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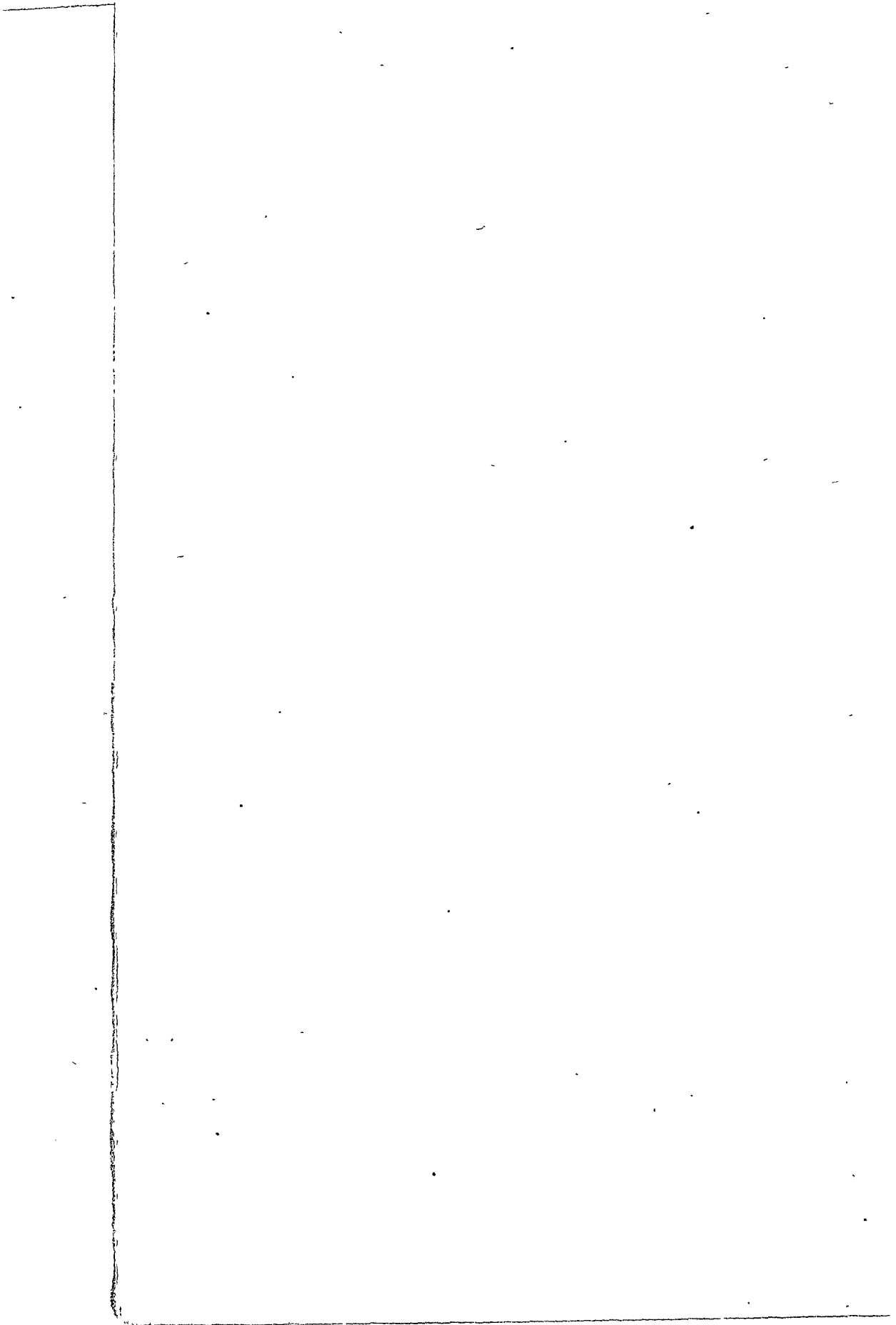
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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN
TE AMSTERDAM.

PROCEEDINGS

VOLUME XXI

N^o. 1 and 2.

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Continuation of § XVI.

The factor by which the double integrals (7) are multiplied, now becomes, with $n = N:v$:

$$\frac{1}{3} \pi n a^2 \times MN = \frac{1}{2} \times \frac{2}{3} \pi N s^3 \times MN \times \frac{a^2}{s^3} \times \frac{1}{v},$$

i. e., as $\frac{2}{3} \pi N s^3 = 4n = (b_\eta)_\infty$, $MN = \alpha$:

$$\frac{1}{2} \times (b_\eta)_\infty \times \alpha \times \frac{a^2}{s^3} \times \frac{1}{v} = \omega \times \frac{a^2}{s^3} \times \frac{1}{v}.$$

With omission of $1:v$ we get, therefore, for the constant of attraction a :

$$a = \omega \times \frac{2a^4}{s(a^2 - s^2)} \left[\int_{\theta_0}^{90} \int_{r_m}^a \frac{dr \times \sin \theta d\theta}{r^2 \sqrt{1 - \frac{a^2}{r^2} \sin^2 \theta + \varphi \left(\frac{a^2}{r^2} - 1 \right) : \left(\frac{a^2}{s^2} - 1 \right)}} + \int_0^{\theta_0} \int_s^a ibid. \right],$$

when also for $F(r)$ and $-F'(r)$ their values according to (8) and (8a) are substituted. When to abbreviate we write k^2 for $s^2 : (a^2 - s^2)$, the above becomes:

$$a = \omega \times \frac{2a^4}{s(a^2 - s^2)} \left[\int_{\theta_0}^{90} \int_{r_m}^a \frac{dr \times \sin \theta d\theta}{r \sqrt{a^2 \cos^2 \theta - (a^2 - r^2)(1 - k^2 \varphi)}} + \int_0^{\theta_0} \int_s^a ibid. \right], \dots (7^a)$$

in which, therefore, $\omega = \frac{1}{2} \times (b_\eta)_\infty \times \alpha$.

Let us first discuss the first integral referring to all the molecules that pass the molecule which is supposed not to move, without coming in collision with it. We may write for it:

$$I_1 = \int_{\theta_0}^{90} \int_{r_m}^a \frac{dr \times \sin \theta d\theta}{r \sqrt{a^2 \cos^2 \theta - (a^2 - r^2)(1 - k^2 \varphi)}}.$$

As was already remarked above, the above calculations only hold for temperatures above a certain limiting temperature T_0 , defined

by $\theta_0 = 90^\circ$, $\sin \theta_0 = 1$. This is namely the lowest temperature at which a value for θ_0 is still possible. From (6) follows namely $\sin^2 \theta_0 = \frac{s^2}{a^2}(1 + \varphi)$, so that $\frac{s^2}{a^2}(1 + \varphi)$ can never become greater than 1, hence φ never greater than $(a^2 - s^2): s^2 = 1:k^2$.

When we represent this limiting value of $\varphi = M: \frac{1}{2}\mu u_0^2$ by φ_0 , we get therefore

$$\varphi_0 = \frac{1}{k^2} = \frac{1-n^2}{n^2}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

when we put the ratio $s:a=n$. Accordingly, as long as φ remains $< \varphi_0$ ($T > T_0$), the quantity $1 - k^2\varphi$ also remains > 0 in the above integral.

θ_0 is $= 90^\circ$ in the limiting case $\varphi = \varphi_0$; then *all* the entering molecules collide, also those that strike at an angle $\theta = 90^\circ$, which just reach the rim of the sphere $r=s$, and will yield there a minimum value for r for the last time.

But as soon as the temperature becomes still lower, and φ becomes $> \varphi_0$, all the entering molecules collide without previous minimum, i. e. they all strike at angles $< 90^\circ$ with the normal. For *these* values of φ we shall therefore have to execute a *separate* integration later on, i. e. for all the values from $\varphi > \varphi_0$ to $\varphi = \infty$ ($T=0$).

Now the integration with respect to r yields:

$$\int_{r_m}^a \frac{dr}{r \sqrt{p^2 r^2 - a^2(p^2 - \cos^2 \theta)}} = \frac{1}{a \sqrt{p^2 - \cos^2 \theta}} \left(Bg \operatorname{tg} \sqrt{\frac{p^2 r^2 - a^2(p^2 - \cos^2 \theta)}{a^2(p^2 - \cos^2 \theta)}} \right)_{r_m}^a,$$

when we put $1 - k^2\varphi = p^2$. As $\sin^2 \theta_0 = \frac{s^2}{a^2}(1 + \varphi)$, $\cos^2 \theta_0$ is therefore $= 1 - \frac{s^2}{a^2}(1 + \varphi) = \frac{a^2 - s^2}{a^2} \left(1 - \frac{s^2}{a^2 - s^2} \varphi \right) = \frac{a^2 - s^2}{a^2} p^2$. Hence the quantity p^2 is also $= \frac{a^2}{a^2 - s^2} \cos^2 \theta_0$, so that $p^2 - \cos^2 \theta$ always remains positive. For $\cos^2 \theta$ is at most $= \cos^2 \theta_0$ in I_1 .

At the limit r_m the quantity under the root sign, viz. $p^2 r^2 - a^2(p^2 - \cos^2 \theta)$ is always $= 0$, because then $dr:dt = 0$ (compare (3^a)). Hence we have after introduction of the limits:

$$I_1 = \frac{1}{a} \int_{\theta_0}^{90} \frac{\sin \theta d\theta}{\sqrt{p^2 - \cos^2 \theta}} Bg \operatorname{tg} \frac{\cos \theta}{\sqrt{p^2 - \cos^2 \theta}} = \frac{1}{a} \int_0^{x_0} \frac{dx}{\sqrt{p^2 - x^2}} Bg \operatorname{tg} \frac{x}{\sqrt{p^2 - x^2}},$$

when we write $-d\cos\theta$ for $\sin\theta d\theta$, and x for $\cos\theta$, so that $\cos\theta_0$ is represented by x_0 . Now $dBg \operatorname{tg} = dx: \sqrt{p^2 - x^2}$, so that we find:

$$I_1 = \frac{1}{2a} Bg^2 \operatorname{tg} \frac{x_0}{\sqrt{p^2 - x_0^2}} = \frac{1}{2a} Bg^2 \operatorname{tg} \frac{1}{k},$$

as $p^2 = \frac{a^2}{a^2 - s^2} x_0^2$ (see above), hence $p^2 - x_0^2 = \frac{s^2}{a^2 - s^2} x_0^2 = k^2 x_0^2$.

Multiplying by the factor $\omega \times \frac{2a^4}{s(a^2 - s^2)}$, we have therefore for the first part of a:

$$a_1 = \omega \times \frac{a^2}{s(a^2 - s^2)} Bg^2 \operatorname{tg} \frac{1}{k} = \omega \times \frac{1}{n(1 - n^2)} Bg^2 \operatorname{tg} \frac{\sqrt{1 - n^2}}{n}. \quad (10)$$

Hence we find for this a value which no longer contains φ (hence T), so that the part of the constant of attraction which refers to the *passing* molecules, appears to be *independent of the temperature*. This seems somewhat strange, because near the limiting temperature, given by φ_0 , θ_0 gets near 90° , so that then the limits of I_1 with respect to θ get nearer and nearer to each other, and finally coincide at $\theta_0 = 90^\circ$ ($\varphi = \varphi_0$). It would therefore be expected that a_1 would become smaller and smaller according as T decreases, and that it would disappear at the limiting temperature. However, this is not the case according to (10). The explanation may be found by an examination of the paths of the molecules, which shows that with the diminution of the velocity u_0 they occupy an *ever larger portion of the path* within the sphere of attraction; to which the circumstance is added that the frequency for the angle, which is proportional to $\sin \theta$, reaches its *maximum* exactly in the neighbourhood of $\theta = 90^\circ$.

When n is near 1, i. e. a near s (very thin sphere of attraction), $Bg^2 \operatorname{tg} \frac{1 - n^2}{n^2}$ approaches $\frac{1 - n^2}{n^2}$, so that then a_1 approaches $\omega : n^2 = \omega$. As

$\sin^2 \theta_0$ is $= \frac{s^2}{a^2} (1 + \varphi)$, $\cos^2 \theta_0 = x_0^2 = 1 - \frac{s^2}{a^2} (1 + \varphi)$, so that x_0^2 will

lie between $\frac{a^2 - s^2}{a^2} = 1 - n^2 = \pm 0$ at high temperatures ($\varphi = 0$), and

(0) at lower temperatures ($\varphi = \varphi_0$). θ_0 lies, therefore, in both cases in the neighbourhood of 90° , hence the limits of integration of I_1 will almost coincide, viz. θ between $\pm 90^\circ$ and 90° at high temperatures, resp. (90°) and 90° at lower temperatures.

In the case $n \rightarrow 1$ the limiting value $\varphi_0 = (1 - n^2) : n^2$ will lie near 0, i. e. T_0 near ∞ , so that the available range of temperature is exceedingly small.

If, however, n is near 0, i. e. a very much larger than s (very

large sphere of attraction), then Bg^2tg approaches $1/4 \pi^2 - \pi n$, hence a_1 approaches $\omega \times \frac{1}{n} \times \frac{1}{4} \pi^2 = \infty$. Now x_0^2 lies between $1 - n^2 = \pm 1$ at high temperatures and (0) at low temperatures, so that at high temperatures θ will lie between $\pm 0^\circ$ and 90° , and at low temperatures between (90°) and 90° . And the limiting value of φ_0 is near ∞ , i.e. T_0 near 0, so that the available range of temperature is very large in this case. That a_1 now becomes *infinite*, is not astonishing, for to obtain a *finite* value, $F(r)$ should decrease much more rapidly with r than is the case on our assumption (8) — viz. in inverse ratio to r^2 . This assumption, however, only holds for not too large values of $a:s$.

§ XVII. Calculation of $(a_2)_1$.

Now we must carry out the second integration in (7^a). This applies, therefore, to all the molecules that can come in *collision*, as θ now remains smaller than the limiting angle θ_0 . It should be carried out in *two* stages, viz. from $x (= \cos \theta) = p$ to $x = x_0$, and from $x = 1 (\theta = 0)$ to $x = p$. For in the general integral with respect to r (see § XVI), viz.

$$\int_s^a \frac{dr}{r \sqrt{p^2 r^2 - a^2 (p^2 - \cos^2 \theta)}},$$

$p^2 - \cos^2 \theta = p^2 - x^2$ will be *positive* in the first case, *negative* on the other hand in the second case. Accordingly the first stage gives rise to a $Bgtg$, the second to a log . The first stage, integrated with respect to r , yields:

$$\begin{aligned} \frac{1}{a \sqrt{p^2 - x^2}} \left(Bgtg \sqrt{\frac{p^2 r^2 - a^2 (p^2 - x^2)}{a^2 (p^2 - x^2)}} \right)_s^a &= \\ &= \frac{1}{a \sqrt{p^2 - x^2}} \left[Bgtg \frac{x}{\sqrt{p^2 - x^2}} - Bgtg \frac{\sqrt{x^2 - x_0^2}}{\sqrt{p^2 - x^2}} \right], \end{aligned}$$

because $p^2 \left(1 - \frac{s^2}{a^2} \right) = x_0^2$ (see § XVI). Hence we have:

$$(I_2)_1 = \frac{1}{a} \left[\int_{x_0}^p \frac{dx}{\sqrt{p^2 - x^2}} Bgtg \frac{x}{\sqrt{p^2 - x^2}} - \int_{x_0}^p \frac{dx}{\sqrt{p^2 - x^2}} Bgtg \frac{\sqrt{x^2 - x_0^2}}{\sqrt{p^2 - x^2}} \right].$$

¹⁾ $Bgtg \frac{\sqrt{1-n^2}}{n}$ is namely $= Bgtg \frac{1}{n} = Bg \cos n = \frac{1}{2} \pi - n$, hence $Bg^2tg = \frac{1}{4} \pi^2 - \pi n$.

The first integral yields $\frac{1}{2} \left(Bg^2 tg \frac{x}{\sqrt{p^2 - x^2}} \right)_{x_0}^p = \frac{1}{2} \left[\frac{1}{4} \pi^2 - Bg^2 tg \frac{1}{k} \right]$,

as $d Bg tg$ is again $= \frac{dx}{\sqrt{p^2 - x^2}}$.

But the second integral cannot so easily be integrated. As then $d Bg tg$ is $= \frac{x}{\sqrt{x^2 - x_0^2}} \frac{dx}{\sqrt{p^2 - x^2}}$, the said integral becomes:

$$\int_{x_0}^p \frac{\sqrt{x^2 - x_0^2}}{x} Bg tg \times d Bg tg = \int_0^{\frac{1}{2}\pi} \frac{y \sqrt{p^2 - x_0^2}}{\sqrt{p^2 y^2 + x_0^2}} Bg tg y \times d Bg tg y,$$

when we put $(x^2 - x_0^2) : (p^2 - x^2) = y^2$, which causes x^2 to become $(p^2 y^2 + x_0^2) : (1 + y^2)$, and $x^2 - x_0^2$ to become $y^2(p^2 - x_0^2) : (1 + y^2)$. With $Bg tg y = \psi$ the last integral passes into:

$$\begin{aligned} \frac{\sqrt{p^2 - x_0^2}}{p} \int_0^{\frac{1}{2}\pi} \frac{tg \psi}{\sqrt{tg^2 \psi + (x_0^2 : p^2)}} \psi d\psi &= \frac{s}{a} \int_0^{\frac{1}{2}\pi} \frac{\sin \psi}{\sqrt{\sin^2 \psi + \frac{a^2 - s^2}{a^2} \cos^2 \psi}} d\psi = \\ &= k \int_0^{\frac{1}{2}\pi} \frac{\sin \psi}{\sqrt{1 + k^2 \sin^2 \psi}} \psi d\psi, \end{aligned}$$

as $\sqrt{p^2 - x_0^2} : p$ in consequence of $p^2 = \frac{a^2}{a^2 - s^2} x_0^2$, hence $p^2 - x_0^2 = \frac{s^2}{a^2 - s^2} x_0^2$, can be replaced by $\frac{s}{a}$, and $x_0^2 : p^2$ by $(a^2 - s^2) : a^2$, while further

$$\sin^2 \psi + \frac{a^2 - s^2}{a^2} \cos^2 \psi = \frac{a^2 - s^2}{a^2} + \frac{s^2}{a^2} \sin^2 \psi = \frac{a^2 - s^2}{a^2} \left(1 + \frac{s^2}{a^2 - s^2} \sin^2 \psi \right)$$

and $s^2 : (a^2 - s^2) = k^2$. The last transcendental, quasi-elliptical integral can now easily (see appendix) be developed into a series, and then be approximated. Previously we may observe that x_0 , hence φ (and therefore also T), no longer occur in it, so that the result — like that of the first part of $(I_2)_1$ — will not be dependent on the temperature, as little as this was the case with I_1 (see § XVI). It is further easy to see that the said integral approaches

$$\int_0^{\frac{1}{2}\pi} \frac{k \sin \psi}{\sqrt{1 + k^2 \sin^2 \psi}} \psi d\psi = \left(\frac{1}{2} \psi^2 \right)_0^{\frac{1}{2}\pi} = \frac{1}{2} \times \frac{1}{4} \pi^2 \text{ in the limiting case } n = 1$$

($a = s$), hence $k = \infty$; and in the opposite limiting case $n = s$ ($a : s = \infty$),

hence $k = 0$, approaches $k \int_0^{1/2\pi} \sin \psi \times \psi d\psi = k \left(-\psi \cos \psi + \int \cos \psi d\psi \right) = k (-\psi \cos \psi + \sin \psi)$, which yields the value k between 0 and $1/2\pi$.

Hence the integral in question lies between $1/8\pi^2$ and $k = s : \sqrt{a^2 - s^2} = s : a = n$ (as in the latter case s is infinitely small with respect to a), so that we can represent it by

$$\varepsilon n \times 1/8\pi^2,$$

in which ε will lie between $\frac{1}{8}$ (when $n = 1$) and $8 : \pi^2 = 0,811$ (when $n = 0$). Accordingly the factor ε is little variable. It appears from the expansion into series (see Appendix A), that ε becomes $0,845$ for $n = 0,6$ (i. e. $s = 0,6a$).

We now have:

$$(I_2)_1 = \frac{1}{2a} \left[\left(\frac{1}{4} \pi^2 - Bg^2 \operatorname{tg} \frac{1}{k} \right) - \varepsilon n \times \frac{1}{4} \pi^2 \right],$$

so that taking the factor $\omega \times (2a^4 : s(a^2 - s^2))$ into account, the following equation is found:

$$(a_2)_1 = \omega \times \frac{1}{n(1-n^2)} \left[\frac{1}{4} \pi^2 (1 - \varepsilon n) - Bg^2 \operatorname{tg} \frac{\sqrt{1-n^2}}{n} \right] \quad (11)$$

If n is near 1 ($a \sim s$), this approaches $\omega \times \frac{1}{1-n^2} [\frac{1}{4}\pi^2(1-n)-(1-n^2)] = \omega \times (\frac{1}{8}\pi^2 - 1) = 0,234 \omega$. The limits of integration p and x_0 are determined by $x_0^2 = 1 - \frac{s^2}{a^2} (1 + \varphi) = \frac{a^2 - s^2}{a^2} = 1 - n^2 = \pm 0$ at high temperatures ($\varphi = 0$), resp. (0) at lower temperatures ($\varphi = \varphi_0$), and $p^2 = \frac{a^2}{a^2 - s^2} x_0^2 = (1)$, resp. (0); so that θ lies between (0°) and $\pm 90^\circ$ at high temperatures, and (90°) and (90°) at lower temperatures.

And if n is near 0 (a great with respect to s), then $(a_2)_1$ approaches to $\omega \times \frac{1}{n} \times [(\frac{1}{4}\pi^2 - 2n) - (\frac{1}{4}\pi^2 - \pi n)] = \omega \times (\pi - 2) = 1,14 \omega$. Then we have as limits of integration ± 1 for x_0 ($\varphi = 0$), resp. (0) at $\varphi = \varphi_0$, and (1), resp. (0) for p ; so that θ lies between (0°) and $\pm 0^\circ$ at high temperatures, and (90°) and (90°) at low temperatures.

When $(a_2)_1$ is added to a_1 , we find for the part of the constant of attraction a that is independent of the temperature (coming from

the passing molecules and from the (not central) colliding molecules):

$$a_{\infty} = a_1 + (a_2)_1 = \omega \times \frac{1-\varepsilon n}{n(1-n^2)^{\frac{1}{4}}} \pi^2 \quad . \quad . \quad . \quad (12)$$

According to the above this part comprises the *almost totality* of the angles of incidence, from 90° to near to 0° , at *high* temperatures; and only a *very small part*, from 90° to near to 90° at *low* temperatures; i. e. in the limiting cases $n = 1$ and $n = 0$. But also in intermediate cases this continues to hold, because at high temperatures p^2 always lies in the neighbourhood of $\frac{a^2}{a^2-s^2} \times \frac{a^2-s^2}{a^2} = 1$, and at low temperatures always in the neighbourhood of $\frac{a^2}{a^2-s^2} \times 0 = 0$.

Hence the region left for the part of a that is *dependent on* the temperature, is the greater as the temperature becomes smaller.

Now the quantity a_{∞} in (12) lies between $\omega \times \frac{1-n}{n(1-n^2)^{\frac{1}{4}}} \pi^2 = \omega \times \frac{1}{n(1+n)} \pi^2 = \omega \times \frac{1}{8n^2}$ for $n = 1$, and $\omega \times \frac{1}{n} \times \frac{1}{4} \pi^2 = \infty$ for $n = 0$.

§ XVIII. Calculation of $(a_2)_2$.

We finally come to the calculation of the part that is dependent on the temperature, and corresponds with the more central collisions of the *second* stage of I_2 . We now have for the integration with respect to r (cf § XVII):

$$\int_s^a \frac{dr}{r \sqrt{p^2 r^2 + a^2 (\cos^2 \theta - p^2)}},$$

in which $\cos^2 \theta - p^2$ remains *positive* between the limits $\theta = 0^\circ$ and $\theta = Bg \cos p$. The integral yields:

$$\begin{aligned} \frac{1}{a \sqrt{x^2 - p^2}} \left(\log \frac{\sqrt{p^2 r^2 + a^2 (x^2 - p^2)} - a \sqrt{x^2 - p^2}}{r} \right)_s^a &= \\ &= \frac{1}{a \sqrt{x^2 - p^2}} \left[\log (x - \sqrt{x^2 - p^2}) - \log \frac{a}{s} (\sqrt{x^2 - x_0^2} - \sqrt{x^2 - p^2}) \right], \end{aligned}$$

when $\cos \theta$ is put again $= x$, and $\cos \theta_0 = x_0$, x_0^2 being $= p^2 \left(1 - \frac{s^2}{a^2}\right)$ (Cf. § XVI). Hence we have:

$$(I_2)_7 = \frac{1}{a} \left[\int_p^1 \frac{dx}{\sqrt{x^2 - p^2}} \log \frac{x - \sqrt{x^2 - p^2}}{p} - \int_p^1 \frac{dx}{\sqrt{x^2 - p^2}} \log \frac{\sqrt{x^2 - x_0^2} - \sqrt{x^2 - p^2}}{s/a \cdot p} \right].$$

We have written $-dx$ for $\sin \theta d\theta = -d \cos \theta$. The minus sign has again been removed by reversing the limits of integration. Besides — for the sake of homogeneity — a factor p has still been introduced under both \log . For $s/a \cdot p$ we may also write $\sqrt{p^2 - x_0^2}$.

The first integral can again be easily integrated. $d \log$ is namely

$$= -\frac{dx}{\sqrt{x^2 - p^2}}, \text{ so that we find for it:}$$

$$\frac{1}{2} \log^2 \left(\frac{x - \sqrt{x^2 - p^2}}{p} \right)_1^p = -\frac{1}{2} \log^2 \frac{1 - \sqrt{1 - p^2}}{p} = -\frac{1}{2} \log^2 \frac{p}{1 + \sqrt{1 - p^2}},$$

for which with a view to \log^2 also $-\frac{1}{2} \log^2 \frac{1 + \sqrt{1 - p^2}}{p}$ may be written.

The second presents again the same difficulties as the corresponding *Bgtg* in § XVII. This becomes namely, $d \log$ now being =

$$= -\frac{x}{\sqrt{x^2 - x_0^2}} \frac{dx}{\sqrt{x^2 - p^2}} : \\ - \int_p^1 \frac{\sqrt{x^2 - x_0^2}}{x} \log \times d \log = \int_1^p \frac{\sqrt{p^2 - x_0^2}}{\sqrt{p^2 - y^2} \cdot x_0^2} \log \sqrt{\frac{1-y}{1+y}} \times d \log,$$

seeing that

$$\log \frac{\sqrt{x^2 - x_0^2} - \sqrt{x^2 - p^2}}{\sqrt{p^2 - x_0^2}} = \log \sqrt{\left(1 - \sqrt{\frac{x^2 - p^2}{x^2 - x_0^2}}\right) : \left(1 + \sqrt{\frac{x^2 - p^2}{x^2 - x_0^2}}\right)},$$

while from $(x^2 - p^2) : (x^2 - x_0^2) = y^2$ follows $x^2 = (p^2 - y^2 x_0^2) : (1 - y^2)$ and $x^2 - x_0^2 = (p^2 - x_0^2) : (1 - y^2)$. Now $\log \sqrt{\frac{1-y}{1+y}} = -Bgtg \text{ hyp } y$,

so that we find with $Bgtg \text{ hyp } y = \psi$:

$$\frac{\sqrt{p^2 - x_0^2}}{p} \int_1^p \frac{1}{\sqrt{1 - \frac{x_0^2}{p^2} \text{tg}^2 h \psi}} \psi d\psi = k \int_{\text{tg } \theta_0 : k}^1 \frac{\cos h \psi}{\sqrt{1 + k^2 \cos^2 h \psi}} \psi d\psi,$$

because $\frac{a^2 - s^2}{a^2} + \frac{s^2}{a^2} \cos^2 h \psi$ can be substituted for $\cos^2 h \psi - \frac{a^2 - s^2}{a^2} \times \sin^2 h \psi$, with $\sin^2 h \psi = \cos^2 h \psi - 1$; and $s^2 : (a^2 - s^2)$ is $= k^2$ (see § XVII). For $x_0^2 : p^2$ we may namely write $(a^2 - s^2) : a^2$, and $(p^2 - x_0^2) : p^2$

is $= s^2 : a^2$. The limits for x are 1 and p , hence $\sqrt{\frac{1-p^2}{1-x_0^2}}$ and 0 for y , i. e. for $tg h \psi$. Thus $\sqrt{\frac{1-x_0^2}{p^2-x_0^2}}$ and 1 for $cos h \psi = 1 : \sqrt{1-tg^2 h \psi}$, or $tg \theta_0 : k$ and 1; $p^2-x_0^2$ being $= k^2 x_0^2$, and x_0^2 being $cos^2 \theta_0$. Evidently the limits for ψ are $log \frac{\sqrt{1-x_0^2} + \sqrt{1-p^2}}{\sqrt{p^2-x_0^2}} =$
 $= log \left(\frac{tg \theta_0}{k} + \sqrt{\frac{tg^2 \theta_0}{k^2} - 1} \right)$ and 0,

as

$$Bg tg h \psi = - log \frac{\sqrt{x^2-x_0^2} - \sqrt{x^2-p^2}}{\sqrt{p^2-x_0^2}} = log \frac{\sqrt{x^2-x_0^2} + \sqrt{x^2-p^2}}{\sqrt{p^2-x_0^2}}.$$

In this $tg \theta_0 : k$ is > 1 , because now $p < 1$.

Thus we obtain an integral of quite the same form as that of § XVII; with only this difference, that now hyperbolic cosinus is put instead of the former sinus. When again we expand into a series (see Appendix B), it appears that both at *high* temperatures ($\varphi = 0$) and at *low* temperature ($\varphi = \varphi_0 = 1 : k^2$) all the terms with higher powers of log with respect to the first term disappear, so that with close approximation we may write:

$$- \frac{1}{2} n \sqrt{1+\varphi} log^2 \frac{\sqrt{1+\varphi} + \sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2\varphi}},$$

in which φ is determined by the relation $\frac{a^2}{s^2} sin^2 \theta_0 = 1 + \varphi$ (cf. equation (6) of the previous paper), in consequence of which $tg^2 \theta_0 : k^2$ becomes $= (1 + \varphi) : (1 - k^2 \varphi)$. (n has again been written for $s : a = k : \sqrt{1+k^2}$).

When we now add the found integral to the first, viz. $\frac{1}{2} log^2 \frac{1 + \sqrt{1-p^2}}{p}$

then (p^2 being $= \frac{a^2}{a^2-s^2} x_0^2 = (1+k^2)x_0^2$, and x_0^2 being $= 1 - sin^2 \theta_0$
 $= 1 - \frac{k^2}{1+k^2} (1 + \varphi)$, so that p^2 becomes $= 1 - k^2 \varphi$) we get:

$$(I_2)_2 = \frac{1}{2a} \left[- log^2 \frac{1+k\sqrt{\varphi}}{\sqrt{1-k^2\varphi}} + n \sqrt{1+\varphi} log^2 \frac{\sqrt{1+\varphi} + \sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2\varphi}} \right],$$

so that taking into account the factor $\omega \times (2 a^4 : s(a^2-s^2))$, we get the following form:

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)} \left[n \sqrt{1+\varphi} \log^2 \frac{\sqrt{1+\varphi} + \sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2}\varphi} - \log^2 \frac{1+k\sqrt{\varphi}}{\sqrt{1-k^2}\varphi} \right] \quad (13)$$

$$\begin{aligned} \text{As } \log \frac{\sqrt{1+\varphi} + \sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2}\varphi} &= \\ &= \frac{1}{2} \log \frac{1 + \sqrt{\frac{(1+k^2)\varphi}{1+\varphi}}}{1 - \sqrt{\frac{(1+k^2)\varphi}{1+\varphi}}} = \sqrt{\frac{(1+k^2)\varphi}{1+\varphi}} + \frac{1}{3} ()^3 + \text{etc.} \\ \log \frac{1+k\sqrt{\varphi}}{\sqrt{1-k^2}\varphi} &= \frac{1}{2} \log \frac{1+k\sqrt{\varphi}}{1-k\sqrt{\varphi}} = k\sqrt{\varphi} + \frac{1}{3} ()^3 + \text{etc.,} \end{aligned}$$

$(a_2)_2$ will evidently at *high* temperature (φ near 0) approach to

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)} \left[n \sqrt{1+\varphi} \frac{(1+k^2)\varphi}{1+\varphi} - k^2 \varphi \right],$$

i. e. with $k^2 = n^2 : (1-n^2)$ to

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)} \left[\frac{n}{1-n^2} \frac{\varphi}{\sqrt{1+\varphi}} - \frac{n^2}{1-n^2} \varphi \right],$$

$$\text{or } (a_2)_2 = \omega \times \frac{1}{n(1-n^2)} \times \frac{n}{1+n} \varphi \quad (\varphi=0) \quad , \quad . \quad . \quad . \quad (13a)$$

when φ is simply written for $\varphi : \sqrt{1+\varphi}$. This becomes therefore properly $= 0$ for $T = \infty$. Then the limits of the original integral $(I_2)_2$, viz. p and 1, are equal, viz. $= 1$, which causes the limits of the angle of incidence θ to lie between (0°) and 0° (see also the end of § XVII).

For *low* temperatures (φ near $\varphi_0 = 1 : k^2$) we shall have:

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)} \left[\log^2 \left(\frac{1}{n} \frac{2}{\sqrt{1-k^2}\varphi} \right) - \log^2 \frac{2}{\sqrt{1-k^2}\varphi} \right],$$

because then $n\sqrt{1+\varphi}$ is $= 1$, and $\sqrt{(1+k^2)\varphi} = \sqrt{1+\varphi} = 1 : n$.

And as $\log \left(\frac{1}{n} \frac{2}{\sqrt{\varphi}} \right) = \log \frac{1}{n} + \log \frac{2}{\sqrt{\varphi}}$, we may finally write with

omission of $\log^2 \frac{1}{n}$ in comparison with the infinitely large terms:

$$(a_2)_2 = \omega \times \frac{1}{n(1-n^2)} \times \log \frac{1}{n^2} \times \log \frac{2}{\sqrt{1-k^2}\varphi} \quad (\varphi = \varphi_0 = 1 : k^2) \quad . \quad (13b)$$

This gets near to *logarithmically infinite*. Now the limits p and 1 are evidently $=0$ and 1, so that θ lies between (90°) and 0° , hence comprises the whole region.

When $n \rightarrow 1$ ($\alpha \rightarrow s$), $(a_2)_2$ does not become $=\infty$ in 13^a . For as φ can never become greater than $1:k^2 = (1-n^2):n^2$, $(a_2)_2$ remains evidently smaller than $\omega \times \frac{1}{n^2(1+n)}$, i.e. $< \omega \times \frac{1}{2}$. Then $(n=1-d)$ $\log(1:n^2)$ becomes $2(1-n)$ in (13^b) , so that $(a_2)_2$ will approach $\omega \times \log \frac{2}{\sqrt{1-k^2\varphi}}$.

If on the other hand $n \rightarrow 0$ (α large with respect to s), then $(a_2)_2$ approaches $\omega \times \varphi$ in (13^a) , whereas this quantity will approach infinite $\times (\log\text{-infinite})^2$ in (13^b) , i.e. will greatly increase, when the temperature becomes lower.

§ XIX. Calculation of a .

When we finally add the part of a that is *independent* of the temperature, viz. $a_\infty = a_1 + (a_2)_1$ according to (12), to the part that is dependent on the temperature according to (13^a) , then we get at *high* temperature, taking $\omega = \frac{1}{2} \times (b_g)_\infty \times \alpha$ into account (compare § XVI):

$$a = \frac{\omega}{n(1-n^2)} \left[(1-\varepsilon n)^{\frac{1}{4}} \pi^2 + \frac{n}{1+n} \varphi \right] = \\ = \frac{1}{2n(1-n^2)} (b_g)_\infty \alpha \left[(1-\varepsilon n)^{\frac{1}{4}} \pi^2 + \frac{n}{1+n} \varphi \right],$$

or also

$$(\varphi \rightarrow 0) \quad a = a_\infty \left[1 + \frac{n}{(1-\varepsilon n)(1+n)^{1/4} \pi^2} \varphi \right] = \frac{a_\infty (1 + \gamma \varphi)}{1}, \quad (14a)$$

in which therefore

$$a_\infty = \frac{1/4 \pi^2 (1-\varepsilon n)}{2n(1-n^2)} (b_g)_\infty \alpha, \quad \text{and} \quad \gamma = \frac{n}{(1-\varepsilon n)(1+n)^{1/4} \pi^2}.$$

We remind the reader of the fact that the coefficient ε (see § XVII) has the value 1 for $n=1$, the value $8:\pi^2 = 0,811$ for $n=0$, and the value 0,845 for $n=0,6$. Further $\alpha = MN$, in which M is the maximum value of the function of force $f(r)$ at contact of the molecules, and N the total number of molecules in the volume v .

At *low* temperatures ($\varphi = \varphi_0 = 1:k^2$) we get according to (13^b) :

$$(\varphi \rightarrow \varphi_0) \quad a = a_\infty \left[1 + \frac{\log 1/n^2}{1/4 \pi^2 (1-\varepsilon n)} \log \frac{2}{\sqrt{1-k^2 \varphi}} \right] \dots \dots (14b)$$

That for $\varphi = \varphi_0$ the value of a becomes *logarithmically* infinite, and does not get near *exponentially* infinite, as is the case on assumption of BOLTZMANN'S temperature-distribution factor (for $f(a) = (e^{a/RT} - 1) : a/RT$ becomes of the order e^∞ for $T = 0$), is already to be esteemed an advantage. But the above found logarithmically infinite will lead to an ordinary *finite maximum*, when we consider that only the *very definite velocity* u_0 , which causes φ to be $= M : \frac{1}{2} \mu u_0^2 = 1 : k^2$, leads to this $\log \infty$. When we take MAXWELL'S law of the *distribution of velocities into account*, the adjacent velocities will not lead to $\log \infty$, and this will accordingly pass into a finite maximum. We shall come back to this later on.

We will, however, point out already here that the logarithmic infinity for $\varphi = \varphi_0$ is *not* bound to our special assumption (8) concerning $F(r)$. We shall see that this *log-infinite* value of a for $\varphi = \varphi_0$ is found on *any* supposition concerning $F(r)$.

But the numerical values of the quantities a_∞ and γ in (14^a) e.g. will of course be dependent on the said supposition. We possess a kind of control for the case $\varphi = 0, n = 1$. According to (14^a) a_∞ then becomes $= \frac{1}{16} \pi^2 \times (b_q)_\infty a$, because $(1 - \varepsilon n)$ then becomes $= 1 - n$, hence $(1 - \varepsilon n) : n(1 - n^2) = 1 : n(1 + n) = \frac{1}{2}$. But according to the ordinary (statical) theory, the attractive virial (see § IX) must be

$$= \frac{2}{3} \pi N n \int_s^a r^3 \frac{dP_r}{dr} dr. \quad \text{When } a = s, \quad r^3 = s^3 \text{ can be brought before}$$

the integral sign, and we have $\frac{2}{3} \pi N n s^3 (P_r)_s^a = \frac{2}{3} \pi N n s^3 (0 - (-M)) = \frac{2}{3} \pi N s^3 \times M N : v$ (as $n = N : v$). Hence we find with $M N = a$ for a the value $(b_q)_\infty \times a$, so that the factor by which we have to multiply, would have to be $= 1$, and not $= \frac{1}{16} \pi^2 = 0,617$, as we have found. In my opinion this conclusion can only be drawn from it, that even in the limiting case $T = \infty$ ($\varphi = 0$) the factor of distribution at the molecule surface (the sphere of attraction is infinitely thin on the assumption $a = s$) is not $= 1$, as we assumed above in the application of the statical method, but slightly less in consequence of the influence of the *passing* molecules, which does not disappear even for $n = 1$, which is the cause that the full maximum value M of the function of force is not reached. And the difference will depend on the nature of the function of force used.

For $n = 0,6$ the factor of $(b_q)_\infty a$ will get the value $\frac{2,467 \times 0,483}{1,2 \times 0,64} = \frac{1,192}{0,768} = 1,55$, which comes to this, that the attraction

might be thought concentrated at a distance $s \sqrt{1,55} = 1,16 s$ from the centre of the considered molecule (the sphere of attraction extends between s and $1,67 s$ for $n = 0,6$).

We saw already that φ represents the quantity $M : \frac{1}{2} \mu u_0^2$. In this u_0 represents the mean relative velocity with which the molecules penetrate the sphere of attraction. But this velocity is augmented by a certain amount within the sphere of attraction, so that u_0 will not be in *direct* relation with the temperature. For *very large volumes* we may, however, entirely neglect this slight modification in the velocity in comparison with the much larger part of the path passed over with the velocity u_0 . Only for small volumes this is no longer allowed, and in consequence of this new complications will make their appearance.

We may now write:

$$\varphi = \frac{M}{\frac{1}{2} \mu u_0^2} = \frac{MN}{\frac{1}{2} \mu N u_0^2} = \frac{a}{2 \times \frac{3}{2} RT} = \frac{\frac{1}{3} a}{RT},$$

because the mean square of the *relative* velocity is twice that of the square of velocity U_0^2 itself, and $\frac{3}{2} RT$ may be written for $\frac{1}{2} \mu N U_0^2$. According to all that was developed above,

$$a = a_\infty \left(1 + \gamma_1 \frac{\frac{1}{3} a}{RT} + \gamma_2 \left(\frac{\frac{1}{3} a}{RT} \right)^2 + \dots \right) \quad (15a)$$

may therefore be written for a , according to (14^a) — at least for not too low temperatures, and when also higher powers of φ are taken into consideration; whereas for *low* temperatures (φ near $\varphi_0 = 1 : k^2$) an expression of the form

$$a = a_\infty \left(1 - \lambda \log \frac{1}{2} \sqrt{1 - \frac{z}{RT}} \right) \quad (15b)$$

will better answer the purpose, according to (14^b). In this $z = k^2 \times \frac{1}{3} a = \frac{n^2}{1-n^2} \times \frac{1}{3} a$, in which it should be borne in mind that the *log* is now negative, so that the minus sign before λ becomes positive again.

We have already pointed out before that the supposition of an *exceedingly* thin sphere of attraction, as is sometimes assumed, must be entirely excluded for several reasons¹⁾. To this comes the circumstance that for $n \rightarrow 1$ the limiting temperature T_0 , in which a will become logarithmically infinite (or at least maximum), is given by $\varphi_0 = 1 : k^2 = (1-n^2) : n^2$, which for $n = 1$ would give the value 0 for φ_0 , i.e. $T = \infty$. And as it has been experimentally found that the said

¹⁾ Cf. our first paper.

maximum lies at very low temperatures (a continues namely to increase, for H_2 for instance, up to at least $1/2 T_k$), the assumption $n = 1$ must be quite rejected.

As the value 0,08 (about) is found for $1/3 a$ with H_2 , the value of $RT_0 = 1/3 a : \varphi_0$ would become $\frac{0,36}{0,64} \times 0,08 = 0,045$ with $n = 0,6$ (i. e. $s = 3/5 a$ or $a = 1 2/5 s$), i. e. T_0 about $12^\circ,3$ absolute. This is very well possible, as we have seen that for H_2 the value of a is still increasing up to 16° abs. (from $a_\infty = 370 \times 10^{-6}$ to $a_{16^\circ} = 740 \times 10^{-6}$ about). What is very remarkable, is the fact that the limiting temperature seems to lie so close to the *triple point* of H_2 , viz. 14° abs.).

Fontanivent, January 1918.

(To be continued).

Physics. — “On the Course of the Values of a and b for Hydrogen at Different Temperatures and Volumes”. IV. (Continued).

By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of March 23, 1918).

§ XX. The value of a below the limiting temperature.

In this case the integrations need no longer take place in different stages, since a minimum distance r_m , which is dependent on θ , need no longer be reckoned with, so that first the integration with respect to θ can be carried out, and then with respect to r . All the entering molecules, from $\theta = 0$ to $\theta = 90^\circ$, will now come in collision; for the limiting temperature T_0 the molecules that strike under an angle $\theta = 90^\circ$ will just pass the rim of the molecule that is supposed not to move. We have, therefore, now to integrate (see § XVI):

$$a = \frac{1}{2} \times (b_\eta)_\infty \alpha \times \frac{2a^4}{s(a^2-s^2)} \int_0^a \int_0^{1/2\pi} \frac{dr \times \sin \theta d\theta}{r \sqrt{a^2 \cos^2 \theta + (a^2-r^2)(k^2\varphi-1)}},$$

in which $k^2\varphi$ is now always > 1 , and in the limiting case $\varphi = \varphi_0 = 1$: k^2 assumes the value 1. When we put $(a^2-r^2)(k^2\varphi-1) = q^2$, we get therefore:

$$a = \frac{1}{2} \times (b_\eta)_\infty \alpha \times \frac{2a^3}{s(a^2-s^2)} \int_s^a \frac{dr}{r} \int_{1/2\pi}^0 \frac{d(a \cos \theta)}{\sqrt{q^2 + a^2 \cos^2 \theta}},$$

in which we may write for the second integral:

$$\log(a \cos \theta + \sqrt{q^2 + a^2 \cos^2 \theta})_{1/2\pi}^0 = \log \frac{a + \sqrt{q^2 + a^2}}{q},$$

so that we have still to integrate:

$$a = \frac{1}{2} \times (b_\eta)_\infty \alpha \times \frac{2a^3}{s(a^2-s^2)} \int_s^a \frac{dr}{r} \log \left(\frac{a}{q} + \sqrt{1 + \frac{a^2}{q^2}} \right). \quad (16)$$

If in the first place φ is near φ_0 , then q approaches 0, and the integral approaches to

$$\int_s^a \frac{dr}{r} \log \frac{2a}{q} = \int_s^a \frac{dr}{r} \left[\log \frac{2}{\sqrt{k^2 \varphi - 1}} - \log \frac{\sqrt{a^2 - r^2}}{a} \right],$$

because q is $= \sqrt{k^2 \varphi - 1} \times \sqrt{a^2 - r^2}$. Hence we have for the integral:

$$\log \frac{2}{\sqrt{k^2 \varphi - 1}} \log \frac{a}{s} - \int_s^a \log \frac{\sqrt{a^2 - r^2}}{a} \cdot \frac{dr}{r}.$$

We have for the last integral with $r: a = x$, $s: a = n$:

$$- \frac{1}{2} \int_n^1 \log(1-x^2) \cdot \frac{dx}{x} = \frac{1}{4} \left(\frac{x^2}{1} + \frac{x^4}{4} + \frac{x^6}{9} + \dots \right)_n^1 = \frac{1}{24} \pi^2 (1 - \varepsilon' n^2),$$

in which $\varepsilon' = 1$ for $n=1$, and $6: \pi^2 = 0,608$ for $n=0$. For

$$\frac{1}{1} + \frac{1}{4} + \frac{1}{9} + \dots = \frac{1}{6} \pi^2, \text{ and } \frac{n^2}{1} + \frac{n^4}{4} + \frac{n^6}{9} + \dots = n^2 \left(1 + \frac{n^2}{4} + \frac{n^4}{9} + \dots \right)$$

is $= \frac{1}{4} \pi^2$ for $n=1$, and $= n^2$ for $n=0$. (For $n=0,6$ $\varepsilon' = 0,674$).

Hence we get finally:

$$(\varphi \gg \varphi_0) \quad a = \frac{1}{2n(1-n^2)} (b_q)_\infty \alpha \left[\frac{1}{12} \pi^2 (1 - \varepsilon' n^2) + \log \frac{1}{n^2} \log \frac{2}{\sqrt{k^2 \varphi - 1}} \right]. \quad (17)$$

When we compare this with (14^b), where we found for values of φ in the neighbourhood of φ_0 (but $< \varphi_0$, while φ remains $> \varphi_0$ in (16)):

$$(\varphi \lesssim \varphi_0) \quad a = \frac{1}{2n(1-n^2)} (b_q)_\infty \alpha \left[\frac{1}{4} \pi^2 (1 - \varepsilon n) + \log^2 \frac{1}{n} + \log \frac{1}{n^2} \log \frac{2}{\sqrt{1-k^2 \varphi}} \right],$$

we observe with regard to the member that is independent of T , a discontinuity appearing at $\varphi = \varphi_0$. [We have added, for a comparison, to the first (finite) term the term $\log^2 \frac{1}{n}$, which was cancelled in § 18 in form. (13^b) by the side of the infinitely large logarithmic term].

For $n=1$ we find (with the factor $\frac{1}{1-n^2}$ from the factor before the sign of integration) in the first case $\frac{1}{12} \pi^2 \frac{1-n^2}{1-n^2} = \frac{1}{12} \pi^2$, in the second case

$$\frac{1}{4} \pi^2 \frac{1-n}{1-n^2} + \log^2 \frac{1}{n} = \frac{1}{8} \pi^2. \text{ And for } n=0 \text{ we find } \frac{1}{12} \pi^2, \text{ resp.}$$

$\frac{1}{4} \pi^2 + \log^2 \frac{1}{n} = \frac{1}{4} \pi^2 + \infty^2$. This difference can be partly accounted for by the sudden disappearance at $\varphi = \varphi_0$ of the terms which refer

to the *passing* molecules, and which, therefore, do not occur any more in (17). But in any case the difference is of no importance, as these terms, which are independent of φ , remain finite with respect to the term that depends on φ , and logarithmically approaches infinity. (In the case $n=0$, where — for infinitely large spheres of attraction — the entire quantity a would become infinite, and accordingly our derivation is no longer valid, the fact that $\log^2 \frac{1}{n}$ becomes infinite, is of no importance at all).

We will still point out that for $\varphi = \varphi_0$ a does not only become logarithmically infinite with the form of $f(r)$ assumed by us, but with any arbitrary assumption about this. Compare for this Appendix C.

We suppose in the second place in (16) φ near ∞ (i.e. T near 0).

For the integral in (16) we may then write, as q becomes very large:

$$\int_s^a \frac{dr}{r} \log \left(\frac{a}{q} + 1 + \frac{1}{2} \frac{a^2}{q^2} \right) = \int_s^a \frac{dr}{r} \times \frac{a}{q} = \frac{a}{\sqrt{k^2 \varphi - 1}} \int_s^a \frac{dr}{\sqrt{a^2 - r^2}},$$

i.e.

$$\begin{aligned} \frac{1}{\sqrt{k^2 \varphi - 1}} \left(\log \frac{a - \sqrt{a^2 - r^2}}{r} \right)_s^a &= \frac{1}{\sqrt{k^2 \varphi - 1}} \left(\log 1 - \log \frac{a - \sqrt{a^2 - s^2}}{s} \right) = \\ &= \frac{1}{\sqrt{k^2 \varphi - 1}} \log \frac{a + \sqrt{a^2 - s^2}}{s}. \end{aligned}$$

When the factor before the sign of integration is taken into account we get therefore:

$$\left(\begin{array}{l} \varphi \rightarrow \infty \\ T \rightarrow 0 \end{array} \right) \quad a = \frac{1}{n(1-n^2)} \times (b_q)_\infty \alpha \times \frac{1}{\sqrt{k^2 \varphi - 1}} \log \frac{1 + \sqrt{1-n^2}}{n}. \quad (18)$$

This approaches 0 therefore, when φ approaches ∞ (T approaches 0). We may write for $k^2 \varphi - 1$, after substitution of the value for φ ,

the expression $\frac{n^2}{1-n^2} \frac{1}{RT} - 1 = \frac{n^2}{1-n^2} \frac{1}{RT}$, when T is near 0.

Hence after the *maximum* for a at $\varphi = \varphi_0$ the attraction steadily decreases, and *disappears* at 0° abs. This result was to be foreseen. In the original integral of the virial of attraction the radical quantity in the denominator becomes namely $= \infty$ at 0° abs., when q becomes $= \infty$. This radical quantity expresses the relative increase of velocity in the sphere of attraction, and as this increase remains *finite* with respect to $u_0 = 0$, the *relative* increase will become infinitely great.

And this relative increase of velocity entirely determines the density in the sphere of attraction, which is in inverse ratio to it.

We observe once more here, that the earlier BOLTZMANN theory would give an *exponentially infinite* value for a at 0° abs., whereas in reality it is $= 0$.

For $n=1$ ($\alpha=s$) the limiting value of $\frac{1}{1-n^2}$ will be $= \log \frac{1+\sqrt{1-n^2}}{n}$
 $= \frac{1}{\sqrt{1-n^2}}$. With $\sqrt{\frac{n^2}{1-n^2}}$ in $\sqrt{k^2\varphi-1}$ (see above) this becomes
 $1:n$, so that then a will approach $(b_g)_\infty \alpha \times \sqrt{\frac{RT}{\frac{1}{2}\alpha}}$.

For $n=0$ (α great with respect to s) the absolute zero coincides with the limiting temperature, given by $\varphi_0=1:k^2=(1-n^2):n$.
 For then $\varphi_0=\infty$ ($T_0=0$). In (18) $\lim \frac{1}{n} \log$ becomes further $= \frac{1}{n} \log \frac{2}{n}$
 so that then a will approach $(b_g)_\infty \alpha \times \frac{1}{n} \log \frac{2}{n} \times \frac{1}{\sqrt{\frac{n^2}{n^2 \frac{1}{2}\alpha} - 1}}$, which

again becomes $= 0$ for $T=0$, so long as n is not absolutely $= 0$ which of course would be practically impossible.

Summarising we can therefore state, in agreement with the above developed exact theory concerning the quantity a for *very large volume*, that a , from a limiting value at $T=\infty$, steadily increases to a *maximum value* at $T=T_0$, after which it decreases again till a has become $= 0$ at the absolute zero. The mentioned limiting temperature T_0 is then determined by $RT_0 = \frac{1}{2}\alpha : \varphi_0$, in which $\varphi_0 = (1-n^2):n^2$. ($n=s:\alpha$, in which s represents the diameter of a molecule, and α the radius of the sphere of attraction). For H T_0 is about $= \frac{1}{2}T_h$, the ratio of the values of a_∞ , a_h , and a_0 being $1:1\frac{1}{2}:2$.

In the next paper we shall briefly discuss the influence of MAXWELL'S distribution of velocity, and then treat the course of the quantity b from $T=\infty$ to $T=0$, likewise at large volume. Then the values of a and b for *small* volumes will be considered, so as to make a complete theoretical insight possible concerning the *whole* course of a and b along the boundary line, both along the vapour branch and along the liquid branch.

Fontanivent, January 1918.

(To be continued).

APPENDIX.

A. The integral $k \int_0^{1/2\pi} \frac{\sin \psi}{\sqrt{1+k^2 \sin^2 \psi}} \psi d\psi$. (addition to § XVII).

When we expand this into a series through repeated partial integration, we get:

$$\int \frac{\sin \psi}{\sqrt{1+k^2 \sin^2 \psi}} \psi d\psi = \int P \cdot \psi d\psi = \frac{\psi^2}{2} P - \frac{\psi^3}{6} \frac{dP}{d\psi} + \frac{\psi^4}{24} \frac{d^2 P}{d\psi^2} - \frac{\psi^5}{120} \frac{d^3 P}{d\psi^3} + \dots,$$

in which (through ψ) all the terms at the lower limit 0 disappear. And for the upper limit all the *odd* differential quotients of P will disappear, because in this $\cos \psi$ occurs as factor. Indeed, when we put $1+k^2 \sin^2 \psi = \omega$, so that $\frac{d\omega}{d\psi}$ becomes $= 2k^2 \sin \psi \cos \psi$, we have:

$$\begin{aligned} \frac{dP}{d\psi} &= -\frac{1}{2} \frac{\sin \psi}{\omega^{3/2}} (2k^2 \sin \psi \cos \psi) + \frac{\cos \psi}{\omega^{1/2}} = \cos \psi \left(\frac{-k^2 \sin^2 \psi}{\omega^{3/2}} + \frac{1}{\omega^{1/2}} \right) = \\ &= \cos \psi \left(\frac{1-\omega}{\omega^{3/2}} + \frac{1}{\omega^{1/2}} \right) = \frac{\cos \psi}{\omega^{3/2}}. \end{aligned}$$

$$\begin{aligned} \frac{d^2 P}{d\psi^2} &= -\frac{3}{2} \frac{\cos \psi}{\omega^{5/2}} (2k^2 \sin \psi \cos \psi) - \frac{\sin \psi}{\omega^{1/2}} = -\sin \psi \left(\frac{3k^2 \cos^2 \psi}{\omega^{5/2}} + \frac{1}{\omega^{3/2}} \right) = \\ &= -\sin \psi \left(\frac{3(1+k^2)}{\omega^{5/2}} - \frac{2}{\omega^{3/2}} \right), \end{aligned}$$

because $k^2 \cos^2 \psi = k^2 - k^2 \sin^2 \psi = k^2 - (\omega - 1) = (1+k^2) - \omega$. We have further:

$$\begin{aligned} \frac{d^3 P}{d\psi^3} &= -\sin \psi \left(\frac{15(1+k^2)}{\omega^{7/2}} - \frac{6}{\omega^{5/2}} \right) (-k^2 \sin \psi \cos \psi) - \cos \psi \left(\frac{3(1+k^2)}{\omega^{5/2}} - \frac{2}{\omega^{3/2}} \right) \\ &= -\cos \psi \left[\left(\frac{15(1+k^2)}{\omega^{7/2}} - \frac{6}{\omega^{5/2}} \right) (1-\omega) + \left(\frac{3(1+k^2)}{\omega^{5/2}} - \frac{2}{\omega^{3/2}} \right) \right] \\ &= -\cos \psi \left(\frac{15(1+k^2)}{\omega^{7/2}} - \frac{12(1+k^2)+6}{\omega^{5/2}} + \frac{4}{\omega^{3/2}} \right). \end{aligned}$$

And also:

$$\begin{aligned} \frac{d^4 P}{d\psi^4} &= -\cos \psi \left(\frac{105(1+k^2)}{\omega^{9/2}} - \frac{60(1+k^2)+30}{\omega^{7/2}} + \frac{12}{\omega^{5/2}} \right) (-k^2 \sin \psi \cos \psi) + \\ &\quad + \sin \psi \left(\frac{15(1+k^2)}{\omega^{7/2}} - \frac{12(1+k^2)+6}{\omega^{5/2}} + \frac{4}{\omega^{3/2}} \right) \end{aligned}$$

$$\begin{aligned}
&= \sin \psi \left[\left(\frac{105(1+k^2)}{\omega^{9/2}} - \frac{60(1+k^2) + 30}{\omega^{7/2}} + \frac{12}{\omega^{5/2}} \right) ((1+k^2) - \omega) + \right. \\
&\quad \left. + \left(\frac{15(1+k^2)}{\omega^{7/2}} - \frac{12(1+k^2) + 6}{\omega^{5/2}} + \frac{4}{\omega^{3/2}} \right) \right] \\
&= \sin \psi \left[\frac{105(1+k^2)^2 - 60(1+k^2)^2 + 120(1+k^2)}{\omega^{9/2}} + \frac{60(1+k^2) + 24}{\omega^{5/2}} - \frac{8}{\omega^{3/2}} \right].
\end{aligned}$$

Etc. Etc. As has been said, all the odd differential quotients disappear for $\psi = \frac{1}{2}\pi$, and as ω becomes $= 1 + k^2$ for $\psi = \frac{1}{2}\pi$, we keep:

$$\begin{aligned}
\left(\frac{d^2 P}{d\psi^2} \right)_{\frac{1}{2}\pi} &= -\frac{1}{\omega^{3/2}} = -\frac{1}{(1+k^2)^{3/2}}; \\
\left(\frac{d^4 P}{d\psi^4} \right)_{\frac{1}{2}\pi} &= \frac{15}{\omega^{5/2}} - \frac{12}{\omega^{3/2}} - \frac{6}{\omega^{5/2}} + \frac{4}{\omega^{3/2}} = \frac{9}{(1+k^2)^{5/2}} - \frac{8}{(1+k^2)^{3/2}} = \frac{1-8k^2}{(1+k^2)^{5/2}}.
\end{aligned}$$

For the sake of brevity we have only taken the part with $\sin \psi$ into account in the last calculation of the two differential quotients:

that with $\cos \psi$ is namely $= 0$. I. e. of $\frac{d^2 P}{d\psi^2}$ only the part $-\frac{\sin \psi}{\omega^{3/2}}$,

and of $\frac{d^4 P}{d\psi^4}$ only the part with $\sin \psi$ in the first of the three lines

belonging to this. The other parts have every time been necessary for the determination of the next higher differential quotient. Proceeding, we should have found:

$$\frac{d^6 P}{d\psi^6} = - \left(\frac{225}{(1+k^2)^{7/2}} - \frac{360}{(1+k^2)^{5/2}} + \frac{136}{(1+k^2)^{3/2}} \right) = - \frac{1-88k^2+136k^4}{(1+k^2)^{7/2}}.$$

The coefficients of the highest powers of $1 + k^2$ are in all these results resp. $= 1^2, (1 \times 3)^2, (1 \times 3 \times 5)^2$, etc. The sum of the coefficients is always $= 1$. ($9 - 8 = 1$; $225 - 360 + 136 = 1$). Hence we get now, taking into consideration that $k: \sqrt{1+k^2} =$

$$= \frac{s}{\sqrt{a^2-s^2}}: \frac{a}{\sqrt{a^2-s^2}} = \frac{s}{a} = n, \text{ and } (P)_{\frac{1}{2}\pi} = 1: \sqrt{1+k^2}:$$

$$\begin{aligned}
k \int_0^{\frac{1}{2}\pi} \frac{\sin \psi}{\sqrt{1+k^2 \sin^2 \psi}} \psi d\psi &= n \left[\frac{(\frac{1}{2}\pi)^2}{2} - \frac{1}{1+k^2} \frac{(\frac{1}{2}\pi)^4}{24} + \right. \\
&\quad \left. + \frac{1-8k^2}{(1+k^2)^2} \frac{(\frac{1}{2}\pi)^6}{720} - \frac{1-88k^2+136k^4}{(1+k^2)^3} \frac{(\frac{1}{2}\pi)^8}{40320} + \text{etc.} \right],
\end{aligned}$$

in which we may also write $1-n^2$ for $1:(1+k^2) = (a^2-s^2):a^2$. The above series is convergent, as is easily seen from the structure of the factors $(1-8k^2):(1+k^2)^{5/2} = 9:(1+k^2)^{5/2} = 8(1+k^2)^{5/2}$, etc.

For *large* values of k ($a = s$, i. e. $n = 1$) it converges very greatly, and rapidly approaches the first term, i. e. $n \times \frac{1}{8}\pi^2$.

For *small* values of k (near 0, i. e. a large with respect to s , $n = 0$) the series becomes:

$$n \left[\frac{1}{2} \left(\frac{1}{2} \right) \pi^2 - \frac{1}{24} \left(\frac{1}{2} \pi \right)^4 + \frac{1}{720} \left(\frac{1}{2} \pi \right)^6 - \text{etc.} \right] = n (1 - \cos \frac{1}{2} \pi) = n.$$

For the two limiting cases $n = 1$ and $n = 0$ we, therefore, find back the same values as we had already found by direct integration in the text of § 17.

When $n = 0,6$, we get $1 - 8k^2 = 1 - 4,5 = -3,5$, $1 - 88k^2 + 136k^4 = 1 - 49,5 + 43,0 = -5,5$, $1 : (1 + k^2) = 0,64$, so that with $\frac{1}{4}\pi^2 = 2,4674$, the integral being put $= \varepsilon n \times \frac{1}{8}\pi$ (cf. the text of § 17), we find from

$$\varepsilon = 1 - \frac{1}{1+k^2} \frac{(\frac{1}{2}\pi)^2}{12} + \frac{1-8k^2}{(1+k^2)^2} \frac{(\frac{1}{2}\pi)^4}{360} - \frac{1-88k^2+136k^4}{(1+k^2)^3} \frac{(\frac{1}{2}\pi)^6}{20160} + \text{etc.}$$

for ε the value

$$1 - 0,1316 - 0,02425 + 0,00107 \dots = 0,8452 \dots = \underline{0,845}.$$

B. The integral $k \int_{\text{tg}\theta_0 k}^1 \frac{\cosh \psi}{\sqrt{1+k^2 \cos^2 h \psi}} \psi d\psi$ (addition to § XVIII).

In entirely the same way as for the above treated integral we find through repeated partial integration:

$$\begin{aligned} k \int_{\text{tg}\theta_0 k}^1 \frac{\cosh \psi}{\sqrt{1+k^2 \cos^2 h \psi}} \psi d\psi = & - \left[\frac{\text{tg}\theta_0}{\sec^3 \theta_0} \frac{\log^2}{2} - \frac{k \sqrt{\frac{\text{tg}^2 \theta_0}{k^2} - 1}}{\sec^3 \theta_0} \frac{\log^3}{6} + \right. \\ & + \text{tg}\theta_0 \left(\frac{3(1+k^2)}{\sec^5 \theta_0} - \frac{2}{\sec^3 \theta_0} \right) \frac{\log^4}{24} - \\ & \left. - k \sqrt{\frac{\text{tg}^2 \theta_0}{k^2} - 1} \left(\frac{15(1+k^2)}{\sec^7 \theta_0} - \frac{12(1+k^2)+6}{\sec^5 \theta_0} + \frac{4}{\sec^3 \theta_0} \right) \frac{\log^5}{120} + \text{etc.} \right], \end{aligned}$$

in which \log represents $\log \left(\frac{\text{tg}\theta_0}{k} + \sqrt{\frac{\text{tg}^2 \theta_0}{k^2} - 1} \right)$.

In this it has been taken into account that $d \cosh \psi = \sinh \psi$ and $d \sinh \psi = \cosh \psi$, and that further $-k^2 \cos^2 h \psi$ can again be replaced by $1 - \omega$ (when namely $1 + k^2 \cos^2 h \psi$ is put $= \omega$) and $-k^2 \sin^2 h \psi$ by $-k^2 \cos^2 h \psi + k^2 = (1 + k^2) - \omega$. Now the terms with odd powers of ψ do not disappear, because at the lower limit the factor $\sinh \psi$, which occurs for these powers, does not disappear (as for the above

treated integral $\cos \psi$ at the upper limit), but becomes $= \sqrt{\frac{tg^2 \theta_0}{k^2} - 1}$, because $\cosh \psi$ then is $= tg \theta_0 : k$. At the upper limit everything disappears, because then $\psi = 0$. (Besides, the terms with odd powers of ψ still contain the factor $\sinh \psi$, which now likewise becomes $= 0$, because $\cosh \psi$ becomes $= 1$ at the upper limit. (Cf. further the text of § 18)). We may, therefore, write:

$$k \int = - \left[\sin \theta_0 \left\{ \frac{\log^2}{2} + \left(\frac{3(1+k^2)}{(1+tg^2 \theta_0)^2} - \frac{2}{1+tg^2 \theta_0} \right) \frac{\log^4}{4} + \text{etc.} \right\} - \right. \\ \left. - \sqrt{\frac{tg^2 \theta_0 - k^2}{1+tg^2 \theta_0}} \left\{ \frac{1}{1+tg^2 \theta_0} \frac{\log^3}{6} + \left(\frac{15(1+k^2)}{(1+tg^2 \theta_0)^3} - \frac{12(1+k^2)+6}{(1+tg^2 \theta_0)^2} + \right. \right. \right. \\ \left. \left. \left. + \frac{4}{1+tg^2 \theta_0} \right) \frac{\log^5}{120} + \text{etc.} \right\} \right].$$

Let us now introduce the quantity φ , determined by equation (6) of the last paper but one, viz.

$$\frac{\alpha^2}{s^2} \sin^2 \theta_0 = 1 + \frac{M}{\frac{1}{2} \mu u_0^2} = 1 + \varphi,$$

in which, therefore, φ depends on the *temperature* (determined by $\frac{1}{2} \mu u_0^2$). For $1 + tg^2 \theta_0$ we may write $\frac{1-k^2 \varphi}{1+k^2}$, because $k^2(1+\varphi) : (1-k^2 \varphi)$ may be substituted for $tg^2 \theta_0 = \frac{s^2}{\alpha^2} (1+\varphi) : \left(1 - \frac{s^2}{\alpha^2} (1+\varphi) \right)$ with $\frac{s^2}{\alpha^2 - s^2} = k^2$. For $tg^2 \theta_0 - k^2$ we find $k^2(1+k^2)\varphi : (1-k^2 \varphi)$, so that we get:

$$k \int = - \left[\frac{k}{\sqrt{1+k^2}} \sqrt{1+\varphi} \left\{ \frac{\log^2}{2} + \frac{(1-k^2 \varphi)(1-3k^2 \varphi)}{1+k^2} \frac{\log^4}{24} + \text{etc.} \right\} - \right. \\ \left. - k \sqrt{\varphi} \left\{ \frac{1-k^2 \varphi}{1+k^2} \frac{\log^3}{6} + \left(\frac{(1-k^2 \varphi)^2 (9-15k^2 \varphi)}{(1+k^2)^3} - \right. \right. \right. \\ \left. \left. \left. - \frac{(1-k^2 \varphi)(8-12k^2 \varphi)}{1+k^2} \right) \frac{\log^5}{120} + \text{etc.} \right\} \right]$$

in which

$$\log = \log \left(\frac{tg \theta_0}{k} + \sqrt{\frac{tg^2 \theta_0}{k^2} - 1} \right) = \log \frac{\sqrt{1+\varphi} + \sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2 \varphi}}.$$

Let us now examine, what are the limiting values to which the found integral approaches at high temperatures, and at low temperatures (φ near $\varphi_0 = 1 \cdot k^2$).

At *high* temperatures ($\varphi = 0$) \log draws near to $\log 1 = 0$, so that all the terms with high powers of \log are cancelled by the

side of the first term, and besides the whole part with $k\sqrt{\varphi}$ disappears. That in this case only the first term with \log^2 remains, follows also from this that $\tan \theta_0 = k^2(1+\varphi):(1-k^2\varphi)$ approaches k for $\varphi = 0$, so that in case of equality of the limits of the original integral the factor $k \cos h\psi : \sqrt{1+k^2 \cos^2 h\psi} = k : \sqrt{1+k^2}$ does not change between them (with respect to the \log that becomes 0 at both the limits), and can accordingly be brought outside the integral sign.

At low temperatures (but higher than the limiting temperature T_0 , determined by $\varphi_0 = 1:k^2$) the whole second part of $k \int$ will again disappear in consequence of the factor $1-k^2\varphi$, which approaches 0, whereas of the first part again only the first term with \log^2 remains. In this case $\cos h\psi = \tan \theta_0 : k = \infty$ at the lower limit, and the factor of $\psi d\psi$ in the integral can again be placed outside the integral sign at this limit, which now prevails since the \log becomes infinite there. At the other limit the \log is namely $= 0$.

With close approximation we may, therefore, write (n has been written for $k : \sqrt{1+k^2} = s : a$):

$$k \int = -\frac{1}{2} n \sqrt{1+q} \log^2 \frac{\sqrt{1+q} + \sqrt{(1+k^2)\varphi}}{\sqrt{1-k^2\varphi}},$$

with neglect of all the terms with higher powers of \log . Only at intermediary temperatures the omitted part can have any influence — but the difference brought about by this might possibly be made to disappear entirely on a somewhat modified assumption concerning $f(r)$ between a and s (see § XVI).

C. The quantity a for $\varphi = \varphi_0 = 1:k^2$. (addition to § XX).

The original integral was (cf § 16):

$$a = \frac{1}{2} \times (b_g)_\infty a \times \frac{2a^4}{s(a^2-s^2)} \int_s^a \int_0^{1/2\pi} \frac{r(-f'(r))dr \times \sin \theta d\theta}{\sqrt{1 - \frac{a^2}{r^2} \sin^2 \theta + \varphi f(r)}}.$$

We may also write for the integral:

$$\int_s^a \int_{1/2\pi}^0 \frac{r^2(-f'(r)) dr d(a \cos \theta)}{\sqrt{r^2 \varphi f(r) - (a^2 - r^2) + a^2 \cos^2 \theta}} = \frac{1}{a} \int_s^a r^2(-f'(r)) dr \log \left(\frac{a}{q} + \sqrt{1 + \frac{a^2}{q^2}} \right),$$

when $r^2 \varphi f(r) - (a^2 - r^2) = q^2$ is put. When $f(r)$ is generally $= \frac{g^t}{r^t}$, so that this duly becomes $= 1$ for $r = s$, then $-f'(r) =$

$\frac{t s^t}{r^{t+1}}$ and $q^2 = \frac{\varphi s^t}{r^{t-2}} - (a^2 - r^2)$. Hence we now have:

$$a = (b_g)_\infty \alpha \times \frac{t a^3 s^{t-1}}{a^2 - s^2} \int_s^a \frac{dr}{r^{t-1}} \log \left(\frac{a}{q} + \sqrt{1 + \frac{a^2}{q^2}} \right),$$

in which the quantity q for the lower limit passes into $\varphi s^2 = (\alpha^2 - s^2)$, which becomes $= 0$ for $\varphi = \frac{a^2 - s^2}{s^2} = \frac{1 - n^2}{n^2} = \frac{1}{k^2}$ as before. The value of a will, therefore, again approach to *logarithmically infinite* for $\varphi = \varphi_0 = 1/k^2$. This is, accordingly, entirely independent of the exponent t in the assumed law of force $f(r) \propto r^{-t}$.

Physiology. — "*On the Peripheral Sensitive Nervous System.*"

By Dr. G. C. HERINGA. (Communicated by Prof. J. BOEKE).

(Communicated in the meeting of February 23, 1918).

When we endeavour to summarize our knowledge of the peripheral sensitive nervous system, which is a time-consuming experience as it involves the perusal of an enormous number of periodicals, we shall find amidst a mass of controversial matter a number of facts received by various controversialists, which, when put together, make up a gratifying whole.

In the neurological clinic the doctrine of neurons is still all but paramount, but in the neuro-anatomic literature it is quite a different thing. There, in spite of this same doctrine of neurons, experiences come to the front pointing to the existence of a very extensive continuous retiform structure of sensory nerves close to the periphery. As has been insisted upon by APATHY there exists a highly delicate texture of anastomotic nerve-fibers close under the surface of the body of invertebrates. This view has hardly been disqualified. It is now getting more and more evident that such a network is also to be found in vertebrates.

Many data regarding the "*rete amielinica subpapillare*" we owe especially to RUFFINI and his school, who based upon them his theory of the "*circuito chiuso delle neurofibrille*." According to the descriptions given by RUFFINI himself, the fibers of this network spring from different sources:

1. end-branches of the ordinary medullated fibers;
2. ultraterminals of endorgans;
3. sympathetic fibers;
4. ultraterminals of fibers belonging to the TIMOFEEV-system.

From all sides (BOTEZAT, LEONTOWITCH, PRENTISS, SFAMENI, DOGIEL) much evidential matter tending in the same direction, has been brought forward, so that no room is left for any doubt as to the principal facts, though there remains some difference of opinion regarding the components of the network, and though several inquirers will not go the length of subscribing to all the inferences of RUFFINI's "*teoria unitaria*."

Two recent publications from the Italian school seem to me to be

interesting in this connection. STEPHANELLI¹⁾ describes an extensive network of nerve-fibers, which he found in the skin of reptiles. This network built up of non-medullated fibers is easily distinguishable from the familiar subepithelial *plexus*, which lies deeper and in which only an interlacement of nerve-fibers, for the greater part still medullated, takes place. The relations of the non-medullated network to the subepithelial plexus are also described minutely by him. In the former, which spreads diffusely as a true network of nerves in the skin, he describes by the side of very few other endings an "organo di senso in stato diffuso," a conception which is the more plausible since the network is immediately connected with an intrapapillary extension of the same nature.

Here lies the link that joins STEPHANELLI's publication to that of VITALI.²⁾

VITALI examined the skin of the nail-bed also after RUFFINI's galvanic chloride method. His results correspond completely with those of similar researches by RUFFINI and others. In succession he describes the presence of many free endings easy to differentiate by the very melodious Italian names: gomitoli, alberelli, espansioni ad arvoiticciati, fiocchetti papillari, grappoli, and also of RUFFINI's MEISSNER's and VATER-PACINI's corpuscles. The principal interest now hinges about the fact that he lays particular stress upon the occurrence of anastomoses between the terminals reciprocally and upon their contact, as a whole, with the rete amyelinica subpapillare, therewith emphasizing the importance attached by RUFFINI long since to the ultraterminals as expounded in his *teoria unitaria* previously mentioned.—Finally VITALI comes to the conclusion that all those terminals together with the rete subpapillare form one connected amyelinic meshwork. When following up the Italian school a little further, we shall see that this meshwork must be placed on a level with STEPHANELLI's diffuse network. Then also the various endorgans of the higher vertebrates will be found to be points of differentiation amidst less developed surroundings. "Eche cos'alt sono," as Simonelli puts it rhetorically, "quello che noi denominiamo espansioni, se non il condensarsi in punti limitati di un simile reticolo diffuso periferico: in altri termini se non punti nodosi

¹⁾ AUGUSTO STEPHANELLI. Nuovo contributo alla cognoscenza della espansione sensitiva dei Rettili e considerazioni sulla tessitura del sistema nervoso periferico. Intern. Monatschrift. f. Anat. u. Phys. XXXII 1916. — Sui dispositivi microscopici della sensibilità cutanea e nella mucosa orale dei Rettili. (Ibid. XXXII 1916).

²⁾ G. VITALI. Contributo allo studio istologico dell'unghia. Le espansioni nervose del derma sotto ungueale dell'uomo. (Ibid. XXXII 1915).

maglie piu serrati di una rete generale, che intimamente involge e compenetrà i tessuti, per meglio localizzare e precusare gli stimoli periferici?"

Thus, according to this view an unbroken series of anastomoses must be traceable in numerous varieties of free endings from the rete amielinica on the one side to the tactile corpuscles inserted in a rete intrapapillare on the other.

It would perhaps be premature to consider this highly pregnant hypothesis as proven. Still, undoubtedly it is equally true that anyone who will take the trouble to look into the literature, will find attestations from other authors also pointing unmistakably in the same direction. It is evident that the border-lines demarcating the various forms of end-organs, classified into various-groups, are by no means established. Nearly coeval with the study of the end-organs itself are the efforts to establish a phylogenetic pedigree of the various end-organs, in which the intricate forms are reduced to more primitive types (MERKEL, KRAUSE, and others). Certain it is also that the more forms are brought to light by modern researchers, the more the border-lines between the various groups are fading out.

With this we are impressed forthwith when looking at the illustrations accompanying the several publications (see e.g. CECCHERELLI ¹⁾ v. D. VELDE). ²⁾ The leading modern authors (BOTEZAT, DOGIEL, SFAMENI and followers of RUFFINI) endeavour to demonstrate anastomoses between the various endings. DOGIEL ³⁾ says in his article about nerve-endings in the external genitalia: "Wenn wir die Beschreibung der Nervenendigungen in den verschiedenen Nervenapparaten, den Genitalkörperchen, den Endkolben und den Meissner'schen Körperchen, welche in der Haut der äusseren Genitalorgane gelegen sind, vergleichen, und zugleich die beigegebenen Zeichnungen betrachten, so müssen wir zu dem Schluss kommen, dass zwischen ihnen kein wesentlicher Unterschied besteht".

SFAMENI ⁴⁾ also describes the relationship between the genital corpuscles and KRAUSE's end-bulbs, GOLGI-MAZZONI's corpuscles and VATER-PACINI's corpuscles on the one side and RUFFINI's corpuscles on the other.

BOTEZAT ⁵⁾ has written a long and comprehensive paper on the system and the interrelationship of the nerve-endorgans.

¹⁾ Intern. Monatschr. XXV 1908.

²⁾ Intern. Mon. XXVI 1909.

³⁾ Arch. Micr. Anat. XLI.

⁴⁾ Arch. di fisiol. I 1904.

⁵⁾ Zeitsch. Wiss. Zool. LXXXIV. 1906.

But what seems to me to be more important than all this, as it falls in with RUFFINI's views, is that also the border-lines between the corpuscles and the "free" endings are gradually falling away. Here the only differential diagnostic is whether or not a capsule is present. The same characteristics of the nerve-fibers, of the supporting tissue, "tactile-cells" or whatever name may be given to the cells found in the endorgans are equally peculiar to either group of end-organs. This may be gathered from the illustrations and the descriptions in all papers. BOTEZAT makes particular mention of this, adding that a capsule round a nerve-ending is not a question of vital importance for it, either functionally or morphologically. On the contrary BOTEZAT very often finds by the side of a capsuled ending its fellow deprived of a capsule. Thus the free "Knäuel" are found side by side with the capsuled "Knäuel" and the bulbs of KRAUSE; side by side with MERKEL's cells GRANDRY's and MEISSNER's corpuscles etc. Moreover BOTEZAT distinguishes all sorts of gradations between the free and the capsuled endings.

In other authors we find the same again. RUFFINI's corpuscles are according to VITALI¹⁾ nothing else but capsuled "alberelli".

DOGIEL²⁾ also speaks of non-capsuled corpuscles of RUFFINI. SFAMENI³⁾ asserts that non-capsuled varieties occur of the same Genital corpuscles, which, as has been observed, are allied to all sorts of tactile-corpuscles. Of MEISSNER's corpuscles there seems to exist a large variety of simple modifications.

SFAMENI describes intermediate forms between MEISSNER's corpuscles and "flochetti papillare" i. e. free endings. DOGIEL's modifications of MEISSNER's corpuscles (RUFFINI calls them DOGIEL's corpuscles) are non-capsuled at the upper-pole from which the axis-cylinders are branching off into free endings. They are types of RUFFINI's "espansioni misti". Other modifications again of MEISSNER's corpuscles (DOGIEL, v. D. VELDE) are characterised by their having a slightly developed capsule and a simplified nervecourse. DOGIEL's "eingekapselte Knäuel" described by him in 1903 as modified MEISSNER's corpuscles must therefore be closely allied to the free endings, perhaps identical with them (see supra). It seems, then, that MEISSNER's corpuscles are, in a higher degree than many other forms, closely allied to free nerve-endings. So when observing the several findings concerning the capsule of these corpuscles, we shall see that LAN-

¹⁾ Int. Mon. XXXI. 1915.

²⁾ Arch. f. Micr. Anat. 1903.

³⁾ l.c.

GERHANS¹⁾ absolutely disproves its existence. He says: "Es besitzt *der Zellhaufen*²⁾ den man Tastkörper nennt, nicht einmal eine eigene umschliessende Membran. Ueberal stossen die peripheren Zellen direct an das umgebende Bindegewebe, und nur nach längerer Einwirkung eines Reagenzes kann es vorkommen, dass das starre Aussehen der Bindegewebsschichten eine eigene Membran vortäuscht".

Likewise ROUGET, TAFANI, IZQUERDO, HOGGAN, LEONTOWITCH absolutely deny the existence of a capsule. MEISSNER, RENAUT, KRAUSE, WOLFF, KOLLMAN and LEFEBURE consider it as a single endothelial membrane. LEFEBURE³⁾: "une simple lame conjoncture doublée sur une face profonde par un feuillet endothelial". From all this it follows that the hypothesis brought forward by DOGIEL, RUFFINI, THOMSA and KOLLIKER that the corpuscles are provided with a true lamella-capsule, is hardly tenable. The very gradations (and they are many) between MEISSNER's corpuscles and the free endings go far to substantiate a priori the opinion of LANGERHANS, who appears to have studied the organs under consideration thoroughly. They also support BOTEZAT's view when he puts MEISSNER's corpuscles on a level with the complicate, non-capsuled MERKEL's corpuscles. In virtue of my personal inquiry I incline to LANGERHANS's view, as will appear lower-down.

Finally let us bestow consideration upon the problem of the genetic connections between the free endings and the tactile bodies with the subpapillary network.

If we confine ourselves to the more modern authors, we mention the names of BETHE, PRENTISS, BOTEZAT, LEONTOWITCH, SFAMENI and DOGIEL⁴⁾, who have, all of them, discussed more or less minutely the subepithelial network and its connections with the nerve-endorgans.

BOTEZAT differs from the other investigators in that he considers the network to be independent of tactile corpuscles. This follows from his opinion that the rete amielinica, is built up of fibers of the so-called 2^d sort⁵⁾. But for the rest, he sides with the Italian School,

1) Arch. f. Micr. Anat. IX 1873.

2) The italics are mine.

3) Revue gen. d'histol. 1909.

4) BETHE. Allgemeine Anat. und Phys. des Nervensystems. Leipzig 1903

PRENTISS. Journ. of Comp. neur. XIV 1904.

BOTEZAT l.c.

LEONTOWITCH Int. Mon. XVIII 1901.

SFAMENI, DOGIEL l.c.

5) Medullated fibers losing their myelin already in the nerve-trunk. It seems doubtful whether these fibers are still to be considered as a separate group.

our starting point, when in speaking about certain free endings, he says that through anastomoses they form a widely spread end-structure, "welcher in der Form eines im allgemeinen weitmaschigen varikösen Netzes von weithin ausgebreiteter Ausdehnung erscheint", which continues into the papillae, and there adheres to ordinary medullated fibers. He looks upon this nerve-complex as a "für sich bestehender sensibeler Apparat der Lederhaut". He finds it again in fishes and amphibia, so it is beyond doubt that he describes the very network which STEPHANELLI discusses in his publication.

DOGIEL, an authority on end-organs, concurs with RUFFINI that the lateral branches of the free papillary endings blend with the rete amielinica: "Wie aus dem mitgeteilten hervorgeht, so hat das aus Marklosen Aestchen und Faden zusammengesetzte subpapilläre Nervengeflecht, die uneingekapselte Nervenknäuel sowie die Schleifenförmig gebogene Bündel und das intrapapilläre Fadennetz einen und denselben Ursprung". Also the TIMOFEEV fibres of the MEISSNER-corpuscles, which DOGIEL reckons among the sensory system, go to make up according to him, the intrapapillary nerve-complex by means of their ultraterminals.

SFAMENI, though far from adhering to the *teoria unitaria* gives a description of the subepithelial plexus and of its connection with tactile corpuscles and free endings, that accords fairly with RUFFINI's. Nor is it on the whole contradicted by PRENTISS and LEONTOWITCH in their publications respectively of *Rana* and the human skin.

It surely will not do to ignore the many differences between the various authors, differences in theoretical conception, in appreciation and in interpretation of their observations. Opposed to DOGIEL, who still holds that interlacement of the fibers is the fundamental principle governing the structure of the network, are BOTEZAT, BETHE, RUFFINI, LEONTOWITCH, and SFAMENI, who are convinced of the fusion of the fibers. PRENTISS wavers. It is a fact that the network is built up of sensitive fibers. However, the question whether also sympathetic elements are fused with it, is as yet unsettled. This depends in some degree on the doubtful character of the TIMOFEEV fibers. Still, though the origin of the sensory part of the network is still uncertain, there is no denying that, also in this respect, observers concur more and more. As we observed before BOTEZAT considers the whole network to be made up of anastomotic free nerve-endings. DOGIEL also looks upon them as the principal components, but according to him also ultraterminals of the TIMOFEEV system of the tactile corpuscles unite with it. SFAMENI believes there is *also* some connection with the genital corpuscles; LEONTOWITCH, BETHE, and PRENTISS assume an

immediate connection of the network with the free endings as well as with corpuscles. All these authors, though theoretically far removed from RUFFINI's neurogenetic conceptions, have brought forward a number of facts corresponding satisfactorily with those insisted upon most emphatically by the Italian school.

In short there is in the literature about the subject a tendency towards the hypothesis that there is, generally speaking, interconnection and coherence in the whole peripheral sensory nervous system.

It is these facts, derived from the literature, that enhance the significance of recent personal studies made by the BIELSCHOWSKY method on the sensory nerve-endings.

The BIELSCHOWSKY method differs from the methylene blue- and the gold-chloride method in that it affords another view of the problems. It does not present those typical appearances, which, when comparatively slight magnifications of rather thick sections are examined, yield a clear survey of the relations. Its efficiency lies in the fact that when preparations counterstained in haem. eosin, are examined under a microscope of the highest power, it brings out in strong relief the relations between the fibrils and their surroundings.

Along this totally different path I arrived at conclusions which, as I hope, will contribute to lend support to the hypothesis that the MEISSNER corpuscles are more related to the free endings than is commonly believed.

In a paper read at last year's Congress for Physics and Medicine at The Hague (1917) (see also: Verslagen Kon. Ak. v. Wetensch. 27 April 1917) I recorded some morphological data, hitherto unknown, concerning the structure of the axis-cylinder. In that paper I set forth that, when tracing an ordinary nerve-fiber from centre to periphery, the following changes in the structure are to be observed in a transverse section. First we find in the medullary sheath the axoplasm, which (in a transverse section) seems to be vacuolar in structure and embraces the neurofibrils in the protoplasmatic septa between the vacuoles. As known, the medullary sheath is surrounded by the protoplasmatic sheath of SCHWANN with its nucleus. More towards the periphery the medullary sheath splits up into several tubes. The always vacuolar axoplasma material with its fibrils spreads over the daughter medullary sheaths. Together they remain embedded in one undivided protoplasmatic mass, which must be considered as a continuation of the sheath of SCHWANN. Still further towards the terminus of the course of the nerve the medullary sheaths disappear from the section, so that the neurofibrils lie free in the protoplasmatic envelopment which, now being of vacuolar structure like

the primitive axis-cylinder, must be assimilated to the sheath of SCHWANN blended with the axoplasm. These formations are seen to get thinner and thinner and their meshes to get ever wider according as they approach the terminus of the nerve. To all appearance they ultimately blend or unite with the connective tissue plasmoderms in which we find the neurofibrils in the ultimate tract of their course¹⁾.

At first I was disposed to think that the described vacuolar dissolution of the axis-cylinder was characteristic of the so-called free nerve-endings, because I saw the medullated nerves force their way into the MEISSNER corpuscles without having undergone any modification.

I can go a step farther this time, and assert on the basis of a profound investigation of MEISSNER's corpuscles that the axis-cylinders inside these corpuscles pass through precisely the same disintegration process, previously described by me for the so-called free nerve-endings, and just now designated as a vacuolar dissolution.

Whereas nowadays it is maintained by many inquirers that the axis-cylinder loses its medullary sheath, before it enters into the corpuscles, I side with ENGELMANN²⁾, LANGERHANS, FISCHER³⁾ KEY—RETZIUS⁴⁾ and LEFEBURE⁵⁾, having been able to ascertain, in preparations treated with Osmic acid, that the medullary sheath, just as the sheath of SCHWANN, is prolonged into the intracorpuseular course of the nerves. Moreover my preparations also proved distinctly that those medullary sheaths split up inside the sheath of SCHWANN exactly as has been indicated above.

I hold with LEFEBURE that most likely the fact that the Osmium method has been abandoned for the modern fibril staining methods, is responsible for the erroneous opinions about the presence or the absence of medullary sheaths, prevailing in the neurological literature.

As to the sheath of SCHWANN, it goes without saying that I must contest the hypothesis that it passes into the formation of the capsule, since to me it is an intrinsic part of the lemmoblastic sheath. (DOGIEL and others⁶⁾). My preparations, which are well impregnated and of good fixation also enable me to ascertain the fate of the axiscylinders

¹⁾ Cf. J. BOEKE. Studien zur Nervenregeneration I, Verh. Kon. Ak. v. Wet. A'dam 2e Sectie Deel, XVIII n^o. 6.

²⁾ Zeitschr. Wiss. Zool. XII 1863.

³⁾ Arch. f. Mikr. Anat. XII.

⁴⁾ Arch. f. Mikr. Anat. IX 1873.

⁵⁾ Revue génér. d'histologie 1909.

⁶⁾ With more justice LANGERHAUS, KRAUSE and others assert that the sheath of SCHWANN passes into the inner capsule of the corpuscles.

inside the MEISSNER corpuscles. For among the cells filling up the core of the MEISSNER-corpuscles we find many of the same vacuolar non-medullated nerve-sections, which we have described, with the fibrils, scattered over the spongy protoplasm.

Now it was but another step to establish in well-chosen objects that those vacuolar axis-cylinders maintain their course in the cells of the core itself. In tangential sections we were in a position to observe with absolute certainty that from the axis-cylinder the fibrils pass *into* the protoplasm of those cells, where they may aid in making up a regular network of the fine fibrils, and where, as a continuation of the vacuolar structure of the axis-cylinder in transverse section, a reticular protoplasm serves as a substratum to the neurofibrils. Just as I observed previously in the corpuscles of GRANDRY, I saw also here a similar diffuse expansion of the network over the cell-protoplasm, as well as the mechanical traction phenomena between protoplasm and fibril-system, so that my interpretation leaves hardly any room for doubt. It is beyond all question that the core cells are indeed parts of the nerve-course itself; consequently it fits in with my view ¹⁾ to term them lemmoblasts *together with* the other elements, building up the course of the nerve. The fibrillar networks described, are by no means terminal. As a rule the fibrils are seen to unite again and pursue their way as a new axis-cylinder. This is an additional argument for classing those cells among the structural elements of the nerve-course itself. In this way I came to the conclusion that *the entire MEISSNER corpuscle is built up of compact lemmoblast cords in structure completely similar to the free nerve-endings*. Now this appears to me to be an important conclusion, the more so when correlated with the above data regarding the connection between the tactile corpuscles and the free endings, as discussed in the literature.

In conclusion I will impart that in the MEISSNER corpuscles I found hardly anything that reminded me of a capsule, certainly not a fine fibrillary texture proper, still less a lamellar system. The enveloping connective tissue is rather of a loose spongy structure. I found in it vacuolar nerve-sections as well as "free" fibrils invested in the plasmoderms. I often despaired that the contours of MEISSNER-corpuscles are very indistinct. Especially in the tactile balls of the cat's paw I rarely found typical MEISSNER corpuscles; often, however, in the papillary connective tissue I found detached groups

¹⁾ Cf. G. C. HERINGA. Le développement des corpuscules de GRANDRY et de HERBST (Arch. néerl. des Sc. Exactes et nat. Serie III B. tome III 1917).

of nerve-sections of the familiar appearance in various sizes. Together they presented precisely the appearance of a transverse section of a MEISSNER corpuscle. Only by studying serial sections it can be ascertained whether we have to do with a MEISSNER corpuscle or rather with some detached axis-cylinders of free endings. Such forms, which must no doubt be classed as modified MEISSNER corpuscles, are in my judgment, as many proofs of the close relationship there is indeed between tactile corpuscles and free endings.

My conclusions, therefore, are the following:

1. the cells found by all inquirers¹⁾ except DOGIEL in the MEISSNER corpuscles are elements of the nerve-course itself, lemmoblasts, as I have endeavoured to demonstrate for GRANDRY-corpuscles.

2. As to structure and behaviour, the nerves in the MEISSNER-corpuscles correspond exactly with those of the so-called free-endings.

3. so that it is very likely that the terminal branches of the MEISSNER corpuscles (ultraterminals) form one connected whole with the free papillary endings.

¹⁾ THOMSA. LANGERHANS, RANVIER, MERKEL, KRAUSE, LEONTOWITCH SPAMENI, RUFFINE, LEFEBURE, VAN DE VELDE and others.

Astronomy. — “*On the Parallax of some Stellar Clusters*” (Second communication). By Dr. W. J. A. SCHOUTEN. (Communicated by Prof. J. C. KAPTEYN).

(Communicated in the meeting of February 23, 1918).

In a former communication it was shown, how it is possible to determine the parallaxes of stellar clusters from the numbers of stars of determined magnitude in the clusters by means of the luminosity curve of KAPTEYN. The calculation was performed for *Messier 3* and *h and χ Persei*. Now the same method is used in order to determine the parallax of some other clusters.

The Small Magellanic Cloud.

H. S. LEAVITT. 1777 Variables in the Magellanic Clouds *Annals Harvard Observ.* Vol. 60, N^o. 4.

A preliminary catalogue containing 992 stars of the Small Cloud and 885 of the Great Magellanic Cloud. The places of 28 stars of catalogues in the neighbourhood of the Small Cloud are also given.

We counted a number of stars and estimated their diameter on a photographic plate, taken at the Harvard Observatory. For orientation we used the catalogue-stars the position of which Miss LEAVITT communicates. In order to reduce the estimates of diameters to magnitudes, we

1^{stly} counted an area of 1000 \square' without the Cloud, and determined from the numbers of stars of every magnitude the magnitude corresponding to every diameter by means of *Publ. Gron.* N^o. 27, Table IV,

2^{ndly} we estimated the diameters of 142 variable stars, the magnitudes of which occur in LEAVITT's catalogue and which are equally distributed over the Cloud, and we have compared these with the mean magnitude, i. e. the average of maximum and minimum, given by Miss LEAVITT,

3^{dly} we have estimated the diameters of the catalogue-stars mentioned above and compared these with the magnitudes in the C. P. D. and the A. G. C.

Finally the magnitude corresponding to each diameter was determined from all these data by graphical smoothing.

We counted an area of $240 \square'$ in the Cloud. The results are given in the table below. In it N_m represents the number of stars from the brightest star to the magnitude under consideration.

Diameter	Magn.	N_m	Magn.	N_m	A_m	Normal	Cluster
25	10.1	1	10.0	1	1	1	—
22	10.4	2					
20	10.7	4	10.5	4	3	—	3
17	11.2	5	11.0	5	1	1	—
16	11.3	6					
15	11.5	13	11.5	16	11	1	10
14	11.7	19					
13	12.0	26	12.0	33	17	1	16
12	12.2	39					
11	12.5	55	12.5	60	27	3	24
10	12.8	87					
9	13.1	122	13.0	122	62	4	58
8	13.4	172					
7	13.7	220	13.5	202	80	5	75
6	14.0	282	14.0	305	103	8	95
5	14.3	358					
4	14.6	467	14.5	438	133	11	122
3	14.9	568					
2	15.2	810	15.0	655	217	16	201
1	15.6	1104	15.5	1064	409	22	387
0	16.0						

The normal number of stars is calculated for the galactic latitude $b = 10^\circ$. As we always use the luminosity curve for whole numbers as values of the argument m and have counted here by half magnitudes, we may deduce from the above table the following two tables:

m	A_m	A_{m+1} / A_m	m	A_m	A_{m+1} / A_m
12.0	33	3.24	11.5	18	3.39
13.0	107	1.81	12.5	61	2.48
14.0	194	2.35	13.5	151	1.79
15.0	455		14.5	270	

The irregular progress of the quotients $\frac{A_{m+1}}{A_m}$ is partly to be explained from our counting only a small part of the cluster.

These numbers give the following values for the parallax:

I	$\pi = 0''.0004$
II	4
III	7
IV	13
V	11
VI	4
Mean	$\pi = 0''.0007 \pm 0''.0002$

From 142 cluster variables that are equally distributed over the cluster and occur in Miss LEAVITT's catalogue, we find for the mean apparent magnitude of these stars $\bar{m} = 14.67$ and $5 \log. \pi = -15.77$, so that the mean absolute magnitude of these δ Cephei variable stars with a short period is $\bar{M} = 3.9$ according to our determination of the parallax.

From some δ Cephei variable stars with a long period HERTZSPRUNG found for the parallax of the Small Magellanic Cloud $\pi = 0''.0001$.

Praesepe.

$$\alpha_{1900} = 8^h 34^m 39^s, \delta_{1900} = +20^\circ 1', b = +33^\circ, l = 169^\circ.$$

Dr. P. J. VAN RHIJN. The proper motions of the stars in and near the Praesepe cluster, Publ. Groningen, N^o. 26, 1916.

The measurement of 2 sets of plates, taken at Potsdam. The catalogue contains 531 stars. The diameters were reduced to photographic magnitudes by means of standard magnitudes, determined by HERTZSPRUNG. The probable error of a magnitude is $\pm 0^m.12$.

We have derived the visual magnitudes from the photographic ones in the same way as VAN RHIJN did on page 10 of his publication. The correction was determined from the value of the colour

index for each *apparent* magnitude that is based on PARKHURST and SEARES' researches. To this objections may be raised, as for the cluster stars we have to deal with *absolute* magnitudes. As, however, the relation between colour index and luminosity is only inaccurately known as yet and as moreover, it cannot be decided whether a given star belongs to the cluster or not, VAN RHIJN's method is the only one possible. VAN RHIJN found that the photographic magnitudes (international scale) between $m = 7.5$ and $m = 14.5$ wanted a constant correction $-0^m.5$ for reduction to the visual Potsdam scale. Therefore by a correction $-0^m.7$ they are reduced to the Harvard scale.

The number of cluster stars of each magnitude we find by diminishing the numbers counted by the normal number, which was determined for this cluster from Publ. Gron. N°. 27, Table V.

It appears at once that the Praesepe stars have faint luminosities. The declivities that we observe in the frequency curve of the magnitudes, are partly smaller than the smallest declivity occurring in KAPTEYN's luminosity curve. That is why we could make only four determinations of the parallax notwithstanding the great interval of magnitudes. These give

$$\pi = 0''.024 \pm 0''.004.$$

This parallax is considerably greater than the one which we found for other stellar clusters.

Messier 52.

N. G. C. 7654; $\alpha_{1900} = 23^h 19^m.8$, $\delta_{1900} = +61^\circ 3'$, $b = +1^\circ$; $l = 81^\circ$; class: D3.

F. PINGSDORF. Der Sternhaufen in der Cassiopeia. Diss. Bonn. 1909. Measurements of three plates, taken by KÜSTNER. The catalogue contains 132 stars up to $15^m.0$. The standard magnitudes have been determined by visual observations by means of gauzes of 25 stars by ZURHELLEN.

We find from 4 determinations:

$$\pi = 0''.002 \pm 0''.0003.$$

Messier 46.

N. G. C. 2437; $\alpha_{1900} = 7^h 37^m.2$, $\delta_{1900} = -14^\circ 35'$, $b = +6^\circ$, $l = 200^\circ$; class: D1.

W. ZURHELLEN. Der Sternhaufen Messier 46. Veröffentl. Kgl. Sternwarte zu Bonn, N°. 11, 1909.

Measurements of three plates, taken by KÜSTNER. The catalogue

contains 529 stars. For standard magnitudes 47 stars were used, the brightness of which was estimated by KÜSTNER or determined by means of gauzes by ZURHELLEN.

We find from 4 determinations:

$$\pi = 0''.002 \pm 0''.0001.$$

Messier 37.

N. G. C. 2099; $\alpha_{1900} = 5^h 45^m.8$, $\delta_{1900} = +32^\circ 31'$, $b = +4^\circ$, $l = 145^\circ$; class: D 1.

J. O. NORDLUND. Photographische Ausmessung des Sternhaufens Messier 37. Inaug. Diss. Upsala 1909, Arkiv för Matematik, Astronomie och Fysik, Band 5, N^o. 17.

Dr. H. GIEBELER. Der Sternhaufen Messier 37. Veröffentl. Kgl. Sternwarte zu Bonn, N^o. 12, 1914.

NORDLUND measures 4 plates and gives the places and magnitudes of 842 stars. The magnitudes are derived from the diameters according to the formula of CHARLIER by means of 214 standard magnitudes that have been determined photometrically by VON ZWEPPEL. Many of the bright stars of the cluster are red (colour index $> 0^m.7$), e.g. some 50 or 70 % of the stars of the 10th magnitude.

GIEBELER discusses 2 plates taken by KÜSTNER and measured by STROBLE. The catalogue contains 1231 objects. The magnitudes have been joined with NORDLUND's scale by comparing those of 450 stars. For the red stars too the photographic magnitude is given.

For our purpose it is a drawback that for the red stars the photographic magnitude is mentioned. This is why the brightest stars, among which many red ones occur, could not be used by us. Excluding these we find from 4 determinations:

$$\pi = 0''.0025 \pm 0''.0004.$$

Messier 36.

N. G. C. 1960; $\alpha_{1900} = 5^h 29^m.5$, $\delta_{1900} = +34^\circ 4'$, $b = +2^\circ$, $l = 142^\circ$; class: D 2.

Dr. S. OPPENHEIM. Ausmessung des Sternhaufens G. C. N^o. 1166. Publ. der v. Kuffner'schen Sternwarte in Wien, Bd. III, pag. 271-307, 1894.

Measurements of three photographic plates. The catalogue contains 200 stars. The magnitudes were derived from the diameters, measured in connection with estimates of visual magnitudes found by Dr. PALISA for the greater part of the stars.

The interval of magnitudes is small. We find from 3 determinations:

$$\pi = 0''.005 \pm 0''.001.$$

20 *Vulpeculae*.

N. G. C. 6885; $\alpha_{1900} = 20^h 7^m.6$, $\delta_{1900} = 26^\circ 10'$, $b = -5^\circ$, $l = 31^\circ$.

H. SCHULTZ. Micrometrisk bestämning af 104 stjernor inom teleskopiska stjerngruppen 20 Vulpeculae. Kongl. Svenska Vetenskaps-Akademiens Handlingar, Bändet 11, N^o. 3, 1873.

The magnitudes have been determined by a photometer in accordance with ARGELANDER'S scale.

A. DONNER und O. BACKLUND. Positionen von 140 Sternen des Sternhaufens 20 Vulpeculae nach Ausmessungen photographischer Platten. Bulletin de l'Acad. Imp. des Sciences de St. Pétersbourg, Série V, Volume II, pag. 77-92, 1895.

Measurements of 2 plates taken by DONNER at Helsingfors. The magnitudes were taken from SHILOV.

M. SHILOV. Grössenbestimmung der Sterne im Sternhaufen 20 Vulpeculae. Bulletin etc. ut supra, pp. 243-251.

The magnitudes of the 140 stars, the position of which was determined by DONNER and BACKLUND, were found by measuring the diameters of the images. As standards those 100 magnitudes were used that SCHULTZ had determined already. SHILOV uses CHARLIER'S formula $m = x - y \log D - zD$. The probable error of a difference $m - m_{\text{SCHULTZ}}$ is $\pm 0^m.25$.

We have not reduced the magnitudes based on ARGELANDER'S scale, to the HARVARD scale, because SHILOV'S magnitudes differ considerably from those of SCHULTZ. We find for the parallax from 7 determinations:

$$\pi = 0''.005 \pm 0''.001.$$

Messier 5.

N. G. C. 5904; $\alpha_{1900} = 15^h 13^m.5$, $\delta_{1900} = +2^\circ 27'$, $b = +45^\circ$, $l = 333^\circ$; class: C3.

M. SHILOV. Positionen von 1041 Sternen des Sternhaufens 5 Messier, aus photographischen Aufnahmen abgeleitet. Bulletin de l'Acad. Imp. des Sciences de St. Pétersbourg, Série V, Vol. VIII, pag. 253-312, 1898.

Measurements of 2 plates, taken resp. by BELOPOLSKY and KOSTINSKY. The magnitudes have been determined in a rather inaccurate manner, viz. by comparing the diameters with the images of stars of 20 Vulpeculae, the magnitudes of which are known.

S. I. BAILEY. Variable Stars in the Cluster Messier 5, Annals Harvard Observ., Vol. 78, Part. II, 1917.

Ninety-two stars are dealt with. For 72 the period is mentioned.

Among these 3 have long periods. Moreover the magnitudes are given for 25 comparison-stars.

In SHILOW's catalogue the magnitudes of 1006 stars are mentioned. The interval of magnitudes is small and the magnitudes are inaccurate. Nor did we succeed in reducing them to a more exact scale by means of BAILEY's magnitudes. We find the results $\pi = 0''.0002$ and $\pi = 0''.0009$; consequently as average value:

$$\pi = 0''.0005^s \pm 0''.0002.$$

According to SHAPLEY the average photogr. magnitude of the variable stars is $15^m.25$ and we found $5 \log. \pi = -16.3$; therefore $M = 15^m.25 - 11^m.3 = 4^m.0$. So we get for the mean absolute magnitude of the variable cluster stars 4.0.

If we determine the parallax from the variable stars with a known period, we find, when making use of HERTZSPRUNG's numbers:

$$\pi = 0''.0002.$$

Messier 13.

N. G. C. 6205; $\alpha_{1900} = 16^h 38^m.1$, $\delta_{1900} = 36^\circ 39'$, $b = +40^\circ$, $l = 26^\circ$; class: C 3.

J. SCHEINER. Der grosse Sternhaufen im Hercules Messier 13, Abhandl. Kgl. Akad. Berlin 1892.

The catalogue contains 823 stars. The magnitudes are uncertain.

H. LUDENDORFF. Der grosse Sternhaufen im Hercules Messier 13. Publ. Astroph. Observ. Potsdam, Bd. XV, N°. 50, 1905.

This catalogue contains 1118 stars. The brightness is not expressed in magnitudes; but the diameters are estimated in 16 "Helligkeitsstufen".

H. SHAPLEY. Studies etc. Second Paper: Thirteen hundred stars in the Hercules Cluster (Messier 13). Contrib. Mt. WILSON Observ. N°. 116, 1915.

The photogr. and photovis. magnitudes of 1300 stars have been determined; but of only 650 stars they have been published. For the statistical investigation 1049 magnitudes and colour indices were used.

We make use of LUDENDORFF's catalogue and we availed ourselves of SHAPLEY's results in reducing the "Helligkeitsstufen" to magnitudes. First we can express the "Stufen" in photographic magnitudes by means of a table in SHAPLEY's work (p. 25, Table VIII) and these may be reduced to photovisual ones by means of the Tables XIV and XVI. No correction is wanted for the difference between the scales of HARVARD and MOUNT WILSON, because the visual Harvard

scale is continued only up to $12^m.0$ and for this magnitude agrees with the MT. WILSON scale.

Now we determine the numbers A_m . For the brightest magnitudes we find then a declivity, which surpasses by far the greatest declivity, found in KAPTEYN's curve. This value, great as it is, may perhaps be explained from the manner, in which the diameters have been reduced to magnitudes. Excluding of these values being undesirable *a priori* and not possible on account of the small interval of magnitudes, we have smoothed the numbers observed by a continuous curve. Then we find from 4 determinations:

$$\pi = 0''.00075 \pm 0''.00006.$$

From SHAPLEY's research (l. c. p. 79) we derive for the mean photographic magnitude of the variable cluster stars which are probably σ Cepheids, $m = 15.2$ and we found $5 \log. \pi = -15.4$, so that according to our determination of the parallax their mean absolute magnitude $= 4.8$ ¹⁾.

From 2 variable stars with known period SHAPLEY (l. c. p. 82) found for the parallax the value:

$$\pi = 0''.00008.$$

Messier 67.

N. G. C. 2682; $\alpha_{1900} = 8^h 45^m.8$, $\delta_{1900} = +12^\circ 11'$, $b = +34^\circ$, $l = 183^\circ$; class: *D 2*.

E. FAGERHOLM. Ueber den Sternhaufen Messier 67. Inaug. Diss. Upsala, 1906.

The catalogue contains 295 stars. The magnitudes were derived from the diameters by means of CHARLIER's interpolation-formula, after the visual magnitudes of 15 stars had been determined photometrically.

H. SHAPLEY. Studies etc. III. A catalogue of 311 Stars in Messier 67, Contrib. MT. WILSON Observ. N°. 117, 1916.

For all stars the fotogr. magnitudes have been determined and also the photovisual ones for all stars within $12'$ of the centre. In this way 232 colour indices were found. SHAPLEY finds a much greater number of back-ground stars than would be expected.

ÖLSSON's catalogue cannot be used on account of the inaccuracy of the magnitudes.

We first make use of FAGERHOLM's catalogue. The magnitudes that are expressed in the *P. D.* scale, are reduced to the Harvard scale by adding a correction $-0^m.2$.

¹⁾ The values of the parallax and the mean absolute magnitude given here, are to be preferred to the preliminary results published in the first communication.

Now we derive from 2 determinations (the interval being only 2 magnitudes):

$$\pi = 0''.001 \pm 0''.0007.$$

According to SHAPLEY (l. c. p. 10) the difference FAG.-MT. W. is constant $= +0^m.24$ and as HARV. = MT. WILSON photovis., we have also: FAG.-HARV. $= +0^m.24$. We have taken FAG.-HARV. $= +0^m.2$, so that the magnitudes used should be correct. Upon closer inquiry, however, the difference FAG.-SHAPLEY appears not to be constant, but to vary with the magnitude. We have determined the errors of FAGERHOLM's scale by comparing the magnitudes of 156 stars, and afterwards we have calculated the numbers A_m for the corrected magnitudes. Now we derive for the parallax from only one determination that can be used:

$$\pi = 0''.002.$$

By telling off SHAPLEY's catalogue we find for the parallax the values $\pi = 0''.001$ and $\pi = 0''.002$. Summing up, we may assume for the parallax of this cluster:

$$\pi = 0''.002.$$

For this cluster SHAPLEY determined the colour indices of *all* the stars, perceptible on the plate within a circle with a radius of $12'$. But here, too, no great value can be attached to a comparison of the distribution of colours, found by SHAPLEY for every M , with SCHWARZSCHILD's table. For it is not certain that all stars up to $13^m.0$ are visible on the plate, and just here the separation of cluster stars and back-ground stars offers great difficulties. According to SHAPLEY the distribution of colours, expressed in percentages of the numbers of stars of determined absolute magnitude, is as follows:

<i>Type</i> \ <i>M</i>	+ 4.0	+ 3.0
<i>B</i>	0	0
<i>A</i>	0	15
<i>F</i>	38	30
<i>G</i>	51	20
<i>K</i>	11	30
<i>M</i>	0	5

Messier 11.

N. G. C. 6705; $\alpha_{1900} = 18^h 45^m.7$, $\delta_{1900} = -6^\circ 23'$, $b = -4^\circ$, $l = 355^\circ$; class: C3¹⁾.

W. STRATONOFF. Amas stellaire de l'écu de Sobieski (Messier 11), Publ. de l'Observ. de Tachkent N^o. 1, 1899.

The catalogue contains 861 stars. From the estimates and measurements of diameters the magnitudes have been derived by means of the Southern B. D.

H. SHAPLEY, Studies etc. IV. The galactic cluster Messier 11, Contrib. Mt. WILSON Observ. N^o. 126, 1916 (A. P. J. Vol. 45, 1917).

For 458 stars the photogr. and photovis. magnitudes have been determined. For statistical research 364 stars were available, after the uncertain magnitudes and the stars upon which the EBERHARD-effect may be of influence had been excluded.

We tell off STRATONOFF's catalogue and we determine the quotients $\frac{A_{m+1}}{A_m}$. It then appears that the magnitudes are too inaccurate and cannot be used.

Now we reduce STRATONOFF's magnitudes to SHAPLEY's scale. In order to do so we compare the magnitudes of 293 stars. The results are given in the table subjoined.

m_{SHAPLEY}	Sh—Strat.	Number of comp. stars
10.0	+ 1.53	30
5	1.94	44
11.0	1.68	38
5	1.39	26
12.0	1.45	11
5	1.21	14
13.0	0.91	50
5	0.80	27
14.0	0.70	53

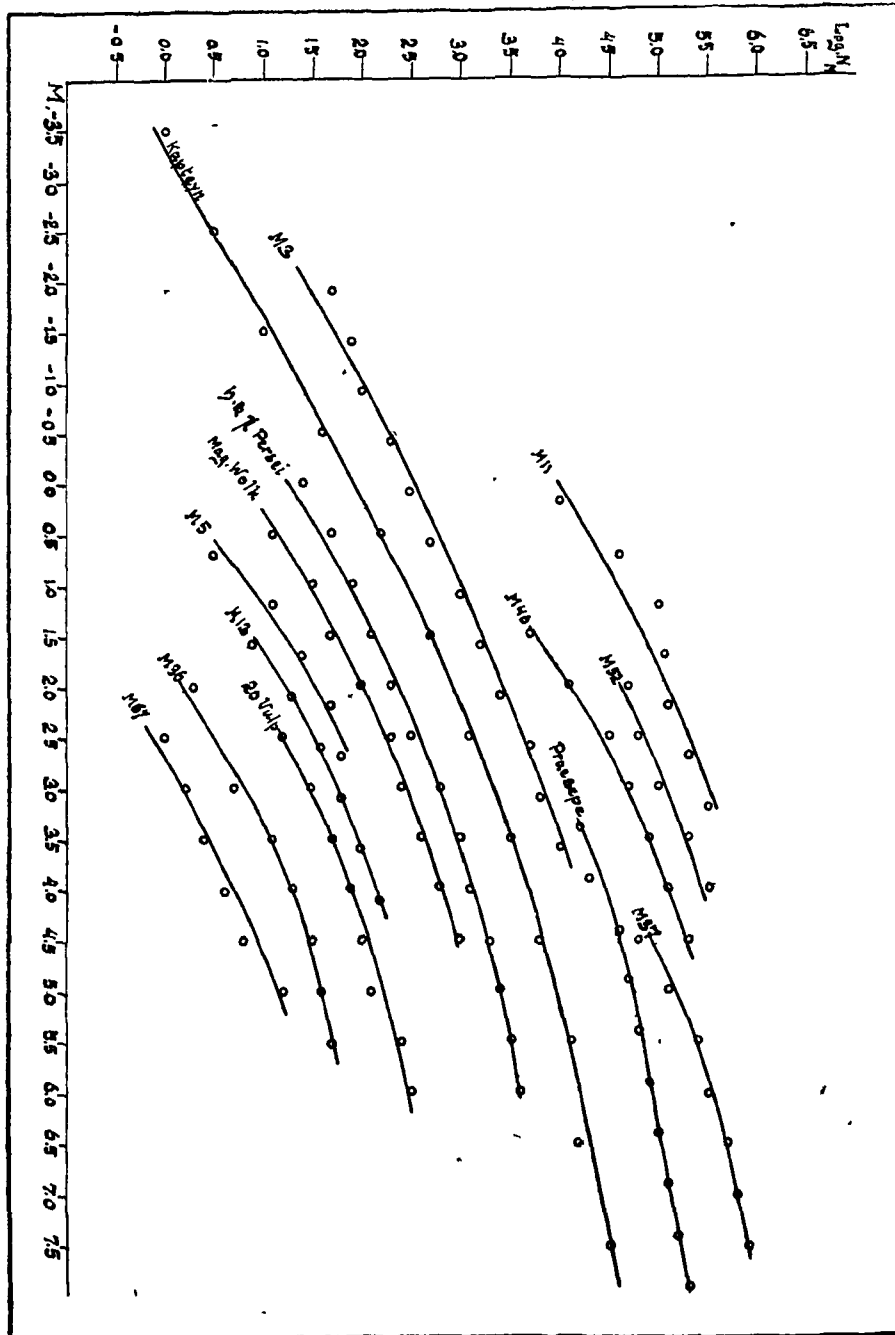
Afterwards we determine by interpolation A_m for the corrected magnitudes. In this way we find for the parallax from 2 determinations:

$$\pi = 0''.00055 \pm 0''.00003$$

¹⁾ SHAPLEY reckons Messier 11 among the open clusters.

The mean parallax of the globular clusters is $0''.0006$ and that of the open clusters (Praesepe excluded) is $0''.003$.

The number of parallaxes, determined at present, is still too small to derive conclusions from them as regards the distribution of clusters in space. Perhaps this will be possible, when we shall have extended



our research to more clusters. It will then also be possible to investigate, how far our results give support to the well-known theory of giant and dwarf stars.

From the figure subjoined it is evident that the luminosity curves of the various clusters greatly resemble that found by Prof. KAPTEYN for the stars in the neighbourhood of the sun. And so this method of determining the parallax, proposed by Prof. KAPTEYN, is justified.

In the graphical representation N_M means the number of stars from the brightest star to the absolute magnitude under consideration. As it is only our purpose to compare the relative frequencies of the various absolute magnitudes, we added in each curve a constant amount to $\log. N_M$.

Amsterdam, December 1917.

Physiology. — *“Experiments with Animals on the Nutritive Value of Standard Brown-Bread and White-Bread.”* By Prof. C. EIJKMAN and Dr. D. J. HULSHOFF POL.

(Communicated in the meeting of April 26, 1918).

Owing to the scarcity of food the old problem has latterly cropped up again whether, instead of baking white-bread, it would not be more practical to make bread of unboltered meal, since through the process of boltering the grain loses 20—30 % of its nutritive value, according to the degree of milling. The modern technique of grinding enables the miller to separate the flour, which contains the constituents of the endosperm or starchy part, nearly entirely from the bran and the germs of the grain.

The current opinion among people that brown-bread is more nourishing than white, is founded chiefly on the belief that brown bread is more satiating and appeases the appetite for a longer period than white bread does. Though this property must not be underrated, it scarcely needs to be pointed out, that it cannot be an index for the content of nutritious matter. The bran (inclusive of the germs) differs from the flour by a smaller amount of starch and more nutritive salts, fat and protein. However it also contains more cellulose, which is all but indigestible for man, and which also renders it difficult for the alimentary canal to utilize the foodstuffs contained in the bran, since they are for the greater part shut up within thick walls of cellulose. This is why many consider the bran to be useless for man, even noxious, and deem it better that only flour should be baked into bread and the bran should be given to the cattle, which can digest cellulose well and return to us the foodstuffs of the bran in the form of flesh and dairy-products. On the other hand it has been argued that this round-about way via the cow, is also attended with great loss, and that, in striking a balance, it will turn out that man gets more food from wheat in the form of brown bread in spite of less digestibility, than from an equal amount of wheat in white bread.

However, it now appears that the problem requires re-consideration, since it has been proved that, besides the foodstuffs alluded to, the bran also contains peculiar constituents, altogether lacking in flour,

that are highly conducive to the building up of the animal body, may be even indispensable for its health and growth, viz. the so-called accessory foodstuffs or vitamins.

Here I refer to a paper read by me (E.) some 20 years ago on a fowl's disease (polyneuritis gallinarum) attended with degeneration of the peripheral nerves and motory disturbances arising from a polished-rice diet, and resulting in death within a few days, unless another diet was had recourse to. When the fowl was fed on unpolished rice, or when polishings were added again to the peeled rice, the disease could be prevented, or, if it had already broken out, it could be cured. It appeared namely, that the rice-polishings contained ingredients which, being diffusible, could be readily extracted with water and possessed the same prophylactic and remedial property as the polishings themselves.

The fowl's disease, which can also be produced in other birds (pigeons, rice-birds) in the manner described, shows in many respects a close resemblance to beri-beri, and the researches by VORDERMAN, and many others after him, demonstrated that much of what was brought forward for the one was also applicable to the other.

It must be especially remembered that what has been said regarding rice, also holds for other kinds of grain. Fowls develop the disease, when fed on bolted meal, but not or exceptionally only when given the whole grain or unbolted meal. In keeping with this is the fact that beri-beri does not only manifest itself where polished rice constitutes the staple diet, but is also observed among a population living chiefly on white-bread (LITTLE).

Also in Holland the tropical beri-beri can break out, as has been proved by the cases that lately occurred among native sailors of the Rotterdam Lloyd, described by KOOLEMANS BEYNEN. It is well-known, moreover, that the so-called Ship beri-beri, a comparatively mild form of the disease, which has been seen from time to time especially on Norwegian ships, is also attributed, on reasonable grounds, to too one-sided and too vitamin-poor a nourishment. Nor is it at all improbable that cases of polyneuritis among men, which do occur every now and then, are in some degree allied to beri-beri.

Fortunately the accessory foodstuffs, playing a part here, occur in many other articles of food, such as peas, beans, potatoes, meat, egg-yolk etc. There need be no fear, therefore, for the immediate appearance of beri-beri, at all events not when foods such as white rice and white-bread are not the principal dish. However, if we bear in mind that, as has been seen from what we said about meat, the relative vitamins form a normal constituent of the animal

body, (not evolved in it but derived from the food), it is but natural that, especially in times of scarcity, a vitamin-poor food should be deleterious to the body, even though not causing actual illness.

Comparative experiments on the nutritive value of brown- and white-bread have repeatedly been undertaken, also when vitamins were not thought of. As early as about seven decades back MAGENDIE observed how a dog, fed exclusively on white-bread, lost flesh, got weaker and weaker, and succumbed after 40 days; another dog, fed on bread made from the whole wheat, kept in good health. Similar results were latterly achieved in HOFMEISTER's laboratory with mice. The evidence from such experiments may be disqualified by contending that the laboratory animals actually starve, because they refuse to eat white-bread much sooner than brown-bread. Those nevertheless who believe in animal instinct will not wholly repudiate the significance of this phenomenon.

We preferred to experiment with fowls, first of all because they react most indubitably upon vitamin-poor food with the typical aspect of polyneuritis and do not succumb under equivocal symptoms; and secondly because when the appetite lessens, they readily submit to forced feeding. Forcible feeding is a method also employed in poultry-yards. Intense inanition may in this way be prevented up to the first indication of the disease, viz. atony of the muscle layer of the crop. This causes a more tardy discharge of the crop, so that the ordinary daily allowance cannot be gone through. The typical weakness in the leg-muscles, reminding so forcibly of a similar disturbance attending beri-beri, generally ensues only after some days, sometimes weeks.

Here we also wish to observe that fowls are no more able to digest the cellulose of the bran than man is. The thick walls of the cells of the so-called aleurone-layer, in which chiefly protein and fat are contained, are left intact in their digestive canal. The vitamins, however, as said above, are easily isolated from the bran. The meal, from which the Standard bread was baked, was composed according to the governmental prescription for the white-bread of 60 % inland wheat- and (or) rye-flour, 10 % American flour and 30 % potato-meal; for brown-bread of 70 % unboltered wheat- and (or) rye-meal, 25 % potato-meal and 5 % grits and (or) pollard. Potato-meal is too pure and, therefore, too one-sided a food. The other nutritive constituents of the potato — protein, salts and also vitamins — get lost in the preparation. They putrefy our public waters. It would have been much more reasonable indeed, to eke bread-meal out with powder from dried potatoes, instead of potato-meal. On the

other hand yeast raises the vitamin-content; it has a protective and curative effect with respect to polyneuritis. An accidental advantage is that during the baking the internal temperature of the dough hardly rises above 100° C. As has been shown by GRIJNS for rice and has been corroborated also by myself for other cereals, vitamins are destroyed by moist heat only at much higher temperatures.

In the writer's laboratory two sets of three fowls have been subjected by Dr. HULLSHOFF POL to feeding-experiments on brown- and white-bread; they were young, strong animals of about the same age (± 2 years) and weight. The best fed animals were taken for the white-bread experiment, their body-weight averaged ca. 1550 grms; that of the brown-bread fowls was ca. 1400 grms. The bread-ration was ca. 100 grms.

The results of the experiments are given in the graphics. S denotes the moment when forced feeding commenced. P that when the typical symptoms of polyneuritis (disturbances in the gait) made their appearance. For purposes of accurate comparison the changes in the body-weight are not expressed in absolute measure, but in percentages of the initial body-weight.

When first studying the whitebread experiments, we shall notice a fall in the body-weight almost immediately, in spite of normal appetite, which fall continued also after we proceeded to forced feeding. At the close of the 11th week the first fowl (III) developed polyneuritis and succumbed after a few days. A second (II) followed a week later. Henceforth it was fed on brown-bread, just as N°. I, which had lost flesh, indeed, but was not yet actually ill. With this diet the diseased animal recuperated and the fall in body-weight was arrested in either of them.

Whereas with a polished-rice diet the fowls develop polyneuritis most often inside of five weeks, not unfrequently even as early as at the end of the 3^d week, this outbreak was considerably retarded in the case of fowls on white-bread. It seems probable that this is due to a protective action of the baker's yeast.

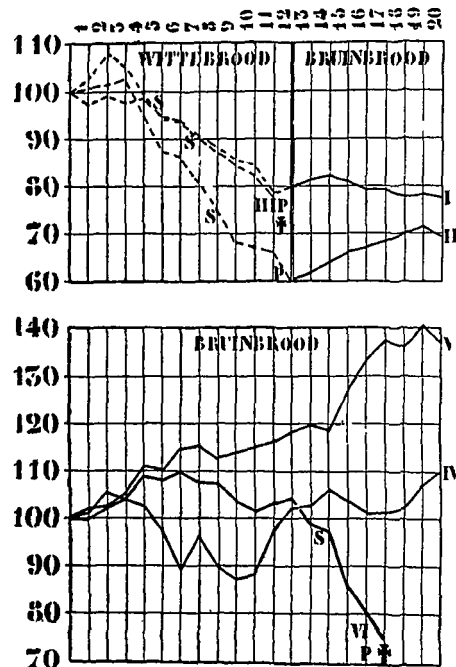
Much more favourable were the results of the brown-bread experiments. N°. IV and V remained perfectly healthy and vigorous up to the conclusion of the experiment, which lasted 20 weeks. They increased in body-weight, N°. V even considerably, so that there was no occasion for forced feeding, although a slight inappetence ensued, as is always the case with a uniform diet.

N°. VI fared worse. For the first fortnight it maintained its original weight, but after this time it lost weight constantly; forced

4*

feeding was of no avail. The animal got anaemic, showed the typical aspect of polyneuritis in the 17th week and died a few days later.

Change in body-weight in percentages
of the initial weight.



Wittebrood = White-bread.

Bruinbrood = Brown-bread.

In resuming it may be allowable to state that brownbread yields undoubtedly more satisfactory results than whitebread. In connection with what we said at the beginning, we believe the same to hold good also for human nourishment. The drawback of partial indigestibility must not be overestimated. Besides, by improvements in the mode of grinding the miller is able to neutralize this drawback by a finer distribution of the bran along the dry or the wet path, or by removing the coarsest and least nutritive outer layers of the grain. This method should henceforth be more generally applied. Nature, as it were, has destined the bran to eke out the flour; it seems unreasonable, therefore, to separate the two and to replace the bran by potato-meal, which last should be admixed only in the second place and preferably in the form of potato-powder. The use of white-bread should be restricted as much as possible.

Foodstuffs that are fit for man, nay that are preferable for human sustenance, must in times of scarcity not be given to the cattle.

The Hygienic Institute of the Utrecht University.

Physics. — “*An indeterminateness in the interpretation of the entropy as $\log W$* ”. By Mrs. T. EHRENFEST-ATANASSJEWA. (Communicated by Prof. J. P. KUENEN).

(Communicated in the meeting of March 23, 1918).

I. A certain quantity of a gas may be given, so large that it may be divided into a great number of portions — great enough for the purpose we are about to discuss — without the usual statistical treatment of the parts losing its value.

Regarding the matter from a thermodynamic point of view we assume:

1. that the entropy of every system strives to attain its maximum.
2. that the entropy of the total mass of gas is equal to the sum of the entropies of the parts.

If in accordance with the kinetic theory, we take the entropy to be the logarithm of the probability of the state of the system, we get the following theses as the analogues of those just given:

1. The state of every system endeavours to approach the greatest probability;
2. The logarithm of the probability of the state of the total mass of gas is equal to the sum of the logarithms of the probability of the states of its parts; or in other words: the probability of the state of the whole is equal to the product of the probability of the states of its parts.

At the same time it may easily be seen that the latter theses are only correct provided the combinations with which we reckon in the determination of the probability of the state of the whole are submitted to certain limitations, which are quite arbitrary *from the combinationary point of view*.

II. We will illustrate this by a simple example, which depends only on the calculus of combinations.

Let us suppose 27 tables, each provided with three holes. In each of the holes a red or a black ball must come to lie. The colour of the ball may be decided by a lottery, in which the chance of drawing a red ball is $\frac{2}{3}$, and of a black ball $\frac{1}{3}$.

In this case for each table separately — if we still distinguish between the three different holes ¹⁾ — the most probable division of the balls is: two red ones and one black one. For this the probability is ²⁾

$$\frac{2}{3} \times \frac{2}{3} \times \frac{1}{3} \times \frac{3!}{2!} = \frac{12}{27}.$$

We must now ask: what is the most probable distribution of the combinations over all the 27 tables? We can here still distinguish between the tables. As the most probable distribution we get that in which on only twelve tables two red balls and one black ball lie, on eight of the others three red ones, on six 2 black ones and one red one, and on the last one three black balls. For this distribution the probability is expressed by

$$W_m = \left(\frac{12}{27}\right)^{12} \cdot \left(\frac{8}{27}\right)^8 \cdot \left(\frac{6}{27}\right)^6 \cdot \left(\frac{1}{27}\right)^1 \cdot \frac{27!}{6! 8! 12!}.$$

On the other hand, the chance that on each of the 27 tables uniformly two red balls and one black ball should come to lie is given by

$$W_u = \left(\frac{12}{27}\right)^{27}.$$

The ratio between the two is

$$\frac{W_u}{W_m} = \frac{12^{27-12} \cdot 6! 8! 12!}{8^8 \cdot 6^6 \cdot 27!},$$

which is very much smaller than 1 ³⁾.

Let us now suppose the number of balls that can lie on a table, and also the number of tables to be greater; the number of different typical possibilities of division on each table separately (varying from all red to all black) then rises, as also the number of ways in which we can find these types of division spread over the collective tables.

The chance of the most probable division for one particular table becomes *smaller*. The probability W_u , that just this division will be found repeated on every table, becomes therefore represented by a high power of a very small fraction.

¹⁾ That is to say, if for a particular combination (e.g. 1 red, 2 black) we count as separate possibilities the cases in which differently coloured balls lie in a given hole.

²⁾ The chance of all three being red is $\frac{8}{27}$, of one red and two black $\frac{6}{27}$, of all three black $\frac{1}{27}$.

³⁾ For $\frac{6!}{6^6} \cdot \frac{8!}{8^8} \cdot \frac{12!}{27!} \cdot \frac{12^{27-12}}{27!} = \frac{6!}{6^6} \cdot \frac{8!}{8^8} \cdot \frac{12}{13} \cdot \frac{12}{14} \cdot \dots \cdot \frac{12}{27}$, in which further $\frac{6!}{6^6} < \frac{1}{64}$, $\frac{8!}{8^8} < \frac{1}{400}$, $\frac{12}{13} < 1$, $\frac{12}{14} < 1$, \dots , $\frac{12}{27} < 1$.

On the other hand, the chance W_m for the realisation of that case, in which the different types are found represented amongst the collective tables in proportion to their probability, will contain a large permutation-factor, and consequently — with a sufficiently large number of tables the ratio W_u/W_m may reach any degree of smallness. It makes a great difference, therefore, — and of course not only to the calculation of the maximum — whether we take the tables collectively as an object of higher order in the calculation of combinations or whether we determine the probability for each table separately and calculate that of the whole as product of the separate probabilities.

III. Suppose that the number of tables and holes for each table are not yet given, but only the total number of hollows in all the tables together, and that it was left to our choice to divide them amongst the tables, then an opinion as to what was the most probable division would be even more arbitrary.

IV. It is obvious, that the above considerations may be applied to the gas, taking into consideration, where necessary, additional conditions.

If we introduce the restriction that in the parts only we attend to all the possible permutations, in defining the most probable division, and that in the system as a whole we do not take into consideration any further permutations between these parts, *only then* does the probability for the state of the whole appear as the product of the probability of the states of the parts.

If on the other hand the total system is regarded as a new object for combinations, an object of a higher order, the probability of the distribution of a special state in the whole is not equal to the product of the probabilities of the parts corresponding to this state. The latter must be corrected by a certain permutation-factor, the magnitude of which is dependent upon the number of the parts, that is either upon the fineness of the division to be chosen at will, or — with a permanently fixed fineness of division — upon the magnitude of the total system.

The question arises: with which $\log W$ should the entropy be identified?

Only when the said permutation-factor is neglected can it be said that the tending of the parts towards the maximum of their entropy brings with it a striving towards a maximum of the entropy of the whole.

If we adopt the latter view, in other words if we say that the $\log W$ of a system is *almost the same* as the sum of $\log w$ of its parts, at the most a sign of inequality is changed into a sign of equality. It is not justifiable, however, to *reverse* the sign of inequality. But this is just what happens when, for instance, the uniform distribution of density in a gas is regarded as the most probable state, and in order to calculate the probability of a distribution slightly deviating from this the relation

$$\log W = \sum \log w,$$

is taken as the basis, for in this way each deviating distribution appears as a less probable one¹⁾.

V The above analysis is by no means intended to call into question the validity of calculations similar to those indicated in the preceding paragraph, as these rest on the thesis that the entropy of the whole is equal to the sum of the entropies of the parts, a thesis that probably is physically better justified than the combinatory reasonings, at least in the circumstances in which they are applied. The analysis is merely intended to make clear that the *decision of the question whether the probability of the state of a system has reached its maximum or not, depends upon the point of view of the investigator*, and that the *ideas formed from purely combinatory reasonings do not form a satisfactory or conclusive foundation to direct our choice amongst many different standpoints to any one in particular*; further that the choice of our standpoint is made on the ground of various physical intuitions, which are outside the pale of the combination-calculus as such.

That is to say, that the combinational reasonings in question cannot be deduced from a higher principle which may be said to rule nature.

VI. We can show this more particularly in the case of a gas. Let us bring together two cubic centimetres of gas at different temperatures. If it should depend upon the "probability principle" which is to happen, it would be quite indefinite whether an equalisation of temperature would take place or not. It would depend upon the question of which is more important in nature; one cubic centimetre or trillions of cubic centimetres. In the latter case our two cubic centimetres might just be those members of our trillion

¹⁾ R. FÜRTH. *Ueber die Entropie eines realen Gases als Funktion der mittleren räumlichen Temperatur- und Dichteverteilung*. Phys. Zschr. 18, p. 395—400, 1917.

system, which ought to have different temperatures in order that the whole may get the most probable division of temperature over its parts (trillion tables, and upon each of them million balls). If it is advanced against this that an inequality of this kind must continually appear in precisely the same cubic centimetres, so that *our* two portions of gas may still equalize their temperature, it must not be forgotten that this demands that at the same moment another arbitrary pair of cubic centimetres would be obliged to change temperature in just the opposite direction.

Further it must be remembered that in the case when the subdivision is continued as far as the single molecules we do actually take up the latter standpoint: the momentary kinetic energy accorded to each separate molecule is in itself not the most probable; over a sufficiently large number of molecules, however, the velocities are divided in such a manner that we can only talk of the most probable distribution for the whole of these molecules (quadrillion tables with one ball on each, or, what comes to the same, one table with quadrillion balls).

Zoology. — “*On the primary character of the markings in Lepidopterous pupae*”. By Prof. J. F. VAN BEMMELN.

(Communicated in the meeting of April 26, 1918.)

On p. 136 of his paper: Zur Zeichnung des Insekten-, im besondern des Dipteren- und Lepidopterenflügels (Tijdschrift voor Entomologie, vol. LIX, 1915) DE MEYERE raises objections against the comparison of the pupal stage in Lepidoptera with the subimaginal instar of Agnatha; a comparison, which as far as I know, was first made by POULTON¹⁾, and to which I have expressed my adhesion in my paper on the pupae of Rhopalocera²⁾.

He says (translated by me): “It is well known that many investigators believe the pupa to have evolved from a flying imagolike form, the limitation of the wings to the last instar having been acquired later on. In these views I cannot agree with my colleague” (viz. VAN BEMMELN). “In what way one may imagine the initial evolution of the pupal stage to have taken place, either from a dormant subimago, or from a dormant larva (the latter alternative according to my view being the more probable), in any case I think to be justified in supposing that the Trichoptera, Panorpata, Diptera and Lepidoptera have differentiated out of Neuroptera, after the latter had acquired the Holometabolic metamorphosis they possess to-day. Now the Neuroptera generally have a faintly coloured pupa, which leads a hidden life, concealed in the earth or in a cocoon, and usually has a thin chitinous skin. Such also is the condition with Panorpata, Diptera, and likewise with a number of lower Lepidoptera, as Micropteryx, Lymacodides and many others.

When therefore we meet with special colour-markings exactly in the freeliving pupae of diurnal butterflies, I am inclined to regard this as a wholly secondary feature (The italics are mine).

This statement leads me to the following remarks:

¹⁾ E. B. POULTON, The external morphology of the Lepidopterous Pupa, its relation to that of other stages and to the origin and history of metamorphosis; Transactions Linnean Society 1890—91.

²⁾ J. F. VAN BEMMELN, Die phylogenetische Bedeutung der Puppenzeichnung bei den Rhopaloceren und ihre Beziehungen zu derjenigen der Raupen und Imagines, Verh. d. Deutschen Zool. Ges. 23 Versamml. 1913.

Against the use of the expression "subimago" in itself, for the pupal stage of Lepidoptera and other Holometabola, DE MEYERE does not seem to have fundamental objections, for as is seen from his own words, he declares that the pupa might be considered as an "inactive subimago," though he himself would prefer the name "inactive larva."

In this preference I cannot agree with him. The conception "larva" implies the presence of provisional organs, as well as the manifestation of a metamorphosis, the moment of which fixes the final point of larval life. Now it is clear, that this point lies at the passage from caterpillar to pupa. Therefore the latter cannot be called an "inactive larva", but only an "inactive subimago". It might even be asserted to represent an "inactive imago", for the provisional larval organs have disappeared, the imaginal organs on the contrary being all present, though still unable to functionate.

But it is especially against the inference, that this subimaginal stage should have been provided with a sufficient mobility to enable it to fly about, after the fashion of the caddisflies when they leave the water, that DE MEYERE raises objection. According to his view, it is much more probable that in none of their phylogenetic stages the Lepidoptera or any of their kin: Panorpata, Diptera, or Neuroptera, were ever on the wing before the very last moult, so before they fully deserved the designation "imago".

Now I must admit, that this supposition of the occurrence of a flying subimaginal instar among the ancestors of these groups of Insects is merely a hypothesis, which can only be supported by arguments of probability, while most assuredly important objections can be opposed against it. One of these difficulties I will indicate myself: Holometabolic Insects may indeed be compared still to other Hemimetabola than precisely the Agnatha, and moreover to Ametabola also, and this comparison may lead to raising the question, if the pupal stage might not best be compared to the last instar but one of these groups, to which belong insects, whose different instars are much more similar to each other than those of Holometabola, because all of them differ less from the imaginal condition, or, what means the same, because they have all deviated in a minor degree from the original Insect-type.

In them we see the wings protrude at an early stage as lateral outgrowths of the dorsal body-wall and increase in size at each following ecdysis, though entering into function at the last one only.

Why should this course of development be less primitive than that of caddisflies? Might not the curious phenomenon, that

the subimaginal instar of the Ephemeridae, after moulting at the surface of the water, flies about for a few moments, then to moult again and immediately afterwards to proceed to copulation, rather be taken as a speciality of the Agnathous life history, without any deeper significance, and therefore of no importance for the explanation of Holometaboly with its dormant pupal-stage.

On this point I dare not pronounce a definite opinion, but should like to point out, that in trying to find an answer to the above stated question, we must take into account various general considerations, in the first place that of the development of wings in its totality, viz. the question how Insects (at least Pterygogenea) acquired their wings. For this decides about the question whether we are to suppose that the ancestors of modern Pterygote Insects never passed through a period, in which they moved about on the wing before attaining sexual maturity, or that the beginning of the functional activity of the wings (howsoever acquired) became more and more postponed to the last instar. If we are right in accepting the second alternative, and therefore in believing that the oldest winged insects could already make use of their wings shortly after their birth, the Agnatha may have retained a last trace of this ancient condition. The apparently absurd fact, that these animals fly about in their subimaginal coat for a few moments only, might then be explained by the assumption, that they gradually postponed the start on the wing to later instars, under the ever increasing influence of their secondary adaptation to life in the water. Then the difference between them and other Hemimetabola would not consist in a greater originality of the latter, but in a different mode of deviation from the primitive condition, viz. by the complete removal of the initiation of real flying to the imaginal instar.

The supposition of such a retardation in the transition to flying life-habits is diametrically opposed to the explanation assumed for many other phenomena in metamorphosis, viz. that the manifestation of new characteristics is gradually removed to ever younger instars. In my opinion the former supposition is as well justified as the latter. When for instance WEISMANN (rightly I think) assumes that changes in colour-markings of certain caterpillars, becoming visible at their last ecdysis only, have been transferred to younger stages in species near akin by a process of precession of development, the opposite course of events may also be considered possible, viz. that a colour-pattern of the wings, which originally came into existence together with the wings themselves, now

only appears a long time after the stage in which the rudiments of the wings first become visible.

Now what is true for the colour-pattern, may as well be applied to the wings themselves.

I do not intend to enter into these considerations more profoundly, as it is irrelevant for the solution of the question, whether or no the colour-pattern on the wing-sheaths of Rhopaloceran pupae possesses phylogenetic significance. • On the contrary it seems to me that in this way the question is made unnecessarily intricate. For the difference between the Lepidopterous pupa and the imago emerging from it, as well as between this pupa and the last instar but one in Hemimetabola, only consists in the limited mobility and the temporary suspension of food-supply and excretion in the pupa. In my opinion there can be no doubt that it has lost these functions, and that this loss happened gradually. For we are justified in considering the sculptured and movable pupae of primitive Lepidoptera as more original forms than the mummie-pupae, which are hardly mobile. Why then should not absence of colour and of markings be the consequence of a gradual regression of these characteristics?

Of course this explanation may be as well applied to Neuroptera as to Lepidoptera; DE MEYERE himself concedes that the pupae of Neuroptera "mostly live hidden in the earth or in cocoons, and that their chitinous envelope is thin *and only poorly coloured*". (The italics are mine).

The causes for the regression of existing colour-patterns — viz. darkness and absence of sharpsighted enemies — which obtain all over the animal kingdom — may therefore have exerted their influence on Neuroptera. But this need not involve that the primitive Neuropterous ancestors of recent Lepidoptera already had concealed and immovable pupae. In any case those ancestors had to pass through a long range of thorough transformations, during which especially the youngest larval instars deviated ever more from the original type of the Insect, and in so doing came to differ from the last instar as well as from the last but one.

Those two stages on the contrary remained alike in all important points, though they came to differ from each other in minor accessory characters, which for the pupae chiefly consisted in the loss of mobility, with all its consequences. But apart from this immobilisation it retained the old primordial characters without or with only small modifications, and where a change still occurred, this depended more on katabolic phenomena, e.g. partial or total extinction of colour-markings, than on progressive alterations.

Therefore I think that we need no more ascribe a secondary character to the pupal stage of Lepidoptera, than we should be inclined to do so to the larval or nymphal instar of Hemi-or Ametabola. A grasshopper during the succession of its moults, passes through a series of successive stages of colour-pattern as well as a moth. The idea that the last stage but one of this series bears a different character from the preceding instars or the following ultimate stage, would never occur to us. Neither is this supposition necessary or useful for the understanding of the Lepidopterous design. That the latter is secondarily modified, is beyond doubt, it has been changed in all stages, but precisely in the pupal stage less so than in the preceding larval instar or the succeeding imaginal state, as SCHIERBEEK has shown by comparing the pupal design with that of the caterpillar in its first instar.

As to the colour-pattern of the pupa, the same considerations can be applied to it as to so many of its further properties. POULTON e.g. has pointed out, that in the pupae of those butterflies, whose forewings show a denticulated outer margin, the wing sheaths do not stop at that broken line, yet clearly marked out on its surface, but continue for a short bit and then end in an unbroken front line. He rightly takes this feature as an indication, that the ancestors of those butterflies at one time possessed normally rounded wings. In the same way he was able to show, that in those moths whose females have only vestigial wing-rudiments (the wings of the male sex being well developed) the female pupae differ much less from the male ones, because their wing-sheaths are only a little bit shorter than those of the males.

Likewise the difference between the sheaths for harbouring the filiform antennae of the females and those for the pectinate ones of the males was found to be smaller than that between these antennae themselves.

Would not all these features be caused by a recapitulation of their phylogeny, by the preservation during the subimaginal stage of former conditions which have lost their original meaning.

On this topic DE MEYERE makes the following remark: "It is difficult to explain the presence of this line" (viz. POULTON's mark) "already on the young pupal wing, otherwise than by anticipation of hereditary tendencies. Anyhow a sufficient number of instances can be adduced of cases in which features of different stages are transferred to the pupa in both directions, as well from the imago as from the larva To this same influence of precocious entrance into activity might also be ascribed the fact, that certain

markings of the imaginal wing are already visible on the pupa, e.g. the submarginal spots of *Vanessidae*. Especially when, as VAN BEMMELLEN has pointed out, the imaginal wing-pattern, during the beginning of its ontogenetic development, at first shows reminiscences of older more generalised types, we can understand, that the pattern of the wing-sheaths precisely reproduces these stages, without our being obliged to assume that the imago received its colour-markings from the pupa, and that the latter once moved about on wings ornamented in the same style".

Referring to these considerations of DE MEYERE I should like to remark, that I do not in the least suppose the imago to have drawn on the pupa for its colour-pattern, as may clearly be seen from the inferences on p. 358 of my paper: On the phylogenetic significance of the wing-markings of *Rhopalocera*, (Transact. 2^d Entom. Congress, Oxford 1912), in which I point out the facts, that: 1. only the external surface of the wing-sheaths, harbouring the developing primaries, wear colour-markings, in contrast to that of the secondaries hidden beneath it, while of course both pairs of the imaginal wings develop a colour-pattern on both their surfaces; and 2. that the primordial or vanishing pattern on these imaginal wings is still more primitive and therefore phylogenetically older than the colour-pattern on the pupal sheath, so that there is as little reason to suppose that the latter received its pattern from the young imaginal wing hidden in its interior, as to make the opposite supposition.

The transference of imaginal features to younger instars seems probable to me also, as may be seen from the foregoing remarks. When however DE MEYERE calls this transference anticipated entrance into activity, he must have in view the activation of latent hereditary factors, and so must admit the presence of those factors in the genetics of the species. They therefore are connected with former periods of phylogenetic development, or in other words: the colour-pattern of the pupal sheaths must once have ornamented the wings of an insect flying about (or at least walking about) with them. Whether this insect was the imago or the subimago, is a question for itself, but in any case DE MEYERE's expression about "anticipated activation" includes the inference, that he also considers the pupal colour-markings as a recapitulation of a phylogenetically older stage.

Trying to enter into his ideas, I suppose them to have taken the following course: The imaginal instar of *Lepidoptera* was of old preceded by an uncoloured pupal stage. In the ancestry of the recent butterflies the peculiar habit was acquired, that their pupae no longer lived in

hidden localities, and therefore came in need of protection by mimicking- or by warning-colours. They provided for this need by means of anticipated activation, viz. by transferring the then existing pattern of their forewings to the external surface of the pupal wing-sheaths.

This pattern persisted on the pupa, even after the wings of the imago had acquired the new pattern, such as is found on them to day, by the further modification of the old one.

Even if this view of the course of phylogenetic development should prove right, which I consider rather improbable, it would not diminish in any way the phylogenetic significance of the pupal pattern, and so there would be no need to consider this pattern as wholly secondary and therefore destitute of all importance for the phylogeny of Lepidoptera. For this it would seem, is what DE MEYERE means by his words mentioned in the beginning of this paper: which fully cited run as follows:

“When precisely in the free-living pupae of the butterflies we find special colour-markings, I would consider this as a wholly secondary feature, the body having first acquired certain pigment-spots, to which sympathetic markings of the wingsheaths afterwards were added. That the latter show a certain connection with the veinal system, cannot astonish us, when we take into consideration the special importance of the veins as respiratory and circulatory vessels”.

Against this view I wish fully to maintain my own, viz. that the colour-markings of the butterfly-pupae — those on the body as well as those on the wing-sheaths — should be considered as an original pattern, the whole-colour of white, yellow, brown or black pupae of most moths resulting from the loss of this primitive design.

Regarding in particular the harmony between abdomen and wings, in colour-hues as well as in design, we may remark that such a similarity is a generally occurring feature, not only with pupae but even and in a higher degree with imagines. Without doubt this harmony will often root in a secondary modification of shades and markings, of the abdomen as well as the wings, which we may ascribe to sympathetic correlation, but this need not oblige us to doubt that both patterns result from a primitive one, or to abstain from searching after the vestiges of this primitive pattern on both those regions of the body.

What is true for the imagines, is certainly right for the pupae, even in a higher degree; remnants of the original design may be more probably expected on them and be found there in a more complete state, because the imagines are exposed to greater versabi-

lity of life-conditions and external influences, even more so than the caterpillars, their habits of moving about and resting, of nourishing and propagating being more varied.

Both caterpillars and imagines in these respects surpass the nearly immovable and lethargic pupae.

DE MEYERE's views on this topic seem to be the cause, that while attaching great importance to the differences between the pattern on the pupal wing-sheaths of nearly related forms, such as *Euchloe cardamines*, *Pieris brassicae*, *Aporia crataegi*, he only pays very slight attention to the facts pointed out by me, viz. the great similarity between the pupal designs in several families of Rhopalocera e. g. Papilionids, Pierids and Nymphalids, a similarity not only far exceeding the resemblance between the wing-patterns of the imagines that emerge from those pupae, but also rooting in the nearer connections of this pupal pattern with the primordial and ephemerid design, which appears on the developing wings during the course of the pupal life, and only gives place to the conclusive imaginal pattern in the very last days before the emergence of the imago.

These vestigial markings on the rudiments of the wings hidden in the pupal sheaths, moreover prove to us that a primordial pattern may easily continue its existence in concealment; therefore such notions as "sympathetic colouration" or "influence of illumination and surroundings" need not be invoked in order to explain the manifestation of such a pattern.

Though the absence of markings may, in all probability, be connected with concealed life-habits and with absence of light, it would not do to consider these influences as the direct and unavoidable causes of the deterioration of the pattern. For the pattern is evidently able also to persist hidden under the pupal sheath, though in some forms it is retained much clearer and more complete than in others, without our being able to find an explanation for this difference.

Now what holds good for the wings inside the pupal sheaths, will probably also apply to those sheaths themselves. Taking this inference for granted, we might expect, that also in some of those Lepidoptera, whose pupae conceal themselves in hidden spots, the original colour pattern, on the body as well as on the wings, might have been more or less preserved.

This turns out to be really the case, as I found when studying the pupae of Chaerocampinae amongst Sphingidae, and of several genera of Geometridae. In contrast with the majority of the genera belonging to these families, whose pupae are black, brown, yellow

or white all over, the genera in question show a well marked and regular design of black markings on a light background. Yet the majority of these pupae certainly live under nearly similar circumstances as those of their relations, i. e. concealed in the earth, in cocoons or between leaves.

It is worth remarking that precisely the Chaerocampinae do not hide in the earth for the object of pupation, as many other Sphingidae do, but remain on the surface and there construct a coarse cocoon of small lumps of earth glued together with threads.

In the same way many Geometridae do not pupate inside the earth, but above it; their tissue often being so loose, that the pupa may be seen inside. I suppose that this may be the cause of the colour-markings on these pupae persisting, whereas those on their near allies have disappeared by obliteration in consequence of total darkness.

Yet the Chaerocampa-pupae in so far undoubtedly show the influence of their concealed habitat, as their markings not only are variable in the highest degree, but also show a marked tendency to obliteration. In this respect they agree with the primordial design on the imaginal wings inside the pupal sheath, and also with the maculated pattern of those butterfly-pupae, in which the original colour-mosaic is replaced by a sympathetic general hue, e.g. the uniformly green pupae of *Pieris napi*, on which the identical spots as on *P. brassicae*, may easily be detected though much smaller and less sharp than on the latter (comp. VAN BEMMELEN, Phylogenetische Bedeutung der Puppen-Zeichnung, and SCHIERBEEK: The significance of the setal pattern in caterpillars and its phylogeny).

Therefore though the colour-design of the Chaerocampa-pupae shows deep traces of obliteration, it nevertheless is clear, that this design is founded on the same groundplan as that of butterflies. In my just-mentioned paper I have proposed a system of names (comp. fig. 6 on p. 115), according to which seven chief ranges of spots might be distinguished, called by me the dorsal, dorsolateral, epistigmal, stigmal, hypostigmal, ventrolateral and ventral rows of spots. In his essay Dr. SCHIERBEEK has pointed out, that the names of W. MÜLLER and WEISMANN, who use the expressions supra- and infrastigmal, have priority.

These rows of spots may all be met again on the pupae of sundry species of *Chaerocampa* as well as on those of *Deilephila* (e. g. *euphorbia* and *elpenor*) in various degrees of clearness and completeness.

No less striking than this correspondence in colour-design between

Sphingidial and Rhopaloceran pupae, is the connection between the markings on the pupae of the Sphinges and on their caterpillars and imagines respectively. Among the material at my disposal I found this similarity most distinctly marked in *Deilephila celerio*, as far as general completeness goes, though for certain details or on special parts of the body, other related forms sometimes showed the similarity still better and more complete, or in a more original form, as I hope to point out in a following communication.

Though I still lacked the occasion to extend my investigations to living caterpillars in their different instars, or to the development of the pupal skin beneath the last larval coat, or the imaginal epidermis inside the pupa, I do not doubt a moment but these transgressive stages will strengthen my conclusions as to the comparability of larval, nymphal and imaginal colour-design, viz. that all three are simply modifications of one and the same ground-plan, which manifests itself clearest in the pupa.

Groningen, April 1918.

Physics. — “*Calculation of some special cases, in EINSTEIN’S theory of gravitation*”. By DR. GUNNAR NORDSTROM. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of April 26, 1918).

As an application of the theorems deduced in two preceding papers for EINSTEIN’S theory ¹⁾ of gravitation, we shall now calculate the gravitation field and the stresses for some special *stationary systems with spherical symmetry*.

First the state at a surface of discontinuity will be investigated.

§ 1. *Introductory formulae.*

In a field with spherical symmetry a surface of discontinuity necessarily is a sphere. This surface will be considered as the limiting case of a layer of finite depth, and we shall only have to pay attention to such surfaces in which in the limit some component of the material stress-energy-tensor increases above every arbitrary limit so that the line-integral across the layer remains finite. In general at such a surface of discontinuity there evidently works a surface-tension P :

$$P = \lim_{r_2 - r_1 = 0} \int_{r_1}^{r_2} \mathfrak{T}_p^p dr, \dots \dots \dots (1)$$

where r_1 denotes the inner radius of the layer, and r_2 the outer one. The radial component of the stress-tensor \mathfrak{T}_r^r on the contrary we shall suppose never to pass every arbitrary limit; in other words we assume that:

$$\lim_{r_2 - r_1 = 0} \int_{r_1}^{r_2} \mathfrak{T}_r^r dr = 0 \dots \dots \dots (2)$$

First we shall consider a general surface of discontinuity and only afterwards we shall introduce special assumptions. We start from the first and third formulae (38) I and from (39) I. (From these three formulae the second formula (38) I may also be derived, but

¹⁾ G. NORDSTRÖM, On the mass of a material system according to the gravitation theory of EINSTEIN These Proceedings XX, 1917, p. 1076 (cited further on as I) and: On the energy of the gravitation field in EINSTEIN’S theory. These Proceedings XX, 1918 p. 1238 (cited further on as II).

we do not need this). The system of coordinates will be fixed by the conditions:

$$v = r, \text{ viz. } p = r \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Putting further:

$$\mathfrak{E} = \sqrt{-g} T = u w T, \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

and applying a simple transformation, we can write for the mentioned starting formulae:

$$-\frac{1}{u^2} \left(1 + 2r \frac{w'}{w} \right) + 1 = r^2 \kappa T_r^r, \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\frac{d}{dr} \left\{ r \left(1 - \frac{1}{u^2} \right) \right\} = r^2 \kappa T_4^4, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

$$\frac{2}{r} (T_p^p - T_r^r) + \frac{w'}{w} (T_4^4 - T_r^r) = \frac{dT_r^r}{dr}. \quad . \quad . \quad . \quad . \quad (7)$$

These formulae hold for each stationary gravitation field with spherical symmetry; the system of coordinates only is determined by the condition (3). The quantities u and w determine (when $p=1$) all components $g_{\nu\sigma}$ of the fundamental tensor according to the formulae (25) I.

When T_4^4 is given, the equation (6) determines u as a function of r . By integration across a layer which afterwards by a passage to the limit is changed into a surface of discontinuity with radius $r_1 = r_2 = R$ and after division by R we obtain

$$\frac{1}{u_1^2} - \frac{1}{u_2^2} = R \kappa \lim_{r_2-r_1=0} \int_{r_1}^{r_2} T_4^4 dr. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

This formula shows that u changes discontinuously at a surface of discontinuity where

$$\lim_{r_2-r_1=0} \int_{r_1}^{r_2} T_r^r dr$$

differs from zero. Such a surface which moreover satisfies the condition (2) will be called a *material surface*. The system of coordinates might be chosen in such a way that at the surface u changes continuously, but then p would change discontinuously. In general at least one of the space-components of the fundamental tensor changes discontinuously at a material surface. With the aid of formula (5) we shall now prove, that w on the contrary changes continuously at our material surface, when only the condition (2) is satisfied. Equation (5) gives

$$2 \frac{w'}{w} = \frac{u^2}{r} \left(1 - r^2 \kappa T_r^r \right) - \frac{1}{r}, \quad . \quad . \quad . \quad . \quad . \quad (9)$$

and by integration across the layer we obtain

$$\log w_2 - \log w_1 = \int_{r_1}^{r_2} \left\{ \frac{u^2}{r} (1 - r^2 \kappa T_r') - \frac{1}{r} \right\} dr \quad (10)$$

We shall only consider gravitation fields in which u is every where finite and when in the limit we pass to an infinitely thin layer the limiting value of the integral on the right-hand side becomes zero according to the assumption (2).

Now we shall apply formula (7) and substitute in it the expression (9) for $\frac{w'}{w}$ and the expression (6) for T_r' . Multiplying further by $\frac{urdr}{2}$, we find

$$u(T_p' - T_r')dr + \frac{1}{4}\{u^2(1 - r^2 \kappa T_r') - u\} \left\{ \frac{1}{\kappa r^2} \frac{d}{dr} r \left(1 - \frac{1}{u^2} \right) - T_r' \right\} dr = \frac{ur}{2} \frac{dT_r'}{dr} dr. \quad (11)$$

This equation must be integrated over a layer and afterwards we must pass to the case of an infinitesimal depth. In order to obtain as a first term on the left-hand side the surface tension P as defined by equation (1) we must moreover multiply by w . We shall however not continue our general investigation, but rather consider two more special cases.

§ 2. Investigation of the state at a material surface.

First we investigate the case that at the limit T_r' surpasses any value, so that the right-hand side does not become zero, but that $\frac{dT_r'}{dr}$ remains finite, so that on both sides of the surface of discontinuity T_r' has the same value.

In (11) we first consider the part of the left-hand side which after integration gives

$$\begin{aligned} I &= \frac{1}{4} \int_{r_1}^{r_2} \left\{ u^2 (1 - r^2 \kappa T_r') - u \right\} \frac{1}{\kappa r^2} \frac{d}{dr} r \left(1 - \frac{1}{u^2} \right) dr = \\ &= \frac{1}{4\kappa} \int_{r_1}^{r_2} \left\{ u^2 (1 - r^2 \kappa T_r') - u \right\} d \left\{ r \left(1 - \frac{1}{u^2} \right) \right\}. \end{aligned}$$

We have to calculate the value of this expression for the limit $r_2 - r_1 = 0$. In this limiting case r constant $= r_1 = r_2 = R$, so that we have

$$d \left\{ r \left(1 - \frac{1}{u^2} \right) \right\} = 2 R \frac{du}{u^3}.$$

We thus obtain

$$\lim_{r_2-r_1=0} I = \frac{1-R^2 \kappa T_r'}{2\kappa R} \int_{u_1}^{u_2} du - \frac{1}{2\kappa R} \int_{u_1}^{u_2} \frac{du}{u^2} = \frac{u_2-u_1}{2\kappa R} \left(1 - \frac{1}{u_1 u_2} - R^2 \kappa T_r' \right).$$

Now we have treated one part of the left-hand side of (11) by integration and by passage to the limit. Of the remaining parts of this left-hand side those containing T_r^r remain zero at the passage to the limit according to our assumption (2), u remaining moreover finite. The part containing T_p^p on the contrary does not become zero. The right-hand side has the value zero at the limit, as we have assumed T_r^r to change continuously at the surface of discontinuity. Multiplying our equation still by w , which quantity we have proved to change continuously at the surface, so that at the limit it may be considered as constant, we obtain:

$$P = -\frac{w}{2\kappa R} (u_2 - u_1) \left(1 - \frac{1}{u_1 u_2} - R^2 \kappa T_r^r \right) \quad . \quad . \quad . \quad (12)$$

Together with (8) this formula expresses the laws for a surface of discontinuity of the kind we now consider. These formulae will be applied to the special case that all matter that is present is situated in the material surface. T_r^r being continuous, we have in this case $T_r^r = 0$. Further we have according to (6) both inside and outside the surface

$$r \left(1 - \frac{1}{u^2} \right) = \text{const.} \quad (r \neq R) \quad . \quad . \quad . \quad (13)$$

When $r = 0$, u cannot be zero, so that the value of the constant within the surface must be zero. We thus find for $r < R$, $u = 1$ and therefore also

$$u_1 = 1. \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

Within the spherical material surface we thus have a euclidian space. (This is of course true for every hollow sphere; the distribution of mass and stress on the outside only has spherical symmetry). Outside the material surface the constant in equation (13) has not the value zero, but a value, proportional to the mass of the system which is given by formula (15) II:

$$m = \frac{4\pi a}{\kappa} \quad . \quad . \quad . \quad . \quad . \quad . \quad (15a)$$

We thus have for u_1 :

$$u_2 = \frac{1}{\sqrt{1 - \frac{\alpha}{R}}} \quad \dots \quad (15)$$

For w we have at our surface:

$$w = c \sqrt{1 - \frac{\alpha}{R}} = \frac{c}{u_2} \quad \dots \quad (16)$$

This may be proved e.g. by putting $\varepsilon = 0$ in formula (12) II which holds outside our surface. Also by putting $r = R$ we obtain the value (16) at the surface, and formula (9) shows afterwards (as within the surface $u = 1$ and $T_{,r} = 0$), that this constant value of w holds also everywhere inside the material surface.

Introducing the expressions u_1 , u_2 , and w , we find for the surface tension P

$$P = -\frac{c}{2\pi R} \left(1 - \sqrt{1 - \frac{\alpha}{R}}\right)^2 \quad \dots \quad (17)$$

This formula expresses the relation between the surface-tension, the mass and the radius. Expressed in the usual units the surface-tension is cP (comp. I p. 1079). The constant of mass α is also connected with the right-hand side of equation (8). After introduction of the values of u_1 and u_2 , this equation gives

$$\alpha = \kappa R^2 \lim_{r_2 \rightarrow r_1} \int_{r_1}^{r_2} T_4^4 dr. \quad \dots \quad (18)$$

In the euclidian space inside the material surface we have not the same velocity of light as at an infinite distance from our system, but a smaller velocity

$$c \sqrt{1 - \frac{\alpha}{R}}.$$

We thus have a representation of EINSTEIN's idea on the influence of distant masses on the velocity of light in our part of the world.

Expanding the expression (17) for P in powers of α/R we obtain:

$$P = -\frac{c}{2\pi R} \left(\frac{1}{4} \frac{\alpha^2}{R^2} + \frac{1}{8} \frac{\alpha^3}{R^3} + \dots \right) \quad \dots \quad (17a)$$

NEWTON's theory gives for cP :

$$cP = -\frac{km^2}{16\pi R^2} \quad \dots \quad (17b)$$

where k is the NEWTONIAN gravitation constant:

$$k = \frac{c^2 \kappa}{8\pi}.$$

Introducing in (17b) the expressions for k and m , we find for P an expression, corresponding to the first term of (17a). As to the terms of lower order the theory of EINSTEIN agrees therefore with that of NEWTON.

§. 3. *Second example of a surface of discontinuity.*

Now we shall consider another kind of surface of discontinuity viz. one in which

$$\lim_{r_2-r_1=0} \int_{r_1}^{r_2} T_4^4 dr = 0 \quad . \quad . \quad . \quad . \quad . \quad (19)$$

but where T_r^r changes discontinuously. Such a surface of discontinuity we have e. g. when an electric charge is spread over the surface.

Formula (8) shows that in the case in question u changes continuously at the surface:

$$u_2 = u_1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

Above we showed already by formula (10) that w changes continuously.

This time too we must multiply formula (11) by w , integrate a layer and pass to the limit of an infinitesimal thickness. As in the last part of the left-hand side all quantities remain finite at the limit, this part gives the limiting value zero. As further u and w change continuously, we obtain

$$P = \frac{R}{2} u w (T_{r_2}^r - T_{r_1}^r),$$

or, introducing the components of the volume-tensor \mathfrak{T}

$$P = \frac{R}{2} (\mathfrak{T}_{r_2}^r - \mathfrak{T}_{r_1}^r). \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The meaning of this equation is trivial. It expresses the equilibrium between the surface-tension P at the spherical surface and the normal force perpendicular to that surface, the magnitude of which is $\mathfrak{T}_{r_2}^r - \mathfrak{T}_{r_1}^r$, per unit of surface. The gravitation has evidently no influence.

When on the surface we have an electric charge e and inside the surface no matter, we find (II, note p. 1240)

$$\mathfrak{T}_{r_1}^r = 0, \quad \mathfrak{T}_{r_2}^r = \frac{u w e^2}{8\pi R^4}. \quad . \quad . \quad . \quad . \quad . \quad (22)$$

Now we shall assume that neither outside the surface there is any matter except the electric field, and we shall calculate the mass

We eliminate $\frac{w'}{w}$ between this equation and (31). In this way we find

$$\frac{2 dp}{(\varrho + 3p)(\varrho + p)} + \frac{\kappa}{3} \frac{r dr}{1 - \frac{\kappa \varrho}{3} r^2} = 0 \quad . \quad . \quad . \quad (34)$$

The integration gives

$$\log \frac{\varrho + 3p}{\varrho + p} - \log \sqrt{1 - \frac{\kappa \varrho}{3} r^2} = \text{const.}$$

The integration constant has to be determined with the aid of the condition that for $r = R$ $p = 0$. We therefore find

$$\frac{\varrho + 3p}{\varrho + p} = \sqrt{\frac{1 - \frac{\kappa \varrho}{3} r^2}{1 - \frac{\kappa \varrho}{3} R^2}} \quad . \quad . \quad . \quad (35)$$

Thus the pressure-scalar p is determined as a function of r .

Eliminating p between this equation and (32) we obtain for w as a function of r the expression:

$$w = \frac{c}{2} \left(3 \sqrt{1 - \frac{\kappa \varrho}{3} R^2} - \sqrt{1 - \frac{\kappa \varrho}{3} r^2} \right) \quad . \quad . \quad (36)$$

In this way we have perfectly determined the gravitation field and the pressure distribution inside our sphere. The formulae we obtained become identical with those of SCHWARZSCHILD when for r we substitute

$$r = \sqrt{\frac{3}{\kappa \varrho}} \sin \chi.$$

§ 5. *On the gravitation field as it may be imagined to exist in the inside of an atom.*

In the theory of atomic structure of RUTHERFORD-BOHR we meet with difficulties arising from the assumption that in an atomic nucleus of very small dimensions there exist units of charge which — at least when they are liberated in the form of electrons — have a greater diameter than the atomic nucleus. As now EINSTEIN's gravitation theory states that the space in a gravitation field when expressed in natural units is non-euclidian, the question arises whether this theory leaves the possibility of the assumption that the atomic nucleus fills a greater space with a narrow neck or perhaps a space which crosses itself at a certain point. This question will be investigated here.

We consider again a stationary system with spherical symmetry. In the same way as above we may define the distance r from the centre of symmetry by putting $p=1$ viz. by demanding that the periphery of a circle with its centre at the centre of symmetry is $2\pi r$, when expressed in natural units. If we do so in the case in question, the state in the field is not a single-valued but within a certain interval at least a more-valued function of r . It is therefore useful to introduce a new radial space-coordinate of which the quantities in the field are single-valued functions. As such a coordinate the distance s from the centre of symmetry expressed in natural units suggests itself. In order to specialize our discussion we can prescribe a relation between the radius defined by the condition $p=1$ and s and investigate afterwards whether this is in agreement with a possible distribution of the components T'_μ of the stress-energy-tensor.

As a trial we put

$$r = \pm s \left(\frac{s^2}{3a^2} - 1 \right), \quad . \quad . \quad . \quad . \quad . \quad . \quad (37)$$

where a is a constant, and we choose the sign thus that a positive value of r corresponds to a positive value of s . For small values of s r and s are proportional and the three-dimensional space is dilated when we come farther away from the centre (viz. from the point $s=0$). For $s=a$ r reaches however a maximum and when s increases still further the space is contracted and crosses itself at a point in the neighbourhood of $s=\sqrt{3}a$. For still higher values of s the space is again dilated.

Before proceeding we still remark that in fact the sign of r does not play a role. Inversing the sign of r in our fundamental formulae (5), (6) and (7) and interchanging also the signs of dr and w' we find from the formulae the same values as above for all remaining quantities. For this reason we take in (37) everywhere the $+$ sign, so that r is taken negative in the interval $0 < s < \sqrt{3}a$.

While the following discussions will be based on the fundamental equations (5), (6), (7), we suppose u , w , r , T'_μ , T^p_μ , T^4_μ to be functions of s . As s is the distance from the centre of symmetry expressed in natural units we obtain, attending to the meaning of the quantity u (see I § 3)

$$ds = u dr, \quad . \quad . \quad . \quad . \quad . \quad . \quad (38)$$

As (37) gives by differentiation

$$dr = \left(\frac{s^2}{a^2} - 1 \right) ds, \quad . \quad . \quad . \quad . \quad . \quad . \quad (39)$$

we find for u

$$u = \frac{1}{\frac{s^2}{a^2} - 1} \quad (40)$$

That u is negative for $s < a$, does not cause any trouble, as the fundamental tensor depends on u^2 only.

Now we must introduce in equation (6) the expressions (37) and (40) for r and u . Introducing to begin with the expressions on the left hand-side only we obtain

$$-\frac{s^2}{a^2} \left(\frac{7}{3} \frac{s^2}{a^2} - 6 \right) = r^2 \kappa T_4^4 \quad (41a)$$

Introducing the expressions on the right-hand side too we find for T_4^4 as a function of s

$$\kappa T_4^4 = \frac{6 - \frac{7}{3} \frac{s^2}{a^2}}{a^2 \left(\frac{s^2}{3a^2} - 1 \right)^2} \quad (41)$$

The formulae derived here hold evidently only inside the material system of which the outer boundary may be indicated by $s = S$. In order that the space occupied by the system may cross itself at any point we must have because of (37).

$$S > \sqrt{3} a.$$

In the limiting surface $s = S$ we have according to (40) $u < 1$. In order that in that surface u may pass continuously into the value it has in the field on the outside, u must also in the outer field be smaller than 1 for $s = S$. This follows also from formula (11) II, when the system has only a sufficient great electric charge. Further it does not matter that u would change discontinuously at the boundary, if only this is a material plane as considered in § 2.

Formula (41) shows that in the interval $\sqrt{\frac{18}{7}} a < s < S$ T_4^4 is negative, which though somewhat startling is not at all absurd. Further formula (41) indicates that T_4^4 becomes infinite for $s = \sqrt{3} a$. Within a finite extension there is however only a finite mass of matter, which follows from the fact that $r^2 T_4^4$ is everywhere finite according to (41).

The equations (40) and (41) for u and T_4^4 involve together with (37) that the fundamental equation (6) is satisfied. Now we must still determine w , T_r^r and T_p^p as functions of s , so that also the equations (5) and (7) are satisfied. As (5), (6) and (7) form the complete set of field equations for a stationary gravitation field, we

may choose for one of the quantities w , T'_r and T''_p an arbitrary single-valued function of s . When also the expressions for r , u and T^4_4 are introduced, the equations (5) and (7) determine now the two quantities. All these possible material systems give — if only the distribution of T^4_4 is the same — a three-dimensional space of the same curvature, because the formulae (25) perfectly determine the space-components of the fundamental tensor (when $p=1$). The curvature of the four-dimensional space-time continuum on the contrary depends also on the distribution of T'_r , which quantity according to (5) influences w . The following simple assumptions might e. g. be made to obtain a definite system: $w = \text{constant}$, $T'_r = 0$ or $T'_r = T''_p$ (normal pressure in all directions). Performing the integration of (15) and (7), we might choose the integration constants in such a way, that at the boundary $s = S$ w takes the value that holds there for the outer field, for, as was proved in § 1, w changes continuously into a surface of discontinuity.

The purpose of our investigation being reached no further calculations will be added. We have shown that EINSTEIN's theory of gravitation really admits such a distribution of the stress-energy-tensor T'_r , that the (three-dimensional) space crosses itself at a certain point. We can also prove without difficulty, that systems can exist in which the space filled with the matter runs out into a narrow neck.

It is still of some importance to investigate the action of the electric forces within the space which is just dilated and afterwards again contracted. We might e. g. investigate the state, when, with constant T^4_4 , T'_r , T''_p for the non electro-magnetic matter, a point charge was placed at the centre of symmetry. The gravitation field will evidently change. We have not only to calculate this field, but also the laws of the equilibrium and the motion of other electric (point)-charges in the new electric field. Here we must treat the matter as perfectly permeable. These indications may however suffice, which show already that EINSTEIN's theory opens wide possibilities to explain the state in the inside of an atom.

Chemistry. — “*Determination of the Configuration of cis-trans isomeric substances*”. By Prof. J. BÖESEKEN and CHR. VAN LOON.

(Communicated in the meeting of May 25, 1918).

1. The appearance in a number of isomers of unsaturated and cyclic compounds, has undoubtedly been a momentous incitement to the acceptance of VAN 'T HOFF's hypothesis on the carbon atom, which is supposed to lie in the centre of its valencies.

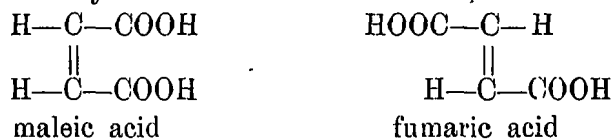
The permanence of the optical activity at moderate temperatures necessitated the attribution of a rather great stability to these valencies. Obviously in cyclic molecules the same rigidity had to be accepted, and also around the double bond.

Apart from objections that may rise against the substance of this supposition — objections connected with hypotheses on the internal structure of the atom — it must be granted that a very elegant interpretation has been given of the existence of the aforesaid isomers.

In fact, only very seldom cis-trans isomerism could not be observed when it was to be expected according to this theory, while on the other hand, if identical radicles are united to one of the unsaturated atoms or members of the ring, and therefore no isomers are to be anticipated, they were indeed not to be found.

2. This interpretation of the existence of cis-trans isomers is little to be doubted; however, it is much more difficult to determine which isomer has the cis- and which the trans-configuration.

By a happy coincidence the classical case of cis-trans isomerism, viz. that of maleic and fumaric acid, has offered, also in this respect, the greatest certainty.



The cause is evident: the configuration determination here is based almost exclusively on properties that may be deduced from the molecules themselves.

The determination namely of the configuration of geometrical isomers takes place along different lines.

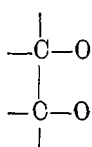
First of all the configuration may be deduced from properties that are to be anticipated in consequence of the reciprocal influence of the groups in the molecule; this is the surest way, if enough (critically examined) data for comparison be available.

Among these properties are: dissociation constants of acids, formation of anhydride, resolution into optical antipodes, *etc.*

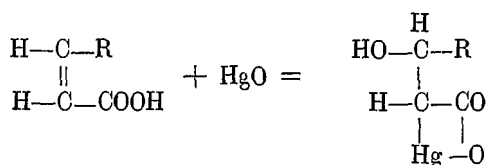
The formation of complex compounds is to be included in so far as the valencies, which are the bearers of cis-trans isomerism, are not attacked.

This is seldom easily established, since the structure of complex compounds is uncertain. Probably we are authorized to use this method in judging the cis-trans isomerism of cyclic glycols by the influence on the conductivity of boric acid,

because the boric acid-radicle is united to the oxygen atoms and not to the carbon atoms, which determine the isomerism. It is doubtful if it may be applied to cis-trans non-saturated acids; if the formation of complex metallic compounds must be represented by the following formula:



BOH



or anyhow, if it is to be supposed that the double bond is attacked, we can rely upon this method as little as on all others, by which the bearers of the isomerism are affected (see below).

Now the contrast between the two groupings H and COOH, which are bound to the very simple skeleton of maleic and fumaric acid, is exceptional; besides, the two carboxyl groups may enhance each other's acidity or react with one another under anhydride formation. Also a mutual repulsion of the COOH groups is to be anticipated, from which could be deduced that fumaric acid is more stable than maleic acid.

The particularly simple structure of these acids, by which the carboxyl groups take the leading position, has rendered the above-mentioned considerations so successful in determining the configurations.

As soon as this reciprocal influence fails or the structure becomes much less simple, we have no longer any certainty.

We will examine α - and *iso*-crotonic acid in this respect:

1. The dissociation constants are: α -crotonic acid $2 \cdot 10^{-5}$.
iso- " " $3,6 \cdot 10^{-5}$.

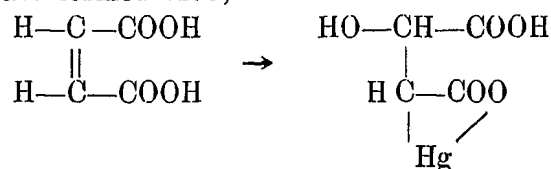
By comparing propionic with acetic acid it could be deduced that a methyl group weakens the acidity, so that in α -crotonic acid the methyl group must lie on the same side as the acid group; in fact acrylic acid ($k = 5,6 \cdot 10^{-5}$) is dissociated in a higher degree than

both crotonic acids, and dimethyl-acrylic acid ($\pm 7 \cdot 10^{-6}$, according to preliminary determinations of Mr. P. E. VERKADE, Dissertation Delft 1915, 2nd Note, p. 66) is weaker still. Also citraconic acid is much weaker than maleic acid.

Still one ought to be cautious, for *iso*-butyric acid is somewhat stronger than propionic acid (1.44 to $1.31 \cdot 10^{-5}$) and the dimethyl succinic acids are much stronger than succinic acid (1.9 and 1.3 to $0.6 \cdot 10^{-4}$).

2. Formation of an anhydride is not possible and therefore cannot help us.

3. Formation of complex compounds: BILMANN has shown that maleic, citraconic and *allo*-cinnamic acid form salts with mercuric acetate, which are soluble in sodium hydroxide, and from which the original acids could not be regenerated by elimination of mercury; in this case β -hydroxy-acids were formed and in consequence B. surmises that the salts were complex mercury salts of these hydroxy-acids, which are formed thus;



In the same way α -crotonic acid remained in solution in the form of a complex mercury salt, which could be precipitated with alcohol. From this salt β -hydroxy-butyric acid was obtained; in consequence one deduces from this too the *cis*-configuration for ordinary crotonic acid with the higher melting point.

In order to corroborate this result we have subjected *iso*-crotonic acid to the same operation and obtained an insoluble basic mercury salt, which, after decomposition by means of H_2S furnished a mixture of *iso*- and α -crotonic acid.

It may be mentioned in passing, that α -crotonic acid must have been formed during the elimination of mercury, for this acid — so far as it originally was present in the *iso*-crotonic acid — was kept in solution as a complex salt and because H_2S does not, or at least extremely slowly, change free *iso*-crotonic acid into α -crotonic acid.

The coincidence of the conclusions from the dissociation constants and from the researches of BILMANN gives some certainty to the configuration of the crotonic acids. It follows that the formula of these complex compounds is probably different from the one that has been proposed by BILMANN. However, this method of discernment is valid exclusively for $\alpha\beta$ -non-saturated acids; other ethylene derivatives, among which are the esters of isomeric acids, cannot be

distinguished in this way, because they all seem to form complex compounds with basic mercury salts¹⁾.

From the dissociation constants of *angelic* and *tiglic acid* we can at the very best suspect that in the first acid a hydrogen atom is situated on the side of the COOH group, in the other one of the methyl groups.

The configurations adopted here are supported by the consideration that the most stable acid will be the one in which the relatively positive group is situated as near as possible to the COOH group.

$\begin{array}{c} \text{H}-\text{C}-\text{COOH} \\ \\ \text{H}-\text{C}-\text{COOH} \end{array}$	$\begin{array}{c} \text{HOOC}-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{COOH} \end{array}$	$\begin{array}{c} \text{CH}_3-\text{C}-\text{H} \\ \\ \text{H}-\text{C}-\text{COOH} \end{array}$	$\begin{array}{c} \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{H}-\text{C}-\text{COOH} \end{array}$	$\begin{array}{c} \text{CH}_3-\text{C}-\text{H} \\ \\ \text{CH}_3-\text{C}-\text{COOH} \end{array}$	$\begin{array}{c} \text{H}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CO} \end{array}$
maleic acid	fumaric acid	<i>iso</i> crotonic acid	<i>γ</i> -crotonic acid	angelic acid	tiglic acid
forms anhydride	no anhydride	—	—	—	—
$k = 1.2 \times 10^{-2}$	9.3×10^{-4}	3.6×10^{-5}	2.0×10^{-5}	5×10^{-5}	1×10^{-5}
complex Hg. salt +	0	0	+	—	—
	stable		stable		stable

About oleic and elaidic acid there is utter uncertainty, because the dissociation constants are not known; it can only be suspected that in the more stable elaidic acid the relatively positive carbon chain is likely to lie on the side of the carboxyl group.

With cyclic cis-trans isomers the importance of cis-trans situated radicles in relation to the ring becomes less as the last widens. [The conception of VON BAEYER that the angle between the directions of the affinities of trans-situated radicles decreases as the ring widens, is not incorrect; only VON BAEYER deduces this decrease from sterical considerations and then it cannot be so very important]; this consideration lessens the certainty of our conclusions about the configuration still more. But now here we meet with the very happy circumstance, that the trans-compounds frequently are asymmetrical and therefore can be resolved into optical antipodes.

If this argument is annulled, as in the case of the hexahydro-terephthalic acids, which are both symmetrical, or if a resolution into optical antipodes has not been tried, there is no certainty at all. This may be backed by the following table: (See following page).

We see that the formation of anhydrides, the most important argument with maleic acid, has all but lost its significance in the case of the cyclohexane derivatives, as both 1-2-dicarboxylic acids and neither of the 1-4-acids form an anhydride.

¹⁾ B. **33** 1340, 1641, 2692, (1900); **34** 1385, 2906 (1901), **35** 2571 (1902); **43** 568 (1910).

			k	Anhydride	Resolvable
cis-cyclopropane-dicarboxylic acid	1.2	4	$\times 10^{-4}$	+	—
trans " "	1.2	2.1	$\times 10^{-4}$	—	+
cis-cyclobutane-dicarboxylic acid	1.2	6.6	$\times 10^{-5}$	+	} not investi- gated
trans " "	1.2	2.8	$\times 10^{-5}$	—	
cis-cyclopentane-dicarboxylic acid	1.2	1.58	$\times 10^{-5}$	+	} "
trans " "	1.2	1.2	$\times 10^{-5}$	—	
cis " "	1.3	5.4	$\times 10^{-5}$	+	} "
trans " "	1.3	5.0	$\times 10^{-5}$	—	
cis-cyclohexane-dicarboxylic acid	1.2	4.4	$\times 10^{-5}$	+	—
trans " "	1.2	6.2	$\times 10^{-5}$	+	+
cis " "	1.3	} not determined		+	} not investi- gated
trans " "	1.3			—	
? cis " "	1.4	3	$\times 10^{-5}$	—	} sym- metrical
? trans " "	1.4	4.6	$\times 10^{-5}$	—	

This is the more true of the dissociation constants, whereof the differences in the case of the cyclopentane-dicarboxylic acids are small already, but leastways such that from the acid with the greater constant an anhydride is known.

About the cyclohexane-dicarboxylic acids in this respect we grope in the dark. The 1-2-acid, which has been resolved into optical antipodes and accordingly is undoubtedly the trans acid, is stronger than the cis acid; both acids easily form an anhydride. If in this case it should have been unknown which acid is resolvable, we should probably have come to a wrong conclusion.

With the 1-4-dicarboxylic acids, the classical case of cyclic cis-trans isomerism, *there is no certainty at all*; the one with the highest melting point, which von BAYER has denominated trans, has the highest dissociation constant and therefore one should perhaps call it the cis acid. As it as little forms an anhydride as the isomer and neither can be resolved into optical antipodes, the only remaining argument in favour of the current conception is the greater stability; an argument that should be termed weak, considering the slight solubility and the high melting point.

Still the case is not entirely hopeless; after having discussed the

chemical methods that can serve to determine the configuration, we will demonstrate that here too there is a way out.

It is evident that, if less characteristic radicles are bound to the nucleus, as in the cyclohexanediols 1-4 or the hexahydro-toluilic acids, with which no discernment by resolution into optical antipodes is feasible, it seems impossible to determine the configuration.

Here the difference which appears in the formation of complex compounds, for instance of the diols with boric acid, has proved promising; this has been evidenced by the configuration determination of some sugars, but on that point we will not expatiate here.

3. Secondly the configuration may be deduced from what happens if the double bond is saturated; the so formed compounds are different as they originate from the *cis* or from the *trans* isomer.

The configuration may also be inferred from the way of formation, either from saturated compounds by elimination of parts of the molecule, or from acetylene derivatives by partial saturation, or by substitution of groups in compounds, of which the configuration is known.

The last mentioned modes of determination, by which the bonds between the atoms are vigorously attacked, have often caused confusion, by which their trustworthiness has been impaired. When applied to fumaric and maleic acid, they at first seemed to answer excellently; we can still assert with satisfaction that fumaric acid is changed by KMnO_4 into racemic acid and maleic acid into *meso*-tartaric acid.

Only, the brilliant researches of WISLICIENUS about the bromination of both acids, followed by elimination of one molecule of HBr , by which fumaric acid furnishes first racemic dibromo-succinic acid and then bromo-maleic acid, and maleic acid first *meso* (*iso*-)dibromo-succinic acid and then bromo-fumaric acid, have turned out to be correct only as far as the final products are concerned.

McKENZIE ¹⁾ and BROR HOLMBERG ²⁾ namely have demonstrated that *iso*-dibromo-succinic acid with the lower m. p. can be resolved into optical antipodes and this entirely overthrows the deduction.

As well at the addition of bromine to both acids, as at the elimination of HBr , exactly the reverse occurs from what we could expect, and this inversion appears to be rather common.

By the action of PCl_5 on aceto-acetic acid two isomeric β -chloro-

¹⁾ Proc. Chem. Soc. 1911, 150.

²⁾ Journ. pr. ch. 84 145 (1911).

crotonic acids are formed, one of which is volatile with steam. This one has a dissociation constant $= 9,5 \cdot 10^{-5}$; the other acid has $k = 14,4 \cdot 10^{-5}$. From this it may be concluded with some certainty, that in the first mentioned acid the chlorine atom lies farther from the COOH group than in the other. Now the relatively weaker acid on reduction furnishes the relatively stronger *iso*-crotonic acid; on the other hand the relatively stronger β -chloro-crotonic acid gives rise to the relatively weaker α -crotonic acid; in both cases an inversion must have occurred and we come to the conclusion, as well as in the series maleic acid \rightarrow *iso*-dibromo-succinic acid \rightarrow bromo-fumaric acid, that an inversion has taken place at the attack of the valency, which governs the configuration.

By catalytic hydrogenation only of phenylpropionic acid in the presence of colloidal platinum 80 % of the theoretically possible amount of *allo*-cinnamic acid was formed; on the other hand, by the action of zinc dust and acetic acid, resp. alcohol, ordinary cinnamic acid was almost exclusively obtained¹⁾. As the catalytic hydrogenation of acetylene compounds appeared to warrant some certainty, we applied it to tetrolic acid, which ought to give chiefly α -crotonic acid.

However during a microchemical investigation, which was executed some years ago with the collaboration of Miss O. B. VAN DER WEIDE, α -crotonic acid could not be found among the reduction products of the sodium salt of tetrolic acid.

By hydrogenation of the free acid under the influence of palladium-sol, crotonic and *iso*-crotonic acid are formed in the proportion of 2 : 1.

We see, therefore, that no more than with the reduction of phenylpropionic acid, this chemical method is capable of giving us sufficient certainty about the configuration.

4. To cyclic cis-trans diols also this unsafe mode of determining the configuration is generally not applicable, because the correspondent saturated diols cannot be obtained.

The hydro-aromatic glycols form an exception, as they can be obtained from aromatic diphenols, which may be considered as cis diols. Of course this case is not quite to be compared to the hydrogenation of acetylene compounds; it is known with rather great certainty that the OH groups of the phenols are situated in the plane of the benzene nucleus; on the other hand it is to be supposed, considering

¹⁾ HOLLEMAN and ARONSTEIN B. 22 1181 (1889); LIEBERMANN and TRUCHSÄSS B. 42 4674 (1909); E. FISCHER, Ann. 386 385 (1912).

the number of isomers, that in acetylene derivatives the substituents lie in a line with the carbon atoms of the acetylene skeleton.

The researches in this field, *viz.* the catalytic hydrogenation of diphenols with the aid of nickel, show, that a *mixture* of the cyclohexanediols is formed; a reduction under the influence of platinum or palladium at a low temperature apparently has not been executed yet.

Now there are general syntheses of these diols, *viz.* from the non-saturated cyclic hydrocarbons, either by direct oxidation by KMnO_4 , or *via* the oxides; we have made use of them to prepare the hydrindenediols. According to current ideas the *cis* diol should be formed exclusively by this reaction¹⁾:

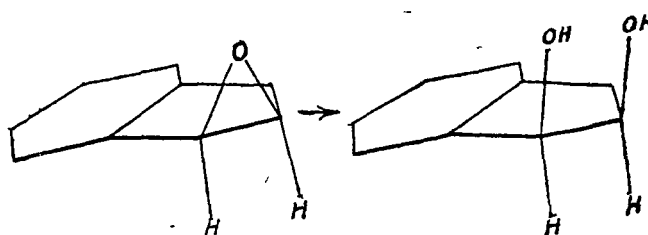


Fig. 1.

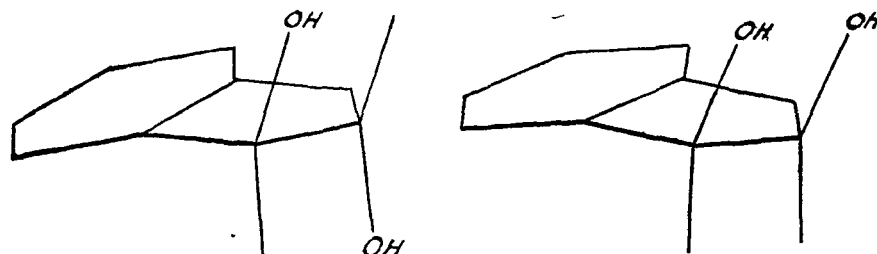
Indene oxide was hydrated as mildly as possible, that is to say at the ordinary temperature in aqueous solution with a very little acetic acid, and still we could isolate a considerable proportion of the *trans* isomer too. At this hydration likewise a valency of one of the carbon atoms that determine the configuration, is violated and a partial inversion takes place.

In judging the *cis-trans* isomerism in this case, the determination of the acidity is left out for the present, as the methods of investigation are not sensitive enough. The forming of an anhydride too cannot yield a good result here, because the bearers of the stereo-isomerism are brought into play, which is *not* the case with the formation of anhydrides of acids, as of maleic or cumaric acid.

Here are only left 1. the resolution into optical antipodes, but this will not be easy and has never been successfully accomplished; 2. the formation of complex compounds, which has proved effectual with the sugars, as we came to know by it the configurations of α - and β -glucose, of α - and β -fructose and of α - and β -galactose. In the case under consideration too the last method has been to the purpose; the isomer melting at the lower temperature namely, increased the conductivity of boric acid, on the other hand the isomer with the higher melting point diminished it in some degree,

¹⁾ Versl. Kon Akad. v. Wet 26, 1272 (1918).

and from this the *cis* configuration could be deduced for the first mentioned diol. If this method had not come to the rescue, the case would have been almost hopeless, because a resolution into optical antipodes cannot enlighten us:



For it is evident that *both* isomers are asymmetrical and therefore can be resolved into optical antipodes.

It has been our intention to draw attention to the fact, that as soon as valencies are attacked of atoms which determine the stereoisomerism, the arrangement of the groups runs a risk of being changed. Of course the phenomenon going by the name of WALDEN's inversion ought also to be included here. In many cases the possible isomers are both formed and very often principally the one, which we should not expect.

This will not occur only with reactions as have been mentioned, by which stereoisomers are formed; in consequence of the formation of stereoisomeric substances, which can distinctly be discerned, the phenomenon was observed here as well as with the inversion of WALDEN. But it stands to reason that it is of a general character and that we may compose the rule:

During a chemical reaction, by which atoms are added, eliminated or substituted, there is always a chance that the arrangement is changed of the valencies of the atom or of the atoms, at which the reaction takes place.

It deserves further consideration to establish whether the arrangement around adjacent atoms or around remote atoms is disturbed, when such a change occurs with the valencies of some atom.

This is not probable fortunately, as it would highly aggravate our task to determine the configuration of compounds, for every relation between optically active substances would fail. Besides the formation of anhydrides of maleic or citraconic acid would be worthless and the differences, that may be observed in the influence of compounds

on the conductivity of boric acid, would lose all significance for the determination of the configuration.

Therefore, if this improbability be excluded and if we assume that an attack of the valencies somewhere in the molecule leaves unaltered the arrangement around the atoms, which are not immediately concerned, then we shall be able to obtain a solution in some apparently hopeless cases.

We have seen that with the two isomeric hexahydro-terephthalic acids a comparison of the dissociation constants does not answer the purpose; neither is resolvable into optical antipodes and besides from neither an anhydride could be obtained.

Of the Δ^2 -tetrahydro-terephthalic acids (see accompanying diagrams)

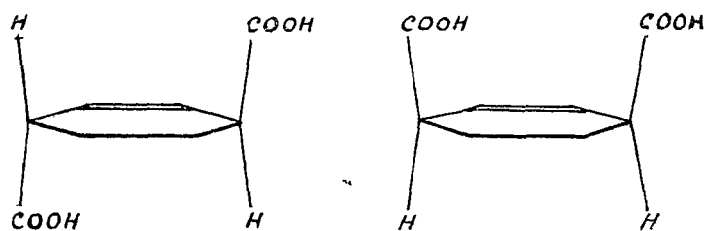


Fig. 2.

the trans acid should be resolvable into optical isomerides and it is thereby to be distinguished from the cis acid, which cannot be resolved.

Now it should be possible to change these acids into the correspondent hexahydro-terephthalic acids by catalytic reduction, without altering the arrangement of the carboxyl groups and therefore the configuration of the last mentioned acids may be definitively established.

•A case bearing an essential relation to this one, is:

Benzoquinone furnishes maleic acid by careful oxidation; from this we may conclude with rather great certainty, that this acid has the cis configuration, as this arrangement is contained in the quinone molecule and because at the elimination of the $-\text{CH}=\text{CH}-$ group, the bonds that bear the isomerism, are not interfered with; if in the case of maleic and fumaric acid we were as badly equipped as with the hexahydro-terephthalic acids, then this mode of formation would have been of preponderant importance for the determination of the configuration.

Chemistry. — "*The Addition of Hydrogenbromide to Allylbromide*".
By Prof. A. F. HOLLEMAN and B. F. H. J. MATTHES.

(Communicated in the meeting of May 25, 1918).

In the many cases that in my laboratory I had trimethylene-bromide prepared by the introduction of HBr gas into allyl-bromide, I was struck with the fact that now an almost quantitative yield was obtained, now a much smaller yield, without our being able to indicate the cause of this varying yield. When now my assistant, Mr. DEN HOLLANDER, had obtained almost exclusively trimethylene-bromide in this addition in a very brightly lighted room, whereas a few years ago Mr. WUITE observed by the side of it considerable quantities of a product that boiled at a lower temperature (propylene bromide) in the ordinary work-room, the supposition suggested itself that daylight exerts an influence on this. Mr. MATTHES undertook to inquire more closely into this matter.

For this purpose a quantity of allyl-bromide was divided into two equal parts; one part was poured into an ordinary bottle, the other in a bottle that had been perfectly blackened on the outside with lacquer. The liquid in the ordinary bottle was exposed as much as possible to the sunlight during and after the introduction of HBr. Every time that no HBr was absorbed any more, it was closed, and left to itself till the next day. After some days no further HBr was absorbed. The blackened bottle was treated in the same way. The absorption of HBr took place a great deal more slowly here, so that the process had to be continued for some weeks, before complete saturation had been attained.

When the contents of the two bottles was afterwards subjected to distillation, the preparation from the ordinary bottle almost entirely went over at constant temperature and at the boiling point of trimethylene bromide. After distillation in vacuum its boiling point amounted to 167°.1 for 760 mm.

The contents of the other bottle, on the other hand, presented a very considerable boiling range, viz. from 100—190°. On fractionated distillation a fraction of about 7 gr., going over between 140°—150°, was obtained, while between 155° and 165° a fraction of 22 gr. went over. The former had about the specific gravity of propylene

bromide, viz. 1.9259 at 23°.2; the latter had the spec. gr. of trimethylene bromide, viz. 1.9801 at 23°.2. Between 100° and 105° a few drops had also been distilled, which were still unchanged allyl-bromide, as appeared from this boiling point. Hence the conclusion is that on addition of HBr to allyl-bromide in bright daylight trimethylene bromide is almost exclusively formed; in the dark, beside this compound as chief product, also pretty much propylene bromide.

Amsterdam, May 1918. Org. Chem. Lab. of the University.

Physics. — “*The variability with time of the distributions of Emulsion-particles*”. By Prof. L. S. ORNSTEIN. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of March 31, 1917).

SMOLUCHOWSKI discussed this problem in different papers and gave a complete survey of his work in three lectures at Göttingen.¹⁾

He deduced a formula for the average change of the number of particles in an element, which at the moment zero contains n particles. This formula is:

$$\bar{\Delta}_n = (v-n) P, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P is the probability that a particle which lies in the element at the time zero, may have come outside in the moment t ; whilst v is the number of particles which at a homogeneous distribution over the whole volume would come to lie in the element in consideration.

Also for the average square with a given number of particles n at the time zero SMOLUCHOWSKI gives a formula, viz.

$$\bar{\Delta}^2_n = [(n-v)^2 + n] P^2 + (n+v) P, \quad . \quad . \quad . \quad . \quad (2)$$

from which follows — if the average also is determined according to n —

$$\bar{\Delta}^2 = 2 v P.$$

These relations are deduced by SMOLUCHOWSKI with the help of calculations of probability, which “nach Ausführung recht komplizierter Summationen (yield) merkwürdigerweise das einfache Resultat”.

It goes without saying, that it must be possible to attain such a simple result also by a less complicated method. That this is indeed the case I want to demonstrate in this paper. At the same time it will be possible to give some extension to the result.

1. Let us think the space divided into a great number of equal elements, which we shall mark by the indices $1 \dots \kappa \dots k$. Let there be at a given moment $t=0$ $n_1 \dots n_\nu \dots n_k$ particles in

¹⁾ Cf. Phys. Zeitschr. 1916, p. 557 and also Phys. Zeitschrift XVI. 1915. p. 323.

these elements. After a time t has passed these numbers have become changed. Let $p_{1\lambda}$ then represent the chance that a particle which at the time $t=0$ is in the element 1, is found at the time t in the element λ , and let $p_{\lambda 1}$ represent the probability of the reversed transition. Then, if there is no predilection for any direction in the movement of the particles, it goes without saying that $p_{1\lambda} = p_{\lambda 1}$.

Further $\sum_{\lambda=1}^{\lambda=k} p_{\lambda\lambda} = P$ if the sum is taken according to all values λ except $\lambda = \lambda$, for the sum represents the probability that the particle has come after the time t in one of the $k-1$ other elements, i.e. outside the element λ .

If an element λ contains n_λ particles the number of particles having passed from λ to λ in a given case will be $\Delta_{\lambda\lambda}$. I shall now calculate first the average values of $\Delta_{\lambda\lambda}$, $\Delta_{\lambda\lambda}^2$, and $\Delta_{\lambda\lambda} \Delta_{\mu\mu}$. The number of cases where $\Delta_{\lambda\lambda}$ has the value s and thus $n_\lambda - s$ particles have remained in the element, amounts to:

$$\frac{n_\lambda!}{(n_\lambda - s)! s!} p_{\lambda\lambda}^s (1 - p_{\lambda\lambda})^{n_\lambda - s} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

as is easily seen; to determine the three average-values this expression must be multiplied by s resp. s^2 and summed from zero to n_λ . Then after quite an elementary calculation of these finite sums, we find

$$\overline{\Delta_{\lambda\lambda}^2} = p_{\lambda\lambda}^2 (n_\lambda^2 - n_\lambda) + p_{\lambda\lambda} n_\lambda \quad . \quad . \quad . \quad . \quad . \quad (5)$$

and

$$\overline{\Delta_{\lambda\lambda}} = p_{\lambda\lambda} n_\lambda \quad . \quad . \quad . \quad . \quad . \quad (4)$$

To determine the average of a double product we need only replace (3) λ by μ and s by t (where t represent the number of emitted particles in a definite case).

If the result obtained in this way is multiplied by (3) and summed with respect to ν from 0 to n_λ and with respect to t from 0 to n_μ , we find

$$\overline{\Delta_{\lambda\lambda} \Delta_{\mu\mu}} = p_{\lambda\lambda} p_{\mu\mu} n_\lambda n_\mu \quad . \quad . \quad . \quad . \quad . \quad (6)$$

With the help of the relations (4), (5) and (6) SMOLUCHOWSKI's formulae can now immediately be deduced. The change ${}_n\Delta_\lambda$, i.e. the total change of the number of particles in the element λ may be represented by

$${}_n\Delta_\lambda = \Delta_{1\lambda} + \Delta_{2\lambda} \dots + \Delta_{k\lambda} - (\Delta_{\lambda 1} + \dots \Delta_{\lambda k}) \quad . \quad . \quad (7)$$

Now we can write Δ_λ for $\Delta_{\lambda 1} + \dots \Delta_{\lambda k}$, i.e. the total number of particles that leaves the element in the time t .

Then we must determine the average of (7) with constant n_λ ,

while all possible values must be given to the number $n_1 \dots n_k$ in the other elements. If now we first take the $n_1 \dots n_r$ constant and determine the average, we find

$${}_n\overline{\Delta}_r = p_{1r} n_1 + \dots p_{kr} n_k - n_r P.$$

If then we proceed to determine the average according to $n_1 \dots n_r$ and keep in mind that $\overline{n}_1 = \dots = \overline{n}_r = v$, we find

$${}_n\overline{\overline{\Delta}}_r = v(p_{1r} + \dots p_{kr}) - n_r P = (v - n_r) P.$$

In order to find ${}_n\overline{\Delta}_r^2$ we proceed in quite an analogous way, we bring (7) into the square. Then we find

$$\begin{aligned} \Delta_r^2 = & \Delta_{1r}^2 + \dots \Delta_{kr}^2 + \Delta_r^2 \\ & + 2 \Delta_{1r} \Delta_{2r} + \dots \\ & - 2 \Delta_r (\Delta_{1r} + \dots \Delta_{kr}). \end{aligned}$$

If now we apply (5) and (6) and determine the average with given $n_1 \dots n_k$ and n_r , we find

$$\begin{aligned} {}_n\overline{\Delta}_r^2 = & (n_1^2 - n_1) p_{1r}^2 + p_{1r} n_1 + \dots + P^2 (n_r^2 - n_r) + n_r P \\ & + 2 n_1 n_2 p_{1r} p_{2r} + \dots \\ & - 2 n P (p_{1r} n_1 + \dots p_{kr} n_k). \end{aligned}$$

Here the average must be determined keeping constant n_r with respect to n_1 etc. And we must bear in mind that $\overline{n_1^2} = \overline{n_2^2} = \dots \overline{n_r^2} = v^2 + v^1$, that further $\overline{n}_1 = v$ and $\overline{n_1 n_2} = v^2$. Consequently we find

$$\begin{aligned} {}_n\overline{\overline{\Delta}}_r^2 = & (v^2 + v) (p_{1r}^2 + \dots p_{kr}^2) \\ & + 2 v^2 (p_{1r} p_{2r} + \dots) \\ & - v (p_{1r}^2 + \dots) \\ & - 2 n v P^2 + P^2 (n^2 - n) + n P. \end{aligned}$$

The three first terms together yield $P^2 v^3$. The result becomes thus

$$\overline{\overline{\Delta}}_r^2 = \{ (n-v)^2 P^2 - n^2 P^2 \} + (n+v) P$$

from which by determining the average according to n the relation

$$\overline{\Delta}^2 = 2 v P$$

arises.

2. The extension of the given formulae may be obtained to the case that the deviation of density in the various elements of volume are not independent, where however concerning the emission of the particles we must still presuppose independence of the events.

In order to introduce the correlation of the densities I make use of the function g , which was defined by Dr. ZERNIKE and myself.¹⁾

¹⁾ We have $n_1 = v + \delta$, $\overline{n_1^2} = v^2 + 2 v \overline{\delta} + \overline{\delta^2} = v^2 + v$.

$\overline{n_1 n_2} = \overline{(v + \delta_1)(v + \delta_2)} = v^2 + v (\overline{\delta_1} + \overline{\delta_2}) + \overline{\delta_1 \delta_2} = v^2$.

²⁾ Chance deviations in density in the critical point of a simple matter. These Proc. XVII, 1914. p. 582.

If δ_0 is the deviation in density in a point $x=0, y=0, z=0$, then we get for the deviation of density δ in a point x, y, z :

$$\bar{\delta} = g(x, y, z) \delta_0 dv \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

where dv is the element of volume.

Further

$$\overline{\delta \delta_0} = g(x, y, z) \overline{\delta_0^2} dv = g(x, y, z) \varrho \quad . \quad . \quad . \quad . \quad . \quad (9)$$

where ϱ is the number of particles per unit of volume.

We now have

$$\overline{{}_n\Delta_r} = n_1 p_{1r} + \dots n_r p_{rr} - n P.$$

Now $\overline{n_1} = v + \overline{\delta_1} dv$, if then we introduce (8) and consider p_{rr} as function of x, y, z , bearing in mind that $\delta_0 = \frac{v-n_r}{dv}$, we find

$$\overline{{}_n\Delta_r} = (v-n) \left\{ P + \int g_{rr} p_{rr} dv \right\}$$

The influence of the second part may become considerable with a strong correlation

Also in determining $\overline{{}_n\Delta^2}$, the correlation can be taken into consideration. Then in the first place we get the old terms, but moreover (9) yields still new terms in $\overline{n_\lambda^2}$, $\overline{n_\lambda}$ and $\overline{n_\lambda n_r}$, $\overline{n_r n_\lambda}$. These terms are:

$$\begin{aligned} & 2 v (v-n) \int p_{rr} g_{rr} dv \\ & - (v-n) \int p_{rr}^2 g_{rr} dv \\ & - 2 n P (v-n) \int p_{rr} g_{rr} dv \\ & + 2 v \int p_{rr} p_{\mu r} g_{\mu r} dv_\lambda dv_\mu. \end{aligned}$$

If then $\overline{\Delta^2}_n$ is determined, only the last term remains and a part of the term before last, so that we get

$$\begin{aligned} \overline{\Delta^2} &= 2 v \left(P + \int p_{rr} p_{\mu r} g_{\mu r} dv_\mu dv_\lambda \right. \\ & \quad \left. + \int p_{rr} g_{rr} dv \right). \end{aligned}$$

These considerations may also be applied, as least approximately, to the changes, which accidental derivations in density undergo in result of diffusion. Our formulae show then that close to a critical point the deviations in density as a result of their correlation, are not only stronger on the average, but also more strongly changeable.

Utrecht, March 1917.

Institute for Theoretical Physics.

Physics. - "*On the Brownian Motion*". By Prof. L. S. ORNSTEIN.
(Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of December 29, 1917.)

VON SMOLUCHOWSKI¹⁾ observed that the function which gives the probability, that in the Brownian Motion a particle accomplishes a definite way in a given time is a solution of the equation of diffusion. For cases in which an exterior force also acts on the particles, he deduced a differential equation for the above-mentioned function of probability by a phenomenological method. Some time after Mr. H. C. BURGER²⁾ deduced this differential equation following a method, which takes the essence of the function of probability more into consideration. Both deductions do not stand in direct connection with the mechanism of the Brownian motion; my object in this paper is to demonstrate, that starting from a relation which Mrs. DE HAAS—LORENTZ³⁾ has used in her dissertation, to determine the average square of the distance accomplished, one is able to determine the function of probability of the Brownian motion. It is worth observing that the way in which different averages depend on the time may be calculated from the results obtained by Mrs. DE HAAS—LORENTZ by a slightly more careful transition of the limit than was necessary for the object she had put herself (viz. the determination of the stationary condition). First I want to determine these averages by a new method, which will offer the opportunity of demonstrating, that the opinion, from which Dr. A. SNETHLAGE⁴⁾ starts in the theory of the Brownian motion that EINSTEIN's theory is in conflict with statistical mechanics, is incorrect.

Besides the function of probability for the distance I shall also deduce that for the velocity. The chain of thoughts which lead to

¹⁾ Compare e.g. M. v. SMOLUCHOWSKI. Drei Vorträge über Diffusion, BROWN'sche Bewegung etc. Phys. Zeitschr. XVII p. 557 1916.

²⁾ H. C. BURGER, Over de theorie der BROWN'sche beweging. Verslagen Kon. Ak. XXV p. 1482, 1917.

³⁾ Mrs. Dr. G. L. DE HAAS—LORENTZ. Over de theorie der BROWN'sche beweging, Diss. Leiden 1912.

⁴⁾ Miss Dr. A. SNETHLAGE, Moleculair-kinetische verschijnselen in gassen etc. Diss. Amst. 1917.

the results given below shows great similarity to the deductions which Lord RAYLEIGH¹⁾ gave utterance to already years ago. Kindred ways of regarding the stationary condition are also found in the work of Dr. FOKKER²⁾ and M. PLANCK³⁾.

§ 1. In the dissertation Mrs. DE HAAS—LORENTZ starts from the equation of motion for a emulsion particle, which she brings in the formula

$$m \frac{du}{dt} = -wu + mF \quad . \quad . \quad . \quad . \quad . \quad (1)$$

Here u is the velocity of the particle, $w = 6\pi\mu a$ the resistance which according to STOKES' formula the spherical particle (radius a) would experience in a liquid with internal coefficient of friction μ . The force expended by the shocks of the molecules is divided into two parts, of which one is that according to STOKES, the second is quite irregular, so that $\bar{F} = 0$. The determination of the average is to be understood in this way that it is to be taken at a given moment for particles which all have had the same velocity u_0 a time before.

Now we are able to integrate the equation (1), if we introduce $\frac{w}{m} = \beta$, we have

$$u = u_0 e^{-\beta t} + e^{-\beta t} \int_0^t e^{\beta t} F(t) dt \quad . \quad . \quad . \quad . \quad . \quad (2)$$

where u_0 is the velocity at the time $t = 0$.

If then we determine the average of this equation in the way indicated, the result is

$$\bar{u} = u_0 e^{-\beta t} \quad . \quad . \quad . \quad . \quad . \quad (3)$$

or expressed in words: when we start from a great number of particles of given velocity, the average velocity decreases in the same way as with large spheres; the damping coefficient also is deduced in the same way from radius and coefficient of friction of the fluid. Let us now calculate also the average of the square of the velocity. For this we find:

¹⁾ Lord RAYLEIGH, Phil. Mag. XXXII, p. 424. 1894. Papers III. Dynamical problems in illustration of the theory of gases.

²⁾ Dr. A. FOKKER, Over de BROWN'sche beweging in het stralingsveld. Diss. Leiden, pg. 523, 1913.

³⁾ M. PLANCK, Ueber einen Satz der Statistischen Dynamik u.s.w. Berl. Ber. p. 324. 1917.

$$\overline{u^2} = u_0^2 e^{2\beta t} + e^{-2\beta t} \left\{ \int_0^t e^{\beta t} F(t) dt \right\}^2 \quad (4)$$

In order to determine the integral in the second member we proceed in the following way. We write for it

$$\int_0^t \int_0^t \overline{F(\xi) F(\eta)} e^{\beta(\xi+\eta)} d\eta d\xi.$$

Now $\overline{F(\xi) F(\eta)}$ is only differing from zero if η and ξ differ very slightly, i.e. there is for short periods a correlation of the forces F . If we introduce $\eta = \xi + \psi$, it is allowed to replace η in the exponent by ξ and to split up the integral into a product of integrals according to ξ and ψ where we may integrate from $-\infty$ to $+\infty$. If then we assume

$$\int_{-\infty}^{+\infty} \overline{F(\xi) F(\xi + \psi)} d\psi = \vartheta \quad (4a)$$

which is a constant characteristic of the problem and if we perform the integration towards ξ , then (4) is transformed after substitution into

$$\overline{u^2} = u_0^2 e^{-2\beta t} + \frac{(1 - e^{-2\beta t}) \vartheta}{2\beta} \quad (5)$$

When applying this equation for $t = \infty$, $\overline{u^2} = \frac{kT}{m}$ and thus we get

$$\vartheta = \frac{kT}{m} 2\beta$$

In the same way we are able to determine the average square of the distance accomplished. From (2) or by direct integration from (1) we get namely

$$u - u_0 = -\beta s + \int_0^t F dt$$

$$\beta^2 \overline{s^2} = \overline{(u - u_0)^2} + \left\{ \int_0^t F dt \right\}^2 \quad (6)$$

For the last integral we find in a quite analogous way

$$\vartheta t$$

If we calculate the first average with the help of (3) and (5) we obtain

$$\beta^2 \overline{s^2} = u_0^2 (1 - 2e^{-\beta t} + e^{-2\beta t}) + \frac{\mathfrak{D}}{2\beta} (-3 - e^{-2\beta t} + 4e^{-\beta t}) + \mathfrak{D}t \quad (7)$$

Consequently for very long periods we find

$$\overline{s^2} = \frac{2kT\mathfrak{D}}{\beta} = \frac{kT}{3a\mu} t \quad (8)$$

which is the well-known formula for the average distance in the Brownian motion. If we determine the average of (7) with reference to all possible initial velocities and if we consider that $\frac{1}{u_0^2} = \frac{\mathfrak{D}}{2\beta}$, we find for the average square of the distance accomplished as an arbitrary initial velocity:

$$\beta^2 \overline{s^2} = \frac{\mathfrak{D}}{\beta} (t\beta - 1 + e^{-\beta t}) \quad (7a)$$

As long as βt is large in relation to $1 - e^{-\beta t}$ the formula of EINSTEIN is thus the right one. For the cases, considered in experiments, the lowest limit for t to be obtained in this way is of the order of 0.01 second.

§ 2. On the basis of statistical mechanics objections have been raised by Prof. J. D. v. D. WAALS JR. and Miss A. SNETHLAGE¹⁾ to the application of the division which has been applied to this case upon the example of EINSTEIN and HOPF in their treatment of another problem.

Starting from the supposition than in an "ensemble".

$$\overline{Ku} = 0$$

where K is the active force, they work out another fundamental formula viz. (with a slight variation in notation)

$$\frac{d^2 u}{dt^2} = -\varrho^2 u + w \quad (9)$$

where \overline{w} has to be taken zero. We can again integrate this equation and obtain then

$$u = u_0 \cos \varrho t + \frac{\dot{u}_0}{\varrho} \sin \varrho t + \frac{1}{\varrho} \int_0^t w(\xi) \sin \varrho (t - \xi) d\xi \quad (10)$$

If taking the average we get:

$$\overline{u} = u_0 \cos \varrho t + \frac{\dot{u}_0}{\varrho} \sin \varrho t$$

The average velocity would in this way possess a definite period. If however we work out $\overline{u^2}$ we arrive at an incompatibility.

¹⁾ Cf. Versl. Kon. Ak. v. Wet. XXIV. 1916. p. 1272.

Because for $\overline{u^2}$ we get

$$\overline{u^2} = \left(u_0 \cos \varrho t + \frac{\dot{u}_0}{\varrho} \sin \varrho t \right)^2 + \frac{1}{\varrho^2} \left\{ \int_0^t w(\xi) \sin \varrho (t - \xi) d\xi \right\}^2. \quad (11)$$

For the integral, if again we make a double integral of it and if we introduce the constant θ

$$\theta = \int_{-\infty}^{+\infty} w(\xi) w(\xi + \psi) d\psi. \quad (12)$$

we can write

$$\frac{\theta}{\varrho^2} \int_0^t \sin^2 \varrho (t - \xi) d\xi = \frac{\theta t}{2\varrho^2} + \text{periodical terms.}$$

Thus we find

$$\overline{u^2} = \frac{\theta t}{2\varrho^2} + \text{periodical terms} \quad (13)$$

This formula shows that $\overline{u^2}$ increases indefinitely with the time, while it is evident according to statistical mechanics that $\overline{u^2}$ must approach $\frac{kT}{m}$.

Consequently if the equation (9) is treated as a differential equation we arrive at results which are not right ¹⁾.

§ 3. Miss Dr. SNETHLAGE and Prof. Dr. J. v. D. WAALS JR. have observed, that the theory of the Brownian motion must be in accordance with a general theorem of statistical mechanics. For the case that we consider a particle, that under the influence of the impacts of the molecules of the liquid executes a movement, the force which the molecules exercise does not depend upon the velocity, but only upon the coordinates. Consequently the product of force and velocity must on the average be zero, as well in a canonical as in a microcanonical as in a time ensemble. Now they are of opinion that EINSTEIN's formula comes into conflict with this. I shall demonstrate that this is only the case to a certain extent.

If we assume in a canonical (or micro-canonical ensemble) all systems selected in which the velocity of our particle at a point of time 0 is equivalent to u_0 and if then we follow this group of particles,

¹⁾ An analogous question is treated by M. PLANCK (Ann. der Phys. 1912. Bd. 37 p. 462) where it is demonstrated that the energy of a resonator subjected to the irregular field of black radiation increases in proportion to the time; the f of PLANCK agrees here with v. D. WAALS' u .

we can work out an average of every arbitrary quantity for the group of systems which after a time t has developed from the group considered at first. The value of the quantity considered varies for the different systems of our group (part ensemble), because the systems where at $t=0$ the velocity of the particle is u_0 , may still show considerable differences, so that e.g. the impulses which the particle gets will be widely different. I shall call this average the *case-average with a given initial velocity*. Moreover the velocity u_0 may be varied and again the case-average may be worked out and then by making u_0 run through all possible values all systems are taken into consideration in determining the average at the time t . If now the case-average of a quantity $g(u)$ for u_0 is $g(u_0)$ and if the number of systems of the group is $N(u_0)$ then — if N represents the total number of systems in the ensemble — the quantity

$$\frac{\sum N(u) g(u)}{N}$$

is the case-average for the entire ensemble.

However, as the ensemble is stationary the case average for a quantity is equal to the average of the corresponding quantity in the ensemble. If in particular $g(u)$ for every u is equal to zero, the average in the ensemble is also zero. I shall now demonstrate that if we start from EINSTEIN's formula the case average of Ku for every initial velocity u_0 is zero, and from this it follows immediately that EINSTEIN's formula does *not come into conflict* with the theory of the ensembles, more particularly that $\overline{Ku^e} = 0$, ($-e$ means determining the average of an ensemble, which — is used everywhere here for the case average).

EINSTEIN's equation comes into conflict with the theory of the ensembles if we select at $t=0$ a group of particles with a given velocity u_0 from the ensemble. For if we determine the average of

the equation it yields $m \frac{du}{dt} = K = -\nu u_0$, whilst according to the

theory of ensembles \overline{K} is independent of the velocity. If however we leave the selected group to itself and if we apply to its motion EINSTEIN's equation which is not right in the first moment, it is evident that in the long run the group moves in such a way that in the long run EINSTEIN's equation can be applied to it. Moreover from the group with particles with a given velocity u_0 those systems can be selected to which (1) applies. From what follows it becomes apparent that for this group in the long run the usual relations

with regard to the averages in a canonic ensemble become the right ones.

Instead of $Ku = 0$ we can also write $m \frac{du}{dt} u = 0$ or $u \frac{du}{dt} = 0$.

If now we multiply the EINSTEIN-HOPF equation by u and work out the case average, we get

$$u \frac{du}{dt} = -\beta \overline{u^2} + u \overline{F}$$

Further we shall demonstrate that for sufficiently long periods the second member is identically zero.

For according to (5) we have got for the first term $-\frac{\partial}{2\beta} \beta$ or $-\frac{\partial}{2}$. We shall now determine the second average. For this purpose we multiply (2) by F and work out the average, and arrive at

$$\overline{uF} = \overline{u_0 e^{-\beta t} F} + e^{-\beta t} F \int_0^t e^{\beta t} F(t) dt$$

In this formula the first average in the second member is zero. To determine the second average we must consider that F for the integral refers to a definite time t . And so only those parts of the integral where the argument differs only slightly from t yield distributions to the average. In the exponent we can again take the argument equivalent to t , so that we can write for the second term

$$\int_{t-\eta}^t \overline{F(t) F(t-\eta)} d\eta \quad \text{or} \quad \int_{-\infty}^0 \overline{F(\xi) F(\xi-\eta)} d\eta$$

Now this integral is just half of the integral of (4a), as it covers half the region of integration, whilst the integrand is of course symmetrically with regard to ξ .

And so in the end we find for the second member identically zero as the two averages first neutralize each other. If now we take (5) into consideration for shorter periods the second member becomes

$$u_0^2 e^{-2\beta t} - \frac{\partial}{2\beta} e^{-2\beta t}$$

This result is also obtained by differentiating (4) with respect to the time.

The case average of $u \frac{du}{dt}$ for finite times not large with reference to $\frac{1}{\beta}$ is consequently not strictly zero. Now we can however determine

the average according to the initial velocity u_0 and so find the ensemble average of $u \frac{du}{dt}$. Then we obtain

$$\overline{u \frac{du}{dt}}^e = \left(\overline{u_0^2}^e - \frac{\vartheta}{2\beta} \right) e^{-2\beta t} = 0$$

as $\overline{u_0^2}^e$ possesses the equipartition value. Thus it is proved that also for short periods the average value of the case average does not come into conflict with statistical mechanics.

4. I shall now deduce the law of frequency for distribution of velocity. If we integrate the equation (1) for a short time τ , we can write for it

$$u - u_0 = -\beta u_0 \tau + x \quad \text{or} \quad u = u_0 (1 - \beta\tau) + x \quad (14)$$

where $x = \int_0^\tau F(t) dt$ and $\overline{x^2} = \vartheta\tau$.

Now there is for x a law of frequency $\varphi(x)$, so that

$$\int_{-\infty}^{+\infty} \varphi(x) dx = 1, \quad \int_{-\infty}^{+\infty} x \varphi(x) dx = 0 \quad \text{and} \quad \int_{-\infty}^{+\infty} x^2 \varphi(x) dx = \vartheta\tau. \quad (15)$$

If now a particle starts with a given velocity u_0 , the number of particles, for which in the time t the velocity lies between u and $u + du$, may be represented by

$$f(u_0, u, t) du$$

or shorter

$$f(u, t) du$$

Let us now consider the distribution of velocity at the time $t + \tau$ and again fix our attention on the particles whose velocity lies between u and $u + du$. These particles have had at t a velocity u' in such a way that

$$u' (1 - \beta\tau) = u - x$$

or

$$u' = u (1 + \beta\tau) - x \quad (16)$$

whilst an interval $du' = (1 + \beta\tau) du$ corresponds to the interval du . The number of particles that is at t in du' and at $t + \tau$ in du consequently amounts to

$$f(u', t) \varphi(x) dx du'$$

and thus we get

$$f(u, t + \tau) du = (1 + \beta\tau) du \int f(u', t) \rho(x) dx. \quad (17)$$

If now we work this out and retain the terms up to the first order in τ and if we take (15) into consideration and if after division by τ , we make τ approach zero, we obtain

$$\frac{\partial f(u, t)}{\partial t} = \beta \frac{\partial}{\partial u} (u \cdot f) + \frac{\partial}{2} \frac{\partial^2 f}{\partial u^2} \quad (18)$$

To the function of frequency for the velocity the extended equation of diffusion is thus applicable, where ν plays the part of coefficient of diffusion. The equation is quite of the same form as that for the Brownian motion under the influence of a quasi-elastic force ($-u$ or $-s$) (cf. also § 4). If we apply (18) to determine the stationary condition we have

$$0 = \beta \frac{\partial}{\partial u} (u f) + \frac{\partial}{2} \frac{\partial^2 f}{\partial u^2}$$

from which follows

$$f = C_1 e^{-\frac{\beta}{2} u^2} + C_2 e^{-\frac{\beta}{2} u^2} \int_0^u e^{\frac{\beta}{2} u^2} du.$$

This last term becomes infinite for $u = \infty$, consequently the integration constant must be taken $c_2 = 0$.

For the law of distribution we thus find the MAXWELL division of velocity quite independent of the initial condition. Moreover RAYLEIGH has carefully investigated this question for his particular example. He has deduced a similar equation for a particle in a highly rarefied gas, where only the constants β and $\frac{\partial}{2}$ have another meaning (cf. loc. cit.). It goes without saying that if one starts from the equation of v. D. WAALS-SNETHLAGE, one arrives at the conclusion that the division after long periods is *not* that of MAXWELL, and that there does not even exist a stationary division of velocity. And on this point also these investigators thus come into conflict with the statistical mechanics of GIBBS, which is the starting-point of their reasonings.

It may further be observed that for a particle beginning with a velocity zero, as long as u is still small with respect to the velocity of the particles, which collide against it, we get as RAYLEIGH has demonstrated

$$\frac{\partial f}{\partial t} = D \frac{\partial^2 f}{\partial u^2}.$$

For the change in velocity we get then at each impact according to RAYLEIGH

$$u' = u \pm 2q v,$$

where q is the relation of the masses of particles and molecules, v the velocity of the molecules. Now the problem treated by RAYLEIGH in this way may be connected directly with the theory of the function of probability for the way in the Brownian motion. If we take the velocity marked as vector, the terminal point is removed $\pm qv$ after every shock. The terminal point of the vector consequently executes a Brownian motion at least according to the scheme which is often given of it (cf. e.g. Mrs. DE HAAS—LORENTZ' dissertation). It is certainly remarkable how Lord RAYLEIGH had already so long ago deduced these results, which came to the foreground only by SMOLUCHOWSKI's work, which opened so many new views.

It may have its advantages now it has become apparent that EINSTEIN's formula is the right one to say something further on the kinetic mechanism. Let us first direct our attention to a single shock of a particle of a great mass with a particle of a small one. If the velocity for the first is before the shock u' , after the impact u , the velocity of the small particle v and the relation of the masses q , where we have $q \ll 1$, then we get for every impact:

$$u = u' (1 - q) \pm q v.$$

If we assume then that again and again after a time τ a collision takes place, then we have

$$\frac{u - u'}{\tau} = -\frac{q}{\tau} u' \pm \frac{q}{\tau} v$$

for every impact. We can only make a differential equation of this equation of differences by taking τ infinitely small. if q is of the same order infinitely small and then we get

$$\frac{du}{dt} = -\beta u \pm \beta v,$$

where F may be written for βv . Thus we see here by a (not very strict approach to the limit) EINSTEIN's equation arise as it were. If now we do not go to the limit, but avail ourselves of the following graphic representation, its meaning becomes even more clearly visible. On one axis we measure out the time (and to make things easier we take again equal intervals between the impacts), on the other the velocity. Between two collisions the velocity is then constant, at an impact the velocity suddenly jumps to another value and this jump consists in every case in two parts; one part proportional to the velocity of the particle before the shock with which

the velocity decreases and one part which may be either positive or negative (and in general may possess all sorts of values dependent upon the conditions of the impacts, which in the simple case investigated by RAYLEIGH is $\pm qv$). The velocity-time curve is thus a discontinuous curve. If the velocity has become large it has the tendency to become smaller by shocks owing to the first part, whilst the second part exercises no systematic influence in a contrary sense. If now we imagine a combination of curves drawn starting from a given velocity, EINSTEIN'S equation will represent for each of these discontinuous curves the differential equation. At the same time if we introduce the curve $u = u_0 e^{-\beta t}$ into the scheme, this line will at all times be an average of the discontinuous velocity time-curves in the diagram.

§ 4. Finally I will deduce the function of probability for the Brownian motion under the influence of an external force. We take this force km , where k depends upon the place (s).

The equation of motion for our particle is then the following

$$\frac{du}{dt} = -\beta u + F + k \dots \dots \dots (19)$$

If now a particle has in the time $t=0$ a velocity u^0 , if in a time $t=\tau$ the velocity has become u' and a way s' is accomplished, and if u and s represent these magnitudes in a time t , we get

$$u - u' = -\beta(s - s') + \int_{t=\tau}^t F dt + \int_{t=\tau}^t k dt.$$

We now consider the time so small that the way accomplished in that time is small enough to treat K in the last integral which depends upon s as a constant.

We have thus

$$u - u' = -\beta(s - s') + \int_{t=\tau}^t F dt + k\tau \dots \dots \dots (20)$$

Now we want $\overline{\Delta s} = \overline{s - s'}$ and $\overline{\Delta s^2}$. In order to determine these we apply (3), this yields

$$\overline{u - u'} = u_0 e^{-\beta t} (1 - e^{-\beta \tau})$$

as we have to take the mean value of Δs for all possible values of u_0 the average of \overline{us} being zero we get

$$\beta \overline{\Delta s} = k\tau \dots \dots \dots (21)$$

and in the same way

$$\overline{\Delta s^2} = \vartheta \tau. \quad (22)$$

In order to arrive then at the differential equation for the function of frequency we reason again in the same way as before. Let $f(s, s_0, t)$ represent the chance that a particle that at the time 0 has the coördinate s_0 possesses at the time τ the coördinate s (with margin ds) where we determine the average according to the initial velocity. Now we follow the movement for a short time τ and build the function of frequency at the time $t + \tau$ from that on time s . If Δs again represents the mean deviation during the time τ , and $\varphi(\Delta s)$ the function of frequency, we know for this deviation that we have

$$\int \varphi(\Delta s) d\Delta s = 1, \quad \int \Delta s \varphi(\Delta s) d\Delta s = k\tau \text{ and } \int (\Delta s)^2 \varphi(\Delta s) d\Delta s = \vartheta \tau \quad (22a)$$

We then obtain

$$f(s, s_0, t + \tau) ds = \int ds' f(s', s_0, t) \varphi(\Delta s) d\Delta s \quad (23)$$

where $s' = s - \Delta s$.

If now we take (20) into consideration we find for the connection of ds' and ds

$$ds' = \left(1 - \frac{1}{\beta} \frac{\partial k}{\partial s} \tau\right) ds.$$

Developing according to (23) up to the first order with respect to τ , we find

$$\frac{\partial f}{\partial t} = -\frac{1}{\beta} \frac{\partial}{\partial s} (kf) + \frac{\vartheta}{2} \frac{\partial^2 f}{\partial s^2} \quad (24a)$$

If we introduce the value for ϑ and β we obtain

$$\frac{\partial f}{\partial t} = -\frac{m}{6\pi\mu a} \frac{\partial}{\partial s} (kf) + \frac{m}{6\pi\mu a^2} \frac{\partial^2 f}{\partial s^2} \quad (24)$$

This equation agrees with that of SMOLUCHOWSKI, if we take D (coefficient of diffusion of the Brownian motion $\frac{kT}{6\pi\mu a}$). The factor

$\frac{1}{6\pi\mu a}$ is the ψ of SMOLUCHOWSKI i.e. the factor with which the force mk must be multiplied in order to calculate the velocity which in a stationary condition was caused by this force.

By DEBYE and his pupil Dr. TUMMERS¹⁾ a differential equation for

¹⁾ DEBYE, Zur Theorie der anomalen Dispersion. Verh. Deutsch Phys Ges. X, p. 790.

J. TUMMERS, Over elektrische dubbelbreking, Diss. Utr. 1914.

the function of the frequency of the axes has been deduced for the case of molecules (particles) which turn in a liquid, which is acted upon by an external couple and by a couple resulting from the molecular impacts. The deduction of the results obtained there follows immediately from our formulae. We need only split up the couple exerted by the molecular movement into two parts, the one $-q\dot{\alpha}$ ($\dot{\alpha}$ be the angular velocity of the particle) $q = 8\pi\mu a^3$ (a radius of the particle) and into a second part of which the average value (case average) is zero. For the motion of the axis we get then

$$P\ddot{\alpha} = -q\dot{\alpha} + X$$

where P is the moment of inertia of the particle.

If we take $\dot{\alpha} = u$, $\frac{q}{P} = \beta$, $\frac{X}{q} = F$, we get for u equation (1), from which appears that the function of frequency can be deduced from a differential equation of the form (24a).

Finally it may be observed that it offers no difficulties to extend our considerations to the Brownian motion of coordinates in systems with an arbitrary number of degrees of freedom.

Utrecht, Dec. 8 1917.

Institute for Theoretical Physics.

put in the place of the equation of LANGEVIN-EINSTEIN, Miss SNETHLAGE differentiates equation (1) according to t . This yields

$$\overline{v \frac{dK}{dt}} = - \overline{K \frac{dv}{dt}} = - \frac{\overline{K^2}}{M} \quad \dots \quad (3)$$

From which she rightly concludes that $\frac{dK}{dt}$ is not independent of v . The nature of this dependence will be known, if for each value of v one knows the average $\overline{\frac{dK}{dt}}^v = F(v)$. Then there may be written for one system:

$$\frac{dK}{dt} = F(v) + w \quad \dots \quad (4)$$

where w is an accidental quantity which on the average is zero ($\overline{w}^v = 0$).

If we want to determine $F(v)$ it is apparently necessary to consider the group of systems with a definite value of v . We shall further on indicate an average in such a " v -group", the same as above by $\overline{}^v$, i. e. the average over the systems where in one definite moment v has a prescribed value, whilst the symbol $\overline{}$ will indicate the average for the whole ensemble. As is proved by the following calculation equation (3) is not applicable, as (4) and (2), to every v -group in particular; and this Miss SNETHLAGE has left out of consideration.

Let K represent the force acting in the x -direction on the particle, v the velocity of this particle in that direction. Equation (1) is then found for the canonical ensemble, when K does not depend upon the velocities, and is exclusively a function of the coordinates $q_1 \dots q_n$.

Let q_1 be the x coordinate of the particle, so that $q_1 = v$. Then we have

$$\frac{dK}{dt} = \frac{\partial K}{\partial q_1} v + \frac{\partial K}{\partial q_2} \dot{q}_2 + \dots + \frac{\partial K}{\partial q_n} \dot{q}_n$$

and for the average at definite v

$$\overline{\frac{dK}{dt}}^v = \overline{\frac{\partial K}{\partial q_1}}^v v + \overline{\frac{\partial K}{\partial q_2}}^v \dot{q}_2 + \text{etc.}$$

In order to reduce the last term we have made use of the well-known independence of the extension in velocity and configuration.

These terms fall out because $\overline{\dot{q}_2}^v = 0$. The same independence has as its result that

$$\frac{\overline{\partial K^v}}{\partial q_1} = \frac{\overline{\partial K}}{\partial q_1}.$$

The last average, is easily calculated from GIBBS' formulae.

$$\frac{\overline{\partial K}}{\partial q_1} = \frac{\int \frac{\partial K}{\partial q_1} e^{-\frac{\epsilon}{\Theta}} dq_1 \dots dq_n}{\int e^{-\frac{\epsilon_q}{\Theta}} dq_1 \dots dq_n}$$

Integrating by parts the denominator yields

$$\frac{1}{\Theta} \int K \frac{\partial \epsilon}{\partial q_1} e^{-\frac{\epsilon_q}{\Theta}} dq_1 \dots dq_n$$

as the integrated part falls out ($\epsilon = \infty$ at the limits).

Now

$$\frac{\partial \epsilon}{\partial q_1} = -K, \text{ and therefore } \frac{\overline{\partial K}}{\partial q_1} = -\frac{1}{\Theta} \overline{K^2}$$

Considering that $\Theta = M \overline{v^2}$, we obtain

$$\frac{d\overline{K^v}}{dt} = -\frac{v}{M \overline{v^2}} \overline{K^2} \dots \dots \dots (5)$$

And so $F(v)$ has been found; equation (4) becomes

$$\frac{dK}{dt} = -\frac{\overline{K^2}}{M \overline{v^2}} v + w \dots \dots \dots (5a)$$

i. e. the very form given to this equation without further proof by V. D. WAALS and Miss SNETHLAGE. (Miss SNETHLAGE equation 24, sees however the note of these Proc. 24, 1278 where a calculation remotely analogous to ours is found, without however our conclusions being drawn from it.)

The fact that $\frac{d\overline{v^v}}{dt} = 0$ and $\frac{d\overline{K^v}}{dt} = -\frac{v}{M \overline{v^2}} \overline{K^2}$ or $\frac{d^2 \overline{v^v}}{dt^2} = -\frac{\overline{K^2}}{M^2 \overline{v^2}} v$

has great importance for the theory of canonical ensembles. If at a given moment one chooses a group of systems in which the suspended particle has a definite velocity-component v , then the formulae found are applicable to this group. Now one ought to consider, that, if one follows these systems in the time, the velocity of the particles does not remain the same for all of them, but that different velocities are going to arise. Moreover our formulae indicate that, if we take the average velocity a very short time τ after the selection of the group, it has become smaller than v . By

substitution of the above results in a series of TAYLOR we find namely:

$$\overline{v}_t = v \left(1 - \frac{\overline{K^2}}{2 M^2 \overline{v^2}} \tau^2 \dots \right)$$

Now it is remarkable that, if we follow the systems back into the time, i. e. determine the average for a moment $-\tau$ for a group where at $t=0$ the velocity of the suspended particle is v , exactly the same formula can be applied. So that we get a reversible process and questions analogous to the problem of the tops of H curves solved by EHRENFEST arise. Our reasonings consequently also give in principle how the objections may be put aside, which ZERMELO has raised to the statistical mechanics of GIBBS (as well as to the molecular theories of BOLTZMANN concerning the H theorem ¹⁾).

The result obtained may shortly be formulated in this way: the properties of a group of systems, chosen so that in all of them the suspension-particle has a velocity v — a v -group —, are dependent on the time elapsed since the selection.

We may also ask now after the change of \overline{vK} with the time for the v -group selected at the moment $t=0$. From the preceding calculation results that

$$\frac{d\overline{vK}}{dt} = \overline{\frac{dv}{dt} K} + v \frac{d\overline{K}}{dt} = \frac{\overline{K^2}}{M} \left(1 - \frac{v^2}{\overline{v^2}} \right) \dots \dots (6)$$

from which it follows that the relation

$$\overline{vK} = 0 \dots \dots \dots (7)$$

which is the right one for the moment in which the group was selected in the ensemble, is *not* right when this group is followed further.

It is true that the average for the last member of (6) for the ensemble is equal to zero, as is necessary with regard to the stationary character of the whole ensemble, which was already used in the deduction of (3).

Consequently we should be very careful in interchanging differentiation and determination of the average. So equation (5) will only be right for the first moment (just as (4)) and consequently also

¹⁾ One ought to bear well in mind that the series-development given here is only right for a short time after the selection of the v -group from the ensemble. If one follows the group during a long time then the systems of which it consists will have spread themselves over the whole phase-extension with the density that belongs to a canonical ensemble.

For the importance of the EINSTEIN-LANGEVIN formula for this process compare the paper of one of us (ORNSTEIN), (preceding paper).

(5a), which accordingly *must not be looked upon as a differential equation*, Or: if we do consider (5a) right for later moments, we do not get in connection with it $\overline{w} = 0$, as it is made use of by Miss SNETHLAGE.

We are able to refute the second objection, viz. that statistical mechanics should not allow that the fluid moves with the particle in an analogous way. For this purpose we shall calculate the derivatives of

$$\overline{\frac{v}{v'}} = 0$$

where v' is the x -velocity of an arbitrary molecule situated in the neighbourhood of the particle.

We have

$$\overline{\frac{d}{dt} \frac{v}{v'}} = \overline{\frac{dv}{dt} \frac{v}{v'}} + v \overline{\frac{dv'}{dt} \frac{1}{v'}} = \overline{\frac{K}{M} \frac{v}{v'}} + v \overline{\frac{K'}{M'}} = 0$$

as $\overline{v'}$ as well as $\overline{K'}$ are zero. Further

$$\overline{\frac{d^2}{dt^2} \frac{v}{v'}} = \overline{\frac{d^2 v}{dt^2} \frac{v}{v'}} + 2 \overline{\frac{dv}{dt} \frac{dv'}{dt} \frac{v}{v'}} + v \overline{\frac{d^2 v'}{dt^2} \frac{1}{v'}} = \overline{\frac{1}{M} \frac{dK}{dt} \frac{v}{v'}} + 2 \overline{\frac{KK'}{MM'}} + \overline{\frac{v}{M'} \frac{dK'}{dt}}.$$

The average of the first term yields

$$\overline{\frac{1}{M} \left\{ \frac{\partial K}{\partial q} \frac{v}{v'} + \frac{\partial K}{\partial q'} \frac{v'^2}{v'^2} + \dots \right\}} = \overline{\frac{1}{M} \frac{\partial K}{\partial q'} \frac{v}{v'^2}} = - \overline{\frac{KK'}{M\Theta} \frac{v}{v'^2}} = - \overline{\frac{KK'}{MM'}}$$

and of the third term

$$\overline{\frac{v}{M'} \left\{ \frac{\partial K'}{\partial q} \frac{v}{v'} + \frac{\partial K'}{\partial q'} \frac{v'}{v'} + \dots \right\}} = \overline{\frac{v^2}{M'} \frac{\partial K'}{\partial q}} = - \overline{\frac{v^2}{M'} \frac{KK'}{\Theta}} = - \overline{\frac{v^2}{v'^2} \frac{KK'}{MM'}}$$

so that

$$\overline{\frac{d^2}{dt^2} \frac{v}{v'}} = \overline{\frac{KK'}{MM'}} \left(1 - \frac{v^2}{v'^2} \right) \dots \dots \dots (8)$$

For the change of v' with the time we have according to the preceding

$$\overline{\frac{dv'}{dt}} = 0$$

$$\overline{\frac{d^2 v'}{dt^2}} = - \overline{\frac{KK'}{MM' v'^2}} v$$

Now K is the sum of the forces in the x -direction, which all other particles exercise on the first, K' the corresponding sum for the second particle.

If we develop the product of these sums, we shall obtain the average of the product of action and reaction that may be assumed

to preponderate, so that we may expect that $\overline{KK'}$ is negative. The second derivative of $\overline{v'}$ consequently has the same sign as v , i.e. the movement of the surrounding matter with the particle, which does not exist at the moment of selection, arises after a short time. According to (8) there is on the average no question of a movement of the surrounding particles with the Brownian particle in an ensemble, as may be expected.

When we want to investigate statistically the qualities of a stationary system of molecules, we can make use of a statistically stationary ensemble and identify the qualities observed with the qualities of the most frequent system in this ensemble or with the corresponding averages.

The system that we consider at an investigation of the Brownian motion — a liquid with a particle suspended in it — is, it is true, not stationary, but all the same it changes only slowly: the moving particle changes its velocity only *slightly* by a *great number* of impacts. Consequently, in order to make use of ensembles for the study of the Brownian motion we must start from a "quasistationary" ensemble and deduce the qualities of the real Brownian motion from the properties of the most usual system in such an ensemble.

The calculations given show, that the groups chosen with definite v from a canonical ensemble do *not* form such quasi-stationary ensembles. However it seems probable to us that such a group, when we follow it a short time, will get to fulfill the requirements, though it will be difficult to show this by direct calculation. The v -group, which has become quasi-stationary at a later moment, would then correspond to the ensemble selected from the canonical ensemble, by selecting those systems in which the particle has already got the velocity v during a short time.

An indication with regard to the length of time required was found along another method by one of us in a former paper ¹⁾.

The above quoted statistic-mechanical objections to the application of the law of Stokes thus probably have no justification for a real system, but only for the first moment of a v -group, i.e. at the very time when it cannot yet be made use of to represent the properties of a real system.

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¹⁾ L. S. ORNSTEIN. l. c. — This time must namely be of the order of the time during which there is a correlation between the irregular impulses, i. e. $\overline{F(\xi)F(\xi + \tau)}$ differs from zero.

Physics. — "*The Scattering of Light by Irregular Refraction in the Sun*". By Prof. L. S. ORNSTEIN and Dr. F. ZERNIKE.
(Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of April 27, 1917).

By the investigation of Dr. J. SPIJKERBOER in his dissertation "*Scattering of Light, and Distribution of Intensity over the Disc of the Sun*", the supposition of JULIUS¹⁾, that besides the scattering by the action of the molecules also the scattering by irregular bending of rays owing to accidental gradients of the optical density must play a part in the origin of the distribution of light over the disc of the sun, has been corroborated.

In this paper it is our object to show, that a mathematical treatment of the problem of the scattering of light by curving of rays is possible. For it is possible to put up an integral-equation for this phenomenon and to transform this with suitable and plausible suppositions into a differential equation with boundary conditions.

The problem treated here is the counterpart of the problem of molecular diffusion in a flat layer of gas, which was solved by SCHWARZSCHILD. The deduction of the integral equation resembles his train of thoughts, but in our case we have the advantage, that the peculiar nature of the problem allows that a differential equation can be deduced from it, which makes mathematical discussion so much easier. It seems to us, that the irregular reflection and the irregular double refraction may be treated in an analogous way, which is important for the theory of the extinction of liquid crystals.

In a medium, in which accidental gradients of the index of refraction arise, a ray of light will be curved in an irregular fashion. If a broad bundle of parallel rays runs through the medium, the different rays will be curved in different ways. And so, if the bundle is broad with regard to regions of a constant index of refraction, a bundle of initially parallel rays will be spread plume-shape. Now we fix our attention on the action of a volume-element on a ray, which goes in a given direction, and imagine that the nature of the irregularity of the index of refraction in the medium

¹⁾ W. H. JULIUS. Verslag Kon. Akad. v. Wet. 18, 195 (1909) and 22, 64—75 (1913).

is such, that after running through the element in question the diffusion of the rays has only taken place over a small cone. A characteristic difference with molecular scattering is, that with the scattering by refraction *not* a great part of the bundle goes on unimpeded and a small part spreads to *all* sides, but that the chief bundle itself gets continually broader.

And so, expressed in mathematical terms: let us follow light of a given direction over a length l , then, if this bundle has an intensity of one per unit of square, the intensity of the light which is found in a cone of the opening $d\omega$, of which the axis formed an angle α with the direction of incidence, will be possible to be represented after running through l by a function:

$$\chi(\alpha, l) d\omega \quad \text{or} \quad \chi(\alpha) d\omega$$

By making use of a particular image the form of the function χ may be determined. This form will be analogous to the law of errors; it is however unimportant for what follows. What is important is the supposition that the function χ possesses a perceptible value only for very small values of α .

If we take the meaning of χ into consideration, we see immediately that of course

$$\int \chi(\alpha) d\omega = 1$$

where the integral, just as everywhere else in what follows, must be taken over the whole unity sphere.

Now we shall deduce the integral equations for the intensity of radiation. Let $f(x, y, z, \vartheta, \varphi)$ represent the intensity of radiation in a point (x, y, z) , whilst the direction is given by the angle ϑ with the x -axis and φ . If now we know the radiation in a point (x, y, z) , we ask this quantity in a point that is situated l further in the direction of the ray ϑ, φ . The coordinates of this point are:

$$x + l \cos \vartheta, \quad y + l \sin \vartheta \cos \varphi, \quad z + l \sin \vartheta \sin \varphi$$

And so the intensity of radiation may be represented by:

$$f(x + l \cos \vartheta, y + l \sin \vartheta \cos \varphi, z + l \sin \vartheta \sin \varphi, \vartheta, \varphi).$$

This intensity must now be equal to the intensity which by the bending of rays comes in the given direction. When ϑ' and φ' are the angles which determine a ray in x, y, z , then, if α represents the angle of this ray with the ray ϑ, φ , the intensity in the second point will also be given by:

$$\int \chi(\alpha) f(x, y, z, \vartheta', \varphi') d\omega'$$

so that the required integral equation is:

$$f(x + l \cos \vartheta, \dots) = \int \chi(\alpha) f(x, y, z, \vartheta', \varphi') d\omega'.$$

Now it is easy to transform this integral equation into a differential equation, if we bear in mind that χ has only perceptible values for small values of α . We express by α the integration-element $d\omega'$ and the angle ψ , which the plane through (ϑ', φ') and (ϑ, φ) makes with that through (ϑ, φ) and the x -axis. So that the value of $d\omega'$ is:

$$\sin \alpha d\alpha d\psi = \alpha d\alpha d\psi.$$

For the difference of the angles ϑ and ϑ' and that of the angle φ and φ' we find going to the second order to α and after elementary reduction:

$$\Delta\vartheta = \vartheta' - \vartheta = -\alpha \cos \psi + \frac{1}{2} \sin \vartheta \cos \vartheta \Delta\varphi^2 = -\alpha \cos \psi + \alpha^2 \frac{\cot \vartheta \sin^2 \psi}{2}$$

$$\Delta\varphi = \alpha \frac{\sin \psi}{\sin \vartheta}.$$

Now we can develop in the integral $f(x, y, z, \vartheta', \varphi')$ with respect to $\Delta\vartheta$ and $\Delta\varphi$ and get in this way:

$$\begin{aligned} & f(x, y, z, \vartheta, \varphi) \int \chi(\alpha) d\omega' + \\ & + \frac{\partial f}{\partial \vartheta} \iint \Delta\vartheta \alpha \chi(\alpha) d\alpha d\psi + \frac{\partial f}{\partial \varphi} \iint \Delta\varphi \alpha \chi(\alpha) d\alpha d\psi + \\ & + \frac{1}{2} \frac{\partial^2 f}{\partial \vartheta^2} \iint (\Delta\vartheta)^2 \alpha \chi(\alpha) d\alpha d\psi + \frac{\partial^2 f}{\partial \vartheta \partial \varphi} \iint \Delta\vartheta \Delta\varphi \alpha \chi(\alpha) d\alpha d\psi \\ & + \frac{1}{2} \frac{\partial^2 f}{\partial \varphi^2} \iint (\Delta\varphi)^2 \alpha \chi(\alpha) d\alpha d\psi \end{aligned}$$

The first integral is equal to unity, the second yields

$$\frac{\pi}{2} \cot \vartheta \int \alpha^3 \chi(\alpha) d\alpha,$$

the third is zero as well as the fifth, whilst the fourth and the seventh yield:

$$\pi \int \alpha^3 \chi(\alpha) d\alpha \quad \text{and} \quad \frac{\pi}{\sin^2 \vartheta} \int \alpha^3 \chi(\alpha) d\alpha$$

Now we can introduce the mean value of α^2 according to

$$\overline{\alpha^2} = \int \alpha^2 \chi(\alpha) d\omega = 2\pi \int \alpha^3 \chi(\alpha) d\alpha$$

And thus we obtain at length, — if we also combine the first term of the second member with the first member and develop according to l — for the differential equation of the diffusion of light by irregular refraction:

$$\frac{\partial f}{\partial x} \cos \vartheta + \frac{\partial f}{\partial y} \sin \vartheta \cos \varphi + \frac{\partial f}{\partial z} \sin \vartheta \sin \varphi = \frac{\alpha^2}{4l} \left(\frac{\cos \vartheta}{\sin \vartheta} \frac{\partial f}{\partial \vartheta} + \frac{\partial^2 f}{\partial \vartheta^2} + \frac{1}{\sin^2 \vartheta} \frac{\partial^2 f}{\partial \varphi^2} \right)$$

For the case important in practice that f only depends on x and ϑ consequently:

$$\sin \vartheta \cos \vartheta \frac{\partial f}{\partial x} = \frac{\alpha^2}{4l} \left(\cos \vartheta \frac{\partial f}{\partial \vartheta} + \sin \vartheta \frac{\partial^2 f}{\partial \vartheta^2} \right) \quad ^1).$$

For this case the boundary conditions are, if we have at $x=0$ a layer, which radiates according to the cosinus law and at d a plane layer through which no inward-radiation takes place:

$$\begin{array}{lll} f=c & \text{for:} & x=0 \quad \cos \vartheta > 0 \\ f=0 & \text{for:} & x=d \quad \cos \vartheta < 0. \end{array}$$

For $\vartheta=0$ and all values of x : f and $\frac{\partial f}{\partial \vartheta}$ continuous, $\frac{\partial^2 f}{\partial \vartheta^2}=0$; for

$$\cos \vartheta = 1 \quad \text{or} \quad -1 \quad \frac{\partial f}{\partial \vartheta} = 0.$$

It is worth observing that the diffusion is determined by the quantity $\frac{\alpha^2}{l}$, i. e. the average square of diffusion per length-unity. This magnitude is specific for the problem, does not depend upon the length, as α^2 is doubled in doubling the length l . The magnitude is related to the nature of the irregularities. It is a constant which still may be different for different layers of the sun. The study of the distribution of intensity over the disc of the sun will be able to supply us with the knowledge of the average value of the characteristic constant of the sun.

Utrecht, April 1917.

Institute for Theoretical Physics.

¹⁾ For the two dimensional problem:

$$\cos \vartheta \frac{\partial f}{\partial x} = \frac{\alpha^2}{4l} \frac{\partial^2 f}{\partial \vartheta^2}.$$

Meteorology. — *“On the diffraction of the light in the formation of halos. II. A research of the colours observed in halo-phenomena”.*
By Dr. S. W. VISSER. (Communicated by Dr. J. P. VAN DER STOK).

(Communicated in the meeting of June 29, 1918).

In the first paper on the diffraction of the light in the formation of halos ¹⁾ a survey of colours observed has been given on pag. 1175 taken from “Thunderstorms, optical phenomena etc. in Holland”.

Prof. Dr. E. VAN EVERDINGEN however informed me, that these records are altogether insufficient because only a small number of colour observations are dealt with in “Thunderstorms”. On his suggestion I have studied a number of records sent in to the “Koninklijk Nederlandsch Meteorologisch Instituut”. In the first place I hope to have set right a neglect against the sincere voluntary observers of the Institute; in the second place this research gave valuable materials for the answer to the question how far and in what manner the diffraction works in the formation of halos.

In this paper a survey of the research is given; the results will be discussed and it will appear, that indeed the diffraction has an important influence on the refraction of light in ice crystals.

I started with all the colour records in the years 1913, '14 and '15. Then the research was extended to the years 1911, '12 and '13. In the first part I soon found, that great prudence was necessary. As an example I take the observations of “rainbow-colours”. In the three years 1913—'15 I find “rainbow-colours” 12 times recorded by 9 observers. There are however 7 who have never sent in another record during all this time. They were evidently led by suggestion and fancy more than by observation power. The personal character also comes to the front. Therefore it was resolved to make a very careful selection and only to use records of those observers known to the Institute as wholly reliable. In this manner the notes are studied of eleven observers, who are mentioned in this paper with the numbers I tot XI.

¹⁾ These Proceedings Vol. XIX.

Omitted were all incomplete observations and those about the moon. 550 Observations were at my disposal, divided over the six years as follows:

	1910	1911	1912	1913	1914	1915	Total
colour-records	125 (6)	107 (7)	114 (7)	81 (8)	66 (8)	57 (7)	550
total	473	480	399	283	325	377	2337
%	26	22	29	29	20	15	24

In parenthesis is mentioned the number of observers.

The row "total" gives the total number of records taken from "Thunderstorms".

The fourth part of all the notes gives reliable records.

31 Colours and colour-groups are mentioned, among which three very anomalous ones: blue IX; violet, red VIII; red, violet, green V. In the first communication are mentioned¹⁾ golden brown (red), yellow, green, violet (3 times by two observers); yellow, violet; golden brown, clear white, blue.

All the colour observations (divided over the two circles, the tangential arcs and the circumzenithic arc) are contained in the table I. (See table following page).

In the table the personal character comes out strongly.

144 observations of red by 10 observers (among which 115 of VII and IX), and 133 orange by 5 (among which 130 of V and X) where in most cases the same colour is meant, this clearly points to the personal estimation of this colour. The same is evident in the groups red-white and orange-white.

The table II also gives an idea of this individual opinion. (See table II page 122).

All the colour records of each observer, separately for the ordinary circle, the parhelion and the tangential arcs have been collected without further observations in this table. From this it appears, that the records of V, VII and X are limited to green (V has one observation of violet on a total number of 158). III also mentions blue, but never violet; VIII notes neither green nor blue, but in 22 records 12 times violet.

This phenomenon however interesting from a physiological point of view, greatly diminishes the value of the records, but without doubt green and blue colour shades often occur, as is further evident in the percentages of the separate colours in the following table (in which parhelion and tangential arc are taken together).

¹⁾ l.c. p. 1330 seq.

TABLE I.

	circle 22	parhelion	tang. arc.	circle 46	circ. zen. arc.	total
white	51 (8)	7 (3)	1 (1)	—	—	59 (8)
red (brown)	119 (10)	14 (3)	9 (4)	2 (2)	—	114 (10) ¹⁾
orange	123 (4)	7 (2)	3 (1)	—	—	133 (5)
yellow	15 (6)	4 (3)	1 (1)	—	—	20 (6)
blue	—	—	—	1 (1)	—	1 (1)
red, white (brown, white)	20 (6)	8 (1)	1 (1)	—	—	29 (6) ²⁾
orange, white	27 (1)	1 (1)	1 (1)	—	—	29 (2)
yellow, white	5 (2)	—	—	—	—	5 (2)
red, orange	4 (1)	—	—	—	—	4 (1)
red, yellow (brown, yellow)	10 (4)	2 (1)	1 (1)	—	—	13 (6) ³⁾
red, green	22 (3)	9 (5)	5 (2)	—	2 (2)	38 (5)
red, blue	10 (3)	2 (1)	2 (2)	1 (1)	—	15 (4)
red, violet	7 (1)	2 (2)	1 (1)	1 (1)	—	11 (2)
orange, yellow	1 (1)	—	—	—	—	1 (1)
orange, green	1 (1)	—	—	—	—	1 (1)
orange, violet	—	1 (1)	—	—	—	1 (1)
violet, red	1 (1)	—	—	—	—	1 (1) ⁴⁾
red, orange, white	—	1 (1)	—	—	—	1 (1)
red, yellow, white	1 (1)	1 (1)	1 (1)	—	—	3 (2)
red, green, white	1 (1)	—	—	—	—	1 (1)
red, orange, green	1 (1)	—	—	—	—	1 (1)
red, orange, violet	—	1 (1)	—	—	—	1 (1)
red, yellow, green	4 (3)	2 (2)	1 (1)	—	4 (1)	11 (3) ⁵⁾
red, yellow, blue	8 (3)	—	1 (1)	—	—	9 (4)
red, yellow, violet	1 (1)	1 (1)	—	—	—	2 (2)
red, green, blue	3 (2)	—	3 (2)	—	—	6 (2)
red, blue, violet	—	—	1 (1)	—	—	1 (1)
red, violet, green	—	1 (1)	—	—	—	1 (1)
red, yellow, green, blue	—	—	2 (2)	—	—	2 (2)
red, green, blue, violet	—	—	1 (1)	—	—	1 (1)
rd., or., yl., gr., bl., vi.	1 (1)	1 (1)	1 (1)	—	2 (1)	5 (3) ⁶⁾
	436	65	36	5	8	550

¹⁾ Among which brown 10 (2).

²⁾ " " brown, white 11 (3).

³⁾ " " brown, yellow 3 (1).

⁴⁾ 1911, April 12: "on the outside reddish, inside violet". VIII. — April 23 VIII records: "on the outside common red".

⁵⁾ An observation of an arc of Lowitz by HISSINK 1910, Sept. 7 at Zutphen was neglected.

⁶⁾ Colours mentioned 2 times.

"All colours" once

"rainbow-colours" twice.

TABLE II.

	Circle of 22°							Parhelion							Tangential arc						
	w	r	o	y	g	b	v	w	r	o	y	g	b	v	w	r	o	y	g	b	v
I	1	3	—	4	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
II	—	4	—	1	—	—	—	—	1	—	—	1	—	—	—	3	—	—	—	4	—
III	2	21	—	5	2	15	—	—	—	—	—	—	—	—	3	—	1	3	1	—	—
IV	—	1	—	—	—	—	—	—	5	1	3	1	1	1	—	1	—	—	—	—	1
V	61	44	82	13	23	—	—	—	6	—	—	6	—	1	2	5	1	—	4	—	—
VI	1	6	1	4	1	4	2	—	—	—	—	—	—	—	1	—	—	—	—	—	—
VII	23	60	1	8	4	—	—	—	5	—	2	2	—	—	—	5	—	1	2	—	—
VIII	2	13	1	2	—	—	8	1	3	3	1	—	—	3	—	1	—	—	—	—	1
IX	11	50	—	7	1	—	—	14	23	2	4	1	2	2	2	6	—	3	—	1	—
X	3	4	73	2	1	—	—	2	1	6	1	1	—	—	—	3	1	—	—	—	—
XI	1	7	—	—	1	2	—	1	1	—	—	1	—	—	—	5	1	2	4	5	2
	105	213	158	46	33	22	10	18	45	12	11	13	3	7	4	30	5	8	13	11	4

	white	red	orange	yellow	green	blue	violet
circle 22°	17.9	36.3	26.9	7.8	5.6	3.8	1.7
parhelion, tang. arc	11.9	40.8	9.2	10.3	14.1	7.6	6.1

Surely the figures for violet are strongly flattered (21 observations of violet among which 12 of VIII). Without the records of VIII the percentages for violet are respectively about 0.3 and 3.8.

Evident is the great variety of colour of parhelion and tangential arc¹⁾.

By adding red and orange, green, blue, and violet the personal influences may be destroyed to some extent. Then I find

	white	red orange	yellow	green blue violet
circle 22°	17.9	63.2	7.8	11.1
parh. tang. arc.	11.9	50.0	10.3	27.8

Against a decrease of white and red we see an increase of the other colours. In more than $\frac{1}{4}$ of all cases colours are recorded approaching green and blue for the parhelion and the tangential arcs. This also happens with one in nine ordinary circles, where colours are made mention of.

¹⁾ Without doubt in the first communication I have slightly misunderstood PERNTNER: the predomination of fixed crystal positions must at all events be very important.

Some colours and groups occur relatively often.

yellow; yellow, white	25 times; 6	observers
red, yellow; red, yellow, white.	16	" 6 "
red, green; red, blue; red, violet	64	" 8 "
red, yellow, green; red, yellow, blue; red, yellow, violet	22	" 7 "
red, green, blue	6	" 2 "
Spectrum colours	5	" 3 "

Green, blue and violet, to escape from personal influences, are again added.

The yellow takes a peculiar place. Yellow circles seem to occur. It is clear, that the yellow is often missing between the red and the green, but on the other hand it is often met with.

As regards the rainbow colours; 5 observations of 3 observers remain in six years.

Separate mention deserve the estimations of breadth by HEMMES at Arnheim in the ordinary circle and the tangential arc.

1911 Dec. 29	red $\frac{1}{2}^{\circ}$ yellow $\frac{1}{2}^{\circ}$ blue 1°
1912 Feb. 18	$\left\{ \begin{array}{l} \text{,, } \frac{1}{4}^{\circ} \text{ ,, } \frac{1}{4}^{\circ} \text{ ,, } \frac{1}{4}^{\circ} \\ \text{,, } \frac{1}{2}^{\circ} \text{ ,, } \frac{1}{2}^{\circ} \text{ especially at the top also blue.} \end{array} \right.$
March 3	
May 10	
March 8	red $\frac{1}{4}^{\circ}$, green $\frac{1}{4}^{\circ}$ blue $\frac{1}{4}^{\circ}$
1912 Jan. 6	$\left\{ \begin{array}{l} \text{red } \frac{1}{4}^{\circ} \text{ yellow } \frac{1}{4}^{\circ} \text{ green } \frac{1}{4}^{\circ} \text{ blue } \frac{1}{4}^{\circ} \end{array} \right.$
1913 June 14	
1911 Dec. 3	red $\frac{1}{4}^{\circ}$ yellow $\frac{1}{4}^{\circ}$ green $\frac{1}{4}^{\circ}$ blue $\frac{1}{4}^{\circ}$.

The fact that the breadth strongly varies also appears from the detailed tables on the circumzenithic arc by BESSON¹⁾: 17 times on 91 arcs BESSON measured the colours. The distance from red to violet varied from $1\frac{1}{2}^{\circ}$ to 3° ($1\frac{1}{2}^{\circ}$: 3 times; 2° : 6 times; $2\frac{1}{2}^{\circ}$ twice; 3° : 3 times). Three times blue and violet are wanting; among these is one arc, with which the breadth of the inside red to the green is 5° . BESSON notes: "très large, très brillant".

These variations of breadth are very important for the theory of diffraction.

Summing up I find as the results of the research after eliminating the individual influences:

1. the pretty large wealth of colours,
2. the variation of colours,
3. the variation of breadth.

¹⁾ Sur la Théorie des Halo's. Paris 1909. p. 62.

These results are not expected by the simple theory of refraction; they demonstrate the action of diffraction. It is these very properties which, for the rainbow, made the ordinary refraction-theory insufficient.

Evidently the conditions for the development of these phenomena of diffraction are present rather frequently. With great certainty this research has established the conclusions-drawn in the first paper. The observations however difficult by the small power of the colours, which generally are to be taken as mixed colours, the records, however often delusive by personal influences sufficiently show, that in the formation of halos the diffraction plays an important part.

Mathematics. — “Nouvelle démonstration du théorème de JORDAN sur les courbes planes”. By Prof. ARNAUD DENJOY. (Communicated by Prof. L. E. J. BROUWER).

(Communicated in the meeting of June 29, 1918).

Le théorème fondamental de JORDAN sur les courbes fermées peut s'énoncer ainsi :

Si les points d'un ensemble Γ et ceux d'un cercle se correspondent réciproquement et continument, chacun à chacun, l'ensemble Γ divise le plan en deux régions.

L'hypothèse faite sur Γ caractérise une courbe de JORDAN. Je me propose dans cette Note de donner une démonstration du théorème ci-dessus énoncé. Je rappellerai d'abord certaines définitions et résultats connus.

Nous caractérisons comme il suit les côtés positif et négatif en un point I d'une ligne HIK formée de deux segments de droite HI, IK , dont I est le seul point commun. Décrivons, dans le sens direct des rotations, un arc circulaire inférieur à 2π , de centre I , ayant son origine sur IK et son extrémité sur HI . Cet arc borne, avec HI et IK , un secteur de cercle ω . Soit L un ensemble continu, tel que, à l'intérieur d'un certain cercle c de centre I et de rayon inférieur à celui de ω , L et HIK aient seulement I en commun. Nous dirons que, au voisinage de I , L est situé du côté positif de la ligne HIK (ou du côté négatif de la ligne KIH) si les points de L intérieurs à c et distincts de I sont tous dans ω .

Il est aisé de voir que, si IK' est du côté positif de HIK , IK est du côté négatif de HIK' .

Si I est un point non extrême d'une ligne brisée λ simple (c'est-à-dire telle qu'un point quelconque de la ligne n'appartient à deux côtés différents que si ce point est origine de l'un et extrémité de l'autre), pour définir les côtés positif et négatif de λ en I , nous considérons un secteur de cercle analogue à ω , limité au côté (ou aux deux côtés) de λ contenant I , et ne rencontrant aucun autre côté de λ .

Soit P un polygone simple, défini avec son sens de parcours. On montre (voir *Comptes Rendus de l'Académie des Sciences de Paris*, 1911) que P divise le plan en deux régions (nous les appelons respectivement positive et négative, et les désignons par P^+ et P^-),

telles que tout continu joignant un de leurs points M au polygone P , atteint celui-ci du côté positif pour P^+ , du côté négatif pour P^- . A et B étant deux points de P , la ligne brisée décrite en parcourant P selon son sens, de A à B est l'arc direct AB de P . L'arc rétrograde AB est géométriquement identique à l'arc direct BA , mais les sens de parcours des deux arcs sont opposés.

Pour démontrer le théorème de M. JORDAN, nous utiliserons le lemme suivant:

Si, en parcourant une fois un polygone P dans un sens invariable, on rencontre successivement les quatre points A, B, C, D de ce polygone, et si $(AC), (BD)$ sont deux continus joignant respectivement A à C, B à D , et dont tous les points, sauf A, B, C, D , sont dans une même région limitée par le polygone, ces deux continus ont au moins un point commun.

Supposons d'abord que (AC) soit une ligne brisée simple. On peut toujours choisir le sens positif de parcours de P , de façon que la région de P contenant (AC) et (BD) , sauf leurs extrémités, soit P^+ .

Considérons alors le polygone π formé de l'arc direct CA de P , et de la ligne (AC) parcourue de A vers C . (AC) atteignant P en A et C du côté positif, l'arc direct AC de P s'écarte de π du côté négatif en A et C . Donc, D qui est sur cet arc est dans π^- . Mais, P et π ayant en commun l'arc CA qui contient B , les côtés positifs de P et de π au voisinage de B coïncident. Donc le continu (BD) est, au voisinage de B , dans π^+ . On en déduit que (BD) rencontre π en un point différent de B . Comme (BD) ne rencontre pas l'arc CA , (BD) rencontre (AC) .

Supposons que ni (AC) ni (BD) ne soient des lignes brisées simples. Si ces continus n'ont pas de points communs, leur distance minimum est un nombre positif α . On remplace le continu (AC) par une ligne brisée simple λ d'extrémités A et C , située, sauf pour ces deux points, dans P^+ comme l'est (AC) , et ayant tous ses points à une distance de (AC) inférieure à α . D'après la première partie de la démonstration, λ rencontre (BD) . Nous aboutissons donc à une contradiction. Donc (AC) et (BD) se rencontrent dans tous les cas.

Nous déduirons de ce lemme une proposition essentielle.

Soit Γ une courbe de JORDAN et O la circonférence de cercle correspondant ponctuellement à Γ . Si un point décrit O dans le sens direct, nous dirons que le point homologue de Γ décrit Γ dans le sens positif. On échange le sens positif de parcours de Γ en transformant le cercle O en lui-même par une symétrie par rapport à un de ses diamètres. Cela posé,

Si A, B, C, D sont quatre points d'un polygone simple P , et A', B', C', D' quatre points d'une courbe de JORDAN Γ ne rencontrant pas P , si $(AA'), (BB'), (CC'), (DD')$ sont quatre continus deux à deux distincts contenant respectivement les points mis en évidence dans leurs désignations et n'en ayant aucun autre de commun avec P ni avec Γ , l'ordre des quatre points A', B', C', D' sur la courbe Γ , et celui de A, B, C, D sur P , l'une et l'autre parcourus dans le sens positif, sont identiques ou inverses.

On voit sans peine qu'en échangeant entre elles, s'il en est besoin, les dénominations des couples associés A et A' , etc., et aussi en modifiant le sens positif de Γ , la proposition serait en défaut dans le cas unique où, A, B, C, D étant rencontrés sur P dans leur ordre d'énonciation, on rencontrerait sur Γ successivement A', C', B', D' . Mais alors le continu (AC) formé de (AA') , de (CC') et de l'arc direct $A'C'$ de Γ , ne rencontrerait pas le continu (BD) formé de (BB') , de (DD') et de l'arc direct $B'D'$ de Γ . Or ces deux continus sont, à l'exception de leurs extrémités A, B, C, D l'un et l'autre dans la région de P contenant Γ . C.q.f.d.

Rappelons maintenant que si l'on forme une subdivision du plan en carrés égaux (γ) par deux familles de droites respectivement parallèles à deux directions rectangulaires, et, si l'on considère les ensembles formés par les carrés ne contenant, ni intérieurement ni sur leur contour, nul point d'un continu E , ces ensembles forment des domaines (réunion d'un continuum et de sa frontière; un continuum est un ensemble connexe dont tous les points lui sont intérieurs) dont chacun est limité par un polygone simple appelé *polygone d'approximation de E , relatif au quadrillage (γ)* . Le sens positif d'un tel polygone π sera défini par la condition que E soit dans π^- .

Tout point H de π est situé sur l'un (ou sur deux) des côtés d'un (ou de deux ou de trois) carré γ dont l'intérieur appartient à π^- et qui contient, intérieurement ou sur son contour, au moins un point de E . L'un de ces points-ci H' , est tel que la distance HH' est minimum. Les points non extrêmes du segment HH' sont situés dans π^- et étrangers à E . D'ailleurs HH' est au plus égal à la diagonale de γ .

Cela étant, soient M et N deux points, distincts ou non, appartenant à une même région limitée par Γ , et P, Q deux points de Γ tels que les segments MP, NQ aient en commun 1° avec Γ , uniquement les points respectifs P et Q , 2° entre eux, éventuellement et seulement certains de leurs points extrêmes (donc si M coïncide avec N , P est distinct de Q et inversement). M et N peuvent être joints par une ligne simple λ dont tous les points sont distincts de

Γ . Soit 4α un nombre inférieur à la distance de λ à Γ , et à la distance rectiligne PQ . ε étant moindre que α , considérons dans un quadrillage de côté ε le polygone π d'approximation de Γ , dont la région positive contient M et N . A partir de P et de Q , les segments PM , QN rencontrent π aux premiers points respectifs M_1 et N_1 . Soit ϑ la plus grande des deux longueurs M_1P et N_1Q . ϑ tend vers zéro avec ε . Si $\vartheta + \varepsilon < \alpha$, sur chacun des arcs directs M_1N_1 , N_1M_1 de π , il existe des sommets, respectivement H , K , tels que les segments HH' , KK' les joignant à leurs correspondants définis plus haut, ne coupent ni M_1P ni N_1Q . Alors, d'après le lemme, H' et K' sont séparés sur Γ par P et par Q .

Cela posé, à un sommet H de l'arc direct M_1N_1 de π ; faisons correspondre P ou Q ou H' , selon que HH' rencontre M_1P ou M_1Q , ou ni l'un ni l'autre de ces segments. Alors, à la suite des sommets de l'arc M_1N_1 correspond une suite de points de Γ , tels que la distance de chacun d'eux au suivant est inférieure à $2\vartheta + 5\varepsilon$. Tous ces points sont sur un même arc PQ de Γ , puisqu'aucun d'eux n'est sur l'arc PQ contenant K' .

De même, sur ce dernier arc, nous pouvons former entre P et Q une chaîne de points, telle que la distance de chacun d'eux au suivant soit inférieure à $2\vartheta + 5\varepsilon$, chacun de ces points étant d'ailleurs distant de moins de 2ε d'un sommet de π . Nous déduisons de là les deux corollaires suivants :

1° *Toute région limitée par Γ admet pour frontière la totalité de Γ .*

Car la région contenant M et N admet pour frontière chacun des deux arcs PQ de Γ .

2° *M et N étant dans une même région de Γ , P et Q étant sur Γ et les segments MP et NQ étant sans points non extrêmes communs, ni avec Γ , ni entre eux; quel que soit le nombre positif η , il est possible de trouver deux lignes brisées λ, λ' dont tous les points sont étrangers à Γ et situés à une distance inférieure à η , respectivement de l'arc direct PQ et de l'arc direct QP de Γ , les extrémités de chacune des deux lignes λ, λ' étant, l'une sur MP , l'autre sur NQ .*

En particulier, si M, N et l'un des arcs PQ sont intérieurs à un cercle c , on peut joindre M à N par une ligne brisée ne rencontrant pas Γ et intérieure à c .

De ces corollaires nous tirons les propositions suivantes :

1° *Toute courbe de JORDAN admettant un arc rectiligne divise le plan en deux régions.*

En effet, soit I le milieu de l'arc rectiligne direct HK appartenant à Γ et ω un cercle de centre I ne contenant aucun point de l'arc KH de Γ . Le diamètre HK divise ω en deux demi-cercles

ω_1 et ω_2 . L'intérieur de ω_1 fait partie d'une même région r_1 limitée par Γ . De même l'intérieur de ω_2 appartient à une même région r_2 limitée par Γ . D'ailleurs, toute région limitée par Γ admet I pour point frontière, donc possède des points dans ω , donc dans ω_1 ou dans ω_2 . Elle coïncide donc avec r_1 ou avec r_2 .

Je dis que r_1 et r_2 sont distincts. Sinon, soient α_1 et α_2 deux points symétriques par rapport à I , et respectivement intérieurs à ω_1 et à ω_2 . S'il était possible de joindre α_1 à α_2 par une ligne brisée simple λ ne rencontrant pas Γ , on pourrait choisir λ sans points communs avec le segment $\alpha_1\alpha_2$ en dehors de ses points extrêmes, et en ajoutant à λ le segment $\alpha_1\alpha_2$, on obtiendrait un polygone fermé ϖ . Le segment HK et le côté $\alpha_1\alpha_2$ de ϖ se coupent en leur milieu I . D'ailleurs HK ne rencontre plus ϖ . Donc, H et K sont dans deux régions différentes de ϖ . Donc, l'arc direct KH de Γ rencontre ϖ , et comme cet arc ne rencontre pas le segment $\alpha_1\alpha_2$, il rencontre λ , ce qui est contraire à l'hypothèse. La proposition est donc démontrée.

2° Toute courbe de JORDAN divise le plan en deux régions.

Soit J un point quelconque de Γ . Soit c un cercle de centre J et laissant à son extérieur un point K_0 de Γ . Il existe un cercle c' concentrique et intérieur à c , tel que, si P est un point de Γ intérieur à c' , l'un des deux arcs PJ de Γ est intérieur à c . La même propriété est dès lors vérifiée pour l'un des deux arcs PQ , si P et Q sont à la fois sur Γ et dans c' .

Il est possible d'entourer K_0 d'un cercle c'' extérieur à c et tel que, si α et β sont deux points de Γ intérieurs à c'' , l'un des deux arcs $\alpha\beta$ de Γ est extérieur à c . Le segment $\alpha\beta$ rencontre en général Γ en d'autres points que α et β , peut-être même en une infinité de points. Ceux-ci forment sur le segment $\alpha\beta$ un ensemble fermé. Soit HK un intervalle contigu à cet ensemble. Le segment HK est une corde de Γ . Ses extrémités seules font partie de Γ . L'un des deux arcs HK de Γ est extérieur à c . L'autre contient J . On peut, quitte à échanger les dénominations de H et de K , supposer que ce dernier arc est l'arc direct KH de Γ .

Soit Γ_1 la courbe de JORDAN obtenue en ajoutant à l'arc direct KH de Γ , le segment rectiligne HK . Dans c , Γ et Γ_1 coïncident, puisque ces deux courbes diffèrent uniquement par leurs arcs directs HK , l'un et l'autre extérieurs à c .

Γ_1 divise le plan en deux régions admettant l'une et l'autre J pour point frontière. Soient M et N deux points appartenant respectivement à ces deux régions et contenus dans c' . Joignons M et N à J . Soient, à partir de M et de N respectivement, P et Q les deux premiers points de rencontre obtenus avec Γ . Les segments

MP , NQ étant intérieurs à c' , où Γ et Γ_1 coïncident, P et Q sont sur Γ_1 et les segments MP , NQ n'ont avec Γ_1 d'autres points communs que P et Q . MP et NQ n'ont pas de points communs entre eux, sauf éventuellement P et Q , si ces points coïncident avec J .

Je dis que tout point S étranger à Γ peut être joint à M ou à N par une ligne brisée ne rencontrant pas Γ . En effet, d'après le premier corollaire, S peut être joint à un point T intérieur à c' et étranger à Γ . T est, relativement à Γ_1 , dans la même région que M ou que N . Soit R le premier point de rencontre à partir de T , du segment TJ avec Γ (et avec Γ_1 , puisque TJ est dans c'). En vertu du second corollaire, on peut joindre T à M (ou T à N) par une ligne brisée $TT_1 M_1 M$ (ou $TT_1 N_1 N$) étrangère à Γ_1 , et intérieure à c , puisque c contient les segments MP , NQ , TR , l'un des deux arcs PR et l'un des deux arcs QR . Comme l'arc direct HK de Γ ne pénètre pas dans c , la même ligne brisée est sans points communs avec Γ . Donc, Γ divise le plan en deux régions au plus.

D'ailleurs, M et N sont dans deux régions différentes de Γ , sinon on pourrait joindre M à N par une ligne brisée étrangère à Γ et située dans c . Donc, cette même ligne ne rencontrerait pas Γ_1 , et par suite M et N seraient dans la même région de Γ_1 , ce qui est faux par hypothèse.

Donc, Γ divise le plan en deux régions et deux seulement. Le théorème de JORDAN est donc démontré. Nous avons au surplus obtenu un procédé pour définir le côté positif de Γ en un point J . On se donne c . On en déduit c' , puis une corde HK de Γ , telle que ni cette corde, ni l'arc direct HK ne rencontrent c . La courbe formée par l'arc direct KH de Γ suivi de la corde HK , limite une région contenant le côté positif de la corde HK . Les points de cette région situés dans c' définissent le côté positif de Γ en J .

On montre sans difficulté que ce côté est indépendant de la corde auxiliaire choisie HK , et que les côtés positifs de Γ en tous ses points appartiennent à une même région limitée par Γ et que l'on peut appeler région positive de Γ .

Physiology. — "*On the spontaneous transformation to a colloidal state of solutions of odorous substances by exposure to ultra violet light.*" By Prof. H. ZWAARDEMAKER and Dr. F. HOGEWIJN

(Communicated in the meeting of April 26, 1918).

The literature contains a number of records concerning the spontaneous transformation to a colloidal state of substances whose molecules contain a noticeably large number of atoms (BLITZ¹⁾ colouring matters) or which are of a considerable molecular weight (J. TRAUBE²⁾ alkaloids). As one of us had noted the spontaneous transformation of eugenol in glycerin, when these substances are rapidly mixed up, and had been able to establish at the same time several details, we resolved to investigate more systematically the transformation of solutions of odorous substances in water, glycerin, and paraffin. After being rapidly mixed up, the solutions were allowed to stand for weeks and subsequently examined upon Tyndall's effect and observed ultramicroscopically³⁾.

It appeared that the following solutions yield a strong Tyndall effect.

<i>In water</i>	<i>In glycerin</i>	<i>In paraffin</i>
Eugenol	Eugenol	Anilin
Cressol	Safrol	Eugenol
Guaiacol	Creosote	Cumidin
Carvacrol	Nitrobenzol	
Citral		
Cumidin	Cressol	
Thymol	Apiol	
Hypnon		

In this table the odorous substances have been arranged according to their degree of transformation. In a number of cases the oblique

¹⁾ BLITZ, Album J. v. BEMMELEN, 1910, p. 110 (boundary value between 50 and 55 atoms)

²⁾ J. TRAUBE, Int. Ztsch. f. Physik. Chem. Biol. Bd. I, p. 35, 1914 (boundary value between 208 – 275 molecular weight).

³⁾ The examination upon Tyndall's effect was performed in the light-cone of a small electric arc-lamp, while watching the complete extinction of the oblique

diffused light has been measured after the method of KAMERLINGH ONNES and KEESOM¹⁾). The values of the quantitative determinations in the series of the aqueous solutions are in the ratio of 43:39:37:20:15:15:10; in the paraffinous solutions 23:18: slight.

Besides the above solutions also the aqueous solutions of apiol, creosol, paraxylol, anisaldehyd appeared to yield a markedly distinct effect. The Tyndal phenomenon is fairly distinct in old aqueous solutions of xylidin, orthotoluidin, chinolin, durol. A moderate effect we discovered of old aqueous solutions of methylcinnamylate, paratoluidin, salicylaldehyd, naphthalin, cumarin, toluol, anthranilic acid methylester, benzylbenzoate. A very slight effect was evinced by aqueous solutions of safrol, vanillin, anthracene, nitrobenzol. Tyndall's effect did not appear in old aqueous solutions of iron, heliotropin, moschus, isomuscon²⁾).

The solutions were fully saturated. This is, however, not necessary for odorous substances with a strong tendency for transformation such as eugenol, cressol, guaiacol, carvacrol etc.

In glycerin solutions the phenomenon is of less frequent occurrence. We demonstrated the absence of Tyndall's effect in a number of old solutions in glycerin of odorous substances, which, when dissolved in water, became colloidal within a few days. Also in a solution in paraffin transformation occurs rarely.

When there is hardly any solubility, Tyndall's effect cannot be expected in the long run with odorous substances, but also, even when e.g. fluorescence shows us that molecules are thrown into solution, transformation to the colloidal state is sometimes lacking altogether, even when the solution has been standing for a long time. Such is the case with heliotropin. Eugenol is the substance that, both in water and in glycerin, attains a more intense colloidal condition than all other odorous substances examined. Also in paraffin eugenol becomes colloidal; anilin, in this solvent, still more so.

Generally speaking, odorous substances becoming intensely colloidal

diffused light by means of a Nicol prism in the large apparatus of ZSIGMONDI. The solutions in glycerin, however, could not be taken up in an ordinary cuvette, the stuff with which the quartz windows are fixed, being soluble in glycerin. In this case we therefore used Zeiss' paraboloid condensor, or a Leitz' darkground-condensor-cuvette.

¹⁾ KAMERLINGH ONNES and KEESOM, Acad. Amst. 29 Feb. 1908.

²⁾ The list of odorous substances that are transformed spontaneously has since been lengthened considerably. Also the alkaloids that become at length colloidal in aqueous solutions, are very numerous. It is interesting to contrast with them the crystalloid condition of nearly all solutions of antipyretica (non-alkaloids).

have a greater molecular weight than those that are not transformed or hardly so; again, the former generally bring about a more considerable lowering of the surface-tension of water. For the solutions examined upon their Tyndall effect the number of droplets decreased in an orderly manner. Calling the number of droplets for pure water 49, that of eugenol is 90, crissol 80, carvacrol 80, citral 72, thymol 72, guaiacol 70, cumidin 65, hypnone 54. This series corresponds approximately with the one holding for Tyndall's effect. On the whole there is an orderly decrease in the power to produce a lowering of the surface tension between air and water, similar to that of the power to bring about a colloidal condition of the saturated or half-saturated solution.

When examining our solutions ultramicroscopically while standing for days and weeks, at various intervals, the number of submicrons appears to augment ¹⁾ to the detriment of the amicrons, which formed the base of the cone. In strong colloid solutions there ultimately appears a precipitate, as in the case of eugenol. By the addition of $\frac{1}{2}$ n. sodium-carbonate solutions the markedly opalescent fluid at once becomes rather more translucent, in which process amicrons re-appear, this time to the detriment of the spontaneous submicrons previously formed.

Prior to and subsequent to transformation the surface-tension of the solution is approximately equal (with a eugenol solution 1 : 1500 fresh 67 and old 67 droplets for the stalagmometer volume). Also the smell-intensity is the same before and after transformation. Upon this basis we feel justified in terming the transformed odorous solutions "suspensoids". Exposed in the usual way in an U-tube to the action of a constant electric current, the particles in these suspensoids were all moved towards the anode. It follows then that the particles themselves must be negatively charged. The arm with the + pole was getting more opalescent, the one with the — pole cleared up.

After reversal of the current the previous state was restored. Likewise the previous intensity of Tyndall's effect is restored by mixing the contents of the two arms. The following table gives the quantitative relations of the light-intensities of the Tyndall effect of the solutions,

¹⁾ The fluids, the colloidal as well as the fresh-prepared control fluids, were instantly filtered in the cuvette through a paper filter. Consequently with pure water only half a dozen submicrons at the most were discernible in a microscopic field. With water a base of amicrons was altogether lacking, similarly with the fresh control-fluids; but in the saturated or partly saturated solutions that through standing had been changed into suspensions, we discerned besides a base of amicrons a very large number of submicrons in active Brownian movement.

tabulated above, after allowing a current to pass through for one hour :

INTENSITY OF THE OBLIQUELY DIFFUSED LIGHT.

	Initially	At the — pole	At the + pole
Eugenol.....	37	33	41
Guaiacol.....	37	29	35
Cressol.....	24	19	23
Carvacrol.....	20	16	24
Citral	20	16	22
Cumidin	15	12	18
Thymol.....	15	10	16
Hypnone.....	10	slight	16

After displacement of the micellæ in the suspensoids through the influence of the current, the surface tension in the arm of the positive pole appears to become somewhat less than in the arm containing the negative pole.

NUMBER OF DROPLETS (CALLING THAT OF WATER 49).

	Previously	At the — pole	At the + pole
Eugenol.....	90	87	89
Carvacrol.....	84	79	80
Cressol.....	80	78	79
Citral	73	71	74
Thymol....	72	70	71
Guaiacol.....	70	70	71
Hypnone	55	54	56

When heating an aqueous eugenol solution 1 : 1200 beyond 40°, the opalescence decreases, whereas it returns on cooling and after a few days becomes more intense than before. Below 30° no change occurs, even when the solution is maintained at 30° for 24 hours.

Similarly a colloidal solution of eugenol in glycerin appeared to be much less opalescent on hot summerdays than on cooler days preceding or following.

The gradual transformation of solutions of odorous substances beginning with the formation of amicrons, that develop into submicrons, appears to be largely influenced by light. When kept in the dark, the process is slow in aqueous solutions. There are even several substances, e.g. chinolin, in which it does not appear at all, but in which it comes forth distinctly in daylight. It should also be observed that the effect of ultra-violet light is much stronger than that of daylight ¹⁾.

When exposing a eugenol-solution in a quartz test-tube at $\frac{1}{2}$ m. distance from the light of a mercury quartz lamp, opalescence is attained within half an hour, which otherwise is not arrived at in a fortnight. An electric arc-lamp has the same effect in a smaller degree. This quickening of transformation does not occur when the quartz-tube is enclosed in stanniol-paper. The same was observed with all other solutions. Even a heliotropin solution, ultramicroscopically empty, shows, after half an hour's radiation, numerous micellae.

Besides by the ordinary light-waves and the ultra violet rays, odorous substances can also be rendered colloidal by radiation with radium kept in vitro. In order to ascertain this we took two perfectly equal glass cuvettes with parallel walls, each filled with saturated odorous solution. In one of the cuvettes a closed glass tube was inserted, in which 200 mgrs of a mixture of radium- and barium-bromide containing 0,18 % RaBr^2 . If the experiment was performed with a saturated heliotropin solution, the control fluid remained ultramicroscopically empty, whereas the solution, in contact with the radium tube, showed in 24 hours a base of amicrons and 10 submicrons per microscopic field. Something similar occurred in a short time also with the other odorous solutions of the table, though with every following substance of the series more time was required to obtain a difference in dispersity between the radium-cuvette and the control-cuvette.

Not only the admitted electro-magnetic waves of the visible light, the ultraviolet light and the γ -rays of the radium, but also the mechanical energy is competent to give to a fresh-prepared, saturated multitomic odorous solution the energy needed for an amount of surface-energy sufficient for the formation of numberless amicrons and submicrons, to be observed in the gradually developed suspensoid. By shaking the fluid forcibly, transformation is largely promoted. In

¹⁾ Besides opalescence also fluorescence is generated. We are unable to decide whether there is any relation between light electricity and the observed highly accelerated transformation to a colloidal state. Cf. HELLWACHS on Light-electricity in Marx's Hab. d. Radiol. Vol. III p. 438.

a heliotropin solution e.g. that remained free from submicrons, even after standing for months, they appear in a rather large number directly after the old solution was shaken for some time in the closed cuvette. The same occurs with glycerinous solutions. Eugenol poured on glycerin without shaking renders the latter non-opalescent in five days. When it is vigorously shaken, however, the fluid is rendered slightly opalescent, and colloidal in the real sense of the word. It also retains its suspensoidal character in the subsequent phase of the process.

It is not likely that chemical energy should also come into play, since the process also takes place in chemically all but indifferent fluids, such as paraffin, though it must also be added that entire deoxidation of paraffin inhibits transformation also in ultraviolet light. However, there must be still another unknown source of energy, apart from the radiation of light and the mechanical energy, which supplies the newly generated micellae with surface-energy, with or without the aid of oxygen, since eugenol solution enclosed in a leaden casket, kept in utter darkness, becomes undoubtedly

TRANSFORMATION TO A COLLOIDAL STATE OF AQUEOUS SOLUTIONS IN THE ANILIN-SERIES.

	Molec. weight	Number of Atoms	Tyndall's effect
Anilin.....	93	14	hardly distinguishable
Toluidin.....	107	17	rather distinct
Xylidin.....	121	20	" "
Cumidin.....	135	23	distinct

ID. IN THE BENZOLSERIES.

	Molec. weight	NUMBER OF ATOMS	Tyndall's effect
Benzol.....	78	12	hardly distinguishable
Toluol.....	92	15	little distinct
Xylol.....	106	18	
Pseudocumol...	120	21	little distinct
Durol.....	134	24	rather distinct

suspensoidal within a few days. However, to obtain this, large dissolved molecules are required. This is clearly shown when comparing the terms of an homologous series inter se.

Odorous substances never have very large molecules.¹⁾ Therefore, there will never be an extremely strong tendency to form amicrons, subsequently submicrons, as soon as the supply of energy that may pass into surface-energy, is established. This accounts for the process being hitherto unobserved. But when working with much larger molecules, we may readily presume that the process of transformation is highly facilitated, and will show itself very distinctly, whenever electromagnetic waves, mechanical energy, or the unknown source of energy, suggested above, are present, from which the particles to be formed, derive their surface-energy.

¹⁾ The odorous substances examined by us, had a molecular weight between 78 and 199; the number of their atoms amounted to from 14 to 27, on the understanding that no multiple of the chemical formula should be taken.

Chemistry. — "*The Passivity of Chromium*". (Third Communication).
By Dr. A. H. W. ATEN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the Meeting of March 23, 1918).

When it is tried to explain the results communicated in the foregoing papers¹⁾ we should in the first place consider the possibility that the hydrogen (or oxygen) present in the surface layer of the metal, has a certain influence on the phenomena.

The phenomena, that render it probable that the hydrogen present in the surface layer of the metal promotes the activity, are among others the following.

When a piece of GOLDSCHMIDT chromium, which contains little hydrogen, is placed in a feeble acid or in very dilute sulphuric acid, it does not go spontaneously into solution with generation of hydrogen. When the chromium is, however, cathodically polarized, so that hydrogen is generated in consequence of this, the chromium goes also into solution as chromous ion. When the current is broken, also the dissolving as chromous ion stops, when the acid is diluted enough. In more concentrated acids, especially in hydrochloric acid, and also at higher temperatures in diluted acids, the dissolving accompanied by hydrogen generation, begins spontaneously after a short time.

From the fact, that the cathodic polarisation causes the solution of the chromium, we may conclude that the hydrogen charge that the metal acquires in this case, is the cause of the activity. At the same time it follows from this that a hydrogen charge corresponding to gaseous hydrogen of one atmosphere is not sufficient to activate chromium, for in this case the activity would have to continue to exist when the current is broken. At that moment, and also some time after, the metal has, namely, a hydrogen charge that is at least equal to one atmosphere, and yet the going into solution ceases spontaneously. The activity disappears even when the cathodic polarizing current is not broken, but only sufficiently weakened²⁾. FLADE³⁾ denies this statement of RATHERT, but describes

¹⁾ These Proc. XX, p. 812, 1119.

²⁾ RATHERT. Zeitschr. f. physik. Chemie 86. 567, (1914).

³⁾ ibid. 88 569 (1914).

an experiment that proves about the same thing. He found, namely, that a passive electrode in diluted sulphuric acid could be cathodically polarized to a feeble hydrogen generation without becoming active.

The behaviour of chromium in acids can be derived from figure 1.

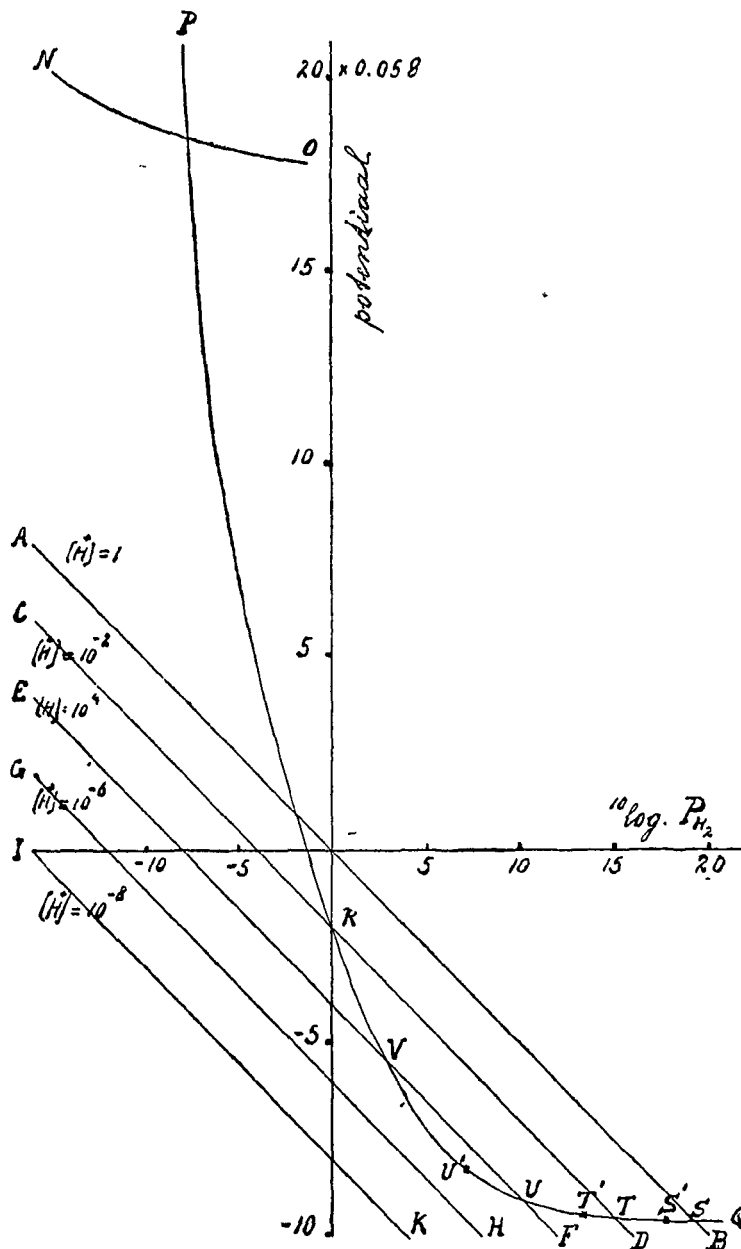


Fig. 1.

The 10 log of the hydrogen pressure has been plotted on the abscissa; the potential on the ordinate. The line AB indicates the

hydrogen charges which an electrode acquires for different potentials when the concentration of the hydrogen ions in the solution is 1.

The same thing is given by the line CD for a hydrogen ion concentration 0.01 etc. These lines are nothing but the graphical representation of the potential of the hydrogen electrode.

Let us now assume that the potential of a chromium electrode in a solution of a given chromium concentration is determined by the density of the hydrogen charge, and can be represented by the line PQ in figure 1. There is little to be said about the course of this line; only on increasing hydrogen charge this line must draw near to a limiting value, which represents the real potential of equilibrium of chromium.

This latter supposition, that the electrode presents a chromium potential, which c.p. is only dependent on the density of the hydrogen charge, goes slightly further than the usual hydrogen hypothesis, according to which the hydrogen would only accelerate the setting in of the equilibrium. According to our conception a certain chromium potential corresponds to a given hydrogen charge. This supposition may seem improbable considered in itself, without it an explanation by the aid of the hydrogen hypothesis is not possible in my opinion. In what way the chromium potential comes about here, will not be discussed.

When we now take a chromium electrode with a gas charge 1, then the potential of this is R , according to figure 1. If this electrode is placed in a solution, which is 0.01 n. of acid, it can generate from it exactly hydrogen of one atmosphere. In consequence of the overvoltage no hydrogen will be generated, but the chromium will not lose its gas charge either. Hence the potential remains unchanged. When the same chromium is brought in an acid in which the concentration of the hydrogen ions is $= 1$, the chromium at the potential R can develop hydrogen in this acid to a pressure of 10^4 atm. In consequence of the increase of the hydrogen charge the potential now descends below R , this causes the hydrogen charge to increase, and thus the potential will continue to descend. The lowest value that *can* be attained, is S . This value *need* not be reached, however. It can only exist for a hydrogen charge of 10^{20} atm., and this is only possible when there is a very great overvoltage for hydrogen generation at chromium.

It appears therefore from this, that chromium with a hydrogen charge 1 will spontaneously activate, when placed in an acid which is stronger than 0.01 n. If the acid is weaker, the chromium does not spontaneously become active. In 10^{-4} n. acid a hydrogen charge

of 10^{-4} atm. corresponds to a potential R , and the hydrogen charge of chromium does, therefore, not become stronger of its own accord. When, however, this chromium is cathodically polarized in 10^{-4} n. acid, the hydrogen charge increases, the chromium potential decreases. If this falls below V , the chromium can be activated further spontaneously till the potential has become U . By stronger cathodic polarisation the potential can become lower than U ; when the current is broken the potential will, however, have to rise again up to U . The potential itself will not stop at U , but become higher. If the hydrogen generation is sufficiently vigorous to maintain a sufficient gas charge on the chromium, the potential can remain between V and U . Then the chromium remains active. When the hydrogen charge becomes smaller than corresponds with V , the potential rises above V , and the activity disappears. Not only when the current is broken can the potential rise above V ; it is also possible that this already takes place in case the polarizing current is weakened. When e.g. with vigorous cathodic polarisation the gas charge becomes greater than V , the gas charge can become smaller than V when the hydrogen generation becomes feebler, and the activity will disappear. This is the above described phenomenon of RATHERT. It is likewise possible that with very weak cathodic polarization the hydrogen charge does not become great enough to lower the potential below U . Then the metal remains passive in spite of the cathodic polarization (FLADE).

The most negative potentials that the chromium can spontaneously assume in 1 n. 0.01 n. and 0.0001 n. acid, are accordingly S , T , and U . These will, however, not be reached, because a very great over-voltage would be required for it. In reality the potentials S' , T' , and U' will e.g. be observed.

The above given considerations account, therefore, sufficiently for the spontaneous activation of chromium in acids, and the activation by cathodic polarization, also in connection with the strength of the acid.

Chromium becoming more easily active in hydrochloric acid than in sulphuric acid or in other acids, there must exist a specific activating action of the chlorine ions. This comes to this that a smaller gas charge is required for the activation in hydrochloric acid, and that the line PQ must therefore be drawn more to the left for hydrochloric acid. The same thing applies for higher temperatures.

It appears then also from figure 1, that chromium can only remain strongly active in a liquid in which it develops hydrogen, and, therefore, maintains its gas charge itself. When now a fresh electrode

the chromium is left in contact with the liquid, the hydrogen present in the boundary surface GF , will for the greater part pass into the solution, or escape in gas form. This causes the concentration of the hydrogen at the boundary surface to become smaller.

In consequence of this the hydrogen diffuses from the metal towards the boundary surface, and after a certain time the concentration of the hydrogen in the chromium will be represented by the line ABC . In the part AB the concentration has remained unchanged, in BC the concentration has changed through diffusion. We shall call the layer EF , in which the diffusion is perceptible, the diffusion layer. The chromium now presents a potential which is determined by the size of FC .

When we now polarize anodically, the first consequence will be, that the hydrogen concentration at the boundary surface FC becomes smaller. This will at any rate be the case when the solution used is so little acid, that the hydrogen potential corresponding to a given hydrogen charge, is more negative than the chromium potential of the same hydrogen charge. This applies therefore to those parts of the hydrogen lines (AB , CD , etc.) that lie under the chromium line PQ in fig. 1. For in case of anodic polarization, the potential of the metal will here lie further above the equilibrium potential of the hydrogen than above that of the chromium, so that the hydrogen will dissolve to a greater extent.

At the same time chromium goes into solution. Hence the boundary layer GF shifts to the left, and gets e.g. at the place $G'F'$. The thickness of the diffusion layer has now become smaller, and the concentration of the hydrogen in this layer is represented by $B'C'$. Now the hydrogen charge at the boundary surface is $F'C'$, hence smaller than before the anodic polarization. When the strength of the current is kept constant, a stationary state will set in, in which $F'C'$ is constant, and also the concentration gradient in the diffusion layer.

When the strength of the current is increased, this stationary state will be another, i.e. so, that $F'C'$ is smaller and the concentration gradient of the hydrogen in the diffusion layer greater than in case of smaller strength of current, because the diffusion layer is thinner.

During anodic polarization the potential will be more positive than before, because the hydrogen concentration at the boundary surface is smaller. When the current is broken, the hydrogen will quickly diffuse towards the boundary surface in consequence of the great concentration gradient in the thin diffusion layer. This causes the hydrogen charge at the boundary surface to rise, e.g. to $F''C''$.

Besides, the diffusion layer becomes thicker again, as the metal no longer dissolves; the point B' , therefore, gets in B'' . C'' must lie higher than C , because at C'' more hydrogen diffuses towards the boundary surface than at C on account of the slight thickness of the diffusion layer. This hydrogen must also pass into the liquid more rapidly, which is only possible when $F' C''$ is greater than $F C$.

When the value C'' has been reached, the hydrogen charge at the boundary surface will decrease again through the continual passing of hydrogen into the liquid, and through the supply of hydrogen from the metal going more slowly, because the diffusion layer becomes thicker. At last a stationary state is again reached, which is equal to the state before the polarization, and in which the hydrogen charge of the boundary surface is $F' C'''$, the concentration of the hydrogen in the diffusion layer $B''' C'''$.

The greater the density of the current, the smaller will be $F' C'$, the thinner will be the diffusion layer, and the higher therefore will C'' lie.

Hence the following particulars will be observed for the potential of electrolytic chromium. When electrolytic chromium with a fresh surface is brought into an electrolyte, the hydrogen charge at the boundary surface is great, FG , and the potential strongly negative. When this chromium is left in contact with the liquid for a long time, the boundary surface of the metal loses part of its hydrogen, the hydrogen charge falls to FC , and the potential becomes more positive. When we polarize anodically, the hydrogen charge decreases to $F' C'$, the potential becomes, therefore, still more positive. When the current is now interrupted, then the hydrogen charge rises to $F' C''$, the potential becomes much more negative, but gradually the hydrogen charge decreases again to $F' C'''$, and the potential rises to the value that it showed before the polarization.

This course is quite in concordance with what was drawn in figure 7 of the second communication.

Accordingly the potential reaches a minimum which is the deeper as C'' lies higher, hence as the strength of the current is greater and consequently the diffusion layer is thinner.

When the strength of the current is very small, and the diffusion layer is thick, it may occur that C'' does not get above C''' , and that the potential does not pass through a minimum, as is the case with the line for $1mA$ in figure 7 of the second communication.

It is clear that the phenomena for anodic polarization will, therefore, chiefly be determined by the hydrogen content of the metal.

These phenomena being different for chromium on copper, on

silver, and on gold i.e. so that the potentials for chromium on copper are the most negative, it must be assumed that chromium deposited on copper contains more hydrogen than chromium on silver, and this more than chromium on gold.

In the same way the existence of a retrogressive current potential line can be explained, as has been drawn in figure 11 of the second communication. These lines refer to the formation of chromate, and we shall, therefore, have to assume that also the potential of chromate formation will be dependent on the hydrogen content. This dependence is e.g. given by the line NO in figure 1.

Here too, in case of anodic polarization the concentration of the hydrogen at the boundary layer will be small, hence the potential high. On increasing current density the diffusion layer becomes thinner, so that in case of interruptions of the current by the commutator the hydrogen charge at the boundary surface *after* the current has been broken will be the greater as the current density was greater.

Hence for greater current density the potential is more negative after the current has been interrupted than for small current density. Moreover it is clear that the retrogressive current potential line can only be found when we work with a commutator. When the potential is measured with continual passage of the current, the potential is the more positive as the current density is greater, because then only the hydrogen charge at the boundary surface is to be reckoned with as it is *during* the polarization.

Accordingly the activation *after* anodic polarization can be satisfactorily accounted for by means of the hydrogen theory.

It remains, however, to explain the phenomenon that on anodic polarization of electrolytic chromium and of activated chromium of GOLDSCHMIDT, the potential becomes more negative also during the passage of the current.

An explanation of this may be arrived at when it is borne in mind, that not immediately after the current is broken or started the state in the diffusion layer is stationary.

When in figure 3 BC represents the concentration of the hydrogen in the diffusion layer of a piece of chromium which has been in contact for a long time with an electrolyte, the hydrogen at the boundary surface has the concentration FC . When this electrode is now anodically polarized, the concentration of the hydrogen will descend to $F'C'$ in consequence of this. Now the concentration of the hydrogen in the diffusion layer will have the course $B'C'$. This will be the state when the current has just been started, and the

boundary surface has, therefore, been only little shifted inward. When the passage of the current is continued, the boundary surface moves more inward, and when it has reached $F'' G''$, a stationary state

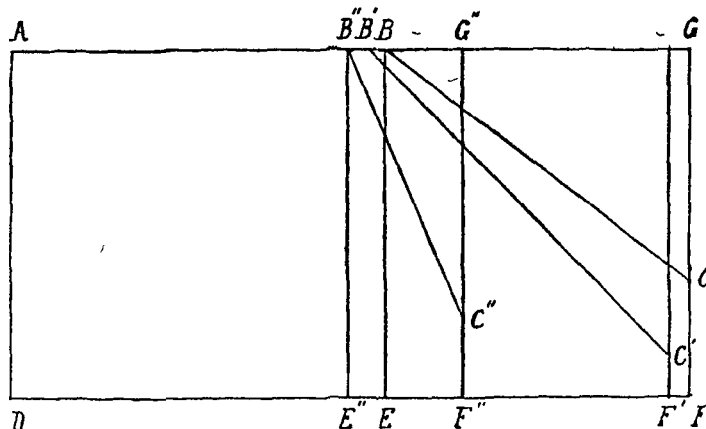


Fig. 3.

will have been reached, in which the thickness of the diffusion layer and the concentration gradient of the hydrogen is stationary. The former is smaller and the latter is greater than when the current had just been started; consequently also the hydrogen charge at the boundary surface $F'' C''$ can now be greater than at first. The course of the potential as function of the time will, therefore, be as follows. Before the polarization the electrode is comparatively active, corresponding to the hydrogen charge $F' C'$. When the current is put on, the potential rises in consequence of the decrease of the hydrogen charge. On continued passage of the current the potential descends again, because the hydrogen charge becomes greater again in consequence of the diffusion layer becoming thinner.

This is what was observed for the anodic polarization of electrolytic chromium, and also of GOLDSCHMIDT chromium which is activated in molten $ZnCl_2$ or $KCl + NaCl$. Also with chromium of GOLDSCHMIDT which has been activated in strong HCl , the same phenomenon is observed. Nevertheless there exists quantitatively a great difference between these two kinds of chromium. With electrolytic chromium the activation proceeds much more quickly during the passage of the current than with GOLDSCHMIDT chromium which has been activated in $ZnCl_2$, and with this again more quickly than with GOLDSCHMIDT chromium that has been activated in hydrochloric acid. For this last the potential continued to become more and more negative for hours with constant strength of the current. For electrolytic chromium this continued only for a few minutes. The difference

in the duration of the phenomenon may be attributed to a difference in the hydrogen content of electrolytic chromium and GOLDSCHMIDT chromium. The former can bear a much stronger current already at the beginning of the anodic polarization than the latter. In consequence of this the displacement of the boundary surface GF to $G''F''$ goes much more quickly for electrolytic chromium than for chromium of GOLDSCHMIDT, hence also the activation on anodic polarization proceeds more quickly for electrolytic chromium.

As has been described in the second paper, a piece of GOLDSCHMIDT chromium that has become active through anodic polarization, can not bear the same strength of current any more when the current has been broken for some time, though the potential is then much more negative than immediately after polarisation. This, too, can be accounted for by the diffusion of the hydrogen in the metal. Before the polarization the concentration of the hydrogen in the diffusion layer is represented by BC in figure 4. When the electrode is

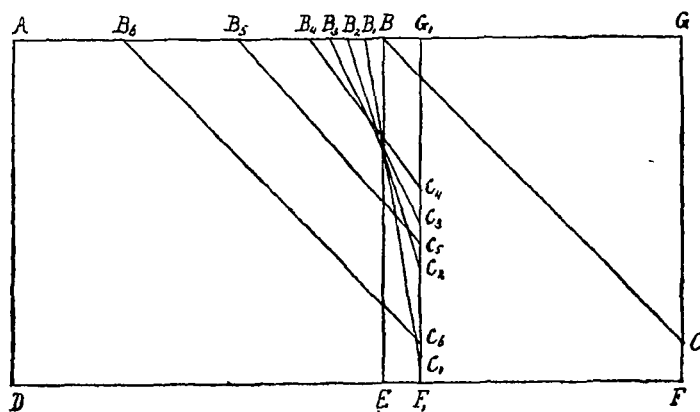


Fig. 4.

anodically polarized, and the strength of the current is slowly carried up, a stationary state will be reached after some time, for which the concentration of the hydrogen in the diffusion layer, which has now become a good deal thinner, is represented by B_1C_1 . When the current is interrupted, the hydrogen concentration at the boundary surface rises in consequence of the great gradient of concentration. Besides the thickness of the diffusion layer increases, which extends inwards in the metal, and is no longer dissolved from outside. The course of the concentration of the hydrogen in the diffusion layer is now successively represented by B_1C_1 , B_2C_2 , B_3C_3 , B_4C_4 , B_5C_5 , and B_6C_6 . With B_6C_6 the concentration of the hydrogen at the boundary surface is greatest, the potential, therefore, most negative.

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When we now anodically polarize with the same strength of current as when the hydrogen concentration was represented by B_1C_1 , the hydrogen charge at the boundary surface will now descend below C_1 , since the thickness of the diffusion layer is now so much greater than immediately after polarization, and the diffusion of hydrogen accordingly proceeds so much more slowly. In consequence of this the chromium gets a more positive potential. In this way it is, therefore, explicable that the chromium can bear a stronger current when this is again put on immediately after the interruption than when the current has remained broken for some time, though in the latter case the potential is more negative in current-less condition. It now also appears that there is no immediate connection between the potential of a chromium electrode in current-less condition, and the possibility of its becoming passive. The former is namely determined by the density of the hydrogen charge at the boundary surface, whereas it depends on the gradient of concentration in the diffusion layer whether the electrode can be made passive. The before described phenomenon that not always the most negative electrode is most difficult to passivate, is in agreement with this.

So far the phenomena can, therefore, be explained by the aid of the hydrogen theory. That the phenomena are caused by a particular state of the metal surface, and not of the liquid, appears from this that they qualitatively remain the same, when the liquid is vigorously stirred, and also when the liquid is entirely renewed. The potential of the electrode only becomes *somewhat* more positive by stirring. This is probably owing to this, that in consequence of the stirring the solution contains more oxygen, and the hydrogen is more quickly withdrawn from the chromium surface. When the stirrer is stopped, the potential falls again.

In these experiments the chromium anode was placed in a saturate solution of KCl, the cathode in a same solution in a porous vessel. This latter liquid became alcalic during passage of the current. The solution round the anode became on the other hand *acid*. To determine the degree of acidity a hydrogen electrode was placed in this solution. It presented a potential -0.58 V. with respect to the n. calomel electrode, corresponding with a hydrogen ion concentration of 10^{-5} . A current of 4 mA had been led through this solution for 20 hours.

That the solution became acid can be explained by a hydrolytic splitting up of the formed CrCl_2 , or by the hydrogen present in the chromium going anodically into solution as H.

As the volume of the solution amounted to about 300 cm^3 , and

the hydrogen ion concentration was 10^{-5} , there has been formed 0.003 mgr. aeq. of hydrogen ions, 3 mF having gone through the solution. Hence the chromium would have to contain 0.1 % hydrogen in order to give the above mentioned degree of acidity to the solution. In reality this must be slightly more, because part of the OH ions has moved from the cathode space to the anode space, and has, therefore, partly neutralized the acid formed.

It also appeared in these experiments that the potential which the chromium electrode presents, is really a chromium potential, or at least no hydrogen potential. In the acid solution the potential was namely -0.59 V. When the solution was then made feebly alcalic, the potential rose to -0.58 V, whereas a hydrogen electrode in the same liquids would have to present a decrease of about 0.2 V. In this and in other experiments the chromium developed hydrogen. This cannot be hydrogen that the chromium developed spontaneously from the liquid, for in this case the potential of the chromium electrode would have to be more negative than that of a hydrogen electrode in the same liquid. This was not the case here; the potential of the hydrogen electrode was -0.58 , that of the chromium electrode -0.52 . Besides the hydrogen generation took just as well place in a feebly alcalic solution as in a feebly acid solution, whereas the potential of the chromium electrode was often pretty much more positive than -0.52 V. It is possible that the chromium contains more hydrogen than dissolves anodically, and that part of it escapes in gaseous form.

Hence it must be assumed that the examined chromium always contained hydrogen. In the case of electrolytic chromium this has been separated at the same time with the chromium in a considerable quantity, whereas the chromium of GOLDSCHMIDT contains a slight quantity. By treatment with molten $KCl + NaCl$ or $ZnCl_2$, the chromium can absorb more hydrogen in consequence of the decomposition of the water present in it by the chromium. On the action of chromium on these molten salts development of a combustible gas and formation of chromium oxide was always observed. That $ZnCl_2$ activates more strongly than $KCl + NaCl$ could be explained by this, that the hygroscopic $ZnCl_2$ contained more water, and can, therefore, yield more hydrogen. The activity which chromium obtains by treatment with hydrochloric acid and by increase of temperature must, however, chiefly or exclusively be attributed to the hydrogen which is naturally present in the metal.

With regard to the hydrogen generation at chromium during the anodic polarization it should still be pointed out that this ceases

after the polarizing current has been broken for some time, and in general is the weaker as the strength of the current is the smaller. This hydrogen generation is, however, in no connection with the other phenomena on anodic polarization, as the hydrogen generation failed to appear in a number of experiments, though the anodic behaviour was the same for the rest.

The explanation of the phenomena on cathodic polarization presents one difficulty, viz. that through the cathodically separated hydrogen, the metal in a solution of KCl is not activated. The metal, indeed, gets a strongly negative potential, but the strength of the current which the chromium anodically can bear, is not greater than before the cathodic polarization. To explain this it should be assumed that the cathodically developed hydrogen only remains at the metal surface, and does not diffuse, or only very slightly, into the metal.

Amsterdam, March 1918.

*Chemical Laboratory of the
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Physiology. — *"On the influence of the increase of the osmotic pressure of the fluids of the body on different cell-substrata."*

By Dr. S. DE BOER. (Communicated by Prof. G. VAN RIJNBERG).

(Communicated in the meeting of March 23, 1918.)

In the following experiments an investigation was made into the influence of the increase of the osmotic pressure of the fluids of the body on the vital functions of frogs. The increase of the osmotic pressure was brought about along different ways, which I intend to indicate here successively, mentioning at the same time the phenomena I observed.

I. Frogs were placed into a hyperisotonic solution of RINGER containing instead of 6.5 gr. (p. L.) NaCl 18 gr. NaCl. Such a quantity of this fluid was poured into the vessel in which the frogs had been removed, that the head and the back projected above it. A considerable part of the surface of the skin was then in contact with the hyperisotonic solution of RINGER. When the frogs had remained in this solution for about 20 hours, they showed a series of phenomena as a consequence of the increase of the osmotic pressure of the fluids of the body. The first phenomenon that is observed, is the comatous condition. The frog sits still in a squatting position with the connective fleeces (membranes) before the eyes, and no longer leaps about. If one stretches out a hindleg, this abnormal posture of the leg is indeed corrected again but very sluggishly. After a longer residence in the hyperisotonic surroundings this correction does not take place. Irritations of the skin have a slight reflectoric effect which in a later stage is likewise reduced to

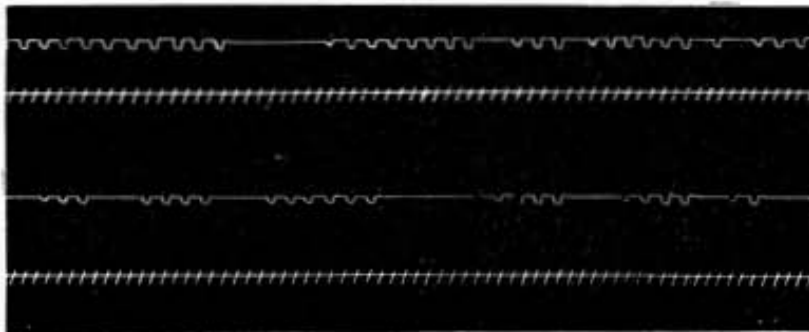


Fig. 1.

a minimum. The muscles show a strong inclination to contractions.

At the same time the respiration shows a periodicity that is known by the name of Cheijne-Stokes' respiration. Groups of dyspnoea alternate here with pauses. In Fig. 1 we see curves of this phenomenon which were registered by suspension of the skin in one of the flanks. During the flank-movements the pharyngeal respiration continued likewise and in such a manner that after each flank-movement a movement of the mouth-bottom could be observed. In the pauses both these movements ceased.

The curves of Fig. 2 were registered with another frog by placing a cork cylinder through which a pin had been pierced, on the back. The up-and downward movements of this cylinder were enlarged by a lever-system and registered on a drum covered by smoked

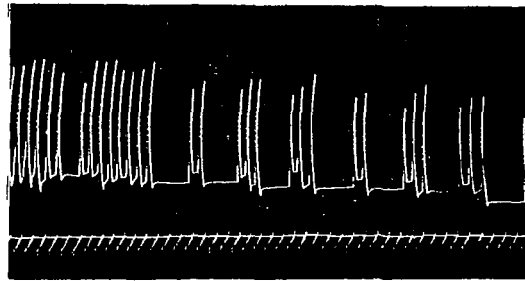


Fig. 2.

paper. The flank-movements were here likewise accompanied by movements of the mouth-bottom, whilst in the pauses both these movements ceased. In both figures we see in the beginning of the groups the ascending degree indicated. The periodic respiration was succeeded by a cessation of the respiration. This cessation was reached, after the animal had remained about 24 to 25 hours in the hyperisotonic solution of RINGER.

I found likewise a constantly occurring deviation at the eye-lenses. The surface of the pupil had the appearance of *cataract*.

The phenomena enumerated above were caused by the increase of the osmotic pressure of the liquids of the body. A few more controlling experiments were made in this respect.

Whilst the periodical respiration was still going on, or likewise whilst a cessation of the respiration had already set in, the frog was put into the water. After the animal had been in the water for 24 hours, all the phenomena mentioned above had disappeared. The frog was then again quite normal, the passivity, the reflectionlessness and coma had entirely disappeared. The respiration was then again normal,

the cataract had entirely or almost entirely disappeared. (After the frog had remained in water for 2 days not a vestige of the cataract was left). The frog could not in any respect be distinguished from a normal one.

A second control experiment was made in the following manner:

The frog was put in the hyperisotonic solution of RINGER, and at the same time a canule was fastened in the dorsal lymph-bag. Slowly water was poured into the lymph-bag through this canule. Under these circumstances the fluids of the body did not become hyperisotonic, as the water that was withdrawn from the frog along the skin, was replaced again along the lymph-bag. In this way the frogs could remain alive during a week without showing the above mentioned symptoms. Without the drainage of the lymph-dorsal-bag the frog dies in the hyperisotonic solution of RINGER within one day and a half.

II. Instead of the hyperisotonic solution of RINGER a hyperisotonic solution of glucose was used (1.38% solution). The frogs behaved in this solution in exactly the same manner.

III. In a third series of experiments fluid was withdrawn from the frogs by placing them in a dry bottle, and sucking through the latter by means of a water-jet-suction pump air that had previously passed through lime-tubes. After one day and a half such a frog had desiccated so much as to show the same symptoms as a frog that had been placed in a hyperisotonic fluid. After it had been removed into the water again a complete restoration set in likewise.

IV. In a fourth series of experiments the blood was replaced from the vena abdominalis by a hyperisotonic solution of RINGER (with 18 gr. NaCl per L.). When the fluid had streamed through the frog for 15 to 20 minutes, the same phenomena of coma, passivity and reactionlessness set in. The respiration was then periodical (Cheyne-Stokes' respiration) or stopped entirely. In the latter case the Cheyne-Stokes' respiration could be restored by placing the frog for a short time into water. A beginning of cataract could already be observed, when the drainage had lasted 15 to 20 minutes. If no further measures were taken, the cataract augmented considerably after the drainage in the course of 10 to 15 minutes.

All phenomena disappeared likewise in this series of experiments when the frog was removed to water.

A short description of an experiment may follow here.

11 $\frac{1}{2}$ o'clock. From the vena abdominalis a frog is drained with a hyperisotonic solution of RINGER during 25 minutes. Coma, passivity

cessation of the respiration, when it is turned on its back, the frog does not move, abnormal position of the leg is not corrected, cataract of both the eyes¹⁾.

At 1 o'clock placed in water.

1½ o'clock. The frog shows now and then a respiration.

2 o'clock Cheyne-Stokes' respirations.

Whilst the frog continues to lie on its back in the bottle of water, the number of respirations per group and the duration of the pauses during some time are registered.

Here follows the result:

9 respirations	58 sec. pause
1 minute pause	14 respirations
9 respirations	62 sec. pause
½ minute pause	11 respirations
5 respirations	45 sec. pause
40 sec. pause	13 respirations
11 respirations	40 sec. pause
70 sec. pause	20 respirations
11 respirations	62 sec. pause

This observation has this advantage over the registration, because on account of the suspension the respiration of the frog varies temporally at least often.

After this the respiratory curves were registered by suspension of the mouth-bottom, as LANGENDORFF did for the first time. The first 8 minutes after the suspension the respiration stopped entirely. Thereupon the groups reappeared again. Fig. 3 represents some of these. The bottom row was registered ½ hour, the top one 10 minutes after the suspension.

When we compare the respiratory-curves of these groups with the curves

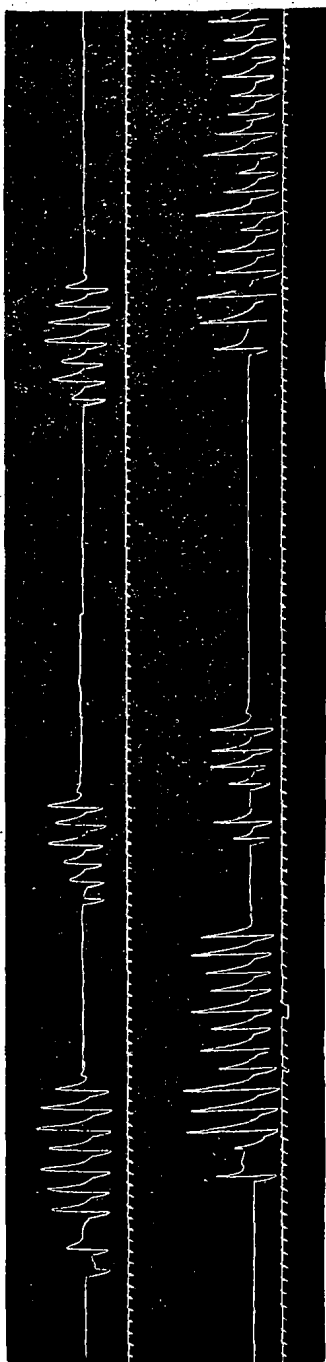


Fig 3.

¹⁾ In order to control the experiment the two lenses were extirpated after the experiment and compared with normal extirpated lenses. The latter were clear and transparent, the former turbid and opalescent.

of the normal respiration, it appears that with each movement of the mouth-bottom one movement of the flanks takes place during these groups.

Only the two first groups of the top-row set in with a separate expiration-movement, which is not followed by a movement of the mouth-bottom. For the rest all groups begin with an expiration, as appears from the fact that the lever descends in the beginning. During the normal respiration the frogs show one flank-movement with some movements of the mouth-bottom. During the groups of the Cheyne-Stokes' respiration every movement of the mouth-bottom is almost always followed by one flank-movement. In this way the frog respire likewise when it is dyspnoeic.

If the blood of frogs is replaced by normal isotonic solution of RINGER instead of hyperisotonic fluid of RINGER the mentioned phenomena do not occur. The respiration remains normal, the lense does not become turpid.

A more explicit discussion of the cataract and the Cheyne-Stokes' respiration follows here.

Cataract.

In whatever way the fluids of the body of frogs may be made hyperisotonic, cataract occurs always. *The cataract disappears however again, when the osmotic pressure of the fluids of the body is made normal again.*

The cataract develops itself very slowly. When after a perfusion during 15 or 20 minutes the respiration has stopped already, the surface of the pupil begins only to become a little dim. If then one waits a short time without continuing to drain the circulation-apparatus, the dimness gradually increases. At last two vertical parallel white stripes are observed on the lense, between which there is a long dark stripe. It makes the impression as if one sees two white walls and between these a deep, dark moat. The direction is usually vertical, sometimes almost vertical. This vertical stripe will correspond to the frontal vertical suture of the lens, as it is described in GAUPP. (*Anatomie des Frosches*). One often sees white, thin lines proceeding in a radiary direction from this vertical line, corresponding to the so-called spokes of the human cataract. It is obvious that the origin of the cataract must be attributed to a congelation of the albuminous substances in consequence of an increase of the saltconcentration of the fluids of the body. As soon as the osmotic pressure of the fluids of the body decreases again, the process is likewise converted. In my opinion another explanation of the phenomenon is impossible.

It is obvious that also every other circumstance by which a con-
gelation of albuminous substances is caused, can bring about lense-
cataract. In my opinion however it is of importance that I have
indicated, that a mere increase of the osmotic pressure of the fluids
of the body can result in cataract.

Cheyne-Stokes' respiration.

The periodical respiration was caused in my experiments by an
increase of the osmotic pressure of the fluids of the body. The
periodical respiration disappeared likewise again as soon as this
pressure did not exist any longer. In order to study the origin of
the Cheyne-Stokes' respiration more accurately the desiccation of the
frogs was continued in a series of experiments so far, that the
Cheyne-Stokes' respiration had not yet set in. Thereupon the mouth-
bottom was suspended and in a warm room the frog was exposed
to further desiccation. Usually the Cheyne-Stokes' respiration slowly
set in there in the course of a few hours. During these experiments
it appeared that besides a periodicity of the flank-respiration we
must distinguish a periodicity of the pharyngeal respiration. In far
advanced stages the two periodicities coincide, so that then during
the groups movements of both the flanks and the mouth-bottom
take place, whilst in the pauses the respiration stops entirely. As
a transition to this complete Cheyne-Stokes' respiration we find a
stage in which the groups are equal to those of the complete Cheyne-
Stoke's respiration, but during this stage the movements of the
mouth-bottom continue. It appears consequently that both ways of
respiration are to a certain degree independent of each other, as
appears indeed also from the normal respiratory curves.

According to the examinations of LANGENDORFF the movement of
the flanks comes off passively without a contraction of the pectoral
muscles. If this is correct, then the movement of the flanks is after
all made possible by an active opening of the glottis. With the
Cheyne-Stokes' respiration the periodicity of the movement of the
flanks is determined by a periodicity of the glottis-muscles. An
opening of the glottis is almost constantly followed by a move-
ment of the mouth-bottom, this however is not necessary either. The
first 2 groups of Fig. 3 set in with an expiration that is brought
about by an opening of the glottis, which is however not followed
by a movement of the mouth-bottom.

One word more about the cause of the Cheyne-Stokes' respiration
in these experiments. As I explained already, this phenomenon

occurs at a hyperisotony of the fluids of the body. This hyperisotony leads in the end to a cessation of the respiration. Like the cataract this cessation of the respiration can be suppressed again by a decrease of the osmotic pressure. Consequently the setting in of the cessation of the respiration in hyperisotonic surroundings, just as the Cheyne-Stokes' respiration that precedes it, and likewise the development of cataract originate in modifications that are reversible.

Chemistry. — “*On the Electrochemical Behaviour of Metals*”. By
Prof. A. SMITS. (Communicated by Prof. ZEEMAN).

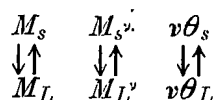
(Communicated in the meeting of March 23, 1918).

1. *Introduction.*

By application of the considerations on which the theory of allotropy is based to the internal state of the metals and to their chemical as well as to their electromotive behaviour, we are enabled to consider all the metals, also those which serve as so-called unattacked electrodes, from the same point of view.

These considerations rest on the more than probable assumption that every metal contains metal atoms, one or more kinds of metal ions, and electrons, which can be in equilibrium under definite circumstances. When a metal is immersed in an electrolyte, then in agreement with NERNST'S views of the phenomenon of solution, the heterogeneous equilibrium between the metal and the boundary layer will be established with so great velocity, that it may be said that this equilibrium always exists.

When we, therefore, restrict ourselves to the simple case that the metal consists of metal atoms, v -valent ions, and electrons, we may say, that when this metal is immersed in an electrolyte the following heterogeneous equilibria will at once set in.



Whether the homogeneous equilibrium will also exist in the two coexisting phases between the metal atoms, metal ions, and the electrons, depends on different circumstances. Whereas it seems that a metal in perfectly dry condition can assume internal equilibrium as a rule only at comparatively high temperature, this often takes place very quickly when in contact with an electrolyte, but it may also occur that the metal gets in equilibrium very slowly, or not at all, under these circumstances at the ordinary temperature.

The velocity with which a metal assumes internal equilibrium under definite circumstances is undoubtedly one of the most characteristic properties of the metal.

2. *The Potential Difference Metal-Electrolyte when
the Metal is Attacked.*

When a metal in contact with an electrolyte superficially assumes internal equilibrium with very great velocity, the internal state in the metal surface remains unchanged, in whatever way the metal may be attacked.

Let us suppose that we immerse zinc in an aqueous solution of hydrochloric acid; then hydrogen generation takes place, because the electron concentration of the metal equilibrium

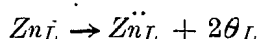


in the solution is greater than the electron-concentration of the hydrogen equilibrium:



Hence the electrons of the equilibrium (1) are removed, and through this the equilibrium is disturbed. It is now the question how the equilibrium can be restored.

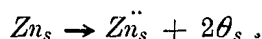
The concentration of the zinc-atoms in the liquid is so small that even if the reaction constant of the conversion



was very large, yet only exceedingly few zinc ions and electrons would be split off per second in this way.

The only way in which the state of equilibrium can be restored is this that the metal sends electrons into solution, which is of course accompanied by zinc ions going into solution, because zinc-ions and electrons, with a difference of only a very small amount, are always present in the same concentration.

Through this process the internal equilibrium in the metal surface is disturbed, which can be restored again by the reaction:



As the heterogeneous equilibrium in the boundary layer sets in with very great velocity, the question whether the metal zinc during solution in an acid will be disturbed, comes to this, whether the internal equilibrium in the surface of the metal sets in with so great velocity that the concentration remains practically unchanged.

This is actually the case for zinc under certain circumstances. Mr. HÜFFER S. J., who examined some metals at my request, found among others, that when the potential difference between zinc and a solution of zinc-chloride is measured during vigorous stirring, and then that between zinc and a zinc-chloride solution of the same

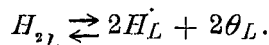
concentration acidified with hydrochloric acid, *the potential difference retains the same value, notwithstanding a strong hydrogen-generation takes place in the latter case.*

The metal zinc is, therefore, not disturbed through solution in hydrochloric acid, and this result is in perfect agreement with what is found when zinc is anodically brought to solution in a zinc-chloride solution. In this process, which likewise rests on the withdrawal of electrons from the metal, the potential difference, zinc-electrolyte, does not change appreciably, even for comparatively great densities of current, so that our investigations about the potential difference *during* the solution of zinc in a hydrochloric acid solution, as well as the measurements of the potential difference of the same metal on anodic solution in a solution of zinc-chloride lead to the result that the equilibrium in the metal zinc in contact with the above-mentioned electrolyte sets in with a velocity which is very great compared with the velocity with which electrons and ions are withdrawn from the metal.

3. General consideration.

When we now consider the phenomenon in general, we can distinguish the following cases.

On immersion of a metal in an acid we have in the simplest case among others the two following equilibria in the electrolyte:



and



The electron-concentrations of these two equilibria are in general different, and a consequence of this is that either the electrons of the metal equilibrium, in the liquid, combine with the hydrogen ions of the hydrogen equilibrium, which causes electrons + ions from the metal to go into solution, or the electrons of the hydrogen equilibrium with the metal ions of the metal equilibrium pass from the electrolyte into the metal.

Let us first imagine the limiting case, viz. this that the internal equilibrium of the metal surface is established with great velocity, so that this velocity is very great with respect to the velocity with which electrons + ions are withdrawn from the metal or are added to the metal, then the metal surface will not change independent of whether one process takes place or the other, and the potential

difference metal-electrolyte will remain equal to the potential difference of the unary metal.

In the second place the case may present itself that the internal equilibrium of the metal surface does not set in so rapidly as was supposed above, and then it will be possible to disturb the metal surface either in one direction or in the other, i.e. it may become either nobler or baser, hence the potential difference can differ from that of the unary metal in noble or base direction.

A third case, which like the first, represents a limiting case, is this that the metal is so inert that the velocity with which it assumes internal equilibrium is very small compared with the velocity with which the electrons and ions are withdrawn from the metal or added to it.

In the first limiting case the potential difference is entirely governed by the state of internal equilibrium of the metal, and in the last case the potential difference is dominated by the electron concentration of the hydrogen equilibrium in the electrolyte.

4. *Nickel as Example of an Inert Metal, the Inertia of which Increases under the Influence of the Dissolved Hydrogen.*

An example of the latter case with this particularity, however, that the just mentioned great inertia is only slowly reached, because the metal is converted to this state after some time through the negative catalytic influence of the dissolving hydrogen, is furnished by nickel. As was shown in a previous communication, the case presents itself that when this metal is immersed in such an acid solution that hydrogen generation would have to take place, this phenomenon does not take place to an appreciable degree, and the metal appears to be disturbed after some time so far in a noble direction that its potential difference has become equal to that of the hydrogen electrode.

On that occasion we already gave an explanation of this phenomenon, and pointed out that, nickel being so inert, the electron concentration of the nickel equilibrium in the electrolyte

$$Ni_L \rightleftharpoons Ni_L^{\cdot\cdot} + 2\theta_L$$

becomes equal to the electron concentration of the hydrogen equilibrium:

$$H_2 \rightleftharpoons 2H^{\cdot} + 2\theta$$

so that finally

$$(\theta_{Ni})_L = (\theta_H)_L.$$

This was demonstrated in the following way. We pointed out

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namely, that on application of the electron equation for the potential difference, metal-electrolyte, for the derivation of the relation for the electromotive force of a circuit consisting of two metals immersed in the corresponding salt-solutions, we arrive at the following equation

$$\Delta_1 - \Delta_2 = \frac{\mu_{\theta_{s_1}} - \mu_{\theta_{s_2}}}{F} - \frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})}$$

so that, taking into consideration, that the first term of the second member denotes the Volta-effect of the two metals, which is a very small quantity, the electromotive force $\Delta_1 - \Delta_2$ will be zero in first approximation, when $(\theta_{L_1}) = (\theta_{L_2})$.

In the case discussed here the metals 1 and 2 are nickel and hydrogen, and experiment has taught that $\Delta_{Ni} - \Delta_{H_2}$ was really practically zero, from which therefore followed $(\theta_{Ni})_L = (\theta_{H_2})_L$.

Through the inertia of the metal nickel, which inertia was still increased by the hydrogen dissolved in the metal, which is here a negative catalyst, as was already stated before, the metal could, therefore, be disturbed so far, that the electron concentration of the nickel equilibrium in the electrolyte had become equal to the electron-concentration of the hydrogen.

We may, therefore, also express ourselves in a different way, and say, that the nickel had been passivated by the acid. Finally the nickel phase and the hydrogen phase present the same potential difference, accordingly these phases, which are in contact with the same electrolyte, can coexist. As in the case discussed here the nickel will of course be covered by a layer of hydrogen, the found potential difference refers to the three-phase equilibrium $Ni + H_2 +$ electrolyte.

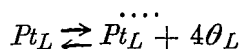
5. *Unattackable Electrodes.*

As follows from the communication cited here, this disturbance is comparatively slowly reached for nickel. There are, however, metals for which this goes much quicker, and these are the metals of which the so-called unattackable electrodes consist, as the platinum metals.

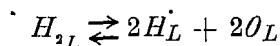
These metals belong to the group of the most inert metals that we know. Even in contact with an electrolyte these metals do not get in internal equilibrium, but they are almost always in passive state, so that the potential difference of the unary metal is not even known to us.

When such a metal is immersed in a solution of HCl or H_2SO_4 ,

and hydrogen is passed through, the electron concentration of the platinum equilibrium in the electrolyte



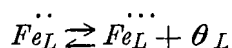
has almost immediately become equal to the electron concentration of the hydrogen equilibrium,



corresponding to the pressure of the hydrogen that passes through, so that e.g. the platinum electrode has almost immediately become electromotively equal to the hydrogen electrode.

For these metals, which behave *ideally inert*, the potential difference is, therefore, governed by the existing electron concentration in the electrolyte. This is also the reason why these exceedingly inert metals may serve not only as gas-electrodes, but also for the determination of the so-called oxidation, resp. reduction potentials.

When e.g. platinum is immersed in a solution in which the equilibrium:



prevails, the electron concentration of the platinum equilibrium in the solution has almost immediately become equal to the electron concentration of the above ferro-ferri equilibrium, so that in the electron equation for the potential difference of the platinum

$$\Delta = \frac{RT}{F} \ln \frac{K_\theta}{(\theta_L)}$$

the electron concentration of the ferro-ferri equilibrium may be written instead of (θ_L) , in consequence of which we get:

$$\Delta = \frac{RT}{F} \ln \frac{K_\theta}{K} \frac{(Fe^{\dots\dots})}{(Fe^{\dots\dots})},$$

as was already stated before.

The peculiar feature of these platinum metals is therefore their extraordinary inertia, which causes them to behave ideally passive in most electrolytes.

6. Considerations in the Light of the Theory of Phases.

It is clear that for the explanation of the phenomena discussed here, considerations as have been introduced by us of late, are indispensable.

Phase-theoretical considerations are inadequate here, but all the same it may be of use to represent the obtained results graphically by means of Δ, x -diagrams.

Let us first consider the case that the metal zinc is immersed in a hydrochloric acid solution of ZnCl_2 ; then it is the Δ - x -figure of the system Zn-H_2 that may serve for the graphical elucidation of the found result.

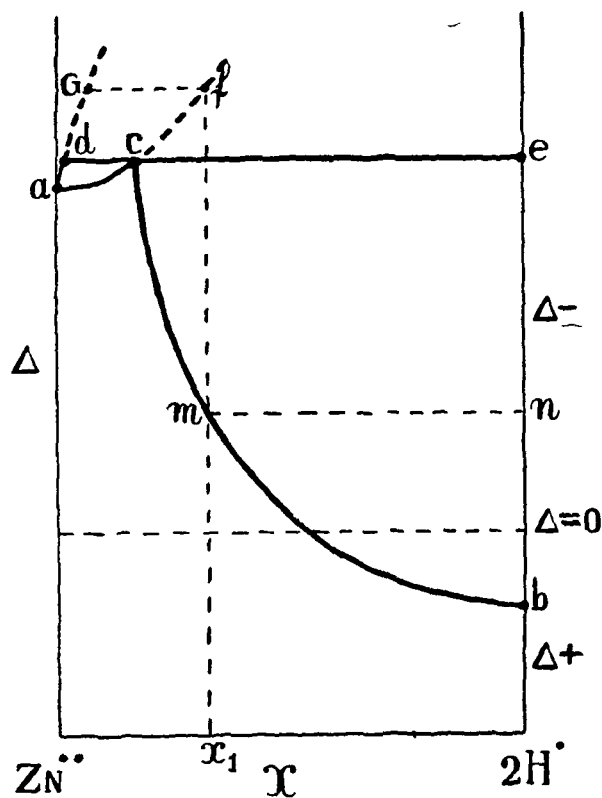


Fig. 1.

Zinc.

A Δ - x -figure holds for constant T, P , and a constant total ion-concentration; for T we choose here the ordinary temperature, and for P the pressure of 1 atm., the total ion-concentration being put here at 2 norm.

The situation of the point C , which represents the electrolyte which coexists with the zinc phase and the hydrogen phase of the pressure of 1 atm., is found from the equation:

$$\frac{RT}{2F} \ln \frac{K_{Zn}}{(Zn_L)} = \frac{RT}{F} \ln \frac{K_H}{(H_L)}$$

from which follows:

$$\frac{K_{Zn}}{K_H} = \frac{(Zn_L)}{(H_L)^2}$$

or also from the equations for the product of solubility of zinc and hydrogen:

$$L_{Zn} = (Zn)'' (\theta)^2$$

and

$$L_{H_2} = (H)^2 (\theta)^2$$

by putting $(\theta)_{Zn} = (\theta)_{H_2}$, in consequence of which:

$$\frac{L_{Zn}}{L_{H_2}} = \frac{(Zn)''}{(H)^2}$$

or

$$\frac{(Zn)''}{(H)^2} = \frac{10^{2 \times -35}}{10^{2 \times -48}} = 10^{26}.$$

When we put for a moment $(Zn)'' = 1$, then:

$$(H)^2 = 10^{-13}$$

We see therefore, that the point C lies so much on one side that practically it coincides with the zinc-axis. Hence the line d , c , e or the line for the three-phase equilibrium zinc-hydrogen-electrolyte lies practically on the same level as the point a , so that the measured potential difference of the zinc, which contains a little dissolved hydrogen, and is besides covered with a layer of hydrogen, is certainly practically equal to the potential difference of the pure hydrogen-free zinc, the measurement of which is impossible here.

Let us now suppose that we immerse zinc in an electrolyte, the composition of which, as regards the zinc- and hydrogen ions, is x_1 ; we then see, that zinc *cannot* be in stable electromotive equilibrium with this liquid, but that hydrogen can.

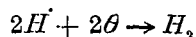
If, however, the hydrogen did not appear as a new phase, but only dissolved in the zinc, a metastable electromotive equilibrium would, indeed, be possible, viz. $g f$, but the potential difference would be more strongly negative than that of the three-phase equilibrium represented by the line d , c , e .

This metastable electromotive equilibrium does not appear, however; on the contrary, we observe a generation of hydrogen, and we will point out here in a few words, how the experimental fact is to be explained that under these circumstances the potential difference zinc-electrolyte is equal to that which corresponds with d , c , e , or what is practically the same thing, with a .

The explanation is this: when zinc is immersed in the electrolyte of the concentration x_1 , the establishment of the three-phase equilibrium between the zinc phase, the electrolytes, and the hydrogen phase takes immediately place in the boundary layer.

Accordingly the concentration c prevails in the boundary layer, whereas the total concentration of the electrolyte is x_1 .

The hydrogen ions now diffuse in the boundary layer, where for the maintenance of the concentration c the reaction:



takes place, in consequence of which, as we have already seen, electrons and zinc ions from the metal phase go into solution. The zinc phase assumes internal equilibrium with great velocity, and consequently it remains unaltered during the hydrogen generation, and the measured potential difference is that of the three-phase equilibrium d, c, e , which practically agrees with that of pure zinc, a .

When a platinum electrode is placed in the same electrolyte, it indicates the hydrogen-potential which corresponds with the line $m n$. The zinc electrode and the hydrogen electrode present therefore entirely different potential differences in the same electrolyte.

This is the graphical elucidation for our conclusion that the potential difference of zinc with respect to a solution of $ZnCl_2$ acidified with hydrochloric acid is determined by the state of internal equilibrium of the zinc.

Nickel.

Let us now proceed to the case that instead of zinc the metal nickel is taken; then it is worthy of note in the first place that under the same circumstances we then find for the composition of the electrolyte c

$$\frac{K_{Ni^{++}}}{K_{H^+}} = \frac{L_{Ni}}{L_{H_2}} = \frac{(Ni_L^{++})}{(H^+)^2} = \frac{10^{2 \times -45}}{10^{2 \times -48}} = 10^6$$

When we now put $(Ni_L^{++}) = 1$, we get $(H^+)^2 = 10^{-6}$ or $(H^+) = 10^{-3}$.

Here, too, the electrolyte c has still a one-sided position. Let us assume that the adjoined figure 2 again holds for 18° , and a pressure of 1 atm. for a total-ion concentration of 2-norm.; then an entirely different phenomenon is observed on immersion of a nickel-electrode in the electrolyte of the concentration x_1 than in the case with zinc discussed just now, because the internal equilibrium in the metal surface cannot maintain itself when electrons and nickel ions go into solution.

The metal is more and more disturbed in noble direction, and the result is, as we demonstrated already, that the electron-concentration of the nickel equilibrium in the solution has become equal to the electron-concentration of the hydrogen-equilibrium in the electrolyte,

in which the potential difference of the nickel electrode has become equal to that of the hydrogen electrode. This may be graphically represented in the way as has been done in fig. 2.

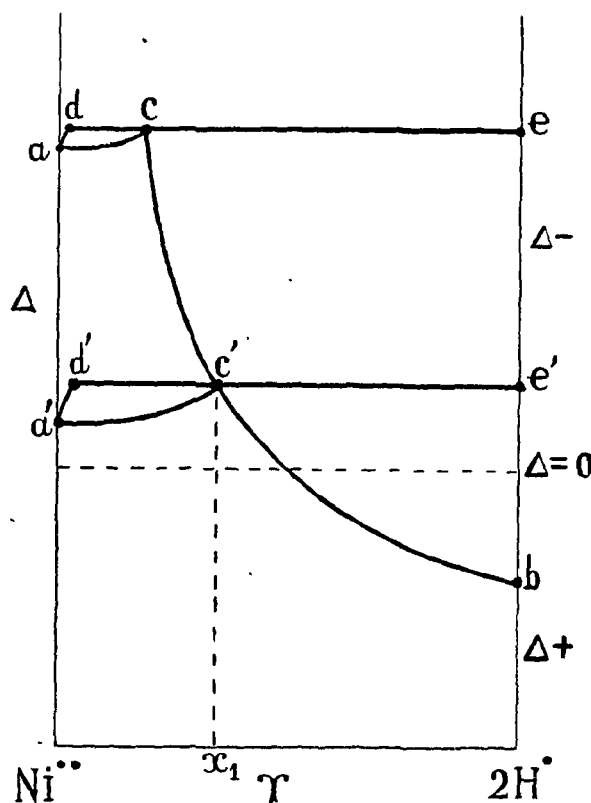


Fig. 2.

In consequence of the disturbance point d has got in point d' , and represents, therefore, the ennobled nickel phase which coexists with c' and the hydrogen phase e' .

It could be derived from our considerations how we have to proceed when we want to know the potential of the unary nickel, or in other words the equilibrium-potential. Then the nickel is to be brought into a solution with a hydrogen-ion-concentration, smaller than that in the electrolyte c . Then our Δ, X -diagram 3 shows that under these circumstances e.g. the electromotive equilibrium between the nickel phase d'' and the electrolyte c'' will be established, the potential difference of which practically coincides with that of the unary metal, which is perfectly free from hydrogen and indicated by a .

It is necessary to point out that when a metal is in electromotive equilibrium with a coexisting electrolyte, the electron-concentration

of the metal equilibrium must always be equal to the electron-concentration which exists in the liquid in consequence of the other prevailing equilibria.

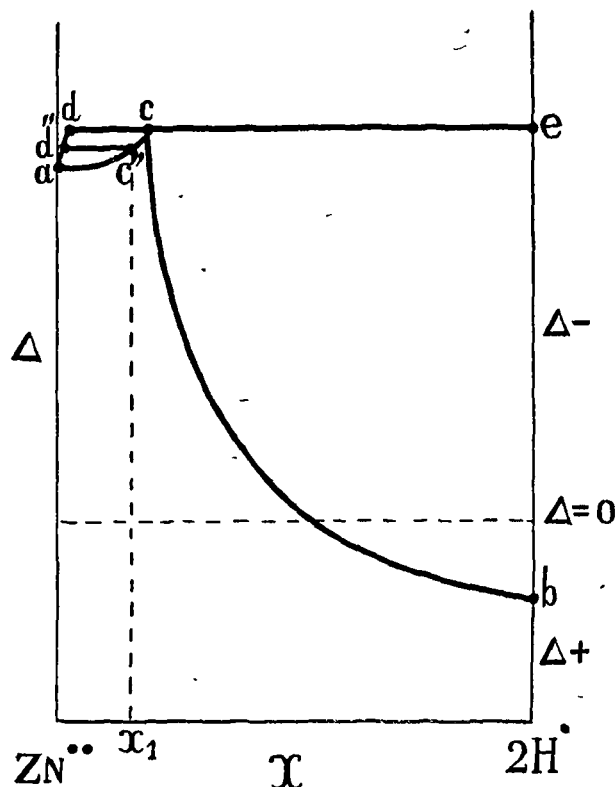


Fig. 3.

In this case we may say, that the metal is really in equilibrium with the electrolyte. When the metal dissolves in an acid, or when a metal is deposited, the just mentioned equality of electron-concentration prevails only in the boundary layer between metal and electrolyte, and diffusion takes continually place in the boundary layer.

The just mentioned equality of the indicated electron-concentrations must, therefore, also exist when in the case mentioned just now the metal nickel has got in equilibrium with the electrolyte. Of course there are always some transformations required for this, but these are soon over, and can, therefore, not give rise to a permanent disturbance, at least if the solution has been freed as much as possible from air and hydrogen by boiling in vacuum.

We have acted upon this principle, and, as was communicated in the preceding paper by Mr. LOBRY DE BRUIN and myself, by this procedure the equilibrium-potential was found of nickel that contained

only a trace of hydrogen, so that the found potential difference will practically very certainly agree with that of the purely unary metal.

It is supposed here that the potential difference between nickel and the nickelsalt solution with the exceedingly small hydrogen-ion-concentration, is measured after the electrolyte has been heated with the nickel electrode in vacuum, after the whole apparatus has been

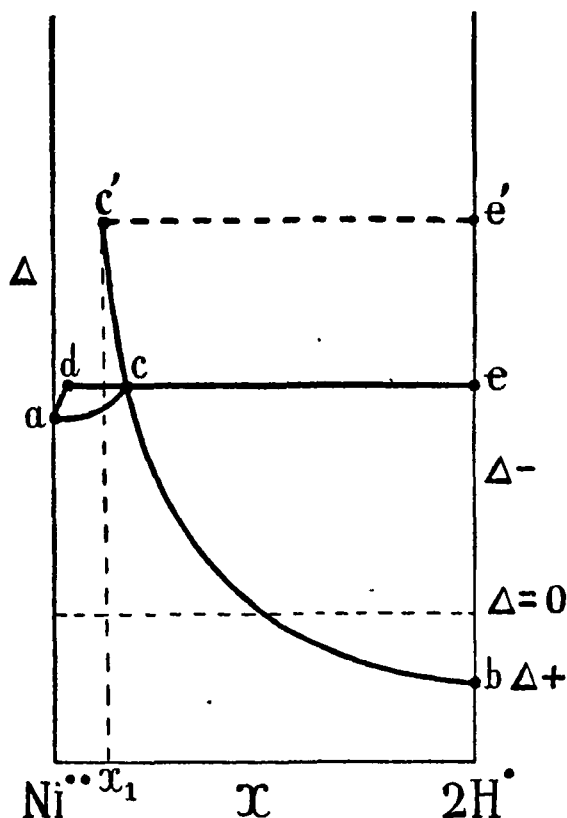


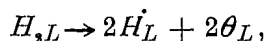
Fig. 4.

filled with the electrolyte and connected with the 1 N. Calomel electrode by means of a siphon and a liquid circuit, so that the pressure under which the electrolyte is, amounts to 1 atm. also in this case.

An entirely different result is obtained when the foregoing measurement does not take place in vacuum, but in a hydrogen current.

In this case the nickel electrode is disturbed, but the disturbance does not take place now in a noble direction, but in a base direction, and as we showed before the potential difference of the nickel has again become equal to that of the hydrogen-electrode. This result can again be brought to expression in an exceedingly simple way by means of a Δ, X -fig. 4.

When we lead hydrogen through the electrolyte, of which the concentration x_1 lies on the lefthand of the point c , the potential of the hydrogen-electrode is indicated by the line $c'e'$. In this mode of procedure the nickel electrode gets in contact with gaseous hydrogen, and in the boundary layer which is simultaneously in contact with nickel and hydrogen, the electrolyte c will be formed in consequence of the reaction:



while electrons and nickel ions (and a few hydrogen ions) are deposited on the metal. This renders the metal baser superficially and both the three-phase equilibrium dce and the point a rise.

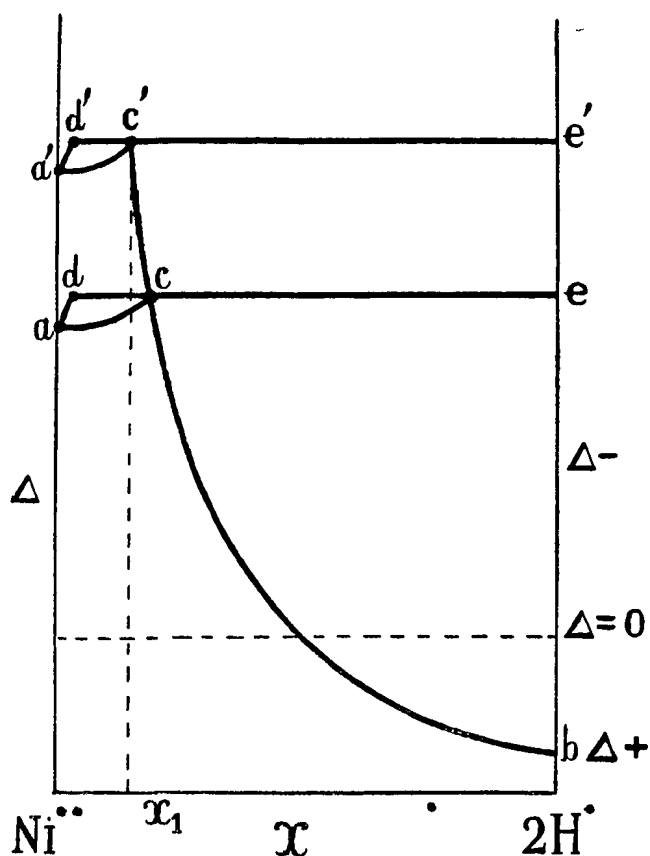


Fig. 5.

This disturbance in base direction continues till the concentration of the electrolyte has become equal to that in the boundary layer.

This is the case when a three-phase equilibrium has formed of which the electrolyte possesses the concentration x_1 , hence at the place where the curve bc intersects the vertical which corresponds with this concentration. As fig. 5 shows, this takes place in point c'

and the three-phase equilibrium, which therefore finally is established, is here indicated by the points $d'c'e'$. Accordingly also in this case the potential difference of the nickel electrode is equal to that of the hydrogen electrode.

When we now consider the metals of which the unattacked electrodes consist, we need only remark that because as was just now demonstrated, these metals are ideally inert, the potential difference metal-electrolyte is in almost all cases exclusively determined by the electron-concentration in the electrolyte. Hence, when e.g. a platinum electrode is immersed in an electrolyte through which hydrogen is led, the platinum shows the hydrogen potential almost immediately, which was the case for nickel only after some time had passed. When we want to express this graphically in a Δ, X -fig., we get, of course exactly the same representation as for the case nickel-hydrogen.

That in aqueous solutions we cannot determine the equilibrium potential of platinum, whereas this is still possible for nickel is owing to this that the electrolyte c has such an one-sided situation for platinum-hydrogen, that an aqueous solution of a platinum salt always possesses a concentration on the righthand side of the point c as regards the platinum and the hydrogen ions, so that a disturbance must always take place.

In a subsequent communication I hope to enter into a fuller discussion of the phenomenon of the "super-tension", which has already been repeatedly referred to in our considerations without having been named.

*Amsterdam, March 1918. , General Anorg. Chemical Laboratory
of the University.*

Anatomy. — "*On the Nervus Terminalis from man to Amphioxus.*" By Prof. J. W. VAN WIJHE.¹⁾

(Communicated in the meeting of April 26, 1918).

Although hardly credible, it is a fact that a good three years ago — in 1914 — a new nerve, arising independently in the brain, was discovered in man. This is the Nervus Terminalis. Naturally it is not visible to the naked eye, but can be seen through the magnifying glass, especially through the dissecting microscope, with the aid of which its discoverer, the American BROOKOVER found it. (Journ. of Comp. Neurology. Vol. 24.)

It has its course through the pia mater, parallel and mesial to the olfactory bulb and tract, running over the middle of the gyrus rectus (vide fig. 1.) When a rectangular piece of the pia mater in this region is taken up and placed under the microscope, the fine fibres of this nerve can be seen. Here and there the fibres are retracted from each other to come together again later on.

The nerve is independent of the olfactory tract and bulb, and in the opinion of BROOKOVER enters the brain at the mesial root of the tract. A number of ganglionic cells, BROOKOVER takes their number at about 50, lie spread in the nerve in its course along the olfactory tract.

The nerve can be followed not only along the tract but also somewhat further distally along the olfactory bulb, but in this vicinity it is embedded in the dura mater, while it has here also partially pierced the former and lies on the lamina cribrosa.

In the vicinity of the bulb the number of its ganglionic cells is considerably larger than is the case along the tract. It was estimated by BROOKOVER at about 100 to 200 cells. Undoubtedly its branches pass through the mesial row of openings in the lamina cribrosa to the mucous membrane of the nasal septum, but the research did not extend as far as this.

In adult man the course of the new nerve is as yet known in the brain-case only, not on its outside.²⁾

¹⁾ Lecture delivered before the meeting of the Neth. Zoological Society, Jan. 26, 1918.

²⁾ Vide, however, the postscript at the end of this article.

As was to be expected, in the adults of the mammals the nerve was not first found in man. The dog and the cat (Mc. COTTER. 1913.) and the rabbit (HUBER & GUILD. 1913.) were the first, but it is remarkable, that in the embryonic stages of the mammals the human embryo was the first in which, although incompletely, the nerve was discovered. This was done by our countryman ERNST DE VRIES, who also observed it in the embryos of the guinea-pig. He described his research (published in the Proceedings of the Royal Academy of Sciences of April the 22nd 1905), which also drew much attention abroad, in an article of four pages, which proves that it is not necessary or even desirable to be loquacious when one has found something of importance.

DE VRIES found ganglionic cells spread in the course of the nerve which supplies the organon vomeronasale, (the organ. of JACOBSON, or better the organ of RUYSCH)¹⁾ near the base of the nasal septum. He moreover found that the so-called olfactory ganglion, by him called the ganglion vomeronasale, does not belong to the fila olfactoria, which are taken collectively as the true olfactory nerve. In his opinion it belongs to the N. Vomeronasalis, which supplies RUYSCH's organ, lined by a layer divided off from the nasal mucous membrane. As the vomeronasal nerve also enters the central nervous system at a different place — the area vomeronasalis — than do the fila olfactoria, DE VRIES drew the conclusion that the N. Vomeronasalis is not, as was the general opinion, a component part of the olfactory nerve, but an independent nerve, homologous to the N. Terminalis in the fish.

A serious difficulty to this explanation however is that, according to the illustrations of DE VRIES, the N. Vomeronasalis issues from the olfactory bulb, while the N. Terminalis of the Dipnoi and the Selachii issues out of the true hemisphere and not out of the bulb.²⁾

This difficulty seems to have escaped DE VRIES's notice. On the first page of his publication he rightly distinguishes between the olfactory lobe and the hemisphere, which are separated from each other laterally by the fissura rhinica, and mesially by the fissura prima. On pages 3 and 4 he states that the area vomeronasalis, where the nerve of this name enters the brain, belongs to the hemisphere. According to his own communication and illustration, however, this area lies at the sulcus circularis bulbi, hence *not* on

¹⁾ Concerning RUYSCH's organ see postscript at the end of this paper.

²⁾ Entering and issuing out of a nerve are used in this address, indiscriminate of the direction in which the impulse moves.

the hemisphere, but on the olfactory lobe. In young embryos the tract is thicker than the bulb, later on this relation is reversed.

It was therefore very desirable that more light were thrown on the question whether the vomeronasal nerve should be considered as the homologue of the N. Terminalis of the fishes.

This happened in 1913 in America, more especially through two publications viz. of JOHNSTON in the Journ. of Comp. Neur. Vol. 23. and of HUBER & GUILD in the Anatomical Record Vol. 7.¹⁾

JOHNSTON examined embryos of the pig, the sheep, and of man. Besides mammals he also examined embryos of tortoises and a larva of Amblystoma.

The elucidation which JOHNSTON brought, consists herein that (as he found) the ganglion and the ganglionic cells do not belong to the N. Vomeronasalis, but to another nerve, which does not enter the brain in the olfactory bulb, but in the true hemisphere, near or in the lamina terminalis, as is the case in the Selachii.

What DE VRIES had considered as one nerve, was in reality two nerves which for the greater part cover each other; one is the N. Terminalis, the other is the true N. Vomeronasalis.

The vomeronasal nerve has no ganglionic cells and arises out of the cells of a part of the nasal mucous membrane which had been split off (Organon Vomeronasale). In structure and development it is exactly similar to the bundles of the olfactory nerve. It also enters the brain in the olfactory bulb, just as the fila olfactoria, which collectively form the olfactory nerve. It is true that it enters the bulb at a special place, on its mesial plane rising high up caudally, but then it is a *specialised* bundle of the olfactory nerve. The peripheral ganglionic cells and the true ganglion belong to the N. Terminalis.

DE VRIES' mistake is easily comprehensible; he used no special methods to make the nerves visible, could not expose his material of human embryos to this risk and was thus compelled to consider the proximal end of the N. Vomeronasalis (split into four bundles according to him) as a root of the Ganglion Terminale, by him incorrectly called the Ganglion Vomeronasale, which is as it were pasted up against it, while the true roots of this ganglion escape observation in cross section through their fineness. That it is possible to make mistakes even when using nerve-staining methods is proved by the work of DÖLLKEN (1909). He examined embryos of mice, rabbits, guinea-pigs and man. Following in the footsteps of DE VRIES

¹⁾ Further literature is found mentioned in these publications.

he also took the roots of the N. Vomeronasalis to be those of the N. Terminalis.

Regarding the mouse he says "Die sog. mediale Riechwurzel von der bereits CAJAL, KAPPERS u. A. behauptet haben, sie sei nicht als eigentliche Riechwurzel zu bezeichnen, ist eine Wurzel des N. Terminalis". No wonder that he continues "Sie hat bedeutende Beziehungen zum Olfactorius".

The second important elucidation appeared, as has already been said, in a communication, also in 1913, of HUBER and GUILD, who had come on this subject á propos of the work of JOHNSTON, which had partly been done in HUBER's laboratory.

These writers examined rabbit embryos by the silver-pyridine method. They could fully confirm JOHNSTON's results that the N. Terminalis and the N. Vomeronasalis were two different nerves, and that the ganglion and the disseminated ganglionic cells belong, not to the N. Vomeronasalis, which is evidently a specialised bundle of the olfactory nerve, but indeed to the N. Terminalis.

While JOHNSTON however was still of opinion that the peripheral termination of the N. Terminalis was limited, principally in any case, to the region of the N. Vomeronasalis, these investigators discovered that this ending is to be found in the foremost part of the nasal septum, reaching caudally to the rear border of the Organon Vomeronasale. It is only a small part of the peripheral branches that reaches this organ and the true olfactory mucous membrane, the region of the fila olfactoria, was free from branches of the N. Terminalis.

Through difference in tint the branches of the Terminalis could well be distinguished from those of the Trigeminal nerve (Nasociliary and Nasopalatine), which are also found in the mucous membrane of the nasal septum.

As will presently become clear, it is of importance in following the nerve to Amphioxus, that the N. Terminalis does not branch in the olfactory mucous membrane.

In 1912 and 1913 Mc. COTTER published his investigations on the N. Vomeronasalis and the N. Terminalis. By means of the dissecting microscope, thus as it were at magnifying glass magnification, he found the latter in the adult dog and cat, but not in the rat, the rabbit, the sheep, the guinea-pig or the opossum. That he did not find it is not to be wondered at considering his method. His opinion that the N. Terminalis ends peripherally at or near the vomeronasal organ is also comprehensible because the bundles here are thicker, the fibres of the N. Terminalis being strengthened by those of the vomeronasal nerve.

This much as regards the *mammals*, which I have considered somewhat more extensively as most, and to my mind the most accurate, investigations have been done on them.

I can be brief about the birds, reptiles, and amphibians.

There does not seem to be much known about the N. Terminalis in the *birds*.

In the *frog* it was found in 1909 by C. JUDSON HERRICK, who also described its central termination more especially; its peripheral branches could not be traced accurately. This was also the case in the *Urodela*, where the nerve was observed by MC. KIBBEN (1914), who could not however find any ganglionic cells in it. Some time later JOHNSTON succeeded in this. He says "In *Amblystoma* the nervus terminalis is ganglionated and supplies the vomeronasal organ, as in reptiles and mammals". Concerning the reptiles he says that the peripheral termination takes place "in the turtle to a medial diverticulum of the nasal sac, which presumably corresponds to the vomeronasal organ or a part of it".

We now come to the *fishes* wherein, setting aside an isolated observation by G. FRITSCH about one of the *Selachii*, the nerve was first found by PINKUS in *Protopterus*. His preliminary communication appeared in 1894 in the "Anatomischer Anzeiger" and was followed in 1895 by his elaborate treatise "Die Hirnnerven des *Protopterus annectens*" in the "Morphologische Arbeiten". PINKUS found that his new nerve originates in the brain, places itself rostrally against the most mesial bundle of the olfactory nerve, takes its course over the nasal mucous membrane and is to be followed to the roof of the anterior nasal opening. The nerve consists of nonmedullated fibres and has in its course a cellular swelling, which is undoubtedly the Ganglion Terminale of later writers, although PINKUS could not convince himself of the ganglionic nature of the cells.

SEWERTZOFF (1902) found the nerve in embryos of *Ceratodus*. He mentions the fact, of importance for the homologisation, that the nerve does not branch in the olfactory mucous membrane and that it terminates in the skin at the external nasal opening. Soon (1904—1905) BING and BURCKHARDT described the nerve in the adult *Ceratodus* also.

Concerning the *Selachii* the treatise of LOCY, which appeared in the "Anatomischer Anzeiger" after several smaller publications, is well known. In this treatise, which is accompanied by a large number of handsome illustrations, he described the structure and development of the nerve in *Acanthias* as seen in series of sections, as well as its course as this is to be seen, by means of the dissecting microscope.

in 20 genera of sharks and rays. At first he held the nerve to be a part of the olfactory nerve, but later on he recognised its homology to the new nerve of PINKUS, and called it the N. Terminalis.

In the Selachii the distance between the nasal sac and the olfactory bulb is small, hence the olfactory nerve is short. Immediately on its appearance out of the nasal sac it is separated into a lateral and a mesial bundle by a small groove into which the distal termination of the N. Terminalis enters.

Scoliodon terrae novae alone has something peculiar. Here the two bundles are not only completely separated from each other, but the division also continues on to the bulb, and even to the distal (foremost) end of the tract, which usually is long in the Selachii. After the N. Terminalis of the Selachii has made its appearance out of the hemisphere, it takes its course along the mesial border of the tract, and when it has reached the bulb it forms a ganglion. In some species two ganglia were observed in the course of the nerve.

LOCY assures that the nerve in its distal ramifications is principally limited to the olfactory mucous membrane, but to my mind he has not proved this. His method was not sufficient to do this, and considering the results of other investigators in other classes of animals this assertion needs corroboration by preparations treated with silver compounds.

In the *Ganoids* the N. Terminalis was first found and clearly represented by PHELPS ALLIS (1897, fig. 64) in *Amia calva*. He could follow it caudally up to the fore-brain. In the larvae he also found its ganglion.

In 1910 BROOKOVER described its development in these fishes. His investigation contains many new finds and interesting communications, but his conclusion that the nerve is a branch of the olfactory nerve cannot in my opinion be correct. In his work in 1914 on the nerve in *Lepidosteus* he also came to this conclusion.

In the *Teleostei* SHELDON and BROOKOVER (1909) found the nerve in the carp and in *Amiurus*. According to them the roots of the ganglion enter the olfactory bulb to reach the hemisphere, contained in the tract. Here however the question arises whether they have not made a mistake analogous to that of DE VRIES in the embryos of man, as this is not the condition in the Dipnoi, in the Selachii, in the amphibians or in the mammals, nor either in man according to what BROOKOVER himself (1914) found in the last-named.

Concerning the lungfishes I can here demonstrate to you two fine models of the fore-end of the brains, with the nerves arising therefrom, of *Ceratodus* and *Protopterus*, both constructed by Dr. VAN DER

HORST in the Institute for Brain Research of Dr. ARIËNS KAPPERS, who was so kind as to lend them for this evening. One sees the N. Terminalis arising out of the hemisphere, and running rostrally quite independent of the olfactory lobe, as is also the case in man according to BROOKOVER (c.f. fig. 1).

Finally I come to *Amphioxus*, on whose cerebral nerves I published a communication in the meeting of the Royal Academy of October the 27th. 1894. As is known the trigeminal nerve of the craniata forms a complex of two dorsal segmental nerves, the components being the N. Ophthalmicus profundus (N. Nasociliaris) and the rest of the N. Trigeminus. I found both these components in the two nerves, of which the one appears before and the other behind the first well developed myotome (which has morphologically to be considered as the second). Before the homologue of the profound ophthalmicus, however, there is in *Amphioxus* still another nerve which supplies the utmost point of the snout. On account of this and because it arises from the morphological fore-end of the cerebral ventricle I called it the N. Apicis.

At first I thought that the N. Apicis would be aborted in the higher chordata, but shortly before the publication of my article the preliminary communication of PINKUS appeared (Anat. Anz. 1894), in which he reported the discovery of a new nerve in *Protopterus*, later named the N. Terminalis by LOCY.

This had to be considered the homologue of the N. Apicis considering its course, ramification and origin, not from the infundibulum as I concluded out of the preliminary communication, but near the Lamina Terminalis as became clear when the more extensive treatise appeared the next year.

I must acknowledge that I have later on sometimes doubted whether this homologisation were correct, when I read the investigations of LOCY in the *Selachii*, of BROOKOVER and SHELDON in the *Ganoids* and *Teleostei*, and of ERNST DE VRIES and DÖLLKEN in the mammals, because all these writers assert that the peripheral termination of the N. Terminalis is wholly or principally limited to the olfactory mucous membrane (or in mammals to the vomeronasal organ, which is covered by a split-off part of the olfactory mucous membrane). In *Amphioxus* on the other hand the N. Apicis stands in no relation whatever to the covering of the olfactory groove.

After however reading the research of HUBER and GUILD (1913) this doubt was dispelled.

Their illustration (c. f. fig. 2) shows the N. Apicis of *Amphioxus* in the rabbit — I could almost say "in optima forma", even to the

disseminated ganglionic cells, which have already been long known in the N. Apicis.

As the N. Apicis is an ordinary cutaneous nerve¹⁾, the relation in which the N. Terminalis stands to the olfactory epithelium in some of the higher animals must be of a secondary nature. It is even possible that the terminal ramification of the nerve has become principally limited to the olfactory mucous membrane, as appears to be the case in many fishes.

Thus has the N. Terminalis completed its course through science in 20 years (1894—1914) beginning in the lung-fishes, I may as well add in Amphioxus, and ending in man. It can no longer be doubted that we have here to do with an independent cerebral nerve and not with a bundle of the olfactory nerve. In most or all of the craniata however branches of both nerves run close alongside of each other, and on account of this it is difficult to distinguish their peripheral distribution.

From Amphioxus to man the N. Terminalis is provided with disseminated ganglionic cells, which can partly be gathered together to one or more ganglia. On the other hand the olfactory nerve (including its specialised bundle, the N. Vomeronasalis of the Amniota) is distinguished by the complete absence of ganglionic cells.

At the end of this summary I want here to express my thanks to Dr. ARIËNS KAPPERS, who was so kind as to send me for perusal a dozen treatises on the N. Terminalis, nearly all of American investigators, which have become the occasion of this address.

POST SCRIPTUM.

Early in March Dr. KAPPERS sent me for perusal a copy of a new work by BROOKOVER, which he had received a few days earlier: "The Peripheral Distribution of the Nervus Terminalis in an Infant" (Journal of Comp. Neurology Vol. 28 N^o. 2).

BROOKOVER found the branching of the N. Terminalis in the nasal septum of the child analogous to that in the rabbit, according to HUBER and GUILD, only much more strongly developed. In it he could count about 1500 ganglionic cells, not considering the Ganglion

¹⁾ It is a well known fact that ganglionic cells are found not only in the first but also in the second cutaneous nerve (N. Ophthalmicus prof.) of Amphioxus. DE QUATREFAGES discovered them here in 1845 already, but held them for mucous cryptes, "cryptes mucipares". Incorrectly it is assumed that peripheral ganglionic cells are not present in the other nerves. I found multitudes of them in the nerves running under the atrial epithelium which covers the intestine and the liver.

Terminale. This ganglion was a compound of 6 to 8 ganglia, combined by a net of nervous fibres.

He mentions nothing about a N. Vomeronasalis, but found a stout nerve without ganglionic cells, which, with a branch of the N. Terminalis, passes through one of the hindmost openings of the Lamina Cribrosa to the nasal septum and anastomoses peripherally with the N. Nasopalatinus.

BROOKOVER considers the above-named stout nerve as a sympathetic anastomosis between the Ganglion Sphenopalatinum and the Ganglion Terminale. To my mind this nerve is the N. Vomeronasalis, which has then not been aborted after birth, in man, as was hitherto the general opinion. In case this conjecture is correct, it must arise behind in the olfactory bulb and supply the vomeronasal organ.

This organ is generally present in the vertebrates higher than the fishes ¹⁾, and seems to be a product of adaptation to terrestrial life. It first appears in the amphibians, and has been lost or is present only in the early stages of development in the higher forms which have secondarily become aquatic again (crocodiles, partly also the Chelonia, the Cetacea, and the Pinnipedia).

Flying also seems to be unfavourable for the development of the organ (birds and some — not all — of the bats).

The organ is usually named after JACOBSON, who found it independently in a large number of mammals, and who also discovered the N. Vomeronasalis. His work became known through the report CUVIER made on it ²⁾.

After the considerable praise which CUVIER bestows on the work, for a part done in his laboratory, one would expect at the end of his report to the "Institut" the advice to have the treatise of JACOBSON, "pensionnaire et chirurgien-major dans les armées de Roi de Danemark", printed. The end of the report, however, reads as follows: "Nous croyons que le Mémoire de M. JACOBSON mérite l'approbation de la classe [de l'Institut] et que cet anatomiste doit être invité à continuer des recherches, qui ont déjà fourni un résultat aussi curieux".

This encouragement does not, however, seem to have had the desired result. At least it is not known that JACOBSON has published his treatise, enlarged or not.

For the rest CUVIER makes a mistake in believing that nobody had observed the organ before JACOBSON, and that it is not present

¹⁾ Cf. R. WIEDERSHEIM, Vergleichende Anatomie der Wirbeltiere, Jena, 1909.

²⁾ G. CUVIER, Rapport fait à l'Institut, sur un Mémoire de M. JACOBSON intitulé: Description anatomique d'un Organe observé dans les Mammifères. Annales du Muséum d'Histoire naturelle, Tome 18, 1811.

in man. It has escaped his attention that RUYSCH, who is cited by him à propos of the Meatus Nasopalatinus, (l.c. p. 414. He writes: RUYSCH) is the discoverer of the organ, and just in man in whom it is normally present as was corroborated later on.

KÖLLIKER¹⁾ and HERZFELD²⁾ found it regularly in children while it is seldom wanting in adults. When this was the case it had probably to be ascribed to former diseases of the nasal septum.

The description of RUYSCH³⁾, who also gives a clear representation of the orifice of the organ, with a sound brought into it, on the nasal septum of a child, reads as follows: "In anteriore et inferiore parte septi juxta palatum in utroque latere foramen apparet, seu osculum cujusdam ductus de cujus usu et existentia nil apud authores legi; inservire mucos excernendo existimo".

JACOBSON also, not knowing RUYSCH's work, is inclined to consider the organ as being secretory, although the powerful innervation pleads for a sensory function, but (l.c. p. 422): "quel agent extérieur pourroit aller se faire percevoir dans un réceptacle si caché, si profond, si peu accessible?"

CUVIER himself still thinks — under reserve — he has to accept a kind of olfactory perception and the later writers do this too. It is usually assumed that the organ serves to smell the food which has already been taken into the mouth; in mammals the odour would then rise up through the Meatus Nasopalatinus. This can however not be the case in the horse or the donkey (nor in the camel or giraffe), because here the Meatus is no longer opened to the buccal cavity, while their Organon Vomeronasale cannot be held to be rudimentary as is the case in man.

The secretory function is evident on account of the numerous glands (KÖLLIKER, l. c. p. 11) which fill the organ with mucus, which streams out through ciliary motion, but the difficulties against accepting

¹⁾ A. KÖLLIKER, Ueber die Jacobsonschen Organe des Menschen. Reprinted from the Festschrift für RINECKER, Leipzig 1877.

²⁾ P. HERZFELD, Ueber das Jacobsonsche Organ des Menschen und der Säugethiere, Zoologische Jahrbücher, Abth. für Anat. und Ontogenie der Thiere Bd. 3, 1889.

HERZFELD gives a summary of the mammals in which the organ had been found by him and others up to 1889, also in connection with the meatus nasopalatinus. He might have added that JACOBSON had also already observed it in the marsupials (kangaroo). Later on it was also found in the Monotremata and Edentata.

³⁾ F. RUYSCH, Thesaurus anatomicus III, Amstelodami, 1724, p. 26, N^o. LXI, 5. Illustration: Tab. IV, fig. 5.

KÖLLIKER (1877) cited the description, mentioned above, from an edition of 1703 p. 49; hence more than 100 years before CUVIER's report.

an olfactory function, already hinted at by JACOBSON, and which KÖLLIKER tries to evade in a peculiar manner, are not to be got out of the way.

In this regard an observation of HERZFELD in connection with the venous sinus, with a strong circular layer of nonstriated muscular fibres, which is found in the wall of the organ of the rat on the inner side of the bony capsule, — cartilaginous in the majority of the mammals — seems to me worthy of attention. He assumes that the air will be sucked into the organ through contraction of the sinus and the lessening of the volume of the wall, inside the rigid capsule, caused by this.

If this appears to be the case in other animals also — the opportunity for research will probably present itself in a veterinary college — then a sort of olfactory function would become comprehensible. It would then also become clearer why the Cetacea and Pinnipedia are nearly the only¹⁾ mammals in which the search for the organ²⁾ of RÜRSCH has been in vain.

It is comprehensible that the Cetacea and Pinnipedia have lost the true olfactory organ, adapted to aquatic life in earlier fishlike ancestors, it became adapted to smelling in the air in later ancestors, which lived on land as mammals. When these, in a still later period, again went back to aquatic life, as Protocetacea and Protopinnipedia, the true olfactory organ could not undergo this change and became rudimentary or disappeared altogether. If the organ of RÜRSCH in terrestrial mammals is always filled with liquid (mucus), and does not need to adapt itself to smelling in the air, then there is not the same reason for its disappearance in the Cetacea and Pinnipedia as there is for the degeneration of the true olfactory organ of the Cetacea.

¹⁾ One would expect the Sirenia here also. It is remarkable however that Manatus, according to STANNIUS (Lehrbuch 1846, p. 399) possesses an exceptionally well developed Organon Vomeronasale. In some bats and catarrhine apes the organ has disappeared through some cause or other, as in the Cetacea and Pinnipedia.

²⁾ The numerous morphological investigations on this organ have taught us very little about its function. On histological grounds a sort of olfactory function is not to be doubted, (c.f. amongst others M. VON LENHOSSEK, Die Nervenursprünge und Endigungen in Jacobsonschen Organ des Kaninchens. Anat. Anzeiger. 1892). This is about the only result, concerning the function which we can, after about 200 years, add to the words of the discoverer: "Inservire mucos excernendo existimo."

J. W. VAN WIJHE: "On the Nervus terminalis from man to Amphioxus".

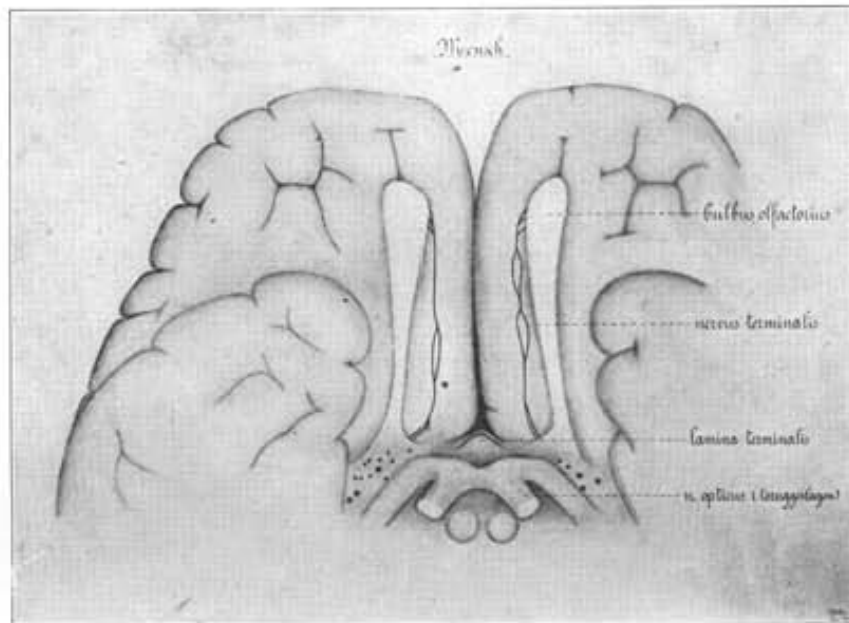
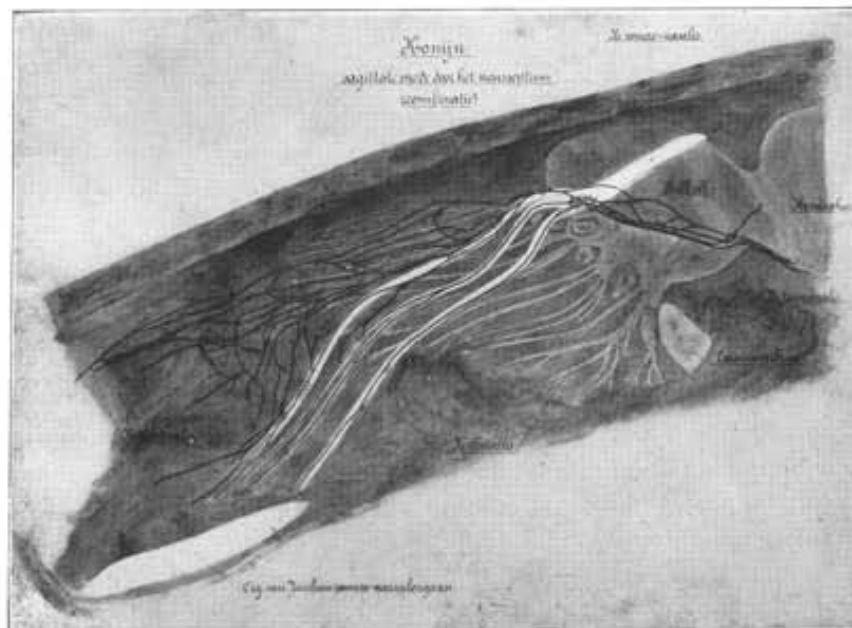


Fig. 1. Shows the lower surface of the foremost part of the brain of man and the intracranial part of the N. terminalis. (According to a figure of BROOKOVER, slightly modified).



Microbiology. — “*The significance of the tubercle bacteria of the Papilionaceae for the host plant*”. By Prof. BEIJERINCK.

(Communicated in the meeting of April 26, 1918).

As there is no reason to doubt of the accuracy of HELLRIEGEL's ¹⁾ experiments, it appears certain that the bacteria of the nodules on the roots of the Leguminosae are indispensable for the fixation of atmospheric nitrogen by these plants. ²⁾ But I shall prove that the theory, at present generally adopted, according to which this process takes place only within the tubercles, cannot be correct. But previously some remarks on the occurrence of the tubercles and the cultivation of bacteria from them.

For some plant species such as serradella (*Ornithopus sativus*) and the yellow lupine (*Lupinus luteus*), it cannot be doubted that only the tubercle-bearing specimens grow vigorously in nitrogen-poor soils and consequently, after the theory, fix the atmospheric nitrogen. It is therefore easy on poor heath fields to find languishing, stunted lupine plants, always devoid of nodules, amid the luxuriantly growing tubercle-bearing ones. Never did I find there well-developed lupine or serradella plants quite without them. But the number of tubercles is of no consequence, it evidently suffices if only few come to development..

In garden experiments on open sandbeds, without supply of nitrogen, but where inevitably more nitrogen compounds occur than in heath soils, also in peas and beans (*Vicia faba*), plants with nodules grow better than those devoid of them.

In fertile garden soil such as in the laboratory garden at Delft, yellow lupine and serradella do not fully develop, and especially their roots make the impression of sickliness; tubercles do not grow on them, not even when the soil has been abundantly provided

¹⁾ H. HELLRIEGEL und H. WILFARTH, Untersuchungen über die Stickstoffnahrung der Gramineen und Leguminosen, Zeitschrift für Rübenzuckerindustrie, Beilageheft November 1888. See further the excellent treatise of HILTNER, Bindung von freiem Stickstoff in höheren Pflanzen, in Handbuch der technischen Mykologie, Bd. 3, 1903—1905.

²⁾ For the objective proof that here free atmospheric nitrogen is fixed see, besides HELLRIEGEL (l. c. p. 191), SCHLÖSING et LAURENT, Fixation de l'azote libre par les plantes, Ann. de l'Institut Pasteur, Tome 6, pag. 65, 1892.

with the concerned bacteria. Whether the latter die in the soil or are not attracted by the roots of the plant is not yet clear. Most other leguminous plants, such as clover, *Vicia*, peas and *Vicia faba*, bear also in fertile soil many nodules, and it is not easy to find specimens wholly devoid of them, unless the soil has been previously sterilised.

On the roots of *Genista anglica* and *Genista pilosa*, growing on poor heath fields, I found after long seeking only very few tubercles, although they and in particular the former, bore many pods with good seeds; the tubercles are, however, never quite absent. When sown in my garden at Delft or brought there as plants, they die after some few years. On the other hand, *Genista tinctoria* thrives as well at Delft as along the highway of Zutphen to Vorden and at both places bears a small number of nodules.

For *Robinia pseudo-acacia* the favourable influence of *B. radicola* only on the young plant, has been stated by NOBBE.¹⁾ As to full-grown specimens on poor heath soil at Gorssel I could after long digging find but few tubercles, while at a small distance, but on somewhat better soil more tubercles occurred, but still so little numerous, that nobody would attribute to them any direct significance for such a large tree, had not the fixation of nitrogen in the tubercles become an inveterate belief. *Sarothamnus vulgaris* and *Ulex europaeus* behave in the same way as *Robinia*. On *Phaseolus vulgaris* on sandy soils I found but few nodules, and then only on thin rootlets and nearly always enclosed by plant remains; in the pure sand the nodules are very rare. In garden soil at Delft *Phaseolus* produces no nodules, but it does in a there arranged sandbed; *Lupinus luteus* and *Serradella* behave likewise.

When comparing the various mentioned plants, all noted in agriculture for their power of ameliorating the soil, as they contain in their dry substance nearly double the quantity of nitrogen found in other plants, for example the grasses, we come to the conclusion that only for lupine and serradella the number and weight of the tubercles is of some significance in regard to the whole weight of the plant. For other species they are of so little volume that even if within them free nitrogen were fixed with great intensity, only an extremely little quantity of fixed nitrogen could be expected, whilst in reality this amount is very considerable. Hence the theory, at present generally accepted, after which the fixation takes place in the

¹⁾ HILTNER l.c. Also BÜSGEN, Bau und Leben unserer Waldbäume, 2te Aufl., Pag 246, 1917.

nodules only, requires reconsideration. Also other experiences make this reconsideration necessary. But previously a few remarks on the isolation of the bacteria from the nodules and from other materials, and on the question of their specificity.

A very convenient medium for isolation was already described in 1888,¹⁾ namely pea leaves- or clover-extract-gelatin with 2 % cane sugar. *B. radicola* grows thereon in soft, white, non-liquefying colonies, while *B. ornithopodis* from *Ornithopus perpusillus*, *O. sativus* or *Lupinus luteus*, when isolated in the autumn or in March, liquefy somewhat, as does *B. herbicola*.²⁾

As a solid medium, poor in nitrogen compounds, I recommend a plate of: Tapwater 100, agar 2, cane sugar 1, starch 1, bipotassium-phosphate 0,05, in which, because of the albuminous matter of the agar, enough fixed nitrogen is present to cause a distinct growth of *B. radicola*, but the colonies remain small. Later a little saltpetre or ammoniumsulphate may be added locally, which makes the tubercle bacteria like the other saprophytes thrive well, showing that they do not assimilate the free atmospheric nitrogen. If on such a plate eventually germs of *Azotobacter*, which is able to assimilate free atmospheric nitrogen, are present, these will grow quite well if no nitrogen compounds are added. Such nitrogen-poor plates are also useful to recognise the spore-bearing soil bacteria, which almost constantly appear at the isolation of *B. radicola*.

I only call tubercle bacteria those species which develop mutually identic colonies by thousands or hundreds of thousands from the externally well-sterilised and cautiously crushed nodules. These bacteria derive for the greater part from within the cells. I consider the deviating and less numerous colonies obtained at the culture experiments as the product of germs accidentally present in the intercellular cavities of the rind of the nodules.³⁾ That the full-grown bacteroids cannot develop on the plates is well-known; hence bacteria may be expected from the tubercles only in the beginning of their development.

It is an important and until now not yet sufficiently investigated circumstance that from the tubercles of the same plant not always the same bacteria are obtained. So I found for *Ornithopus perpusillus*

¹⁾ Botan. Zeitung. 1888 Pag. 764.

²⁾ Occasionally a great number of colonies of *B. herbicola* are obtained from the tubercles; whoever is unacquainted with this species may make mistakes in the isolation of *B. radicola*. But even with this knowledge the isolation of serradella- and lupine-bacteria is difficult. Good descriptions of these forms do not exist.

³⁾ Besides *B. radicola* *B. herbicola* can also occur within the living cells.

the bacteria I had isolated in March different from those grown in October, whilst the tubercles came from plants growing side by side and being in the same state of development. With the yellow lupine and serradella I had similar results. In most other cases, however, for example with *Pisum*, *Lathyrus*, *Vicia*, and *Trifolium*, the similarity of the various mutually independently isolated stocks is so complete and the image of *B. radicum* can so distinctly be recognised, that the above observation requires nearer confirmation. But we cannot now enter upon this point.

When trying to isolate *B. radicum* from materials other than the nodules, for example from the soil and from the dying surface cell-layers of the root, it proves very difficult to recognise this species amid the numerous other saprophytes, especially when the number of the germs of the different species is to be determined quantitatively. *B. fluorescens liquefaciens* causes much trouble by the liquefying of the gelatin plates, and yet it is necessary to use these plates as on them the colonies of all the species lie free from one another, while on agar they are overgrown and rendered unrecognisable by *B. fluorescens*, which extends strongly sideways.

Concerning the question if only one or more species of tubercle bacteria exist the following.

Already in 1892 experiments thereabout were made by the late HELLRIEGEL ¹⁾ in the experimental station at Bernburg with pure cultures of the bacteria made by myself at Delft. Of his results HELLRIEGEL sent me two reports. In the first, dated 24 July 1892, he gives as "Augenblickliches Hauptresultat: "Es gelingt mit den Reinkulturen von *B. radicum* var. *Pisi* oder von *Vicia faba*, die Erbsen und Bohnen, und mit denen des *Bac. radic.* var. *Lupin.* oder *Ornithopodis* Lupinen und Serradella erfolgreich zu infizieren und zum Wachstum resp. der Assimilation des freien Stickstoffs zu bringen, und das ist was unsere anfängliche Behauptung bestätigt". Already earlier HELLRIEGEL had arrived at the conclusion that the bacteria of *Lupinus* and *Ornithopus* belong to a species different from that of *Pisum* and *Vicia*, which was also my own opinion.

In later years many interesting experiments were made in this direction, especially by HILTNER. Yet the evidence is unsatisfactory as it proved hitherto impossible in the sand cultures ²⁾ to bring Leguminosae to complete development by infection with

¹⁾ He died 24 September 1895 of a stomach disease and was already suffering when I visited him at Bernburg in 1892.

²⁾ It is a well-known fact that the Papilionaceae, when cultivated in liquids, do not fix the atmospheric nitrogen indifferently whether they produce tubercles or not.

B. radicumicola only and with exclusion of all other microbes. Such cultures are always at the end of the vegetation period rich in various other species, in particular in *B. fluorescens liquefaciens* and the nitrogen-fixing spore-forming *Granulobacter* (*Clostridium*) *pasteurianum* and *Helobacter cellulosae*. This observation holds good as well for the first experiments made by myself as for those of others, and this should never be lost sight of when reading the descriptions of the infection experiments with the so-called "pure cultures". It had not escaped HELLRIGEL's attention, and we see it in all the photographs of his above mentioned treatise at the film of the glass vessels, wherein he cultivated his plants (in bright daylight), which film consisted of Chlorophyceae and various other species of microbes, but he thought it of no consequence (l. c. p. 169). For myself I have observed in nitrogen-free sand, besides the mentioned species, *Chlorella* and *Cystococcus* and sometimes also *Palmella cruenta* and many Cyanophyceae. Many of my later efforts to bring clover plants to complete growth on agar with nutrient salts and *B. radicumicola* in large cotton-plugged ERLIENMEYER-flasks, failed as the plants ceased to grow before they blossomed, although the nodules developed very well.

The tubercle bacteria do not fix the atmospheric nitrogen when cultivated in nutrient media.

I will now call attention to my chief subject namely the want of power of the tubercle bacteria to fix the free atmospheric nitrogen. They do this neither when cultivated out of the plant nor within the nodules.

Regarding the first point the experiment is very simple. We have but to crush the nodules and bring the thus obtained material into culture soils used for the ordinary experiments to fix free nitrogen and then cultivate at 20° to 30° C.; or we use the pure cultures for infection of the same media. A convenient medium is: Tapwater 100, Glucose 2, Dikaliumphosphate 0,05, lime 2, fresh garden soil 2. This liquid, to which the garden soil is added as a catalyst, must previously be sterilised to kill the germs of *Azotobacter*, *Granulobacter* and *Helobacter*; notwithstanding the sterilisation, the soil preserves its catalytic power very little impaired. The spores of the nitrogen-fixing *Helobacter* and *Granulobacter* often adhere to the nodules and, when present, fermentation phenomena show that the experiments cannot be relied upon, *B. radicumicola* not causing fermentation. Commonly, however, these fermenting and nitrogen-

fixing microbes can be removed by thoroughly washing of the nodules with alcohol and water. In the course of many years I have experimented in this way with numerous species of tubercle bacteria, and with many modifications in the nutrient media as well in the temperature as in the source of carbon. Moreover I have, as said, tried to grow pure cultures of the bacteria themselves in the liquid culture medium as also on solid culture soils of various compositions, and at first I thought I had observed a rather considerable increase of these organisms. This increase, however, proved to be really very slight, so slight that gain of atmospheric nitrogen is not proved, whilst the obvious augmentation of dry weight of the sown bacteria derives from the formation of thick slime walls, that is of nitrogen-free, cellulose-like substances around the hardly augmented original protoplasmic material.¹⁾

Only when cultivating the microbes in plant extracts with cane sugar, wherein nitrogen compounds are evidently present, I could observe a very slight and by no means convincing increase of the total nitrogen rate of the liquid in consequence of the growth of *B. radiculicola*. But when performing these experiments I was not yet acquainted with the circumstance that laboratory air contains sufficient carbon and nitrogen compounds to be made perceptible by the growth of microbes which can feed on them. This was afterwards demonstrated by Ir. A. VAN DELDEN and myself in our investigation on *Bacillus (Actinobacillus) oligocarboophilus*.²⁾

There exists moreover an aërobic spore-producing bacterium³⁾, hard to kill by sterilisation of the nutrient liquids, which fixes free nitrogen; at that time it was still quite unknown to me and even now it is very imperfectly understood. It may have been present at my experiments likewise as at those of other investigators who think they have observed fixation of free nitrogen out of the plant in the pure cultures of *B. radiculicola*.

With sufficient precautions the results of such experiments are however always the same: The bacteria of the nodules do in no way fix the free atmospheric nitrogen. When the experiments are performed, not with

¹⁾ The slime formation is of importance for the explanation of the "slime threads" (erroneously called "infection threads") within the nodules. See "Die Natur der Fäden der Papilionaceenknöllchen." Centralbl. für Bakteriologie. Bd. 15, pag. 928, 1894.

²⁾ Ueber eine farblose Bakterie deren Kohlenstoffnahrung aus der atmosphärischen Luft herrührt. Centralbl. f. Bakteriologie 2te Abt. Bd. 10, pag. 33, 1903.

³⁾ *Bacillus danicus*, T. WESTERMANN and F. LÖHNIS, Centralbl. f. Bakteriologie, 2te Abt. Bd. 22, pag. 250, 1909).

nutrient liquids, but with a solid medium, the results are quite the same: fixation of nitrogen does not take place then either. Stress must be laid on the latter fact as it seems impossible to fix free nitrogen by the Papilionaceae when cultivated in liquid media even under the best circumstances and whether tubercles are produced or not. So it seems probable that for this process a direct contact with the air is necessary, which cannot be realised in the liquid culture media, but very well in solid ones.

Further it must be observed that the plate cultures of some of the nodule organisms,¹⁾ for example the forms from *Pisum*, *Vicia*, and *Trifolium*, on glucose-agar-potassiumphosphate plates, in absence of purposely added nitrogen compounds, at superficial view make the impression of being quite able to develop, but here too, it is only the formation of much wall substance, as already described above, and not of nitrogen-rich protoplasm, which explains the voluminosity of the colonies.²⁾ With other slime-producing bacteria, as *B. radiobacter* and *Aerobacter viscosum*, of which it is quite certain that they cannot live on the atmospheric nitrogen, extensive colonies may likewise be grown on the said nitrogen-poor medium with fit carbon food. By a better nitrogen nutrition such colonies may even be greatly reduced in volume, the wall substance then serving as food under a strong increase of the bacterial protoplasm, which gives rise to very interesting experiments. It is only when being acquainted with these facts by personal observation that we can understand how in the literature so many statements can occur on the nitrogen fixation by the nodule bacteria, which does not take place.

Within the nodules the atmospheric nitrogen is neither fixed.

The preceding gives rise to the question, whether the protoplasm of the host plant might be the catalyst that enables the invading bacteria, in their bacteroidal state, to fix the free nitrogen. However improbable this hypothesis may appear, being in contradiction with the laws of heredity, still it deserves attention because the rate of

¹⁾ The wonderful "experiments" of MAZÉ (Annales de l'Institut Pasteur T. 11, pag. 44, 1897, T. 12, pag. 1 and pag. 128, 1898), who asserts that on broth gelatin plates at the same time ammoniumcarbonate is produced and fixation of free nitrogen by *B. radicola* takes place, need not be considered, although they are taken up uncriticised in the handbooks of Plantphysiology.

²⁾ Likewise for the ordinary saprophytic bacteria the want of nitrogen compounds varies very much: the large-celled *Bacillus megatherium* requires very little, the small celled *Bacterium fluorescens* very much.

albuminous matter in the nodules is so very high. I myself found about 4% nitrogen, which is about 25% albumen in the dry matter of pease-nodules. Others found 5 to 6% nitrogen. It is noteworthy that the bacterial colonies on agar plates, grown out of the plant, contain but 1 to 2% nitrogen of the dry weight, which consists for the greater part of carbohydrates. So it is certain that the bacterial body is very much modified by its entrance into the plant cell as well morphologically as physiologically. Therefore it was tried gazometrically to state nitrogen absorption in the tubercles. If the hypothesis is founded it must be possible, with a great quantity of tubercles in a closed space and under favourable physiological conditions, easily to observe that absorption. For the number of tubercles, for example of the woody papilionaceae, being as said very small, while yet these plants are noted in agriculture for their considerable nitrogen-fixing power, the action of the tubercles must necessarily be very intense.

To test the hypothesis we acted as follows.¹⁾ First small, later larger quantities of lupine and serradella tubercles were placed in wide glass tubes which could readily be connected with the gas burettes, then put in thermostats at about 25° C. The tubercles respiring vigorously we had to keep account with a rapid assimilation and supply of the oxygen. Further it was only necessary to determine the quantity of nitrogen still present after deduction of the carbonic acid and the oxygen. The only difficulty we met with was that the nodules, which by their abundant content of albuminous matter are an excellent food for bacteria, when they touch each other and get moist, easily give rise to fermentations in particular by *Bacterium aërogenes*. Hereby hydrogen and much carbonic acid are produced, so that it is then necessary also to determine the hydrogen. But this fermentation may be prevented by introducing the material very loosely into the burette, so that there are but few points of contact between the nodules, and the air can freely pass between. Under such conditions there is no danger that free nitrogen will be formed; this only occurring through the action of the denitrifying bacteria on nitrates, which substance is in the nodules completely absent.

Of the tubercles of yellow lupine we used in our experiments quantities of 100 grs., 500 grs., and later even of 1 kil. In some

¹⁾ In some of these experiments I was assisted by Ir. D. C. J. MINKMAN, formerly assistant to the Laboratory for Microbiology of the Technical High School at Delft.

experiments we had the root tubercles cut off, in others the roots with the tubercles were left united with large pieces of the stem, so that eventually formed nitrogen compounds might be able to flow into the stem. All our estimations, however, showed that not in a single case the slightest fixation of nitrogen by the tubercles was observable. As at first we doubted of the accuracy of our results obtained with relatively little material, we afterwards used the just mentioned larger quantities, but this did not make any difference either. Besides the two said species we still examined several times 10 to 20 grs. of the nodules of *Vicia faba*, and once about 15 grs. nodules of *Robinia pseudo-acacia*, but other results were not obtained.

As our researches did not last longer than 12 to 20 days it might be objected that we have not sufficiently imitated the conditions of the plants in the field. Further, that in these experiments the growth of the tubercles, together with that of the whole plant, was excluded. Although these objections have not been refuted in the preceding, it is still highly improbable that nitrogen fixation would be associated with the growth of the tubercles and not with the augmentation of the bacteria out of the plant. Principal, however, is the fact that if within the nodules nitrogen fixation were to take place, which might have escaped our attention, the concerned quantity must certainly be extremely small. When we now consider how difficult it is to collect a few grams of tubercles for example of *Robinia*, it is clear that if this material is to be of any significance for such a great tree, its nitrogen-fixing power must be enormous. The experiments, however, show that the tubercles are wholly inactive or nearly so, hence there can be no question of attaching to them any importance concerning the nitrogen nutrition, whilst yet nitrogen fixation by this tree is as certain as for lupine and serradella and even on a much larger scale. So the nitrogen nutrition of the Papilionaceae can only be indirectly connected with the bacteria of the nodules. In my opinion this relation can only exist in the herbaceous species and in the germ plants of the shrubs and trees of that plant order, but in full-grown specimens of the woody species such as *Robinia pseudo-acacia* the presence or the absence of the nodules is wholly indifferent. Likewise on the roots of shrubs, such as *Sarothamnus vulgaris*, *Spartium scoparium*, *Genista anglica*, and *Genista pilosa* in full-grown condition, the number of tubercles is so small, their volume so insignificant to that of the whole plant, that even if they were able to assimilate some free nitrogen their slight activity could not possibly explain the rich nitrogen store of the whole plant.

Hence, the at present generally accepted explanation of the peculiar

behaviour of the Papilionaceae cannot be correct. New researches, especially with *Phaseolus*, are desirable.

From the preceding follows:

For various Papilionaceae, excelling by their abundance of nitrogen compounds, even when cultivated in media without such compounds, the number and volume of the tubercles is so small, that if only within them the fixation of free nitrogen should take place, the intensity of the process in these tubercles must necessarily be very great. We have not, however, succeeded gazometrically in observing the process in the tubercles at all.

Neither do the tubercle bacteria fix the atmospheric nitrogen when cultivated out of the plant in nutrient liquids or in plate cultures, nor enclosed in solid media.

The contradictory statements in the hand books of Plantphysiology are erroneous.

Physics. — “*On the rotational oscillations of a cylinder in an infinite incompressible liquid*”. By D. COSTER. (Communicated by Prof. J. P. KUENEN).

(Communicated in the meeting of May 25, 1918)

The method to be followed in the discussion of the problem will be in the main the same as that used by Prof. VERSCHAFFELT in the analogous case of the sphere¹⁾. We consider the rotational swings about its axis of an infinitely long cylinder which executes a forced vibration. Our object will be to ascertain the motion in the liquid which will establish itself after an infinite time (in practice after a relatively short time²⁾) in order to compute the frictional moment of forces exerted on the cylinder by the liquid. For the sake of simplicity the calculations will be referred to a height of 1 cm.

The motion of the cylinder may be represented by $\alpha = a \cos pt$ where α is the angle of rotation. An obvious assumption to be made is that the liquid will be set in motion in coaxial cylindrical shells each of which will execute its oscillations as a whole. On this assumption it is not difficult to establish the differential equation for the motion of the liquid.

Let ϱ be the density of the liquid.

μ the viscosity of the liquid.

ω the angular velocity of a cylindrical shell.

r the radius of the shell.

The frictional force per unit surface of one of the shells will then be $F = r\mu \frac{\partial \omega}{\partial r}$ and the frictional couple on a cylindrical surface

of radius r : $2\pi r^3 \mu \frac{\partial \omega}{\partial r}$.

Taking a shell of thickness dr its equation of motion will be

$$2\pi r^3 dr \varrho \frac{\partial \omega}{\partial t} = \frac{\partial}{\partial r} \left\{ 2\pi r^3 \mu \frac{\partial \omega}{\partial r} \right\} dr,$$

which reduces to

$$\frac{\varrho}{\mu} \frac{\partial \omega}{\partial t} = \frac{\partial^2 \omega}{\partial r^2} + \frac{3}{r} \frac{\partial \omega}{\partial r} \quad \dots \quad (1)$$

¹⁾ Comp. Proceedings 18 p. 840. Sept. 1915. Comm. Leiden 148b.

²⁾ Comp. Comm. 148b. pag. 22 footnote.

It is important to note that equation (1) may also be deduced from the general equation of hydrodynamics without its being necessary to neglect the second power of the velocities, as is the case in many problems of that kind. For an infinitely long time of vibration i. e. for uniform rotation (1) simplifies to

$$0 = \frac{d^2\omega}{dr^2} + \frac{3}{r} \frac{d\omega}{dr} \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The solution of (2) is $\omega = \frac{c_1}{r^2} + c_2$, c_1 and c_2 being integration-constants. If the solid cylinder (radius R) rotates with uniform speed Ω in an infinite liquid, the result will be $\omega = \frac{R^2 \Omega}{r^2}$, giving for the frictional couple as is well known the expression

$$- 4\pi\mu R^2 \Omega \quad . \quad . \quad . \quad . \quad . \quad . \quad (2')$$

In order to arrive at a possible solution of (1) we have to make our assumption regarding the motion of the liquid a little more definite by assuming that the angular displacement of each shell is represented by

$$\alpha_r = f(r) \cos (pt - \varphi(r)) \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We may also consider (3) as the real part of the complex function ue^{ipt} , where u is a function of r the module of which gives the amplitude of the oscillation and the argument the phase-shift $\varphi(r)$.

Remembering that $\omega = \frac{\partial \alpha}{\partial t}$ equation (1) may be reduced to

$$\frac{d^2 u}{dr^2} + \frac{3}{r} \frac{du}{dr} - \frac{i\varrho p u}{\mu} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Equation (4) is closely related to the differential equation of the cylindrical functions. Indeed by the substitution $y = zv$ BESSEL's equation of the 1st order $\frac{d^2 y}{dz^2} + \frac{1}{z} \frac{dy}{dz} + \left(1 - \frac{1}{z^2}\right)y = 0$, changes to

$$\frac{d^2 v}{dz^2} + \frac{3}{z} \frac{dv}{dz} + v = 0.$$

It follows that the general solution of equation (4) is

$$u = \frac{1}{r} \{ A J_1(cr) + B N_1(cr) \} \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where $c = \sqrt{\frac{-i\varrho p}{\mu}}$, A and B being complex integration-constants.

J_1 is the cylindrical function of the 1st kind and 1st order, N_1 that of the 2nd kind and 1st order¹⁾.

As regards c an agreement must be come to. We shall choose the root with the negative imaginary part i.e. $c = ke^{-\frac{i\pi}{4}}$, where $k = |c| = \sqrt{\left|\frac{ep}{\mu}\right|}$.

As a first boundary-condition we have $\lim_{r=\infty} r\alpha_r = 0$ ²⁾. As this relation must hold for all values of t , it follows that $\lim_{r=\infty} ru = 0$.

The cylindrical functions with complex argument all become infinite at infinity with the exception of the so-called functions of the 3rd kind or HANKEL's functions $H_p^{(1)}$ and $H_p^{(2)}$. Of these $H_p^{(1)}$ disappears at infinity in the positive imaginary half-plane and on the contrary becomes infinite in the negative half, whereas the opposite is true for $H_p^{(2)}$. By our choice of c in the negative imaginary half we are led to the function $H_1^{(2)}$. For the integration-constants in equation (5) this gives the relation $B = -iA$ ³⁾, so that (5) becomes

$$u = \frac{A}{r} H_1^{(2)}(cr) \quad . \quad . \quad . \quad . \quad . \quad (6)$$

For the determination of A we have to use the 2nd boundary-condition $\alpha_R = a \cos pt$, R being the radius of the cylinder. We therefore assume that there is no slipping along the wall.

$$\text{Hence } A = \frac{aR}{H_1^{(2)}(cR)},$$

so that

$$\alpha_r = R \frac{aR}{H_1^{(2)}(cR)} \frac{H_1^{(2)}(cr)}{r} e^{ipt} \quad . \quad . \quad . \quad . \quad . \quad (7)$$

The symbol R is intended to indicate, that the real part has to be taken of the function which stands after it.

If we had chosen for c the root with the positive imaginary part, we should have had to utilize the function $H_1^{(1)}$. It is quite easy to verify that this would not have made any essential change in the solution (7).

¹⁾ Comp. JAHNKE u. EMDE. Funktionentafeln pp. 90 and 93.

NIELSEN. Cylinderfunktionen. Instead of N NIELSEN uses the symbol Y .

²⁾ Prof. VERSCHAFFELT puts $\lim_{r=\infty} \alpha_r = 0$, which in my opinion is not quite correct, as the linear velocity has to disappear at an infinite distance. Comm. 148b p. 22.

³⁾ Between J , N , and H a linear relation holds. Comp. J. u E. p. 95.

For large values of x (real, positive) $H_1^{(2)}(x\sqrt{-i})$ approaches asymptotically to

$$-\frac{e^{-\frac{x}{\sqrt{2}}}}{\sqrt{\frac{1}{2}\pi x}} e^{-i\left(\frac{x}{\sqrt{2}} - \frac{\pi}{8}\right)};$$

therefore for (kR) sufficiently large:

$$\alpha_r \approx -\frac{aR}{|H_1^{(2)}(cR)|} \frac{e^{-\frac{kx}{\sqrt{2}}}}{\sqrt{\frac{1}{2}\pi k r^{1/2}}} \cos\left(pt - \frac{kx}{\sqrt{2}} + \frac{\pi}{8} - \varphi\right) \quad (8)$$

where $\varphi = \text{argument } H_1^{(2)}(cR)$.

From (8) it appears that damped waves are propagated from the cylinder to infinity, the velocity of propagation being

$$v = \frac{p}{k/\sqrt{2}} = \frac{p\sqrt{2}}{k} = \sqrt{\frac{2p\mu}{\rho}}$$

and the wave-length

$$\lambda = vT = \frac{2\pi v}{p} = \frac{2\pi\sqrt{2}}{k} = 2\pi \sqrt{\frac{2\mu}{\rho p}} \quad (8')$$

The frictional moment on the wall of the vibrating cylinder is

$$2\pi\mu R^3 \left[\frac{\partial \omega}{\partial r} \right]_R \quad \text{where } \omega = \frac{\partial \alpha}{\partial t}. \text{ First we determine } \left[\frac{\partial \alpha_r}{\partial r} \right]_R \text{ from (7)}$$

$$\left[\frac{\partial \alpha_r}{\partial r} \right]_R = R \left[-\frac{a}{R} e^{ipt} + ac \frac{H_1^{(2)'}(cR)}{H_1^{(2)}(cR)} e^{ipt} \right] \quad (9)$$

For the reduction of the 2nd part on the right hand side of (9) we make use of the well-known recursion-formula of the cylindrical functions:

$$\frac{dH_1^{(2)}(z)}{dz} = H_0^{(2)}(z) - \frac{1}{z} H_1^{(2)}(z)$$

By its application (9) obtains the form

$$\left[\frac{\partial \alpha_r}{\partial r} \right]_R = R \left[-\frac{2a}{R} e^{ipt} + ac \frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)} e^{ipt} \right] \quad (10)$$

giving for the frictional couple

$$K = 2\pi\mu R^3 \left[\frac{\partial \omega}{\partial r} \right]_R = -4\pi\mu R^3 \omega + R \frac{d}{dt} \left[2\pi\mu R^3 ac \frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)} e^{ipt} \right] \quad (11)$$

For an infinite time of swing, i. e. $p = 0$, but with a rotational velocity differing from 0, $|c| = \sqrt{\frac{\rho p}{\mu}}$ becomes 0. In that case the

second term on the right of (11) disappears on two grounds:
 (1) because $c = 0$ (2) $\lim_{cR=0} \frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)} = 0$; only the first term then remains, which agrees with (2').

Moreover

$$\lim_{cR=\infty} \frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)} = -i. \quad ^1)$$

It appears from the accompanying graphs ²⁾ of the module and argument of $\frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)}$ that this limiting value is practically reached at

$$\left. \begin{aligned} |cR| &= k \cdot R = 10 \\ |c| &= k = \frac{2\pi \sqrt{2}}{\lambda} \quad (\text{cf. } 8') \end{aligned} \right\} \dots \dots \dots (12)$$

The condition $|cR| \geq 10$ means, that the radius of the cylinder must be about equal to or larger than the wave-length. If R is small compared with λ the second part of the frictional couple is negligible. For $|cR| \geq 10$ the 2nd term on the right-hand side of (10) becomes

$$-a c i e^{i\omega t} = -a k e^{i\left(pt + \frac{\pi}{4}\right)} \quad \left(\text{since } c = k e^{-\frac{i\pi}{4}} \right)$$

Hence equation (11) now becomes:

$$K = -4\pi\mu R^2 \omega - 2\pi\mu k R^2 \frac{d}{dt} \left(a \cos \left(pt + \frac{\pi}{4} \right) \right) \quad (13)$$

where

$$\omega = \frac{d}{dt} (a \cos pt).$$

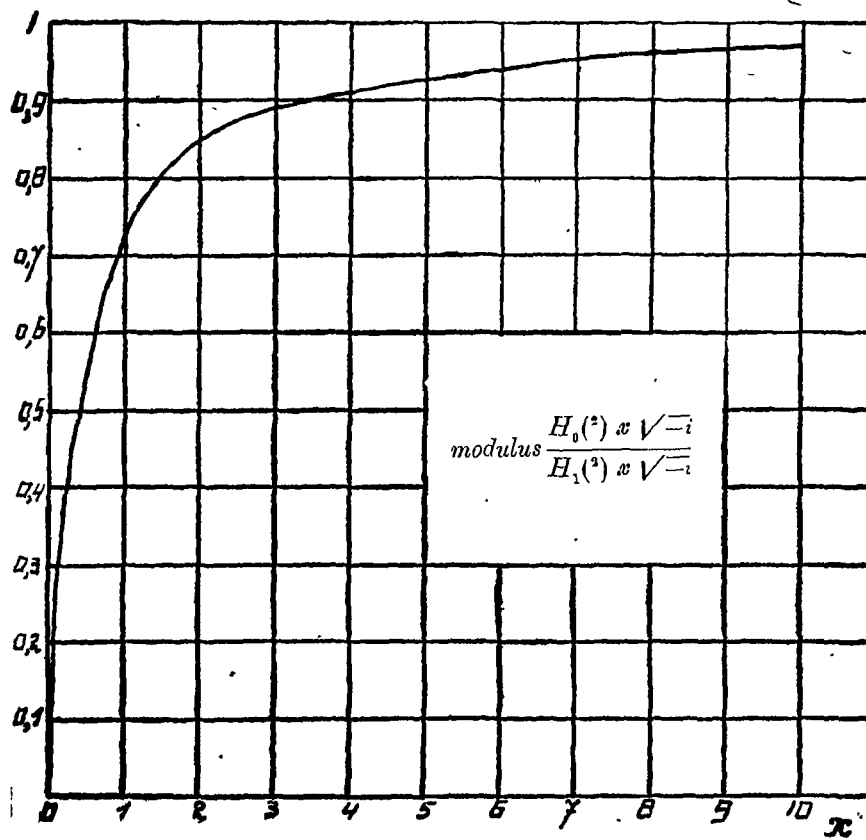
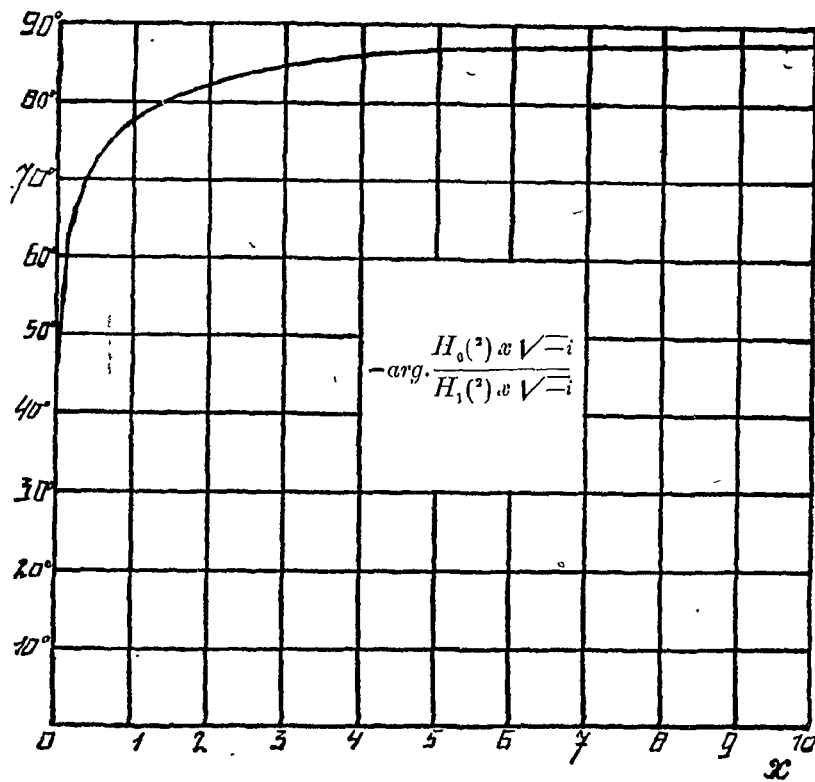
The frictional couple thus divides into two parts, one which does not contain the density of the liquid and another, in which it occurs and which therefore refers to the emission of waves. In the transition to the limit of uniform rotation the first part only remains.

In the discussion of the 2nd part of the frictional moment the quantity $k = \sqrt{\frac{p\rho}{\mu}}$ is an important factor. If we take a time of oscillation of 2π seconds, so that $p = 1$, we have $k = \sqrt{\frac{\rho}{\mu}}$.

This gives the following values for k .

¹⁾ Comp. J. u. E. l. c.

²⁾ Tables for $H_0^{(1)}$ and $H_0^{(2)}$ will be found J. u. E. p. 139, 140.



	ρ	μ	$k = \sqrt{\frac{\rho}{\mu}} (p = 1).$
Water 16°	1	0.011	9.5
Atm. air 0°	0.0013	0.000171	2.8
Air 0.01 atm. ¹⁾			0.28
Air 0.001 atm. ¹⁾			0.09
Hydrogen 1 atm. 0°	0.0000898	0.000085	1

From this table it appears that, except for dilute gases, R has to be relatively small in order that the 2nd part may be neglected with respect to the first. For instance for atmospheric air with $R = 0.5$ c.m. $kR = 1.4$ and $\left| \frac{H_0^{(2)}(cR)}{H_1^{(2)}(cR)} \right| = 0.80$, so that the amplitude of the 2nd term of the frictional couple is still 56 % of that of the first (see equation (11)), every thing calculated for a time of oscillation of 2π seconds.

There is a further special limiting case of equation (13), which is of some interest. Let R become infinite, and let a at the same time disappear, in such a manner that Ra converges to a finite limit b . We thus approach the one-dimensional problem of the oscillation of an unlimited flat plate in its own plane in an infinitely extended liquid. The frictional force per unit of surface is found from (13) to be

$$F = -\mu k \frac{d}{dt} \left(b \cos \left(pt + \frac{\pi}{4} \right) \right) \quad . \quad . \quad . \quad (14)$$

a formula which is well-known from hydrodynamics ²⁾. A term analogous to $-4\pi\mu R^2 \omega$ does not occur in the one-dimensional problem, the reason evidently being that with a uniform translation of the plate a condition of equilibrium does not arise, until the whole liquid away to infinity proceeds with the velocity of the plate.

Finally it is of importance to ascertain for what frequency the amplitude of the forced vibration becomes a maximum, in other words to what frequency the system cylinder-liquid resounds, if the cylinder is urged back to the position of equilibrium by a quasi-elastic force.

¹⁾ At these pressures μ has not become much smaller. Comp. KUNDT u. WAR. BURG. Pogg. Ann. 1875 Band CLV.

²⁾ Comp. LAMB. Hydrodynamics, 3rd edition 1905, p. 559.

The differential equation for the forced oscillation in complex notation is as follows:

$$\theta \frac{d^2 \alpha}{dt^2} + L \frac{d\alpha}{dt} + M\alpha = E e^{i\mu t} \quad (15)$$

Here in our case L is a complex quantity $L = L' + iL''$, where

$$L' = (4\pi \mu R^2 + \sqrt{2} \pi \mu k R^2)$$

$$L'' = \sqrt{2} \pi \mu k R^2.$$

If we only concern ourselves with the particular solution of (15) which gives the forced oscillation, we can also write (15) in the form:

$$\left(\theta + \frac{L''}{p} \right) \frac{d^2 \alpha}{dt^2} + L' \frac{d\alpha}{dt} + M\alpha = E e^{i\mu t} \quad (16)$$

We see therefore that in consequence of the motion of the liquid an apparent increase of the moment of inertia arises.

Putting

$$\theta + \frac{L''}{p} = \theta'$$

the particular solution of (16) becomes:

$$\alpha = \frac{E}{\sqrt{(M - \theta' p^2)^2 + L'^2 p^2}} e^{i(\mu t - \varphi)}$$

in which the phase-angle φ is determined by the constants of the differential equation.

Resonance occurs for $M - \theta' p^2 = 0$

or

$$\theta p^2 + L'' p - M = 0 \quad (17)$$

Now L'' is proportional to k and $k = \sqrt{\frac{pq}{\mu}}$, so that we may conveniently write $L'' = Np^{\frac{1}{2}}$, N being a constant.

(17) is now replaced by

$$\theta p^2 + Np^{\frac{1}{2}} - M = 0 \quad (18)$$

This equation which is bi-quadratic in \sqrt{p} determines the frequencies to which the system resounds. On closer examination there appears to be but one resonance-frequency. Naturally we are only concerned with the real roots p of equation (18). There are found to be two of such, one for which \sqrt{p} is positive, and another for which \sqrt{p} is negative. Now it follows from our calculation that we have assumed \sqrt{p} , which occurs in k to be essentially positive. For if we substitute a negative value for \sqrt{p} in our equations, we obtain a system of waves which moves from infinity towards the cylinder.

But the amplitude of this system is infinite at infinity, so that our first boundary-condition would not be satisfied.

We may also choose our boundary-conditions differently. We may for instance imagine the liquid limited on the outside by a second cylinder co-axial with the first and at rest. It is then advisable to write the general solution of equation (4) in the following form

$$u = \frac{1}{r} \{ C H_1^{(2)}(cr) + D H_1^{(2)}(cr) \} \dots \dots \dots (19)$$

At a sufficient distance from the axis of the cylinders two systems of waves then arise, one of which is propagated outwards and the other inwards. At the surface of the exterior cylinder we obtain reflection with reversal of phase, so that the liquid there is at rest. For the determination of the integration-constants C and D we obtain comparatively complicated relations which may be omitted here as they do not yield anything of further interest.

The problem of the free oscillation does not now give any further special difficulties.

We must now seek a solution of equation (1) of the form

$$a_r = f(r) e^{-k't} \cos(k''t - \varphi(r)),$$

which for $r = R$ becomes $a_R = a e^{-k't} \cos k''t$. Again we may write $a = u e^{nt}$, where $n = -k' + ik''$.

The same method of solution may now be followed. Instead of (7) we obtain:

$$a_r = \frac{aR}{H_1^{(2)}(c'R)} \frac{H_1^{(2)}(c'r)}{r} e^{nt}, \dots \dots \dots (20)$$

where $c' = \sqrt{-\frac{n\rho}{\mu}}$, if for c' the root with the negative imaginary part is chosen. Hence

$$\left[\frac{d\alpha_r}{dr} \right]_R = -\frac{2a}{R} e^{nt} + ac' \frac{H_0^{(2)}(c'R)}{H_1^{(2)}(c'R)} e^{nt}. \dots \dots \dots (21)$$

$$\lim_{|c'R|=\infty} \frac{H_0^{(2)}(c'R)}{H_1^{(2)}(c'R)} = -i$$

Therefore:

$$\left[\frac{d\alpha_r}{dr} \right]_R = -\frac{2a}{R} e^{nt} - a \sqrt{\frac{n\rho}{\mu}} e^{nt}, \dots \dots \dots (22)$$

if for $\sqrt{\frac{n\rho}{\mu}}$, we take the root with the positive real term.

The frictional moment now becomes:

$$2\pi\mu R^2 \left[\frac{d\dot{\alpha}}{dr} \right]_R = -2\pi\mu R^2 \left[\frac{2}{R} + \sqrt{\frac{nQ}{\mu}} \right] \dot{\alpha}_R$$

The differential equation for the free vibration is:

$$K \frac{d^2\alpha}{dt^2} + L \frac{d\alpha}{dt} + M\alpha = 0 \quad . \quad . \quad . \quad . \quad . \quad (23)$$

giving for the natural frequencies of the system the equation

$$Kn^2 + Ln + M = 0 \quad . \quad . \quad . \quad . \quad . \quad (24)$$

The quantity L here contains \sqrt{n} .

If we put $L = P + Q\sqrt{n}$, where

$$P = 4\pi\mu R^2 \text{ and } Q = 2\pi\mu R^2 \sqrt{\frac{Q}{\mu}},$$

(24) assumes the form :

$$Kn^2 + (P + Q\sqrt{n})n + M = 0 \quad . \quad . \quad . \quad . \quad . \quad (25)$$

Equation (25) is bi-quadratic in $z = \sqrt{n}$. On further examination it is found to have 2 complex roots z in the right hand portion of the complex plane and 2 in the left portion, only the former of which we can use (comp. equation (22)); hence the system has but one natural frequency. Further $z^2 = n$ is found to contain a negative real term, as indeed could not be expected otherwise.

Chemistry. — “*Investigations on PASTEUR’S Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry: V. Optically active complex-salts of Iridium-Trioxalic Acid*”. By Prof. F. M. JAEGER.

(Communicated in the meeting of June 29, 1918).

§ 1. A short time ago I published¹⁾ some data about the properties of *racemic Potassium-Iridium-Oxalate*: $\{K, Ir(C_2O_4)_3\} + 4\frac{1}{2}H_2O^2$, and on that occasion I announced experiments undertaken with the aim of splitting this compound into its optical antipodes. It was our purpose to gain in this way the necessary information to enable us to indicate the correct configuration in space of these optically active complex ions, in comparing it with that attributed to the corresponding *rhodium*-derivatives, in consequence of the arguments brought forward on that occasion. At the same time I hoped to investigate in this way, what influence the substitution of the central *rhodium*-atom in these complex ions by the homologous *iridium*-atom appeared to have upon the magnitude and the specific character of the optical rotation and its remarkable dispersion. It may be considered of importance, of course, to know the relation existing between the two functions just mentioned, especially in connection with our former studies on the analogously constituted complex salts of *cobalt* and *rhodium* combined with three molecules of *ethylenediamine*, where the problem arose as to the true configurative relations between the salts of these homologous metals of the eighth group of the periodic system, when rotating the plane of polarisation in the same direction³⁾.

In the following the fission-experiments mentioned and the results obtained by them are recorded in details. Thus for the first time the possibility of a “partial” asymmetry⁴⁾ has been proved, in the case of *iridium* as the central atom; the series of the metals showing

¹⁾ F. M. JAEGER, *Proceed. R. Acad. Amsterdam*, **20**, 263. (1917).

²⁾ C. GIALDINI, *Rend. Acad. d. Linc., Roma*, (5a), **16**, II, 551. (1907); *Proceed. Acad. Amsterdam*, loco cit. p. 278.

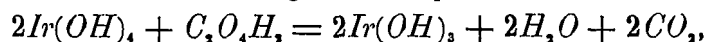
³⁾ F. M. JAEGER, *Proceed. R. Acad. Amsterdam*, **17**, 49. (1915); **20**, 244. (1917); *conf. Zeits. f. Kryst. u. Miner.* **55**, 209. (1915).

⁴⁾ F. M. JAEGER, *Lectures on the Principle of Symmetry*, *Amsterdam*, (1917), p. 235.

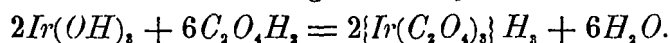
this phenomenon being herewith extended to *chromium*, *iron*, *cobalt*, *platinum*, *rhodium*, and *iridium*. With respect to the dispersion of some of these salts, we hope yet to furnish some new data in the near future.

§ 2. The required *racemic Potassium-Iridium-Oxalate*: $K_3\{Ir(C_2O_4)\} + 4\frac{1}{2}H_2O$ was obtained in the following way. A 3% solution of pure, hydrated *iridiumchloride* of commerce (HERAEUS) is treated by a solution of *potassiumhydroxide* in excess. A dirty brownish precipitate is formed, which dissolves in the excess of *KOH* to form *potassium-iridiate*. The alkaline solution is heated, and then some *perhydrol* (30% H_2O_2) added: the colour changes to dark blue, and the principal part of the *iridium* precipitates as $Ir(OH)_4$. Another part of it remains in the solution as a colloidal suspension of great stability, not being precipitated or coagulated from it, even after addition of electrolytes. These solutions are therefore better evaporated, and the residue transformed into *ammonium-chloro-iridiate* to be used afterwards in other experiments.

The blue precipitate is washed by decantation with water slightly acidified by means of *oxalic acid*; the filtrates and washings are also later converted into the mentioned compound. When the removed liquid gets colourless, the decantation may be considered complete, and the precipitate is brought into a round bottom flask, the superfluous liquid removed after some hours, standing, and a hot, concentrated solution of *oxalic acid* added. The contents of the vessel are boiled under a reflux-condenser during 30 or 40 hours, a part of the *oxalic acid* is thereby decomposed, and the tetravalent *iridium* reduced to trivalent according to the equation:



while *iridium-trioxalic acid* is then formed from the derivative of the trivalent *iridium*, conforming to the equation:



The gold-yellow solution finally obtained is filtered, and almost perfectly neutralised by means of $KHCO_3$; it is then concentrated on the waterbath, and the successive fractions of the crystals formed are separately collected. Almost pure *potassium-oxalate* is first deposited, and afterwards, besides this, the orange crystals of the salt required, which is very soluble. These crystals have to be separated mechanically, and they are afterwards recrystallised for purification¹⁾.

The *racemic* compound crystallises in pale orange-coloured crystals,

¹⁾ Dr. J. KAHN has aided most effectively in the preparation of a part of this *racemic* compound, and in the troublesome working up of the *iridium*-residues.

which have already been investigated and described in a former paper¹⁾. They are triclinic-pinacoidal, and completely isomorphous with the corresponding racemic *rhodium*-salt, so that the direct isomorphous substitution of the metals *Rho* and *Ir*, also in their complex salts, has been hereby definitely proved. As we shall see, this proof has now also been given in the case of the *optically-active components* of such complex salts.

§ 3. *Fission of the racemic Potassium-Iridium-Oxalate* ($+4\frac{1}{2}H_2O$) *into its optically-active components.*

27,5 Grams of pure *strychnine-nitrate* are dissolved in 1300 ccm. boiling water; then a solution of 15,5 grams of the racemic salt in 250 ccs water of 60° C. is rapidly poured into the boiling solution under perpetual stirring. The flask with the golden yellow liquid is allowed to cool slowly for twelve hours to room-temperature. The deposited, highly yellowish coloured, felty-like crystals are sharply sucked off at the water-pump, washed with some strong alcohol, afterwards with some ligroine, and dried at room-temperature in an air-current. The mother-liquid is evaporated on the waterbath to about $\frac{2}{3}$ of its original volume; on cooling highly yellow, needle-shaped crystals are again deposited, which are treated in the same way. While the first fraction, however, represents the *strychnine*-salt of the *dextrogyratory* component, — the *laevogyrate* antipode was immediately obtained from the second precipitate. On further evaporation of the filtrate, some paler coloured fractions are consecutively obtained, all of which give the *laevogyratory potassium*-salt. The sixth and the seventh fraction finally consisted of pure *strychnine*, accompanied by some of its *nitrate*, while in the last fractions crystals of the free, *racemic potassium*-salt together with some of the *laevo*-salt, and also some *potassium-nitrate*, appeared. The rotation of this last fraction as a whole, after removing the *potassium-nitrate*, was negative, amounting only to about $\frac{1}{7}$ of the rotation of the pure *laevogyrate* salt, so that a considerable amount of racemic salt is evidently admixed. Probably a partial hydrolysis during the repeated evaporations has taken place, so that the free *potassiumsalt* accumulates in the last fractions.

The *strychnine*-salt of the *dextrogyratory* component has the formula: $\{Ir(C_2O_4)_3\}_2(C_{21}H_{22}N_2O_2)_2 + 3\frac{1}{2}H_2O$; it appears as pale yellow, very fine needles. For a series of wave-lengths the rotation of this strongly active salt was determined; the solution used contained 0,4763 grams of the hydrated salt in 100 ccs. of the liquid.

¹⁾ F. M. JAEGER, Proceed, R. Acad. Amsterdam, 20, 278, (1917).

The following data were found:

ROTATION-DISPERSION OF STRYCHNINE- <i>d</i> -IRIDIUM-OXALATE (+ 3½ H ₂ O).		
Wave-length in A. U.:	Observed Rotation:	Molecular Rotation:
5105	+ 1.02	+ 20997°
5260	0.86	17703
5430	0.65	13379
5610	0.38	7822
5800	0.27	5558
6020	0.21	4323
6260	0.17	3499
6530	0.15 ^s	2676

In the same way the composition of the corresponding *strychnine*-salt of the *laevogyrate* component appeared to be: $\{Ir(C_2O_4)_3\}C_{21}H_{22}N_2O_2 + 3H_2O$. This salt too crystallises in needles, somewhat thicker than those of the first. The substance is strongly *laevogyra-*tory, and its dispersion is smaller than in the case of the other salt, as may be seen from the following data, and the graphic representation in fig. 1:

ROTATION-DISPERSION OF STRYCHNINE- <i>l</i> -IRIDIUM-OXALATE (+ 3 H ₂ O).		
Wave-length in A. U.:	Observed Rotation:	Molecular Rotation:
5105	— 0.33	— 17236°
5260	0.28	14624
5430	0.24	12535
5610	0.19	9994
5800	0.15	7835
6020	0.12 ^s	6057
6260	0.09	4701
6530	0.08	4178

This solution contained 0,1886 grams of substance in 100 grams of the liquid.

It is remarkable that the laevogyrate *strychnine*-salt has a somewhat greater molecular rotation than the corresponding *potassium*-salt itself; the dextrogyrate *strychnine*-salt rotates more strongly than the free *potassium*-salt.

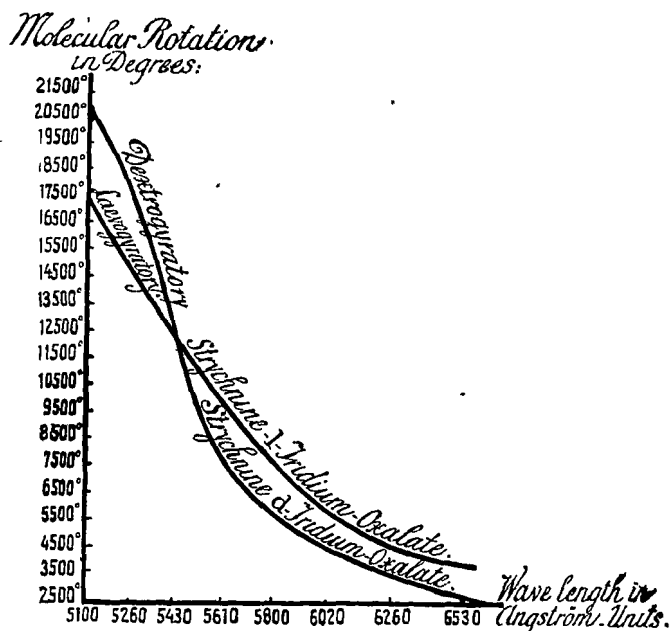


Fig 1. Molecular Rotation Dispersion of *Strychnine-d-Iridium-Oxalate* ($\frac{1}{3}\text{H}_2\text{O}$) and of *Strychnine-1-Iridium-Oxalate* ($\frac{1}{3}\text{H}_2\text{O}$).

§ 4. The different fractions were mixed with about six times their weight of finely pulverized *potassium-iodide*, and then ground together in a mortar, some cold water being added to the mixture. When all *potassium-iodide* has just been dissolved, the yellow liquid is sharply sucked off from the white precipitate, this last washed with a very small quantity of cold water, and the yellow filtrate precipitated by the addition of an excess of 95 % alcohol. A yellow deposit is formed, which is sucked off on the BUCHNER-filter, washed with alcohol, and recrystallised from water. On heating on the waterbath the solution does not autoracemise notably. By slow crystallisation at roomtemperature, beautiful trigonally-shaped, orange crystals are formed, which are dried between filterpaper. They can grow in their mother-liquid to considerable size. The optically-active components are extremely soluble, more than the very soluble racemic compound; on this account the crystallisation of the active components was executed in smaller and somewhat deeper crystallisation-dishes.

§ 5. The rotation-dispersion of these optically-active *iridium-salts* was measured in the same way as formerly by means of a great polarimeter of SCHMIDT and HAENSCH, with threefold field, and equipped with a monochromator. The tube was always 20 cm. long, and determinations were made for a whole series of wave-lengths. Even in thin layers of the liquid the spectral region of the transmitted light appeared to be appreciably limited by absorption, also in the case of not very concentrated solutions.

Waves larger than 6850 A.U. were never transmitted to a sufficient degree, while even in a solution of 1 % no exact determinations could be made for wave-lengths smaller than 5300 A.U. To investigate the shape of the dispersion-curve also for shorter wavelengths, it was therefore necessary to use very dilute solutions, of 0,2 % and 0,1 % or less. We have used four such solutions for this purpose, containing respectively one grammolecule of the hydrated salt in 14,57 Liters (a) of the solution, in 57,73 Liters (b), in 228,86 Liters (c), and in 413,7 Liters (d).

In the following table the mean values are taken into account, and the molecular rotations calculated from them; in fig. 2 these results are moreover graphically plotted, in their relation to the light used:

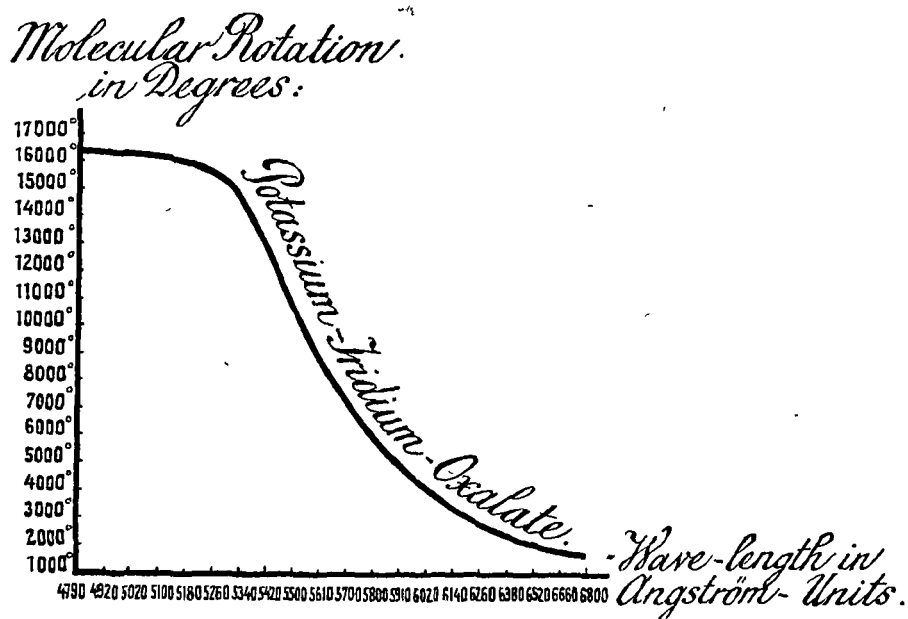


Fig. 2. *Molecular Rotation-Dispersion of the Optically active Potassium-Iridium-Oxalates.*

The values obtained with the different solutions agreed very well

together. In the table are therefore quoted those values which approached nearest to the curve of the mean values. The dispersion-curve shows a tendency to get more and more horizontal for wave-lengths beneath 5100 A.U.

ROTATION-DISPERSION OF DEXTROGYRATE POTASSIUM-IRIDIUM-OXALATE (+ 1 H ₂ O).		
<i>Wave-length in A. U.:</i>	<i>Observed Rotation in Degrees:</i>	<i>Molecular Rotation in Degrees:</i>
4790	+ 0.79 (<i>d</i>)	+ 16340°
4920	0.785 (<i>d</i>)	16237
5020	0.78 (<i>d</i>)	16134
5100	0.78 (<i>d</i>)	16134
5180	0.77 (<i>d</i>)	15927
5260	0.75 (<i>d</i>)	15514
5340	1.28 (<i>c</i>)	14647
5420	4.36 (<i>b</i>)	12586
5510	14.42 (<i>a</i>)	10508
5610	11.94 <i>id.</i>	8699
5700	9.88 <i>id.</i>	7198
5800	8.17 <i>id.</i>	5952
5910	6.86 <i>id.</i>	4998
6020	5.49 <i>id.</i>	4000
6140	4.73 <i>id.</i>	3446
6260	3.86 <i>id.</i>	2813
6380	3.32 <i>id.</i>	2446
6520	2.61 <i>id.</i>	1901
6660	2.33 <i>id.</i>	1698
6800	2.10 <i>id.</i>	1530

Although the dispersion of these orange-coloured solutions is extraordinarily strong, the slope of the curve is quite different from that found in the case of the corresponding *rhodium*-salt. This fact proves the preponderant influence of the special nature of the

central metal-atom on the specific light-absorption (colour) of these salts and on the whole character of the rotation-dispersion.

The yellow crystals obtained on evaporating the original mother-liquid of the *strychnine*-salts to $\frac{2}{3}$ or $\frac{1}{2}$ of its volume, gave after treatment with potassium-iodide a fraction which appeared to be the *pure laevogyrate* salt. The following measurements, made with a solution containing one grammolecule of the hydrated salt in 42.97 Liters of the liquid, may make this clear:

ROTATION-DISPERSION OF THE LAEOGYRATE POTASSIUM-IRIDIUM-OXALATE (+ 1H ₂ O).		
Wave-length in A. U.:	Observed Rotation in Degrees	Molecular Rotation in Degrees:
5340	— 6° 66	— 14287°
5430	5.72	12289
5520	4.89	10506
5610	3.86	8293
5700	3.26	7004
5800	2.70	5801
5910	2.28	4898
6020	1.95	4189
6140	1.63	3502
6260	1.35	2900
6340	1.07	2299
6520	0.88	1891
6660	0.74	1590
6800	0.70	1504

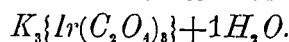
A comparison of the rotations for the same wave-lengths in the case of the corresponding *rhodium*-salt with the here described

Salt:	Molecular Rotation:	Atomic Volume of the metal:
$K_3 \{Rho(C_2O_4)_3\} + H_2O.$	$M_{4930} = 14200^\circ; M_{5800} = 790^\circ; M_{5970} = 0^\circ; M_{6660} = -1215^\circ$	8.50
$K_3 \{Ir(C_2O_4)_3\} + H_2O.$	$M_{4930} = 16230^\circ; M_{5800} = 5952^\circ; M_{5970} = 4500^\circ; M_{6660} = +1698^\circ.$	8.61

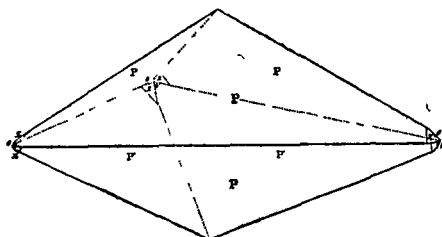
iridium-salts, teaches us, that the rotation of the *iridium*-salt is always appreciably *greater* than that of the *rhodium*-salt, although the atomic volume of *iridium* differs only slightly from that of *rhodium*, and even exceeds it by a small amount.

If we were able to demonstrate later, that for $\{Ir(Aeïne)_3\}I$, the rotations are smaller than those of the corresponding *rhodium*-salt, then we should have proved that the influence of the atomic volume on the magnitude of the rotation, may be in this or in the opposite direction, according to there being either basic or acid substituents attached to the central-atom.

§ 6. DEXTROGYRATORY POTASSIUM-IRIDIUM-OXALATE:



Beautiful, rather large, orange-coloured, and very lustrous crystals, which are commonly regularly developed in the shape of flattened, triangular bipyramids. They are well built and geometrically easily determinable, allowing very exact measurements. The deviations of the angular values from those found with the corresponding *rhodium*-



Dextrogyratory Potassium-Iridium-Oxalate.

Fig. 3.

salt are more appreciable than ordinarily stated in the case of rigorously isomorphous crystals.

The symmetry of the two series of crystals is however exactly the same, and their form-analogy is sufficiently great, to consider the optically-active salts of the two series as quite isomorphous, also with respect to the doubtless isomorphy between the racemic salts of the *rhodium*-, and the *iridium*-series. The more deviating values of the angles and axial parameters are probably connected with the rather great difference of atomic weight of the metal-atoms. Analysis teaches us, that also these optically-active salts crystallise with only one molecule of water.

Trigonal-trapezohedral.

$$a : c = 1 : 0.9520. \text{ (BRAVAIS); } \alpha = 100^\circ 20'. \text{ (MILLER).}$$

Forms observed. $P = \{11\bar{2}2\} [52\bar{1}]$, as positive trigonal bipyramid,

14*

predominant and yielding good reflexes; $o = \{10\bar{1}1\} [100]$, positive rhombohedron of the first kind, well reflecting, but in most cases only with rather small facets; $x = \{1\bar{1}01\} [2\bar{1}2]$, a negative rhombohedron of the first kind, commonly much broader than o , somewhat less lustrous; $y = \{2\bar{1}\bar{1}1\} [4\bar{2}1]$, a negative trigonal bipyramid, about as large as x , but much smaller than P , commonly yielding good mirror-images; $r = \{1\bar{1}02\}$, as a narrow obtusion of the edges of the rhombohedron o , ordinarily absent, but in the other case very lustrous. Sometimes a very narrow and rudimentarily developed prism $m = \{11\bar{2}0\}$ was observed, truncating the basal edges of P . The crystals are mostly very regularly developed as flat trigonal bipyramids; but occasionally more or less deformed, table-shaped individuals are met with, showing the same combination of forms. The faces of P are often striated parallel to the edges $P:o$. (Fig. 3). Also crystals are found, where o is about twice as large as P ; in this case the striation on P was observed in all cases.

Finally we met with individuals showing only P and o in about equal size, P having its characteristic striation; besides them also y was found occasionally, but very small and subordinate, especially in the case of the dextrogyrate component.

<i>Angular Values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$P:P'' = (11\bar{2}2):(1\bar{2}12) = *$	73° 20'	—
$P:P' = (11\bar{2}2):(11\bar{2}\bar{2}) =$	92 49	92° 49'
$P:o = (11\bar{2}2):(10\bar{1}1) =$	21 40	21 43
$x:o = (1\bar{1}01):(10\bar{1}1) =$	43 28	43 26
$x:y = (1\bar{1}01):(2\bar{1}\bar{1}1) =$	28 20	28 21
$y:o = (2\bar{1}\bar{1}1):(10\bar{1}1) =$	28 24	28 21
$P:o = (1\bar{2}12):(10\bar{1}1) =$	60 48	60 50½
$o:o = (10\bar{1}1):(0\bar{1}11) =$	79 30	79 40
$o:r = (10\bar{1}1):(1\bar{1}02) =$	39 43	39 50
$m:P = (11\bar{2}0):(11\bar{2}2) =$	46 30	46 25

No distinct cleavage was observed.

Optically uniaxial, without noticeable circular polarisation. The character of the birefringence is negative.

The specific gravity of the crystals at 20° C. was: 2,734; the molecular volume is therefore: 217,77, and the topical parameters are: $\chi:\omega = 7,0618:6.7230$, if calculated with respect to hexagonal axes, and $\chi=\psi=\omega = 6,1321$, with respect to rhombohedral axes.

§ 7. The crystals of the laevogyrate antipode ordinarily showed only the bipyramid P , which must be considered as a *lefthanded* bipyramid here, because all phenomena are in agreement in this case with PASTEUR's law, as is proved beyond doubt by the hemihedral symmetry of the crystals. Therefore to this bipyramid must be attributed the symbol $\{2\bar{1}\bar{1}2\} [5\bar{1}2]$, besides the forms o , x , and y , y having the symbol $\{11\bar{2}1\} [4\bar{1}2]$, appear subordinately here. Because o and x were in most crystals about equally large, and could not be discerned in any other way, the external habit of these lefthanded crystals was not different from that of dextrogyrate salt, the latter being brought into the same position as the lefthanded by a rotation through 60° round the trigonal axis, with the only difference, that the forms x and o are thereby interchanged. However, if x and o are of unequal size, the occurrence of mirror-images could be seen immediately in the crystals. The zonal relations may be made clear by the subsequent stereographical projections (Fig. 4). Just as in the case of oppositely rotating *rhodium*-salts, a non-superposable hemihedrism accompanies here the contrary power of rotation.

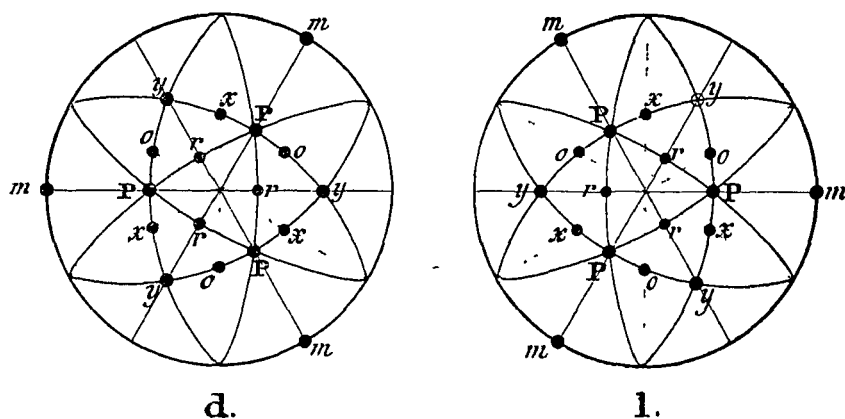


Fig. 4. Stereographical Projection of the Crystalforms of *d*- and *l*-Potassium-Iridium-Oxalate (only the top-ends of the crystals).

§ 8. The specific gravities of the formerly investigated *rhodium*-salts, were determined at $d_{40}^{20} = 2,171$ for the racemic compound ($4\frac{1}{2} H_2O$), corresponding to a molecular volume of 260,34; and at $d_{40}^{20} = 2,255$ for each of the optically-active salts ($+1H_2O$), which corresponds to a molecular volume of 222,70. From this the topical axes of these salts are calculated at:

$\chi : \psi : \omega = 6,8980 : 6,4274 : 6,6306$, for the racemic *rhodium*-salt, and $\chi : \omega = 7,2660 : 6,4944$, for the optically-active salts, with respect to hexagonal axes, and $\chi = \psi = \omega = 6,1856$, with respect to rhombohedral axes.

Comparison with the corresponding parameters of the here studied *iridium*-salts ¹⁾:

Salt:	Topical Parameters:
<i>racemic</i> $K_3 \{ Rho (C_2 O_4)_3 \}, 4\frac{1}{2} H_2 O.$	$\chi : \psi : \omega = 6,8980 : 6,4274 : 6,6306.$
<i>racemic</i> $K_3 \{ Ir (C_2 O_4)_3 \}, 4\frac{1}{2} H_2 O.$	$\chi : \psi : \omega = 6,7454 : 6,2626 : 6,5162.$
<i>optically-active</i> $K_3 \{ Rho (C_2 O_4)_3 \}, H_2 O.$	$\chi : \omega = 7,2660 : 6,4944; \chi' = 6,1856.$
<i>optically-active</i> $K_3 \{ Ir (C_2 O_4)_3 \}, H_2 O.$	$\chi : \omega = 7,0618 : 6,7230; \chi' = 6,1321.$

teaches us, that the substitution of the central *Rho*-atom in the complex oxalate by the isomorphous *Ir*-atom, produces a diminution of the topical parameter ω in the case of the racemic salts, but a slight increase, in the case of the optically active antipodes, although the values for χ and χ' are in this case smaller with the corresponding *Rho*-salt.

In the same way as in the case of the previously described *rhodium-oxalate*, all phenomena observed in the fission of *potassium-iridium-oxalate* are really in full agreement with the sense of PASTEUR'S law.

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Groningen, June 1918.

¹⁾ The specific gravity of *racemic* $K_3 \{ Ir (C_2 O_4)_3 \} + 4\frac{1}{2} H_2 O$ was at 18° C. determined at: $d_{40}^{18} = 2,688$; the molecular volume is thus: 243,82.

Chemistry. — “*Investigations on PASTEUR's Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry: VI. On the Fission of Potassium-Rhodium-Malonate into Its Optically-active Components.*” By Prof. F. M. JAEGER and WILLIAM THOMAS. B. Sc.

(Communicated in the meeting of June 29, 1918).

1. Some time ago one of us¹⁾ described the crystalform of *racemic Potassium-Rhodium-Malonate*: $K_3\{Rho(C_3H_2O_4)_3\} + 3H_2O$, and hinted at the possibility of separating this salt into its optically-active components. In the following we are now able to describe the results of the respective experiments, which have led to a positive result, and to give a review of the highly remarkable rotation-dispersion of these new salts.

The racemic salt necessary for these experiments was prepared in the following way. A 3 % -solution of pure $Na_3RhoCl_6 + 9H_2O$ was heated to 40° C, and then precipitated by means of a 10 % solution of caustic potash, so much of the base being added, that the liquid showed a feeble alkaline reaction. The precipitate is separated from the excess of potash as well as possible by repeated decantation in high cylindrical vessels; it settles down extremely slowly, so that this operation takes much time. Then the precipitate is brought into a round bottom distilling-flask and heated under a reflux-cooler some forty hours with a solution of the calculated amount of *potassium-bimalonate*: $KHC_3H_2O_4$, and some free *malonic acid*, until the precipitate no longer diminishes in quantity. The red coloured liquid is then filtered, and concentrated on the water-bath: on slow evaporation at room-temperature there soon appear red flat crystals of the complex malonate, which are once more recrystallised from water for purification. The residue in the flask is again changed into the complex *sodium-rhodium-chloride*: $Na_3RhoCl_6 + 9H_2O$ in the usual way, and afterwards precipitated as described in the above.

§ 2. After a series of attempts we succeeded in separating this salt, which crystallises in beautiful monoclinic crystals²⁾, into its optically-active components by the aid of its *cinchonine-salt*.

¹⁾ F. M. JAEGER, *Proceed. Kon. Acad. Amsterdam*, **20**. 276. (1917).

²⁾ *loco citato*, p. 277.

For this purpose the *potassium*salt is first converted into the *barium*salt, by adding a strong solution of 3 molecules of *barium-chloride* to a concentrated solution of 2 molecules of the *potassium*-salt: a yellow precipitate is formed, which dissolves rather easily in hot water, but which can be almost completely precipitated from its aqueous solution by the addition of 97 % alcohol. This *barium*-salt was now dissolved in water at 50° C, and then a solution of one equivalent *cinchonine-sulphate* ¹⁾, also heated to 50° C, was added to it. The solutions need not be too concentrated, because the *cinchonine-rhodium-malonate* will otherwise partly precipitate, as it is only sparingly soluble. The *barium*sulphate formed is carefully sucked off, and by washing with water of 45° C. all the included yellow *cinchonine*-salt eliminated. On standing for 24 hours in a large crystallising-dish, the liquid begins to deposit beautiful, pale yellow and often in rosettes united needles of the *cinchonine*-salt of the *laevogyrate* component, as will soon be shown. On repeated partial evaporation of the mother-liquid on the waterbath, the successive fractions were separately collected and investigated. The first three fractions appeared to contain the *lefthanded* component; the fourth fraction gave the almost pure *dextrogyrate* antipode, the fifth and sixth fractions the pure *dextrogyrate* component immediately. It is a remarkable fact that the *cinchonine-l-malonate* and the *cinchonine-d-malonate* are both *dextro*-gyratory, notwithstanding the very large rotation of opposite sign of the complex ions present therein. This peculiar behaviour was checked by us by a special control, namely by preparing the free *potassium*-salts again from the *cinchonine*-salts used in the polarimetric measurements. We could easily prove in this way, that the salts thus obtained, really represented the right and left antipodes. From the pure *laevogyrate potassium*salt we once more prepared the corresponding *cinchonine*-salt by means of the *barium*-salt; the rotations determined with this especially prepared salt proved to be positive, and they agreed very well with those formerly found. We have also investigated the influence of the addition of three molecules of *cinchonine* to a solution of the optically-active *potassium*-salts, and the rotations found with these solutions were compared with those

¹⁾ Originally we tried to reach our purpose by means of the *strychnine*-salt, as in the case of the *rhodium-oxalate*. However, these experiments had no result, the *potassium*salt prepared from the carefully fractionated *strychnine*-salt by *potassium-iodide* being always optically-inactive. It is difficult to say whether racemisation or partial racemism is the cause of this; but only after several failures we passed to the use of *cinchonine*.

of *cinchonine* itself: the observed rotations appeared to be practically identical with those of the *cinchonine-l-rhodium-malonate*, so that evidently the influence of the three molecules of *cinchonine* far outweighs that of the laevogyrate *rhodium-malonate-ion* itself.

The last fractions of the crystallisation-series of the *cinchonine*-salt finally gave pure *cinchonine*, a small amount of the dextrogyrate salt and a certain quantity of the racemic salt remaining in the last mother-liquids. Evidently also here the repeated evaporation on the waterbath, just as in the case of the corresponding *oxalate*, seems to cause a partial hydrolysis. Analysis taught us that the *cinchonine-d-rhodium-malonate* crystallises with $3 H_2O$; the corresponding *cinchonine-l-rhodium-malonate* with $\frac{1}{2} H_2O$. This last mentioned salt could not be heated above $100^\circ C$, being less stable than the right-handed salt, it is rapidly decomposed with formation of a dirty brown powder.

For the rotation-dispersion of the *cinchonine*-salts we found the following values:

I. CINCHONINE- <i>d</i> -RHODIUM-MALONATE (+ 3 H ₂ O).		
Wave-length in A. U.:	Observed Rotation in Degrees:	Molecular Rotation in Degrees:
5105	+ 1,37	+ 30010°
5260	1,23	26943
5420	1,14	24972
5610	1,07	23406
5800	0,99	21686
6020	0,94	20591
6260	0,88	19277
6520	0,84	18400

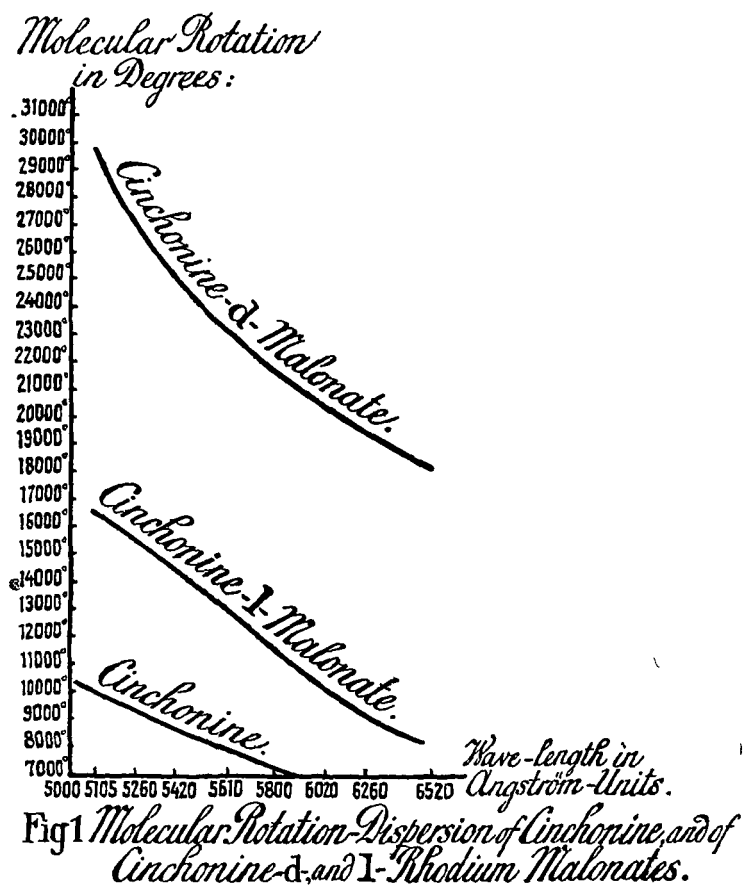
The solution investigated contained 0,3070 grams of the hydrated salt in 100 grams of the liquid.

The results obtained are plotted in the figure 1. It shows us, that *both* curves are situated *above* that of pure *cinchonine*, notwithstanding the fact, that one of them contains the strongly negatively rotating complex *rhodium-malonate-ion*; of a simple superposition of the optical activities there is therefore no question.

The transformation of the *cinchonine*-salts into the corresponding *potassium*-salts was carried out in the following way. The pure

II. CINCHONINE- <i>l</i> -RHODIUM-MALONATE (+ $\frac{1}{2}$ H ₂ O).		
Wave-length in A.-U..	Observed Rotation in Degrees:	Molecular Rotation in Degrees.
5105	+ 0,65	+ 16647°
5260	0,61	15622
5420	0,57	14598
5610	0,52	13384
5800	0,45	11525
6020	0,40	10244
6260	0,36	9220
6520	0,32	8195

The solution used had 0,2538 grams of the hydrated salt in 100 grams of the liquid.



cinchonine-salt is ground with about ten times its weight of potassium-iodide, and a small amount of water added to the finely pulverized mass. The mixture is allowed to stand for 24 hours at room-temperature; the yellow liquid is then sucked off as sharply as possible from the precipitate. The reddish yellow filtrate is precipitated by 97 % -alcohol, and the pale yellow precipitate of *potassium-rhodium-malonate* thus formed recrystallised from a little water. During the evaporations on the waterbath a noticeable racemisation does not occur. It is advisable to add as little water as possible during the transformation of the *cinchonine*-salt by means of potassium-iodide, as otherwise the precipitation with alcohol is very incomplete.

3. The optically-active components are, like the racemic salt, but in yet higher degree, very soluble; at ordinary temperatures the racemic form is therefore doubtless the stabler phase in comparison with the optically-active components, so that there is no chance to execute a fission by spontaneous crystallisation¹⁾. The solutions possess a beautiful orange or bloodred colour. For a series of wave-lengths the rotations were determined in the case of both antipodes; the values obtained agreed completely in both cases with exception of the algebraic sign. The concentrations of the solutions used in these experiments must be varied over wide limits, if measurements are to be made over a greater spectral range, because the absorption of the light in layers of 20 cm. is very intensive. In the visible part of the spectrum no distinct absorption-bands occur; but at both ends it is abruptly cut off. a 1,5 % solution allows the transmission of waves from 5190 to 6800 A. U.; a 0,75 % solution the transmission of the whole red, yellow, green, and blue part of the spectrum to 4870 A. U.; a 0,37 % solution in the same way to 4420 A. U.; etc. With a 1,48 % solution these limits were found at: 5020 and 6900 A. U.

For the polarimetric determinations we used solutions which contained respectively 1,503 grams (A), 0,511 grams (B), and 0.305 grams (C) of the *laevogyrate* anhydrous salt in 100. grams of liquid; in the case of the *dextrogyratory* antipode we used a solution containing 0,804 % of the anhydrous salt. The results of these measurements are reviewed in the following table, and in fig. 2 they are plotted in a diagram. The data have been calculated with respect to the anhydrous salt.

¹⁾ Conf.: F. M. JAEGER, The Principle of Symmetry and Its Applications to All Natural Sciences, *Amsterdam*, (1917), p. 209, 210.

ROTATION-DISPERSION OF LAEVO- AND DEXTROGYRATORY POTASSIUM-RHODIUM-MALONATE.								
Wave-length in A.U.	Observed (ν) and Molecular (M) rotations of the left salt:						Observed (ν) and Molecular (M) Rotations of the right salt:	
	A.		B.		C.		D.	
	α :	M :	ν	M :	α :	M	ν :	M :
4730	—	—	—	—	$-0,19$	2436°	—	—
4870	—	—	—	—	0,19	2436	—	—
5020	—	—	—	—	0,19	2436	—	—
5105	—	—	$-0,49$	-2524°	—	—	—	—
5180	—	—	0,49	2524	0,20	2564	—	—
5260	—	—	0,50	2575	—	—	—	—
5340	—	—	0,50	2575	0,20	2564	$+0,86$	$+2614^{\circ}$
5420	$-1,50$	-2621°	0,51	2627	—	—	0,87	2645
5515	1,53	2673	0,52	2678	0,21	2692	0,88	2675
5610	1,59	2778	0,54	2781	—	—	0,90	2736
5700	1,61	2812	0,55	2833	0,22	2820	0,92	2797
5800	1,63	2847	0,56	2884	—	—	0,93	2827
5910	1,55	2708	0,53	2730	0,21	2692	0,89	2706
6020	1,47	2568	0,50	2575	—	—	0,85	2584
6140	1,44	2516	0,49	2524	0,20	2564	0,82	2493
6260	1,41	2463	0,48	2472	—	—	0,81	2462
6380	1,38	2410	0,47	2420	0,19	2436	0,74	2402
6520	1,35	2358	0,46	2369	—	—	0,78	2371
6660	—	—	0,45	2317	0,19	2436	—	—
6800	—	—	—	—	0,19	2436	—	—

From fig. 2 the very remarkable shape of the dispersion-curves may be seen, which at a wave-length of about 5800 A. U. show a maximum. For wave-lengths smaller than 5800 A. U. the rotation of the plane of polarisation increases with *increasing* wave-length, while for those greater than 5800 A. U. it diminishes with increasing

wave-lengths, as in ordinary cases. In the neighbourhood of 5800 A. U., the absorption-spectrum, however, does not manifest a single line or band. However the occurrence of such an anomalous rotation-

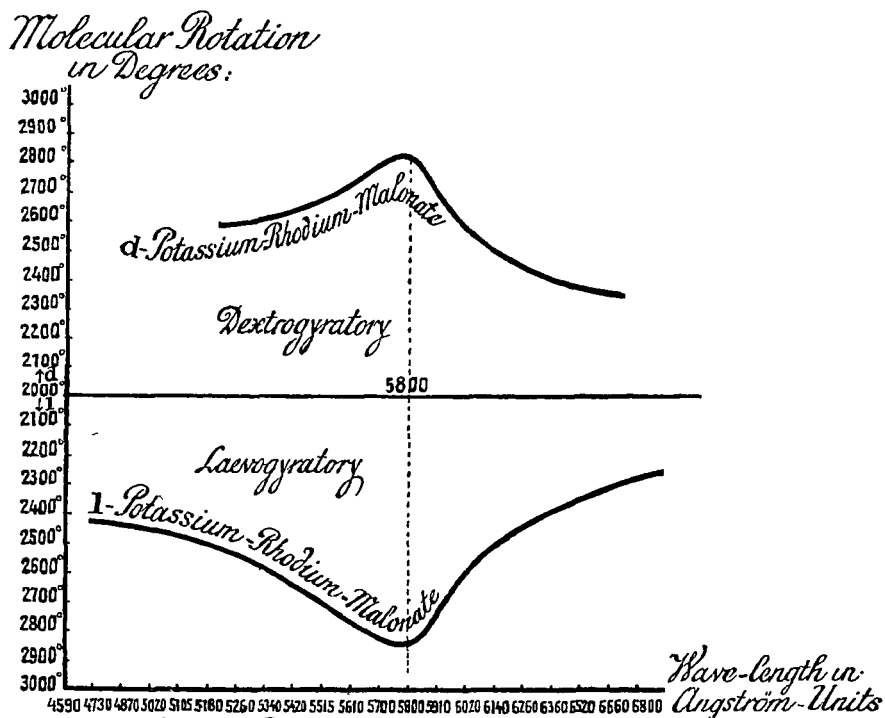
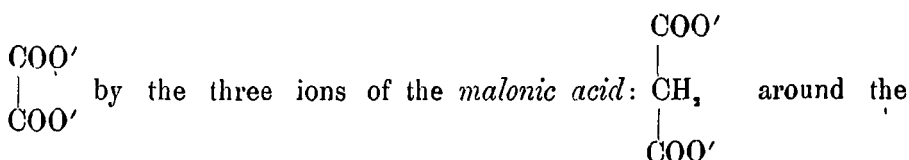


Fig 2. *Molecular Rotation Dispersion of dextro and laevogyrotary Potassium-Rhodium-Malonate.*

dispersion under these circumstances seems to be theoretically explicable, if the assumption may be made that at least two kinds of active ions are present ¹⁾.

Besides this anomalous rotation-dispersion, the whole character of which is in sharp contrast to that of the regular one, the *absolute* activity of these salts appears in general to be appreciably *smaller* than that of the analogously constituted *oxalates*, unregarded the passing through the zero-point in the case of the *oxalate* at 5970 A. U., formerly mentioned. The substitution of the *oxalic acid*-ions:



¹⁾ DRUDF, Lehrbuch der Optik, (1900), p. 382.

central *rhodium*-atom, is evidently followed by a very radical change of the character of the optical rotation of the molecule, which affects not only the magnitude, but also the algebraic sign of the molecular rotation for a number of corresponding wave-lengths. The special chemical nature of the substituents placed dissymmetrically round the central atom therefore appears to have as much influence on the magnitude of the rotation, as the chemical nature of the central metal-atom itself.

§ 4. After many attempts we were able to obtain the crystals of the optically-active salts in a measurable form. The laevogyrotory component set free from the *cinchonine*-salt of the first fractions, appeared, as already mentioned, to be extremely soluble; the solutions manifested a strong tendency to supersaturation.

By this circumstance the formation of well measurable crystals

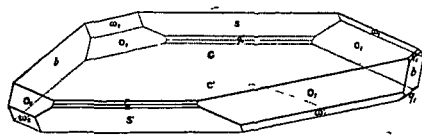


Fig. 3. *Laevogyrotory*
Potassium-Rhodium-Malonate.

is severely hindered; and, as generally occurs in such cases, the crystals finally obtained appeared to be badly formed. Because of the vicinal facets present, most crystal-faces yield multiple mirror-images, causing the angular values to oscillate often more than 30' round their mean-values. Hence it was at first thought, that triclinic crystals were present here. But the repeated determinations, in connection with the optical investigation proved to us finally, that the salt crystallises monoclinically, and more especially in forms differing from their mirror-images.

The analogy of the parameters of the optically-active salt and those of the racemic compound is most remarkable, as becomes clear, if the directions of the *a*- and *c*-axes in our former determinations are interchanged¹⁾.

Monoclinic-sphenoidical

$$a : b : c = 1,0637 : 1 : 1,1667.$$

$$\beta = 85^{\circ}27\frac{1}{4}'.$$

Forms observed: $c = \{001\}$, predominant, and mostly very lustrous; $b' = \{0\bar{1}0\}$, broad and lustrous; $b = \{010\}$, very narrow, often absent and always yielding good reflexes; $o_1 = \{111\}$, broad and lustrous; $\omega_1 = \{\bar{1}11\}$, narrower than o_1 , yielding multiple reflexes; $o_2 = \{\bar{1}11\}$,

¹⁾ F. M. JAEGER, *Proceed. R. Acad. Amsterdam*, 20. 277. (1917). There the ratio $a' : b : c$ was equal to: 1,0783 : 1 : 1,2309; with $\beta = 86^{\circ}36'$.

and $\omega_2 = \{\bar{1}\bar{1}1\}$, about equally broad, giving sharp reflexes; $s = \{\bar{1}01\}$, broad and well reflecting, but as all faces of the orthodiagonal-zone, often showing oscillating angles; $r = \{101\}$; extremely narrow and dull; $a = \{100\}$, hardly observable, in most cases totally absent; $q = \{021\}$, very narrow and dull. The external habit is that of hemimorphic thin plates parallel to $\{001\}$, with a slight elongation in the direction of the b -axis.

No distinct cleavage could be found.

Angular Values:	Observed: Calculated:	
$b' : \omega_2 = (0\bar{1}0) : (\bar{1}\bar{1}1) =$	*50° 46'	—
$c : \omega_2 = (001) : (\bar{1}\bar{1}1) =$	*60 14	—
$c : o_2 = (001) : (1\bar{1}1) =$	*55 45	—
$c : a = (001) : (100) =$	85 41	85° 27 $\frac{1}{4}$ '
$c : s = (001) : (\bar{1}01) =$	50 4	50 8
$o_1 : \omega_1 = (111) : (1\bar{1}1) =$	64 5	64 1
$s : \omega_2 = (\bar{1}01) : (\bar{1}\bar{1}1) =$	39 23	39 14
$q : c = (012) : (001) =$	ca. 31 0	30 11
$b' : o_1 = (0\bar{1}0) : (\bar{1}\bar{1}1) =$	52 49	52 58

On $\{001\}$ the directions of extinction are orientated parallel to and normal to the orthodiagonal. The crystals are not appreciably dichroitic; their birefringence is feeble. The optical axial plane is $\{010\}$, with a feeble, inclined dispersion; one axis emerges on $\{001\}$ at the border of the field.

The crystal-form of the corresponding dextrogyratory antipode is reproduced in fig. 4.

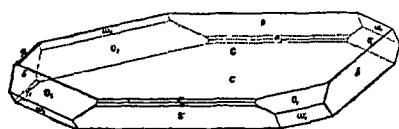


Fig. 4. *Dextrogyratory*
Potassium-Rhodium-Malonate.

The specific gravity of the crystals was at 18° C. found to be: $d_4^{180} = 2,317$; the molecular volume is therefore: 238,76, and the topical parameters become: $\chi : \psi : \omega = 6,1471 : 5,7790 : 6,7423$. Analysis proved that the

salt contains $1\frac{1}{2} H_2O$; on heating at 120° C. it is decomposed, assuming a brown colour.

If the specific gravity of the racemic compound be also taken into account, ($d_{180}^{40} = 2,251$; $V = 257,80$), it appears, in comparing it with the corresponding *potassium-rhodium-oxalate*¹⁾, that the sub-

¹⁾ The topical parameters of the *racemic malonate*, after interchange of the a - and c -axis, becomes: $\chi : \psi : \omega = 6,2484 : 5,7947 : 7,1329$.

stitution of the *malonic acid* for the oxalic acid, causes a diminution of the topical parameters in two, but an enlargement in the third direction as well in the case of the racemic as in that of the optically-active compounds.

At all events this investigation has brought full evidence of the fact, that the salts of the complex *rhodium-trimalonic acid* may also be split into optically-active components, and that the phenomena observed in their study are in agreement with PASTEUR's law in its fullest scope.

*Laboratory for Inorganic and Physical
Chemistry of the University.*

Groningen, June 1918.

Chemistry. — “Investigations on PASTEUR's Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry: VII. On optically active Salts of the Tri-ethylenediamine-Chromi-series.” By Prof. F. M. JAEGER and WILLIAM THOMAS.

(Communicated in the meeting of June 29, 1918).

§ 1. Some time ago it was already found ¹⁾ by one of us, that *racemic tri-ethylenediamine-chromichloride*: $\{Cr(Ene)_3\}Cl_3 + 3H_2O$, was completely isomorphous with the corresponding *cobalti-* and *rhodium-* compounds. We prepared this salt according to a method indicated by PFEIFFER ²⁾, from the *tripyridyl-chromi-chloride*: $\{Cr(Pyr.)_3\}Cl_3$ by heating this product with ethylenediamine, and subsequent purification. Then it was separated into its optical antipodes by means of *sodium- α -camphor-nitronate* ³⁾, and these were obtained in this way as the pure *iodides*.

In this fission 6 grams of the *racemic* salt were dissolved in 20 ccm water, and a solution of 6 grams of pure *sodium- α -camphor-nitronate* in 15 ccm water subsequently added. A pale yellowish precipitate of *d-triethylenediamine-chromi-d-camphornitronate* is formed; it is sucked off and to the mother liquid 2 more grams of *sodium- α -camphornitronate* are then added, and the solution allowed to stand for a few hours, when some more of the precipitate is separated.

After filtration the mother liquid was used for preparing the corresponding *laevogyrate* component. The precipitate, thoroughly washed with alcohol and ether, was ground in a mortar with an excess of finely pulverised *sodium-iodide*, some water added, and the dark yellow liquid sucked off from the precipitate, which was well washed with alcohol and ether, dissolved in a small quantity of water, and again precipitated by an excess of *sodium-iodide*.

The mother liquid formerly mentioned, containing the *camphornitronate* of the *laevogyrate* salt, was precipitated by addition of 5 grams *sodium-iodide*. The precipitate formed appeared, after being thoroughly washed, to be the *racemic iodide*. The remaining

¹⁾ F. M. JAEGER, Proceed. R. Acad., Amsterdam. **20**. 247. (1917).

²⁾ P. PFEIFFER, Zeits. f. anorg. Chemie, **24**. 282, 286. (1900).

³⁾ A. WERNER, Ber. d. deutsch. Chem. Ges. **45**. 865. (1912).

mother liquid, however, was now treated in an analogous way with 8 grams of sodium-iodide; the precipitate appeared to be this time the *laevogyrate triethylenediamine-chromi-iodide*. It is difficult to obtain these iodides in well measurable crystals, and they are moreover ordinarily very small.

§ 2. The rotation-dispersion of these salts was determined in the usual way, already frequently indicated. As the orange coloured liquids already manifested a very appreciable absorption of the transmitted light in layers of 20 c.m. thickness, the measurements for the limiting wave-lengths had to be made with very dilute solutions. These measurements agreed very well with those made in the case of more concentrated solutions, so that for all solutions we have given the mean values of the molecular rotations obtained. In the case of the dextrogyratory component solutions were used, containing 1,0133 grams (A), 0,5070 grams (B), 0,2535 grams (C), and 0,0325 grams (D) of the anhydrous salt respectively in 100 grams

*Molecular Rotation
in Degrees:*

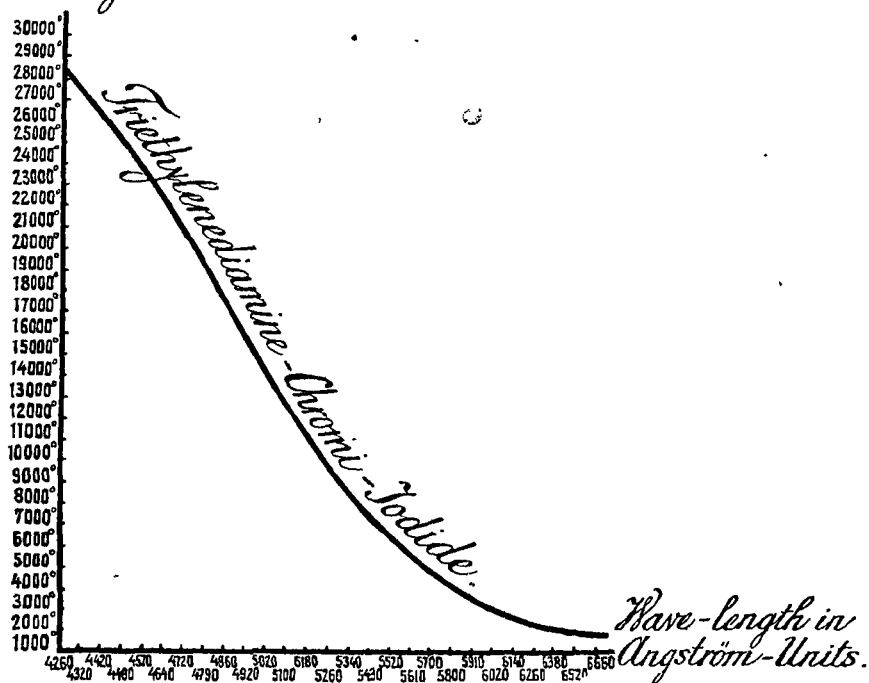


Fig.1. *Molecular Rotation-Dispersion of the Optically active
Triethylenediamine-Chromi-Iodides.*

ROTATION-DISPERSION OF THE OPTICALLY-ACTIVE TRI-ETHYLENEDIAMINE- CHROMI-IODIDES.		
<i>Wave-length in A. U.:</i>	<i>Observed Rotation:</i>	<i>Molecular Rotation: (positive and negative)</i>
4260	0.30 (D)	28263°
4320	0.29 <i>id.</i>	27321
4420	0.27; 0.35 (D, K)	25385
4480	0.26; 0.34 <i>id.</i>	24552
4570	0.25; 0.33 <i>id.</i>	23619
4640	0.23; 0.31 <i>id.</i>	22053
4720	0.22; 0.29 <i>id.</i>	20858
4790	0.20; 0.28; 0.27 (D, I, K)	18652
4860	0.18; 0.26; 0.24 <i>id.</i>	17610
4920	0.16; 0.23; 0.21 <i>id.</i>	15128
5020	0.14; 0.40; 0.21 (D, H, I)	13267
5100	0.97; 0.36; 0.18 (C, H, I)	11714
5180	0.88; 0.32; 0.16 <i>id.</i>	10579
5260	1.60; 0.79; 1.07 (B, C, G)	9647
5340	1.43; 0.71; 0.95 <i>id.</i>	8578
5430	1.27; 0.64; 0.84 <i>id.</i>	7634
5520	1.12; 0.57; 1.46; 0.72 (B, C, F, G)	6692
5610	0.96; 0.48; 1.22; 0.62 <i>id.</i>	5741
5700	1.63; 0.81; 0.41; 2.18 (A, B, C, E, F, G)	4891
5800	1.33; 0.67; 0.33; 1.85 <i>id.</i>	4093
5910	1.15; 0.56; 0.28; 1.55 <i>id.</i>	3422
6020	0.96; 0.47; 0.24; 1.30 <i>id.</i>	2912
6140	0.86; 0.43; 0.22; 1.16 <i>id.</i>	2621
6260	0.77; 0.38; 0.19; 1.04 <i>id.</i>	2328
6380	0.70; 0.35; 0.18; 0.94 <i>id.</i>	2133
6520	0.65; 0.32; 0.16; 0.88 <i>id.</i>	1951
6660	0.61; 0.30; 0.15; 0.82 <i>id.</i>	1820

For these last wave-lengths only the rotations of the solutions A, B, C, and E are reviewed.

of the liquid; in the case of the laevogyrate antipode the six different solutions employed contained 1,3512 grams (*E*), *half* or a *quarter* of this (*F*, *G*) in 100 grams of the liquid, and 0,0927 grams (*H*), 0,0464 grams (*I*), and 0,0232 grams (*K*) respectively of the anhydrous salt in 100 grams of the liquid.

The dispersion-curve for the molecular rotation, shewn by measurements is plotted in the diagram (fig. 1). It has much analogy with that of the corresponding *cobalti*-salts, but only a slight analogy with that of the *triethylenediamine-rhodium*-compounds.

Probably the magnitude of the rotation for corresponding wave-lengths in the case of these analogously built complex ions greatly depends on the magnitude of the *atomic volume* of the central metallic atom, in such a way that the rotation appears *higher*, if the atomic volume of the metal is *smaller*. As for instance:

COMPLEX SALT:	MOLECULAR ROTATION OBSERVED:	ATOMIC VOLUME OF THE METAL
{Co (Eine) ₃ } I ₃ + H ₂ O.	$M_{5800} = 7230^\circ$; $M_{5100} = 21580^\circ$; $M_{6600} = 2114^\circ$	6.76
{Cr (Eine) ₃ } I ₃ + H ₂ O.	$M_{5800} = 4093^\circ$; $M_{5100} = 11714^\circ$; $M_{6600} = 1880^\circ$	7.72
{Rho (Eine) ₃ } I ₃ + H ₂ O.	$M_{5800} = 3125^\circ$; $M_{5100} = 3965^\circ$; $M_{6600} = 2243^\circ$	8.50

The values for $\lambda = 6600$ A. U., are mentioned at the same time for the purpose of demonstrating that this antiparallelism of rotations and atomic volume is surely *not* true for *all* wave-lengths: for rays of *great* wave-length, as e. g. in the visible red part of the spectrum, — the rotation of the *Rho*-salt surpasses even that of both the other salts; only in the domain of appreciable dispersion, is the said regularity met with.

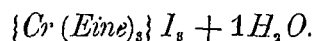
As regards the absorption, we were able to state the following. In a layer of the solution of 20 c.m., a liquid containing.

1,1212% of the salt, allows the passage of all red and yellow rays up to those of 5380 A.U.
 0,5606% " " " " " " " " " " " " " " " " 5220 A.U.
 0,2803% " " " " " " " " " " " " " " " " 5030 A.U.
 0,1402% " " " " " " " " " " " " " " " " 4850 A.U.
 0,0701% " " " " " " " " " " " " " " " " 3940 A.U.

§ 3. Numerous attempts were made to win these *chromi*-salts in well measurable crystals, and to investigate the validity of PASTEUR's law also in this case. But a heavy impediment in reaching this aim was created not only by the facility with which those salts decompose in solution, especially under the influence of the light, — but also

by the great solubility of these salts, inducing us always to work with only small volumes of concentrated solutions, from which good crystals are ordinarily deposited with difficulty. For the same reason the transformation of the iodide into the chloride or bromide could not be of any use, so that these for our purpose so very important salts, could not be made use of in this case.

RACEMIC TRIETHYLENEDIAMINE-CHROMI-IODIDE.



On slow crystallisation this compound presents itself in the form of very small, orange, apparently octahedral crystals. Crystallisation must occur in the dark, because this salt, in the same way as all the *triaethylenediamine-chromi*-salts, becomes violet under the influence of the light. Also increase of temperature must be avoided, because the solutions change from an orange colour to a dark reddish violet by the transformation into salts of the violet *aquo*-type. The crystals measured were not larger than a pinhead, and often they were disfigured and distorted in rather a strange way. Some of them showed under the microscope the appearance of fig. 2a, without

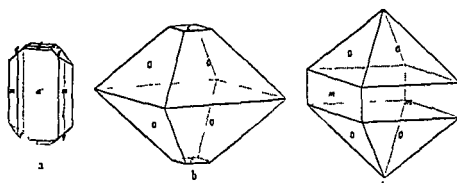


Fig. 2. *Racemic Triethylenediamine-Chromi-Iodide*. (+ H_2O).

it being possible however to determine the MILLERIAN indices of their facets with complete certainty; the crystals pictured in fig. 2b and 2c manifested however some measurable forms.

Rhombic-bipyramidal.

$$a:b:c=0,8632:1:0,8652.$$

The crystals are pseudo-tetragonal, and perfectly isomorphous with the corresponding crystals of the *cobalti*-¹⁾, and of the *rhodium*-²⁾ compound, just as we were able to prove this before in the case of the trigonal *chloride* of this series ³⁾. The colour of the crystals was orange or red; by partial loss of water of crystallisation, they sometimes get locally yellow and opaque.

¹⁾ F. M. JAEGER, *Proceed. R. Acad. Amsterdam*, 18. 62 (1915).

²⁾ F. M. JAEGER, *Proceed. R. Acad. Amsterdam*, 20. 250. (1917)

³⁾ F. M. JAEGER, *Proceed. R. Acad. Amsterdam*, *ibid.* 247. (1917).

The forms observed are: $o = \{111\}$, great and very lustrous; $c = \{001\}$, small, but well developed and yielding good reflections; $m = \{110\}$, broad, but commonly with curved and rudimentary facets, and thus practically not well measurable. Probably also a form $q = \{021\}$ occurs, and in the case of the crystals of fig. 2a doubtless $a = \{100\}$, as a broad pinacoidal face, and $r = \{h\ o\ k\}$.

<i>Angular values:</i>	<i>Observed:</i>	<i>Calculated:</i>
$c : o = (001) : (111) =$	$52^\circ\ 56'$	—
$p : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$62\ 49$	—
$o : o = (111) : (1\bar{1}\bar{1}) =$	$74\ 10$	$74^\circ\ 8'$
$o : o = (111) : (\bar{1}\bar{1}\bar{1}) =$	$74\ 27$	$74\ 19$

No distinct cleavability was found.

There cannot be the least doubt about the complete isomorphism with the corresponding *Co*- and *Rho*-salt:

Cr-salt $a : b : c = 0,8632 : 1 : 0,8652$.

Co-salt $a : b : c = 0,8700 : 1 : 0,8699$.

Rho-salt $a : b : c = 0,8541 : 1 : 0,8632$.

Up till now we have had no opportunity to prove this isomorphism also in the case of the optical antipodes, because no suitable crystals could be obtained. There can be however no doubt, that the said relation also exists in this case.

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Groningen, June 1918.

Anatomy. — "*The Involution of the Placenta in the Mouse after the Death of the Embryo*". By Dr. A. B. DROOGLEEVER FORTUYN. (Communicated by Prof. J. BOEKE).

(Communicated in the meeting of June 29, 1918).

In various species of mammals which are pregnant with several embryos at the same time it accidentally occurs that one or more embryos die before birth. The subsequent fate of the placenta has been controlled in only a few cases and it appears to be intimately connected with the structure of the placenta. Now this structure in the mouse considerably deviates from that in many other mammals. So it seemed to be worth while to investigate in this animal too, as has not yet been done, the involution of the placenta after interruption of the pregnancy. For this purpose the uteri of 8 mice were at my disposal containing together besides many normal egg-chambers 20 egg-chambers without an embryo. Judging from the degree of development of the normal egg-chambers one of the 8 mice had been killed on the 13th day of the pregnancy, one on the 15th, four on the 16th, one on the 17th and one on the 18th day.

The 20 empty egg-chambers are more fully described in a paper that I offered to the "Tijdschrift der Nederlandsche Dierkundige Vereeniging". Here I shall only communicate the results in a general way.

Never was any other trace of the embryo left than some free cells which could not be duly recognised. Many portions of the foetal membranes survived the embryo, but they did not all do so during the same time. So among the empty egg-chambers some groups could be recognised with more or less remainders of the foetal membranes.

In the first group the giant-cells (in the mouse trophoblastic cells which are greatly enlarged and have become independent) and the membrane of REICHERT were left and moreover parts of the ectoplacental cone and of the proximal or distal entoderm of the yolk-sac or of both. The proximal entoderm of the yolk-sac could be well recognised by the appearance of the cells, but it had always been broken into pieces. The distal entoderm of the yolk-sac sometimes lined large pieces of the membrane of REICHERT internally; besides free cells of it occurred. The ectoplacental cone

never inclosed embryonic blood-vessels, but sometimes some connective tissue of the allantois entering the ectoplacental cone together with the large blood-vessels. Always the cells or the syncytium of the ectoplacental cone could be recognised. In some cases they changed into young giant-cells, which in normal circumstances too can originate from cells of the ectoplacental cone. Often spaces filled with maternal blood lay between the cells of the ectoplacental cone, as is the case in normal egg-chambers. REICHERT's membrane could easily be recognised as the homogeneous membrane that develops beneath the trophoblastic epithelium when it changes into free giant-cells. After the disappearance of the embryo the contraction of the uterine wall had pressed the greater part of the ectoplacental cone into the space previously occupied by the embryo. Moreover this contraction had folded REICHERT's membrane. Sometimes this membrane had much diminished in size, but it always showed the aperture through which the cells of the ectoplacental cone previously cohered with the allantois.

Generally the giant-cells very clearly showed their power to ingest erythrocytes and other portions of the maternal decidual tissue, but they had hardly changed in this group. This was not so in the second group of empty egg-chambers where, as to the foetal elements, only the distal entoderm of the yolk-sac, the membrane of REICHERT and the giant-cells were left. There several of the latter cells had grown out till they reached dimensions that were extraordinary even for giant-cells. In normal egg-chambers it is the task of the giant-cells to attack the decidual tissue and the maternal blood and to leave part of the ingested food to the embryo. As soon as they have been loosened from the trophoblastic epithelium or the ectoplacental cone they lead an independent life. After the death of the embryo the only change is the fact that of course the giant-cells can provide no longer any food to the embryo. They keep all to themselves and consequently thrive extraordinarily. In all directions they acquire the same dimensions, as the pressure of the embryo which in normal egg-chambers flattens them much, has been suspended. Therefore the space occupied by the giant-cells is much larger than in normal egg-chambers. Their number only seems to me to be larger, because they are not dying away so soon as in normal egg-chambers, not because more of them would have developed. Yet here too the fate of the giant-cells is to die away. This is more conspicuous in another group of empty egg-chambers where giant-cells are the only foetal element that is left. Especially here one sees the body of the giant-cell losing its affinity for the dyes

and dissolving, leaving the naked nucleus behind. Afterwards the nucleus submits to the same fate.

The giant-cells have not been able to consume the whole layer of decidual tissue before they disappear. Yet this layer must be removed if the normal situation of the uterine-wall is to return. Therefore the giant-cells are supported by another type of cells, apparently amoeboid wandering cells with phagocytal qualities. These cells are of a hitherto unknown kind and in normal egg-chambers they do not occur, not even post partum. Their shapes and sizes are very variable. They have a nucleus which generally lies ex-centrally and sometimes two or more nuclei. Their cytoplasm stains remarkably intensely with eosin dissoluble in water, whereas eosin dissoluble in alcohol stains them, it is true, but not extraordinarily. I propose to call these cells eosinophilous phagocytes. About their origin nothing is known to me, but I think that they are maternal cells. The eosinophilous phagocytes were lacking only in one of the twenty empty egg-chambers, and this one obviously had been preserved within a day after the death of the embryo. In the first place they appear in small groups between the group of giant-cells and the layer of unattacked decidual tissue. These groups enlarge into constantly thicker layers, which are always situated either between the decidual tissue and the giant-cells or between the former and the uterine cavity. The eosinophilous phagocytes attack only the maternal decidual tissue and not the giant-cells and they continue to do so after the disappearance of the giant-cells. So a fourth group of empty egg-chambers exists where one sees no foetal rests at all, but only eosinophilous phagocytes which remove the layer of decidual tissue, which has in the mean time greatly diminished in size. I could not observe the disappearance of the eosinophilous phagocytes.

As is known, in egg-chambers of the mouse the uterine cavity disappears at the mesometrical side of the embryo to extend at the antimesometrical side of the embryo starting therewith from the portions of the uterine cavity that are lying between the egg-chambers. Before the parts of the new uterine cavity reach one another in the middle of the egg-chamber, which occurs on the 17th day of the pregnancy, a more or less thick partition of decidual tissue in the egg-chamber separates the parts of the new uterine cavity, which approach one another. Now this partition can be found in many empty egg-chambers, but in some it has been ruptured, in others it is attacked by eosinophilous phagocytes, and in still others it has been removed prematurely by eosinophilous phagocytes.

I cannot even guess the cause of the death of the embryo, but I observed that the embryo may perish at different ages. At least I think I have met with a case where this occurred on the 8th day and with another where this occurred on the 16th day. He who disposes of younger specimina (my youngest embryos were of the end of the 13th day) probably will also find eggs that have perished before the 8th day. Moreover it appears that in one and the same uterus embryos may die away at very different ages. I discovered in the same uterus one of the empty egg-chambers with the smallest and one with the greatest quantity of foetal rests, and I conclude that one embryo had been dead a much longer time than the other.

Leiden.

Anatomisch Kabinet.

Physics. — “*The Limit of Sensitiveness in the String galvanometer.*”

By Prof. I. K. A. WERTHEIM SALOMONSON.

(Communicated in the meeting of June 29, 1918).

In EINTHOVEN's stringgalvanometer the deflectional constant is subjected to the same law as holds good in the movable needle- and movable coil galvanometer: it is proportional to the square of the periodic time of the movable part. In the string instruments the duration of the oscillations is modified by altering the tension of the string. The sensitiveness finally depends on this tension as well as on the dimension and material of the string, and lastly on the strength of the magnetic field.

The tension of the string can only be altered within certain limits. The upper limit is given by a tensile stress exceeding the elastic strength. The lower limit is the total absence of tension. But even when no pull is exerted, the string can still vibrate transversally. The frequency of the vibrations it then makes, is a function of the dimensions of the wire and two properties of the material i.e. density and the elasticity-modulus, and may be represented by

$$N = \frac{m^2 d}{8\pi l^2} \sqrt{\frac{E}{g}} \dots \dots \dots (1)$$

in which N denotes the frequency, l the length, d the diameter of the string, g being the density and E YOUNG's modulus, whereas m is the smallest root of the transcendental equation $\cos m \cosh m = 1$. The value $m = 4.730 \dots$ (RAYLEIGH On sound I. Art. 174).

As we may discard the influence of temperature on the elasticity, this formula gives the lowest frequency for transverse vibrations obtainable in strings, which in a definite material and with given dimensions cannot be lessened. We may therefore say that the periodic time of the string in the EINTHOVEN galvanometer, and consequently the sensitiveness of the latter is limited by the impossibility to lessen the frequency; and as the elasticity of the material is responsible for transverse vibrations which might occur in a perfectly relaxed wire, the true limit of the sensitiveness is to be found in the elasticity, and as we shall see also in the density and specific resistance of the material of the strings.

With the formula (1) we can always calculate the minimum of

the frequency of the transverse vibrations of the string, if we know its dimensions and the material of which it is made. In table I a few numerical data are given regarding various materials which may be used for making strings. In this table the length is taken as 10 cm and the diameter as one micron (10^{-4} centimeter).

TABLE I.

	$E \frac{1}{98100000}$	g	$N/\text{sec.}$	T
<i>Cu</i>	11000	8.9	0.3100	3.32"
<i>Ag</i>	7500	10.5	.2356	4.25
<i>Au</i>	7500	19.2	.1724	5.80
<i>Al</i>	6750	2.7	.4408	2.27
<i>Pt</i>	16500	21.4	.2448	4.08

It is very difficult to measure directly the vibrations per second in wires of 1 micron diameter. The air resistance in this case is so considerable as to cause the movement to come to a dead stop. We should have to examine such strings in a perfect vacuum. Furthermore we are not able to make wires of 1 micron except in platinum, and perhaps in aluminium and gold. Silver wires of 1 micron are as yet not attainable. But the dimensions used in this table and the figures in the last columns permit us to calculate in a simple way, e.g. with a slide rule, any periodic time when other dimensions are given: the vibration time being proportional to the square of the length and inversely proportional to the diameter.

A wire clamped at the end without any tensile stress will sag under the influence of a load P , uniformly distributed over the total length. The maximum deflection h will be

$$h = \frac{P l^3}{EI 384} \dots \dots \dots (2)$$

where I represents the axial moment of inertia of a section of the wire. As for a round wire $I = \frac{\pi d^4}{64}$, we get

$$h = \frac{P l^3}{6\pi E d^4} \dots \dots \dots (3)$$

In the string galvanometer the transverse load P is equal to Hil Dynes, if H be the strength of the magnetic field in Gauss, i

the current strength in Webers ($=10$ ampere) and l the length of the wire in centimeters. If we put this value for P in 3):

$$h = \frac{H l^4}{6\pi E d^4} \dots \dots \dots (4)$$

giving the deflection of the middle of a string clamped at the ends without tension, and of a length l and a diameter d , placed in a magnetic field H , as soon as a current of i Weber passes through the string. We need hardly insist on the fact that this formula gives the absolute limit for the sensibility for small currents.

The next table II shows this limit for strings made of different materials. For the dimensions of the string we again take 10 cm and 1 micron, for the current-strength 10^{-13} Weber (10^{-12} ampere), for the field intensity 10000 Gauss. The last column gives the deflection in millimeters if the absolute deflection of the middle be magnified 1000 times. We can use the figures of this column, if we wish to calculate the possible deflection with strings of other dimensions in a field of a different strength, and when observed magnified to another scale. The deflections are proportional to the fourth power of the length and the inverse of the diameter of the string.

TABLE II.

	$E \frac{1}{98100000}$	$\frac{Hi}{6\pi E}$	De- { $V = 1000 \times, d = 1\mu$ flection { $l = 10 \text{ cm}, i = 10^{-13} \text{ WEBER}$ }
<i>Cu</i>	11000	4916.10 ⁻²⁰	49.16 mm
<i>Ag</i>	7500	7210.10 ⁻²⁰	72.10 "
<i>Au</i>	7500	7210.10 ⁻²⁰	72.10 "
<i>Al</i>	6750	8012.10 ⁻²⁰	80.12 "
<i>Pt</i>	16500	3277.10 ⁻²⁰	32.77 "

The figures in the last column may also serve to calculate figures for existing strings. With an aluminium string of 2 microns and 56 millimeters' length in a field of about 16000 Gauss, I found a deflection of 0.40 millimeters for 10^{-12} ampere, which took place in about 20 seconds. From the figure in the table we calculate that the deflection ought to be 1.20 millimetres. In EINTHOVEN's publications on silvered quartz fibres we equally find figures about the possible sensibility, the order of which does not disagree greatly with the theoretically possible deflection if we take for the sensitiveness with silvered quartz fibres the same value as in the case of silver

wires. The same may be said about my own observations with quartz fibres. Generally the deflection actually observed is some 3—5 times smaller than we ought to expect from the theory. The explanation is found when we consider the behaviour of silver strings of 16.5 microns and of copper strings of 15 microns diameter. These wires still give vibrations when the tension is reduced as far as possible, but in every case the frequency is about 1.5 to 2.1 times greater than that calculated from formula (1). With a silver string of 16.5 μ and 53 mm length I could not reduce the frequency under 20 per second instead of 14 as calculated. When magnified 47 times 1 microampere caused a deflection of 1.31 millimeter; the string being placed in a field of 14000 Gauss. The theoretical value is 3.7 millimetres with 14 vibrations, which would come to about 1.8 millimeters with 20 vibrations. As there may be a slight difference between the figure taken for the diameter and the actual diameter, the agreement may be considered not unsatisfactory, the more so as the value of E must also be considered as merely an approximate one. Finally we must state that the string was not an entirely straight one, and that in being mounted it had probably retained a slight torsional stress.

In a few other observations of the same kind with wires of different material I found a deflection of 8.1 mm where 9.1 mm was expected; also one of 36 mm, where 40 had been calculated. Generally speaking, the agreement was by far the best with the thicker wires. Yet in all cases the agreement was close enough to allow an extension of the theory to the sensitiveness for small potential differences.

From the formula (4) we find an expression for the sensibility for small potential differences by dividing both parts by w , the resistance of the string:

$$\frac{h}{w} = \frac{Hl^4}{6\pi E d^4 w} \dots \dots \dots (5)$$

This formula gives the deflection in centimeters of the middle part of the string when a potential difference of 10 Volts is applied to the terminals. But with this formula we have not taken count of the damping. The movement of the string in the EINTHOVEN galvanometer is damped partly by air friction, partly by electromagnetically generated counter-electromotive force. In the following cases we shall consider only the electromagnetic damping; which with thick wires greatly exceeds the air resistance. As the electromagnetic damping is caused by the number of the lines of force

cut by the string during its movement, the form taken by the string in its deflected condition is of the greatest significance as well as the strength of the magnetic field. A string under tension deflected in a homogeneous magnetic field takes the form of a parabola. In that case the damping factor is

$$D = \frac{2}{3} \frac{H^2 l^2}{w \cdot 10^9} \dots \dots \dots (6)$$

Whenever the string would take another form whilst being deflected, the factor $\frac{2}{3}$ would take another value. This factor represents the mean deflection taken over the whole string as compared with the maximum deflection. A perfectly relaxed string, clamped at the ends, and uniformly loaded takes the form given by the formula

$$y = \frac{P}{EI} \frac{l^3}{24} \left(\frac{x^2}{l^2} - 2 \frac{x^3}{l^3} + \frac{x^4}{l^4} \right) \dots \dots \dots (7)$$

in which y gives the deflection for a point at distance x from the end. If we put $x = \frac{1}{2}l$ we get the deflection for the middle of the string, which has already been given in formula (2). In order to find the mean deflection we integrate (7) over the whole length:

$$y \int_0^l dx = \frac{P}{EI} \frac{l^4}{720} \dots \dots \dots (8)$$

Comparing (2) and (8) we find

$$y \int_0^l dx / y_{\max} = \frac{8}{15}$$

so that we may state

$$D = \frac{8}{15} \frac{H^2 l^2}{w \cdot 10^9} \dots \dots \dots (9)$$

Taking M as the mass of the string, we can always represent the time of vibration as

$$\frac{1}{N} = 2\pi \sqrt{\frac{M}{K}} \dots \dots \dots (10)$$

if K be a lateral force and if we suppose the damping to be very slight. If the string should make critically damped vibrations, the damping would be

$$D = \sqrt{4MK} \dots \dots \dots (11)$$

Eliminating K from (10) and (11) we get, in connection with (9)

$$4\pi MN = \frac{8}{15} \frac{H^2 l^2}{w \cdot 10^9} \dots \dots \dots (12)$$

In (12) we substitute for the mass $M = \pi d^2 l \rho$ and for the resistance $w = \frac{l \rho}{\pi d^2}$, giving:

$$H^2 = 7.5 \pi 10^3 \cdot g \rho N. \quad (13)$$

which shows a simple relation between the allowable and necessary strength of the magnetic field, the frequency and the density and resistivity of the material. If we were at liberty to choose any figure for N , the length and the thickness of the string would seem to be of no consequence. But we started from the premise that the frequency should be as small as possible with a string of predetermined length and thickness, and elasticity. Hence we must put the value for N taken from (1) in (13) giving

$$H = 1.45 10^5 \sqrt{\frac{d}{l^2} \sqrt{g E \rho^2}}. \quad (14)$$

Now we can substitute this value for H in (5) and by likewise substituting $w = \frac{\rho l}{\pi d^2}$ we arrive at a formula for the sensibility for potential differences:

$$\frac{h}{w} = 6040 \frac{l^2}{d \sqrt{d}} \sqrt{\frac{g}{E^3 \rho^2}}. \quad (15)$$

This expression for h/w gives the extreme limit for the sensibility of a completely relaxed string in a magnetic field of a strength exactly calculated to render the movements of the short-circuited string critically damped. The volt-sensibility increases by l^2 and decreases by $d \sqrt{d}$. It also depends on the density, resistivity, and elasticity of the material. In table III we find the constants for different materials and in the fourth column the comparative "material-factor" for each material. These have been multiplied by 10^5 so as to indicate deflections per microvolt with strings of 1μ

TABLE III.

	g	$E \cdot \frac{1}{98100000}$	$\rho \cdot 10^6$	$6040 \cdot \sqrt{\frac{g}{E^3 \rho^2}} \cdot 10^5$	H	N/sec
<i>Cu</i>	8.9	11000	1.62	774	325	0.3100
<i>Ag</i>	10.5	7500	1.75	1034	320	0.2356
<i>Au</i>	19.2	7500	2.20	1073	417	0.1724
<i>Al</i>	2.7	6750	2.87	622	284	0.4408
<i>Pt</i>	21.4	16500	9.40	295	1078	0.2448

diameter and 10 c.m. length with a microscopic magnification of 1000 times. The next column shows the strength of the field H in Gauss, and the last column contains once more the frequencies.

Gold fibres, if critically damped, will give a larger deflection than strings of any other material, but of the same dimensions. The time of vibration, and consequently the time of deflection is larger than with other strings. Hence we cannot easily compare the results. This table is only useful if we wish to calculate the possible deflection with strings of other dimensions. In order to get comparable figures we shall have to consider strings of the same diameter, which have the same vibration time. A formula for this case can be given by calculating

$$\frac{h}{w} \cdot N = 5400 \frac{1}{\sqrt{d}} \cdot \frac{1}{\sqrt{Eq^2g}} \dots \dots \dots (16)$$

This formula represents the deflection caused by 10 Volts through a string of a diameter d , completely relaxed, and vibrating once a second, whilst placed in a magnetic field of a strength, sufficient to cause the movement of the string to be entirely damped. In this case the length is predetermined for any material by the condition that the frequency is one per second.

In table IV we give a few figures which can be calculated by this last formula.

TABLE IV.

	$\frac{5400}{\sqrt{Eq^2g}}$	H	l	w	Deflection per μV . with $d = 1\mu$. and $V = 1000 \times$
<i>Cu</i>	2410	590	5.56	1150	241 mm
<i>Ag</i>	2448	658	4.85	1080	245 "
<i>Au</i>	1878	997	4.15	1163	188 "
<i>Al</i>	2757	426	6.63	2430	276 "
<i>Pt</i>	726	2190	4.95	5940	73 "

From this table we see that aluminium is the best material for strings in an EINTHOVEN galvanometer if used for the measuring of small potential differences. A string of 1μ , completely relaxed and 6.65 cm in length, gives vibrations of one second. With it we can get a deflection of 276 mm for 1 microvolt, if the field be adjusted at 997 Gauss; and the microscopic magnification amounts

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to 1000 times. If the string were placed in a perfect vacuum the movement would be critically damped. Silver follows with 245 mm deflection if the length be 4.85 cm. Copper requires a longer string viz. of 5.56 cm and gives about the same deflection. Practically we shall have to make our choice between aluminium, silver, or copper, whenever we want a high sensitiveness for small potential differences with a critically damped movement. From the formula we conclude that with a given material the thinner the string the higher will be the sensibility for small potential differences.

Finally we shall have to consider one other possibility for rendering the voltsensibility as high as possible.

We take again the case of a perfectly relaxed string, clamped at the ends. If the weight P be uniformly distributed over the entire length l , we must use the formula (1). But if the string is loaded in the middle only with the weight P , the deflection will be exactly twice as large:

$$h = \frac{P}{EI} \frac{l^3}{192} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

If we put the string, of a length l in a stronger magnetic field H' but of a very short length λ so as to make $Hl = H'\lambda$, and if we suppose λ to be very small as compared with l , we shall come very near the conditions represented by the last formula (17). Especially if we use strings of not too small a diameter there will be scarcely any difficulty of making the magnetic field 10—20 times stronger and the string 10—20 times longer than the field. In this case we practically double the deflection, but at the same time the damping will have become too great. The damping factor will have become nearly 1.0 instead of 8/15. Hence the magnetic field must be made $\sqrt{2}$ times weaker. Finally the sensibility for small potential differences will become only $\sqrt{2}$ times greater.

Anatomy. — "*The egg-cleavage of Volvox globator and its relation to the movement of the adult form and to the cleavage types of Metazoa.*" By Dr. H. C. DELSMAN. (Communicated by Prof. J. BOEKE).

(Communicated in the meeting of June 29, 1918).

For the zoologist still more than for the botanist *Volvox* is an interesting object. Already in this organism, where it is still dubious whether we have to consider it as a plant or as an animal, we see indicated the main lines along which the phylogenetic development of the Metazoa has taken its course. BUTSCHLI¹⁾ rightly observes that *Volvox* is no longer to be considered as a colony of Protozoa, but as a pluricellular organism of simple structure. Not only do the cells communicate with each other by plasmodesms, forming thus one single mass of protoplasm, but also there is a difference between mortal somatic and potentially immortal propagation cells as is characteristic of Metaphyta and Metazoa. Between these two *Volvox* holds an intermediate position, reminding one more of the former by the possession of chlorophyll but pointing more in the direction of the animal kingdom by the rest of its organisation.

Long ago the first stage of development in Metazoa, the blastula, has been compared to *Volvox* and was termed by HUXLEY²⁾ e.g. "the animal Volvox". The resemblance afterwards appeared to be still greater than HUXLEY could have suspected, for *Volvox* is by no means a homaxone sphere rotating indiscriminately in all directions, but shows a distinct opposition between an animal and a vegetative pole. The line joining them can be described as the main axis of the organism, which is not strictly globular, but a little elongated in the direction of the main axis. With the animal pole directed forwards it swims with a rotary movement round the main axis just as is the case with the pelagic larvae of lower Metazoa and also still of *Amphioxus*. At the animal pole the cells are smaller and further from each other and contain also less chlorophyll than those at the vegetative pole which are darker green, by reason of the higher

¹⁾ O. BUTSCHLI, 1883—1887, Protozoa II, p. 775, in BRONN's Klassen und Ordnungen des Thierreichs.

²⁾ T. H. HUXLEY, 1877. The Anatomy of Invertebrated Animals, p. 123, 678.

proportion of chlorophyll, and communicate by more numerous and broader plasmodesms. The cells at the animal pole each contain a red stigma as characteristic of flagellates sensible to light (to which also the Volvocineae belong), whilst those at the vegetative pole are lacking them. The two kinds of cells pass quite gradually into each other. The propagation cells are restricted to the vegetative half. Any one having an opportunity to study *Volvox* can easily verify all this.

The propagation occurs either by means of egg-cells and spermatozoa, or parthenogenetically by so-called parthenogonidia. The latter mode occurs, just as in Rotatoria and Infusoria, during a number of generations, the former mode at the close of such a period, the encysted egg being the result. The cleavage stages of the egg and of the parthenogonidia in which development proceeds in a similar manner, exhibit again a striking resemblance to those of Metazoan eggs. The figures given of these stages for *Volvox*, *Pleodorina*, *Eudorina*, *Pandorina*, and *Gonium*, remind one especially of stages of the spiral cleavage type, which probably we may designate as the original cleavage type of the Zygoneura or Protostomia, and which is still found with Polyclads, Nemertines, Polychaetous Annelids and most Molluscs. It therefore seemed to me very interesting to find out how far the cleavage of *Volvox* corresponds to the spiral type. The statements made by former investigators appear to be insufficient and too contradictory to answer this question in a satisfactory way¹⁾.

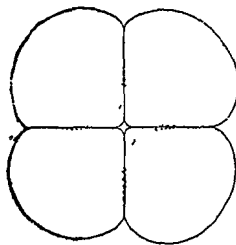


Fig. 1. *Volvox globator*, parthenogonidium, four-celled stage, seen from the vegetative side.

When, therefore, the opportunity presented itself to study more closely the cleavage of the parthenogonidia in *Volvox*, which appeared

¹⁾ Statements on the cleavage of *Volvox* are found in:

J. GOROSHANKIN, 1875, Genesis im Typus der palmellenartigen Algen. Versuch einer vergleichenden Morphologie der Volvocineae. Mitt. Kaiserl. Ges. naturf. Freunde in Moskau, Bd. 16 (Russian, an extract is found in Botan. Jahresber. f. 1875, p. 27).

E. OVERTON, 1889, Beitrag zur Kenntniss der Gattung *Volvox*. Botan. Centralbl., Bd. 10, p. 177.

L. KLEIN, 1890, Vergleichende Untersuchungen über Morphologie und Biologie der Fortpflanzung bei der Gattung *Volvox*. Ber. naturf. Ges. Freiburg, Bd. 5, p. 15.

to occur in considerable number in the *Victoria regia*-basin of the Leyden botanical garden, I readily seized it. The study was made on living material. During development the parthenogonidium, which continues to communicate by plasmodesms with the surrounding cells, considerably increases in size¹⁾, so that the older stages are often easier to study than younger ones, for which the use of oil-immersion as a rule is to be preferred.

By two meridional cleavages the parthenogonidium is first divided into four equal cells, which each will give rise to a quadrant. The eight-celled stage has already been figured repeatedly for *Volvox* and other Volvocinea, but not the transition of the four- into the

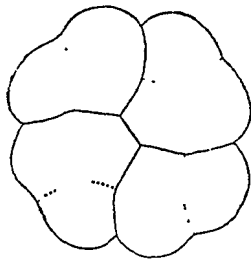


Fig. 2. Beginning of the third cleavage, animal side

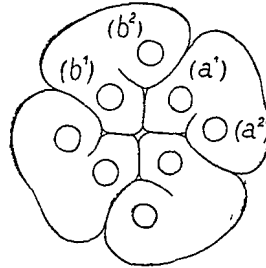


Fig. 3. Transition 4—8, vegetative side

eight-celled stage. Figs. 1, 2, and 3 teach us that during this cleavage a torsion amounting to 45° occurs between what we may call for the sake of shortness the four vegetative cells and the four animal cells. In the terminology of the spiral cleavage type we should call this torsion a dextrotropic one since, if we look at the egg from the side of the animal pole, the four animal cells appear to lie to the right of the four lower cells.

It seemed to me interesting to make out if this third cleavage always takes place in the same way or if, as could equally be imagined, it is sometimes dextrotropic and sometimes laetotropic. In the cleavage of *Balanus*, which shows a similar torsion, I found e.g. both possibilities occurring indiscriminately²⁾. In the spiral cleavage type the third cleavage is always dextrotropic with the exception of inversely wound Gasteropoda where the whole cleavage proceeds in an inverse manner. So not only the adult form but equally the earliest cleavage stages present the reflected image of what we find in dextral Gasteropods.

¹⁾ All the figures in this article have been drawn the same size.

²⁾ H. C. DELSMAN, 1917. Die Embryonalentwicklung von *Balanus balanoides* Linn Tijdschr. Nederl. Dierk. Ver. (2), Dl. 15.

I found that in *Volvox* the third cleavage always proceeds in a dextrotropic manner, and the suggestion lies at hand that here too some peculiarity of the adult form might stand in a certain relation to this phenomenon. What, for example, is the direction in which *Volvox* rotates round the main axis, is this always the same or at one time dextrotropic and at another laeotropic? As has been already observed by earlier investigators and as I can confirm here once more, the rotation always occurs in this way that, seeing it from the animal pole, we may designate it as clockwise, i.e. in the direction of the hands of a clock or dextrotropic. It lies at hand to suggest a relation between these phenomena, as has been stated equally in *Gasteropods*. That in the latter there can be no question of a direct causal relation between the torsion of the adult animal and that of the cleavage cells will be evident at once if we bear in mind that the spiral cleavage type occurs equally well in forms that are not wound at all, as *Lamelibranchiata*, *Chitons*, *Polychaetous Annelids* etc. We will revert to the question whether possibly in *Volvox* we might think of a more direct relation between the torsion during cleavage and the direction of the rotation during movement.

In the eight-celled stage (fig. 4, 5) which has been figured already

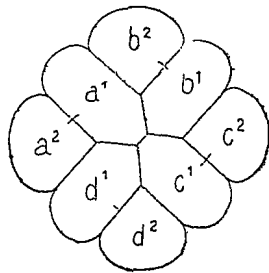


Fig. 4. Stage 8,
animal side.

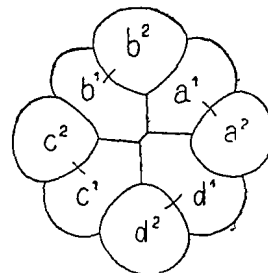


Fig. 5. Stage 8,
vegetative side.

more than once, the four vegetative cells alternate with the four animal cells. They constitute together a little cell-plate representing phylogenetically the *Gonium*-stage, but which at the border already begins to curve in. This curving in accentuates itself during the transition into the 16-celled stage and in *Volvox* evidently manifests itself somewhat earlier than in *Pleodorina*, *Eudorina*, and *Pandorina*, where also in the stage 16 the cells are still lying in a concave little plate, while in *Volvox* it has then already passed into a hollow globule with an opening, the "phialoporus". The eggs always have the vegetative side, with the phialopore, directed to the surface of the maternal organism.

The passage of the eight- into the sixteen-celled stage, which in the spiral type is always performed by a laeotropic cleavage, is characterised in *Volvox* by a progressive torsion of the cells of the vegetative side with regard to those of the animal side and this in

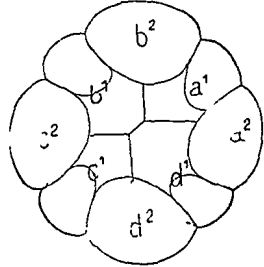


Fig. 6. Beginning of the fourth cleavage, vegetative side.

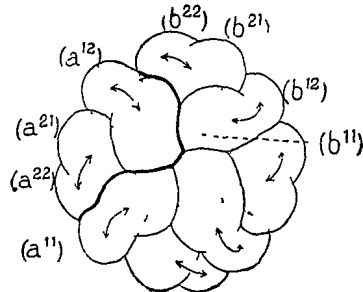


Fig. 7. Transition 8—16, animal side

the same direction in which it has already manifested itself in the foregoing cleavage, which is what we may call dextrotropic. This expresses itself in the shape of the cells immediately when the fourth cleavage sets in, as fig. 6 teaches us. The torsion here has already become a little greater than 45° as becomes evident if we compare the situation of the inferior parts of the vegetative cells (a_4 — d_4) with regard to the cross of the cleavage furrows at the animal pole. The fourth cleavage (fig. 7, 8), therefore, under the influence of

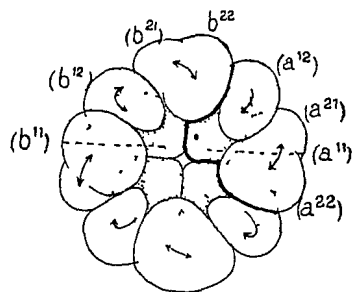


Fig. 8. Transition 8—16, vegetative side.

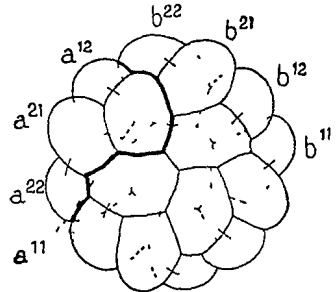


Fig. 9. Stage 16, animal side.

the above torsion, must be described as dextrotropic. For this reason, and in regard to the further cleavage, I think it inadvisable to apply here the nomenclature proposed by CONKLIN for the spiral type, but will modify this a little. I call the cells of the four quadrants resp. a , b , c , and d , and to their descendants I give each time the exponent 1 to the cell that lies to the animal side, and the exponent 2 to that lying to the vegetative side. Thus all the cells with the letter a are descendants of the cell a of the four-celled stage, forming

together one quadrant which, moreover, I have surrounded with a thick line in the figures. Now fig. 9 answers wholly to the image presented by a 16-celled stage of the spiral cleavage type, however, one would expect the cells a^{11} , a^{12} , b^{21} and b^{22} to represent together one quadrant. This has been shown not to be the case, and if one takes a view of figs. 8 and 9, the dextrotropic torsion that has occurred during the cleavage, at once strikes the eye. Between a^{11} and a^{22} this torsion now amounts to between 45° and 90° . The phialopore is surrounded by the cells $a^{22}-d^{22}$ and $a^{12}-d^{12}$, the former constituting the four longer, the latter the four shorter sides of the octangular phialoporic border. Sometimes one of the cells $a^{21}-d^{21}$ also reaches the border, the latter then being formed by nine cells.

The fifth cleavage, leading to the 32-celled stage, is again laeotropic, as is shown as well by a view from the animal (fig. 10) as from the vegetative side (fig. 11). Thus the dextrotropic torsion is again

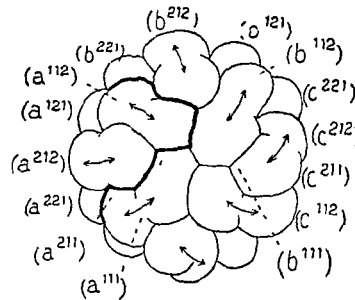


Fig. 10. Transition 16—32,
animal side.

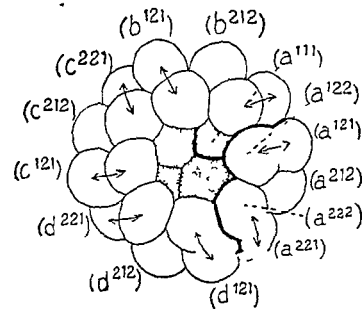


Fig. 11. Transition 16—32,
vegetative side.

continued here, and as fig. 11 and especially fig. 13 shows, this torsion of the vegetative extremity of each quadrant with regard to the animal extremity (the cell a^{111}) now amounts to nearly 90° . While the cell a^{212} forces itself between a^{12} and a^{22} , as was already the case in the 16-celled stage, so that a^{221} is pushed aside a little (figs. 11, 13), a^{12} while dividing is pushed to the phialoporic border by a^{11} , which also divides. As a consequence $a^{122}-d^{122}$ now form the longer, $a^{222}-d^{222}$ the shorter sides of the octangular phialopore. Often also all eight sides are of equal length.

The arrangement of the cells in the 32-celled stage is so regular (figs. 12 and 13) that no doubt one would not suspect from it the torsion stated here by watching the cleavages.

The last cleavage studied by me is the one that leads from the 32-celled to the 64-celled stage (figs. 14 and 15). The direction of

the divisions gradually becomes subject to more variation, yet the equatorial direction just as in former cleavages — though with a

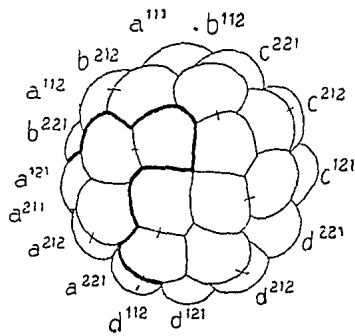


Fig. 12. Stage 32, animal side.

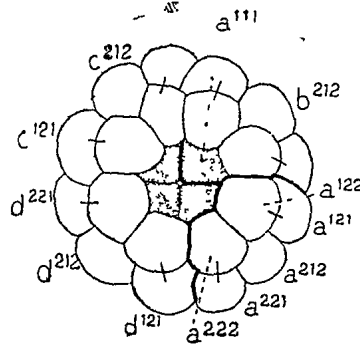


Fig. 13. Stage 32 (the same egg), vegetative side.

deviation caused by the torsion — continues to predominate. That the torsion still proceeds is evident from fig. 15, which shows that it is already more than 90° .

At the beginning of this investigation I almost expected to find that *Volvox* divides according to the spiral cleavage type. The figures given by some investigators seemed to me to point in this direction. No doubt this result would have been interesting with regard to the derivation of the different cleavage types of Metazoa and their mutual relation. A more direct relation between *Volvox* and the lowest forms with a spiral cleavage type would not then appear improbable, since, as shown above, there are other points of agreement. That *Volvox* possesses chlorophyll would be no insuperable obstacle

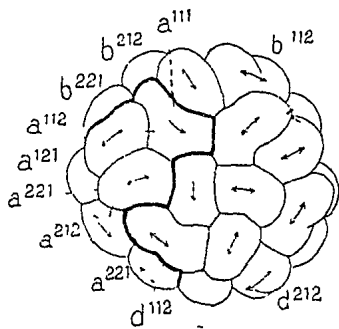


Fig. 14. Transition 32—64, animal side.

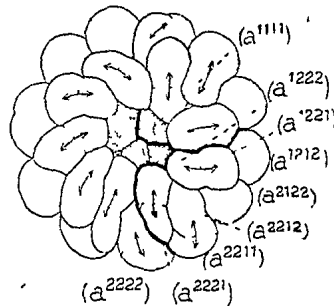


Fig. 15. Transition 32—64, vegetative side.

since it can hardly be doubted that animals must descend from organisms with chlorophyll. No production of organic from inorganic substance would have been possible otherwise.

We have seen, however, that the cleavage of *Volvox* may not be counted as belonging to the spiral type in the form in which it occurs in Metazoa, though the arrangement of the cells is more in a spiral than it is with the latter. Though there are certain points in common I yet refrain from further speculations in this direction.

In another respect, however, the results reached seem to me to be interesting. We have been able to state during the cleavage a progressive torsion of the vegetative cells with regard to the animal cells which becomes especially manifest from a comparison of figs. 2, 4, 7, 9, 10, 12, and 14 and of figs. 3, 5, 6, 8, 11, 13, and 15. So we have every reason to assume that in the adult form also a similar arrangement of the cells prevails. In the spiral cleavage type the succeeding dextrotropic and laetotropic divisions nearly annul the effect of each other, so that in the blastula the cells belonging to one quadrant nearly occupy an area situated between two meridians distant 90° from each other, as is represented fig. 16a. Fig. 16b shows the situation of the cells belonging to one quadrant in the case where the torsion does not surpass 90° . How great the latter has become in the adult *Volvox* cannot be made out. Now in the same dextrotropic direction also the rotation occurs, as we have seen, and it seems to me probable that in this case we may look for a more direct relation between the two phenomena than with the torsion of Gasteropods. Let us assume to this end that not only the colony but also each of the cells of *Volvox* has a certain polarity and thus a main axis in the direction from the animal to the vegetative pole of the colony. This polarity of the cells e.g. manifests itself in the corresponding direction in which all the flagella beat causing a water current from in front backwards, which makes the organism move

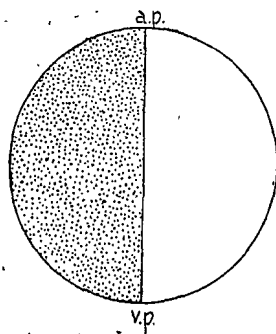


Fig. 16a.

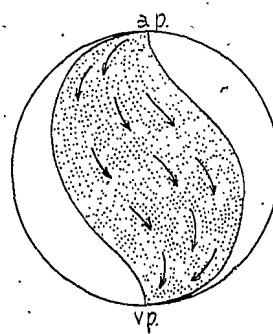


Fig. 16b.

in the direction of the animal pole. If a *Volvox* be pressed between a cover-slip and an object-slide so that it cannot move anymore, this

water current can easily be demonstrated by watching the little particles suspended in the water. If further we assume that by the dextrotropic torsion, during the cleavage the direction of the main axis of the cells undergoes a dextrotropic deviation and the flagella thus beat in the direction of the arrows in fig. 16b, then the dextrotropic rotation of the colony follows directly from this assumption. That indeed the flagella beat in this way needs no further proof, but follows from the rotation itself.

It would be interesting no doubt if a variety of *Volvox globator* rotating to the left, were discovered. It can hardly be expected otherwise than that the cleavage here will equally belong to the inverse type.

Have we accounted now for the rotating movement of *Volvox* by the torsion presenting itself during the cleavage? In a causal sense we have, if our suggestion is right. But how is the torsion of the cleavage cells to be accounted for? Phylogenetically now I should feel inclined to consider the torsion during the cleavage rather as a consequence of the rotation of the adult animal than as its cause. The study of ontogeny ever anew teaches us that we must not consider the structure of the adult animal phylogenetically as a product of the developmental processes, but we rather must account for the latter by the structure of the adult animal. Thus I would see also in the torsion during the egg cleavage of *Volvox* nothing but a very precociously appearing character of the adult form related to the movement of the latter. This character, which cannot be demonstrated in the adult form, could be revealed only by the study of its development.

Physics. — “Contributions to the study of liquid crystals. III. Melting and congelation-phenomena with para-azoxy-anisol.” By Dr. W. J. H. MOLL and Prof. L. S. ORNSTEIN. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of September 29, 1917).

In our second paper on the extinction of liquid crystals we observed, that among others with para-azoxy-anisol there is, with regard to the extinction, a difference between the liquid crystalline condition which arises by melting the solid crystals (“exsolid”) and that which arises in cooling the isotropic liquid (“exliquid”). Where with para-azoxy-anisol we had stated the existence of two solid phases, the question lay at hand whether in exsolid and exliquid we had perhaps got two different liquid crystalline phases. To make this out a research after the exact position of the points of transition was desirable.

Method of Research.

There we made use of a kind of radiation calorimeter, which is schematically represented in figure 1.

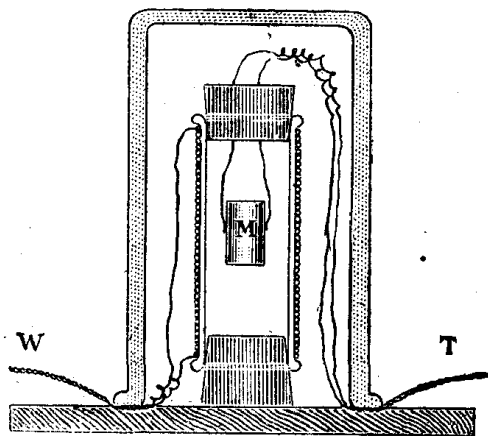


Fig. 1.

schematically represented in figure 1. The substance to be examined (about $\frac{1}{4}$ c.m.³) half filled a gold beaker *M* with thin walls, against which on the exterior on the one side a brass wire, on the other a constantane wire has been soldered. The two wires form a thermoelement, by the help of which the temperature of the beaker and its contents is measured ¹⁾ and serve at the same time to hang it within a brass cylinder. This

¹⁾ Before we came to this way of fixing up the “thermobeaker”, we had followed the usual method for our determination of the temperature, i.e. we had placed a thermometer and later on a thermoelement within the substance to be melted. Then a number of “Schmutzeffekte” were produced, which on close investigation had to be ascribed to convection currents. Our method is of course quite free from this disturbance.

cylinder is closed by a cork at the top and one at the bottom and, that it may be heated electrically, it is provided with a layer of isolated wire. The whole stands on a little table under a glass, which only allows of passage to the wires of the heating-current W and those of the thermocurrent T .

The research consisted in the determination of the temperature-time curve with a constant heating current. If this heating current is closed, the temperature first rises quickly, then more slowly and asymptotically approaches a limit value. If now (also before the limit-temperature is reached) the heating current is weakened and then kept constant, the temperature first falls rapidly, then more slowly till a second lower limiting temperature is reached.

When within the temperature-region in observation the substance in the beaker melts, congelates, or in general undergoes some change of phase, this will be observable on the T - t curve. So during the supply of heat to the beaker the melting will appear as a sharp twist in the ascending branch. The place of the twist indicates the melting-temperature and, that with a much higher degree of accuracy, than would even be possible with a measuring of the temperature within the substance.

The second contact place of the thermo-element was in melting ice during the time of observation. The thermo-current was measured by a quick-indicating galvanometer of MOLL. To keep the deviations within bounds the thermoforce was first for the greater part compensated with the help of a constant current-source and a shunt, and besides the sensitiveness of the galvanometer was strongly reduced.

The deviations of the galvanometer were registered and the T - t curves thus photographed. The figures 2—6 are reduced reproductions of our original photos. The figures put underneath give in an arbitrary measure the temporal value of the heating-current.

An abscisslength of 8 cm. corresponds to a quarter of an hour.

The dotted line indicates the same temperature of about 118° in the different figures.

Discussion of the Results.

Fig. 2. The two ascending branches fully agree and at A the first point of transition shows itself sharply, i.e. the melting point of the solid substance. This temperature, which amounts to about 118° , we have always chosen as point of departure. The strong oscillations

17*

of temperature at *B* are without importance for our investigation and may be left apart¹⁾.

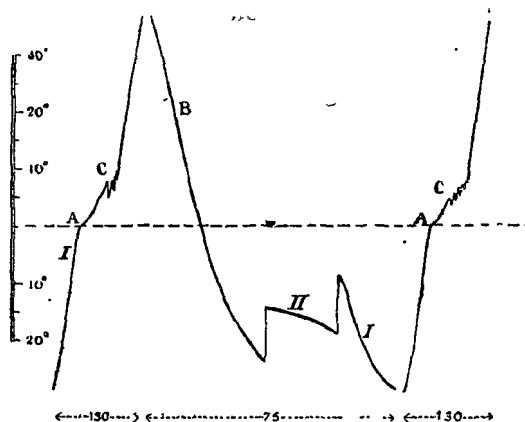


Fig. 2.

The second point of transition is difficult to observe in the ascending branch on account of its steepness, in the descending branch it appears more clearly at *B*. Further we observe in the descending branch a strong undercooling to far below 100° and then a sudden development of heat and congelation. The highest temperature reached in this process ($13^{\circ},5$ below the zero-line) is the point where a very unstable solid phase congeals, which we shall call phase II (phase I has the melting point at about 118°), and which after a short time spontaneously and under the development of heat passes into another

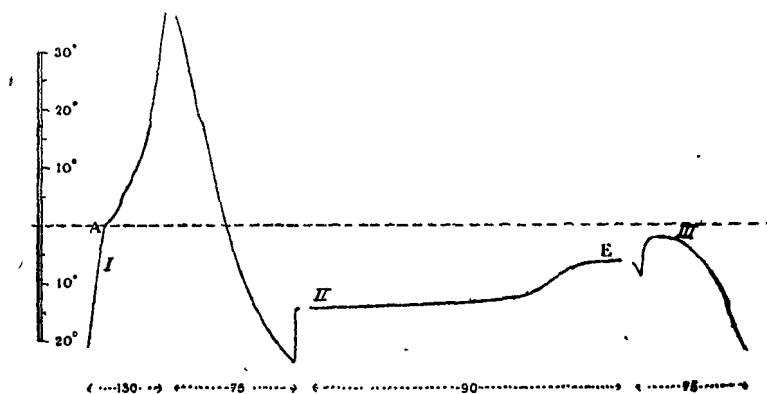


Fig. 3.

¹⁾ They have their cause in the fact that the volume of para azoxy-anisol changes considerably in melting. The internal sidewall of the beaker gets for this reason detached from its contents and can temporarily rise to a higher temperature, so that a drop, dripping from the solid centre, again occasions a sudden falling of the temperature.

phase. Probably directly into phase I, for at a supply of heat the same melting point of about 118° shows itself.

Fig. 3. After the same initial development as in the case represented by fig. 2 the same deep undercooling is again followed by the appearance of the solid phase II. But now we have to take care that immediately after this phase arises, heat is supplied by strengthening the heating-current, and that to such value that phase II is melted but the arising liquid crystalline phase remains undercooled. Whilst at E its temperature has become constant, we have, in order to hasten the process of congelation, reduced the heating-current, and in result of this the temperature has scarcely fallen a few degrees before under the development of heat the liquid crystalline substance congeals and now at a temperature of 2° below the zero-line. We call this new condition solid phase III.

Fig. 4 also gives the origin of phase III from the undercooled

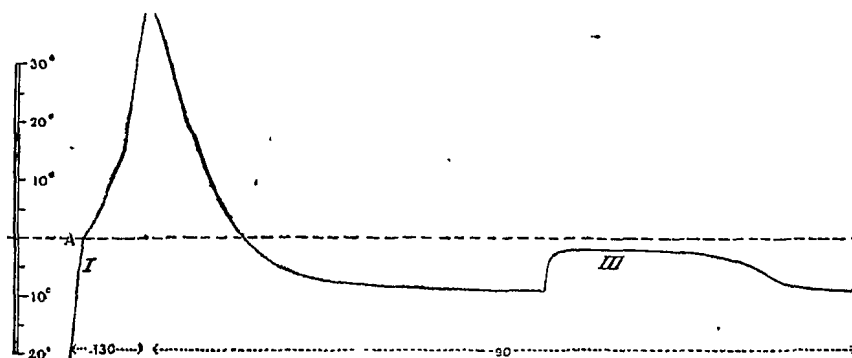


Fig. 4.

liquid crystalline phase. The heating-current during the preceding cooling was chosen in such a way that the formation of phase II was excluded.

Fig. 5 gives once again the origin of phase III with the exclusion of phase II. But where the undercooled liquid crystalline phase in fig. 4

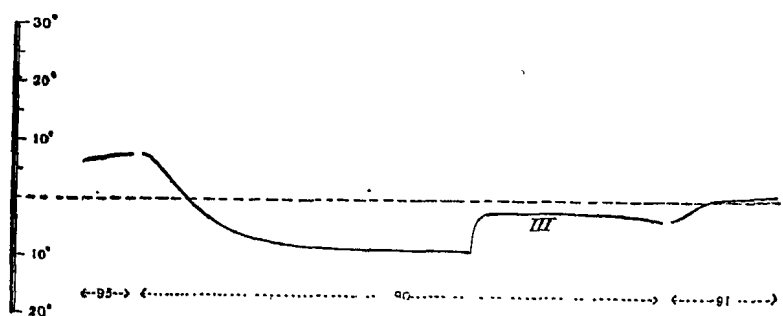


Fig. 5.

was ex-liquid, we have taken it ex-solid in fig. 5. Besides this figure also gives the melting of phase III and there the remarkable pheno-

menon presents itself, that phase III melts at a temperature which we know as the melting point of phase I. Thus it is shown that in this way phase III, during its formation, gradually passed into phase I.

Fig. 6 is reproduced as it allows of studying the second point of transition. At *F* ex-solid, at *G* ex-liquid pass into the isotropic

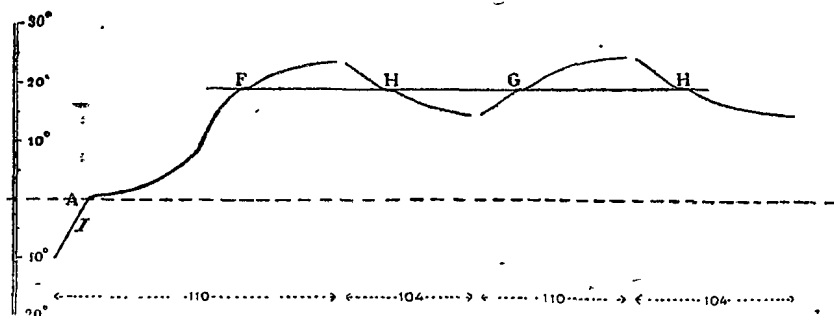


Fig. 6.

phase under the absorption of heat, *H* gives the phenomenon of transition while heat is developed and the three transitions *F* *G* and *H* happen really at the same temperature.

CONCLUSION.

Whilst thus, as far as the situation of the points of transition is concerned, we have found no indication of a difference between exsolid and exliquid with para-azoxy-anisol, we have discovered several phases in the solid condition of aggregation in our investigation. Beside the three phases which we have distinguished as I, II and III, there certainly still exists a fourth¹⁾, with a melting-point of about 108°. It seems that this phase, which during this investigation never once showed itself, can only exist in capillary layers (between glass).

This short, more or less schematic summing up of the most striking facts, which present themselves in an investigation of the melting- and congelation phenomena of para-azoxy-anisol, must suffice, however interesting a closer examination of this substance and perhaps of other substances according to the method indicated may be from a standpoint of phase-theory, for our interest is greater for problems of a different nature.

Physical Laboratory, Institute for Theoretical Physics.

Utrecht, September 1917.

¹⁾ Cf. our second contribution. Verslag Kon. Acad. v. Wetensch. XXV, p. 1114.

Physics. — "*Contributions to the study of liquid crystals. IV. A thermic Effect of the Magnetic Field*". By Dr. W. J. H. MOLL and Prof. L. S. ORNSTEIN. (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of March 23, 1918).

The fact that the particles of liquid crystalline substances are directed by a magnetic field, justifies the question whether perhaps the action of the field, may entirely or partially manifest itself as heat. We shall in this paper develop the results of an investigation into this matter.

We made use of an arrangement for this investigation, which in the main points is the same as that described in our previous paper ¹⁾ on the subject. The p-azoxy-anisol was again heated in a little gold beaker, being within a little oven which was heated by electricity. But our little oven had to serve in this case as thermostat, and above all it was necessary, that the temperature inside of the oven was as far as possible equal everywhere, so that a temperature gradient within the substance to be investigated would be excluded. Instead of our original, very primitive little oven we fitted up as such a brass tube 10 cm. long and 2 cm. wide, provided along pretty well the whole length with a single widening of their manganin wire, closed off at the bottom by a brass plate, at the top by a brass screw-stopper, in which only a narrow opening to leave passage to the thermo-element. To present a current of air along the heating-wire, the latter was wrapped up in chenille, and closely around this there was a double brass mantle, through which water circulated of the temperature of the room.

This arrangement was put (with the axis of the little oven in a vertical direction) between the poles of a Dubois-magnet, and its (horizontal) field may be looked upon as homogeneous at the place of the beaker. The magnet could be turned round a vertical axis.

The electromotive force of the thermo-element was almost fully compensated, the changes arising were registered by photography.

In our investigation as to whether the connection of the magnetic field has a thermic effect, we arrived in the beginning at results,

¹⁾ Compare the foregoing paper.

apparently in contradiction to each other; until at last with the help of a thermo-element of a peculiar structure we have come to understand the phenomena which dominate the effect.

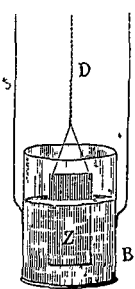


Fig. 1. anisol.

In fig. 1 this thermo-element is represented, as it is hung within the gold beaker *B*. (The wall of the little beaker must be thought transparent). *B* is attached by two pins *S* to the screw-stopper of the little oven; *D* are two wires twisted together, brass and constantane, which are soldered by their ends to a thin plate of silver-plate *Z* (5×7 mm., 0,02 mm. thick), which is immersed for somewhat more than half in the p-azoxy-

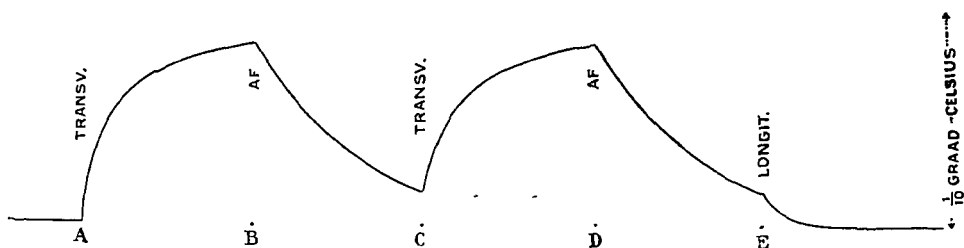


Fig. 2

Fig. 2 may make this clear; a curve, taken by photography, is represented. At *A* a transversal field is connected with the result that the temperature of the silver-plate rises slowly; 15 sec. later at *B* the field is broken up and a still slower cooling of the plate is the result; 15 sec. later, at *C* (before the temperature has as yet regained the original value) the transversal field is put on for the second time; 15 sec. later at *D* it is again broken up; and at last 15 sec. later a longitudinal field is put on at *E* and this causes a quicker reaching of the thermostat temperature. A new connection of the longitudinal field remains without effect¹⁾.

The principal conclusion from our experiments is this, that the effect observed must have its origin in the immediate vicinity of

¹⁾ It need hardly be mentioned, that in the isotropic phase the connection and disconnection of the magnetic field offers a thermic effect.

the metal wall, and that within the liquid crystalline matter a magnetic field offers no thermic effect or only a very slight one. For *then* the effect of a transversal and a longitudinal field would have to be equal.

Where the influence of a magnetic field means in the end the direction of the more or less stretched particles of the liquid crystalline substance we come to the conclusion that against this directing there is only important resistance to be overcome near the wall.

Now we have accepted an action of the wall for the explanation of some extinction phenomena ¹⁾, and that in such a way that the wall directs the particles parallel to itself. The resistance which is to be overcome for a transversal field is quite in accordance with this way of seeing the question.

Then as regards the nature of this resistance, we might imagine it to be of elastic origin; the particles would then get another form at the cross-action of field against wall (heating), and return at the disappearance of the field again elastically to their original form (cooling), in which process the longitudinal field hastens this return.

Conclusion.

With para-azoxy-anisol the thermoeffect of a magnetic field is investigated with the help of a thermo-element of peculiar structure.

The investigation shows that an effect is only apparent at the wall of the thermo-element, which effect probably has its origin in the elastic change of form of liquid crystalline particles.

Utrecht, Febr. 1918.

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for Theoretical Physics.*

¹⁾ See our first and second papers.

Mathematics. — “*The primitive Divisor of x^k-1 .*” By J. G. VAN DER CORPUT. (Communicated by Prof. J. C. KLUYVER).

(Communicated in the meeting of September 29, 1917).

This paper is an extension of the article of Prof. J. C. KLUYVER: “*The primitive Divisor of x^m-1 .*” (These Proceedings, Vol. XIX, page 785.

Definition 1. If k be a positive integer, the product $\prod_{\sigma} (x - e^{\frac{2\pi i \sigma}{k}})$, extended over all the values σ of a reduced rest-system, modulo k , is called the primitive divisor $F_k(x)$ of x^k-1 .

Definition 2. If k be a positive integer, $\varphi = \varphi(k)$ represents the number of positive integers $\leq k$, which are prime to k .

Proposition 1. If k be a positive integer, then the primitive divisor of x^k-1 is a polynome of the degree φ .

Definition 3. The numbers A_λ ($\varphi \geq \lambda \geq 0$) are defined by the relation

$$F_k(x) = \sum_{\lambda=0}^{\varphi} A_\lambda x^\lambda,$$

k being an arbitrary positive integer.

Definition 4. In the functions $\chi_\nu(n, k)$ of the variable integer n (k being a positive integer), which are called the arithmetical characters of n , modulo k , ν represents an arbitrary integer, prime to k .

The functions $\chi_\mu(n, k)$ and $\chi_\nu(n, k)$ are identical or different, according as μ and ν are mutually congruent or incongruent, modulo k . Hence it follows, that there are φ different arithmetical characters $\chi_\nu(n, k)$, modulo k and these functions possess the following properties:

- I. $\chi_\nu(m, k) \chi_\nu(n, k) = \chi_\nu(mn, k)$.
- II. $\chi_\nu(m, k) = \chi_\nu(n, k)$ if $m \equiv n \pmod{k}$.
- III. The modulus of $\chi_\nu(n, k)$ is equal to 0 or 1, according as n and k are commensurable or incommensurable.
- IV. $\chi_1(n, k)$ is equal to 0 or 1, according as n and k are commensurable or incommensurable.
- V. $\chi_{-1}(n, k)$ is equal to the symbol $\left(\frac{n}{k}\right)$ of LEGENDRE.
- VI. $\chi_\nu(1, k) = 1$.

$$\text{VII.} \quad \sum_{n=1}^{\varphi} \chi_{\nu}(n, k) = 0, \text{ if } \nu \not\equiv 1 \pmod{k}.$$

$$\text{VIII.} \quad \chi_{\nu}(n, k_1) \chi_{\nu}(n, k_2) = \chi_{\nu}(n, k),$$

if k be equal to the product of the two incommensurable integers k_1 and k_2 .

Definition 5. $\chi_{\nu}(n, k)$ and $\overline{\chi}_{\nu}(n, k)$ are two conjugate functions; they are, therefore, identical, if $\chi_{\nu}(n, k)$ is real and they are conjugate imaginary, if $\chi_{\nu}(n, k)$ is an imaginary function.

Proposition 2. $\overline{\chi}_{\nu}(n, k)$ is an arithmetical character of n , modulo k .

Proof. Each function of n , satisfying the conditions 4.I, II and III, is an arithmetical character of n , modulo k .

Definition 6. The functions $a_{\nu}(n, k)$ of the variable integer n , (ν and k being incommensurable numbers) are defined by the relation

$$\sum_{m=1}^k \overline{\chi}_{\nu}(m, k) e^{\frac{2\pi i m n}{k}} = a_{\nu}(n, k) \sum_{m=1}^k \overline{\chi}_{\nu}(m, k) e^{\frac{2\pi i m}{k}}.$$

Proposition 3. If k be the product of the two incommensurable numbers k_1 and k_2 , each of which is prime to the integer ν , then we shall have

$$a_{\nu}(n, k_1) a_{\nu}(n, k_2) = a_{\nu}(n, k).$$

Proof. In the expression

$$\sum_{m_1=1}^{k_1} \overline{\chi}_{\nu}(m_1, k_1) e^{\frac{2\pi i m_1 n}{k_1}} \sum_{m_2=1}^{k_2} \overline{\chi}_{\nu}(m_2, k_2) e^{\frac{2\pi i m_2 n}{k_2}} = \sum_{m_1=1}^{k_1} \sum_{m_2=1}^{k_2} \overline{\chi}_{\nu}(m_1, k_1) \overline{\chi}_{\nu}(m_2, k_2) e^{\frac{2\pi i (m_1 k_2 + m_2 k_1) n}{k}}$$

we have $m_1 = 1, 2, 3, \dots, k_1$ and $m_2 = 1, 2, 3, \dots, k_2$. We may make $m_1 k_2 + m_2 k_1$ congruent to $m \pmod{k}$ and $k \geq m \geq 1$. Then we have $m = 1, 2, 3, \dots, k$ and

$$\overline{\chi}_{\nu}(m, k) = \overline{\chi}_{\nu}(m, k_1) \overline{\chi}_{\nu}(m, k_2) \quad (\text{according to 4, VIII})$$

$$= \overline{\chi}_{\nu}(m_1 k_2, k_1) \overline{\chi}_{\nu}(m_2 k_1, k_2) \quad (\text{according to 4, II})$$

$$= \overline{\chi}_{\nu}(k_2, k_1) \overline{\chi}_{\nu}(k_1, k_2) \overline{\chi}_{\nu}(m_1, k_1) \overline{\chi}_{\nu}(m_2, k_2) \quad (\text{according to 4, I}).$$

Consequently

$$\overline{\chi}_{\nu}(k_2, k_1) \overline{\chi}_{\nu}(k_1, k_2) \sum_{m_1=1}^{k_1} \overline{\chi}_{\nu}(m_1, k_1) e^{\frac{2\pi i m_1 n}{k_1}} \sum_{m_2=1}^{k_2} \overline{\chi}_{\nu}(m_2, k_2) e^{\frac{2\pi i m_2 n}{k_2}} = \sum_{m=1}^k \overline{\chi}_{\nu}(m, k) e^{\frac{2\pi i m n}{k}}$$

and (make $n = 1$)

$$\overline{\chi}_{\nu}(k_2, k_1) \overline{\chi}_{\nu}(k_1, k_2) \sum_{m_1=1}^{k_1} \overline{\chi}_{\nu}(m_1, k_1) e^{\frac{2\pi i m_1}{k_1}} \sum_{m_2=1}^{k_2} \overline{\chi}_{\nu}(m_2, k_2) e^{\frac{2\pi i m_2}{k_2}} = \sum_{m=1}^k \overline{\chi}_{\nu}(m, k) e^{\frac{2\pi i m}{k}}.$$

The first two factors occurring in these formulae, are according to 4, III not equal to zero, because k_1 and k_2 are incommen-

surable. If the last two formulae be divided one by the other, we shall obtain, according to definition 6

$$a_1(k_1, n) a_1(k_2, n) = a_1(k, n).$$

Proposition 4. If the following conditions are satisfied:

k_1 and k_2 are two squareless incommensurable numbers and their product is equal to k ,

n is an arbitrary integer and v an arbitrary number, prime to k ,

D_1 is the G. C. D. of $v-1$, k and k_1 ,

D_2 is the G. C. D. of $v-1$, n and k_2 ,

D is the G. C. D. of $v-1$, n and k ,

then we have

$$\mu(D_1) \varphi(D_1) \chi_v\left(n, \frac{k_1}{D_1}\right) \mu(D_2) \varphi(D_2) \chi_v\left(n, \frac{k_2}{D_2}\right) = \mu(D) \varphi(D) \chi_v\left(n, \frac{k}{D}\right).$$

Proof. D_1 and D_2 are incommensurable, because k_1 and k_2 are incommensurable. The numbers D_1 and D_2 , therefore also $D_1 D_2$, are divisors of D and D is a divisor of $D_1 D_2$; consequently $D_1 D_2 = D$. Hence it follows

$$\mu(D_1) \mu(D_2) = \mu(D),$$

$$\varphi(D_1) \varphi(D_2) = \varphi(D)$$

and

$$\chi_v\left(n, \frac{k_1}{D_1}\right) \chi_v\left(n, \frac{k_2}{D_2}\right) = \chi_v\left(n, \frac{k}{D}\right),$$

according to 4, VIII.

Proposition 5. If v be an integer, prime to the positive integer k and the integers n and n' satisfy the relation $nn' \equiv 1 \pmod{k}$, then we shall have $\chi_v(n, k) = \overline{\chi}_v(n', k)$.

Proof. From the relation $nn' \equiv 1 \pmod{k}$ it follows that n and n' are prime to k and according to definition 5 and 4, III $\chi_v(n, k)$ and $\overline{\chi}_v(n, k)$ are two conjugate functions with modulus 1.

Consequently

$$\chi_v(n, k) \overline{\chi}_v(n, k) = 1.$$

Moreover we have, according to 4. I, II, and VI,

$$\overline{\chi}_v(n', k) \overline{\chi}_v(n, k) = \overline{\chi}_v(nn', k) = \overline{\chi}_v(1, k) = 1,$$

hence

$$\chi_v(n, k) = \overline{\chi}_v(n', k).$$

Proposition 6. If k be a squareless number, prime to v and D represents the G. C. D. of $v-1$, n and k , then we have

$$a_v(n, k) = \mu(D) \varphi(D) \chi_v\left(n, \frac{k}{D}\right).$$

Proof I. k is a prime number

α). k is a divisor of $v-1$ and n ; consequently $D = k$.

$$\begin{aligned}\mu(D) \varphi(D) \chi_v \left(n, \frac{k}{D} \right) &= (-1)(k-1) \chi_1(n, 1) \\ &= -(k-1), \quad \text{according to 4. IV,} \\ \sum_{m=1}^k \overline{\chi_v}(m, k) e^{\frac{2\pi i m n}{k}} &= \sum_{m=1}^{k-1} 1 = k-1\end{aligned}$$

and

$$\sum_{m=1}^k \overline{\chi_v}(m, k) e^{\frac{2\pi i m}{k}} = \sum_{m=1}^{k-1} e^{\frac{2\pi i m}{k}} = -1,$$

consequently, according to definition 6,

$$a_v(n, k) = -(k-1) = \mu(D) \varphi(D) \chi_v \left(n, \frac{k}{D} \right).$$

β). If k be a divisor of n and not of $v-1$, we shall have

$$\begin{aligned}D &= 1, \\ \chi_v \left(n, \frac{k}{D} \right) &= \chi_v(n, k) = 0, \quad (\text{according to 4. III}),\end{aligned}$$

$$\begin{aligned}\sum_{m=1}^k \overline{\chi_v}(m, k) e^{\frac{2\pi i m n}{k}} &= \sum_{m=1}^k \overline{\chi_v}(m, k) \\ &= 0, \quad (\text{according to 4. VII}),\end{aligned}$$

consequently

$$a_v(n, k) = 0,$$

so that now both members of the sought relation are equal to zero.

γ). Let k be no divisor of n , so that we may make

$$nn' \equiv 1 \pmod{k}, \quad mn \equiv m' \pmod{k}, \quad k \geq m' \geq 1.$$

According to proposition 5

$$\chi_v(n, k) = \overline{\chi_v}(n', k),$$

consequently

$$\chi_v(n, k) \overline{\chi_v}(m', k) = \overline{\chi_v}(n', k) \overline{\chi_v}(m', k) = \overline{\chi_v}(m'n', k) = \overline{\chi_v}(m, k),$$

because

$$m'n' \equiv mnn' \equiv m \pmod{k}.$$

Hence it follows

$$\sum_{m=1}^k \overline{\chi_v}(m, k) e^{\frac{2\pi i m n}{k}} = \chi_v(n, k) \sum_{m'=1}^k \overline{\chi_v}(m', k) e^{\frac{2\pi i m' n'}{k}},$$

consequently

$$a_v(n, k) = \chi_v(n, k) = \mu(D) \varphi(D) \chi_v \left(n, \frac{k}{D} \right),$$

because $D = 1$.

II. k is the product of two different prime factors. Take $k = k_1 k_2$,

(k_1 and k_2 are two different prime numbers). According to I we have

$$a_v(n, k_1) = \mu(D_1) \varphi(D_1) \chi_v\left(n, \frac{k_1}{D_1}\right),$$

$$a_v(n, k_2) = \mu(D_2) \varphi(D_2) \chi_v\left(n, \frac{k_2}{D_2}\right),$$

D_1 being the G. C. D. of $v-1$, n and k_1 ;

D_2 being the G. C. D. of $v-1$, n and k_2 .

If these two formulae are multiplied, we shall obtain

$$a_v(n, k) = \mu(D) \varphi(D) \chi_v\left(n, \frac{k}{D}\right)$$

according to the propositions 3 and 4.

III. k is the product of three or four different prime-factors.

Take k equal to the product of the two incommensurable numbers k_1 and k_2 , each of which is equal to a prime number or to the product of two different prime numbers. The proof is given in the same way as in II. etc.

Proposition 7. If k be a squareless number, prime to the integer v and $D_{n+\lambda}$ represents the G. C. D. of $v-1$, $n+\lambda$ and k , then the in definition 3 defined coefficients A_λ satisfy the relation

$$\sum_{\lambda=0}^{\varphi} A_\lambda \mu(D_{n+\lambda}) \varphi(D_{n+\lambda}) \chi_v\left(n+\lambda, \frac{k}{D_{n+\lambda}}\right) = 0,$$

whatever be the value of the integers n and v .

Proof.

$$\overline{\chi}_v(m, k) e^{\frac{2\pi i m n}{k}} \sum_{\lambda=0}^{\varphi} A_\lambda e^{\frac{2\pi i \lambda m}{k}} = 0,$$

for, if m and k have a common factor, $\overline{\chi}_v(m, k) = 0$ according to

1, III and if m is prime to k , $e^{\frac{2\pi i m}{k}}$ is a primitive root of the equation $x^k - 1 = 0$, i.e. a root of the equation

$$F_k(x) = \sum_{\lambda=0}^{\varphi} A_\lambda x^\lambda = 0,$$

so that then the last factor is equal to zero. Hence

$$\begin{aligned} 0 &= \sum_{m=1}^k \overline{\chi}_v(m, k) e^{\frac{2\pi i m n}{k}} \sum_{\lambda=0}^{\varphi} A_\lambda e^{\frac{2\pi i \lambda m}{k}} \\ &= \sum_{\lambda=0}^{\varphi} A_\lambda \sum_{m=1}^k \overline{\chi}_v(m, k) e^{\frac{2\pi i m (n+\lambda)}{k}}, \end{aligned}$$

consequently

$$0 = \left\{ \sum_{\lambda=0}^{\varphi} A_\lambda \mu(D_{n+\lambda}) \varphi(D_{n+\lambda}) \chi_v\left(n+\lambda, \frac{k}{D_{n+\lambda}}\right) \right\} \left\{ \sum_{m=1}^k \overline{\chi}_v(m, k) e^{\frac{2\pi i m}{k}} \right\},$$

according to definition 6 and proposition 6.

The last factor is not equal to zero, for then the sum

$$\sum_{m=1}^k \bar{\chi}_v(m, k) e^{\frac{2\pi i m n}{k}} = \mu(D_n) \varphi(D_n) \chi_v\left(n, \frac{k}{D_n}\right) \sum_{m=1}^k \bar{\chi}_v(m, k) e^{\frac{2\pi i m}{k}}$$

would be equal to zero if $n = 1, 2, 3, \dots, k$, that is the equation

$$\sum_{m=1}^k \bar{\chi}_v(m, k) x^m = 0$$

would possess the root zero and k different roots $e^{\frac{2\pi i m}{k}}$, and this is impossible, since the coefficients $\bar{\chi}_v(m, k)$ are not identically equal to zero, according to 4, III.

Consequently we conclude

$$\sum_{\lambda=0}^{\varphi} A_{\lambda} \mu(D_{n+\lambda}) \varphi(D_{n+\lambda}) \chi_v\left(n+\lambda, \frac{k}{n+\lambda}\right) = 0.$$

Proposition 8. If k be squareless, then we have

$$\sum_{\lambda=0}^{\varphi} A_{\lambda} \mu(D'_{n+\lambda}) \varphi(D'_{n+\lambda}) = 0,$$

$D'_{n+\lambda}$ being the G. C. D. of $n+\lambda$ and k . In this formula n may be any integer number whatever.

(This formula is to be found in the above mentioned article of Prof. J. C. KLUYVER).

Proof. Make in proposition 7 $v = 1$; then we shall have

$$D_{n+\lambda} = D'_{n+\lambda}$$

and

$$\chi_v\left(n+\lambda, \frac{k}{D_{n+\lambda}}\right) = \chi_1\left(n+\lambda, \frac{k}{D'_{n+\lambda}}\right) = 1,$$

according to 4, IV, since $n+\lambda$ and $\frac{k}{D'_{n+\lambda}}$ have no common factor, because k is squareless.

Hence it follows

$$\sum_{\lambda=0}^{\varphi} A_{\lambda} \mu(D'_{n+\lambda}) \varphi(D_{n+\lambda}) = 0,$$

Proposition 9. If k be an odd squareless number, then we have

$$\sum_{\lambda=0}^{\varphi} A_{\lambda} \left(\frac{n+\lambda}{k}\right) = 0,$$

$\left(\frac{n+\lambda}{k}\right)$ being the symbol of Legendre. In this formula n may be any integer whatever. (This formula is also to be found in the article of Prof. J. C. KLUYVER).

Proof. Make in proposition 7 $\nu = -1$: then we have $D_{n+1} = 1$, since $\nu - 1 = -2$ and k is odd.

Hence

$$\begin{aligned}\mu(D_{n+1}) &= \mu(1) = 1, \\ \varphi(D_{n+1}) &= \varphi(1) = 1, \\ \chi\left(n+1, \frac{k}{D_{n+1}}\right) &= \chi_{-1}(n+1, k) = \left(\frac{n+1}{k}\right),\end{aligned}$$

according to 4, V. Consequently

$$\sum_{\lambda=0}^{\frac{\varphi}{2}} A_{\lambda} \left(\frac{n+1}{k}\right) = 0.$$

Definition 7. If k be an integer > 2 , the coefficients B_{λ} and C_{λ} $\left(\frac{\varphi}{2} \geq \lambda \geq 0\right)$ are defined by the relation

$$\prod_{\sigma} \left(x - e^{\frac{2\pi i \sigma}{k}}\right) = \sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} x^{\lambda}$$

and

$$\prod_{\tau} \left(x - e^{\frac{2\pi i \tau}{k}}\right) = \sum_{\lambda=0}^{\frac{\varphi}{2}} C_{\lambda} x^{\lambda},$$

in which the products are extended over all the values σ and τ of a reduced rest-system, modulo k , for which $\left(\frac{\sigma}{k}\right) = +1$ and $\left(\frac{\tau}{k}\right) = -1$.

Proposition 10. If k be an odd squareless number, we have

$$\sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} b_{n+\lambda} = 0 \quad \text{and} \quad \sum_{\lambda=0}^{\frac{\varphi}{2}} C_{\lambda} c_{n+\lambda} = 0,$$

if we make

$$b_{\lambda} = \mu\left(\frac{k}{D'_{\lambda}}\right) \varphi(D'_{\lambda}) + \left(\frac{\lambda}{k}\right) i^{1/4} (k-1)^2 \sqrt{k}$$

and

$$c_{\lambda} = \mu\left(\frac{k}{D'_{\lambda}}\right) \varphi(D'_{\lambda}) - \left(\frac{\lambda}{k}\right) i^{1/4} (k-1)^2 \sqrt{k},$$

D'_{λ} being the G. C. D. of λ and k . In these formulae n may be any integer whatever.

Proof. D'_m is greater than 1, if $\left(\frac{m}{k}\right) = 0$, according to 4, IV; consequently

$$\sum_{\substack{d|k \\ d|m}} \mu(d) = \sum_{d|D'm} \mu(d) = 0 \quad \text{if } \left(\frac{m}{k}\right) = 0.$$

If $\left(\frac{m}{k}\right) = 1$, the equation $\sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} x^{\lambda} = 0$ has a root $e^{\frac{2\pi im}{k}}$, hence

$$\sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} e^{\frac{2\pi im\lambda}{k}} = 0 \quad \text{if } \left(\frac{m}{k}\right) = 1.$$

Consequently

$$\left\{1 + \left(\frac{m}{k}\right)\right\} \sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} e^{\frac{2\pi im\lambda}{k}} \sum_{\substack{d|k \\ d|m}} \mu(d) = 0,$$

for the third, second or first factor is equal to zero, according as $\left(\frac{m}{k}\right)$ is equal to 0, 1 or -1 .

Hence

$$S_1 + S_2 = \sum_{m=1}^k e^{\frac{2\pi imn}{k}} \left\{1 + \left(\frac{m}{k}\right)\right\} \sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} e^{\frac{2\pi im\lambda}{k}} \sum_{\substack{d|k \\ d|m}} \mu(d) = 0,$$

$$\begin{aligned} S_1 &= \sum_{m=1}^k e^{\frac{2\pi imn}{k}} \sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} e^{\frac{2\pi im\lambda}{k}} \sum_{\substack{d|k \\ d|m}} \mu(d) \\ &= \sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} \sum_{d|k} \mu(d) \sum_{\rho=1}^{\frac{k}{d}} e^{\frac{2\pi i\rho(n+\lambda)}{d}} \quad (\text{make } m = \rho d) \\ &= \sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} \sum_{d'|k} \mu\left(\frac{k}{d'}\right) \sum_{\rho=1}^{d'} e^{\frac{2\pi i\rho(n+\lambda)}{d'}} \quad \left(\text{make } \frac{k}{d} = d'\right) \\ &\quad \sum_{\rho=1}^{d'} e^{\frac{2\pi i\rho(n+\lambda)}{d'}} \end{aligned}$$

Because the sum $\sum_{\rho=1}^{d'} e^{\frac{2\pi i\rho(n+\lambda)}{d'}}$ is equal to d' or 0, according as $(n+\lambda)$ is divisible or not by d' , we have

$$S_1 = \sum_{\lambda=0}^{\frac{\varphi}{2}} B_{\lambda} \sum_{\substack{d'|k \\ d'|(n+\lambda)}} \mu\left(\frac{k}{d'}\right) \cdot d'$$

Since k is squareless, $\frac{k}{D'_{n+\lambda}}$ and $\frac{D'_{n+\lambda}}{d'}$ have no common factor, so that $\mu\left(\frac{k}{d'}\right) = \mu\left(\frac{k}{D'_{n+\lambda}} \cdot \frac{D'_{n+\lambda}}{d'}\right)$ is equal to $\mu\left(\frac{k}{D'_{n+\lambda}}\right) \cdot \mu\left(\frac{D'_{n+\lambda}}{d'}\right)$. Moreover we have

$$\sum_{d'|D'_{n+\lambda}} \mu\left(\frac{D'_{n+\lambda}}{d'}\right) d' = \varphi(D'_{n+\lambda}),$$

consequently

$$\begin{aligned} S_1 &= \sum_{\lambda=0}^{\frac{\varphi}{2}} B_\lambda \mu\left(\frac{k}{D'_{n+\lambda}}\right) \sum_{d'|D'_{n+\lambda}} \mu\left(\frac{D'_{n+\lambda}}{d'}\right) d' \\ &= \sum_{\lambda=0}^{\frac{\varphi}{2}} B_\lambda \mu\left(\frac{k}{D'_{n+\lambda}}\right) \varphi(D'_{n+\lambda}). \end{aligned}$$

If m and k have a common factor, $\left(\frac{m}{k}\right) = 0$ and in the other case we shall have

$$\sum_{\substack{d|k \\ d|m}} \mu(d) = \mu(1) = 1,$$

hence

$$\left(\frac{m}{k}\right) \sum_{\substack{d|k \\ d|m}} \mu(d) = \left(\frac{m}{k}\right)$$

and

$$\begin{aligned} S_2 &= \sum_{m=1}^k e^{\frac{2\pi i m n}{k}} \left(\frac{m}{k}\right) \sum_{\lambda=0}^{\frac{\varphi}{2}} B_\lambda e^{\frac{2\pi i m \lambda}{k}} \sum_{\substack{d|k \\ d|m}} \mu(d) \\ &= \sum_{\lambda=0}^{\frac{\varphi}{2}} B_\lambda \sum_{m=1}^k \left(\frac{m}{k}\right) e^{\frac{2\pi i m (n+\lambda)}{k}} \\ &= \sum_{\lambda=0}^{\frac{\varphi}{2}} B_\lambda \left(\frac{n+\lambda}{k}\right) i^{1/4(k-1)^2} \sqrt{k}, \end{aligned}$$

according to the theorem of Gauss. Hence we conclude

$$\begin{aligned} 0 &= S_1 + S_2 = \sum_{\lambda=0}^{\frac{\varphi}{2}} B_\lambda \left\{ \mu\left(\frac{k}{D'_{n+\lambda}}\right) \varphi(D'_{n+\lambda}) + \left(\frac{n+\lambda}{k}\right) i^{1/4(k-1)^2} \sqrt{k} \right\} \\ &= \sum_{\lambda=0}^{\frac{\varphi}{2}} B_\lambda b_\lambda. \end{aligned}$$

By changing the symbols of Legendre everywhere into their opposite values, we find in the same way the relation

$$\sum_{\lambda=0}^{\frac{\varphi}{2}} C_\lambda c^\lambda = 0.$$

Physics. "*On the Evaporation from a Circular Surface of a Liquid*".

By Dr. H. C. BURGER (Communicated by Prof. W. H. JULIUS).

(Communicated in the meeting of December 29, 1917.)

In a publication recently published Miss N. THOMAS and Dr. A. FERGUSON¹⁾ communicate observations concerning the evaporation from circular water surfaces. These observations are made under different circumstances viz. in a dark, very quiet room, in a lighted room and in the open air. It appeared, that in every case the quantity of water evaporated in unit time, might be represented by:

$$E = K r^n,$$

in which r is the radius of the water surface and K and n are constants that, except on the external circumstances, also depend upon the distance of the surface of the liquid and the rim of the basin in which this is contained. Now while, as the writers remark, usually in the literature the opinion is found, that the evaporation is proportional to the area of the surface, i. e. that $n = 2$, it was shown by their experiments that this exponent was always between 1 and 2. Now STEFAN²⁾ has treated the evaporation from a circular surface of a liquid, supposing that the vapour diffuses in the space above the plane in which the level of the liquid lies, while at the liquid the concentration of the vapour is a constant.

The result of the computation is, that the speed of evaporation is proportional to the radius of the surface. So it is apparent that in the experiments of THOMAS and FERGUSON the conditions that STEFAN supposes in treating the problem, are not fulfilled.

As I have already been engaged for some time upon the theoretical and experimental treatment of the diffusion in a flowing liquid³⁾, it was of importance to inquire whether my results agreed with the above mentioned investigations. For this purpose we must extrapolate the values of the exponent n for the case that the surface of the liquid is on a level with the rim of the basin. When this is

¹⁾ Phil. Mag. XXXIV p. 308, 1917.

²⁾ Wied. Ann. XVII p. 550, 1882.

³⁾ My principal purpose in this is to investigate whether the solution at the surface of the crystal is saturated or if perhaps, when the solving takes place sufficiently rapidly, an undersaturation arises.

not the case it hardly seems possible to apply the mathematical analysis to the problem.

For the three cases the extrapolated exponent is resp. 1.4, 1.5 à 1.6 and 1.65. In the last case, in which we are most certain that the air above the liquid is in continuous movement, n proves to agree quite sufficiently with the theoretical value $5/3 = 1.67$, which will be deduced hereafter, so that therefore in this case we may be sure, that the air-currents effect the evaporation. In experiments in more quiet air, the values of n approach the value $n = 1$ more closely, which value is found by STEFAN.

In the following sections we will give a theoretical treatment of the diffusion in a flowing gas. As the evaporation from an arbitrarily formed surface is easily deduced from that of a rectangular one, we firstly choose this last shape. We imagine the space above the plane $z = 0$ filled with a flowing gas, while the plane $z = 0$ itself is formed by a fixed wall, of which a part consists of a surface of the liquid. Let this part have the shape of a rectangle with its sides parallel to the axes of x and y , situated at positive y and bounded by the axis of x . Further we will choose the velocity of the gas to be parallel to the axis of y and to be proportional to z , so $v_y = az$. As namely the gas at the plane $z = 0$ through external friction must have a velocity equal to zero, we may put:

$$v_y = az + a_2 z^2 + a_3 z^3 + \dots,$$

and we may neglect the second and following terms of this series when as will generally be the case, the vapour is concentrated in a thin layer above the plane $z = 0$.

When we put c for the concentration of the vapour and D for the coefficient of diffusion then, as is easily seen, c fulfills the altered equation of diffusion:

$$\frac{\partial c}{\partial t} = D \Delta c - \text{div} (v c) \quad (I)$$

Further we suppose that c at the surface of the liquid fulfills the boundary condition:

¹⁾ The last term in the second member may be explained in this way: In the element of volume $dx \, dy \, dz$ flows through the element of surface $dy \, dz$ an amount

of vapour: $cv_x \, dy \, dz$ inward and $\left\{ cv_x + \frac{\partial}{\partial x} (cv_x) \right\} dy \, dz$ outward. By computing

these amounts also for the axes of y and z , we get for the total amount that flows outward $\text{div} (cv) \, dx \, dy \, dz$, when v is the velocity, considered as a vector.

$$c = C^1)$$

in which C is the concentration of the saturated vapour.

Now we will suppose that the state is stationary, i. e. that $\frac{\partial c}{\partial t} = 0$.

Then c satisfies the equation:

$$D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) = az \frac{\partial c}{\partial y} \quad . \quad . \quad . \quad . \quad . \quad (II)$$

while $v_x = v_z = 0$ and $v_y = az$. In this equation we will further take $\frac{\partial^2 c}{\partial x^2} = 0$. Of course this is only approximately true for the values of x that concern points within the rectangle. For points beside the rectangle c will be very small only when $\sqrt{\frac{D}{a}}$ is small with respect to the dimensions of the rectangle, which we will always suppose. So we will treat the problem as a twodimensional one, i. e. as if the rectangle has an infinite breadth in the direction of X^2). So we will neglect $\frac{\partial^2 c}{\partial x^2}$.

Finally we remark that $\frac{a}{D}$ being large, consequently $D \frac{\partial^2 c}{\partial y^2}$ may be neglected with respect to $az \frac{\partial c}{\partial y}$. One might object to this when c is zero or very small, but then is $c = C$ or at least then c is approximately a constant, so all terms of the differential equation are zero or very small, and so it will be allowed to omit $\frac{\partial^2 c}{\partial y^2}$. That $D \frac{\partial^2 c}{\partial z^2}$ may not be neglected, notwithstanding the small factor D , is caused by the fact that the evaporated substance will be concentrated in a thin layer, so that c varies rapidly with z ; $\frac{\partial c}{\partial z}$ and $\frac{\partial^2 c}{\partial z^2}$ therefore are large.

After these simplifications the differential equation for c becomes:

$$\frac{\partial^2 c}{\partial z^2} = \frac{a}{D} z \frac{\partial c}{\partial y} \quad . \quad . \quad . \quad . \quad . \quad (III)$$

As, in consequence of a sufficiently rapid stream, a diffusion

¹⁾ When by the rapid evaporation an undersaturation arises, this will probably be proportional to the speed of evaporation.

²⁾ Experiments with crystals that solve in a flowing liquid, have confirmed this supposition.

against the stream is impossible, we suppose with regard to the fact that the arriving gas is free from vapour that $c = 0$ for $y = 0$. For the same reason we may further assume that the surface of the liquid extends from $y = 0$ to $y = \infty$, while for arbitrary y the concentration will not be influenced by the presence of liquid at the boundary $z = 0$ at greater values of y . As was already said we take for $z = 0$ the boundary-condition $c = C$, while for $z = \infty$ c of course must be zero.

Problems of this kind may be solved in a general way by making the range in which z may vary finite, further by constructing a solution with the aid of a series of proper functions, and finally by going to the limit, whereby the range is made infinite. I hope to explain this method at length in my dissertation; here however it may suffice to give a much simpler treatment, because the purpose is only to find how the quantity of liquid evaporated in unit time depends upon the length of the rectangle, i. e. upon y .

When we introduce in (III) as a new variable:

$$\xi = z \sqrt{\frac{a}{D}},$$

this equation assumes the form:

$$\frac{\partial^2 c}{\partial \xi^2} = \xi \frac{\partial c}{\partial y} \quad \dots \quad (IIIa)$$

The boundary conditions of c are here:

$$c = 0 \quad \text{for} \quad y = 0$$

$$c = C \quad ,, \quad \xi = 0$$

$$c = 0 \quad ,, \quad \xi = \infty$$

The solution of the transformed equation will not contain a or D , because these quantities occur neither in the differential equation nor in the boundary conditions.

Therefore is:

$$c = \varphi(\xi, y) = \varphi\left(z \sqrt{\frac{a}{D}}, y\right).$$

The quantity of the liquid that evaporates in unit time from the part of the surface between $y = 0$ and y is found by computing the quantity of substance that flows through a plane perpendicular to the axis of y . As the velocity of the gas is az , the quantity of vapour that flows in unit time through a unit surface perpendicular to the axis of y , is azc ; so the total mass of vapour that flows away per unit breadth in the direction of x , amounts to:

$$E = \int_0^{\infty} a z c dz = a \int_0^{\infty} z \varphi \left(z \sqrt{\frac{a}{D}}, y \right) dz.$$

When now we introduce again $\zeta = z \sqrt{\frac{a}{D}}$, this quantity becomes:

$$E = a \cdot \left(\sqrt{\frac{D}{a}} \right)^2 \int_0^{\infty} \zeta \varphi(\zeta, y) d\zeta = a^{1/2} D^{3/2} \psi(y) \quad (IVa)$$

We may transform (III) also by putting:

$$\eta = y \cdot \frac{D}{a}.$$

Then we get the equation:

$$\frac{\partial^2 c}{\partial z^2} = z \frac{\partial c}{\partial \eta} \quad (IIIb)$$

To this belong the boundary conditions:

$$\begin{aligned} c &= 0 & \text{for } \eta &= 0 \\ c &= C & \text{,, } z &= 0 \\ c &= 0 & \text{,, } z &= \infty. \end{aligned}$$

Here again the solution will be independent of a and D viz.:

$$c = f(z, \eta) = f\left(z, y \frac{D}{a}\right).$$

From this we find:

$$E = \int_0^{\infty} a z c dz = a \int_0^{\infty} z f\left(z, y \frac{D}{a}\right) dz = a F\left(y \frac{D}{a}\right) \quad (IVb)$$

When now we compare the found values of E , (IVb) proves to agree with (IVa) only when:

$$F(p) = A \cdot p^{2/3},$$

where A is a constant. So E becomes:

$$E = a \cdot A \frac{y^{2/3} D^{2/3}}{a^{2/3}} = A a^{1/3} D^{2/3} y^{2/3} \quad (IVc)$$

Of this result the fact that in the first place interests us is that E proves to be proportional to $y^{2/3}$.

To deduce from the acquired result what E becomes for a surface of an arbitrary shape we imagine that this surface is divided into narrow strips with the long sides parallel to the axis of y i. e. to the current. As the breadth of these strips may not be taken too small when we wish to apply the acquired results, but on the other hand may not be too broad when we want to consider them as

rectangles, it proves that the circumference of the surface of the liquid may not be too irregular and also that the linear dimensions of this surface may not be too small with respect to $\sqrt{\frac{D}{a}}$.

Then however for each of these rectangles E is proportional to the breadth and to the $2/3^{rd}$ power of the length. The total value of E is found by integrating over the whole surface, and it is easily seen that this quantity for conform figures is proportional to the $5/3^{rd}$ power of the linear dimensions, of which this exponent $2/3$, as it were refers to the length and $3/3$ to the breadth.

As all circles are conform it is proved by this that the evaporation from a circular surface of a liquid is proportional to the $5/3^{rd}$ power of the radius as is also found by Miss THOMAS and Dr. FERGUSON, when the circumstances were in agreement with those that are used at the theoretical treatment given above.

The theory that is given here I have found confirmed by experiments of the solving of crystals in a flowing liquid, which will be treated in my dissertation. The quantity of the solved substance proved to be proportional to the $1/3^{rd}$ power of the velocity of the liquid, with the breadth and with the $2/3^{rd}$ power of the length.

Institute for theoretical Physics.

Utrecht, December 1917.

Anatomy. — "*On the topographical relations of the Orbits in infantile and adult skulls in man and apes*". By Prof. L. BOLK.

(Communicated in the meeting of March 23, 1918).

In the Proceedings of this Academy of 1909 two papers by the present author were published, dealing with the position, shifting and the inclination of the Foramen magnum in the Primates. In these papers it was shown that the topographical relations of this Foramen in the infantile skulls of the Primates and more particularly with the Anthropomorphous apes present only small deviations from those in the human skull. It is only in their subsequent growth that a difference between the development in man and the Primates becomes apparent. This difference comes in the main to this that in man the original topographical relations, such as are found in the infantile skull, are permanent, the skull retaining infantile characteristics; in the remaining Primates, on the other hand, and especially in the Anthropoid apes, these juvenile conditions are replaced by others. The chief phenomenon, which may be briefly stated afresh here, is that in infantile skulls of man and anthropoid apes the foramen magnum lies in the middle of the cranial base, and during growth is shifted backwards over a longer or shorter distance in the direction of the occipital pole of the cranium, while in man it remains situated in the anterior half of the cranial base. It is difficult to reconcile this result of my investigations with the conception, often met with in literature, that the more occipital position, as found in these apes, would be the original one, so that it would be in man that a forward shifting would take place. Now of such a forward displacement, presumed on theoretical grounds, nothing appears during individual development in man. On the contrary. From about the eighth year, i.e. in conjunction with the commencement of the loss of the milk-teeth, also in man a slight backward shifting is stated, which is not of much significance, however. So the characteristic difference between the human and anthropoid skulls is that in the former infantile, not to say foetal, characteristics are retained. While the infantile skulls of man and anthropoid apes thus show a great similarity in this respect, the adult skulls grow dissimilar, and it is not the

human but the antropoid skull which deviates more and more from its original shape.

The object of the following communication is to draw the attention to an analogous phenomenon in an entirely different part of the skull, namely in the orbital region, and regarding more particularly the following question: what are the topographical relations of the orbits in infantile and adult skulls of Primates? The answer to this question gives an insight into the phenomena of growth in this border-region between the cerebral and facial skull. These are well fitted to give a definite shape to our conception about the morpho-genetic relation between the human and anthropoid skull. In this

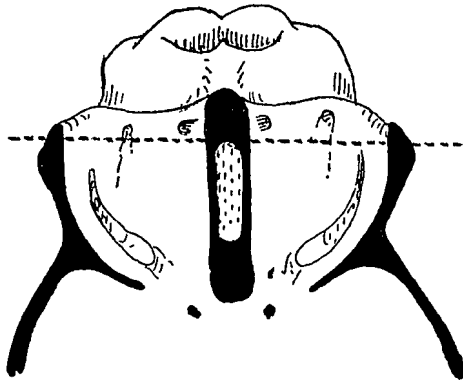


Fig. 1.

communication the main points only will be stated, the more extensive paper will be published elsewhere. For the present purpose the best starting-point is a form in which the differences in topography between the infantile and adult skull are as large as possible, their character thus being clearly revealed. The Gorilla skull serves this purpose well.

We shall mainly deal with the topographical relation of the orbits in regard to the cranial cavity. The easiest way of surveying this

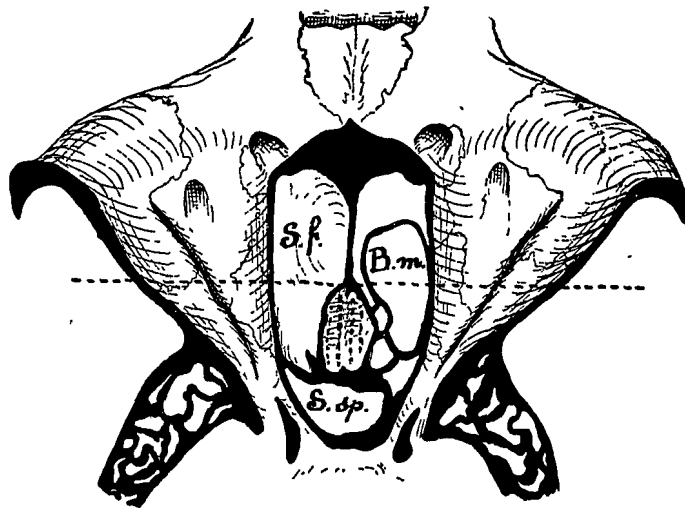


Fig. 2.

is by means of horizontal sections, passing through the middle of the orbits. In fig. 1 such a section is sketched through the skull of a young Gorilla child, in fig. 2 through that of an adult male individual.

In the lateral wall of the orbit in the infantile skull two parts may be distinguished, an anterior one which borders the orbit outwardly and forms the free outer wall of the orbit, and a posterior one forming a partition between the orbit and the fossa media of the cranial cavity. Between these two parts the lateral wall of the cerebral cranium is connected with the lateral wall of the orbit. This arrangement implies that the cranial cavity partly extends laterally of the orbit, in other words that this cavity partly enters into the Cavum cranii, so that there exists a common partition-wall between the Cavum orbitae and the Cavum cranii. Upwards in the direction of the roof of the orbit this partition-wall between the two cavities becomes larger, as the cranial wall frontally more and more joins the supra-orbital ridge. The free exterior wall thus becomes smaller and is entirely lacking near the roof of the orbit in the youthful Gorilla skull, as the cranial wall is attached to the orbital roof along the supra-orbital arch. Thus the whole orbital roof has become the partition between this cavity and the Cavum cranii. This means that in the infantile Gorilla the orbits lie entirely under the cranial cavity.

How is this in the adult skull?

It appears from fig. 2 that now on the lateral wall of the orbit the just-described two parts can no longer be distinguished; the posterior intracranial part has disappeared, since the lateral wall of the skull is attached as far backward as possible to the lateral wall of the orbit. The whole lateral wall has become an outer wall. From a topographical viewpoint this means that the orbit no longer enters into the cranial cavity, but has come to lie before it. This conclusion is confirmed by a closer examination of the orbital roof. In the infantile skull the frontal wall of the cranial cavity is attached to the orbital roof along the circumference of the orbit, which means that the whole roof of the orbit forms a partition between the cranial and orbital cavities and does not form a free exterior wall. In the adult individual, on the other hand, the cranial roof is attached to the orbital roof very much towards the back, as is seen from fig. 3, representing a sagittal section through the orbit of an adult Gorilla. The roof of the orbit has here for the greater part become a free exterior wall.

From this short comparison it already appears that the topographical relations of the orbit with regard to the cranial cavity are

very different in the young and the adult Gorilla. This difference may be briefly summarised as follows: in the young individual the orbit for the greater part enters into the Cavum cranii, in the adult

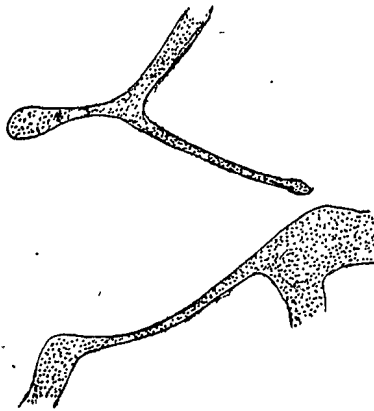


Fig. 3.

individual it lies *before* the cranial cavity. So there is a forward displacement during growth, caused by lengthening of the orbit in a forward direction only. By the aid of figs. 1 and 2 this can easily be proved if the Septum orbitale is particularly kept in view. In both figures the section passes exactly above the Lamina cribrosa, i. e. through the anterior extreme part of the cranial cavity.

In the septum orbitale of the infantile skull three parts may be distinguished, a middle one, formed by the Lamina cribrosa, an anterior and a posterior part. Also in the adult skull these three parts are visible in spite of the pneumatizing. Comparison now shows, that the lengthening of the septum is almost entirely brought about by the increase in length of that part of it which lies before the lamina cribrosa. One has only to compare the dotted lines in the two figures, indicating the plane through the anterior edge of the Lamina cribrosa. These lines are also serviceable for gaining an insight into the forward shifting, resulting from this mode of growth. In the small young skull almost the whole of the orbital cavity lies behind this line, in the adult skull only the posterior part.

Thus the growth of the skull of Gorilla has an evident influence on the position of the orbits with regard to the cranial cavity. That this is accompanied by a considerable change in the shape of the orbital cavity, is also perceived by comparing figure 1 and 2. In the adult skull the posterior part of the orbit has been drawn out in the shape of a funnel or canal.

The change of position of the orbit caused by growth can be illustrated in a simple manner by projecting the outlines of this cavity on the median plane, which is easily done by means of the well-known Martin pantograph. Fig. 4 shows such a projection taken from the skull of a Gorilla child in which the tooth-change had commenced (the medial incisors have been changed; fig. 5 a similar projection of the skull of an adult man¹⁾). The cranial base is partly, the

¹⁾ Fig. 5 is on a smaller scale than fig. 4.

outline of the cranial cavity entirely indicated. Position and direction of the lamina cribosa are also shown. To the transformation of the cranial cavity during growth, chiefly consisting in a flattening,

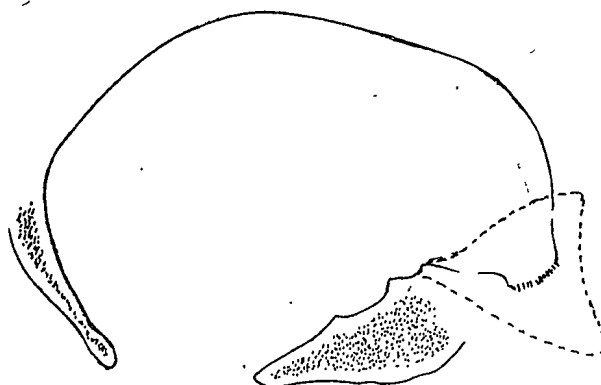


Fig. 4.

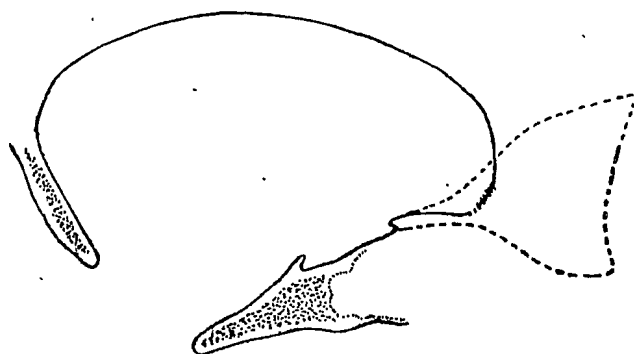


Fig. 5.

attention may be passingly drawn. These figures require little explanation, the change in the topographical relation of the orbits with regard to the cranial cavity is seen at a glance. It should only be pointed out that the shifting of the orbits quite before the cranial cavity must be regarded as the direct cause of the origin of the very strong bony ridge characterising the anterior part of the cerebral skull of Gorilla. This bone-ridge is, as also appears from fig. 3, nothing but the necessary upward enclosure of the orbital cavity, the newly-grown roof of this cavity. Without this bone-ridge the orbit would lack an upper bony enclosure.

Before proceeding to a description of the conditions in man, we shall briefly sketch those in the two other anthropoids by means of a few projection figures. Figures 6 and 7 refer to a young Orang still in possession of its complete milk-dentition, and to an adult individual of this genus. More strongly still than was the case with Gorilla the topographical change of the orbits with regard to the

cranial cavity appears in these two individuals. This is mainly the result of the circumstance that the little skull of the Orang child was so much younger than that of the Gorilla child. With this

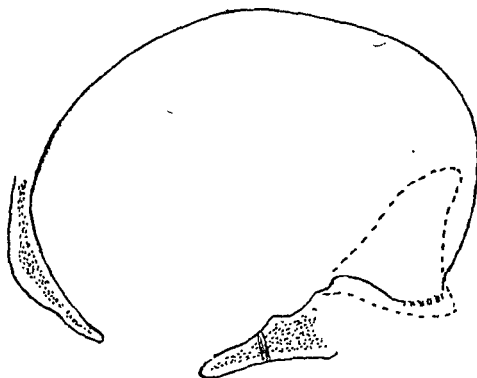


Fig. 6.

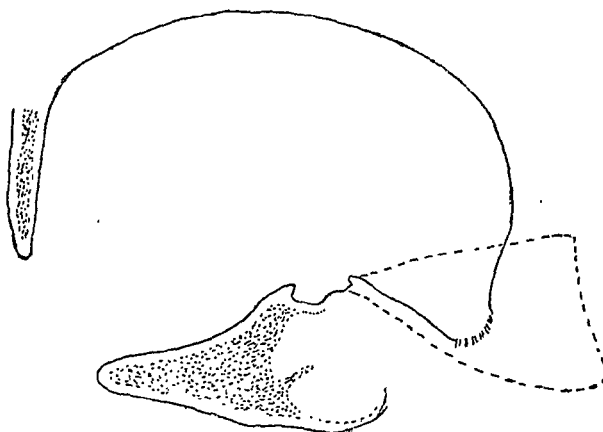


Fig. 7.

very young Orang the orbit is still entirely enclosed by the cranial cavity, the whole roof of the orbit is here still the floor of the anterior cranial cavity. In the adult Orang the orbit has come much more forward. So here also a considerable forward shifting has taken place. In orang this was not accompanied by the formation of a ridge as in Gorilla, firstly because the orbits and in particular their roof did not advance so far before the cranial cavity, and secondly because the anterior cranial wall in Orang had thickened evenly.

The changes in the topographical relations with Chimpanzee appears when we compare figures 8 and 9. With this genus the forward shifting is smaller again than with Orang, although still considerable. The projection in fig. 8 has been taken from a little skull with complete milk-dentition, that of fig. 9 from an adult skull.

From this short summary it appears that the three anthropoids agree in this that as the result of certain phenomena of growth the topographical relation of the orbits with regard to the cranial cavity

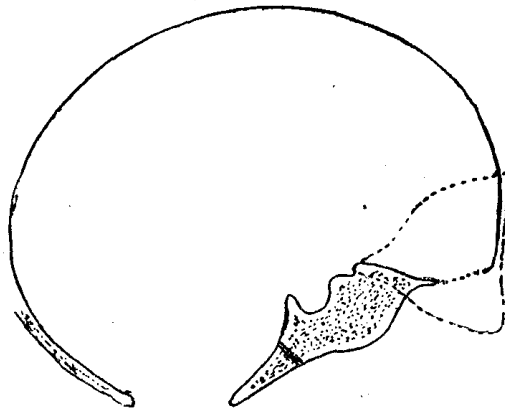


Fig. 8.

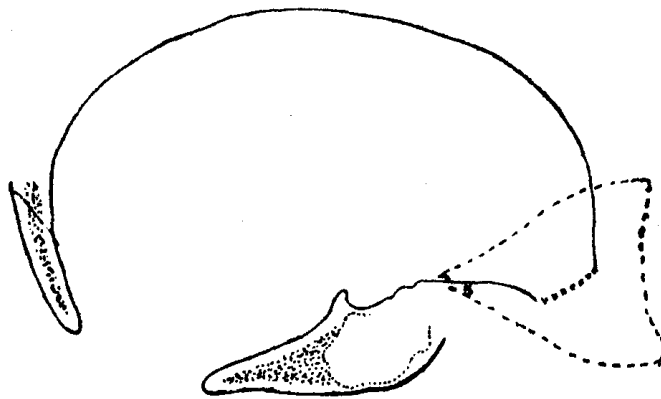


Fig. 9.

is altered. The chief change is that in the infantile antropoid ape the orbits lie under the cranial cavity, in the adult individual more in front of it. This is most strongly seen in Gorilla, where almost the whole orbit lies before the cranial cavity. The sagittal sections

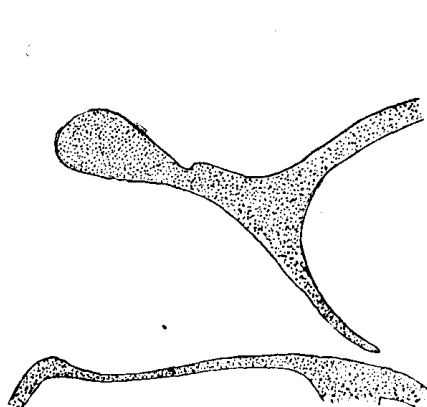


Fig. 10.

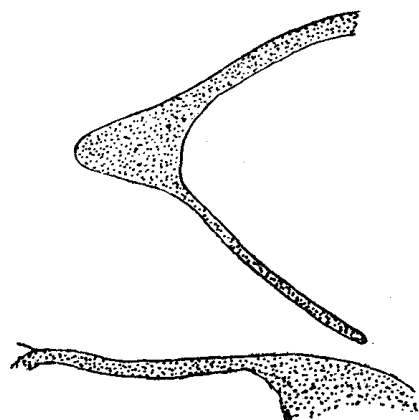


Fig. 11.

through the orbit in fig. 10 (Chimpanzee) and fig. 11 (Orang) when compared with those of fig. 3 (Gorilla) show this difference in shifting with the three Anthropoids very distinctly.

What is now observed in man? We refer in the first place to figs. 12 and 13. In 12 a horizontal section is given through the orbits of a new-born infant, in 13 through the orbits of an adult individual. In both figures a dotted line indicates as before the frontal plane passing through the anterior edge of the lamina cribrosa, i.e.

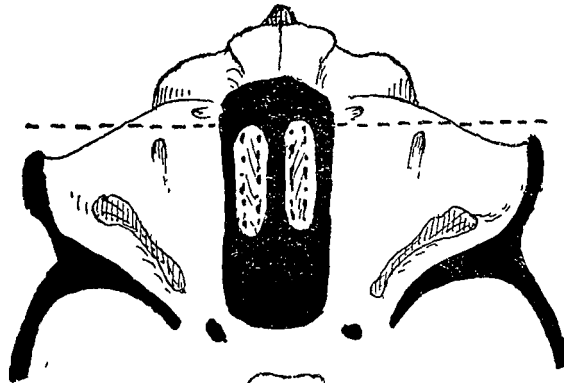


Fig. 12.

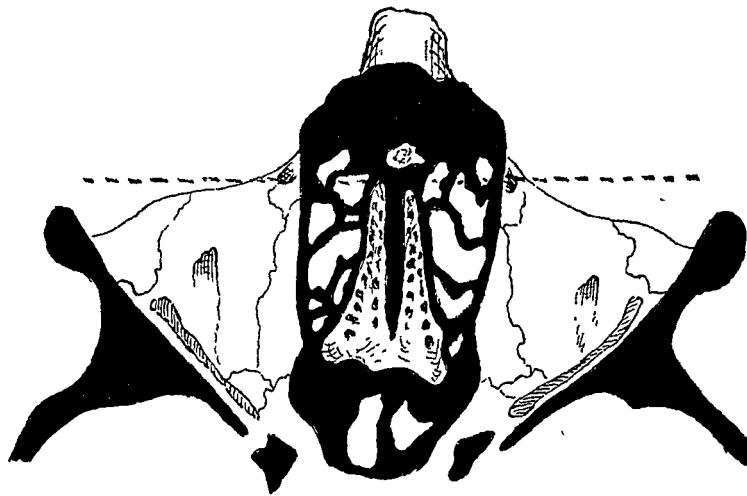


Fig. 13.

through the anterior border of the cranial cavity. When therefore we wish to answer the question whether the orbits are also in man shifted during growth, and, if the answer is affirmative, to what extent this happens, we have only to compare the position of the orbits in both figures with regard to this line. It then appears that there is no evidence of such a shifting. For in the infantile as well

as in the adult skull nearly the whole orbit lies behind this line. As to the topography of the orbits with regard to the cranial cavity, in man no change is observed during growth, such as was found with the Anthropoids. We come to the same conclusion when comparing the anatomy of the lateral wall of the orbits in the two figures. When dealing with the Gorilla skulls it was pointed out that in the infantile skull two parts could be distinguished in this wall, an intracranial part, partitioning the orbital and cranial cavities, and an anterior part, bordering the orbit outwardly. Between these two parts the cranial wall joins the orbital wall. In the adult Gorilla the intracranial part has disappeared, the cranial wall is attached to the posterior part of the orbital wall.

In man nothing appears of these altered anatomical relations. As well in the young as in the adult skull the intracranial part is found, which means that in the adult as well as in the infantile skull the posterior part of the lateral wall of the orbit has remained a partition between this and the cranial cavity. In man the orbital cavity always enters into the cranial cavity, which is moreover proved by the fact that the frontal wall of the cranial cavity is attached along the anterior border of the roof of the orbital cavity, as well in infantile as in adult skulls.

Thus in regard to the phenomena of growth in the orbital region of the skull there is a very noticeable difference between man on one side and the Anthropoids on the other. This difference is that in man infantile topographical relations remain permanent. In their juvenile stage these relations are the same in man as in the anthropoid apes. While in these latter they are replaced by other relations, however, so that the adult skull becomes very unlike the infantile one, the human skull retains its infantile cranial characteristics. As has been stated in the beginning of this paper, the same holds good for the Foramen magnum. From this ensues that when we compare the human and anthropoid skull those of the anthropoid apes may not be considered as primitive forms from which the human skull should be derived.

Mathematics. — “Null-Systems in the Plane”. By Prof. JAN DE VRIES.

(Communicated in the meeting of January 26, 1918).

1. In a null-system $\mathfrak{N}(\alpha, \beta)$ a group of α straight lines n passing through a point N is associated to that point; to a straight line n belongs a group of β points N lying on n . A point is called *singular*, when it is null-point of ∞ null-rays; a straight line is called *singular* if it has ∞ null-points.

The null-systems, for which α or β is equal to 1 (*linear null-systems*) are characterized by the fact that they always have singular null-points if $\alpha = 1$, always show singular null-rays if $\beta = 1$. Considerations concerning the case $\alpha = 1$ are to be found in my papers “On plane Linear Null-Systems” (These Proceedings vol. XV, page 1165) and “Lineare ebene Nullverwandtschaften” (Bull. de l’Acad. des Sciences du Sud de Zagreb, July 1917, Auszug aus der im Rad. Bd. 215, S. 122 veröffentlichten Abhandlung).

That a non-linear null-system does not necessarily possess singular elements, appears among others from the consideration of the null-system $\mathfrak{N}(3, 3n-6)$ formed by the points of inflection and their tangents appearing in a general net of curves of order n ¹⁾. Only for $n = 3$ we have in general a group of 21 singular null-rays, viz. the straight parts of the binodal figures.

2. Let us suppose that a $\mathfrak{N}(\alpha, \beta)$ possesses σ singular points S , which are singular null-points on each ray drawn through them, and σ_* singular points S_* , which replace two null-points on each ray²⁾. We further suppose that there are $\bar{\sigma}$ singular rays s and $\bar{\sigma}_*$ singular rays s_* ; the latter are characterized by the fact that they represent two coinciding null-rays for each of their points.

If the straight line n is caused to revolve round the point P , the β null-points N describe a curve (P) of order $(\alpha + \beta)$, which has an α -fold point in P .

Analogously the null-rays n , which have a null-point N on the

¹⁾ See my paper “Two null-systems determined by a net of cubics” (These Proceedings vol. XIX, page 1124)

²⁾ In the linear null-system formed by the tangents and their points of contact of a pencil (c^n) the base-points are singular points S_* , the nodes singular points S .

straight line p , envelop a curve (p) of class $(\alpha + \beta)$, of which p is a β -fold tangent.

Through a point S pass $(\alpha + \beta)$ tangents of (p) ; from this it is evident that the null-points on the rays of the pencil S form a curve $(S)^{\alpha+\beta}$. Now, S is always one of the null-points, so that an arbitrary ray of the pencil bears only $(\beta-1)$ points N outside S . Consequently $(S)^{\alpha+\beta}$ has an $(\alpha+1)$ -fold point in S .

Analogously we find that $(s)_{\alpha+\beta}$ has the straight line s as $(\beta+1)$ -fold tangent, while a straight line s_* is a $(\beta+2)$ -fold tangent of the curve $(s_*)_{\alpha+\beta}$.

3. The curve $(P)^{\alpha+\beta}$ is of class $(\alpha + \beta)(\alpha + \beta - 1) - \alpha(\alpha - 1)$. Through P pass therefore $(2\alpha + \beta)(\beta - 1)$ more tangents, which touch it elsewhere. To them belong evidently the straight lines PS_* , as S_* represents two coinciding null-points. *Consequently the null-rays bearing a double null-point envelop a curve of class $(2\alpha + \beta)(\beta - 1) - \sigma_*$.*

The complete enveloping figure contains moreover the σ_* class-points S_* .

It is of course possible that the enveloped curve breaks up. This e. g. happens with the null-system that arises if each tangent of a pencil (c^n) is associated to the $(n-2)$ points, in which it moreover intersects the c^n (satellite points of the point of contact).

We have to distinguish then between the envelope of the stationary tangents, which each bear *one* double null-point, and the envelope of the bitangents, which each contain *two* double null-points. The curve (P) is now the so-called *satellite-curve*¹⁾.

In a similar way we find: *The locus of the points N , for which two of the null-rays n have coincided is a curve of order $(\alpha + 2\beta)(\alpha - 1) - \bar{\sigma}_*$.*

4. The curves $(p)_{\alpha+\beta}$ and $(q)_{\alpha+\beta}$ have the α null-rays of the point pq in common. To the remaining common tangents the singular rays s and s_* evidently belong²⁾. There are therefore $(\alpha + \beta)^2 - \alpha - \bar{\sigma} - \bar{\sigma}_*$ rays n , a null-point N of which lies on p , another null-point N' on q .

This number has another meaning yet. If N describes the straight

¹⁾ Cf. my paper "On linear systems of algebraic plane curves" (These Proceedings vol. VII, page 712) or "Faisceaux de courbes planes" (Archives Teyler, série II, t. XI, p. 101).

²⁾ If $\beta = 1$, (p) and (q) have, besides the α null-rays of pq , *only* singular rays in common; consequently we have $\bar{\sigma} + \bar{\sigma}_* = \alpha^2 + \alpha + 1$. The tangents and points of contact of a tangential pencil provide an example of this.

line p , the remaining null-points N' of the null-rays n borne by N will describe a curve $(N')_p$. Its order is evidently equal to the number of rays n , which have a null-point on p and another on q .

Let us now consider the points that $(N')_p$ has in common with p .

Each of the β null-points of p is associated to each of the remaining $(\beta-1)$ null-points, and therefore is a $(\beta-1)$ -fold point of the curve (N') . The remaining points N' lying on p are evidently double null-points on one of the null-rays determined by them. Hence:

The locus of the double null-points is a curve (N_2) of order $\alpha^2 + 2\alpha\beta - \alpha + \beta - \sigma - \sigma_$.*

The consideration of the curves (P) and (Q) produces analogously:

The double null-rays envelop a curve (n_2) of the class $\beta^2 + 2\alpha\beta + \alpha - \beta - \sigma - \sigma_$.*

5. By means of an arbitrary conic φ^2 another null-system may be derived from a given null-system. Let N be one of the null-points of the ray n , N^* the intersection of n with the polar line of N with regard to φ^2 . A new null-system arises now if on each straight line n the null-points N are replaced by the corresponding points N^* ¹⁾. The number β remains intact. In order to find what α passes into, we observe that the null-rays n of the new null-point N^* must have one of their old null-points N on the polar line p of N^* . The null-rays n of the points of p envelop the curve $(p)_{\alpha+\beta}$. On each of the $(\alpha + \beta)$ tangents which it sends through N^* is N^* one of the new null-points.

By the harmonical transformation $\Re(\alpha, \beta)$ is therefore transformed into a $\Re^(\alpha + \beta, \beta)$.*

If N lies on φ^2 while one of its null rays touches at φ^2 , N^* becomes an arbitrary point of n , and n a singular straight line of \Re^* .

In order to determine the number of these singular rays, we associate to each tangent n of φ^2 the β tangents p , which meet n in its β null-points N .

The envelop $(p)_{\alpha+\beta}$ determined by p has evidently $2(\alpha + \beta)$ tangents in common with φ^2 . Besides the straight line p , which, as β -fold tangent of the envelope (p) , replaces β common tangents, $(2\alpha + \beta)$ rays n are associated to p . The correspondence between p and n has $2(\alpha + \beta)$ coincidences; on φ^2 lie therefore $2(\alpha + \beta)$ points N , of which one of the rays n touches at φ^2 . In other words $\Re^*(\alpha + \beta, \beta)$ has $2(\alpha + \beta)$ singular rays more than $\Re(\alpha, \beta)$.

¹⁾ The "harmonical" transformation dually corresponding to this I applied formerly to a $\Re(1, \beta)$ (vide "Plane Linear Null-Systems").

By the dual transformation $\mathfrak{N}(\alpha, \beta)$ passes into a $\mathfrak{N}^*(\alpha, \alpha + \beta)$, which has $2(\alpha + \beta)$ singular points more than \mathfrak{N} .

6. The harmonical transformation may be replaced by a more general transformation in the following way.

The polar curve π of a point N with regard to a given curve Φ^{m+1} intersects the null-ray n in m points N^* , which we shall consider as new null-points of n . In the new null-system \mathfrak{N}^* each straight line has then $m\beta$ null-points N^* .

As N^* lies on the polar curve π^m of N , N belongs to the polar line p of N^* with regard to Φ^{m+1} . Now $(\alpha + \beta)$ tangents of the curve (p) pass through N^* ; they are the null-rays of N^* for \mathfrak{N}^* . I. e. $\mathfrak{N}(\alpha, \beta)$ is transformed into a $\mathfrak{N}^*(\alpha + \beta, m\beta)$ by the new transformation.

In opposition to the harmonical transformation this transformation produces no new singular straight lines.

7. If we write $\alpha = 1$, $\beta = 1$, $m = 2$, we find from a bilinear null-system a $\mathfrak{N}^*(2, 2)$ for which the three singular straight lines of $\mathfrak{N}(1, 1)$ are also singular.

We may indicate the bilinear null-system by

$$y_1 : \xi_2 \xi_3 = y_2 : \xi_1 \xi_3 = y_3 : -2 \xi_1 \xi_2$$

and the curve Φ^3 by

$$x_1^3 + x_2^3 + x_3^3 + 3x_1x_2x_3 = 0.$$

The polar curve of (y) is then expressed by

$$y_1(x_1^2 + x_2x_3) + y_2(x_2^2 + x_1x_3) + y_3(x_3^2 + x_1x_2) = 0.$$

For the null-system $\mathfrak{N}(2, 2)$ we have therefore

$$\left. \begin{aligned} \xi_2 \xi_3 (x_1^2 + x_2x_3) + \xi_1 \xi_3 (x_2^2 + x_1x_3) - 2 \xi_1 \xi_2 (x_3^2 + x_1x_2) &= 0 \\ \xi_1 x_1 + \xi_2 x_2 + \xi_3 x_3 &= 0 \end{aligned} \right\} \quad (1)$$

In order to find the equation of the curve $(P)^4$ we have to combine these two equations with

$$p_1 \xi_1 + p_2 \xi_2 + p_3 \xi_3 = 0.$$

Elimination of ξ_k then produces for $(P)^4$

$$(p_1x_3 - p_3x_1)(p_2x_1 - p_1x_2)(x_1^2 + x_2x_3) + (p_3x_2 - p_2x_3)(p_2x_1 - p_1x_2)(x_2^2 + x_1x_3) - 2(p_3x_3 - p_3x_1)(p_1x_3 - p_3x_1)(x_3^2 + x_1x_2) = 0.$$

The equations (1) determine the two null-points of the straight line (ξ) as intersections of (ξ) with a conic. As a condition for the coincidence of the two null-points we find after some reduction the equation

$$\xi_1 \xi_2 \xi_3^4 - (\xi_1^3 + \xi_2^3) \xi_3^3 - 3 \xi_1^2 \xi_2^2 \xi_3^2 - 2 \xi_1 \xi_2 \xi_3 (\xi_1^3 + \xi_2^3) - 4 \xi_1^3 \xi_2^3 = 0.$$

It shows that the rays that bear two coinciding null-points, envelop a curve of the 6th class.

From this it ensues that the curve $(P)^4$ has no other singularities outside the node P .

Combination of (1) with the equation

$$\pi_1 w_1 + \pi_2 w_2 + \pi_3 w_3 = 0$$

produces for the curve $(p)_4$ by elimination of w_k the equation

$$\begin{aligned} & [(\pi_3 \xi_2 - \pi_2 \xi_3)^2 + (\pi_1 \xi_3 - \pi_3 \xi_1)(\pi_2 \xi_1 - \pi_1 \xi_2)] \xi_2 \xi_3 + \\ & [(\pi_1 \xi_3 - \pi_3 \xi_1)^2 + (\pi_3 \xi_2 - \pi_2 \xi_3)(\pi_2 \xi_1 - \pi_1 \xi_2)] \xi_1 \xi_3 = \\ & 2 [(\pi_3 \xi_2 - \pi_2 \xi_3)(\pi_1 \xi_3 - \pi_3 \xi_1) + (\pi_2 \xi_1 - \pi_1 \xi_2)^2] \xi_1 \xi_2. \end{aligned}$$

This is always satisfied by $\xi_k = 0$, $\xi_l = 0$. This was to be expected as the straight lines $O_1 O_2$, $O_2 O_3$, $O_3 O_1$ must be singular rays.

Mathematics. — "*Cubic involutions of the first class*". By Prof.
JAN DE VRIES.

(Communicated in the meeting of February 23, 1918).

1. By the "*class*" of an involution in the plane we understand the number of pairs of points on an arbitrary line. In a paper printed in volume XVI¹⁾, I have proved that the *cubic involutions of the first class* may be reduced to six principal species provided that it be supposed that there are no collinear triplets.

I will prove now that these involutions, with a few exceptions, may be determined by *nets of cubics*.

Let a net $[c^3]$ be given with *six* base-points C_k . All c^3 that yet pass through a point X , form a pencil (c^3), have therefore still two points X' and X'' in common, which form with X a group of an involution I_1 . On an arbitrary straight line $[c^3]$ determines a cubic involution I_2 , of the second rank; the neutral pair consists of two basepoints X', X'' , consequently is I_1 , an involution of the *first class*²⁾.

To $[c^3]$ belongs the γ^3_k , which has a nodal point in C_k . If X is chosen on this nodal γ^3_k , one of the points X', X'' comes in C_k ; so C_k is a *singular point* that forms groups of the I_1 with the pairs of an I_2 , lying on the singular curve γ^3_k . Each of the two points of γ^3_k lying in C_k , belongs to a pair of the I_2 ; from this it ensues that the pairs of this I_2 are lying on the tangents of a conic (*curve of involution* of the I_2).

To $[c^3]$ belongs also the figure formed by the conic γ^2_6 , which contains the points C_1, C_2, C_3, C_4, C_5 , and a certain straight line c_6 , on which C_6 lies. As $[c^3]$ determines on c_6 the pairs X, X' of an I_1 , c_6 is a *singular straight line*.

The involution I_1 has therefore *six singular points and six singular straight lines*.

The points X'' , which complete the pairs of the I_1 lying on c_6 into triplets of the I_2 , lie evidently on γ^2_6 . Let Y'' be the projection of X'' on c_6 , out of a fixed point of γ^2_6 ; there exists a relation (2,1) between Y'' and X , so that Y'' coincides three times

1) "Cubic involutions in the plane". These Proceedings XVI, 974—987.

2) If the rays XX', XX'' are associated to each point X , a null-system $\mathfrak{N}(2,2)$ arises.

with X . From this it ensues that the rays XX'' envelop a curve of the third class, which evidently has C_1 as bitangent. The straight lines $x = X'X''$, which are indicated by the triplets of the I_3 , form the triplets of an involution of rays i_3 . For this involution too, c_k is singular, as it belongs to ∞^1 groups, the straight lines x', x'' form an i_2 , for which γ_k^2 is the curve of involution.

2. When a point X describes the straight line p , the rays x', x'' , which connect X with X'', X' , envelop a curve $(p)_4$ of the fourth class, which has p as bitangent. The curves $(p)_4$ and $(q)_4$ have 16 tangents in common; to them belong the rays x', x'' , which emanate from $X = pq$, and the six singular straight lines c_k . There are consequently 8 straight lines x'' , for which X lies on p , and X' on q . In other words, if X describes the straight line p , X' and X'' describe a curve p^8 . The latter intersects p in the first place in the pair of the I_3 lying on p , and further in six points X , which have each coincided with a point X' , consequently are coincidences of the I_3 . *The coincidences of the I_3 form therefore a curve of the sixth order, γ^6 .*

If two base-points of a pencil meet in a point B , there is a curve that has a nodal point in B . So γ^6 is at the same time curve of JACOBI for the net $[c^3]$, has consequently nodal points in the six base-points C_k . In each of these points it has the tangents in common with the nodal curve γ^3_k . Outside the points C the lines γ^6 and γ^3_k have only two more points in common; they are the coincidences of the involution (X, X') lying on γ^3_k .

The curve (p) is of order 10, is therefore cut by p in 6 points. For each of these intersections X , x'' coincides with x' , consequently X' with X'' . The locus of the "branch points", the "complementary curve" is consequently also a curve of the sixth order, x^6 . It has nodal points in the singular points C_k , because γ_k^3 bears two coincidences. The curves γ^6 and x^6 have besides the 6 points C moreover 12 points in common, they are united in pairs into triple points of the I_3 . So there are in I_3 six groups, in which the three points are united in one point.

The above mentioned curve p^8 has a triple point in C_k , because γ_k^3 has three points X in common with p , for which X'' lies every time in C_k .

The pairs of the I_3 , which are collinear with an arbitrary point P , lie on a curve $(P)_4$, which passes twice through P and contains the singular points C^1). So p^8 and $(P)_4$ have in C_k 18 points in common;

¹⁾ For C_k this curve consists of γ_k^3 and the straight line C_k .

the intersections X of p with $(P)^4$ supply further 4 common points X' . The remaining 10 points which they have moreover in common form 5 pairs X', X'' , of which the line of connection x passes through P . In other words, if X describes a straight line, x envelops a rational curve of the *fifth class*.

3. Let us now consider the case that three base-points B_1, B_2, B_3 of a $[c^3]$ lie on a straight line α , while the remaining three, C_1, C_2, C_3 , have been chosen arbitrarily.

To the net belongs a pencil, each curve of which consists of the straight line α and a conic that passes through C_1, C_2, C_3 and a certain point A . These conics determine an I_2 on α , the pairs of which are completed by A into groups of the I_3 . So A is a *singular point*, α a *singular straight line*.

To the *singular points* C_1, C_2, C_3 the nodal curves γ_k^3 are again associated as before; to the *singular points* B_1, B_2, B_3 now belong curves β_k^2 , which pass through the points C and A . Each β_k^2 forms, as is known, with α the net-curve that has a node in B_k .

On the pair of lines $AC_1, C_2 C_3$, $[c^3]$ determines a system of groups of the I_3 , a point of which lies every time on $C_2 C_3$, so that AC_1 contains an I_2 of pairs X, X' . The three straight lines $c_k \equiv AC_k$ are therefore *singular*, they form with the singular straight line α the curve $(P)^4$ of the point A (see § 2).

For $C_k, (P)^4$ consists of γ_k^3 and c_k , for B_k of β_k^2, α and a singular straight line b_k . There are consequently *seven singular points* (A, B_k, C_k) and *seven singular straight lines* (α, b_k, c_k).

The straight line α is component part of the *Jacobian*, the *curve of coincidences* is now a γ^5 that passes through the three points B and has nodes in the three points C .

The curves $(p)_4$ and $(q)_4$ have now only 7 tangents x' , in common, which connect a point X of p with a point X' of q . In connection with this p^8 is now replaced by a p^1 , which passes three times through C_k , twice through B_k .

Between the points X of p and the points X^* , which are every time produced by the intersection of x on p , a correspondence exists, each coincidence of which is at the same time a coincidence of the I_3 ; hence x envelops a curve of the *fourth class*, when X describes a straight line.

4. Let us now suppose that one of the six base-points of $[c^3]$ is collinear with the base-points B_1, B_2^* , and with the base-points

B_3, B_3^* ; let this base-point be indicated by A_1 , while the sixth base-point will be indicated by C .

Now $[c^3]$ contains a threeside formed by $a_3 \equiv A_1 B_2 B_3^*$, $a_3 \equiv A_1 B_3 B_3^*$ and a straight line a_1 , which contains C and forms with γ^3 the curve $(P)^4$ of C . The *singular straight line* a_1 bears an I_2 , of which the pairs are completed into groups of the I_3 by A_1 .

To a_2 belongs again (as in § 3) a pencil of conics, the curves of which are completed by a_2 into figures c^3 . This (c^3) has as base-points B_3, B_3^*, C and a point A_2 , which is *singular*, because it forms groups of I_3 with the pairs of the I_2 , which (c^3) produces by the intersection with a_2 . Analogously there is a *singular point* A_3 to which an I_2 belongs placed on a_3 .

To the pencil (c^3) , which is associated to a_2 , belongs the figure formed by $a_3 \equiv B_3 B_3^*$, and the straight line CA_2 ; the latter is therefore identical with the third straight line a_1 of the threeside mentioned above. Analogously a_1 and a_2 form one of the conics that are associated to a_3 . From this we conclude that the *singular points* C, A_2 and A_3 are collinear, and lie on the *singular straight line* a_1 .

To the pencil associated to a_2 belongs also the pair of lines $CB_3, A_2 B_3^*$; on the second of these lines the net determines an I^3 or pairs (X, X') , which are each completed into triplets by a point of CB_3 . So the lines $A_2 B_3^*, A_2 B_3, A_3 B_2^*$ and $A_3 B_2$ are *singular*; we may indicate them by b_3^*, b_3, b_2^*, b_2 .

Finally there is moreover a *singular straight line* c , which passes through C and forms with the threeside $a_1 a_2 a_3$ the curve $(P)^4$ of C . It contains an I_2 of pairs X, X' , which are every time base-points of pencils out of $[c^3]$. If we now take two arbitrary fixed points M and M' , and if we associate the two c^3 , which each of the pencils in question sends through M and M' , two (c^3) are on account of this made projective. As any two homologous c^3 intersect each other in three points of c , and the two pencils have a curve c^3 in common, the figure produced by them consists of c^3 , the line c , and a conic γ^2 ; the latter therefore is the locus of the point X'' .

Summarizing we find that this I_3 has *eight singular points* and *eight singular straight lines*.

Its *coincidences* lie on a γ^4 , which passes through the points B and twice through C .

In an analogous way, as in § 3, it appears that X envelops a curve of the *third class*, when X describes a straight line.

5. Let us now suppose that the base-points B_1, B_2, B_3 are respec-

tively lying on the sides A_2A_3, A_3A_1, A_1A_2 of the triangle which has the base-points A_k as vertices.

In the same way as with the preceding I_2 , there belongs to the straight line $\alpha_1^* \equiv A_2A_3B_1$ a (c^2) , the base of which consists of A_1, B_2, B_3 and a certain point A_1^* , which is again *singular* and belongs to an I_2 lying on α_1^* . Analogously there are moreover two other *singular points*, A_2^* and A_3^* , which are related to involutions I_2 on α_2^* and α_3^* . It appears now from the consideration of the threeside formed by α_1^*, α_2^* and by the straight line α_3 , which must pass through B_3 , that α_3 contains the points A_1^* and A_3^* (see § 4).

Evidently the *singular straight lines* $\alpha_1, \alpha_2, \alpha_3$ belong respectively to the singular points A_1, A_2, A_3 .

The *nine singular points* are now placed in such a way, that each point B_k is the intersection of the lines α_k and α_k^* ; the triangles $A_1A_2A_3$ and $A_1^*A_2^*A_3^*$ are consequently circumscribed to the points B_1, B_2, B_3 .

Besides the six singular straight lines α_k, α_k^* there are moreover *three singular straight lines* $b_k \equiv A_k^*A_k$. For, on the pair of lines $A_1A_1^*, B_2B_3$ [c^3] determines groups of the I_2 , of which every time one point lies on B_2B_3 , while the other two form a pair on b_1 .

The *curve of coincidence* is now a γ^3 , which passes through the points B . To a straight line p a p^3 is associated, while the straight line X envelops a curve of the *second class*, when X describes the straight line p .

For B_1 the curve $(P)^4$ consists of a β_1^2 ($A_1B_1B_2B_3A_1^*$) and the lines α_1, α_1^* ; for each of the remaining singular points it consists of four lines easily to be indicated.

For further particulars I refer to my paper mentioned above.

6. We now consider a net [c^3] that has the vertices A_{kl} of a fourside, with sides α_k , as base-points. To the straight line α_1 a (c^3) is associated, which has as base-points A_{23}, A_{24}, A_{34} and a certain point A_1 ; each of these c^3 forms with α_1 a figure of the net. To these figures belongs the *threeside* that is composed of α_1, α_2 and a third straight line α_{12} , which must pass through A_{34} , but cannot but contain the *singular point* A_1 . But this threeside may at the same time be considered as compound of the straight line α_1 with a pair of lines of the (c^2) , which has as base-points A_{13}, A_{14}, A_4 and a certain point A_2 ; consequently the third straight line α_{12} passes through A_{34} and A_2 . The *singular straight line* α_{12} contains therefore the three *singular points* A_1, A_2, A_{34} .

Besides the *six singular points* A_{kl} , which have each a straight

line a_{kl} as corresponding singular line, the I_s has as appears from the above, moreover *four* other singular points A_m , which are in pairs collinear to the points A_{kl} , and that in such a way that A_m and A_n are connected with A_{kl} by the singular straight line a_{kl} . In other words, there are *ten singular points* and *ten singular straight lines*, which form a fourside and a complete quadrangle, in which the former is inscribed in such a way to the latter that a configuration 10_3 of DESARGUES has arisen.¹⁾

The *curve of coincidences* is now a *conic*, as the four straight lines a_k form part of the *Jacobian*. This may moreover also be confirmed by paying attention to the common tangents of the curves $(p)_4$ and $(q)_4$; they have besides the two straight lines x indicated by the point pq and the 10 singular straight lines, moreover 4 straight lines x in common, which each connect a point X of p with a point X' of q . To a line p as locus of X corresponds therefore a curve p^4 as locus of the pairs X', X'' and the latter intersects p in two coincidences. It is easy to find now that the straight line $X \equiv X'X''$ describes a *plane pencil*.

The I_s here described has been known longest; it may properly be called the involution of REYE.

7. With this *five* of the involutions I_s found in the above mentioned paper have been deduced from nets of cubics. The sixth I_s is obtained if each c^2 passing through the points E, F_1, F_2, F_3 is intersected by each c^2 passing through the points E, G_1, G_2, G_3 . This I_s was amply discussed in my paper "A quadruple involution in the plane". (These Proceedings XIII, 82—91).

When the base-points B_1, B_2, B_3 of a $[c^3]$ lie on a straight line $b_{1,2,3}$ and the base-points B_4, B_5, B_6 on a straight line $b_{4,5,6}$, this net contains a pencil, each figure of which is composed of the two straight lines mentioned and a ray s of a plane pencil whose centrum be indicated by A .

On each ray s $[c^3]$ determines an I_s ; here we have therefore a cubic involution in the plane, which contains *collinear triplets only*, and consequently was excluded from the investigation mentioned above. Neither is it of the first class, for on an *arbitrary* straight line does not lie a single pair.

The Jacobian of this net consists of the lines $b_{1,2,3}, b_{4,5,6}$ and a

¹⁾ In a more symmetrical way the points and lines of the 10_3 are indicated by the symbols kl and klm ; the points kl, km, lm , lie on the straight line klm (k, l, m to be replaced by 1, 2, 3, 4, 5)

curve γ^4 , which contains the *coincidences* of the cubic involutions lying on the rays.

Analogous results are arrived at by considering the net of which the six base-points lie on a conic.

8. Let a *net of nodal cubics* be given, which all pass through the base-points B_1, B_2 and have their node in D .

To $b_1 \equiv B_1 D$ belongs a pencil of conics passing through D, B_2 and two other points A_1 and A_1^* . Analogously to $b_2 \equiv B_2 D$ a (c^2) with base D, B_1, A_2, A_2^* . The two pencils $[c^2]$ indicated by this have the threeside in common, which consists of b_1, b_2 and a third line d . From this it ensues that d must contain the points A_1, A_1^*, A_2 and A_2^* .

On the *singular straight line* d , $[c^2]$ determines an I_2 ; here too we have consequently a triple involution, which was excluded in the investigation mentioned above, because it has collinear triplets.

On the pair of lines $DA_1, B_2 A_1^*$ $[c^2]$ determines groups of the I_3 , which have each a point on DA_1 and a pair of points on $B_2 A_1^*$. The last mentioned line is therefore *singular*, and the same holds good for the lines $B_2 A_1, B_1 A_2$ and $B_1 A_2^*$.

Taking into consideration that the *curve of coincidences* is a γ^4 with *triple point* D , we can now deduce from the combination of two curves $(p)_4$ that besides the *five singular straight lines* mentioned there can be no others. For, $(p)_4$ has d as *bitangent*, so that d represents four common tangents of $(p)_4$ and $(q)_4$. And, as to p , on account of γ^4 , a curve p^6 is associated, as locus of X' , $(p)_4$ and $(q)_4$ can only be touched yet by four singular straight lines.

As none of the singular lines passes through D , the curve $(P)^4$ for $P \equiv D$ will have a *triple point*. On this d^4 , which passes through B_1, B_2 and the points A , lies an I_2 , of points X, X' , for which X'' is lying in D ; the straight line XX' envelops a curve of the 3^{rd} class.

For B_1 the curve $(P)^4$ consists of a conic β_1^2 (which contains an I_2) and the straight lines $B_1 A_2, B_1 A_2^*$.

The *singular points* A_1, A_1^* form triplets with each of the points of b_1 ; to them no singular straight line is therefore associated. For A_1 the curve $(P)^4$ consists of the straight lines $A_1 B_2$ and b_1 together with the twice to be counted line d .

The curve $(p)_4$ is evidently of order 8 (two bitangents); it is consequently intersected by p in 4 points. Consequently the *complementary curve* is of the fourth order. As it has nodes in D, B_1, B_2 , it can have besides these points but $16 - 2 \times 3 - 2 \times 2$ or 6 points in common with γ^4 . In this I_2 only *three groups* occur of which the three points have coincided.

It possesses *seven singular points* and *five singular straight lines*.

9. In § 7 there was a reference to a triple involution that has only collinear groups. Another I_3 with only collinear triplets is determined by the projective nets

$$ka_x^3 + lb_x^3 + mc_x^3 = 0, \quad kA_x + lB_x + mC_x = 0.$$

Each triplet consists of base-points of a pencil (c^4) belonging to the net $[c^4]$ indicated by

$$\begin{vmatrix} \alpha & \beta & \gamma \\ a_x^3 & b_x^3 & c_x^3 \\ A_x & B_x & C_x \end{vmatrix} = 0,$$

which has *thirteen* fixed base-points S_k . For the curves $a_x^3 B_x = b_x^3 A_x$ and $a_x^3 C_x = c_x^3 A_x$ have in common the three points indicated by $a_x^3 = 0$, $A_x = 0$, and they do not lie on the net-curve $b_x^3 C_x = c_x^3 B_x$. The curves of $[c^4]$ pass therefore through 13 fixed points.

Any straight line contains three base-points of a pencil (c^4). If it is represented by $kA_x + lB_x + mC_x = 0$, which is always possible, the pencil in question is found by writing

$$k\alpha + l\beta + m\gamma = 0$$

in

$$\begin{vmatrix} k\alpha + l\beta + m\gamma & \beta & \gamma \\ ka_x^3 + lb_x^3 + mc_x^3 & b_x^3 & c_x^3 \\ kA_x + lB_x + mC_x & B_x & C_x \end{vmatrix} = 0$$

Then we find the pencil

$$\beta \begin{vmatrix} \sum_3 ka_x^3 & c_x^3 \\ \sum_3 kA_x & C_x \end{vmatrix} = \gamma \begin{vmatrix} \sum_3 ka_x^3 & b_x^3 \\ \sum_3 kA_x & B_x \end{vmatrix}$$

and it has as base-points the intersections of

$$\sum ka_x^3 = 0 \quad \text{with} \quad \sum kA_x = 0.^1)$$

The thirteen points S_k are *singular*, for each point S forms a triplet with each of the pairs that is produced by the intersection of the pencil with centre S_k on the nodal curve σ_k^4 , which has S_k as node and belongs to $[c^4]$.

The groups of the I_3 that are collinear with the point P lie on a curve $(P)^4$, which passes through the points S , consequently also belongs to $[c^4]$.

¹⁾ An arbitrary net $[c^4]$ has 12 base-points at most and intersects a straight line in the groups of an involution I^2_1 (of the second rank), which has three neutral pairs. Here the three pairs are replaced by a neutral triplet.

Any net-curve contains a point P , for which it serves as curve $(P)^4$. For the *Jacobian* γ^3 , at the same time *curve of coincidences* of the I_1 , has nodes in S_k and intersects a c^4 of the net consequently moreover in 10 points R , which must be coincidences of the I_1 . Let R_1 be one of those points; the tangent in R_1 at c^4 has two more points in common with that curve; one of them forms with R_1 a triplet of I_1 . Let P be the second of those points. The $(P)^4$ belonging to P has now in common with c^4 the 13 points S , the point P and the triplet of the I_1 determined by R_1 ; but the two curves are identical then and the tangents at c^4 meet in the 10 points R in P .

From this it ensues at the same time that the *lines* t containing the coincidences of I_1 envelop a curve τ of the *tenth class*.

10. In S_k six tangents of σ_k^4 meet; each of the tangents in S_k replaces two straight lines t , so that τ has a node in S_k .

If $(P)^4$ has a node D , PD replaces two straight lines t and P is a point of τ .

If $(P)^4$ has two nodes D_1 and D_2 , P is node of τ and PD_1 , PD_2 are the tangents in P .

Analogously τ has a cusp in P , if $(P)^4$ is a cuspidal c^4 .

Consequently τ has besides the 13 nodes S_k , moreover 225 nodes and 72 cusps.¹⁾

Hence we find further that τ is a *curve of order 27* and of *genus 15*.

It must correspond in genus to the curve of coincidence γ^3 ; in fact the latter is also of genus 15, because it has 13 nodes.

As σ_k^4 contains six coincidences besides S_k , the *complementary curve* x has a *sextuple point* in S_k . On each $(P)^4$ lie 10 points of x , viz. on the straight lines t , which meet in P . So $(P)^4$ and x have $10 + 13 \times 6$ points in common, x is consequently a curve of order 22.

The curves γ^3 and x^{22} can only touch outside the points S ; and in each of those points of contact the curves of a pencil (c^4) have an osculation. From $9 \times 22 - 13 \times 2 \times 6 = 42$ it appears therefore that I_1 has 21 groups of which the three points have coincided.

11. Let us now consider the case that the curves indicated in § 9 by $a_x^3 = 0$, $b_x^3 = 0$, $c_x^3 = 0$ have a node in S_6 . The net $[c^4]$ may now be represented by

¹⁾ A net $[c^n]$ without multiple base points has $\frac{3}{2}(n-1)(n-2)(3n^2-3n-11)$ binodal and $12(n-1)(n-2)$ cuspidal curves. (Cf. e.g. my paper in volume VII, p. 631-633).

$$\begin{vmatrix} \alpha & a_x^2 x_3 + a_x^3 & x_1 \\ \beta & b_x^2 x_3 + b_x^3 & x_2 \\ \gamma & c_x^2 x_3 + c_x^3 & x_3 \end{vmatrix} = 0$$

in which a_x^2 etc. are functions of x_1 and x_2 . All c^4 have a node in S_0 .

The groups of the I_3 on the rays passing through S_0 consist of the point S_0 twice to be counted and a point of the curve c^4 , indicated by

$$\begin{vmatrix} a_x^2 x_3 + a_x^3 & x_1 \\ b_x^2 x_3 + b_x^3 & x_2 \end{vmatrix} = 0,$$

which has a *triple point* in S_0 .

As $(P)^4$ has a node in the singular point S_0 , P bears *eight* straight lines t , so that τ is now of class 8. The curve of coincidence γ^9 intersects $(P)^4$ in the points of contact of the 8 straight lines t and twice in each of the 9 *singular points* S_k (single base-points of $[c^4]$); from this it ensues that γ^9 passes *five times* through S_0 .

We now consider two arbitrary pencils of the net $[c^4]$ and associate to each c^4 of a pencil the curves of the other, which curves intersect it on γ^9 . The product of the pencils that consequently are in an (8,8) consists of the twice counted curve γ^9 , eight times the c^4 , which the pencils have in common, and the *complementary curve* x . From $64 - 2 \times 9 - 8 \times 4 = 14$ it now appears that x is a curve of order 14.

The curve c_k^4 belonging to S_k has nodes in S_k and S_0 ; consequently is S_k *quadruple point* of x . A combination of $(P)^4$ with x^{14} now leads to the conclusion that x^{14} possesses a *sextuple point* in S_0 .

We now find by the combination of γ^9 and x^{14} that I_3 contains 12 groups in which the three points have coincided.

The characteristic numbers of τ are easy to find, as this curve corresponds in genus to γ^9 , and has the 12 points of contact of γ and x as points of inflexion. It appears to be of order 20.

12. If in

$$\begin{vmatrix} \alpha & a_x^2 & x_1 \\ \beta & b_x^2 & x_2 \\ \gamma & c_x^2 & x_3 \end{vmatrix} = 0$$

a_x^2 etc. again represent functions of x_1 and x_2 , all the curves of $[c^4]$ in $O_3 = S_0$ have a *triple point*. The groups of the I_3 are now determined by

$$ka_x^3 + lb_x^3 + mc_x^3 = 0 \quad \text{and} \quad kx_1 + lx_2 + mx_3 = 0.$$

The first of these equations shows that the rays have been arranged by S_0 into the triplets of an involution of the second rank.

If two rays of a group coincide, we have¹⁾.

$$ka_1 + lb_1 + mc_1 = 0$$

$$ka_2 + lb_2 + mc_2 = 0.$$

We find, therefore, for the *curve of coincidences*

$$\begin{vmatrix} a_1 & b_1 & c_1 \\ a_2 & b_2 & c_2 \\ a_3 & b_3 & c_3 \end{vmatrix} = 0,$$

i.e. a γ^5 with *quadruple point* S_0 .

This result was to be foreseen; for the net $[c^4]$ has moreover 4 single base-points S_k ; the JACOBIAN has consequently 4 nodes S_k and an octuple point S_0 , breaks up, therefore, into four rays S_0S_k and a γ^5 .

If the three rays of a group of the involution I_1^2 coincide, we have

$$\begin{vmatrix} a_{11} & b_{11} & c_{11} \\ a_{12} & b_{12} & c_{12} \\ a_{22} & b_{22} & c_{22} \end{vmatrix} = 0.$$

There are consequently three groups of the I_1^2 in which the three points coincide; their lines t are stationary tangents of the curve τ .

As $(P)^4$ has now a *triple point* in S_0 , P bears only *four* straight lines t . The curve τ is consequently of class 4; as it must be of the genus null and has 3 stationary tangents, it is a curve of order three.

The I_1^2 has a neutral pair; these two straight lines form a c^4 with the conic that passes through the five singular points.

13. The net determined by

$$\begin{vmatrix} \alpha & \alpha_x^2 & A_x^2 \\ \beta & \beta_x^2 & B_x^2 \\ \gamma & \gamma_x^2 & C_x^2 \end{vmatrix} = 0$$

has 12 base points, consequently produces an I_4 . If, however, the 6 conics corresponding to the 6 quadratic functions, all pass through a point S_0 , the curves of $[c^4]$ have a node in S_0 and pass further through 9 fixed points besides. The variable base-points of the pencils (c^4) form now an I_3 . This *triple involution of the third class* I have fully investigated in a paper, printed in volume XVII, p. 134 of these "Proceedings". In a paper published in volume XVII, p. 105, a *triple involution of the second class* is to be found; its groups are arrived at by intersecting any conic of a pencil with any curve of a pencil (c^3) ; the two pencils viz. have three base-points in common.

¹⁾ By a_{kl} is meant $\frac{\partial a}{\partial x_k}$, by a_{kl} the form $\frac{\partial^2 a}{\partial x_k \partial x_l}$.

Mathematics. — “*Linear Null-Systems in the Plane*”. By Professor
JAN DE VRIES.

(Communicated in the meeting of April 26, 1918).

1. A linear null-system $\mathfrak{N} (1, m)$ may be determined by two equations of the form

$$\begin{aligned}\xi_1 x_1 + \xi_2 x_2 + \xi_3 x_3 &= 0 \\ \xi_1 A_1 + \xi_2 A_2 + \xi_3 A_3 &= 0,\end{aligned}$$

where A_k indicates a function of order m , in x_k .

When the straight line n revolves round the point $P(y_k)$, its m null-points N , viz. the intersections of $\xi_x = 0$ with the curve $\Sigma \xi_k A_k = 0$, describe a curve of order $(m + 1)$. As $\xi_y = 0$, this *null-curve* $(P)^{m+1}$ has as equation,

$$\begin{vmatrix} y_1 & y_2 & y_3 \\ x_1 & x_2 & x_3 \\ A_1 & A_2 & A_3 \end{vmatrix} = 0.$$

The curves $(P)^{m+1}$ form a net that is represented on the point-field by the points P ; for each netcurve belongs to a definite point P .

The net has $(m^2 + m + 1)$ *base-points*. For, if for the sake of brevity its equation is written in the form

$$y_1 B_1 + y_2 B_2 + y_3 B_3 = 0,$$

it appears that the curves $B_1 = 0$ and $B_2 = 0$ have in the first place the points indicated by $x_3 = 0$, $A_3 = 0$ in common, which, however, do not lie on the curve $B_3 = 0$. For the $(m^2 + m + 1)$ points S_k , which they have moreover in common, we have the relation

$$A_1 : x_1 = A_2 : x_2 = A_3 : x_3.$$

These points lie consequently at the same time on $B_3 = 0$.

Each of the base-points S_k bears ∞^1 null-rays n , is therefore a *singular point* of the null-system.

Two null-curves $(P)^{m+1}$ and $(Q)^{m+1}$ have in the first place the m null-points of the straight line PQ in common; the remaining intersections must be singular as they bear each two null-rays; they are therefore identical with the $(m^2 + m + 1)$ *singular points* S .

If the point O_s is laid in one of the singular points we have to write $A_k = \alpha^{(k)} x_1^{m-1} + \dots$, where $\alpha^{(k)}$ indicates a linear function of x_1 and x_2 .

We find then for null-curve of O

$$(x_1 a^{(2)} - x_2 a^{(1)}) x_3^{m-1} + \dots = 0,$$

from which it is evident that the null-curve σ_k^{m+1} of S_k has a node in S_k .

This result was to be expected, but of course holds good only in the case of S being single null-point for an arbitrary ray passing through S .

2. If a point N describes the straight line p , its null-ray n envelops a curve of class $(m+1)$, which will be indicated by the symbol $(p)_{m+1}$. For the null-curve of an arbitrary point Q intersects p in $(m+1)$ points N , of which the null-rays pass through Q . Evidently p is an m -fold tangent of $(p)_{m+1}$.

The null-curves $(p)_{m+1}$ and $(q)_{m+1}$ have a common tangent in the null-ray of the point pq . Each of the remaining common tangents is a straight line n , of which one of the null-points N lies on p , another null-point N' on q . If N describes the straight line p , the remaining null-points N' describe consequently a curve (N') of order $(m^2 + 2m)$.

Each of the null-points of p is to be considered $(m-1)$ times as point N' , so that (N') in those null-points has $m(m-1)$ points in common with p . In each of the remaining $3m$ intersections of p with (N') a point N' coincides with a point N into a double null-point $N^{(2)}$ of the corresponding straight line n .

In a double null-point the curves (P) of a pencil have a common tangent, one of the pencil-curves has a node there. The locus of the double null-points (*curve of coincidence*) coincides with the *Jacobiana* of the net of the curves (P) . As the latter is in general a curve of order $3m$, the conclusion may be drawn from the above made statement that the null-system possesses in general *no singular straight lines*. For, if a straight line has each of its points as null-point, it is common tangent of null-curves $(p)_{m+1}$ and $(q)_{m+1}$.

The curve of coincidence γ^{3m} has, as Jacobiana, $(m^2 + m + 1)$ nodes S_k .

This may be confirmed as follows. Through P pass $(m^2 + m - 2)$ tangents of $(P)_{m+1}$: their points of contact are double null-points, consequently points of γ^{3m} . The remaining $3m(m+1) - (m^2 + m - 2)$ intersections of (P) with γ must lie in the singular points, but then γ must have a node in each point S .

3. Let us now consider the locus κ of the groups of $(m-2)$ null-points, lying on the null-rays t , which possess a double null-point.

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Through each point S pass $(m^2 + m - 6)$ tangents of the null-curve σ^{m+1} of S ; as they bear a double null-point each, S is an $(m^2 + m - 6)$ -fold point of the complementary curve α . Besides the points S , α has moreover the groups of $(m-2)$ null-points in common with $(P)^{m+1}$; these points lie on the $(m^2 + m - 2)$ straight lines t , which meet in P . The two curves have consequently in common $(m^2 + m + 1)(m^2 + m - 6) + (m^2 + m - 2)(m - 2)$ points. For the order of α we find from this $(m^4 + 3m^3 - 5m^2 - 9m - 2) : (m + 1)$, i. e. $m^3 + 2m^2 - 7m - 2$, or $(m - 2)(m + 4m + 1)$.

4. The straight lines t envelop a curve τ of the class $(m + 2)$ $(m - 1)$.

If a curve c^{m+1} of the net has a node D , DP replaces two of the rays t meeting in P ; P is then a point of τ and PD the tangent in P at that curve.

If P lies on a binodal c^{m+1} , with nodes D and D' , PD and PD' replace each two straight lines t and are tangents in a node of τ .

If a c^{m+1} has a cusp in K , PK replaces three straight lines t , and P is a cusp of τ .

Now the net $[c^{m+1}]$ contains according to a well-known proposition $\frac{1}{2}m(m-1)(3m^2 + 3m - 11)$ binodal and $12m(m-1)$ cuspidal curves.

If we moreover take into consideration that the base-points S are nodes of τ , it appears that τ possesses $\frac{1}{2}(9m^4 - 40m^3 + 35m + 2)$ nodes and $12m(m-1)$ cusps.

We can now determine the remaining characteristic numbers of τ .

From the formula $v = n(n-1) - 2d - 3r$ it ensues at once that the order of τ is $3m^2$.

From $3n - r = 3v - \rho$ we deduce for the number of points of inflexion $3(m-2)(2m+1)$.

The genus of τ is equal to that of γ^{3m} , viz. equal to $\frac{1}{2}m(7m-11)$.

And we now finally arrive from

$$g = \frac{1}{2}(v-1)(v-2) - (\delta + \rho)$$

at the number $\frac{1}{2}(m-2)(m-3)(m^2 + 7m + 4)$ of bitangents.

It appears from the results arrived at that $\mathfrak{R}(1, m)$ has $3(m-2)(2m+1)$ rays with triple null-point $N^{(3)}$ and $\frac{1}{2}(m-2)(m-3)(m^2 + 7m + 4)$ rays that have two double null-points each.

By means of these two numbers it would be possible to determine again the order of the complementary curve. For the curves γ and α will touch in the triple null-points and must intersect in the coupled double null-points; they have further in each singular point

$2(m^2+m-6)$ points in common. Taking this into account we find indeed for the order of κ the number arrived at above.

5. Till now we have supposed that the singular points are all single and different, but moreover that each point S is *single null-point* on a ray arbitrarily drawn through S . An example of a $\Re(1, m)$, of which the singular points are partly *double null-points*, is furnished by a pencil of curves c^r , when each straight line is associated to its points of contact with curves of the pencil. A ray passing through a base-point of (c^r) is touched outside that point by $2(r-2)$ curves, while an arbitrary straight line has $2(r-1)$ null-points; so each base-point is to be considered as double null-point. The remaining singular points of this null-system $\Re(1, 2r-2)$ lie in the nodes of the nodal curves c^r ; they are evidently *single null-points* on the straight lines drawn through them.

We shall now suppose that $\Re(1, m)$ has s_2 singular points $S^{(2)}$, which are *double null-points* of their rays. As a ray passing through $S^{(2)}$ outside that point bears $(m-2)$ null-points the *null-curve* $\sigma^{(2)}$ has a *triple point* in $S^{(2)}$. The complementary curve now consists of the s_2 null-curves $\sigma^{(2)}$ and a curve κ^* of order $(m-2)(m^2+4m+1) - (m+1)s_2$, while the curve τ has been replaced by a curve τ^π of class $(m+2)(m-1) - s_2$ and the s_2 class-points $S^{(2)}$.

If it is taken into consideration that $\sigma_k^{(2)}$ contains all singular points $S_k^{(2)}$ and S_m it is found that κ^* passes through each point S with $(m^2+m-6-s_2)$ branches and with $(m^2+m-8-s_2)$ branches through each point $S^{(2)}$.

6. In order to arrive at a determination of the number of triple null-points $N^{(3)}$, we associate to each point $N^{(2)}$ of a ray t the $(m-2)$ null-points N' of t , and consider the correspondence which arises in consequence of this in a plane pencil with centre T . As the points $N^{(2)}$ lie on the curve γ^{3m} , the points N' on the curve κ' , the characteristic numbers of this correspondence are evidently $3m(m-2)$ and $(m-2)(m^2+4m+1) - (m+1)s_2$, while any ray t passing through T produces an $(m-2)$ -fold coincidence. The number of the remaining coincidences amounts to

$$3m(m-2) + (m-2)(m^2+4m+1) - (m+1)s_2 - (m+m-2-s_2)(m-2) \text{ i.e. } (m-2)(6m+3) - 3s_2.$$

There are consequently $3(m-2)(2m+1) - 3s_2$ null-rays with a triple null-point.

In order to find the number of coupled double null-points $N^{(2)}$ we associate to each point N' of a ray t each of the remaining

null-points N'' of t . The involutory relation which arises in consequence of this in the plane pencil T has as characteristic number $[(m-2)(m^2 + 4m + 1) - (m+1)s_2](m-3)$; any ray t passing through T represents now $(m-2)(m-3)$ coincidences. The remaining coincidences to the number of $2(m-3)[(m-2)(m^2 + 4m + 1) - (m+1)s_2] - (m^2 + m - 2 - s_2)(m-2)(m-3)$ form pairs of double null-points.

There are consequently $\frac{1}{2}(m-2)(m-3)(m^2 + 7m + 4) - \frac{1}{2}(m-3)(m+1)s_2$ rays which each bear two double null-points.

A null-system $\mathfrak{N}(1, m)$ with $(m^2 + m + 1)$ simple singular points has therefore $3(m-2)(2m+1)$ null-rays with a triple null-point and $\frac{1}{2}(m-2)(m-3)(m^2 + 7m + 4)$ null-rays with two double null-points.

With this the results of § 4 are confirmed.

For the null-system $\mathfrak{N}(1, 2r-2)$ mentioned above $s_2 = r^2$; the number of triple null-points amounts therefore to $3(7r^2 - 22r + 12)$. For $r=3$ we find from this 27. For each pencil (c^3) each base-point is point of inflexion on three curves c^3 ; the number 27 consequently arises from the fact that the 9 base-points serve each on three null-rays as triple null-point. As this observation holds good for each pencil (c') the number of points $N^{(3)}$ outside the base-points will be equal to $3(6r^2 - 22r + 12)$. In such a point a c' has four coinciding points in common with its tangent. In general a pencil (c^r) has therefore $6(r-3)(3r-2)$ curves that have a *point of undulation*¹⁾.

7. If the curves $A_k = 0$ (§ 1) have an r -fold point in O_3 , $S_0 \equiv O_3$ is an r -fold null-point on each of its rays. Outside the singular null-point S_0 there are then moreover $(m^2 + m + 1) - r^2$ simple singular null-points S .

The null-curve of S_0 has as equation $A_1 x_2 - A_2 x_1 = 0$; hence it has in S_0 an $(r+1)$ -fold point.

The null-curve $(P)^{m+1}$ has in S_0 an r -fold point, consequently sends through P $(m^2 + m - 2) - (r^2 - r)$ tangents t , of which the points of contact lie on the curve of coincidence γ . The latter has nodes in the points S ; so of its intersections with $(P)^{m+1}$ there lie in S_0 $3m(m+1) - (m^2 + m - 2 - r^2 + r) - 2(m^2 + m + 1 - r^2) = (3r-1)r$ points.

From this it ensues that γ has in S_0 a $(3r-1)$ -fold point.

In order to determine the order of the complementary curve, we consider two pencils of null-curves (c_1^{m+1}) and (c_2^{m+1}) , and associate

¹⁾ Another deduction of this number I gave in "Faisceaux de courbes planes". (Archives Teyler, sér. II, t. XI, p. 99).

to each c_1^{m+1} the $(m^2 + m - 2 - r^2 + r)$ curves c_2^{m+1} , which it intersects on γ^{3m} , outside the points S . The figure produced by the pencils coupled in this way consists of twice the curve γ , of $(m^2 + m - 2 - r^2 + r)$ times the curve c^{m+1} , which belongs to both pencils and of the complementary curve κ . We now find as its order $(m^2 + m - 2 - r^2 + r)(m + 1) - 6m$ i. e. $(m - 2)(m^2 + 4m + 1) - (m + 1)r(r - 1)$.

With regard to § 3 we conclude from this that the null-curve of S_0 is to be considered $r(r - 1)$ times as component part of κ .

Applying the method of § 6 again, we now find the number of *triple null-points* from

$$3m(m-2) + (m-2)(m^2 + 4m + 1) - (m+1)r(r-1) - (m-2)(m^2 + m - 2 - r^2 + r)$$

i. e.

$$(m-2)(6m+3) - 3r(r-1).$$

Analogously we find for the number of null-rays with *two double null-points*

$$\frac{1}{2}(m-2)(m-3)(m^2 + 7m + 4) - \frac{1}{2}(m-3)(m+4)r(r-1).$$

8. A very particular linear null-system is obtained by supposing that the functions A_k (§ 1) only contain x_1 and x_2 . In that case

$$\xi_1 A_1 + \xi_2 A_2 + \xi_3 A_3 = 0$$

represents an involution of rays of the second rank, of which the ∞^2 groups, each of m rays, correspond projectively to the straight lines of the plane.

The null-curves have now in $S_0 \equiv O_3$ an m -fold point, are consequently rational; the null-curve of S has degenerated into $(m + 1)$ rays, which each contain one of the simple singular null-points S .

If the derivatives of A_k with regard to x_1 and x_2 are indicated by $(A_k)_1$ and $(A_k)_2$, we find for the *locus of the double null-points* the equation

$$\begin{vmatrix} x_1 & x_2 & x_3 \\ (A_1)_1 & (A_2)_1 & (A_3)_1 \\ (A_1)_2 & (A_2)_2 & (A_3)_2 \end{vmatrix} = 0$$

This curve of order $(2m - 1)$ has in S_0 a $(2m - 2)$ -fold point. By the $(m + 1)$ rays $S_0 S_k$ it is completed into the Jacobiana of the net of the null-curves.

The rays ι with the double null-points envelop a curve τ of class $(2m - 1)$; for $(P)^{m+1}$ is now of class $(m + 1)m - m(m - 1) = 2m$.

The triple rays of the above mentioned involution are indicated by

$$\begin{vmatrix} (A_1)_{11} & (A_2)_{11} & (A_3)_{11} \\ (A_1)_{12} & (A_2)_{12} & (A_3)_{12} \\ (A_1)_{22} & (A_2)_{22} & (A_3)_{22} \end{vmatrix} = 0.$$

Their number amounts therefore to $3(m-2)$.

There are consequently $3(m-2)$ null-rays with *triple null-point*; they are evidently *stationary tangents* of the curve τ enveloped by the null-rays t .

Analogously the *bitangents* of that curve are intersected in their points of contact by the pairs of double rays that occur in the groups of the involution. Their number, as is known, amounts to $2(m-2)(m-3)$.

For the order of τ we find now m ; it has no cusps, but $\frac{1}{2}(m-1)(m-2)$ nodes. It is, just as γ^{2m-1} , rational.

The involution has $\frac{1}{2}(m-1)(m-2)$ neutral pairs. Each pair belongs to ∞^1 groups and corresponds projectively to a plane pencil of null-rays. In connection with this the null-curve of the centre of that pencil consists in the corresponding neutral pair of rays and a curve of order $(m-1)$, which has an $(m-2)$ -fold point in S_0 .

The null-curve of a singular point S_k consists of the ray $S_k S_0$ and a curve of order m with $(m-1)$ -fold point S_0 .

Mathematics. — “*Null-Systems determined by two linear congruences of rays*”. By Professor JAN DE VRIES.

(Communicated in the meeting of April 26, 1918).

1. A twisted curve α^p intersected by a straight line a in $(p-1)$ points, determines a linear congruence $(1,p)$, of which each ray u rests on a and on α^p . Analogously a curve β^q intersected by the straight line b in $(q-1)$ points determines a congruence $(1,q)$, of which the rays v rest on b and β^q .

Through the point N pass in general *one* ray u and *one* ray v . If the plane $v \equiv uv$ is associated as null-plane to N a null-system arises in which a plane v has in general pq null-points, viz. the intersections of the p rays of u with the q rays of v .

If N describes a straight line l , the rays u and v describe two ruled surfaces, which are successively of order $(p+1)$ and order $(q+1)$, and intersect along a curve (l) of order $(pq+p+q)$. An arbitrary plane v passing through l has with (l) the pq null-points of v in common, and moreover $(p+q)$ points lying on l , which belong each as null-point to a definite plane v . In other words, the straight line l is $(p+q)$ times *null-ray*. In R. STURM's notation the null-system has therefore the characteristic numbers $\alpha = 1, \beta = pq, \gamma = p+q$, may consequently be indicated by $\Re(1, pq, p+q)$.

2. If v coincides with u , any point of that straight line has any plane passing through that straight line as null-plane. Now, the congruences $(1,p)$ and $(1,q)$ have in general $(pq+1)$ rays in common. There are consequently $(pq+1)$ *singular straight lines* s .

The curves α^p and β^q are also *loci of singular points*. Through a point A^* of α^p passes a ray v^* and a plane pencil of rays u . In any plane passing through v^* lies *one* ray v ; so A^* is null-point to any plane of a pencil that has v as axis. The straight lines v^* form a *ruled surface* of order $p(q+1)$; for a plane passing through b contains p rays v^* and a point of b bears pq rays v^* . Finally the points of a and b too are *singular null-points*. A point A_* of a bears *one* ray v_* and ∞^1 rays u , which form a cone of order p with $(p-1)$ -fold generatrix. Any plane passing through v_* contains p rays u , so that A_* is to be considered as p -fold null-point. The rays v_* form a *ruled surface* of order $(q+1)$. A straight line u

(or v) is null-ray to any of its points; in connection with this the curve (l) degenerates for $l \equiv u$ or $l \equiv v$.

3. If a plane v continues to pass through the point P , its null-points describe a surface (P) of order $(p+q+1)$. For a straight line l passing through P bears $(p+q)$ points N , which send their null-plane through P .

The straight lines u and v , which intersect in P , lie on (P) ; for each of their points sends its null-plane through P .

On (P) lie further the $(pq+1)$ singular rays s and the singular curves α^p , β^q , while the singular straight line a is evidently a p -fold line, the singular straight line b a q -fold line. The surfaces (P) and (Q) have, in connection with this, the singular lines s , a , b , α and β in common and intersect further along the curve (l) , which belongs to $l \equiv PQ$.

4. As the straight line l intersects the ruled surface (v^*) in $p(q+1)$ points, the curve (l) contains evidently $p(q+1)$ singular null-points A^* and thus $q(p+1)$ singular null-points B^* .

There are further $(q+1)$ planes passing through l , which bear a p -fold null-point A_* each, and consequently $(p+1)$ planes each with a q -fold null-point B_* .

Let R be a point outside the straight line l . To the intersections of the surface (R) with the curve (l) belong in the first place the pq null-points of the plane lR . Further the $p(q+1)$ points A^* and the $q(p+1)$ points B^* . The remaining common points to the number of $(p+q+1)(p+q+pq) - pq - p(q+1) - q(p+1)$ i.e. $p^2(q+1) + \alpha q^2(p+1)$ must be lying in the $(q+1)$ points A_* and the $(p+1)$ points B_* . As α on (R) is a p -fold line each of the $(q+1)$ points A_* must be a p -fold point of the curve (l) . Analogously has (l) in each of the $(p+1)$ points B_* a q -fold point. The curve α^p is rational, sends consequently $2(p-1)$ tangent planes through l . In each of these tangent planes two rays u coincide, so there are q double null-points, so that the plane is q -fold tangent plane of (l) . Analogously β^q sends through l $2(q-1)$ tangent planes which are p -fold tangent planes of the curve (l) . As l is intersected by (l) in $(p+q)$ points, the rank of l is equal to $2(p-1)q + 2(q-1)p + 2(p+q)$, i.e. $4pq$.

5. Let us inquire in how far the results arrived at are altered when the congruence of rays $(1,q)$ is replaced by the congruence $(1,3)$ of the bisecants v of a twisted cubic β^3 .

Let B^* be a point of β^3 , u^* the ray which the congruence $(1,p)$ sends through that point. Any plane passing through u^* contains two straight lines v , which intersect in B^* ; B^* is consequently a double null-point.

The surface $(P)^{p+4}$ has consequently β^3 as *nodal curve*; it further contains the curve α^p , the $(3p+1)$ singular straight lines s and passes p times through the singular straight line a .

The ruled surface (v^*) is of order $4p$, the ruled surface (u^*) of order $(3p+3)$, while the straight lines v_* , as bisecants of β^3 , form a ruled surface of the fourth order.

If the congruence $(1,p)$ is also replaced by the congruence $(1,3)$ of the bisecants of a curve α^3 , a null-system $\Re(1, 9, 6)$ arises. The surface $(P)^7$ has α^3 and β^3 as nodal curves and contains 10 singular straight lines s ; $(P)^7$ and $(Q)^7$ have moreover a curve $(l)^{15}$ in common. The ruled surfaces (u^*) and (v^*) are of order 12.

6. For $p=1$, $q=1$ we have a bilinear null-system $\Re(1, 1, 2)$, in which the rays u rest on two straight lines a, a' , the rays v on two straight lines b, b' .

The singular figure consists then of the straight lines a, a', b, b' and their two transversals s, s' . For each singular point the null-planes form a pencil; the axes of those pencils form four quadratic systems of generatrices. The surface $(P)^3$ has a triple tangent plane¹⁾ in the null-plane of P .

¹⁾ Cf. my paper "On bilinear null-systems" (These Proceedings, vol. XV, p. 1160).

Experimental Psychology. — "*The Psychology of Conditions of Confusion*". By Prof. E. D. WIERSMA.

(Communicated in the meeting of April 26, 1918).

The contents of our consciousness distinguish themselves by their intensity. When attentiveness is directed on them they have a high grade of consciousness. When our attention is scattered over many psychical contents or there is a weakening or depression of the attentiveness, we speak of a generally low grade of consciousness, by which we have to understand a condition in which external impressions or also our own thoughts can not, or with difficulty, cross the threshold of consciousness; in which associations do not, or incompletely, come to pass; in which the formation of syntheses is hampered, in other words, a condition in which the precision, the clearness and the velocity of conception of the contents of consciousness is diminished. Such depressions of consciousness occur in many forms, normally as well as pathologically. The momentary weakenings of consciousness cause normally the phenomena of depersonalisation and of "*fausse reconnaissance*", as was proved by the investigations of HERMANS, and pathologically the epileptic fits as the psychology of epilepsy teaches us.

More prolonged depressions occur normally in dullness, exhaustion, sleepiness, and sleep, and pathologically in the conditions of acute confusion as we meet them in or after acute infectious diseases, in some intoxications, and sometimes in meningitis.

These processes can make their appearance in many different forms. At one time the stupor is more pronounced, then again the confusion and desorientation, strong disturbances of memory, hallucinations, delusions, and motor restlessness. In whatever form the disease presents itself the characteristics of a lowered grade of consciousness are always clearly present. The constant presence of this one symptom with the great change in all other phenomena, makes it probable that the former is primary to those other symptoms. This opinion is strengthened by the fact that all the symptoms of confusion disappear for a moment if we are able to obviate or lessen the intensity of the depression of attentiveness. In a raving fever patient, in a patient with delirium tremens, with uraemia or

with meningitis one can often let all symptoms disappear for a short time by heightening the psychical level or by concentrating the attention on something. The patient is then no longer confused, gives the right answers, knows his bearings, and has no more hallucinations.

Moreover there is so strong a correspondance between normal depressions of consciousness such as sleep and the dream, and the acute pathological conditions of confusion, that of old a comparison was readily made between these conditions. If now the low grade of consciousness or the depression of the attentiveness is the cause of the various symptoms of acute conditions of confusion, then it is to be expected that such symptoms will also make their appearance, albeit in rudimentary form, in normal and pathological conditions in which the grade of consciousness has sunk.

To determine this I have made a series of investigations on persons of whom it could with certainty be assumed that the groups in which they were classified would show large differences in attentiveness. Among these were patients with obvious intellectual disturbances, sufferers from melancholia with strong obstruction and depression, hysterics with a narrowed consciousness, and normal persons. After the grade of consciousness had been determined by an examination of the attentiveness, several other psychical functions, which are more or less disturbed in acute conditions of confusion, were further investigated.

In a number of other subjects I limited this examination to a few psychical functions only, viz. to the annihilation of weak impressions by later stronger ones. The results of this later examination I shall mention immediately after describing the arrangement of the test, while the results of the first experiments, in which various methods of examination have been used, will follow after a description of the methods has been given, so that in this way a better survey is obtained for comparing the results.

It is well known that there are many good methods for measuring the voluntary attentiveness, which gives us an idea of the grade of consciousness. I have made use of two of these viz. the Esthesiometer, which was first used by GRIESBACH ¹⁾ to determine fatigue, and the marking method ²⁾ as this has been used in the determination of the psychical after-effects of school children.

¹⁾ GRIESBACH Ueber Beziehungen zwischen geistiger Ermüdung und Empfindungsvermögen der Haut. Arch. f. Hygiene Bd. 24. 1895.

²⁾ WIERSMA. Psychische Nachwirkungen. Zeitschr. für de ges. Neur. u. Psych. Bd. XXXV H 3.

Opinions vary strongly as regards the value of the esthesiometric method, but I do not want to dwell upon that now. I have used the method as described by BINET¹⁾ and for the sake of brevity I refer to the original description.

The subjects of the experiment were touched on the back of the hand with the ends of two blunt needles of a certain thickness, which were fixed at various distances from each other in pieces of cardboard.

The distances between the needles were 0 (one needle only); 1; 1.5; 2; 2.5 and 3 cm. The needles must be placed on the skin simultaneously and always with the same amount of pressure. With such a set of needles the subject is touched in irregular order, but with the same distance equally often. These experiments were repeated on five consecutive days at the same time of day.

Then the percentage of double and single touches was determined for each distance. For the purpose of judging the attentiveness I used as a criterion the fact that a touch with one needle had always to be felt as one point, and with two needles 2.5 or 3 cm. apart always as two points. This has been proved by a prolonged investigation of various normal people. If a mistake is made here it has usually to be considered as a disturbance of the attentiveness. By computing the average number of mistakes it was possible to get an opinion of the attentiveness. It was evidently necessary not to reckon with the border values only, because some patients suffering from dementia and often also those suffering from Melancholia, always answer over all distances with 2 or with 1. In these patients one would come to very misleading results. On the other hand it has been proved, also by investigations of BINET, that it must not always be ascribed to inattentiveness when a touch with one needle is felt doubly. A high degree of attentiveness could sometimes be the cause of this. There is therefore no doubt about it that this method does not always yield trustworthy results, but it is serviceable for measuring larger differences of attentiveness, as are found in pathological cases.

The second method of investigation consists of the marking tests. It is accurately explained to the person experimented upon what he is expected to do. A large piece of paper, on which there are printed 50 lines of groups of dots, is placed before him. These groups, of which there are 25 on each line, consists of three, four, or five dots. The order of the various groups, which are more or less equal in number, is extremely irregular.

¹⁾ BINET. An. ps. XI. 1905.

The person to be examined was now instructed to mark the groups of four dots with a vertical and those of three dots with a horizontal line, in pencil, in as short a time as possible. The end of every minute was notified by the investigator and had to be recorded by a line. At the end of three minutes there was an interval of two min. and then the work was started again for three minutes, but then with this difference that now the marking was reversed, the groups of four being indicated by a horizontal, and those of three by a vertical line. This was repeated on five consecutive days, however so that on the even days the reversed marking had to be done in the third minute before the interval. The standard of attentiveness could be determined from the results of this work in different ways:

1. By the number of dot groups that had been examined by the subject.

2. By the number of mistakes.

After the grade of attentiveness had been determined in this way I have investigated whether the phenomena of confusion were to be found in the persons when the grade of consciousness sank.

The memory was examined by the following method:

The so-called "Treffer" Method of MÜLLER and PILZECKER.

This consisted herein that during five days eight pairs of words, which were typed on a piece of paper and between whom an associative connection had been avoided as much as possible, were laid before the subject on each day. One of the lists follows here;

Poplar	Air
Clock	John
Grey	Willow
Jacob	Sleep
Match	Chestnut tree
Violet	Charles
Letter	Garret
Earth	Brown

These words are slowly read aloud in pairs and are then withdrawn from the subject's observation. The first word of each pair was then mentioned by the examiner whereupon the subject had to name the corresponding word. By computing the number of correct, incorrect, and missing answers one could form an idea of the memory.

2. The above named pairs of words were chosen in such a way

that three ideas, which could be combined in the same general conception, appeared three times on each list. In the list above there are three trees, three christian names, and three colours. In other lists there are limbs, coins, birds, names of cities etc. A quarter of an hour after the examination with the "Treffer" method, during which other tests had been made, the subject was asked which trees, christian names, colours etc. were on the list he had seen. Here again the percentage of correct, incorrect, and missing answers was computed.

The further investigations were for the purpose of determining the faculty of inculcation, and the annihilation of freshly received impressions by later and stronger ones.

Inculcation and reproduction of numbers of two figures.

A row of five numbers, which has been carefully selected so that in each test numbers of the same tens, the combination of the same figures, and round tens, were avoided, was placed before the person to be examined. After he had read them aloud slowly twice he had to repeat them after an interval of one minute. Then the same test was repeated, but now with this difference that additions of two figures had to be done as quickly as possible during the interval. This test was repeated during five days and the results with the subsequent impediment, and without it, compared.

Recognition of numbers of two figures.

The test described above was afterwards made in a modified form. The numbers which had been observed and read aloud had now not to be mentioned, but were to be selected from a list three times as large.

The percentage of good bad and nil-achievements in both tests was computed. A comparison between the reproduction through association and through recognition, and between the annihilations of subsequent work in these psychical functions was hereby possible.

Inculcation, Reproduction, and Annihilation of Observations of simple little figures.

The person to be examined is placed in a dark room before a box in which an opening of 10 cm² has been made on the foreside. In the box there is an electric lamp, which throws its light on the opening. Small glass plates to which small drawings on white paper,

that has been blackened on the back-side, have been attached, are pushed into this opening. In front of the box there is another lamp, which is lighted during one second automatically. As this light falls on the drawings they are exposed to the subject during one second. The subject has been told to remember the order of the drawings. The number of exposures necessary before he can do this is a measure for the faculty of inculcation.

• Then the same test is again put, but with the drawings in a different order and with this modification that the lamp in the box is turned on immediately after the exposure of the drawings, so that the full light out of the box falls on the eyes of the subject during several seconds after observation of the drawings. By determining how often under these circumstances the observation had to take place for the subject to be able to name the correct order, one could now determine the retrograde annihilating influence of the strong light.

Persons of various ages were examined by this method. The number of observations, the average of two tests, necessary to determine the order of the drawings, without and with the subsequent strong light, is expressed in the following table:

Age	Number	Without obstacle	With subsequent light
10—15 years	19	2.3	4.2
16—40 „	22	2.4	4.3
above 40 „	12	2.6	5.2

The children have thus to see the drawings 2.3 times. In each observation they then remember $\frac{10}{23}$ or 43.5 % and with a subsequent strong impulse $\frac{10}{42}$ or 23.8 %. When expressed in percentages we get the following table:

Age	Number	Without obstacle	With subsequent light
10—15 years	19	43.5	23.8
16—40 „	22	41.7	23.3
above 40 „	12	40	19.2

We now get a measure of the obstructions by expressing the differences in percentages of the amounts of inculcation.

Age	Obstruction
9—15 years	45 %
16—40 "	44.1 %
over 40 "	52 %

From these tables it is apparent that this investigation proves what is to be expected, that the inculcation is smallest above 40 years of age, and that the destruction of impulses received is then also strongest.

These lamp-tests were modified in such a way that this investigation became serviceable for clinical purposes. Just as with the former tests we experimented on five different days, now however not in a dark room, but in broad daylight. Four round coloured discs were pasted on a piece of grey cardboard. These colours were shown to the subject during 2 seconds. Then, after an interval of 15 sec. he had to name the colours in the right order. If the answer was not correct, the colours were exposed till the correct answer was given twice in succession.

The tests were then again repeated, but with this difference that, after the observation of the colours, the light of an electric lamp, in a little box, of which the cardboard with the colours formed the foreside, was exposed by the removal of the cardboard and the light allowed to shine in the eyes of the subject during 15 seconds. The influence of the subsequent strong light could be determined by investigating how often the test had to be repeated to get the correct answer twice.

This test was subsequently repeated in precisely the same way with four figures e.g. \times \circ \triangle \square which are drawn in pairs next to each other on the cardboard, and afterwards also with three colours and three figures, which were drawn in such a way that there was a colour next to each figure.

The result of these tests was such that in normal people a very slight destruction was caused by the subsequent impulse, but in persons suffering from dementia this was the case to an important degree. At my instigation these experiments have been repeated in a slightly modified form and the results obtained will be published in a thesis.

Sound tests.

In a quiet room the ticking of an electric bell was deadened, by distance and by wrapping the bell in a box with cotton-wool, to such a degree that the intensity of the sound was only just above the border value. On the table in front of the subject, who regularly heard the ticking, there was a hubbub-maker of BARANY, which could be set going automatically through an electric contact, immediately after each tick. By having observations made after the tick, with and without subsequent noise in irregular order, it can precisely be determined how often the weak impulse is lost by the retrograde power of the stronger noise.

In thirteen normal persons and in three suffering from dementia (2 dem. paralytica and 1 dem. arteriosclerotica) twenty tests were made daily on each person during five days.

Average number of observations.

	Number	Without subsequent strong sound.	With subsequent strong sound.
Normal	13	97.1	88.9
Dement	3	50.0	0

The great disturbances in the observation and the enormous destruction in the sufferers from dementia are immediately apparent.

Touch tests.

It can be easily verified that the observation of a slight roughness, which one feels by stroking the fingers over a flat surface, disappears when the observation is followed by a strong touch impulse. It is not necessary that the strong subsequent impulse should act on the same locality, but the preceding weak observation also disappears if the subsequent strong impulse acts on another part of the finger, or even when it acts on one of the fingers of the other hand.

Tests were put in the following way, on one half of a smooth disc a layer of paper 3 mm. thick was pasted. When the disc revolves swiftly, the fingers, resting on the disc, clearly feel the unevenness. If now a larger elevation is placed at some distance from this unevenness so that the finger will collide with this elevation during the revolution, after it has passed the smaller uneven-

ness, then the first and weaker impulse will not be felt if the subsequent stronger impulse is not too far removed from it. By regulating the distance between the two impulses one can determine the retrograde destructive influence of the stronger impulse. In experiments made with people of various ages it became clear that there are strong individual differences.

These tests are excellently suitable to demonstrate the retrograde influence of strong impulses, but there are so many sources of errors that I shall give up the description of the individual differences.

A much better method consists herein that the observation of a weak electric impulse on one hand, which is noticed regularly, disappears when it is followed by a strong electric impulse on the other hand.

After the description of the tests and the communication of the results I shall communicate the results of the examination of the subjects on whom the various methods of investigation had been applied.

Fifty-three persons were examined viz. 14 normals, 9 neurotics, 13 melancholics, and 17 with intellectual defects. This preliminary communication would become too extensive if I were to give a more detailed description of the subjects. I want only to state that in the group of the neuroses there were 4 sufferers from hysteria and 5 from psychasthenia, while the latter also exhibited hysterical stigmata. The melancholics were obstructed and depressed and some of them had micromanias which were not present in others. Among the sufferers from dementia there were patients with senile dementia, dem. paralytica, dem. praecox and dem. epileptica. The intensity of the dementia was strongly varying, but in no case was it so great that it caused any difficulty in this fairly long investigation.

In accordance with the aim of the research, to acquire more knowledge concerning the influence of a depression of consciousness on the various psychical functions, it is sufficient for the present to communicate the differences which appear in the various groups of subjects in which there was a very large difference in the grades of consciousness.

Esthesiometer.

The attentiveness of the melancholics and especially of the patients with dementia is considerably worse than of normals and of the neurotics.

The good achievements of the neurotics prove that the narrowed

	Number	Percentage of correct answers.
Normals	14	96.9
Neurotics	9	98.1
Melancholics	13	87.9
Dements	17	76.9

consciousness of the hysterics and the psychical disturbances of the psychasthenics caused them no difficulty in concentrating their attentiveness for a short time on work which interests them.

Underlining tests.

	Normal underlining average work per minute	Normal underlining N°. of mistakes ‰	Reversed underlining average work per minute	Reversed underlining N°. of mistakes ‰
Normals	86.0	4.7	71.1	17.4
Neurotics	74.6	5.5	59.9	23.8
Melancholics	66.8	7.1	52.9	91.0
Dements	54.8	26.5	42.6	110.7

The great differences in attentiveness is apparent from the number of normal and reversed underlinings as well as from the number of mistakes. The automatic after-action, the perseverance, is increased strongly simultaneously to the diminution of the attentiveness. This appears out of the stronger influence of the normal underlining on the quantity as well as on the quality of the reversed during a depression of the attentiveness. Perseverance, continuing to cling to observations, conceptions or actions is a phenomenon that frequently occurs in dreams and in acute confusion.

It is also clear that the neurotics now, as opposed to the esthesiometric test, achieve considerably less than the normals, probably on account of the circumstance that their attentiveness had now to be settled on a work for a longer time.

Test with the method.

Parallel to the descent of the grade of consciousness the number

Percentage of answers.

	Correct	Incorrect	No answer
Normals	43.2	24.2	32.6
Neurotics	35.3	31.2	33.6
Melancholics	24.5	30.5	45.1
Dements	23.0	35.7	41.2

of correct answers decreases and the number of incorrect ones increases. The lessening of the fixation of associations must be considered as an indication of the very defective conception in acute confusion, in which it is often a striking symptom so that, no matter what trouble the patient takes, it is not possible to digest, to assimilate the external impressions.

The increasing number of incorrect answers indicates a loosening of the associations which must be considered as a rudimentary form of a lack of the connection between the conceptions in the same way as this makes its appearance in acute confusion. This falling out of the associative connection is so essential in this disease that this has been named after it.

In our subjects the difficulty of fixation of impressions causes disturbances of memory, as are found in acute confusion of a very high degree, and which correspond to the depression of consciousness.

Reducing specialised conceptions to general ones.

Percentage of answers.

	Correct	Incorrect	No answer
Normals	67.3	4.4	28.3
Neurotics	63.9	5.2	30.9
Melancholics	53.2	8.3	37.8
Dements	42.2	12.8	44.7

While the associations by contiguity and by simultaneousness were examined more especially in the preceding test, the association by agreement plays the greatest role in this the last research, i.e. the reduction of a special to a general conception.

Here again it is apparent that the impulses are more strongly fixed in the presence of a better attentiveness.

The increasing number of incorrect answers and the strong lowering of the grade of consciousness indicate that the paramnesias, which occur in acute confusion in a much higher degree, so that they then often occasion confabulation, are dependent on these.

Inculcation and reproduction of numbers, with and without subsequent work.

	Without			With		
	Correct	Incorrect	None	Correct	Incorrect	None
Normals	68.3	28.9	2.9	54.3	33.1	12.6
Neurotics	66.2	26.7	7.1	52.9	27.6	19.6
Melancholics	60.9	31.7	7.4	38.8	41.2	20.0
Dements	44.0	38.1	17.9	26.4	48.0	25.6

It is in the first place apparent from these tests that the number of correct reproductions, with as well as without obstruction, here decreases sharply with the stronger lowering of the grade of consciousness, and in such a way that the minute lessening of the attentiveness in the neurotics is accompanied by a slight disturbance of memory, while the much stronger depression of attentiveness in the sufferers from dementia is accompanied by a much stronger one.

If we compare the correct answers with and without obstruction it is clear that the destruction of remembrances is caused by the subsequent work. When we consider the decrease of the achievements in the percentages of the correct answers, with and without subsequent work, we come to the following table.

Destruction by subsequent work.

Normals	20.5
Neurotics	20.1
Melancholics	36.3
Dements	40

The retrograde destruction by subsequent work thus increases in accordance to the lowering of the degree of consciousness. This

phenomenon makes its appearance in much stronger measure in acute confusion, in which often nothing is remembered. Freshly received impressions were immediately destroyed by subsequent psychical contents.

There is another phenomenon worth mentioning. The number of incorrect answers increases in accordance to the lowering of the grade of consciousness. This has also been proved by the preceding tests. The neurotics however form an exception to this rule. Of all the people examined they give the smallest number of incorrect answers. This phenomenon is explained by the characteristics of the psychasthenics, who are withheld from giving an answer by all sorts of scruples unless they are absolutely certain. The normals on the other hand will guess at a number if they have remembered one figure only. In tracing all the answers separately this becomes clear.

The stronger inclination of the psychasthenics to keep silence rather than give an incorrect answer also becomes clearly apparent if we compare the percentage of incorrect and nil-answers of the total number of answers which were not correct.

Answers that were not correct.

	Percentage incorrect	Percentage unanswered
Normals	90.9	9.1
Neurotics	79.0	21.0
Melancholics	81.1	18.9
Dements	68.0	32.0

The number of incorrect answers is smaller in the dements than in the melancholics.

Recognition of numbers, with and without subsequent work.

	Without			With		
	Correct	Incorrect	Unans- wered	Correct	Incorrect	Unans- wered
Normals	80.6	19.4	0	78.0	21.7	0.3
Neurotics	82.2	13.3	4.4	72.9	20.0	7.1
Melancholics	69.5	25.2	5.2	62.8	30.5	6.8
Dements	57.2	36.2	6.6	48.5	42.1	9.4

An important influence of the grade of consciousness is here perceptible. There is hardly any difference between the neurotics and the normals. The power of raising conceptions of remembrance through observations is thus lessened in accordance to the loosening of the attentiveness. If this phenomenon makes its appearance in such a degree that the observations remain independent and that no conceptions of remembrance can be brought into connection with them, then desorientation takes place, a phenomenon that is usually present in acute confusion. The retrograde influence of subsequent work is here not so strong by a great deal as was the case in the preceding test. This is especially apparent from the following table.

Destruction by subsequent work

Normals	3.2
Neurotics	11.3
Melancholics	9.6
Dements	15.2

In the normals the retrograde influence is nearly absent, in the dements on the other hand it is very clear.

The uncertainty of the psychasthenics is apparent in these tests in the same way as in the preceding and again becomes clear if we compare the percentages incorrect answers mutually and the nil-answers mutually, of all the answers that were not correct.

Answers that were not correct

	Without subsequent obstruction		With subsequent obstruction	
	percentage incorrect	percentage unanswered	percentage incorrect	percentage unanswered
Normals	100	0	98.6	1.4
Neurotics	74.7	25.3	73.8	26.2
Melancholics	82.6	17.4	82.0	18.0
Dements	84.6	15.4	81.7	18.3

The number of incorrect answers is smallest in the neurotics, while here the number of nil-answers is largest.

Inculcation, reproduction and destruction of the observation of simple figures.

These tests were not made on the 53 subjects mentioned above,

but on 41. They were repeated during five days. The method of experimenting and of computing the results was the same as that which has been described more in detail above.

	Number	Without subse- quent light	With subse- quent light	Destruction
Normals	12	81.1	38.4	52.7
Neurotics	3	66.7	31.2	53.2
Melancholics	6	58.6	25.5	56.7
Dements	10	29.5	11.6	60.4

It is remarkable that the inculcation decreases regularly as the depression of consciousness becomes larger, and that the dements especially achieve much less. The destruction of the newly received impulses increases as the grade of consciousness becomes lower.

By this research it is apparent that the phenomena of acute confusion are present in the bud in the normal and pathological subjects examined, and that they increase as the grade of consciousness becomes lower.

Mathematics. — “On the direct analyses of the linear quantities belonging to the rotational group in three and four fundamental variables”. By Prof. J. A. SCHOUTEN. (Communicated by Prof. CARDINAAL).

(Communicated in the meeting of September 29, 1917).

Quantities and direct analyses.

By a (geometric or algebraic) quantity existing with a definite transformation-group we mean, according to F. KLEIN, any complex of numbers (characteristic numbers of the quantity), that is transformed *into itself*¹⁾ by the transformations of that group. Quantities only have any signification and only exist with definite transformation-groups and may be “disturbed” as such with other groups, whose transformations do not transform the characteristic numbers into themselves. They are completely determined by their *mode of orientation*, i.e. the mode of transformation of their characteristic numbers. The variables of the group are called *fundamental variables* and are the characteristic numbers of a *fundamental element*. If the group is the linear homogeneous one in n variables, the simplest quantities are those, whose characteristic numbers are transformed as the determinants in a matrix of p fundamental elements independent of each other, $p = 1, \dots, n$. With a homogeneous interpretation of the fundamental variables they correspond to the linear R_{n-p} -complexes in R_{n-1} , provided with a number-factor. All the quantities, whose characteristic numbers are transformed in that way under the transformations of the *rotational group*, we call *linear quantities*.

By a *direct analysis* we mean a system of an addition and some multiplications by means of which we can express the relations among quantities of a definite kind left invariant under the transformations of a definite group. Every quantity is in the analysis a higher complex number. Till recently suchlike analyses were brought about by choosing for multiplications some characteristically distributive combinations conspicuous in geometry or mechanics, and uniting them into a system as well as might be. Owing to the great number of existing combinations of this kind arbitrariness could not fail to arise, and this led to the formulation of many systems, the adherents of which have been involved in a violent polemic for these twenty five years.

¹⁾ e. g. F. KLEIN, *Elementarmathematik vom höheren Standpunkte aus*. Leipzig (09) II p. 59.

Application of KLEIN's Principle of Classification.

The author of this paper observed in 1914¹⁾ that it follows from the application of KLEIN's principle of classification to analyses belonging to definite quantities, that to a given group of transformations and given quantities belongs a completely determined system, which may simply be computed. This was practically done for $n=3$, the rotational group, and quantities up to the second order inclusive. In a more exhaustive investigation contemplating four different sub-groups of the linear homogeneous group the same was executed for arbitrary values of n and for quantities of an arbitrary degree²⁾. We shall briefly state some results of this investigation bearing on linear quantities, in particular for $n=3$ and $n=4$, founded on the:

rotational group ($a_1^2 + \dots + a_n^2$ invariant, $\det. = +1$)

and availing ourselves of the:

orthogonal group ($a_1^2 + \dots + a_n^2$ invariant, $\det. = \pm 1$)

special-affin. group (lin. hom. with $\det. +1$)

equivoluminar group (lin. hom. with $\det. \pm 1$)

linear homogeneous group

for further classification of the quantities existing with the rotational group.

General symmetrical and alternating multiplication.

Three multiplications of fundamental elements exist with all the sub-groups of the linear homogeneous group and for all the values of n , viz. the *general*, the *symmetrical* and the *alternating* one.

The *general product* of p fundamental elements has n^p characteristic numbers, being the products of the characteristic numbers of the factors. Their mode of transformation is entirely determined by this definition. We express the product in this manner:

$$a_1 \circ a_2 \circ \dots \circ a_p = a_1 \overset{\circ}{\dots} a_p \dots \quad (1)$$

By *isomers* of $a_1 \dots a_p$ we mean all the general products that can be formed by permutation of the factors from $a_1 \overset{\circ}{\dots} a_p$. An even respectively odd isomer is concomitant with an even resp. odd permutation. The *symmetrical product* of $a_1 \dots a_p$ is the sum total of all the isomers divided by their number $p!$:

$$a_1 \smile a_2 \smile \dots \smile a_p = a_1 \overset{\smile}{\dots} a_p = \frac{1}{p!} \sum a_{i_1} \overset{\circ}{\dots} a_{i_p} \dots \quad (2)$$

The *alternating product* is the sum of all the even isomers dimi-

¹⁾ Grundlagen der Vektor- und Affinoranalysis, Leipzig (14).

²⁾ Ueber die Zahlensysteme der rotationalen Gruppe. Nieuw Archief voor Wiskunde 1919.

nished by the sum of all odd ones divided by $p!$ and may be expressed as Cayleyan determinant:

$$a_1 \frown a_2 \frown \dots \frown a_p = a_1 \frown \dots \frown a_p = \frac{1}{p!} \begin{vmatrix} a_1 & \dots & a_p \\ \vdots & & \vdots \\ a_1 & \dots & a_p \end{vmatrix} \begin{matrix} \text{(to be} \\ \text{developed} \\ \text{according} \\ \text{to rows)}. \end{matrix} \quad (3)$$

The alternating product of p fundamental elements is a linear quantity for $p \leq n$. For $p > n$ it is zero. A symmetrical product is never a linear quantity.

The Associative Systems R_n .

Classifying up to the lin. homog. group inclusive, the system belonging to the linear quantities is R_n^l , which is an associative system, entirely determined by the rules:

$$\begin{aligned} e_i + e_j &= -e_j + e_i = e_{ij} \quad e'_i + e'_j = -e'_j + e'_i = e'_{ij} \\ e_i + e_i &= k \quad e'_i + e'_i = k' \\ e_i e_j \dots e_l &= e_{ij\dots l} \quad e'_i e'_j \dots e'_l = e'_{ij\dots l} \\ e_{12\dots n} &= I \quad e'_{12\dots n} = I' \\ e_1 = \kappa^n e'_2 \dots e'_n I, \quad e_1 + e'_1 &= e'_1 + e_1 = \kappa, \quad e'_1 = \kappa^n e_2 \dots e_n I' \\ I I' &= I + I' = I' + I = \kappa^{n-1} \quad i, j, \dots, l = 1, \dots, n. \\ \kappa &= (-1)^{\frac{n(n-1)}{2}}. \end{aligned}$$

e_1, \dots, e_n are the covariant *fundamental units*, i. e. units of a fundamental element, and e'_1, \dots, e'_n are the contravariant fundamental units belonging to characteristic numbers, transforming themselves contragrediently relative to the fundamental variables.

When classifying up to the equiv. group incl., the system R_n^a is constituted, being obtained from the preceding one by the identification

$$I = I'$$

and being entirely determined by the rules:

$$\left. \begin{aligned} e_i + e_j &= -e_j + e_i = e_{ij} \\ e_i + e_i &= k \\ e_i e_j \dots e_l &= e_{ij\dots l} \\ e_{12\dots n} &= I \end{aligned} \right\} i, j, \dots, l = 1, \dots, n. \quad (4)$$

$$I^2 = I + I = \kappa^{n-1}$$

Quantities, whose units, apart from an eventual factor I , do not contain two equal fundamental units as factors, exist unlike the

¹⁾ In a more exhaustive investigation "Die direkte Analysis zur neueren Relativitätstheorie", Verhand. der Kon. Akad. v. Wet. Sectie I Deel XII N°. 6 we consider

also not linear quantities and we write $e_i e_j = e_{ij}$ and $e_i + e_j = \frac{e_i e_j - e_j e_i}{2} = e_{ij}$

etc. For more convenience we write here $e_i + e_j = e_{ij}$.

others with the lin. homog. group too, and are called *projective quantities*. Then they are of the *sub-degree* (Dutch: ondertrap, German: Unterstufe) p , when the number of the factors of the units is p , $p = 1, \dots, 2n$, and we write them ${}_p a$. The others are called *orthogonal quantities*. All linear quantities may be composed of projective ones and powers of k .

When classifying up to the special affin. group inclusive, for n odd the system R_n^s is obtained from the preceding one by the identification:

$$I = \varepsilon \dots \dots \dots (5)$$

The sub-degree p , $p \leq n$ coincides with the sub-degree $(n-p)$ and forms the *degree* (trap, Stufe) p . For n even no system is feasible here, because

$$I + e_i = -e_i + I, \dots \dots \dots (6)$$

hence identification of I with an ordinary number is impossible.

When classifying up to the orth. group inclusive, R_n^0 arises out of R_n^a , by the identification

$$k = \varepsilon \dots \dots \dots (7)$$

The system makes no difference between projective and non-projective quantities. The sub-degree p , $p \leq n$ coincides with the sub-degree $(2n-p)$ and forms the *by-degree* (neventrap, Nebenstufe) p .

When classifying up to the rotational group inclusive, for n odd, R_n^r arises out of R_n^a by the identification

$$I = k = \varepsilon \dots \dots \dots (8)$$

Neither does this system make any difference between projective and non-projective quantities. The sub-degrees p , $(n-p)$, $(n-p)$ and $(2n-p)$ coincide and constitute the *principal degree* (hoofdtap, Hauptstufe) p ; $p \leq n'$, $n' = \frac{n-1}{2}$ for n odd and $n' = \frac{n}{2}$ for n even. In all these systems the associative product of dissimilar fundamental units is equal to the alternating one.

The systems R_n are the products of *original systems* and *principal rows*¹⁾ according to the general formulae:

$$\left. \begin{aligned} R_n^r &= O_2^{\frac{n-1}{2}} \\ R_n^s &= H_n O_2^{\frac{n-1}{2}} \\ R_n^0 &= H_1 O_2^{\frac{n-1}{2}} \\ R_n^a &= H_1 H_n O_2^{\frac{n-1}{2}} \end{aligned} \right\} \dots \dots \dots (9)$$

¹⁾ Cf. Grundl. pages 11—18.

for n odd and

$$\left. \begin{aligned} R_n^o &= O_{2^{\frac{n}{2}}} \\ R_n^a &= H_n O_{2^{\frac{n}{2}}} \end{aligned} \right\} \dots \dots \dots (10)$$

for n even, where O_i denotes an original system of the order i and H_i a principal row of the order i . But for some divergence in $+$ and $-$ signs the systems R_n^0 are identical with CLIFFORD's n -way algebras¹⁾.

If none of the units is privileged the choice of the numbers occurring in the identifications is altogether determined by the dualities existing in the different groups. There are four altogether, and we shall call them:

$$\begin{aligned} \mathbf{a} - n-1\mathbf{a} & \quad \alpha - \beta \\ \mathbf{a} - n+1\mathbf{a} & \quad \alpha - \gamma \\ \mathbf{a} - 2n-1\mathbf{a} & \quad \alpha - \delta \\ \mathbf{a} - \mathbf{a}' & \quad \alpha - \varepsilon \end{aligned}$$

From the mode of transformation we conclude for the existence of these dualities as subjoined:

Duality:	$\alpha - \beta$		$\alpha - \gamma$		$\alpha - \delta$		$\alpha - \varepsilon$
Group:	n even	n odd	n even	n odd	n even	n odd	
linear homog.	—	—	—	—	—	—	+
equivo-lumin.	$\begin{smallmatrix} + \\ \text{for } n=2 \\ \text{identity} \end{smallmatrix}$	—	$\begin{smallmatrix} + \\ \text{for } n=2 \\ \text{identity} \end{smallmatrix}$	—	+	+	$= \alpha - \delta$
special-affin	+	+	identity	identity	$= \alpha - \beta$	$= \alpha - \beta$	$= \alpha - \beta$
orthogon.	$\begin{smallmatrix} + \\ = \alpha - \gamma \end{smallmatrix}$	—	$\begin{smallmatrix} + \\ = \alpha - \beta \end{smallmatrix}$	—	identity	identity	identity
rotation	identity	identity	identity	identity	identity	identity	identity

+ = existing, — = not existing.²⁾

¹⁾ CLIFFORD's systems have been worked out by J. JOLY, Proc. Roy. Ir. Acad. 5 (98) 73—123, A manual of quaternions (05) 303—309. He gives geometrical applications after the manner of the quaternion-theory without decomposition of the product. A. M'AULEY has elaborated this matter as well, Proc. Roy. Soc. Edinb. 28 (07) 503—585. These papers do not aim at a foundation on the theory of invariants or a closer investigation of the fundamental groups.

²⁾ The squares of the dualities not founded on contragredience have been indicated by blacker demarcation. These dualities only exist when n is even.

The associative Systems R_3 and R_4 .

If we call the unities of the sub-degrees $(n-1)$, $(n+1)$, and $(2n-1)$ corresponding to $e_i: e_i', \bar{e}_i$ and \bar{e}_i' and the contragredient unities e_i' , the rules of calculation for $n=3$ are:

R_3^l	$e_1 =$	$-e'_{23}I$	$\alpha - \beta: -$ $\alpha - \gamma: -$ $\alpha - \delta: -$ $\alpha - \varepsilon: -$ $\kappa = -1$ $\text{cycl. } 1, 2, 3^1).$
	$e_{23} =$	$-e'_1I$	
	$e_{123} = I$	$e'_{123} = I$	
	$-e_1I' =$	e'_{23}	
	$-e_{23}I' =$	e'_1	
	$II' =$	$I'I = +1$	
	$e_{11} = k$	$e'_{11} = k'$	
	$e_1 + e'_1 =$	$e'_1 + e_1 = -1$	

R_3^a	$e_1 =$	$-e'_{23}I =$	$\bar{e}_1I =$	$-\bar{e}'_{23}I$	$\alpha - \beta: - (1)$ $\alpha - \gamma: -$ $\alpha - \delta: +$ $\alpha - \varepsilon = \alpha - \delta$ $= I^2 = -k^3 = +1 \text{ cycl. } 1, 2, 3$
	$e_{23} =$	$e'_1 =$	$\bar{e}_{23} =$	$-\bar{e}'_1I$	
	$e_{123} =$	$-e'_{123}I =$	$-\bar{e}_{123}I =$	\bar{e}'_{123}	
	$-e_1I =$	$e'_{23} =$	$\bar{e}_1 =$	\bar{e}'_{23}	
	$-e_{23}I =$	$-e'_1I =$	$-\bar{e}_{23}I =$	\bar{e}'_1	
	$e_{123}I =$	$-e'_{123} =$	$-\bar{e}_{123} =$	$\bar{e}'_{123}I$	
	$e_{11} = k$	$e'_{11} = -k^2$	$\bar{e}_{11} = k$	$\bar{e}'_{11} = -k^2$	

R_3^s	$-k e_{23} =$	$e_1 =$	$e_{23}' =$	$-k e_1' =$	$\alpha - \beta: +$ $= I = k^3 = -1, \alpha - \gamma: \text{identity} (12)$ $\alpha - \delta = \alpha - \beta.$ $\alpha - \varepsilon = \alpha - \gamma'$ $\text{cycl. } 1, 2, 3.$
	$k^2 e_1 =$	$e_{23} =$	$e_1' =$	$k^2 e'_{23} =$	
		$e_{123} =$	$e_{123}' =$		
	$e_{11} = k$	$e_{11}' = -k^2$			

R_3^o	$-e_{23}I =$	$e_{123}I =$	$-\bar{e}_{123} =$	$-e_{23}I$	$= -k^3 = +1$ $\alpha - \beta: -$ $\alpha - \gamma: - (13)$ $\alpha - \delta: \text{identity.}$ $\alpha - \varepsilon: \text{identity.}$ $\text{cycl. } 1, 2, 3.$
	$-e_1I =$	$e_{23} =$	$\bar{e}_{23} =$	e_1	
		$e_{123} =$	$-\bar{e}_{123}I =$		
		$e_{11} = -1$	$\bar{e}_{11} = -1$		

¹⁾ "Cycl 1, 2, 3, ..., n" means that the numbers 1, ..., n may be substituted by any even permutation of these numbers.

$\mathbf{e}_1 = \mathbf{e}_{23}$ $\mathbf{e}_{123} = -1$ $\mathbf{e}_{11} = -1$	$\alpha\text{-}\beta$ identity $\alpha\text{-}\gamma$ „ $\alpha\text{-}\delta$ „ $\delta\text{-}\varepsilon$ „ cycl. 1, 2, 3.	(14)
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With a non-homogeneous rectangular interpretation of the fundamental variables \mathbf{e}_1 is a polar vector, \mathbf{e}'_1 an axial bivector, $\bar{\mathbf{e}}_1$ an axial vector, $\bar{\mathbf{e}}'_1$ a polar bivector¹⁾, \mathbf{I} a projective, and \mathbf{k} an orthogonal “pseudoscalar”, $\mathbf{k}\mathbf{e}_1$ a polar, and $\mathbf{k}^2\mathbf{e}_1$ an axial versor (quaternion with tensor 1) without scalar part. R_3^a includes and discriminates all these quantities, R_3^s identifies polar quantities with axial ones and \mathbf{I} with an ordinary number, R_3^o identifies all the polar quantities and all the axial ones as well, and \mathbf{k} with a common number, whereas in R_3^r only the difference between vectors and ordinary numbers exists.

The rules of calculation for $n = 4$ are:

$\mathbf{e}_1 =$ $\mathbf{e}_{12} =$ $\mathbf{e}_{34} =$ $\mathbf{e}_{234} =$ $\mathbf{e}_{1234} =$ $\mathbf{e}_1 \mathbf{I}' =$ $-\mathbf{e}_{12} \mathbf{I}' =$ $-\mathbf{e}_{34} \mathbf{I}' =$ $\mathbf{e}_{234} \mathbf{I}' =$ $\mathbf{I} \mathbf{I}' =$ $\mathbf{e}_{11} = \mathbf{k}$ $\mathbf{e}_1 \mathbf{e}'_1 =$	$\mathbf{e}'_{234} \mathbf{I}$ $-\mathbf{e}'_{34} \mathbf{I}$ $-\mathbf{e}'_{12} \mathbf{I}$ $\mathbf{e}'_1 \mathbf{I}$ \mathbf{e}'_{1234} \mathbf{e}'_{234} \mathbf{e}'_{34} \mathbf{e}'_{12} \mathbf{e}'_1 $\mathbf{I}' \mathbf{I}$ $\mathbf{e}'_{11} = \mathbf{k}'$ $\mathbf{e}'_1 \mathbf{e}_1$	$\alpha - \beta: -$ $\alpha - \gamma: -$ $\alpha - \delta: -$ $\alpha - \varepsilon: +$ $\kappa = +1$ $= +1$ cycl. 1, 2, 3, 4. $= +1$
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¹⁾ In space these quantities have the symmetry-properties of a line-part with direction, a plane-part with rotative direction, a line-part with rotative direction and a plane-part with + and - side, all conceived as parallel removable with respect to themselves. For n odd it holds good that polar quantities change their sign, when the + direction of all axes is inverted, and that axial ones do not change their signs.

e_1	$=$	$-ie'_{234}$	$=$	$-i\bar{e}_1$	$I=$	$\bar{e}'_{234} I$	
e_{12}	$=$	$-e'_{34}$	$I=$	\bar{e}_{12}	$=$	$\bar{e}'_{34} I$	
e_{34}	$=$	$-e'_{12}$	$I=$	\bar{e}_{34}	$=$	$-\bar{e}'_{12} I$	
e_{234}	$=$	$-ie'_1$	$=$	$-i\bar{e}_{234}$	$I=$	$\bar{e}'_1 I$	$\alpha-\beta: +$
e_{1234}	$=$	e'_{1234}	$=$	\bar{e}_{1234}	$=$	\bar{e}'_{1234}	$\alpha-\gamma: +$
$e_1 I$	$=$	$-ie'_{234} I$	$=$	$-i\bar{e}_1$	$=$	\bar{e}'_{234}	$\alpha-\delta: +$
$-e_{12} I$	$=$	e'_{34}	$=$	$-\bar{e}_{12} I$	$=$	\bar{e}'_{34}	$\alpha-\varepsilon = \alpha - \delta$
$-e_{34} I$	$=$	e'_{12}	$=$	$-\bar{e}_{34} I$	$=$	\bar{e}'_{12}	cycl. 1, 2, 3, 4.
$e_{234} I$	$=$	$-ie'_{234}$	$=$	$-i\bar{e}_{234}$	$=$	\bar{e}'_1	
$e_{1234} I$	$=$	$e'_{1234} I$	$=$	$\bar{e}_{1234} I$	$=$	$\bar{e}'_{1234} I$	$= I^2 = k^4 = +1$
$e_{11} = k$		$e'_{11} = k^3$		$\bar{e}_{11} = k$		$\bar{e}'_{11} = k^3$	

(15)

	$e_{1234} I =$	$\bar{e}_{1234} I =$		$= I^2 = +1$
$e_{234} I =$	$e_1 =$	$-ie'_{234} =$	$-i\bar{e}_1 I$	
$-e_{34} I =$	$e_{12} =$	$\bar{e}_{12} =$	$-\bar{e}_{34} I$	$\alpha-\beta: +$ (complicated)
$-e_{12} I =$	$e_{34} =$	$\bar{e}_{34} =$	$-\bar{e}_{12} I$	$\alpha-\gamma = \alpha-\beta$
$e_1 I =$	$e_{234} =$	$-i\bar{e}_1 =$	$-i\bar{e}_{234} I$	$\alpha-\delta: \text{identity}$
	$e_{1234} =$	$\bar{e}_{1234} =$		$\alpha-\varepsilon: \text{identity}$
	$e_{11} = +1$	$\bar{e}_{11} = +1$		$= I$ cycl. 1, 2, 3, 4.

(16)

The dualities $\alpha-\beta$ are complicated ones in this case, i. e. dualising leads say for $\alpha-\beta$ from e_i to e'_i , from e'_i to $-e_i$, from $-e_i$ to $-e'_i$, and from $-e'_i$ again to e_i . This complicated duality always exists for n even¹⁾, as long as one of the units is not privileged. If one of the units is privileged, or, to put it otherwise, if we derive the system belonging to the group, leaving invariant the quadratic form

$$-a_0^2 + a_1^2 + \dots + a_{n-1}^2$$

we find, when classifying up to the orthogonal groups inclusive, the system:

¹⁾ The complicated duality exists also in GRASSMANN's *Ausdehnungslehre* for n even.

$$\begin{array}{lcl}
\begin{array}{l}
\mathbf{e}_0 = \overline{\mathbf{e}_{123}} \\
\mathbf{e}_1 = -\overline{\mathbf{e}_{023}} \\
\mathbf{e}_{01} = -\overline{\mathbf{e}_{01}} \\
\mathbf{e}_{12} = +\overline{\mathbf{e}_{12}} \\
\mathbf{e}_{00} = +1 \\
R_4^0 \mathbf{e}_{11} = -1 \\
\mathbf{e}_{0123} = \mathbf{I} \\
\mathbf{e}_0 \mathbf{I} = \overline{\mathbf{e}_0} \\
\mathbf{e}_1 \mathbf{I} = +\overline{\mathbf{e}_1} \\
\mathbf{e}_{01} \mathbf{I} = \mathbf{e}_{23} = \overline{\mathbf{e}_{23}} \\
\mathbf{e}_{12} \mathbf{I} = -\mathbf{e}_{03} = \overline{\mathbf{e}_{03}}, \quad \mathbf{I}^2 = -1,
\end{array}
&
\begin{array}{l}
\overline{\mathbf{e}_0} = \mathbf{e}_{123} \\
\overline{\mathbf{e}_1} = -\mathbf{e}_{023} \\
\overline{\mathbf{e}_{01}} = +\mathbf{e}_{01} \\
\overline{\mathbf{e}_{12}} = -\mathbf{e}_{12} \\
\overline{\mathbf{e}_{00}} = +1 \\
\overline{\mathbf{e}_{11}} = -1 \\
\overline{\mathbf{e}_{0123}} = -\mathbf{I} \\
-\overline{\mathbf{e}_0} \mathbf{I} = \mathbf{e}_0 \\
-\overline{\mathbf{e}_1} \mathbf{I} = +\mathbf{e}_1 \\
-\overline{\mathbf{e}_{01}} \mathbf{I} = \overline{\mathbf{e}_{23}} = \mathbf{e}_{23} \\
-\overline{\mathbf{e}_{12}} \mathbf{I} = -\overline{\mathbf{e}_{03}} = \mathbf{e}_{03}
\end{array}
&
\left. \begin{array}{l}
\alpha-\beta: + \\
\alpha-\gamma = \alpha-\beta \\
\alpha-\delta: \text{iden-} \\
\quad \text{tity.} \\
\alpha-\varepsilon: \text{iden-} \\
\quad \text{tity.} \\
\text{cycl. 1, 2, 3.}
\end{array} \right\} (17)
\end{array}$$

with non-complicated duality. This system may also be obtained from the preceding system R_4^0 (page 334) by the transition $\mathbf{e}_1 \rightarrow \mathbf{e}_0$, $-i\mathbf{e}_2 \rightarrow \mathbf{e}_3$, etc., $\overline{\mathbf{e}_1} \rightarrow \overline{\mathbf{e}_0}$, $i\overline{\mathbf{e}_2} \rightarrow \overline{\mathbf{e}_3}$, etc. It is noteworthy that, for $n=4$ the theory of relativity (for the space-element) exactly corresponds to this more simple system.

For non-homogeneous rectangular interpretation of the fundamental variables, \mathbf{e}_1 and \mathbf{e}_{123} are a vector, resp. a trivector of the first kind and $\mathbf{I}\mathbf{e}_1$ and $\mathbf{I}\mathbf{e}_{123}$ are the corresponding quantities of the second kind¹⁾. \mathbf{I} is a projective and \mathbf{k} an orthogonal pseudoscalar. R_4^0 contains and distinguishes all these quantities. R_4^0 identifies a vector resp. a trivector of the first kind with a trivector resp. a vector of the second kind and \mathbf{k} with an ordinary number.

Decomposition of the Associative Product.

The associative product of two projective quantities of the sub-degrees p' and q' and the principal degrees p and q , $p', q' \leq n$, $p \leq q$, consists in the most general case of $p+1$ parts, each of which being a product of a projective quantity with a certain number of factors \mathbf{k} . As a distributive combination each of these parts is a product itself. The number of factors \mathbf{k} is called the transvection-number of this product and this number is at most equal to the smallest of the numbers p' and q' . We call these products, if p' and q' are both \leq or both $\geq n'$, beginning from the lowest and otherwise beginning from the highest in sequence:

¹⁾ The customary distinction for n odd between polar and axial quantities does not hold good for n even.

(first) vectorial product \times
 second „ „ „ \times_2
 (only for p even) α -th middle product, $\alpha = \frac{p}{2} + 1$.
 second scalar product \cdot
 first scalar product \cdot .

With this notation, which is in agreement with the existing dualities, products that are identical with the rotational group obtain the same name and the same symbol. Owing to the identification of \mathbf{I} and \mathbf{k} with common numbers the first middle-product is identical with the product of ordinary numbers mutually and with other quantities, hence its symbol may be omitted as being customary.

The rule of transvection.

If each factor is an alternating product of fundamental elements:

$$\begin{aligned} {}_{p'}\mathbf{a} &= \mathbf{a}_1 \cdot \dots \cdot \mathbf{a}_{p'} \\ {}_{q'}\mathbf{b} &= \mathbf{b}_1 \cdot \dots \cdot \mathbf{b}_{q'} \end{aligned}$$

we can form the combination:

$(\mathbf{a}_{p'} \cdot \mathbf{b}_1) (\mathbf{a}_{p'-1} \cdot \mathbf{b}_2) \dots (\mathbf{a}_{p'-i+1} \cdot \mathbf{b}_i) \mathbf{a}_1 \dots \mathbf{a}_{p'-i} \mathbf{b}_{i+1} \dots \mathbf{b}_{q'}$,
 repeat the same for all $p'!$ resp. $q'!$ modes of notation of ${}_{p'}\mathbf{a}$ and ${}_{q'}\mathbf{b}$ and add the results.

The sum then consists of $p'! q'!$ terms, equivalent to each other in groups of $(p'-i)! (q'-i)! i!$. This sum divided by $(p'-i)! (q'-i)! i!$, or, stated more briefly, the sum of $(p'_i) (q'_i) i!$ arbitrary different terms, is called the i -fold-combination of ${}_{p'}\mathbf{a}$ and ${}_{q'}\mathbf{b}$. The i -fold combination is now equal to the product with the transvection-number i . The transvection-number of a product being known, we can hence write it down from memory by this rule.

The free rules for R_2 and R_3 .

Hence the free rules for R_2^l , R_3^a , R_3^s , R_3^o and R_3^r are:

Transv. numb.:		
0	$\mathbf{a} \times \mathbf{b}$	= quantity of the second sub degree.
1	$\mathbf{a} \cdot \mathbf{b}$	= scalar in \mathbf{k} resp. 1.
0	$\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \mathbf{a} \times \mathbf{b} \cdot \mathbf{c}$	= scalar in \mathbf{I} resp. 1. ¹⁾
1	$\mathbf{a} \times (\mathbf{b} \times \mathbf{c})$	$= (\mathbf{a} \cdot \mathbf{b}) \mathbf{c} - (\mathbf{a} \cdot \mathbf{c}) \mathbf{b}$
1	$\mathbf{a} (\mathbf{b} \times \mathbf{c} \cdot \mathbf{d})$	$= (\mathbf{a} \cdot \mathbf{b}) (\mathbf{c} \times \mathbf{d}) + (\mathbf{a} \cdot \mathbf{c}) (\mathbf{d} \times \mathbf{b}) + (\mathbf{a} \cdot \mathbf{d}) (\mathbf{b} \times \mathbf{c})$
1	$(\mathbf{a} \times \mathbf{b}) \times (\mathbf{c} \times \mathbf{d})$	$= (\mathbf{b} \cdot \mathbf{c}) (\mathbf{a} \times \mathbf{d}) - (\mathbf{b} \cdot \mathbf{d}) (\mathbf{a} \times \mathbf{c}) + \dots$
2	$(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d})$	$= (\mathbf{b} \cdot \mathbf{c}) (\mathbf{a} \cdot \mathbf{d}) - (\mathbf{b} \cdot \mathbf{d}) (\mathbf{a} \cdot \mathbf{c})$
2	$(\mathbf{a} \times \mathbf{b}) (\mathbf{c} \times \mathbf{d} \cdot \mathbf{e})$	$= (\mathbf{b} \cdot \mathbf{c}) (\mathbf{a} \cdot \mathbf{d}) \mathbf{e} - (\mathbf{b} \cdot \mathbf{d}) (\mathbf{a} \cdot \mathbf{c}) \mathbf{e} + \dots$
3	$(\mathbf{a} \times \mathbf{b} \cdot \mathbf{c}) (\mathbf{d} \times \mathbf{e} \cdot \mathbf{f})$	$= (\mathbf{c} \cdot \mathbf{d}) (\mathbf{b} \cdot \mathbf{e}) (\mathbf{a} \cdot \mathbf{f}) + (\mathbf{c} \cdot \mathbf{e}) (\mathbf{b} \cdot \mathbf{f}) (\mathbf{a} \cdot \mathbf{d}) + \dots$

¹⁾ In alternating products the brackets have been omitted for the association (..), so that we write the alternating product of $\mathbf{a}_1, \dots, \mathbf{a}_p$:

$$\mathbf{a}_1 \times \mathbf{a}_2 \times \dots \times \mathbf{a}_{n'} \times \mathbf{a}_{n'+1} \cdot \mathbf{a}_{n'+2} \cdot \dots \cdot \mathbf{a}_p.$$

The four systems differ only by the different signification attached to **I** and **k**. R_3'' is the common vector-analysis, in which no difference is made between polar quantities and axial ones and between vectors and bivectors. R_3^o distinguishes between polar quantities and axial ones. In GIBBS's form of this vector-analysis, owing to the groundlessly introduced $+$ sign in $\mathbf{e}_1 \cdot \mathbf{e}_1 = -1$, the formulae acquire apparently irregular changes of $+$ and $-$ signs and the transvection-rule becomes ineffectual, so that the formulae stand side by side independent of one another and can be used only by means of a table. When applied to units the rules for R_3^o and R_3'' are:

$$\begin{array}{lcl}
 \mathbf{e}_1 \times \mathbf{e}_2 = -\mathbf{e}_2 \times \mathbf{e}_1 = \mathbf{e}_{12} & \mathbf{e}_{23} \times \mathbf{e}_{12} = \mathbf{e}_{31} & \\
 \mathbf{e}_1 \cdot \mathbf{e}_1 = -1 & \mathbf{e}_{12} \cdot \mathbf{e}_{12} = -1 & \\
 R_3^o \mathbf{e}_1 \cdot \mathbf{e}_{23} = -\mathbf{I} & \mathbf{e}_{12} \mathbf{I} = \mathbf{I} \mathbf{e}_{12} = -\mathbf{e}_3 & \\
 \mathbf{e}_1 \times \mathbf{e}_{12} = -\mathbf{e}_2 & \mathbf{I}^2 = +1 & \\
 \mathbf{e}_1 \mathbf{I} = \mathbf{I} \mathbf{e}_1 = -\mathbf{e}_{23} & &
 \end{array} \left. \begin{array}{l} \\ \\ \\ \\ \end{array} \right\} \text{cycl. } 1, 2, 3.$$

$$R_3' \left. \begin{array}{l} \mathbf{e}_1 \times \mathbf{e}_2 = -\mathbf{e}_2 \times \mathbf{e}_1 = \mathbf{e}_3 \\ \mathbf{e}_1 \cdot \mathbf{e}_1 = -1 \end{array} \right\} \text{cycl. } 1, 2, 3. \quad (20)$$

The rules (18) and (20) can be dualised according to all existing dualities as given in the table.

The free rules for R_4^a and R_4^o are:

Transv.
numb.

0	$\mathbf{a} \times \mathbf{b} = \text{quantity of the second sub-degree}$	(21)
1	$\mathbf{a} \cdot \mathbf{b} = \text{scalar in } \mathbf{k} \text{ resp. } 1$	
0	$\mathbf{a} \times (\mathbf{b} \times \mathbf{c}) = \mathbf{a} \times \mathbf{b} \times \mathbf{c}$	
1	$\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = (\mathbf{a} \cdot \mathbf{b}) \mathbf{c} - (\mathbf{a} \cdot \mathbf{c}) \mathbf{b}$	
0	$\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c} \times \mathbf{d}) = \mathbf{a} \times \mathbf{b} \times \mathbf{c} \cdot \mathbf{d} = \text{scalar in } \mathbf{l} \text{ resp. } 1$	
1	$\mathbf{a} \times (\mathbf{b} \times \mathbf{c} \times \mathbf{d}) = (\mathbf{a} \cdot \mathbf{b}) (\mathbf{c} \times \mathbf{d}) + (\mathbf{a} \cdot \mathbf{c}) (\mathbf{d} \times \mathbf{b}) + (\mathbf{a} \cdot \mathbf{d}) (\mathbf{b} \times \mathbf{c})$	
1	$\mathbf{a} (\mathbf{b} \times \mathbf{c} \times \mathbf{d} \cdot \mathbf{e}) = (\mathbf{a} \cdot \mathbf{b}) (\mathbf{c} \times \mathbf{d} \times \mathbf{e}) - (\mathbf{a} \cdot \mathbf{c}) (\mathbf{b} \times \mathbf{d} \times \mathbf{e}) + \dots$	
0	$(\mathbf{a} \times \mathbf{b}) \times (\mathbf{c} \times \mathbf{d}) = \mathbf{a} \times \mathbf{b} \times \mathbf{c} \cdot \mathbf{d}$	
1	$(\mathbf{a} \times \mathbf{b}) * (\mathbf{c} \times \mathbf{d}) = (\mathbf{b} \cdot \mathbf{c}) (\mathbf{a} \times \mathbf{d}) - (\mathbf{b} \cdot \mathbf{d}) (\mathbf{a} \times \mathbf{c}) + \dots^1$	
2	$(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d}) = (\mathbf{b} \cdot \mathbf{c}) (\mathbf{a} \cdot \mathbf{d}) - (\mathbf{b} \cdot \mathbf{d}) (\mathbf{a} \cdot \mathbf{c})$	
1	$(\mathbf{a} \times \mathbf{b}) \cdot (\mathbf{c} \times \mathbf{d} \times \mathbf{e}) = (\mathbf{b} \cdot \mathbf{c}) (\mathbf{a} \times \mathbf{d} \times \mathbf{e}) + \dots$	
2	$(\mathbf{a} \times \mathbf{b}) \times (\mathbf{c} \times \mathbf{d} \times \mathbf{e}) = (\mathbf{b} \cdot \mathbf{c}) (\mathbf{a} \cdot \mathbf{d}) \mathbf{e} + \dots$	
2	$(\mathbf{a} \times \mathbf{b}) (\mathbf{c} \times \mathbf{d} \times \mathbf{e} \cdot \mathbf{f}) = (\mathbf{b} \cdot \mathbf{c}) (\mathbf{a} \cdot \mathbf{d}) (\mathbf{e} \times \mathbf{f}) + \dots$	
2	$(\mathbf{a} \times \mathbf{b} \times \mathbf{c}) \times (\mathbf{d} \times \mathbf{e} \times \mathbf{f}) = (\mathbf{c} \cdot \mathbf{d}) (\mathbf{b} \cdot \mathbf{e}) (\mathbf{a} \times \mathbf{f}) + \dots$	
3	$(\mathbf{a} \times \mathbf{b} \times \mathbf{c}) \cdot (\mathbf{d} \times \mathbf{e} \times \mathbf{f}) = (\mathbf{c} \cdot \mathbf{d}) (\mathbf{b} \cdot \mathbf{e}) (\mathbf{a} \cdot \mathbf{f}) + \dots$	
3	$(\mathbf{a} \times \mathbf{b} \times \mathbf{c}) (\mathbf{d} \times \mathbf{e} \times \mathbf{f} \cdot \mathbf{g}) = (\mathbf{c} \cdot \mathbf{d}) (\mathbf{b} \cdot \mathbf{e}) (\mathbf{a} \cdot \mathbf{f}) \mathbf{g} + \dots$	
4	$(\mathbf{a} \times \mathbf{b} \times \mathbf{c} \cdot \mathbf{d}) (\mathbf{e} \times \mathbf{f} \times \mathbf{g} \cdot \mathbf{h}) = (\mathbf{d} \cdot \mathbf{e}) (\mathbf{c} \cdot \mathbf{f}) (\mathbf{b} \cdot \mathbf{g}) (\mathbf{a} \cdot \mathbf{h}) + \dots$	

independent of the units used, viz. $\mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3, \mathbf{e}_4$ or $\mathbf{e}_0, \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$.

¹⁾ The index 2 under * is for simplicity omitted.

When applied to units the rules for R_4^0 and for e_1, e_2, e_3, e_4 are

$$\begin{array}{ll}
 e_1 \times e_2 = -e_2 \times e_1 = e_{12} & e_{12} * e_{23} = e_{13} \\
 e_1 . e_1 = +1 & e_{12} . e_{12} = -1 \\
 e_1 \times e_{23} = e_{123} = i \bar{e}_4 & e_{12} . e_{234} = e_{134} \\
 e_1 . e_{12} = e_2 & e_{12} \times e_{123} = -e_3 \\
 e_1 . e_{234} = I & e_{12} I = I e_{12} = -e_{34} \\
 e_1 \times e_{123} = e_{23} & e_{123} \times e_{234} = -e_{14} \\
 e_1 I = -I e_1 = e_{234} = -i \bar{e}_1 & e_{123} . e_{123} = -1 \\
 e_{12} \times e_{34} = I & e_{234} I = -I e_{234} = e_1 \\
 & I^2 = +1
 \end{array} \left. \begin{array}{l} \\ \\ \\ \text{cycl. 1, 2, 3, 4.} \\ \text{dual } e - \bar{e} \\ \text{(compli- (22)} \\ \text{cated)} \end{array} \right\}$$

and for e_0, e_1, e_2, e_3 :

(See for formula (23) page 339).

The quantities of an even by-degree form a sub-system with 4 units and the rules:

$$\begin{array}{ll}
 i_1 * i_2 = -i_2 * i_1 = i_3 & j_1 * j_2 = -j_2 * j_1 = -i_3 \\
 i_1 * j_2 = -j_2 * i_1 = j_3 & j_1 * i_2 = -i_2 * j_1 = j_3 \\
 i_1 . i_1 = -1 & j_1 . j_1 = +1 \\
 I i_1 = i_1 I = -j_1 & I j_1 = j_1 I = +i_1 \\
 i_1 \times j_1 = j_1 \times i_1 = I & \left(\begin{array}{l} i_1 = e_{23} \\ j_1 = e_{01} \end{array} \right) \\
 I^2 = -1 &
 \end{array} \left. \begin{array}{l} \\ \\ \\ \\ \text{cycl.} \\ \text{1, 2, 3. (24)} \end{array} \right\}$$

But these are the same rules as those for the units $e_1, e_2, e_3, i e_1, i e_2, i e_3$ of R_3^1 with ordinary complex coefficients, so that the free rules for R_4^1 also hold good for quantities of an even by-degree of R_0^4 if, instead of \times and $.$ we introduce the symbols $*$ and $\times = . + \times$:

$$\begin{array}{l}
 2a * 2b = \text{quantity of the second by-degree} \\
 2a \times 2b = \text{scalar in } I \text{ and } 1 \\
 2a \times (2b * 2c) = 2a * 2b \times 2c \\
 2a * (2b * 2c) = (2a \times 2b) 2c - (2a \times 2c) 2b \\
 2a (2b * 2c \times 2d) = (2a \times 2b) (2c * 2d) + \dots \\
 (2a * 2b) * (2c * 2d) = (2b \times 2c) (2a * 2d) + \dots \\
 (2a * 2b) \times (2c * 2d) = (2b \times 2c) (2a \times 2d) + \dots \\
 (2a * 2b) (2c * 2d \times 2e) = (2b \times 2c) (2a \times 2d) 2e + \dots \\
 (2a * 2b \times 2c) (2d * 2e \times 2f) = (2c \times 2d) (2b \times 2e) (2a \times 2f) + \dots
 \end{array} \left. \begin{array}{l} \\ \\ \\ \\ \\ \\ \\ \end{array} \right\} . \quad (25)$$

Hence these rules may be written down from memory, as well as the others.

The System R_4^0 and the theory of relativity (in an element of four dimensional space).

Fragments of R_4^0 have been used by various authors¹⁾ on the theory of relativity. With them five products occur and two of these

¹⁾ H. MINKOWSKI, M. ABRAHAM, A. SOMMERFELD, M. LAUE, PH. FRANK.

and for e_0, e_1, e_2, e_3 :

$$e_0 \times e_1 = -e_1 \times e_0 = e_{01} = -\bar{e}_{01}$$

$$e_1 \times e_2 = -e_2 \times e_1 = e_{12} = \bar{e}_{12}$$

$$e_0 \cdot e_0 = +1, \quad e_1 \cdot e_1 = -1$$

$$e_1 \times e_{23} = e_{123} = \bar{e}_0, \quad e_0 \times e_{12} = e_{012} = -\bar{e}_3$$

$$e_1 \cdot e_{12} = -e_2 \cdot e_1 = e_{10} = -\bar{e}_0, \quad e_0 \cdot e_{01} = e_1$$

$$e_0 \cdot e_0 = 1, \quad e_1 \cdot e_1 = -1$$

$$e_0 \times e_1 = -e_2 = -\bar{e}_{23}$$

$$e_1 \times e_2 = e_{03} = -\bar{e}_{03}$$

$$e_0 I = -I e_0 = e_{123} = \bar{e}_0$$

$$e_1 I = -I e_1 = e_{023} = -\bar{e}_1$$

$$e_{01} \times e_{23} = I$$

$$e_{01} * e_{02} = -e_{12} = -\bar{e}_{12}, \quad e_{01} * e_{12} = -e_{02} = \bar{e}_{02}$$

$$e_{23} * e_{31} = e_{12} = \bar{e}_{12}$$

$$e_{01} \cdot e_{01} = +1, \quad e_{12} \cdot e_{12} = -1$$

$$e_{01} I = I e_{01} = e_{23} = \bar{e}_{23}, \quad e_{12} I = I e_{12} = -e_{03} = \bar{e}_{03}, \quad -e_{01} I = -I e_{01} = e_{23} = e_{23}, \quad -e_{12} I = -I e_{12} = -e_{03} = e_{03}$$

$$I^2 = -1$$

$$\bar{e}_0 \times \bar{e}_1 = -\bar{e}_1 \times \bar{e}_0 = \bar{e}_{01} = -e_{01}$$

$$\bar{e}_1 \times \bar{e}_2 = -\bar{e}_2 \times \bar{e}_1 = \bar{e}_{12} = e_{12}$$

$$\bar{e}_0 \cdot \bar{e}_0 = +1, \quad \bar{e}_1 \cdot \bar{e}_1 = -1$$

$$\bar{e}_1 \times \bar{e}_{23} = \bar{e}_{123} = e_0, \quad \bar{e}_0 \times \bar{e}_{12} = \bar{e}_{012} = -e_3$$

$$\bar{e}_1 \cdot \bar{e}_{12} = -\bar{e}_2 \cdot \bar{e}_1 = \bar{e}_{10} = -e_0, \quad \bar{e}_0 \cdot \bar{e}_{01} = \bar{e}_1$$

$$\bar{e}_0 \cdot \bar{e}_0 = -1, \quad \bar{e}_1 \cdot \bar{e}_1 = -1$$

$$\bar{e}_0 \times \bar{e}_1 = -\bar{e}_{23} = -e_{23}$$

$$\bar{e}_1 \times \bar{e}_2 = \bar{e}_{03} = -e_{03}$$

$$-\bar{e}_0 I = I \bar{e}_0 = \bar{e}_{123} = e_0$$

$$-\bar{e}_1 I = I \bar{e}_1 = \bar{e}_{023} = -e_1$$

$$\bar{e}_{01} \times \bar{e}_{23} = -I$$

$$\bar{e}_{01} * \bar{e}_{02} = -\bar{e}_{12} = -e_{12}, \quad \bar{e}_{01} * \bar{e}_{12} = -\bar{e}_{02} = e_{02}$$

$$\bar{e}_{22} * \bar{e}_{31} = \bar{e}_{12} = e_{12}$$

$$\bar{e}_{01} \cdot \bar{e}_{01} = +1, \quad \bar{e}_{12} \cdot \bar{e}_{12} = -1$$

$$(-I)^2 = -1$$

cycl.
1, 2, 3.

(23)

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said products are doubled by introducing the "dual" bivector (dualer sechervektor)¹⁾. E. WILSON and G. LEWIS have further elaborated the system and obtain all the products, but three²⁾. All these conclusions are founded on analogies with the common vector-analysis and the multiplications form no parts of the associative multiplication. Therefore the free calculation-rules cannot immediately be put down from memory according to the transvection-rule, but in so far as they exist they only allow a use by means of a table. The names scalar and vectorial too, have been divided over the existing multiplications by analogy and not in agreement to the duality $\alpha-\gamma$.

WILSON-LEWIS		SOMMERFELD, LAUE, etc.
$+ a \times b$	$a \times b = {}_2c$	$[a b]$, vectorial product
$- a \cdot b$	$a \cdot b = c$	$[a b]$, scalar „
$+ a \times {}_2b$	$a \times {}_2b = {}_3c$	$Ic = [a {}_2b^*]$, vect. pr. w. dual bivect.
$+ a \cdot {}_2b$	$a \cdot {}_2b = c$	$- [a {}_2b]$, vect. pr.
$\pm k a = \pm a k$	$a I = - I a = {}_3b^*)$	
$+ a \times {}_3b$	$a \cdot {}_3b = {}_4c^*)$	$I {}_4c = ({}_2a {}_2b^*)$, scal. pr. w. dual biv. $[{}_2a {}_2b]$, vector pr. (G. MIE) $- ({}_2a {}_2b)$, scal. pr. $- {}_2b = + {}_2a^*$
$- a \cdot \bar{b}$	$a \times {}_3b = {}_2c$	
$+ {}_2a \times {}_2b$	${}_2a \times {}_2b = {}_4c^*)$	
	${}_2a * {}_2b = {}_2c$	
$- {}_2a \cdot {}_2b$	${}_2a \cdot {}_2b = c$	
$\pm k {}_2a = \pm {}_2a k$	${}_2a I = I {}_2a = {}_2b^*)$	
$k k = -1$	$I^2 = +1^*)$	
$\pm k {}_3a = \pm {}_3a k$	${}_3a I = - I {}_3a = b^*)$	
	${}_3a \cdot {}_2b = {}_3c$	
$- {}_3a \cdot {}_2b$	${}_3a \times {}_2b = c$	
$+ {}_3a \cdot \bar{b}$	${}_3a \cdot b = c$	
	${}_3a \times b = {}_2c$	

¹⁾ This is not a proper duality, because in the only duality existing with the orthogonal group, $\alpha-\gamma$, a bivector e.g. e_{12} is not dualistic to the "dual" bivector Ie_{12} , but to e_{12} itself.

²⁾ The connection with an associative CLIFFORD algebra and the absence of three products has already been briefly pointed out by J. B. SHAW, "The WILSON and LEWIS Algebra for Four-Dimensional Space" Bull. of the int. ass. for quat. (13) 24-27.

Therefore this duality does not attain expression, not even in the system of WILSON and LEWIS, though they use units of the kind $\mathbf{e}_0, \mathbf{e}_1, \mathbf{e}_2, \mathbf{e}_3$.

The foregoing table (subjoined p. 340) presents a summary of the products used by various authors.

The table has been arranged dualistically. Each product has been indicated by an example. For the multiplications we used in the columns 1 and 3 the author's own notation, but for the quantities we used all through the notations adopted in this paper. The dual bivector only has been written with the customary asterisk, while the commutative scalar of WILSON and LEWIS has been indicated by k . The products marked with *) do not correspond exactly to the other systems, because these systems do not contain the non-commutative scalar \mathbf{I} .

The system R_4^0 contains the existing fragments and all the existing multiplications and rules, and owing to the free rules of calculation (21 and 25) it is eminently suited for practical purposes.

The system R_4^0 and the elliptic and hyperbolic geometry in three dimensions.

With a homogeneous interpretation of the fundamental variables R_4^0 corresponds to a projective geometry in three dimensions, a non degenerated quadratic surface being invariant. If the units are selected according to (16) the equation of the absolute surface in point- resp. plane-coordinates is:

$$x_1^2 + x_2^2 + x_3^2 + x_4^2 = 0$$

$$u_1^2 + u_2^2 + u_3^2 + u_4^2 = 0$$

and the geometry is elliptic. If, on the other hand the units are selected according to (17) the geometry is hyperbolic. The free rules of the system are the same for both cases. To a fundamental element a point with a number-value corresponds, to a quantity of the second degree a sum of linear elements (Dyname) and to a quantity of the third degree a planar element. The sub-system of the quantities of the second by-degree is a form of biquaternions, which was first mentioned by CLIFFORD¹⁾ as a system of linear elements in a non-euclidian three-dimensional space. Hence the system R_4^0 completes these biquaternions to a system which also contains points and planar elements.

¹⁾ Preliminary sketch of biquaternions. Proc. Lond. Math. Soc. 4 (73) 381—395; Further notes on biquaternions. Coll. Math. Papers (76) 385, 395.

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ONNES).

(Communicated in the meeting of Febr. 23, 1918).

§ 1. *Introduction.* In a communication by Prof. H. KAMERLINGH ONNES and myself¹⁾ attention was drawn to the considerable deviation from the law of corresponding states which shows itself in the comparison of the viscosity of argon and helium. This circumstance brought out the importance of an investigation of the viscosity of neon down to the lowest temperatures to be reached with this substance. In this connection we also planned an investigation of the heat conductivity of these gases at the lowest temperatures to which measurements can be extended. Indeed according to the kinetic theory a very close connection exists between internal friction and conduction of heat. The two are only distinguished by a factor (specific heat \times numerical factor) and for monatomic gases, where the theory as regards viscosity is confirmed in many respects, this factor is independent of the temperature. According to the theory of heat conduction and viscosity the same law of dependence on the temperature will therefore be found in the two cases and it is immaterial which of the two quantities is submitted to investigation. If both are measured, the results afford a means of mutual control.

Personal circumstances allowed me, before the research above sketched out could be carried out at Leiden, to undertake the investigation of the heat conduction of gases in the physical laboratory of the PHILIPS *Incandescent Lamp Factories*. It was there, that the research contained in this communication was carried out. Only that part which refers to the lowest temperatures will still have to be performed at Leiden.

The neon required for this investigation was put at my disposal by Prof. KAMERLINGH ONNES, who had prepared it from a large supply of gas-residue rich in neon presented to him by G. CLAUDE²⁾; I am glad to offer him my sincere thanks. According to a commu-

¹⁾ Leiden Comm. N°. 134c April 1913.

²⁾ Leiden Comm. N°. 147c p. 38.

nication from Prof. KAMERLINGH ONNES the gas probably still contained a trace of nitrogen. For this reason I purified it once more by GEHLHOFF's method¹⁾.

Whichever of the known experimental methods²⁾ one may choose for the investigation of the heat conductivity of gases, there are always two sources of error which will have to be specially considered: the difference of temperature between the surface and the gas in contact with it and the convection. With diminution of pressure of the gas the influence of the convection becomes smaller, that of the temperature-drop greater. For the latter, similarly to the analogous quantity in the internal friction, the slipping along the wall³⁾, depends on the ratio of the mean free path to the dimensions of the apparatus.

Whereas it has been found impossible to calculate the influence of convection⁴⁾ on the heat conduction, M. KNUDSEN⁵⁾ and M. VON SMOLUCHOWSKI⁶⁾ have been able to bring the theoretical investigation of the temperature-drop to a successful issue.

In accordance with KUNDT and WARBURG⁷⁾ the temperature-drop $\Delta\theta$ at the solid wall is defined as follows:

$$\Delta\theta = -\gamma \cdot \frac{d\theta}{dn},$$

where n represents the direction of the normal and θ the temperature. KUNDT and WARBURG by their experiments established the fact, that γ is proportional to the mean free path λ .

VON SMOLUCHOWSKI based his first investigation on the kinetic theory as developed by CLAUSIUS and was led to the following approximate formula, in which I have introduced the accommodation-coefficient as defined by KNUDSEN⁸⁾.

$$\gamma/\lambda = 0,70 + \frac{4(1-a)}{3a} \quad \dots \quad (1)$$

Later on SMOLUCHOWSKI made a new calculation of γ , in this

¹⁾ GEHLHOFF, Verh. d. D. Physik Ges. 13. (1911) p. 271.

²⁾ Comp. A. WINKELMANN, Handbuch der Physik III, 1906 p. 525.

³⁾ H. KAMERLINGH ONNES, C. DORSMAN and S. WEBER. These Proc. XV (2) p. 1386

⁴⁾ A. OBERBECK. Wied. Ann. VII, 1879, p. 291 and L. LORENZ, Wied. Ann. XIII. 1881, p. 582.

⁵⁾ M. KNUDSEN. Ann. d. Ph. (4) 3 4, (1911), p. 655.

⁶⁾ M. VON SMOLUCHOWSKI, R. v. SMOLAN. Wien. Sitz. Ber. [2a] 107, (1898), p. 304; 108, (1899), p. 5.

⁷⁾ A. KUNDT and E. WARBURG. Pogg. Ann. 156, (1875), p. 177.

⁸⁾ M. KNUDSEN. loc. cit. p. 608.

case starting from MAXWELL's hypothesis¹⁾, that the molecules may be looked upon as centres of force which repel each other with a force proportional to r^{-5} . In this way he found

$$\gamma/\lambda = \frac{15}{2\pi} \cdot \frac{2-a}{2a} \cdot \dots \dots \dots (II)$$

In these formulae λ_1 represents the mean free path as determined in CLAUSIUS's theory, therefore:

$$\lambda_1 = \frac{\pi\sqrt{2\pi}}{4} \cdot \frac{\eta}{\sqrt{p \cdot \varrho}}$$

If the mean free path, as found by O. E. MEYER's²⁾ method of calculation,

$$\lambda = \sqrt{\frac{\pi}{8} \cdot \frac{1}{0,30967} \cdot \frac{\eta}{\sqrt{p \cdot \varrho}}} \dots \dots \dots (III)$$

is introduced into formula II, we find:

$$\gamma/\lambda = 2,32 \cdot \frac{2-a}{2a}$$

§ 2. In a paper³⁾ which has appeared in the *Annalen der Physik* and to which the reader may here be referred, the absolute value of the heat-conductivity at 0° C., K_0 , has been investigated for a number of pure gases. In the experimental determinations SCHLEIERMACHER's⁴⁾ method was used modified in such a manner that it was possible to eliminate the influence of convection on the heat conduction. Simultaneously the value of the temperature-drop at 0° C. was determined for the same gases and an excellent agreement was found between the experimental value and the one calculated from formula II, if for a the results obtained by KNUDSEN⁵⁾ were used. Amongst the gases experimented on was the same distilled neon, with which the present experiments were made.

The result of the measurements for neon was

$$K_0 = 0.00010890 \text{ gr. cal./grad. sec. cm. and } \gamma/\lambda = 2.391.$$

For pure neon and bright platinum KNUDSEN found $a = 0.653$, hence:

$$\gamma/\lambda = 2.32 \cdot \frac{2-a}{2a}$$

¹⁾ J. CL. MAXWELL. Scientific papers Vol. II, p. 23.

²⁾ O. E. MEYER. Kinet. Theorie der Gase p. 111.

It makes no difference whether MEYER's calculation or a different one is followed here, seeing that the factor which has a different value in the various results drops out from the final result by the introduction of the pressure.

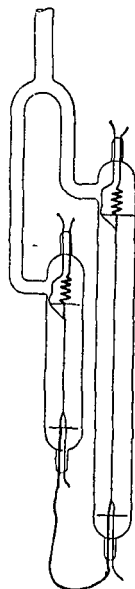
³⁾ SOPHUS WEBER. Ann. d. Ph. (4), 54, (1917), p. 342.

⁴⁾ A. SCHLEIERMACHER. Wied. Ann. 34, (1888), p. 623.

⁵⁾ M. KNUDSEN. Ann. d. Ph., (4) 46, (1915), p. 641.

The value of K_0 is certainly accurate to 2‰ and agrees well with the measurement made by BANNAWITZ¹⁾ on neon, which Professor KAMERLINGH ONNES had drawn for him from the same vessel from which he had supplied me with the gas I used.

§ 3. For the determination of the temperature-coefficient of the heat conductivity for neon the same apparatus could not be used as for the absolute measurement, and on this account I resolved to apply GOLDSCHMIDT's²⁾ method. This method introduces another important improvement into SCHLEIERMACHER's method. The loss of heat at the ends of the wire is eliminated in a simple manner by making measurements first with a long wire and then with a short one of the same diameter, and heating the wire in both cases with the same electric current. The difference between the amount of energy developed in the short and in the long wire gives the energy which is lost radially by a wire of the same section and of a length equal to the difference of the two experimental wires.



The first apparatus which was used in testing GOLDSCHMIDT's method is represented in the figure, the constants and the dimensions being collected in table I³⁾. The figure shows that the thin platinum wires are stretched along the axis of the glass tubes by means of platinum springs.

In the measurements the two wires and a normal resistance of 1Ω are connected up in series. When the condition has become stationary, the potential-differences between the terminals of the long and the short wires E_l and E_k are measured, as also the difference at the terminals of the normal resistance I . The potential differences were measured with a compensation-apparatus by WOLFF which is free of thermo-effects, possible thermo-forces outside the apparatus being eliminated by commutation.

From the resistance the mean temperatures of the platinum wires t_l and t_k are calculated. Using these results the following expressions

¹⁾ E. BANNAWITZ. Ann. d. Ph. (4), 48, (1915), p. 577.

²⁾ R. GOLDSCHMIDT. Physik. ZS. 12 (1911), p. 418.

³⁾ The value given here for $2r_0$ was found by weighing, since it is only used in the correction for the temperature-drop and not in the calibration itself, as this was carried out with atmospheric air (see further on).

TABLE 1.

	App. a	App. b
Diameter of the platinum wire	$2r_0 = 0.005246 \text{ cm}$	$2r_0 = 0.005246 \text{ cm}$
Length " " " "	$l = 11.843 \text{ "}$	$k = 3.138 \text{ "}$
Electric resistance at 0°C of the platinum wire	$W_0 = 5.4187 \Omega$	$w_0 = 1.4481 \Omega$
Temperature-coefficient of W_0 , α_{0-100}	$\alpha_{0-100} = 0.003888$	$\alpha_{0-100} = 0.003888$
Conductivity of the platinum wire	$\gamma = 0.1649$	$\gamma = 0.1649$
Diameter of the glass tube	$2R = 1.449 \text{ cm}$	$2R = 1.449 \text{ cm}$
$4 \frac{A\gamma}{l}$, where A = section of the platinum wire	$4 \frac{A\gamma}{l} = 1.2039 \cdot 10^{-6}$	$4 \frac{A\gamma}{k} = 4.5437 \cdot 10^{-6}$

for L and S may be computed:

$$L = 0.2388 \cdot E_l \cdot I \cdot \frac{1}{l \cdot t_l} \quad \text{and} \quad S = 0.2388 \cdot E_k \cdot I \cdot \frac{1}{k \cdot t_k}$$

If the loss of heat at the ends could be neglected, L and S would represent the radial loss of heat per degree and per cm for the long and for the short wire respectively (in a surrounding of 0°C). In that case L and S as well as the quantity D defined below would all be equal.

Attending now to the difference in length of the two platinum wires we may according to GOLDSCHMIDT assume, that the heat given off by this portion of the wire is not influenced by the heat conduction of the terminals. If D represents the loss of heat per unit length of a wire of the same section in an infinite cylinder of the same shape with a temperature-difference of one degree with the outside at 0°C , and if the loss of heat may be taken proportional to the temperature difference, t_Δ being the temperature-difference of the uniformly heated wire with the surroundings, we have

$$t_\Delta = \frac{W - w - (W_0 - w_0)}{\alpha(W_0 - w_0)} \quad \text{and} \quad D = 0.2388 (E_l - E_k) \cdot I \cdot \frac{1}{(l - k) \cdot t_\Delta}$$

From the value of D the mean conductivity K on the way which the heat follows between the wire and the wall may be calculated according to the relation ¹⁾.

$$D = \frac{2\pi K}{\ln \frac{R}{r_0} + \gamma \left(\frac{1}{r_0} + \frac{1}{R} \right)} \cdot \dots \cdot \dots \cdot (IV)$$

¹⁾ M. VON SMOLUCHOWSKI. W. A. 64, (1898) p. 101.

where γ is the coefficient of the temperature-drop at the wall.

Using this apparatus I have made a few experiments to test GOLDSCHMIDT's theory.

In a set of measurements with the apparatus filled with dry pure carbon dioxide the temperature of the bath being 0°C . the following values amongst others were found for t_l, t_k, L, S, t_Δ and D .

$$\begin{array}{llll} p=21.61 \text{ cm} & t_l = 5.409 & t_k = 4.630 & t_\Delta = 5.693 \\ & L = 413.0 \cdot 10^{-7} & S = 485.2 \cdot 10^{-7} & D = 391.6 \cdot 10^{-7} \\ & L_{\text{cor.}} = 391.9 \cdot 10^{-7} & S_{\text{cor.}} = 391.9 \cdot 10^{-7} & \\ \\ p=6.28 \text{ cm} & t_l = 5.453 & t_k = 4.669 & t_\Delta = 5.739 \\ & L = 409.7 \cdot 10^{-7} & S = 481.1 \cdot 10^{-7} & D = 388.5 \cdot 10^{-7} \\ & L_{\text{cor.}} = 388.7 \cdot 10^{-7} & S_{\text{cor.}} = 388.2 \cdot 10^{-7} & \end{array}$$

These measurements show very clearly that entirely erroneous values may be arrived at for K , if the loss of heat along the ends of the wire is not taken into account.

It can now be shown by means of a simple calculation that the value found for L or S after having been corrected for the heat carried away along the ends agrees with the value of D . The quantities of heat Q_1 and Q_2 which in the stationary condition are conducted away through the surface and the ends of an electrically heated wire respectively (apparatus a) are given by ¹⁾

$$\frac{Q_1}{t-t_0} = c(x^2 + m^2), \quad \frac{Q_2}{t-t_0} = c \frac{x Tgx}{1 - \frac{1}{x} Tgx} \quad \text{and} \quad \frac{Q}{t-t_0} = c \left(m^2 + \frac{x^2}{1 - \frac{1}{x} Tgx} \right)$$

where $c = \frac{4A \cdot x}{l}$ and $m^2 = \frac{0.2388}{c} \propto W_0 \cdot l^2$, x being an auxiliary quantity which is determined by the third equation.

In these equations Q is the entire quantity of heat developed in the wire (app.a, $Q = L \cdot l \cdot t_l$), t the mean temperature of the wire, t_0 the temperature of the glass wall, l the current and W_0 , A , x and l the resistance at t_0 , the section, the conductivity and the length of the heated wire respectively; Tgx stands for the hyperbolic tangent of x .

When the values found for Ll and Sk are corrected in this manner, the figures given under $L_{\text{cor.}}$ and $S_{\text{cor.}}$ are obtained; they are seen to agree very well with D . In this way it appears, that the application of GOLDSCHMIDT's method is allowable, if the dimensions of the apparatus are chosen correctly.

¹⁾ S. WEBER. Ann. d. Ph. (4) 54, (1917), p. 169.

§ 4. In the determinations with neon an apparatus was used the dimensions of which are contained in table 2.

In order to be able to use the apparatus at the temperatures of liquid air it is necessary to compare its resistance with the resistance of a platinum thermometer, whose resistance is known. If this thermometer is calibrated, so that from its resistance the absolute temperature on the Kelvin-scale can be deduced, it becomes possible from the resistance of the conduction-apparatus to determine the corresponding absolute temperature. For this purpose I have chosen the platinum thermometer Pt_1 , the standard thermometer of the cryogenic laboratory at Leiden. For this thermometer there is a table ¹⁾ which gives the relation between $\frac{W}{W_0}$, or properly speaking $\frac{W}{W_0}$, and the absolute temperature.

TABLE 2.			
App. 1		App. 2.	
$2r_0$	$= 0.005240 \text{ cm}$	$2r_0$	$= 0.005240 \text{ cm}$
l	$= 9.992 \text{ „}$	h	$= 3.373 \text{ „}$
$2R$	$= 1.526 \text{ „}$	$2R$	$= 1.526 \text{ „}$
W_0	$= 4.5762 \Omega$	w_0	$= 1.5416 \Omega$
α_{0-100}	$= 0.003891$	α_{0-100}	$= 0.003891$

I have carried out the comparison in the following manner: in a closed cryostat, provided with a stirring arrangement and filled with pure liquid oxygen, the double conduction-apparatus and an oxygen-thermometer according to Stock ²⁾ are mounted side by side. When the condition had become stationary, the resistance of the apparatus $w' = W - w$ was measured and simultaneously the vapour-pressure of the oxygen-thermometer was read. The following corresponding values were obtained in this way.

Vapour-pressure of oxygen $p = 742.35 \text{ mm}$ and $w' = 0.75828 \Omega$.

From p according to KAMERLINGH ONNES and BRAAK ³⁾ the absolute temperature T of the oxygen-bath is calculated by means of the following relation which holds from 83 and 91° K:

¹⁾ G. HOLST. Leiden Comm. N°. 148a.

²⁾ A. STOCK and C. NIELSEN. Ber. d. D. Chem. Ges. 39 (11), 1906, p. 2066.

³⁾ H. KAMERLINGH ONNES and C. BRAAK. Leiden Comm. N°. 107a, comp. HOLST loc. cit.

$$T = \frac{369.83}{6.98460 - \log p}.$$

This gives $T = 89.896^\circ K$.

From the table for Pt_I the following mutually corresponding values are found:

T	$\frac{w'}{w'_0}$	$\left(\frac{W}{W_0}\right)_{Pt_I}$
89.896	0.24988	0.25079

The two platinum-thermometers can now be compared at each temperature with an accuracy sufficient for our purpose¹⁾ by means of NERNST's formula

$$\left(\frac{W}{W_0}\right)_{Pt_I} - \frac{w'}{w'_0} = \alpha \left(1 - \frac{W}{W_0}\right)_{Pt_I}$$

Introducing the above value in this formula we find $\alpha = 0.001221$.

Using this value for α it is now possible to calculate the value of $\left(\frac{W}{W_0}\right)_{Pt_I}$ corresponding to each value of $\frac{w'}{w'_0}$ as measured and hence by means of the table for Pt_I to determine the temperature on the Kelvin-scale.

The apparatus is then placed in a bath of finely ground ice and distilled water and by means of dry air free of carbon dioxide and of pure neon the denominator in eq. IV, $\ln \frac{R}{r_0} + \gamma \left(\frac{1}{r_0} + \frac{1}{R}\right)$, is determined, which gives $\frac{R}{r_0}$, whereas R is found by calibrating the

tube with mercury. When these measurements are completed, the apparatus is put in a bath of solid carbon dioxide and benzene, and new measurements with neon are made; this time, however, the measurements are conducted in the following order: first the resistance $W - w$ is measured without the wire being heated, whereby the temperature of the bath is determined; then the conductivity measurements are made, first at higher pressure, then at lower pressure and again at the higher pressure, as shown in the tables, and finally the resistance of the wire is determined once more without heating.

The temperature of the bath was found not to have changed during the measurements.

The correction for radiation is calculated from the dimensions of

¹⁾ See G. HOLST Leiden Comm. N^o. 148 and P. G. CATH, H. KAMERLINGH ONNES and J. M. BURGERS Leiden Comm. N^o. 152c.

the apparatus and the formula for the complete radiation of platinum¹⁾. The corrections as used were as follows: $R_{100} = 1.70 \cdot 10^{-6}$, $R_0 = 0.48 \cdot 10^{-6}$, $R_{-78} = 0.13 \cdot 10^{-6}$ and $R_{-183} = 0.005 \cdot 10^{-6}$, R being the radiation per degree.

The measurements are collected in the following tables.

In these tables column I gives the pressure p_{cm} in cms Hg ; reduced to $0^\circ C.$ and 45° latitude; column II Δt , the temperature-difference between the central portion of the long wire and the bath;

column III $D = \frac{Q}{(l-k) \cdot \Delta t}$, where Q is the difference of the quantities of heat given off by the two wires expressed in gr.cal./sec.; column

Atm. air at $0^\circ C.$				
p_{cm}	Δt	D	$D'_{\Delta t=17.50}$	$D'_{corr.}$
28.355	17.428	0 0004358	0.0004353	0.0004367
13.069	17.495	4342	4337	4367
3.010	17.860	4258	4251	4378

Neon at $0^\circ C.$				
p_{cm}	Δt	D	$D'_{\Delta t=9.20}$	$D'_{corr.}$
33.791	9.029	0.0008165	0.0008162	0.0008222
20.182	9.077	8122	8118	8219
10.181	9.192	8023	8018	8215
5.729	9.367	7878	7872	8215
1.894	10.252	7220	7206	8160
0.709	12.726	5868	5840	7900
0.217	23.109	3349	3292	7078

¹⁾ In the paper quoted above (Ann. d. Phys. (4) 54, 1917, p. 330), where the complete radiation was investigated for platinum and tungsten, it was pointed out, that the correction for radiation cannot be determined by a separate experiment in vacuo. This is due to the fact that the distribution of temperature along the heated wire is quite different in vacuo than in a gas.

Neon at 99°.81 C.				
p_{cm}	Δt	D	$D'_{\Delta t=12.00}$	$D'_{corr.}$
37.454	9.945	0.0009965	0.0009971	0.00010077
20.225	10.044	9867	9872	10067
7.473	10.389	9547	9547	10057
4.290	13.795	9241	9205	10064
1.718	15.772	8123	8072	9952
0.673	21.362	6081	6000	9570
9.329	13.136	9690	9661	10075
21.262	12.830	9914	9888	10074
38.973	12.721	9998	9973	10072

Neon at 194°.72 K. (Solid carbon dioxide in benzene).				
p_{cm}	Δt	D	$D'_{\Delta t=8.02}$	$D'_{corr.}$
39.915	7.934	0.0006584	0.0006583	0.0006608
21.649	7.966	6557	6556	6603
13.453	8.000	6530	6529	6606
6.844	8.102	6451	6450	6597
5.046	8.169	6398	6397	6597
40.167	7.944	6576	6575	6600

Neon at 99°.0 K. (Liquid oxygen).				
p_{cm}	Δt	D	$D'_{\Delta t=3.54}$	$D'_{corr.}$
32.342	3.481	0.0003740	0.0003740	0.0003746
20.543	3.480	3741	3741	3751
10.309	3.510	3710	3710	3718
5.127	3.514	3706	3706	3746
2.642	3.558	3663	3663	3739
0.826	3.728	3506	3505	3739
32.165	3.490	3730	3730	3737

IV $D' = D - R$, where R is the radiation (as Δt is not quite constant, $D - R$ has been reduced to the same temperature-difference) and column V D'_{corr} , arising by the correction of D' for the temperature-drop at the wall. The latter correction is made by the formula (comp. formula IV on p. 346):

$$D'_{corr.} = D' \left(1 + \frac{\gamma_1}{p_{cm}} \right), \text{ where } \gamma_1 = \frac{\frac{1}{R} + \frac{1}{r_0}}{\ln \frac{r_1}{r_0}} \cdot \gamma p_{cm}.$$

With the differences of temperature which are used we may assume with sufficient accuracy, that K corresponds to the temperature $t_0 + \frac{\Delta t}{2}$; hence we have:

Atm. air: $T = 273.1 + 8.75$	$D'_{corr.} = 0.0004371$
neon: „ $= 273.1 + 4.60$	„ $= 0.0008218$
„ „ $= 273.1 + 99.81 + 6.00$	„ $= 0.0010071$
„ „ $= 194.72 + 4.01$	„ $= 0.0006602$
„ „ $= 89.90 + 1.77$	„ $= 0.0003740$

Hence taking the temperature-coefficient of the conductivity for air as 0.0033, the following results are obtained:

Atm. air: $T = 273.1$	$D'_{corr.} = 0.0004248$
neon: $T =$ „	„ $= 0.0008135$

For the conductivity at 0°C.^1 of dry air free of carbon dioxide I have found $K_0 = 0.00005680$; using this value K'_0 for neon is found as follows:

$$K'_0 = \frac{8135}{4248} \cdot 0.00005680 = 0.0001087 \text{ gr.cal./sec grad.cm.}$$

in good agreement with my previous determination $K'_0 = 1089.10^{-7}$.

This result shows that the two calibrations of the apparatus are in good mutual agreement; the following results are now obtained for neon:

T	K'	$K'_{calc.}(S)$	$K'_{calc.}(\beta=5)$
$273.09 + 105.81$	0.0001344	0.0001344	0.0001364
273.09	1087	1087	1087
$273.09 - 74.37$	0879	0869	0869
$273.09 - 181.43$	0499	0468	0505

¹⁾ S. WEBER. Ann. d. Phys. (4) 54, (1917), p. 352.

Column I contains the absolute temperature T ; column II the conductivity found K' ; column III the values computed by means of SUTHERLAND's formula. The value of C in this formula, 57.5 for neon, was derived from the first two measurements ¹⁾.

It appears, therefore, that SUTHERLAND's formula cannot represent the dependence on the temperature of the conductivity for neon at the lower temperatures. That SUTHERLAND's formula is not satisfactory at low temperatures, was proved before by investigations on the

¹⁾ In connection with the value of C and the high viscosity of neon $\eta_0 = 2981 \cdot 10^{-7}$, it is of interest to calculate the diameter σ of the neon-molecule. Using CHAPMAN's formula (London Phil. Trans. A. Vol. 216, 1916, p. 279)

$$\eta = 0.491 (1 + \epsilon_a) \cdot \frac{\bar{c} \cdot Q}{\sqrt{2 \cdot \pi \sigma^2 \cdot n \left(1 + \frac{C}{T}\right)}},$$

where the small correction ϵ_a is determined by C , we find, with $n = 2.77 \cdot 10^{19}$, $\sigma = 2.32 \cdot 10^{-8}$.

An approximate value of σ may also be obtained by means of the critical constants. From VAN DER WAALS's formulae in the notation of H. KAMERLINGH ONNES and W. H. KEESOM: Die Zustandsgleichung, Comm. Suppl. N^o. 23, Fussn. 284 it follows, using

$$p_k = K_1 \cdot \frac{a_{wf}}{b_{wf}} \quad \text{and} \quad R_{wf} \cdot T_k = K_1 \cdot \frac{a_{wf}}{b_{wf}}$$

that :

$$b_{wf} = \frac{K_2}{K_1} \cdot R_{wf} \cdot \frac{T_k}{p_k}$$

According to VAN DER WAALS (see Fussn. 459 l.c.) $\frac{K_2}{K_1}$ is approximately equal to the theoretical value $\frac{1}{8}$, hence:

$$b_{wf} = \frac{R}{8} \cdot \frac{T_k}{p_k} = \frac{2}{3} \pi \cdot N \cdot \sigma^3$$

Using $N = 62 \cdot 10^{22}$ and by means of the critical constants $p_k = 26.86$ (intern. atm.) and $T_k = 44^\circ.75$ K. (H. KAMERLINGH ONNES, C. A. CROMMELIN and P. G. CATH: Comm. N^o. 151b) we find $\sigma = 2.36 \cdot 10^{-8}$.

If we use the isothermals for neon at 0° and 20° C. (H. KAMERLINGH ONNES and C. A. CROMMELIN Comm. N^o. 147d) and assume, that a in VAN DER WAALS's equation of state is independent of the temperature, one finds (comp. H. KAMERLINGH ONNES, Comm. N^o. 102a p. 5)

$$b_w = \frac{B_{20} - B_0}{20 R} = 0.001398.$$

From the value of the virial-coefficient C_A at 0° C. one obtains

$$b_w = \sqrt[3]{\frac{C_A}{RT}} = 0.00136$$

Using the former of the two values the result is $\sigma = 2.90 \cdot 10^{-8}$.

viscosity of helium and hydrogen (comp. H KAMERLINGH ONNES and SOPHUS WEBER; Comm. N^o. 134). I have therefore tried, whether an improvement is not brought about — as appeared to be the case in Comm. N^o. 134 — by using a formula of the form $\frac{K}{K_0} = \left(\frac{T}{T_0}\right)^{\frac{1}{2}} + \frac{1}{\beta}$.

As shown by column IV $\beta = 5$ gives a very good agreement. According to MAXWELL's theory in a more general form¹⁾, where the forces between the molecules are taken proportional to r^{-n} , we should have to take for neon $2\beta + 1 = n = 11$.

The measurements give for the temperature-coefficient between 0° and 100° C., β_{0-100} , 0.00226; this agrees very closely with the temperature-coefficient of the viscosity, for which RANKINE²⁾ found 0.00225.

§ 5. From the experimental values of D' and the corresponding pressures p the values of D'_{cor} , and γ_1 can be determined according to the relation $D'_{cor} = D' \left(1 + \frac{\gamma_1}{p}\right)$. In this manner the following results for γ_1 were obtained:

T	γ_1	γ_{1calc}	γ_{1calc}
384.90	0.400	0.363	0.408
282.29	0.250	0.250	0.250
202.7	0.157	0.168	0.154
93.4	0.055	0.0676	0.055

The values found for D'_{cor} , are given in the 5th column in the tables on p. 350 and p. 351. In the tables for 0° and 100° C. D'_{cor} will be found to become too small below about $p = 4$ cm.; this is quite intelligible seeing that the theory about the temperature-drop is derived under the assumption that the mean free path λ is small compared to the dimensions of the apparatus. For neon at 0° C. and $p = 4$ cm. $\lambda = 0.000375$ cm., $2r_0$ the diameter of the experimental wire being 0.0005240 cm., hence $\frac{2r_0}{\lambda} = 1.4$. It appears therefore that the theory for the temperature-drop given by KUNDT, WARBURG and SMOLUCHOWSKI is applicable

¹⁾ S. CHAPMAN. London Phil. Trans. A. 211, (1912), p. 433 and 216, (1916), p. 279.

²⁾ A. O. RANKINE. Physik. Z. S. 11 (1910) p. 497 and 745.

over a wider range than might have been expected according to the kinetic theory.

It follows from $\gamma \cdot p = \frac{\ln \frac{R}{r_0}}{\frac{1}{R} + \frac{1}{r_0}} \cdot \gamma_1$ that $\gamma \cdot p = \frac{0.250}{68.44}$; at $9^\circ.2$ C.

when the pressure p is measured in dyne/cm² and λ in cms. we find according to O. E. MEYER (p. 344) from the viscosity $p\lambda = 18.93 \cdot \left(\frac{T}{T_0}\right)^{1.2}$. This gives at the temperature of the wire $t = 9^\circ.2$ C.

$$\gamma/\lambda = 2.46$$

Hence with $\alpha = 0.653$

$$\gamma/\lambda = 2.38 \cdot \frac{2-\alpha}{2\alpha}.$$

The agreement is not so close as it was with the value found previously, but the deviation is not larger than can be explained by accidental errors.

It appears from the table that γ_1 changes with the temperature; this was to be expected as λ depends on the temperature according to the relation $\lambda = \lambda_0 \cdot \left(\frac{T}{T_0}\right)^{1.2}$. Calculating the values of γ_1 which have to be expected at the various temperatures, the results $\gamma_{1\text{ calc}}$, given in column 3 are obtained. On comparing these with the experimental results the latter are seen to change more rapidly with the temperature. This can be explained by the assumption that the accommodation-coefficient α is not independent of the temperature. The same assumption is also rendered probable by the results for hydrogen; KNUDSEN ¹⁾ found that in this case α had a negative temperature-coefficient -0.001 . Assuming the value -0.00076 for the temperature-coefficient of α for neon we find for γ_1 the results given in column 4 under $\gamma_{1\text{ calc}}$.

§ 6. By the aid of the principle of "similar motions" as given by H. KAMERLINGH ONNES ²⁾ a comparison may be made between the heat conductivity of different substances for which the conduction through the molecules themselves may be disregarded. It is found that at equal reduced temperatures we must have:

¹⁾ M. KNUDSEN. Ann. d. P'h. (4) 34, (1911) p. 632.

²⁾ H. KAMERLINGH ONNES. Verh. Kon. Akad., 21, p. 22, 1881.

$$\frac{K_1}{M_1^{-\frac{1}{2}} \cdot P_{k,1}^{\frac{2}{3}} \cdot T_{k,1}^{-\frac{1}{6}}} = \frac{K_2}{M_2^{-\frac{1}{2}} \cdot P_{k,2}^{\frac{2}{3}} \cdot T_{k,2}^{-\frac{1}{6}}} = \dots$$

where P_k and T_k are the critical constants.

When a comparison is made in this manner by means of the experimental results between the conductivity of helium and argon with that of neon¹⁾, it seems in the mean time as if the reduced heat conductivity of neon changes in a different manner with the reduced temperature from that of argon and helium; in order to obtain more evidence on this point it becomes even more important than before, also in view of J. J. THOMSON's theory (that neon would consist of two isotopic elements with molecular weights of 20 and 22 respectively), to determine the conductivity of neon at reduced oxygen- and neon-temperatures and that of helium at reduced hydrogen-temperatures; as was mentioned in the beginning of this paper, it is the intention to carry out this research in the cryogenic laboratory at Leiden.

In conclusion I am happy to express my sincere thanks to Dr. Ir. G. L. F. PHILIPS for his kindness through which I was enabled to carry out this research.

I also wish to thank Mr. H. J. MICHIELSEN for the excellent manner in which he assisted me in the measurements and the calculations.

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of the Philips Incandescent Lamp Factories.*

¹⁾ S. WEBER. Ann. d. Ph. (4) 54, (1917), p. 460.

Physics. — “On the shape of small drops and gas-bubbles”. By J. E. VERSCHAFFELT. Supplement N°. 42c to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 29, 1918).

§ 1. It is well known that the meridian-section of a liquid drop or gas-bubble (which we shall suppose to be bodies of revolution) cannot be represented by a finite equation by means of known functions. The differential equation to the section

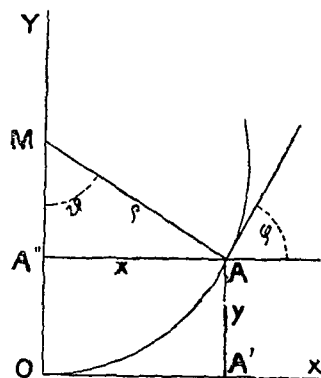


Fig. 1.

$$\frac{1}{R_1} + \frac{1}{R_2} = \frac{1}{x} \frac{d}{dx} \left(\frac{xy'}{\sqrt{1+y'^2}} \right) = k(h+y)^{-1} \quad (1)$$

has as a first integral the equation

$$x \sin \varphi = \frac{1}{2} khx^2 + \frac{k}{2\pi} u, \quad (2)$$

where φ represents the angle which the tangent forms with the x -axis (fig. 1; OY is the axis of revolution)

and $u = 2\pi \int_0^x xy dx^2$, but the computation of u and consequently

¹⁾ In this equation k stands for the expression $\frac{(\mu_1 - \mu_2)g}{\sigma}$, σ being the surface tension, $\mu_1 - \mu_2$ the difference of the densities below and above the surface in its top, g the acceleration of gravity; k is therefore positive or negative according as the liquid is below the top of the surface, as with a drop resting on a plane, or above it, as with a hanging drop; y is the height of a point of the surface above the tangent plane at the top. h is determined by $kh = \frac{2}{R_0}$, R_0 being the radius of curvature at the top; R_0 will be reckoned as positive when the surface is hollow upwards, negative in the opposite case.

²⁾ u is evidently the volume of the body which is originated by rotation of the surface $OA'A'O$ (fig. 1) about the y -axis. Equation (2) may be written in the form

$$2\pi x \sigma \sin \varphi = (\mu_1 - \mu_2)g (\pi x^2 h + u), \quad (3)$$

the further integration of the differential equation can only be carried out by successive approximations or a development in series.

In the case that the drop or bubble deviates little from the spherical shape, y is small compared to h ¹⁾. In first approximation y may thus be neglected by the side of h , i. e. we may put $y = 0$; as a second approximation a circular meridian section is then obtained; if the expression for y corresponding to this as a function of x is substituted in u , a first deviation from the sphere is found as a third approximation, etc.²⁾.

which is also found directly, when, for instance by applying the so called "weight-method", the rise in a capillary tube is calculated. The contradiction found by A. FERGUSON (Phil. Mag., (6), 28, (1914) p. 128) between the result of the integration of the differential equation and that of the application of the weight-method is merely due to an error of computation in the approximation of equation (2), owing to which FERGUSON's formula (7) is incorrect.

Equation (2) can also be written as follows

$$x \sin \varphi = \frac{1}{2} kx^2 (h + y) - \frac{k}{2\pi} v, \quad (2')$$

where $v = \pi x^2 y - u$ represents the volume arising by the rotation of the surface $OAA''O$. (2) gives:

$$2\pi x \sigma \sin \varphi = \pi (\mu_1 - \mu_2) g x^2 (h + y) - (\mu_1 - \mu_2) g v, \quad (3')$$

which expresses for instance, that the resultant of the forces acting along the edge of a section of a hanging drop makes equilibrium with the hydrostatic pressure on the section and the weight of the portion below it, in other words the surface tension does not balance the weight of a hanging drop alone, a fact which may also be derived from a simple consideration of the equilibrium (cf. on this point TH. LOHNSTEIN, Ann. d. Phys., (4) 20 (1906) p. 238).

¹⁾ Hence R_0 is also small compared to h or to $\frac{2}{kR_0}$, that is kR_0^2 is a small number.

²⁾ Cf. for instance A. WINKELMANN, Handb. der Physik, 2e Aufl. I (2), 1143—1144, 1908.

Putting $y = R_0 - \sqrt{R_0^2 - x^2} + z$, where z is considered infinitely small as compared to y , and supposing that z' is also infinitely small compared to y' , $\sin \varphi = \frac{y'}{\sqrt{1 + y'^2}}$ may be developed in a series, which gives, if z_1 represents the first approximation of z :

$$z_1 = \frac{1}{6} k \frac{R_0^4}{\sqrt{R_0^2 - x^2}} - \frac{1}{6} k R_0^3 + \frac{1}{3} k R_0^3 \log \frac{R_0 + \sqrt{R_0^2 - x^2}}{2R_0},$$

as is also found by FERGUSON (loc. cit.) although in a somewhat circuitous manner. This expression, however, does not hold near $x = R_0$, as z_1 is there no longer infinitely small with respect to y' , but of the same order of magnitude (viz. of the order $(kR_0^2)^{-\frac{1}{2}}$; this fact has been overlooked by FERGUSON (loc. cit.).

§ 2. The introduction of polar coördinates, choosing as origin the centre of curvature at the top M (fig. 1), gives the advantage that there is no discontinuity at $\vartheta = \frac{\pi}{2}$; in that case

$$x = \rho \sin \vartheta \quad \text{and} \quad y = R_0 - \rho \cos \vartheta \quad . \quad . \quad . \quad (4)$$

and the equation (1) becomes

$$\frac{\rho \sin \vartheta - \rho' \cos \vartheta}{\rho \sin \vartheta (\rho^2 + \rho'^2)^{1/2}} + \frac{\rho^2 + 2\rho'^2 - \rho\rho''}{(\rho^2 + \rho'^2)^{3/2}} = \frac{2}{R_0} + k(R_0 - \rho \cos \vartheta). \quad (5)$$

If we now put

$$\rho = R_0(1 - \tau) \quad \text{and} \quad \tau = \tau_1 + \tau_2 + \tau_3 + \dots \quad . \quad . \quad . \quad (4')$$

where τ_1, τ_2 , etc. represent the successive approximations to the infinitely small quantity τ , we can, as long as τ and τ' are infinitely small, separate equation (5) into a series of other ones, the first of which being

$$\tau''_1 \sin \vartheta + \tau'_1 \cos \vartheta + 2\tau_1 \sin \vartheta = kR_0^3 (1 - \cos \vartheta) \sin \vartheta; \quad . \quad . \quad (5')$$

hence¹⁾

$$\tau_1 = \frac{1}{8} kR_0^3 \left[(1 - \cos \vartheta) + 2 \cos \vartheta \log \left(\frac{1 + \cos \vartheta}{2} \right) \right], \quad . \quad . \quad (6)$$

an expression which remains valid from $\vartheta = 0$ to $\vartheta = \pi$ throughout.

§ 3. The result of the third approximation is as follows

$$u = \frac{1}{8} \pi R_0^3 (1 - \cos \vartheta)^2 (1 + 2 \cos \vartheta) + \frac{1}{8} \pi k R_0^5 (1 - \cos \vartheta)^2 \cos^2 \vartheta + \\ + \frac{1}{8} \pi k R_0^5 \sin^2 \vartheta (1 - 2 \cos \vartheta + 2 \cos^2 \vartheta) \log \left(\frac{1 + \cos \vartheta}{2} \right). \quad . \quad . \quad (7)$$

and

$$v = \frac{1}{8} \pi R_0^3 (1 - \cos \vartheta)^2 (2 + \cos \vartheta) - \frac{1}{8} \pi k R_0^5 (1 - \cos \vartheta)^2 (2 + \cos \vartheta) - \\ - \frac{1}{8} \pi k R_0^5 \sin^2 \vartheta \log \left(\frac{1 + \cos \vartheta}{2} \right). \quad . \quad . \quad . \quad (7')$$

§ 4. Between the angles ϑ and φ the following relation holds:

$$\sin \varphi = \frac{\rho \sin \vartheta - \rho' \cos \vartheta}{\sqrt{\rho^2 + \rho'^2}} = \sin \vartheta + \tau' \cos \vartheta + \dots;$$

¹⁾ In order to integrate these equations we have to bear in mind, that

$$\cos \vartheta (\tau'' \sin \vartheta + \tau' \cos \vartheta + 2\tau \sin \vartheta) = \frac{d}{d\vartheta} [\sin \vartheta (\tau \sin \vartheta + \tau' \cos \vartheta)]$$

and

$$\tau \sin \vartheta + \tau' \cos \vartheta = \cos^2 \vartheta \frac{d}{d\vartheta} \left(\frac{\tau}{\cos \vartheta} \right).$$

The integration does not offer any special difficulties, but the calculations are long, that of τ_2 being already very laborious; for that reason we have confined ourselves to τ_1 .

It is easily seen, that $R_0 \tau_1 = z_1 \cos \vartheta$.

and correspondingly

$$\vartheta_A(\vartheta_{A'}) = \frac{\pi}{2} - \psi_A = \frac{\pi}{2} - \frac{1}{6} k R_0^2 (2 \log 2 + 1)^{1/2} \quad (10')$$

and

$$y_A(y_{A'}) = R_0 - R_0 \psi_A = R_0 - \frac{1}{6} k R_0^2 (2 \log 2 + 1)^{1/2} \quad (10'')$$

§ 6. From the equations (6) and (8') it follows that in the neighbourhood of $\vartheta = \pi$, putting $\vartheta = \pi - \varepsilon$,

$$\tau_1 = -\frac{1}{3} k R_0^2 \left(\log \frac{\varepsilon^2}{4} - 1 \right) \quad \text{and} \quad \tau'_1 = \frac{2}{3} k R_0^2 \frac{1}{\varepsilon}; \quad (11)$$

in order therefore that these equations may still be valid in that region, seeing that τ'_1 has to be small, it is necessary, that ε must remain large with respect to $k R_0^2$. This is still the case in B , where y has its maximum, for (comp. 4, 6 and 11)

$$y = 2 R_0 - \frac{1}{2} R_0 \varepsilon^2 + \frac{1}{3} k R_0^2 \left(\log \frac{\varepsilon^2}{4} - 1 \right), \quad (11')$$

so that it follows from $\frac{dy}{d\varepsilon} = 0$ that

$$\varepsilon_B = \sqrt{\frac{2}{3} k R_0^2}, \quad y_B = 2 R_0 \left[1 + \frac{1}{6} k R_0^2 \log \left(\frac{1}{6} k R_0^2 \right) - \frac{1}{3} k R_0^2 \right] \quad (12)$$

and, also to a third approximation,

$$x_B = R_0 \varepsilon_B = R_0 \sqrt{\frac{2}{3} k R_0^2} \quad (12')$$

These coordinates are only real, when k is positive.

If k is negative, φ has a maximum in B' (fig. 1) corresponding to a value of ε which is determined by $0 = \frac{d\varphi}{d\vartheta} = 1 + \frac{d\psi}{d\vartheta}$ (see eq. 8); this gives:

$$\varepsilon_{B'} = \sqrt{-\frac{2}{3} k R_0^2}; \quad \text{hence} \quad y_{B'} = 2 R_0 \left[1 + \frac{1}{6} k R_0^2 \log \left(-\frac{1}{6} k R_0^2 \right) \right] \quad (13)$$

$$x_{B'} = R_0 \sqrt{-\frac{2}{3} k R_0^2} \quad \text{and} \quad \varphi_{B'} = \pi - 2 \sqrt{-\frac{2}{3} k R_0^2} \quad (13')$$

§ 7. It is possible to go a step further in the analysis of the meridian section of the capillary surface. Close to $\vartheta = \pi$ the curve has a sharp bend (fig. 3): BCD with a double point E for $k > 0$,

¹⁾ Obviously this expression is also found by putting $\frac{dx}{d\vartheta} = 0$.

²⁾ $\varepsilon_{B'}$ may also be found by putting $0 = \frac{d^2 y}{d\varepsilon^2} = \frac{1}{R_0^2} \frac{d^2 y}{d\varepsilon^2}$, (see eq. 11').

$B'C'D'$ with two points of inflexion B' and D' for $k < 0$; the dotted line (two circular arcs) represents the transition between the two cases for $k=0$.

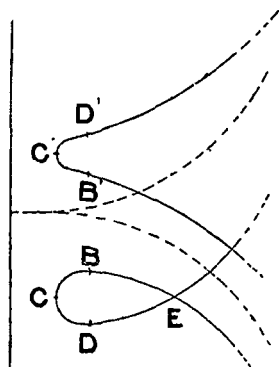


Fig. 3.

In that region the equation to the surface may be written in the form

$$\frac{1}{R_1} + \frac{1}{R_2} = k(h_C + \eta) \quad . \quad . \quad (7')$$

where $h_C = h + y_C$, y_C being the ordinate of C (or C'), and $\eta = y - y_C$. In the region under consideration, however, η is small compared to R_0 , so that in second approximation η may be neglected with respect

to h_C and therefore with the same degree of accuracy to which hitherto the deviation from the circular shape was calculated we may write:

$$\frac{1}{R_1} + \frac{1}{R_2} = kh_C = \text{constant} \quad . \quad . \quad . \quad (14)$$

In third approximation BCD is thus a part of the curve which was called nodoid by PLATEAU, $B'C'D'$ a part of an onduloïd.

The equations of these curves are known¹⁾; but in our case they may be materially simplified. Putting $kh_C = \frac{2}{r_0}$ ²⁾ the first integral of (14) in the case of the nodoid ($\sin \varphi = 0$ for $x = x_B$) will be

$$r_0 x \sin \varphi = x^2 - x_B^2 \quad . \quad . \quad . \quad (15)$$

If x_1 and x_2 ($= x_C$) are the maximum- and minimum-values of x corresponding to $\sin \varphi = 1$ and $\sin \varphi = -1$ we have approximately since x_B is very small with respect to r_0 (see eq. 12')

$$x_1 = r_0 = R_0 \quad x_2 \text{ of } x_C = \frac{x_B}{r_0} = \frac{2}{3} k R_0^2 \quad . \quad . \quad (16)$$

Further it follows from (15), as long as x is small with respect to r_0 ³⁾

$$\pm \eta = x_2 \log \frac{x + \sqrt{x^2 - x_2^2}}{x_2} - \frac{1}{2R_0} x \sqrt{x^2 - x_2^2} \quad . \quad . \quad (17)$$

¹⁾ See for instance WINKELMANN, loc. cit., p. 1150.

²⁾ In first approximation $r_0 = R_0$; in second approximation $kh_C = k(h + 2R_0) = \frac{2}{R_0} + 2kR_0 = \frac{2}{R_0} (1 + kR_0)$, so that $r_0 = R_0 (1 - kR_0^2)$.

³⁾ Here x_1 belongs to the nodoid and has thus not the same meaning as x_A in § 5.

⁴⁾ Since in that case

$$\pm \frac{d\eta}{dx} = \frac{x_B^2 - x^2}{\sqrt{r_0^2 x^2 - (x_B^2 - x^2)^2}} = \frac{x_B^2 - x^2}{\sqrt{r_0^2 x^2 - x_B^4}} = \frac{R_0 x_2 - x^2}{R_0 \sqrt{x^2 - x_2^2}}.$$

This gives for $x = x_B$

$$\eta_B = -\frac{1}{3} k R_0^3 \log \left(\frac{1}{6} k R_0^2 \right) - \frac{1}{3} k R_0^3. \quad (18)$$

whence

$$y_C = y_B - \eta_B = 2R_0 + \frac{2}{3} k R_0^3 \log \left(\frac{1}{6} k R_0^2 \right) - \frac{1}{3} k R_0^3, \quad (16')$$

and similarly, if x_D, y_D and the coördinates of D ,

$$x_D = x_B = R_0 \sqrt{\frac{2}{3} k R_0^2} \quad y_D = y_C - \eta_B = 2R_0 + k R_0^3 \log \left(\frac{1}{6} k R_0^2 \right) \quad (19)$$

§ 8. In the case of the unduloid, where $\sin \varphi$ goes through a minimum in B' , we have

$$r_0 x \sin \varphi = x^2 + x_B^2. \quad (20)$$

The maximum- and minimum-values of x ($\sin \varphi = 1$) are now approximately

$$x_1 = R_0 \quad x_2 = x_C = \frac{x_{B'}^2}{R_0} = -\frac{2}{3} k R_0^3 \quad (21)$$

Moreover in that case

$$\pm \eta = x_1 \log \frac{x + \sqrt{x^2 - x_2^2}}{x_2} + \frac{1}{2R_0} x \sqrt{x^2 - x_2^2}. \quad (22)$$

whence

$$\eta_B = -\frac{1}{3} k R_0^3 \log \left(-\frac{1}{6} k R_0^2 \right) + \frac{1}{3} k R_0^3 \quad (23)$$

$$y_C = y_{B'} - \eta_{B'} = 2R_0 + \frac{2}{3} k R_0^3 \log \left(-\frac{1}{6} k R_0^2 \right) - \frac{1}{3} k R_0^3 \quad (21')$$

$$x_{D'} = R_0 \sqrt{-\frac{2}{3} k R_0^2}, \quad y_{D'} = 2R_0 + k R_0^3 \log \left(-\frac{1}{6} k R_0^2 \right) - \frac{2}{3} k R_0^3 \quad (24)$$

§ 9. It follows from (7') that the volume of a drop from the top to the horizontal plane passing through B or B' ($\vartheta = \pi - \varepsilon$), in second approximation is given by

$$v = \frac{4}{3} \pi R_0^3 (1 - k R_0^2) \quad (25)$$

With the same degree of approximation this is also the volume of a hanging drop up to the level of the neck; indeed the volume

¹⁾ If x is large with respect to x_2 we have

$$\pm \eta = x_1 \log \frac{2x}{x_2} - \frac{x^2}{2R_0}, \quad (17'')$$

so that the equation to the branch CBE (fig. 3) is

$$y = y_C + \eta_+ = 2R_0 - \frac{1}{3} k R_0^3 + \frac{1}{3} k R_0^3 \log \frac{x^2}{4R_0^2} - \frac{x^2}{2R_0}$$

in agreement with (11') (since $\varepsilon = \frac{x}{R_0}$).

From this the abscissa of the node E ($y_E = y_C$) is found to be

$$x_E^2 = -\frac{2}{3} k R_0^4 \log k R_0^2.$$

between the planes passing through point of inflection and neck is found to contribute a negligible amount to the total.

In connection with this it follows from eq. (2') in fourth approximation:

$$x_B = \sqrt{\frac{2}{3} k R_0^3 (1 - k R_0^2)}, \text{ en } x'_c = \pm k R_0^3 (1 - \frac{2}{3} k R_0^2) \quad , \quad (19')$$

the upper sign corresponding to the upper index.

§ 10. Starting from the points D and D' (fig. 3) the analysis may be further continued in a manner similar to the one used above. Indeed the meridian curve of the complete capillary surface consists approximately of a series of nearly semi-circular arcs connected each time by parts of an unduloid or nodoid¹⁾. The centres of these arcs are situated at the heights $R_0, 3 R_0, 5 R_0$, etc. successively; with each (n^{th}) arc we therefore place the origin in the corresponding (n^{th}) centre and as in § 2 write:

$$x = \rho \sin \vartheta, \quad y = (2n-1) R_0 - \rho \cos \vartheta, \quad \rho = R_0 (1 - \tau) \quad . \quad (26)$$

τ is determined by:

$$\tau'' \sin \vartheta + \tau' \cos \vartheta + 2\tau \sin \vartheta = k R_0^2 (2n-1 - \cos \vartheta) \sin \vartheta, \quad (26')$$

whence it follows, introducing the condition that the arcs and intermediate pieces form a continuous curve:

$$\begin{aligned} \tau = & \left[\frac{1}{8} + \frac{1}{8} (n-1) - \frac{1}{8} + \frac{1}{8} \log 2 + \frac{1}{8} n (n-1) - \sum \frac{4(n-1)}{3} \log (n-1) - \right. \\ & - \frac{2}{3} n (n-1) \log (\pm \frac{1}{8} k R_0^2) \cos \vartheta + \frac{n}{3} \cos \vartheta \log (1 + \cos \vartheta) - \\ & \left. - \frac{2(n-1)}{3} \cos \vartheta \log (1 - \cos \vartheta) \right] k R_0^2, \quad . \quad . \quad . \quad (27) \end{aligned}$$

For the connecting curves equations (17), (22) and $x_s = x_c = \frac{x_B}{R_0}$

are each time satisfied.

The successive arcs and their connecting curves can only be realised in separate parts, for instance between two horizontal plates or between two vertical coaxial cylinders. Not every surface, however, obtained in that way is a part of the surface whose meridian-section was analysed above by approximation. As an instance, if the surface is formed between two cylinders which are moistened by the liquid, the fraction $\frac{(x_c)_{n-1}}{(x_A)_n}$ represents the ratio between the radii of the cylinders and this fraction cannot in the analysis of § 10 assume any arbitrary (small) value, as long as n represents a whole number. Still, putting $2(n-1) = a$ and admitting an arbitrary (positive or

¹⁾ Cf. WINKELMANN, loc. cit., p. 1141, fig. 404.

negative) value for α , the equations (26) and (26') remain valid and

$$\tau = kR_0^2 \left[a + \frac{1}{2} \alpha + b \cos \vartheta + \frac{1}{2} \left(\frac{5}{6} - a \right) \cos \vartheta \log (1 + \cos \vartheta) - \right. \\ \left. - \frac{1}{2} \left(\frac{1}{6} - a \right) \cos \vartheta \log (1 - \cos \vartheta) \right], \quad . \quad . \quad . \quad (28)$$

where a and b are integration-constants. R_0 is still undetermined, as also h , which remains connected with R_0 through the relation

$$kh = \frac{2}{R_0}; \text{ as regards the value of } \alpha, \text{ this may be chosen at will}^1).$$

With small values of ϑ the curve shows a minimum for y or a point of inflexion²⁾ according as $(\frac{5}{6} - a)k > 0$; for a value of ϑ which differs but little from π the curve has a maximum for y , if $(\frac{1}{6} - a)k > 0$ or a point of inflexion, if $(\frac{5}{6} - a)k < 0$.²⁾

§ 12. Here again the meridian-section consists of a series of curves which, however, now extends indefinitely upwards as well as down-

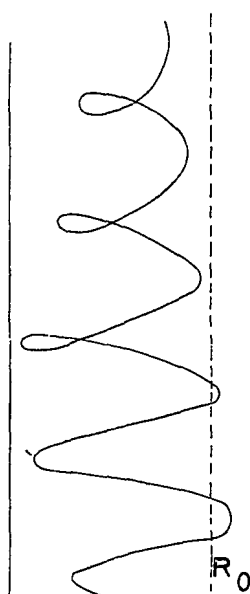


Fig. 4.

wards. For $k > 0$ the higher curves in the series show maxima and minima for y , the lower ones points of inflexion, as represented diagrammatically in fig. 4. For $k < 0$ on the other hand the upper curves have points of inflexion and the lower ones maxima and minima of y , which case is obtained by turning fig. 4 upside down. Putting $\frac{1}{6} - a = \beta$ the successive minima and maxima of x satisfy the relations

$$x_{min.} = \pm \left(\beta + \frac{2n}{3} \right) kR_0^2 \\ x_{max} = R_0 - \left[\frac{1}{2} \alpha - \beta + \frac{2n+1}{6} \right] kR_0^2. \quad (29)$$

At the point where $\beta + \frac{2n}{3}$ changes its sign (smallest value of x_{min}) is the transition between the two kinds of curves. If accidentally $\beta = \frac{2m}{3}$, m being a whole number, the smallest value of x_{min} becomes zero and the case reduces to that of the meridian-sections discussed in § 10.

¹⁾ Supposing for instance the meniscus to be formed between two co-axial cylinders which are moistened by the liquid, the radii of the cylinders being R and r , where r has to be small with respect to R a and R_0 are determined by the conditions $x_C = r$ and $x_A = R$; α and b may still be chosen at will; one might for instance take $\alpha = 0$, while determining b by putting $y_D = 0$.

²⁾ In general therefore in this case the presence of a minimum or maximum for y is not, as in the section 6 sqq, bound to $k > 0$ or the existence of a point of inflexion to $k < 0$.

Physics. — “*On the measurement of surface tensions by means of small drops or bubbles.*” By J. E. VÉRSCHAFFELT. Supplement N°. 42d to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of June 29, 1918).

§ 1. The usual methods for the determination of surface tensions by means of small drops or gas-bubbles, to which properly speaking the method of the capillary rise also belongs, are based on the measurement of the difference of hydrostatic pressure between the two media inside and outside the drop or bubble; indeed the surface-tension is given by the formula

$$\sigma = \frac{1}{2} (\mu_1 - \mu_2) g h R_0, \quad (1)$$

where $\mu_1 - \mu_2$ is the difference of the densities of the two contiguous media, g the acceleration of gravity, R_0 the radius of curvature at the top of the meniscus and h the pressure-difference on the two sides of the surface, measured as a column of the liquid in the surrounding medium. If the drop (or the bubble) is so small, that it may be considered as spherical, we may take for R_0 half of the diameter of the drop (or bubble), or the radius of the capillary tube, in which the liquid ascends, at least if there is no angle of contact; in order, however, that the approximation obtained in that way may be sufficiently close ¹⁾, the radius must be taken so small, that as a rule the relative accuracy of the measurement of the radius remains far behind that which can be reached in the measurement of h , whereas naturally it is desirable to know R_0 and h with the same relative accuracy. In order that this may be possible, it is necessary to make the measurements on drops or bubbles which are not too small, in which case at the same time the necessity arises of a correction on account of the deviation from sphericity. ²⁾

¹⁾ The relative error is of the order $k R_0^2$, where $k = \frac{(\mu_1 - \mu_2) g}{\sigma}$ (cf. eq (2)).

²⁾ R_0 can also be measured directly by an optical method (cf. H. SIEDENTOPF, Diss. Göttingen, 1897); it may also be determined by measurements on photographs (cf. for instance A. FERGUSON, Phil. Mag., (6), 23, (1912) p. 417. A high accuracy is, however, not obtained in that way.

§ 2. Putting $x_A = r$ in eq. (10) of the previous communication (Suppl. N°. 42c) it reduces to

$$R_0 = r + \frac{1}{6}kr^3 - \frac{1}{18}k^2r^5 (3 \log 2 - 2), \quad (2)$$

from which R_0 may be calculated, when r is given and k is known approximately. This value substituted in (1) gives

$$h = \frac{2}{kr} - \frac{1}{3}r + \frac{1}{6}kr^3 (2 \log 2 - 1). \quad (3)$$

or

$$\sigma = \frac{1}{2}(\mu_1 - \mu_2) ghr \left[1 + \frac{1}{3}\frac{r}{h} - \frac{1}{3}\frac{r^2}{h^2} (2 \log 2 - 1) \right]. \quad . . (4)$$

formulae which are already known¹⁾ and by means of which the surface tension can be calculated to a third approximation from the capillary rise h in a tube of radius r , which is completely moistened by the liquid.²⁾

These equations, when proper account is taken of the signs of the various quantities, are applicable in every case, where the width of a drop or bubble can be measured as also the pressure necessary to form it. As an instance, when the liquid does not moist the wall (mercury) the liquid may be forced up by an excess of pressure from a very wide into a narrow communicating tube, until it protrudes from the narrow tube in the form of a drop; h then is the height of the liquid surface in the wide tube above the top of the meniscus on the top of the capillary.³⁾ Similarly when the capillary is moistened by the liquid, the meniscus may be forced down by the pressure of a gas, until a bubble is formed at the bottom of the capillary.⁴⁾

¹⁾ See for instance A. WINKELMANN, Handbuch der Physik, 2e Aufl., I, (2), 1144 and 1159, 1908.

²⁾ For the case, when there is an angle of contact i , the following relation is found by putting $x = r$ and $\varphi = \frac{\pi}{2} - i$ in eq. (9) of the previous communication (Suppl. N°. 42c)

$$\sigma = \frac{1}{2}(\mu_1 - \mu_2) ghr \sec i \left[1 + \frac{1}{3}\frac{r}{h} \sec^3 i (1 - \sin i)^2 (1 + 2 \sin i) + \right. \\ \left. + \frac{1}{3}\frac{r^2}{h^2} \sec^6 i (1 - \sin i)^3 (1 + \sin i + 2 \sin^2 i) + \frac{2}{3}\frac{r^3}{h^3} \sec^2 i \log \frac{1 + \sin i}{2} \right] \quad (5)$$

³⁾ In this case eq. (3) and (4) remain valid without any modification, as both h and R_0 , therefore also r , change sign (see previous comm.). This simple method, which is independent of the angle of contact and which allows the capillary surface being refreshed by removing the drop, does not appear to have been ever applied to mercury.

⁴⁾ Cf. A. WINKELMANN, l.c., p 1162. See also further down in § 9. In this manner, however, it is not the surface tension of the pure liquid in contact with its vapour which is determined, but that of the binary system liquid gas.

§ 3. In dealing with a hanging drop, $\mu_1 - \mu_2$ and h change sign (see Suppl. N^o. 42c) and eq. (4) becomes

$$\sigma = \frac{1}{2} (\mu_2 - \mu_1) g h r \left[1 - \frac{r}{h} - \frac{r^2}{h^2} (2 \log 2 - 1) \right] \quad (4')$$

The practical application of this equation is not so simple, however, as that of eq. (3), as a hanging drop formed at the end of a capillary which communicates with a wide tube is not in stable equilibrium¹⁾. But the equilibrium may be made stable by also taking a narrow tube for the one with which the capillary communicates, say by making the drop hang from a single capillary, as in SENTIS's method²⁾; in that case, however, account must be taken of the curvature of the meniscus in the narrow tube. If h_1 is the distance between the tops of the two menisci, and h_2 the ascension of the liquid in the narrow tube (which can be obtained from a separate measurement), it is evident, that in eq. (4') the substitution:

$$h = h_1 - h_2.$$

has to be made.

§ 4. Let us return to the case of a drop, say a mercury drop, forming on the top of a capillary under the influence of an excess of pressure from the liquid in a very wide communicating tube (section 2). When the mercury by raising the liquid in the wide tube has reached the edge of the capillary, the meniscus protruding above it begins to curve more and more as the liquid gets higher, so that the difference in level h between the two tubes, which had remained constant so far, now increases. Soon the meniscus attains the maximum-curvature and at the same time the difference in level h reaches a maximum.

This maximum occurs at the moment that R_0 has its smallest value³⁾ which happens when R_0 is all but equal to \bar{r} , the radius of the capillary (for simplicity R_0 is here taken as positive). Putting

¹⁾ An imperceptible fall of the level in the wide tube is sufficient to give an appreciable increase to the radius of the hanging drop, through which h becomes larger, while the capillary counter-pressure diminishes; consequently the liquid flows continuous. With a lying drop on the other hand h diminishes and within definite limits the equilibrium is stable (see also §§ 4 and 7).

²⁾ SENTIS, J. d. phys 6 (1887) p 571.

³⁾ Seeing that between h and R_0 the relation $h = \frac{2}{R_0}$ holds (see previous comm. in these proceedings).

$\vartheta = \frac{\pi}{2} + \omega$, where ϑ has the meaning given in § 2 of the previous communication and ω represents an infinitely small angle, equation (9) of the same communication, in view of (see eq. 8 and 8' l.c.)

$$\varphi = \vartheta + \psi = \frac{\pi}{2} + \frac{1}{8} k R_0^2 (2 \log 2 + 1) + \omega,$$

takes the form:

$$r = R_0 - \frac{1}{2} R_0 [\omega + \frac{1}{8} k R_0^2 (2 \log 2 + 1)]^2 - \frac{1}{8} k R_0^3 + \frac{1}{36} k^2 R_0^5 (6 \log 2 - 1). \quad (6)$$

It follows, that the minimum of R_0 is reached for

$$\omega_1 = -\frac{1}{8} k R_0^2 (2 \log 2 + 1), \quad . \quad . \quad . \quad . \quad . \quad (7)$$

therefore for $\varphi = \frac{\pi}{2}$, that is: exactly when $x_A = r$. The surface tension is thus given by the relation (4), when r now represents the radius of the capillary and h the greatest difference in level of the mercury in the wide tube above the capillary; conversely for given r and h the greatest difference in level is given by equation (3).

§ 5. The mercury can still be raised to a higher level in both tubes. The radius of curvature R_0 at the top of the drop then again increases, so that h becomes smaller. All the same the mercury continues to rise in the wide tube, that is: the height $H = h + y$ of the liquid in the wide tube above the top of the capillary (y represents the height of the drop and is therefore here taken with the positive sign) still increases. But this height also soon attains a maximum.

Putting again $\vartheta = \frac{\pi}{2} + \omega$, we have (eq. 4 of previous comm.)

$$H = h + y = \frac{2}{k R_0} + R_0 + R_0 \omega, \quad . \quad . \quad . \quad . \quad (8)$$

from which, joined to the condition $x = \text{const} = r$, it follows that H is a maximum when

$$\omega_2 = \frac{1}{8} k R_0^2 (1 - \log 2), \quad (R_0)_2 = r + \frac{1}{8} k r^3 - \frac{1}{72} k^2 r^5 (12 \log 2 - 17), \quad (9)$$

so that

$$H_m = \frac{2}{k r} + \frac{2}{3} r + \frac{1}{12} k r^3, \quad . \quad . \quad . \quad . \quad (10)$$

whence

$$\sigma = \frac{1}{2} (\mu_1 - \mu_2) g H_m r \left(1 - \frac{2}{3} \frac{r}{H_m} - \frac{1}{6} \frac{r^2}{H_m^2} \right) \quad . \quad . \quad (11)$$

§ 6. To test the use of the method sketched out in sections 4 and 5 a few trials were made with mercury in contact with air. The wide tube was so wide (± 2 cm in radius), that the meniscus could be

considered as flat; the radius of the narrow tube at the top which was sensibly flat was 1.090 mm. Through a rubber tube the wide tube was connected with an adjustable funnel filled with mercury; by slowly raising the funnel the moments are easily marked at which first h and then H attain a maximum¹⁾.

The maximum-values of h and H were found to be to a high degree dependent on the slowness with which the drop was being formed. From these experiments therefore a definite value for the surface tension mercury-air did not follow. As an instance for a drop which had been exposed to the air for a very long time $h_m = 0.490$ (at $t = 17^\circ.3$) was found, which by means of eq. (4) $\mu_1 - \mu_2 = 13.55 \text{ g} = 981$ leads to

$$\sigma = 0,355 (1 + 0,074 - 0,006) = 379,$$

whereas immediately after the formation of a new drop the observation gave $h = 0.592$, whence $\sigma = 454$.

Similarly an experiment where the mercury ran over about 1 minute after the surface being renewed gave $H_m = 0.708$ (at $18^\circ.2 \text{ C.}$) whence (eq. 11)

$$\sigma = 513 (1 - 0,102 - 0,004) = 459,$$

whereas for a drop which did not flow over till after half an hour $H_m = 0,659$, c. e. $\sigma = 423$; after some hours these values had even gone down to $H_m = 0,619$, $\sigma = 393$.²⁾

¹⁾ The maximum of h can be very easily observed by using a micrometer with moveable cross-wire, the fixed horizontal wire I is set on the meniscus in the wide tube, the moveable wire II, also horizontal, on the meniscus in the narrow tube. The funnel is first moved up until the mercury protrudes above the narrow tube as an almost hemi-spherical meniscus: by now raising it very slowly or by adding mercury a drop at the time, so that I and II rise slowly, the distance I—II is seen to increase slowly and attain a greatest value. After that I and II continue to rise, but the distance I—II now diminishes. At the same time the drop above the narrow tube is seen to bulge out more and more, to exceed distinctly the half-sphere and finally fairly suddenly to swell and flow over the edge of the tube; at that moment the level I falls very rapidly, so that H has gone through a maximum.

²⁾ This diminution of the surface tension of mercury which is exposed to the air was first observed by QUINCKE (Pogg. Ann. 1 (1858) p. 105). Similarly GRÜNMACHER (Ann. d. Phys., (4) 28 (1909) p. 247; method of capillary waves) found a much higher value of σ for fresh surfaces ($\sigma = 491,2$ at about 18°) than for surfaces which had been exposed to the air for half an hour ($\sigma = 405,0$). See also WINKELMANN, loc. cit., p. 1168.

Volatile vapours in the air also appear to lower the surface tension of mercury very considerably; it was found in the experiments of § 6 that it was sufficient to bring a piece of blotting paper soaked in benzene or alcohol near a practically hemispherical drop in order to make it flow over at once.

The usefulness of the method is sufficiently demonstrated by these experiments. Moreover they can easily be so arranged, that the surface tension is determined in vacuo, in which case probably a gradual change of σ with the time would not show itself¹⁾.

§ 7. Instead of forming the mercury drop on the top of a capillary it is possible to make it form at the bottom. This can be done by closing a wide tube at the bottom by a plate with a small circular hole; mercury being poured in, a small hanging drop is formed at the orifice, which gives way at a definite maximum height of the mercury in the tube, after which the mercury runs out. From the observed maximum height and the radius of the opening the surface tension of the mercury may be derived.

If H represents the height of the liquid in the wide tube above the opening, $H = h' - y$, h' being the height of the mercury in the wide tube above the bottom of the hanging drop and y again representing the height of the drop. In this case k is negative (see Suppl. N°. 42c), hence $h = \frac{2}{kR_0} = -h'$ and $H = -(h + y)$. The condition for the maximum of H at constant $x = r$ then leads to the same equations as in § 5, except that k and H have to receive the negative sign.

It follows in the first place that ω_1 (eq. 9) is negative; that is: the drop begins to fall before φ has reached the value $\frac{\pi}{2}$ (see § 3), so that h in this case cannot reach its maximum value (§ 4). In the second place according to eq. (11), H_m being reckoned as positive,

$$\sigma = \frac{1}{2}(\mu - \mu_1)g H_m r \left(1 + \frac{2}{3} \frac{r}{H_m} - \frac{1}{6} \frac{r^2}{H_m^2} \right) \quad (11')$$

§ 8. By this method also a determination was made of σ for mercury. For this purpose a tube of 1.5 cm radius was closed at the bottom by a plate, through a hole of which a short piece of glass capillary ($r = 0.522$ mm) had been stuck. When mercury was put into the tube a drop at a time, a drop was formed at the lower end of the capillary which gave way before the hemisphere had been reached.

Here again the value of H_m was very strongly dependent on the time elapsing while the drop was being formed; the greatest value

¹⁾ In a vacuum FÜRTH (Wien. Sitz.-Ber. [2a], 126 (1917) p. 329) found $\sigma = 440$ to 445 at 18°C; in this no trace of a change of σ with the time was observed.

observed was $H_m = 1.230$ which gives:

$$\sigma = 427(1 + 0.028 - 0.003) = 438$$

When the tube was filled to a smaller height and then left to itself, the drop could be seen to bulge out more and more and finally give way in consequence of the diminution of σ .

§ 9. When in a capillary tube, in which a liquid ascends, pressure is exerted by means of a compressed gas, so that the meniscus is forced down, until a gas bubble is formed at the bottom of the capillary, the bubble is found to escape at a definite maximum value of the difference between the gas-pressure and the hydrostatic pressure at the bottom of the capillary. From this maximum of the pressure-difference the surface-tension of the liquid (in contact with the gas) may be derived¹).

The phenomenon is of entirely the same nature as the one described in § 5 and the theory may be developed in the same manner²). If H represents the said difference of pressure, whereas $h = \frac{2}{kR_0}$ again represents the capillary pressure at the lowest point of the meniscus and y the height of the bubble, then, as in § 5, $H = h + y$ and, as k and R are also positive, the same equations are obtained in this case as in section 5³).

In this case h also obtains a maximum-value, which might also be used as the basis for a determination of the surface-tension; in that case eq. (4) would again apply. But the measurement of H is simpler than that of h and therefore preferable from a practical point of view.

§ 10. Several observers have derived surface tensions from measure-

¹) The first to use this method was SIMON (Ann. d. ch. et d. phys. (3), 32, 5, 1851), who assumed without sufficient proof, that the maximum pressure-difference is determined by the capillary rise, which is only correct for very narrow tubes. SIMON's method was used by several other experimenters later on (see WINKELMANN, l.c., p. 1162).

²) See also: M. CANTOR, Ann. d. Phys. (3), 47 (1892) p. 413; R. FEUSTEL, Ann. d. Phys. (4), 16 (1905) p. 61; A. FERGUSON, Phil. Mag., 28, 1914 p. 135, and E. SCHRÖDINGER, Ann. d. Phys., (4), 46 (1915) p. 413.

³) In accordance with what was found by SCHRÖDINGER, (l.c.). It is not astonishing that CANTOR, FEUSTEL and FERGUSON find an incorrect expression for the second correction-term in these equations, seeing that — apart from errors of calculation by CANTOR and FERGUSON — the authors in their reductions assume a spherical shape for the drop, although the second correction-term is actually determined by the deviation from the spherical shape.

ments on drops without pressure-measurements.¹⁾ With small drops the surface tension is then derived from the deviation from the spherical shape; in that case principally equations (10) and (10'') of the previous communication (or (2) of the present paper) are to be applied, which lead to the relations:

$$\sigma = \frac{1}{8} \frac{r^3}{R_0 - r} (\mu_1 - \mu_2) g \left[1 - 2 \frac{R_0 - r}{r} (3 \log 2 - 2) \right], \quad . \quad . \quad (12)$$

$$\sigma = \frac{1}{8} (\mu_1 - \mu_2) g \frac{r^3}{r - y} \log 2, \quad . \quad . \quad . \quad (13)$$

r being the largest radius of the drop (its half breadth) and y the distance from the top to the plane of the section with radius r .

Seeing that here the determination of σ depends on the exact knowledge of the numerical value of terms which only served as correction-terms in the method of the pressure-measurement, this method cannot but give much less accurate results than the previous one. But its use seems indicated for liquids which can only be obtained in very small quantities.

§ 11. A third manner of determining surface-tensions by mean of small drops consists in measuring the weight of small falling drops.

It follows from the equations (25) and (19') of the previous communication, that the volume of a small constricted hanging drop is.

$$v = \frac{2\pi r' \sigma}{(\mu_2 - \mu_1) g} \left(1 - \frac{r'}{R_0} \right), \quad . \quad . \quad . \quad (14)$$

r' being the radius of the circular neck. When the drop is made to fall from a very thin rod — this would be the method, if the liquid moistens the wall — or from a very narrow tube — in the opposite case — ²⁾ r' is not equal to the radius r of the rod or tube, but the difference is very small. Indeed the drop does not fall at the moment, when $r = r'$; before it falls away the drop

¹⁾ See WINKELMANN, loc. cit., p. 1160. See also J. E. VERSCHAFFELT and CH. NICAISE, Bull. Acad. de Belg., 1912, p. 192.

²⁾ Properly speaking equation (14) only holds for a drop hanging in equilibrium and not for a drop forming from a tube while flowing (cf. WINKELMANN loc. cit. p. 1162). It appears from § 7. that a constricted drop cannot hang in equilibrium from the opening of a tube, if the drop is in free connection with liquid in a wide tube. A strongly constricted drop is only possible, if the connection with the free surface in the wide tube is broken, for instance by the interposition of a tap; by opening the tap very little the drop may be made to form very slowly, until it falls: at any moment it can then be looked upon as in equilibrium and its further deformation may be prevented by closing the tap. Similarly a strongly constricted drop may form at the end of a long capillary, through which the liquid flows very slowly (cf. also § 3).

contracts a little more, the volume thereby increasing slightly, until it reaches a maximum. For according to eq. (17) of the previous communication, when $x=r$ differs very little from $x_2=r'$, the volume contained between the circles of radii r and r' is equal to $\pi r'^2 \sqrt{2r'(r-r')}$, so that the volume of the drop up to the plane of suspension is equal to

$$v' = \frac{2\pi r'\sigma}{(\mu_2 - \mu_1)g} + \dots + \pi r'^2 \sqrt{2r'(r-r')},$$

and this is a maximum, when

$$r' = r(1 - \frac{1}{8} k^2 r^4) \dots \dots \dots (15)$$

The maximum-volume will still be represented with sufficient accuracy by eq. (14), if r' is replaced by r .

When the maximum is reached, the smallest further supply of liquid must necessarily make the drop break off. If G is the weight of the drop ¹⁾, it follows from eq. (14) with r instead of r' that

$$\sigma = \frac{G}{2\pi r} \left(1 + \frac{r}{R_0}\right) = \frac{G}{2\pi r} \left(1 + \sqrt{-\frac{2}{3}kr^2}\right) = \frac{G}{2\pi r} \left(1 + \sqrt{\frac{3}{4} \frac{\pi r^2}{v}}\right)^2 \quad (16)$$

This is therefore the formula which in the case of a very small drop has to replace the simpler expression used by QUINCKE ²⁾.

¹⁾ $G = (\mu_2 - \mu_1)gv$; G is therefore the apparent weight, not reduced to a vacuum.

²⁾ It is perhaps not superfluous to point out, that the expression (16) may be deduced in the following simple manner. The molecular forces (surface tension) along the circular neck of the drop make equilibrium with its weight and the hydrostatic pressure on the plane of the neck; hence according to (3') of the previous communication

$$2\pi r\sigma = G + \frac{2\sigma}{R_0} \cdot \pi r^2,$$

where the term $-\pi r^2(\mu_2 - \mu_1)gy$ has been neglected. This equation agrees with the relation which is found in calculating the capillary rise by the so-called weight-method (see previous comm.); in a certain sense, however, it must be considered as its opposite: in both cases the surface tension balances a hydrostatic pressure and a weight, but whereas in the case of the capillary rise the weight is introduced as a correction, here on the other hand the same is true for the hydrostatic pressure.

Seeing that for mercury $k=30$ about and for water $k=13$, r must not be greater than 0,07 to 0,11 mm. in order that the correction-term $\frac{r}{R_0}$ be 0,1. In order that this term may be still further reduced, as is necessary for the accuracy of the method, in view of the further unknown terms which have been neglected, much narrower capillaries would have to be used and this would diminish the accuracy of the measurement of r . This shows that the method of the weighing of falling drops is not a very suitable one for the determination of surface tensions.

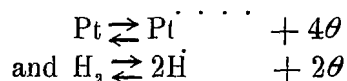
³⁾ Pogg. Ann., 134, (1868) p. 365. See also WINKELMANN, loc. cit., p. 1147 and 1161, and TH. LOHNSTEIN, Ann. d. Phys., 20, (1906) p. 238.

Chemistry. "*The Phenomenon Electrical Supertension*". By Prof. A. SMITS. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of June 29, 1918).

It has already been pointed out in a previous communication¹⁾ that the metals which furnish the so-called unattackable electrodes, differ from the other metals in this that they are ideally inert, so that the potential difference of such a metal electrode with respect to an electrolyte is governed by the prevailing electron-concentration in this electrolyte. Let us now suppose that a smooth platinum-electrode immersed in an aqueous solution of hydrochloric acid, is made cathode, it is then easy to see what will happen.

The two equilibria that are to be considered here, are:

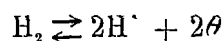


the former of which is entirely determined by the electron concentration of the hydrogen equilibrium.

When we immerse a platinum electrode in a solution of hydrochloric acid, the platinum ion-concentration in the electrolyte will be imperceptibly small. Yet we can speak of a platinum equilibrium in the electrolyte, which, as was already remarked, is entirely determined by the electron-concentration of the hydrogen equilibrium.

In virtue of this it may be said that platinum is a hydrogen-electrode from the very first, but so long as the hydrogen has not yet appeared as second phase, the platinum will be a hydrogen-electrode, corresponding with a hydrogen pressure smaller than the pressure under which the electrolyte is.

When we make the platinum cathode, there are electrons added to it, and a consequence of this will be that hydrogen-ions from the electrolyte are deposited on the metal surface, and are dissolved in it, from which it appears that the hydrogen is of course not immediately present as a new phase. When the internal equilibrium:



sets in very rapidly on the metal surface, this internal equilibrium would already have been established in the metal surface in spite

¹⁾ These Proc.

of the supply of electrons. But above a certain current density, which evidently lies very low, this is no longer the case, and the metal-surface will contain more hydrogen ions and electrons than corresponds with the internal equilibrium. In consequence of this the potential difference, as appears from the formula

$$\Delta = -\frac{RT}{F} \ln \frac{K_H (H_s)}{(H_L)}$$

will be more negative than when internal equilibrium had been established. Let us now suppose that the current density is continually increased, the potential difference becoming continually more negative, then at a given moment super-saturation of hydrogen will set in in the metal surface, and at a certain degree of super-saturation hydrogen will be generated as second phase. When the current density is kept constant, the potential difference can now diminish a little, but on increase of the current density the potential difference will now also increase further, because, even when hydrogen generation takes place, this process can yet be accompanied with an increase of the concentration of the hydrogen ions in the surface of the electrode, and besides because the formation of the gas bubbles through the diminution of the surface of contact metal-electrolyte, causes the current density to increase very greatly. As at the moment that the hydrogen begins to separate as second phase, the metal surface contains more hydrogen ions and electrons than corresponds with the internal equilibrium, the potential difference at this moment will be more strongly negative than corresponds with the state of internal equilibrium, which is in accordance with the above mentioned formula. This internal equilibrium sets in when without passage of a current, hydrogen of a pressure of 1 atmosphere is conducted round the platinized platinum electrode. The difference between this equilibrium potential of the hydrogen and the potential difference, at which during the passage of the current, the hydrogen begins to separate as second phase on the unattackable electrode for the first time, is called "*supertension*". It is clear that in the light of the newer views this phenomenon is not distinguished from the phenomenon of the cathodic polarization in any respect. The supertension of hydrogen is, accordingly, nothing but a consequence of the retardation in the establishment of the internal equilibrium during its electrolytic separation, and the supertension in case of all the other gas-generations can be explained in exactly the same way.

It has been found that the amount of the supertension for the same current density is still dependent on the nature of the metal

electrode; nor is this strange in the light of these considerations, for the different metal electrodes will exert a different catalytic action on the establishment of the internal hydrogen equilibrium. But not only the nature of the electrode, but also the condition in which a certain electrode is, will be of influence on the supertension. A polished platinum electrode or a platinized platinum electrode do not give the same result; in the latter case the supertension is practically zero, which can be explained by the fact that the much larger surface of the catalyst causes a rapid establishment of the internal equilibrium, to which is added that the actual current density is much smaller than is supposed, exactly in consequence of this larger surface. Finally also the electrolyte can exert influence on the setting in of the internal equilibrium, and thus we see that the polarization phenomena at gas-generations can be surveyed and accounted for with all other electrolytic polarization phenomena from the same point of view.

Considerations in the light of the theory of phases. A so-called unattackable metal as hydrogen electrode.

In my preceding communication "On the Electromotive Behaviour of Metals" ¹⁾ I have already treated the unattackable electrodes and their efficiency as gas-electrodes. In this I have demonstrated that the result of these considerations can be given in a Δ, x -fig. in a lucid way.

That a platinum electrode, immersed in an acid solution, and surrounded by hydrogen of one atmosphere indicates the hydrogen potential in correspondence with this pressure, is elucidated by the adjoined fig. 1, which holds e.g. for atmospheric pressure and constant total-ion-concentration.

Though the equilibrium-normal-potential of platinum is not known to us in consequence of its great inertia, yet it may be said with certainty that this potential of the equilibrium, if it could be measured, would be very strongly positive with respect to the hydrogen. The concentration of the electrolyte c would therefore practically quite coincide with the axis for the hydrogen. With a view to lucidity I have however purposely not made the point c coincide with the H_2 -axis in this schematic drawing.

Let us now imagine that a platinum electrode is immersed in

¹⁾ l. c.

an electrolyte of the concentration x_1 , and that the electrode is surrounded with hydrogen of a pressure of 1 atm., then our conclusion from the preceding communication that namely the platinum equilibrium in the liquid is governed by the electron concentration of the hydrogen equilibrium in the electrolyte, or in other words that

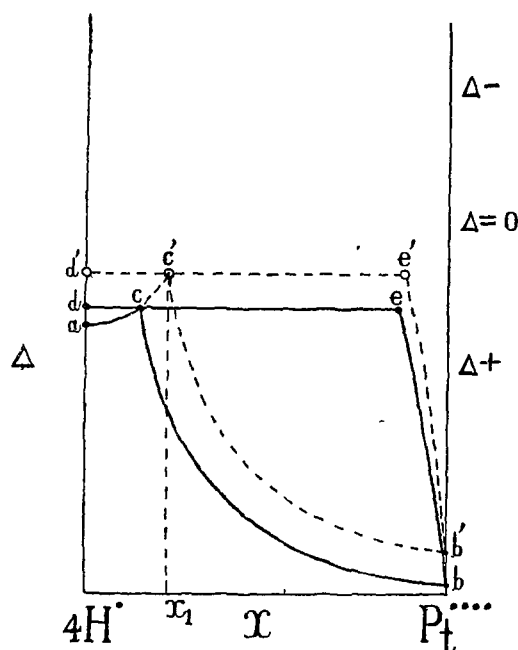


Fig. 1.

the platinum electrode becomes hydrogen electrode, has the following meaning:

It appears from the Δ, x -fig. 1 that the potential difference of the hydrogen with respect to the electrolyte x , is indicated by point c' , lying on the metastable prolongation of ac .

Now it follows, however, from the considerations given here that platinum will present the same potential difference as hydrogen in the experiment mentioned here, and that the electrolyte will, therefore, not only be electromotively in equilibrium with hydrogen, but also with platinum. This means therefore that c' does not only lie on the prolongation of ac , but at the same time on a line that has taken the place of bc . The line bc referred to the electrolytes which coexist electromotively with platinum in internal equilibrium, whereas we now have to do with a curve that indicates the electrolytes that can coexist with a state of platinum disturbed in a base direction; hence this curve lies above bc , and is here indicated by $b'c'$.

The potential difference, which we therefore measure at the platinum electrode in the case supposed here, is the potential difference for the three-phase equilibrium $d'c'e'$, in which a' represents the hydrogen phase, c' the electrolyte, and e' the hydrogen-containing platinum phase. It is clear that in this binary figure it is in fact impossible to indicate the composition of the platinum electrode as the electrode contains atoms and ions of platinum and hydrogen as well as electrons. The composition of the electrode is in consequence of this indicated in platinum and hydrogen in total.

As was already said c lies practically on the hydrogen axis, and as in the case that an attackable electrode is used as hydrogen electrode, the unattackable electrode is immersed in an electrolyte which is practically free from the ions of the electrode material, the concentration x_1 lies likewise entirely on the hydrogen side, so that like c also the point c' will practically coincide with a , i.e. the different unattackable electrodes, applied as hydrogen electrode, will practically present the same potential difference under the same circumstances.

The Supertension Elucidated by Means of the Δ, x -Fig.

When we immerse a smooth platinum electrode in a large quantity of an electrolyte of the concentration x_1 , and when we then make it cathode, fig. 2 gives the successive states. Before the platinum electrode is made cathode, we have electromotive equilibrium between the electrolyte m and the disturbed hydrogen-containing platinum phase n . As soon as the platinum becomes cathode, platinum- and hydrogen ions are deposited on the metal surface, and as the establishment of the equilibrium in the metal surface cannot keep pace with the ion-separation, we get a platinum surface that is still more greatly disturbed, in which there are more platinum and more hydrogen ions and also more electrons present than corresponds with the state of equilibrium. Hence a moment after the passage of the current the point n' indicates the potential difference and the composition of the disturbed, hydrogen-containing platinum electrode, so that now m' and n' represent the coexisting phases.

With increasing density of the current the electromotive two-phase equilibrium moves continually upwards in our Δ, x -figure, and it might be thought that the hydrogen can be separated for the first time *as phase* at the very moment that the line indicating the electrolytes that can coexist with a platinum electrode of definite

disturbance, passes through the point c'' , or in other words at the moment that the disturbance of the platinum electrode has increased to such an extent that the potential difference is indicated by a horizontal line passing through c'' .

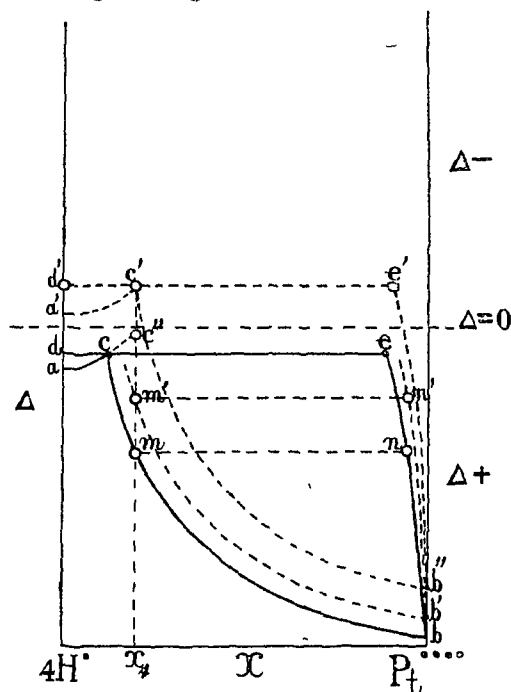


Fig. 2.

This would, however, be the case when the hydrogen could have assumed internal equilibrium in the metal surface, and when there was, therefore, no supertension. As was already said the supertension is just to be explained by this that also the establishment of the internal equilibrium of the hydrogen cannot keep pace with the ion-separation. Hence the hydrogen appears as second phase for the first time not when the potential difference of the metal phase has risen to c'' , but to a higher point, e.g. c' . In correspondence with the concentration of the electrolyte, the curves $a'c'$ and $b''c'$ intersect in this point, which curves refer to the electrolytes which can coexist with a disturbed hydrogen phase, resp. platinum phase.

The hydrogen phase d' , which therefore is generated, is a disturbed hydrogen phase, as it contains more hydrogen-ions and electrons than corresponds with the state of internal equilibrium.

The supertension can now directly be read from the figure; it is equal to the distance $c'c''$.

Now it should be borne in mind that the point c practically coincides with the hydrogen axis, and that when a platinum elec-

trode is immersed in an aqueous solution of an acid, the concentration x_1 practically coincides with the hydrogen point, and consequently the point of intersection c' will likewise practically lie on the hydrogen axis.

It is clear that the considerations given here are general, and will, therefore, also apply to the supertension of other gases.

As was demonstrated there is no essential difference between the phenomenon of supertension and that of polarization. The former is only a little more complicated in so far that here also an unattackable electrode has been inserted into the system.

When, however, we consider the phenomenon of supertension at non-unattackable electrodes, every difference with the ordinary phenomenon of polarization has disappeared.

Amsterdam,
June 18, 1918.

*General and Anorganic-Chemical Laboratory
of the University.*

Chemistry. — "*On the Periodic Passivity of Iron, II*". By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of June 29, 1918).

Periodic passivity in experiments with sealed-in iron electrodes.

In a previous communication ¹⁾ on this subject we have shown how we have succeeded in calling forth the phenomenon of periodic passivity on anodic polarisation of iron in a solution of 0,473 gr. mol Fe SO_4 + 0,023 gr. mol Fe Cl_2 per litre. In these experiments we made use of an iron electrode 0.3 cm. long with an area of $\pm 0.3 \text{ cm}^2$, which was sealed into the short leg of a U-shaped tube by means of shellac. The considerations that led us to these investigations were the following. During the anodic solution of iron in a solution of Fe SO_4 , the internal equilibrium in the metal surface above a certain density of current, can be disturbed so greatly that passivity appears. When into the solution Cl, Br., or I-ions are introduced in a sufficient concentration, which need, however, be only exceedingly small, activation of the iron suddenly makes its appearance. It follows from this that for a definite density of current, given by the velocity of solution of the iron, it must be possible to find a halogen-ionconcentration, for which at a definite moment the chance that the iron remains passive, is equally great as the chance that it becomes active.

When at this moment the density of current is slightly diminished, the transition passive-active is sure to take place.

The iron anode in the passive state will dissolve only exceedingly little, the iron, which has now become active, will, however, go very greatly into solution.

In consequence of this the contact of the halogen-ions with the iron will diminish, and as the iron is now almost entirely withdrawn from the catalytic influence of the halogen-ions, it can again pass into the passive state.

Since, however, as has been said, the passive iron dissolves very little, and the processes which now take place at the anode consist

¹⁾ These Proc.

of the discharge of the SO_4^{--} -ions with the subsequent O_2 -generation, and further of a concentration increase of the halogen-ions, activation will again make its appearance through this latter process at a given moment etc.

This surmise was perfectly confirmed, and using Dr. MOLL's excellent galvanometer, we photographed some exceedingly regular periodic curves, the maxima and minima of which differed 1.74 Volt in situation. These graphs were, however, still incomplete in so far that the lines of time still failed.

In our further researches we made use of a photographic registration arrangement with time-signal-apparatus manufactured at this laboratory, so that also the time-lines are visible on the new photos, and accordingly a better idea of the regularity of the phenomenon can be formed.

We intend to answer several other questions by means of this arrangement, but before proceeding to do so we will first give a photographic representation of the phenomenon of the periodic passivity, under about the same circumstances as before, but now with registration of the time.

This photograph is given in Fig. 1. The potential difference again ranges here from about $-0,3$ Volt with respect to the 1 norm. calomel electrode in the active state, to about $+1,4$ Volt, in the passive state, the current density retrogressing from 33 m.Amp. to 28 m.Amp. per cm^2 . Since the time-lines, which are at a distance of 3,3 seconds from each other, are now also drawn, the regularity of the phenomenon can be much better observed than before. The maxima lie 6,15 seconds apart. Fig 1 shows further that the iron was only a short time active, and comparatively long passive. The electrode was sealed in as before, and 1,5 cm. long, and the siphon of the auxiliary electrode was halfway of the height of the electrode. The solution contained 0,72 gr. mol. FeSO_4 and $\pm 0,014$ gr. mol. FeCl_2 per litre solution.

The content of FeCl_2 was, therefore, much smaller than before, hence the periodicity appeared here already at a smaller current density. Fig. 2 refers to an experiment with the same electrode, but taken with a slightly smaller current density, viz. 30—25 m.Amp. As is very apparent from this photograph, this has caused the periods to become longer, and the time during which the iron was in active state to become about equally long as the time in which the iron was passive.

It is remarkable that when we endeavour to proceed in the same direction, and try to make the active state last still longer

by diminishing the current density still more, this can only be maintained for a short time, and a state soon sets in again as reproduced here.

*Periodic passivity in experiments with iron electrodes
that were not sealed in.*

The following experiment was made with an electrode that was not sealed in, but in which an iron electrode was simply immersed 1.5 cm. deep into the electrolyte, the siphon of the auxiliary electrode being placed quite at the bottom against the iron electrode. In this case there was always an activating influence, starting from the iron at the height of the liquid level, but in preliminary experiments we had already found that this activating influence did not, however, prevent the iron at the bottom of the electrode, which was 1.5 cm. long, from exhibiting pretty regular periodic passivity.

Fig. 3 shows the result obtained in this experiment. The phenomenon is, indeed, not quite so regular as with the sealed-in electrodes, but the difference is not great.

Periodic passivity at different heights under the liquid level.

We will now examine what is the behaviour of a non-sealed electrode at different heights under the liquid level.

For this purpose experiments were made with an electrode which was immersed much deeper, viz. more than 5 cm. under the liquid surface. When the auxiliary electrode was again placed quite at the bottom, a pretty regular periodicity was observed, just as in case of less deep immersion; this is shown by Fig. 4. When the auxiliary electrode was placed 1.5 cm. above the lower end against the iron electrode, the activating influence exerted from above, was already very clearly noticeable. Thus Fig. 4a shows that though the phenomenon is still regular, the character of the curve has been greatly modified. The periods are much shorter and the passive state lasts very short, and what is very remarkable, now a longer duration of the activity than of the passivity can be maintained.

In the following experiment we have placed the auxiliary electrode halfway up the immersed part, hence ± 2.5 cm. from the bottom, and under these circumstances still greater modifications were found, consisting in this that the iron did not always become equally strongly active, and that regularly two less active states were followed by a more active one, or that alternately a more active and a less active state followed, as is clearly shown by Fig.



Fig. 1. Sealed-in iron electrode 1.5 cm. long, of a diameter of 3 mm. Solution contains per Liter 0.72 gr. mol. $\text{FeSO}_4 \pm 0.014$ gr. mol. FeCl_2 . Potential measured halfway the height. Current density 28—33 milli-ampère/cm². 1 period 6.15 seconds. Difference of the extreme values ± 1.7 Volt.



Fig. 2. Electrode, solution and arrangement siphon for potential measurement as in experiment in fig. 1. Current density 25—30 milli-ampère/cm². 1 period 7.8 seconds.



Fig. 3. Electrode 1.4 cm. long, of a diameter of 3 mm., not sealed in, solution as in the experiment in fig. 1. Potential measured at the bottom of the electrode. Current density 32—36 milli-ampère/cm². 1 period 5.25 sec.



Fig. 4. Electrode 5.1 cm. long, of a diameter of 3 mm., not sealed in. Solution as in the experiment in fig. 1. Potential measured 1 mm. from the bottom. Current density 24—39 milli-ampère/cm². 1 period ± 5.1 seconds.



Fig. 4a. Iron electrode 5.3 cm. long of a diameter of 3 mm. not sealed in. Solution as in the experiment in fig. 1. Potential measured 1.5 cm. from the bottom. Current density 38—43 milli-ampère/cm². 1 period 2.7 seconds.



Fig. 5. Iron electrode 5.1 cm. long of a diam. of 3 mm. not sealed in. Potential measured halfway the height. Current density 30—34 milli-ampère/cm². 1 period 2.2 seconds.



Fig. 5a. Electrode, solution and arrangement siphon for potential measurement as in fig. 5. Current density 28—32 milli-ampère/cm².



Fig. 6. Electrode and solution as in fig. 5. Potential measured 1 mm. under the liquid level. Current density 47—53.5 milli-ampère/cm². 1 period 3.65 seconds.



Fig. 7. Electrode ± 60 cm. long of a diameter of 3 mm. electrode spirally wound in 5 windings. Potential measured at the second winding from the top. Strength of the current regularly periodical at ± 0.5 ampère.

5 and 5a. The next figure 6 refers to the phenomenon that occurs when the auxiliary electrode is placed only 1 mm. under the liquid level against the iron electrode, and from this we see how greatly the activating influence issuing from the iron at the level of the liquid surface, disturbs the periodicity; the regularity now consists only in this that the most active state recurs at pretty regular times.

As might be expected the strength of the polarising current was perfectly regularly periodic.

Influence of the area of the surface on the periodic passivity.

In conclusion we have examined what is the influence of an enlargement of the immersed surface. For this purpose we have made an experiment with a spiral, of which 5 windings, with a joint length of 60 cm. were immersed into the electrolyte. The cathode was placed inside the windings, the auxiliary electrode being placed against the second winding from above. While the strength of the current was again regularly periodic, the potential difference exhibited very irregular oscillations, as Fig. 7 clearly shows. The irregularity was such that even the most active state did not recur regularly, and the whole curve, therefore, shows the periodicity under the influence of great disturbances. Hence it could be clearly perceived when observing the iron electrode, that this was never passive resp active throughout the whole area at the same moment, but that different parts were activated at different times.

This curve is a very fine demonstration of the fact observed by us already before that a piece of iron can be passivated with the more difficulty as the surface is greater.

Amsterdam,
June 27, 1918.

General and Anorg. Chemical
Laboratory of the University.

Chemistry. — "*On the System Iron-Oxygen*". By Prof. A. SMITS
and J. M. BIJVOET. (Communicated by Prof. S. HOOGWERFF).

(Communicated in the meeting of June 29, 1918).

The equilibria to which the reactions between iron-oxides and reducing gases as carbon oxide and hydrogen give rise, have already repeatedly been a subject of a scientific research.

Thus of the gas phase of the three-phase equilibria $\text{FeO} + \text{Fe} + \text{G}$ and $\text{Fe}_3\text{O}_4 + \text{FeO} + \text{G}$ the ratio $\frac{(\text{CO})}{(\text{CO}_2)}$ resp. $\frac{(\text{H}_2)}{(\text{H}_2\text{O})}$ was studied ¹⁾.

Three-phase systems of three components were studied, i.e. systems that were monovariant at constant pressure. In this there was, however, no need to keep the pressure constant, because the above-mentioned relations are independent of this. As result the researches with CO as reducing gas yielded two equilibrium curves, which may be called three-phase curves for the homogeneous equilibrium in the gas phase which coexists with two solid phases, namely one for $\text{FeO} + \text{Fe} + \text{G}$, and another for $\text{Fe}_3\text{O}_4 + \text{FeO} + \text{G}$, of which SCHEFFER ²⁾ showed that they had to intersect in virtue of the heat-effect of the conversions.

Researches with H_2 as substance of reduction did not only give the situation of the three-phase line for $\text{Fe} + \text{FeO} + \text{G}$, but also that for $\text{Fe} + \text{Fe}_3\text{O}_4 + \text{G}$. The latter was made probable by REINDERS, who also computed the situation of the three-phase line for $\text{Fe}_3\text{O}_4 + \text{FeO} + \text{G}$ in this system from the corresponding line for the reduction with CO by the aid of the water-gas equilibrium. When we trace the three-phase curves for $\text{Fe}_3\text{O}_4 + \text{FeO} + \text{G}$ and for $\text{FeO} + \text{Fe} + \text{G}$ for the case $\text{G} = \text{CO} + \text{CO}_2$, we get the following figure when $\log K$ is drawn as function of T , in which figure a third three-phase line for $\text{Fe} + \text{Fe}_3\text{O}_4 + \text{G}$ must start from the point of intersection, which is here a quadruple point as SCHEFFER has noticed.

¹⁾ A survey of the literature of these researches has been given in REINDERS' paper on: the equilibria of iron-oxide with hydrogen and water vapour. Chem-Weekblad 15, 180 (1918).

²⁾ These Proc. Vol. XIX, p. 630.

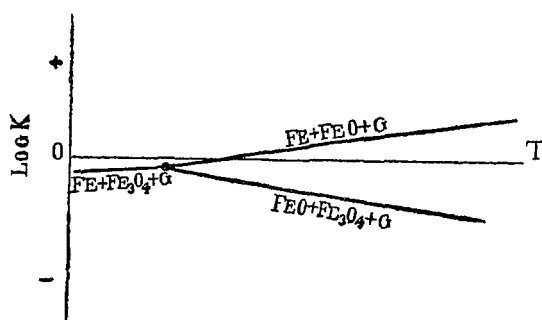


Fig. 1.

On the mixture of the solid phases Fe_2O_3 and Fe_3O_4 .

Now the question presents itself whether there exists also a three-phase line for $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{G}$ ¹⁾.

SOSMAN and HOSTETTER²⁾ think that they have to derive from their determinations about the tension of dissociation and the diffraction of light of mixtures $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$ that the oxides Fe_2O_3 and Fe_3O_4 in the solid state are miscible if not in all proportions, yet very near the concentration Fe_3O_4 . If there really existed a continuous mixed crystal series here, there would not appear a three-phase curve for $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{G}$, and the figure discussed here would be complete.

It is, however, the question whether on the ground of SOSMAN and HOSTETTER's researches we may conclude to a continuous mixed crystal series. When we draw up a p, x -section of the system oxygen-iron corresponding to the temperature 1100° , on the assumption that Fe_2O_3 and Fe_3O_4 are only miscible to a limited degree in the solid state, we arrive at the schematic representation drawn in fig. 2.

In this p, x -section, in which it is assumed that the oxides present a certain mixture in the solid state, the line df represents the mixed crystals that are rich in Fe_2O_3 , and which coexist with the vapours be , the line gh referring to mixed crystals rich in Fe_3O_4 , which can coexist with the vapours eh .

A point on the line df , here p , corresponds with the concentration Fe_2O_3 , and thus a point of the line gh , viz. q , corresponds with concentration Fe_3O_4 .

It follows immediately from this what curve we must get, when

¹⁾ These Proc. 19, 175 (1916) REINDERS has supposed the existence of such an equilibrium but the results of the experiments of SOSMAN and HOSTETTER, were unacquainted at that time.

²⁾ Journal Amer. chem Soc. 38, 837 (1916).

we start from Fe_2O_3 , and every time take away a quantity of the

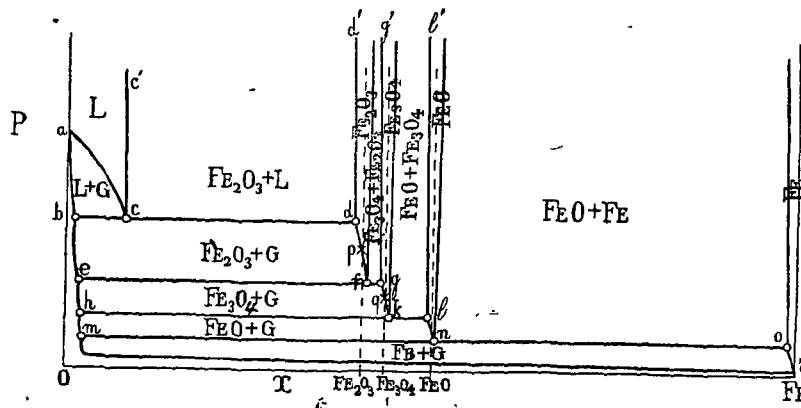


Fig. 2.

vapour phase at the constant temperature of e.g. 1100° . The total concentration will then change in the direction from Fe_2O_3 to Fe_3O_4 , and in this the pressure will also be subjected to a change.

First the pressure will gradually descend from p to f . During this decrease of pressure two phases coexist, viz. mixed crystals rich in Fe_2O_3 and vapours consisting almost exclusively of oxygen. When the pressure has fallen to that of the three-phase equilibrium efg , a mixed crystal phase g rich in Fe_3O_4 will be deposited by the side of the mixed crystal phase f rich in Fe_2O_3 , and a three-phase system arises of which the phase rule demands that the pressure remains constant in case of equilibrium. On continued withdrawal of a part of the gas phase, during which the total concentration continually moves to the right, the pressure therefore remains constant until the last trace of the mixed crystal phase rich in Fe_2O_3 has entirely disappeared. At this moment only the vapour and the mixed crystal phase g rich in Fe_3O_4 coexist, and on further withdrawal of the gas phase the pressure will again descend regularly, in which the solid phase moves downward along gk .

When we now draw the vapour tension as function of the total concentration, theory predicts that on partial mixing of the two oxides Fe_2O_3 and Fe_3O_4 in the solid state, a broken line as is schematically represented in fig. 3, will be found, the middle part of which runs horizontally.

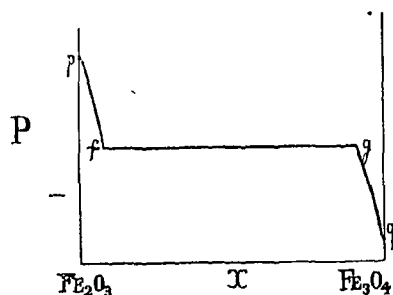


Fig. 3.

This is the theoretical curve, and now it is directly to be seen,

in what the experimentally determined curve will differ from it.

In the first place it is self-evident that through all kinds of disturbing influences of these small pressures, as e.g. the presence of traces of adsorbed gases or contaminations, and the slow progress of the dissociation, there is a great chance that the middle part will not be found to be horizontal, but more or less sloping;

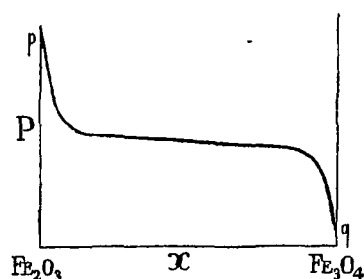


Fig. 4.

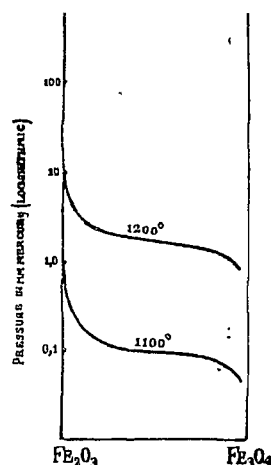


Fig. 5.

and in the second place the transition of the two sloping parts to the horizontal part will not be found to be discontinuous, but always continuous, especially when many observations are made in the immediate neighbourhood of f and g . Instead of the above given broken line the continuous curve of fig. 4 will, therefore, be found in the most favourable case.

When with these curves we compare the lines found by SOSMAN and HOSTETTER, which have been reproduced in fig. 5, we see that the found curves closely resemble those which theory led us to expect for only *partial* mixture of Fe_2O_3 and Fe_3O_4 in the solid state.

Everything depends on this whether the non-horizontal course of the middle portion is essential or not, for if this is essential and the observed pressures correspond with the states of equilibrium, this course of the isotherm would really plead in favour of the existence of a continuous mixed crystal series. SOSMAN and HOSTETTER see a confirmation of the view that the mixing of Fe_2O_3 and Fe_3O_4 is continuous in the fact that the indices of refraction of the mixtures change far from proportionally with the quantity Fe_3O_4 between hematite ($n = 2,78$) and magnetite ($n = 2,42$).

They give namely the following results.

Concentration of the mixture	ε for 700 $\mu\mu$
Hematite	2.74
0.58 % FeO	2.74
5.60 " "	2.73
12.99 " "	2.72
16.11 " "	2.71
17.79 " "	2.71
—	—
Magnetite (31.03 % FeO)	$n = 2.42$

It seems to us that they overlook in this that in case of unmixing it is by no means impossible that the phase rich in Fe_3O_4 of the equilibrium of unmixing would show a much stronger refraction in consequence of its content of Fe_2O_3 than the pure magnetite. This possibility is by no means improbable, because it already follows from the above determinations that independently of the fact whether or no unmixing is assumed, the refraction must diminish much more rapidly somewhere in the optically not investigated region than on the Fe_2O_3 side.

It should besides be considered that, as also SOSMAN¹⁾ remarked, if we assume a continuous series of mixing between the hexagonal hematite and the regular magnetite, this would be an instance of a continuous mixture between non-isomorphous substances, which has not yet been experimentally observed in a single case.

Now if we assume that from the p, x -figure at 1100° and 1200° we must actually conclude to a continuous mixed crystal-series between Fe_2O_3 and Fe_3O_4 , the said difficulty can still be obviated by the assumption that at this temperature the two oxides are isomorphous; as SOSMAN and HOSTETTER found that the homogeneous mixed crystal phases are bi-refringent, magnetite would have to possess a point of transition below 1100°, above which point the regular form is metastable. This not very probable change of crystal class has, however, not been observed, and can besides not render the continuous mixing plausible for temperatures below that of the point of transition.

However this may be, the existence of a continuous series of mixing of $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4$ does not seem proved to us, and we

¹⁾ Journ. of the Washington Ac. of Science 7, 10 (1917).

deem it, therefore, desirable to consider the possibility that in fig. 1 there should be added another three-phase curve, viz. that for $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{G}$ lying under that for $\text{FeO} + \text{Fe}_3\text{O}_4 + \text{G}$.

This situation gives rise to the question, whether this new three-phase line can intersect another. If it intersected the three-phase line for $\text{Fe} + \text{Fe}_3\text{O}_4 + \text{G}$, the mutual relation would be as given in fig. 6.

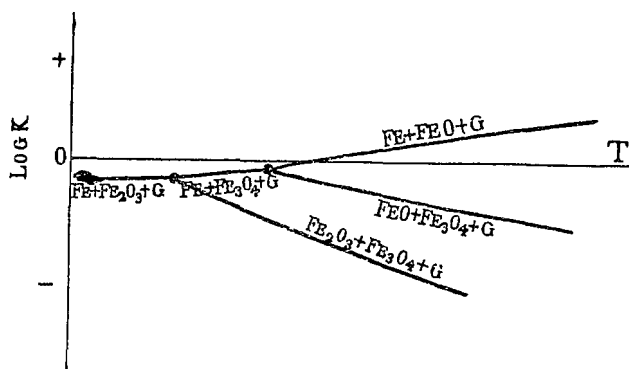
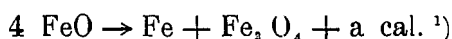
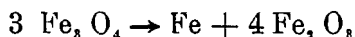


Fig. 6.

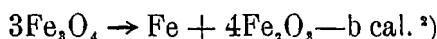
The conclusion that the three-phase lines for $\text{Fe} + \text{FeO} + \text{G}$ and $\text{Fe}_3\text{O}_4 + \text{FeO} + \text{G}$ intersect, and that this point of intersection indicates, therefore, the lowest temperature at which FeO can occur stable by the side of the gas phase G , is entirely in accordance with the sign of the conversion which must take place in this point on withdrawal of heat, viz.:



When also the three-phase lines for $\text{Fe} + \text{Fe}_3\text{O}_4 + \text{G}$ and $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{G}$ intersected in the way indicated here, then the conversion:



would have to take place in this point of intersection on withdrawal of heat, but this is in contradiction with the heat-effect of this reaction. It follows namely from the measurements that:



The supposition expressed in fig. 6 should, therefore, be rejected.

Now there remain two possibilities, namely these that the two three-phase lines for $\text{Fe}_3\text{O}_4 + \text{FeO} + \text{G}$ and $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{G}$ intersect at higher temperature, but that melting sets in, before this intersection takes place. In this case we get a situation as has been schematically given by fig. 7.

¹⁾ Comptes Rendus 120, 623 (1895).

²⁾ loc. cit.

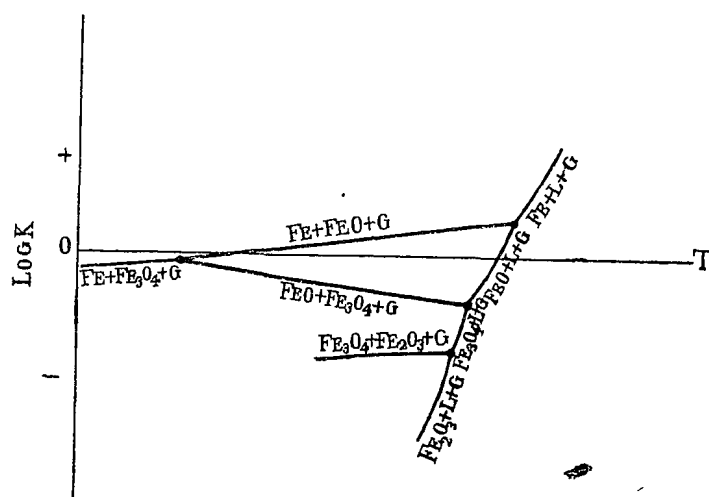


Fig. 7.

Another possibility is this that the just mentioned intersection does take place in the stable region, and then the situation of the lines is represented in fig. 8.¹⁾

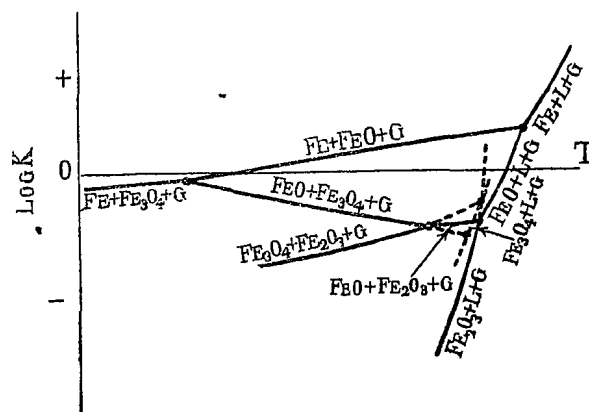


Fig. 8

It will be pretty easy to decide experimentally which of these two figures represents what really takes place. We will draw the attention on the fact that the transition point of iron is intensionally not considered here.

The Blast-Furnace Process.

What precedes gives time a survey of the three-phase lines and

¹⁾ It is clear that when Fe_2O_3 and Fe_3O_4 become miscible above a definite temperature in all proportions, the line for $\text{Fe}_3\text{O}_4 + \text{Fe}_2\text{O}_3 + \text{G}$ ends abruptly.

the two-phase regions in the system $\text{Fe}-\text{CO}-\text{CO}_2$ (resp $\text{Fe}-\text{H}_2-\text{H}_2\text{O}$), and this has rendered it possible to elucidate the *reduction processes*, which e. g. take place in blast-furnaces, from beginning to end by means of a graphical representation ¹⁾.

For this purpose we choose one of our last two figures, e. g. the

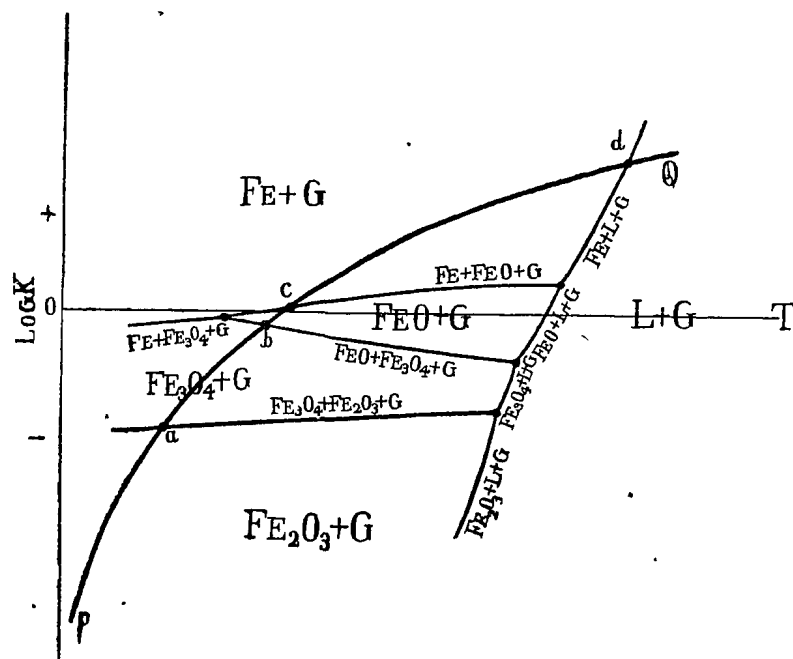
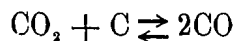


Fig. 9.

more probable one, fig. 7, and draw in this the line pQ for the equilibrium



as this is situated in the blast-furnace.

Thus arises fig. 9, and the processes that take place in the blast-furnace are read from the graphical representation bearing in mind that then the course of this line of equilibrium should be followed through the different regions given here. We then start from point P and end in point Q .

In this way we see that theoretically the reduction from Fe_2O_3 to Fe_3O_4 takes place for the first time in the point a . then in b the reduction from Fe_3O_4 to FeO , in c that from FeO to Fe , and finally in d melting of the iron. Hence we shall remain in each of these

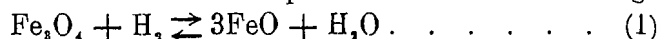
¹⁾ The Figure can easily be completed considering the formation of cementite but this is omitted here intentionally. REINDERS (Proceedings 19, 175 (1916) has already indicated partly the equilibria with cementite.

points of intersection which represent four-phase equilibria on addition of heat, until one of the phases has been completely converted.

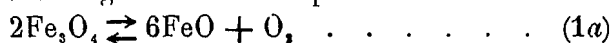
It is known that especially the equilibria with carbon are comparatively slowly established below 800°, which is the reason that in experiments with flowing gas, the just mentioned stage-wise reactions are found at temperatures above those corresponding with the points *a*, *b*, and *c*.

Derivation of the P,T-Figure of the System O—Fe from the Equilibria of the Iron-Oxides with Reducing resp. Oxidising Gases.

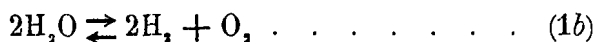
When it is borne in mind that an equilibrium as the following



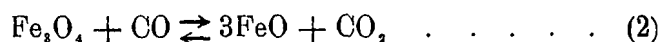
may be conceived as consisting of the two equilibria:



and



and likewise



as consisting of the equilibria:



and



it is clear that from the equilibria (1) and (1b) resp. (2) and (2b) the situation of (1a) can be derived, and the same thing may be said in reference to the other equilibria that are considered here.

It also follows from this that where the three-phase line for $\text{FeO} + \text{Fe}_3\text{O}_4 + (\text{CO} + \text{CO}_2)$ was studied, also $\text{FeO} + \text{Fe}_3\text{O}_4 + \text{O}_2$ were in equilibrium with each other. Hence the shape of part of the P,T-projection of the system O + Fe can be derived from the situation of the determined lines of equilibrium.

Thus it is immediately seen that, the three-phase lines for $\text{Fe} + \text{FeO} + (\text{CO} + \text{CO}_2)$ and for $\text{FeO} + \text{Fe}_3\text{O}_4 + (\text{CO} + \text{CO}_2)$ intersecting this must also be the case with the three-phase lines of $\text{Fe} + \text{FeO} + \text{G}$ and of $\text{FeO} + \text{Fe}_3\text{O}_4 + \text{G}$ in the system O—Fe.

When we express this in a diagram, and when we also assume the existence of the three-phase line $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{G}$, we arrive at the following P,T-projection (Fig. 10) on the assumption, as was also supposed in fig. 7, that the three-phase lines $\text{FeO} + \text{Fe}_3\text{O}_4 + \text{G}$ and $\text{Fe}_3\text{O}_4 - \text{Fe}_2\text{O}_3 + \text{G}$ do not intersect in stable points.

Accordingly this projection presents the peculiarity, which up to now has never yet been observed in a case like this, that

namely two three-phase lines for two solid phases and vapour, intersect, without inverse melting taking place in the system. In case of inverse melting such an intersection must take place, as was before demonstrated by one of us¹⁾; the case of such an

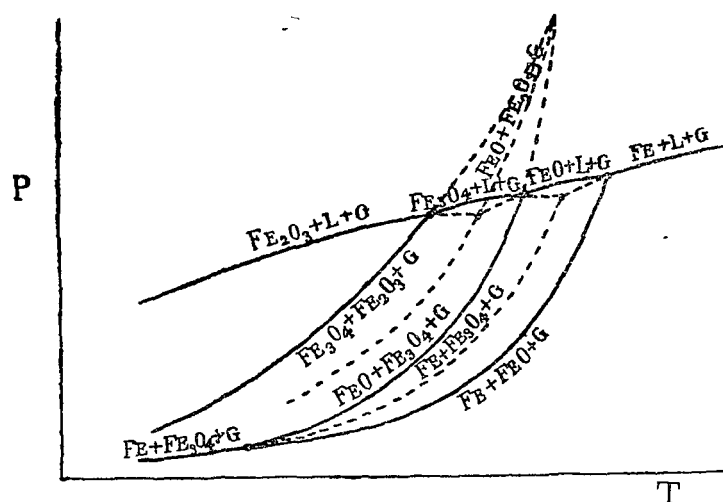


Fig. 10.

intersection without inverse melting, had however not yet been considered, so that the system O—Fe teaches us something new here.

When we now consider the possibility of a stable intersection of the two three-phase lines for $FeO + Fe_3O_4 + G$ and $Fe_3O_4 + Fe_2O_3 + G$,

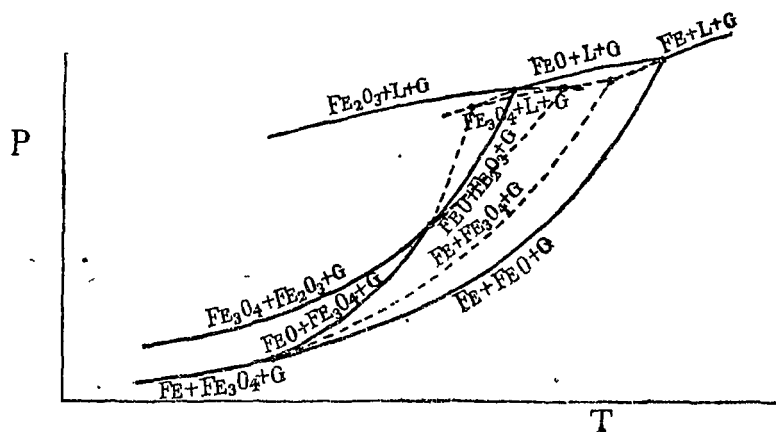


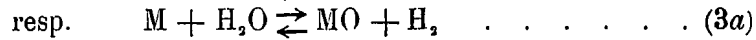
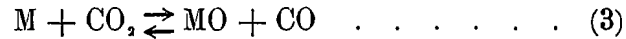
Fig. 11.

according to the supposition in fig. 8, we get a shape for the P, T-projection of the system O—Fe as indicated in fig. 11. In this case the three-phase line for $Fe_2O_3 + L + G$ would, therefore, be metastable.

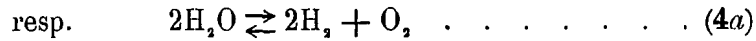
¹⁾ A. SMITS. Zeitschr. f. Elektr. Chem. 18, 1081 (1912).

Calculation of the Oxygen-Pressure of the Dissociation-Equilibria.

When we know the constant of equilibrium of an equilibrium like



and likewise the constant of equilibrium of the equilibrium:



at the same temperature, the oxygen pressure follows immediately from these data.

From (3) follows namely

$$K = \frac{P_{CO}}{P_{CO_2}}$$

and from (4)

$$K_{P_{CO_2}} = \frac{P_{CO}^2 P_{O_2}}{P_{CO_2}^2}$$

so that

$$K_{P_{CO_2}} = K^2 P_{O_2}$$

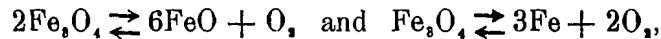
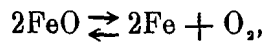
or

$$P_{O_2} = \frac{K_{P_{CO_2}}}{K^2}$$

hence

$$\log P_{O_2} = \log K_{P_{CO_2}} - 2 \log K \quad (5)$$

In this way the oxygen pressures for the equilibria of dissociation:



have been calculated by us between 400° C. and 1000° C.

We had to use for this an equation of $\log K_P$ for the CO_2 dissociation equilibrium. Wishing to apply this equation for temperatures between $\pm 500^\circ$ and $\pm 1000^\circ$, we have substituted the heat-effect corresponding to the temperature of about 800°, viz. — 133000 cal. for E in the equation:

$$\frac{d \ln K_e}{dT} = -\frac{E}{RT^2}$$

and put $\Sigma i c_v = 0$, so on integration we got:

$$\log K_e = -\frac{133000}{4.571 T} + C \quad (6)$$

or:

$$\log K_p = -\frac{133000}{4.571 T} + \log T + C' \quad (7)$$

Then C' is chosen so that agreement is obtained with the experimental data¹⁾. Thus was found e. g. when p is indicated in atmospheres:

$$\log K_{p(T=1300^\circ)} = -13,45.$$

When we substitute this value in our equation for $\log K_p$, we find:

$$C' = 5,8$$

and then equation (7) becomes:

$$\log K_p = -\frac{133000}{4,571 T} + \log T + 5,8 \quad . \quad . \quad . \quad (8)$$

or

$$\log K_p = -\frac{29100}{T} + \log T + 5,8 \quad . \quad . \quad . \quad (9)$$

When we now calculate $\log K_p$, by means of this equation for temperatures between 400° C. and 1000° C., we find what follows:

TABLE I.

t	$\log K_{p_{CO_2}}$
	(p in Atmospheres)
400	— 34.6
450	— 31.5
500	— 28.9
550	— 26.7
600	— 24.6
650	— 22.8
700	— 21.1
750	— 19.6
800	— 18.3
850	— 17.1
900	— 15.9

When at the same temperatures and pressure we now also know the values of $\log K$ for the equilibrium in the gas phase of the different three-phase equilibria in the system $Fe - CO - CO_2$, then follow from equation (5) the values for the oxygen tensions at the different temperatures.

The values of $\log K$ for the equilibria $Fe + CO_2 \rightleftharpoons FeO + CO$, $3 FeO + CO_2 \rightleftharpoons Fe_3O_4 + CO$ and $3 Fe + 4 CO_2 \rightleftharpoons Fe_3O_4 + 4 CO$, have

¹⁾ ABEGG, Handbuch III, 2. 183.

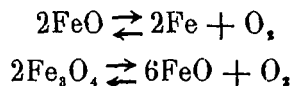
TABLE II.

	$\log K_{p_{CO_2}}$	$Fe + CO_2 \rightleftharpoons FeO + CO$		$3 FeO + CO_2 \rightleftharpoons Fe_3O_4 + CO$		$3 Fe + 4 CO_2 \rightleftharpoons Fe_3O_4 + 4 CO$	
		$\log K_3$	$\log K_{p_{CO_2}} - 2 \log K_3 = \log P_{O_2}$	$\log K_2$	$\log K_{p_{CO_2}} - 2 \log K_2 = \log P_{O_2}$	$\log K'_3$	$\log K_{p_{CO_2}} - 2 \log K'_3 = \log P_{O_2}$
400	- 34.6					- 0.16	- 34.3
450	- 31.5					- 0.10	- 31.3
500	- 28.9					- 0.05	- 28.8
550	- 26.7	- 0.01	- 26.7	- 0.11	- 26.5		
600	- 24.6	+ 0.06	- 24.7	- 0.17	- 24.3		
650	- 22.8	+ 0.12	- 23.0	- 0.23	- 22.3		
700	- 21.1	+ 0.18	- 21.5	- 0.29	- 20.5		
750	- 19.6	+ 0.22	- 20.0	- 0.34	- 18.9		
800	- 18.3	+ 0.27	- 18.8	- 0.39	- 17.5		
850	- 17.1	+ 0.31	- 17.7	- 0.44	- 16.2		
900	- 15.9	+ 0.34	- 16.6	- 0.49	- 14.9		
			$\log P_{Fe + FeO + O_2}$ (in atmospheres)		$\log P_{FeO + Fe_3O_4 + O_2}$ (in atmospheres)		$\log P_{Fe + Fe_3O_4 + O_2}$ (in atmospheres)

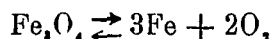
been borrowed from REINDERS' s paper on "The Equilibria of Iron and Iron Oxides with Watervapour and Hydrogen" ¹⁾.

The results of these calculations of the oxygen tensions have been expressed in the following table 2. (See table 2 pag. 398).

In this table we find, therefore, the oxygen-dissociation tensions of the equilibria:



and



and we see from this that these expressions are very small, as was to be expected.

No importance is, of course, to be attached to the absolute values of these pressures, from which we should have to conclude to the presence of one gas-molecule in many litres, when we continue to consider the ordinary gas-laws as valid, because the formulae which we used in our calculation rest on the supposition that we have to do with a great number of molecules. Yet at the lower T the real oxygen pressures corresponding to these calculated numerical quantities will be so exceedingly small that the question suggests itself whether the oxidation of the reducing gas, which in this case proceeds with pretty great velocity, can still be considered as a homogeneous gas reaction. ²⁾

P,T-Projection of the System O—Fe.

By the aid of these data we are now able to indicate part of the *P,T*-projection of the system O—Fe, when we put the found oxygen-pressure equal to the total pressure.

When in this projection we also indicate the points *p* and *q* which would follow from SOSMAN and HOSTETTER's observations for the vapour pressure of the equilibrium $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{G}$, corresponding to the temperatures 1100° and 1200°, starting from the supposition that the almost horizontal part of the isotherms of disso-

¹⁾ l. c

²⁾ Entirely analogous questions suggest themselves in the study of the mechanism of the reactions between e.g. solutions and salts, or between metals with very small solubility-product and electrolytes. Especially in the latter case the numerical values, which denote the electron concentration, in solution, can be exceedingly small, as one of us showed already. *)

*) Zeitschr. für physik. Chemie **92**, 1 (1916).

ciation found by them actually refers to this three-phase equilibrium, we get the P, T figure (12).

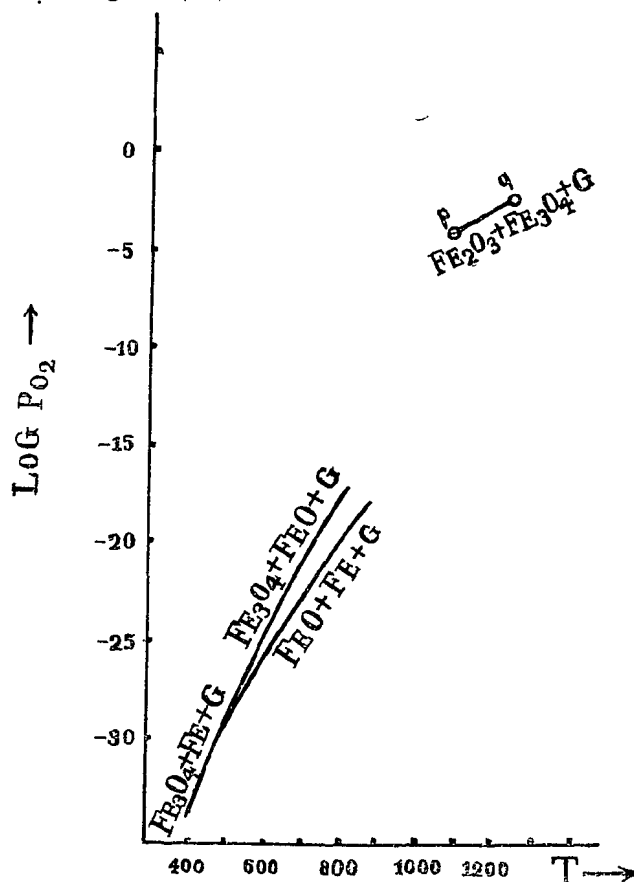


Fig. 12.

Of course these two last mentioned isotherms are perfectly inadequate to determine the direction of the three-phase line for $\text{Fe}_2\text{O}_3 + \text{Fe}_3\text{O}_4 + \text{G}$ with any certainty; we will, therefore, only point out that the situation of this three-phase line, as it would follow from these two data, with respect to other three-phase lines, would be in good agreement with the expectation expressed schematically in fig. 10 or fig. 11.

*General and Anorganic Chemical
Laboratory of the University.*

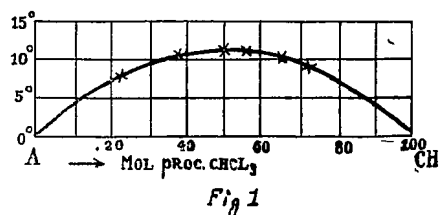
Amsterdam, June 28, 1918.

Chemistry. — “*On the System Ether-Chloroform*”. By Prof. A. SMITS and V. S. F. BERCKMANS. (Communicated by Prof. S. HOOGEWERFF).

(Communicated in the meeting of June 29, 1918).

1. Our investigation on the system ether-chloroform was prompted by a remark of a physician addressed to one of us. He namely drew our attention to the comparatively great generation of heat which occurs when these two substances are mixed, a phenomenon that was first observed by GUTHRIE¹⁾, and had given occasion to the assumption of the existence of a so-called molecular compound of the composition $(C_2H_5)_2O \cdot CHCl_3$, because the heat-effect just reaches a maximum value for a mixture of this concentration, as follows from the adjoined figure 1.

GUTHRIE thought he found a further support for this assumption



in the results of his researches on the volume contraction and the vapour tension of ether-chloroform-mixtures, and it seems that he has also tried to test his assumption by means of determinations of the point of solidification.

He namely says: “The liquid of the said concentration solidifies below 0° to a white crystalline mass at a constant temperature, which I shall state when I shall have determined it accurately”. GUTHRIE has, however, not come back to these determinations of the point of solidification.

Afterwards DOLEZALEK and SCHULZE’s²⁾ researches on the generation of heat and volume contraction led them to the result that these phenomena are maximum for an equimolecular mixture of ether and chloroform. In the conviction that these phenomena were to be ascribed to the formation of a compound they have tried by fractionated crystallisation to separate this compound and found in

¹⁾ Phil. Mag. 5 18, 508 (1884).

²⁾ Zeitschr. f phys. Chem. 83, 45 (1913).

this way about -80° for the point of solidification, when using a pentane thermometer. Like GUTHRIE before them, DOLEZALEK and SCHULZE arrive in this way in virtue of their observations at the conclusion that in the system ether-chloroform an equimolecular compound makes its appearance, which is more or less dissociated in the liquid phase.

2. In order to be able to answer with perfect certainty the question whether or no a compound is formed, it is necessary to determine the melting-point figure of the system, and this is the reason why this inquiry has been taken in hand.

The results recorded in the adjoined table were obtained by means of DE LEEUW and ZERNIKE's quick and sensitive resistance thermometer, a manufacture of the Amsterdam anorganic-chemical laboratory.

When these results are represented in a T, X -diagram, we get the following figure.

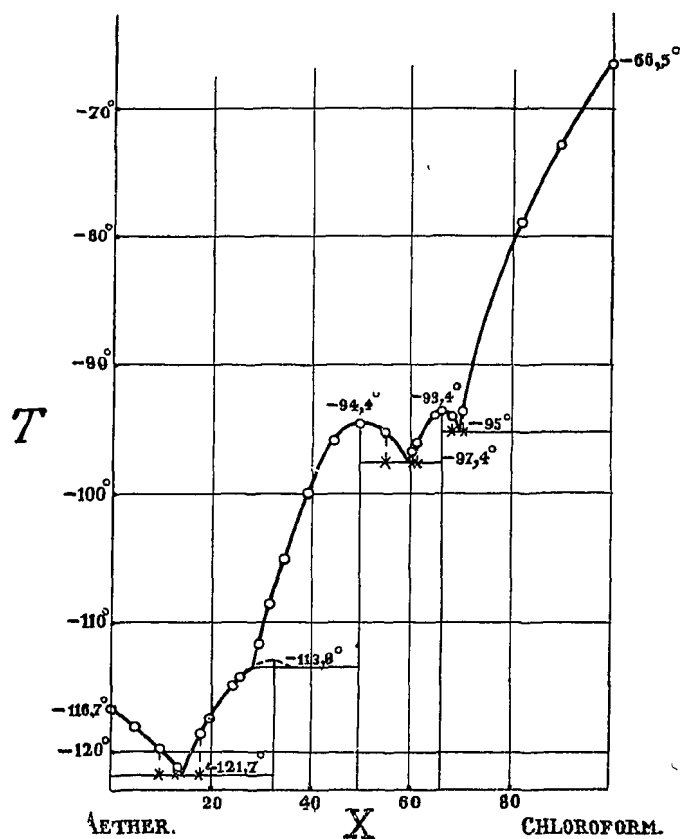
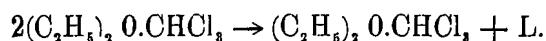


Fig. 2.

This figure (2) shows in the first place that the supposition of GUTHRIE, DOLEZALEK, and SCHULZE is correct, and that in this system

Number of the mixing	Weight in grammes		Molecule percentages		1st point of solidification		Final point of solidification
	CHCl ₃	(C ₂ H ₅) ₂ O	CHCl ₃	(C ₂ H ₅) ₂ O		Repetition with old mixture	
1	—	—	100.00	—	— 66.5		
2	21.545	1.479	90.04	9.96	— 72.6	— 72.3	
3	21.509	2.975	81.77	18.23	— 78.7		
4	8.358	2.223	70.00	30.00	— 93.5		— 95.3
5	15.807	4.226	69.89	30.11	— 94.2	— 93.8	— 95.1
6	8.119	2.371	68.00	32.00	— 93.6		
6a	8.119	2.371	68.10	32.00	— 93.5		— 94.7
7	7.952	2.468	66.66	33.33	— 93.5		
7a	7.952	2.468	66.66	33.33	— 93.3		
8	7.761	2.594	65.00	35.00	— 93.6	— 93.6	
8a	7.761	2.594	65.00	35.00	— 93.9		
9	7.283	2.890	61.00	39.00	— 96.0		— 98.1
10	7.164	2.964	60.00	40.00	— 96.4		— 97.4
11	14.328	6.022	59.62	40.38	— 96.8	— 96.4	
12	6.567	3.335	55.00	45.00	— 95.1		— 97.4
13	11.947	7.414	50.00	50.00	— 94.4	— 94.4	
13a	5.970	3.705	50.00	50.00	— 94.4		
14	11.956	9.021	45.13	54.87	— 95.8		
15	4.776	4.446	40.00	60.00	— 99.7		
15a	11.41	10.609	40.03	59.97	— 99.9	— 99.8	
16	4.179	4.817	35.00	65.00	—104.8	—105.1	
16a	4.179	4.817	35.00	65.00	—104.9		
17	3.976	4.935	33.33	66.66	—108.1		
18	7.798	11.266	30.05	69.95	—111.4	—110.5	
18a	3.582	5.196	29.97	70.03	—111.4		
18b	3.582	5.226	29.84	70.16	—111.4		
19	3.224	5.409	27.00	73.00	—114.3		
20	2.985	5.558	25.00	75.10	—114.7		
20a	2.985	5.558	25.00	75.10	—114.3		
21	4.798	11.888	20.03	79.97	—117.2	—117.5	
21a	2.388	5.928	20.00	80.00	—117.6		
22	4.327	11.717	18.65	81.35	—118.4	—118.3	—121.7
23	1.791	6.302	14.99	85.01	—121.5		—121.7
24	1.991	11.113	10.01	89.99	—119.9	—120.1	—121.6
24a	1.993	11.133	9.99	90.01	—120.2		
25	0.616	7.063	5.13	94.87	—118.3		
26	—	—	—	100.00	—116.4	—116.4	

an equimolecular compound with a point of solidification lying at -94.4° , is actually present; but —, and this particularly gives evidence how necessary the study of the melting point figure is to obtain full certainty about the appearance of compounds, — we see at the same time, that besides the mentioned two other compounds appear, viz. of the concentration $2(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{CHCl}_3$ and $(\text{C}_2\text{H}_5)_2\text{O} \cdot 2\text{CHCl}_3$; the latter of these has a point of solidification at -93.3° , and the former does not present a stable melting-point, but before this temperature has been reached, viz. at -113.8° , it is subjected to the following conversion:



It is now interesting to consider in connection with this the p, x -figures of the same system, as they have been found first by KOHNSTAMM and VAN DALFSEN, and then by DOLEZALEK at $33^\circ, 25^\circ$; 60° , and 100° . (fig. 3).

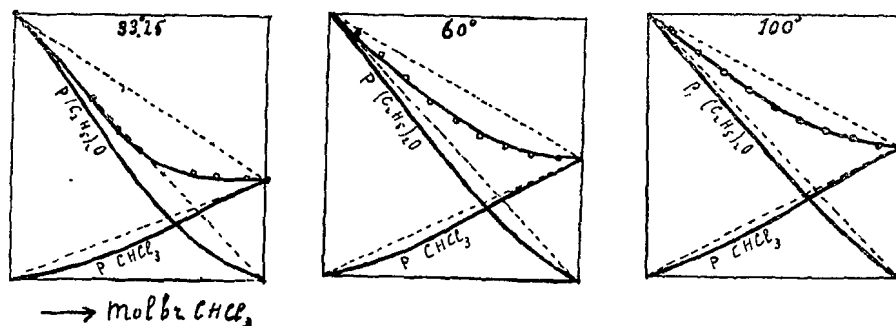


Fig. 3.

It is now very probable that the peculiar shape of these p, x -figures, especially that for the lowest temperature, is influenced not only by physical forces, but *by the side of them* also by chemical forces.

*General and Anorganic-Chemical Laboratory
of the University.*

Amsterdam, June 26, 1918.

Physics. — "*Investigation by means of X-rays of the crystal-structure of white and grey tin. I*". Communication N°. 1 from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht. By A. J. BIJL and N. H. KOLKMEIJER. (Communicated in behalf of Prof. W. H. KEESOM, Director of the Laboratory, by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 29, 1918).

Till now three methods of investigation by means of X-rays of the inner structure of crystals have been used. That of FRIEDRICH, KNIPPING and LAUE¹⁾ and that of the BRAGG's²⁾ can only be used, when rather large, well-formed crystals, of which the crystal-system is known, can be procured. On the contrary the use of DEBIJE and SCHERRER's³⁾ method requires a great number of differently orientated minute crystals⁴⁾. For that reason this method is the most adapted for the investigation of the crystal-structure of those materials that are not or only with difficulty obtainable in larger crystals, e.g. of those metals — eventually of those modifications of those metals — that are only known in a micro-crystalline state. Another example of the probable applicability of the method of DEBIJE and SCHERRER is found in the solidified gases, which till now are not to be obtained in sufficiently large crystals of exactly defined orientation.

The investigation of different modifications of the same material, e.g. allotropic states of an element, is specially interesting. This investigation has already been initiated by OLIE and BIJL, who published lately in these Proceedings their interference-photos of graphite and diamond.⁵⁾ In the meantime DEBIJE and SCHERRER⁶⁾ investigated the same materials and also so called amorphous carbon

¹⁾ W. FRIEDRICH, P. KNIPPING and M. LAUE, Sitz.-Ber. d. K. Bayer. Akad. d. Wiss. Math.-Phys. Kl. 1912, p. 303.

²⁾ W. H. and W. L. BRAGG, X-Rays and Crystal-Structure. London, 1916.

³⁾ P. DEBIJE and P. SCHERRER, Nachr. d. K. Ges. d. Wiss. zu Göttingen. Math. Phys. Kl. 1916, p. 1.

⁴⁾ A. W. HULL, Phys. Rev. (2) 10 (1917), p. 661, evidently arrived independently of DEBIJE and SCHERRER, at rather the same method.

⁵⁾ J. OLIE and A. J. BIJL, Proceedings Roy. Ac. Amst. XIX (1917), p. 920.

⁶⁾ P. DEBIJE and P. SCHERRER, Physik. ZS. 18 (1917), p. 291.

and succeeded in determining the structure of these modifications of carbon.

In connection with the investigations, which have already been made of silicium, lead, and the modifications of carbon, we have in this investigation set ourselves the task, to determine the structure of still another element of this group of the periodical system, the tin namely in two of its modifications, the grey and the white ones.

The X-rays were for the greater part of our photos furnished by a Röntgen-tube, constructed after a drawing, which Prof. DEBIJE and Dr. SCHERRER kindly procured us, and which must be considered as a modification of the tube, constructed by RAUSCH VON TRAUBENBERG ¹⁾. The anticathode was a copper one, the parallel-spark-length (point-disc) measured 6 cm. The X-rays left the tube by an aluminium window of 0,02 mm. thickness, afterwards passed a lead screen, thickness 34 mm. with an opening of 2 mm. diameter and entered then a cylindrical camera of 27,3 mm. radius. In the axis of the camera the material, to be investigated, was placed in the form of a bar of 2 mm. diameter. The white tin bar was filed from a thicker bar, which for the diminution of the crystals and in order to obtain irregular orientation of these, was beaten for some time with the hammer. The grey tin was pressed into a small bar. We obtained this material through the kindness of Prof. COHEN, to whom we therefore render our thanks. A photographic film (thickness 0,2 mm.) was stretched along the wall of the camera and pressed against it by springs. The exposition-time was 4 hours.

During the preparative experiments we observed that in excess of the interference-lines of the tin, still others were obtained, of two different kinds. The first resembled hyperbolas, the centre of which was in the point, where the beam of characteristic rays, after having passed the investigated preparation on both sides, fell on the film. They must be ascribed to the interference of rays, which are diffracted by the silver-bromide of the film. The second kind had the same direction of curvature as the lines, which originated from the preparation in the axis of the camera, they intersected these lastmentioned however at some points, which indicated, that here too the origin was not to be sought for in the preparation. We got the evidence, that the origin of them was to be found in the back-opening of the lead screen, which opening was in the wall of the camera. We got rid of the first kind of undesired lines by making a circular hole in the film, at the place, where the beam

¹⁾ H. RAUSCH VON TRAUBENBERG, Physik. ZS. 18 (1917), p. 241.

fell upon the film, as indeed DEBIJE and SCHERRER already did too. The coming up of the second kind of undesired lines was avoided by extracting the lead screen a little from the surrounding brass tube, so that the rays coming from the lead, were screened from the camera by the remaining wall of the camera, or by widening the end of the screen, which was directed to the film so much, that the rays, emerging from the back edge of the not-widened part of the screen, were arrested by the widened part of it.¹⁾

On the photos, obtained by us of the white, as well as of the grey tin there appear points on the lines, as were also observed by DEBIJE and SCHERRER on their photo of silicium. They must be ascribed to larger crystal-parcels.²⁾

In order to facilitate the comparing of the results for white and grey tin, we have indicated in the drawing underneath, one under the other for both these materials, by vertical lines the places, where the interference-cones intersect the film in a plane, perpendicular to the axis of the preparation. The numbers at the bottom give the distances of the lines to the intersection of the axis of the penetrating beam with the film in mm. By greater or smaller thickness of the lines at the top and the bottom respectively the intensity of the lines is given, as it was estimated by us in five degrees, namely:

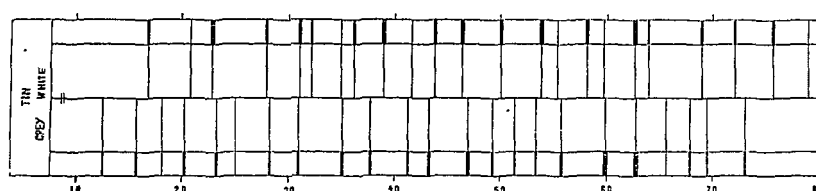
¹⁾ Perhaps it is worth while, to state, that the criticism, exerted by TAYLOR, Physik. ZS. 17 (1916) p. 316 on articles of LAUB, Physik. ZS. 15 (1914) p. 732, 844, seems not to be founded, now that we too found, that characteristic X-rays when going through a leaden screen, can give interference-lines, originating from the edges of the screen.

²⁾ The length-direction of these oblong points is the same as the direction of the interference lines. The explanation of this is as follows. On a single point of a plane out of the atom-net of such a crystal-parcel there falls, on account of the imperfect parallelism of the beam, which has passed the screen, a convergent conical beam of rays (first cone). If the net-plane, mentioned, has such a position that for a direction of rays in the axis of this last beam the condition for favourable interference is fulfilled, then there are in this beam still other directions of rays, for which this condition is just as well fulfilled. The collection of these directions is found by describing a cone, with the normal on the plane mentioned, as axis and the axis of the first cone as one of the describing lines (second cone). All the describing lines of the second cone that are within the first cone, fulfill the condition for favourable interference. After their reflection all these rays form together a diametrically opposite part of the second cone. Just there however the second cone is tangent to the third cone, formed by the reflected rays, which are obtained by letting the reflecting plane take all possible positions favourable for interference. Now, where the film intersects with both the last cones, the intersection-lines will be tangent to each other. One of these intersection-lines is an interference line, the other such an oblong point.

very feeble, feeble, moderate, strong, and very strong. On the axis of the drawing the greatest error, that possibly is made at the readings is indicated by the distance of two little lines (to the left).

From the photo of the grey tin it follows in the first place that this material is crystalline, which fact, so far as we could find, at present was unknown.¹⁾ Further there appears to be a difference between the crystal-structure of grey and of white tin. We intend soon to communicate the composition of both the atom-nets.

In concluding we thank Prof. KESOM very much for the kindness with which he placed all the requisite apparatus for the experiments at our disposition and for his interest and cooperation.



¹⁾ [Note, added during the translation]. After this communication had been printed in the Dutch edition, we found, that VON FOULLON (Jahrb. d. Kais.-Kön. Geol. Reichsanst. Wien. 34 (1884), p. 367) as well as FRITSCH (Ber. d. d. Chem. Ges. 2 (1869), p. 112 and 540) assert, that grey tin is crystalline. It does not appear in what manner these scientists have verified the crystalline condition.

Geology. — "*On Tin-ore in the Island of Flores*". By Prof. A. WICHMANN.

(Communicated in the meeting of June 29, 1918).

Some years ago I maintained on the ground of geological studies that tin-ore does not occur in the island of Flores, at all events not to an amount worth mentioning¹⁾. As appeared from a memoir brought forward last year by Prof. S. J. VERMAES, the author is otherwise-minded²⁾. I think it worth while to study the author's arguments, which he pretends to be based on the doctrine of the deposition of ore, on ethnography and on metallurgy.

Geological researches have not been made in Flores of late years, so that in this respect there was no need for revising my paper. Nevertheless Prof. VERMAES supposes he has been fortunate enough to make a discovery, which throws a new light upon the matter³⁾. This finding appears to be nothing else but a piece of tin-ore, exposed in the Colonial Museum at Harlem, "weighing 131 grms and composed of chlorite and tin-ore with fissures, in which occurs some kaoline. Besides the two mentioned minerals a single grain of chalcopyrite is also noticeable".

Prof. VERMAES altogether fails to see that the finding place "Gunung Rokka", indicated on the label must be fictitious, since the mountain — the Inije Rije of the natives — is a volcano and even now is in the condition of solfataric activity⁴⁾. Indeed, not one of the researchers has ever found the least indication of the occurrence of ores on that mountain and even C. J. VAN SCHELLE, who never shrank from a bold hypothesis, has wisely refrained from making inquiries after tin-ore in the volcanoes of Flores. He looked

¹⁾ "On the tin of the Island of Flores". These Proceedings Amsterdam. Vol. 17, 1914, p. 474—490.

²⁾ Tinerts op Flores. De Ingenieur. 32. 's Gravenhage 1917, p. 584—590.

³⁾ l. c. p. 584.

⁴⁾ J. J. PANNEKOEK VAN RHEDEN. Overzicht van de geographische en geologische gegevens, verkregen . . . van het eiland Flores in 1910 en 1911. Jaarboek van het Mijnwezen in Ned.-O.-Ind. 40. 1911. Batavia 1913, blz. 219—220. — Eenige geologische gegevens omtrent het eiland Flores. Jaarboek van het Mijnwezen. 39. 1910. Batavia 1912. Verhandelingen, p. 135—136.

for it, at haphazard in a district supposed by him to contain tin-ore, which was partly overlaid by volcanic formations¹⁾.

As to his arguments based on metallurgy, it strikes us that Prof. VERMAES has deemed it unnecessary to inquire further into the matter as regards tin, or he could not have written as follows: "He (WICHMANN) also cites what he wrote before, namely that tin-ore could not be reduced by burning grass. I have often seen alang-alang burning, still I *would not make bold to say on metallurgical grounds what WICHMANN presumes*"²⁾. A geologist will not confine himself to merely "see" an alang-alang field "burning", but will also try to watch the effect such a fire has on the components of the soil under it. I myself experienced that the volcanic sand and the lapilli of augite-andesite at the foot of the Batu angus baru in the Minahassa did not change a bit. Nor could anything else be expected, for the grass (*Imperata cylindrica* Beauv.) furnishes such an insignificant quantity of fuel that it is burnt away in a trice. This short burning process does not even extend as far as the roots, so that when the West Monsoon sets in, the grass begins to sprout again.

Prof. VERMAES continues: "We read, however, in VAN SCHELLE's report: "When the forests are on fire, part of the ore seems to be reduced'", after which Prof. VERMAES concludes: "If, therefore, a mass of tin-ore is imbedded near the surface in the root-leaves of a large tree and, after felling the tree, a pile of combustible materials is kindled at the stump, *there is no doubt but that the tin-ore is reduced to metal*"³⁾.

First and foremost I wish to quote a passage from P. VAN DIEST's well-known work on Banca: "The remainders of a charcoal-furnace⁴⁾ are identified by the natives as the spot near which it is supposed that tin was first discovered in Banca, that is after the burning of part of the forest near the spot⁵⁾. The belief in those stories is negated even more, when we reflect that the heat produced by a burning pile of tree-trunks is not adequate to reduce tin-ore without a certain amount of coal being mixed with them, especially

¹⁾ Verslag van het onderzoek naar het voorkomen van tinertshoudende gronden op Flores. Extra-Bijvoegsel der Javasche Courant. Batavia 1890. N^o. 10. (Uittreksel: Tijdschr. voor Nederl.-Indië. Zaltbommel 1890. 2, p. 79).

²⁾ The italics are mine.

³⁾ The italics are mine.

⁴⁾ On the Sambong giri hill near the Lindjoe mine.

⁵⁾ Tradition says this happened in 1710. (F. EPP, Schilderungen aus Archipel. Indiens Heidelberg 1841, p. 134; J. H. CROOCKEWIT. Banka, Malakka and Billiton. The Hague 1852, p. 134).

not in the case of the coarse-granular ore at the foot of this hill¹⁾).

This assertion is apparently founded on the fact that tin-ore is one of the minerals that are difficult of fusion, but that it is easily reduced to tin by the addition of charcoal. This assertion does not satisfy us any more than VERMAES's pronouncement that "*there is no doubt but that the tin-ore is reduced to metal*", by means of a burning pile of wood. An experiment does not seem to have ever been made.

The melting point of tin-ore as established by R. S. CUSACK at 1127° C.²⁾, seems to me to be too low, as higher points are found³⁾ for much more fusible minerals, e. g. for augite 1100°—1200° (according to C. DOELTER⁴⁾) and for plagioclases (labradorite to oligoclase) 1130°—1300°⁵⁾. Anyhow CUSACK's melting point (1127°) being even higher than the heat produced by the burning of living wood — the only wood we have to deal with — it is obvious that a burning wood cannot reduce tin-ore to tin. Moreover, whereas along-along fires may occur repeatedly every year towards the close of the West-monsoon, forest-fires are decidedly the exception, so that even on this account the required amount of tin could not have been produced in this way.

Furthermore, it still remains to be seen whether the expected result can be obtained even at high temperatures. In modern mineralogical textbooks and manuals — with a few exceptions — the hypothesis is advanced that tin-ore does not undergo any change, when the blowpipe is applied. This squares entirely with the results most inquirers are capable of achieving in connection with the difficulty of mastering some facility in handling the blowpipe. Years ago BERZELIUS wrote: "Das Oxyd verändert sich und schmilzt nicht, aber von einem starken und anhaltenden Reduktionsfeuer kann reines Zinnoxid ganz und gar ohne Zusatz zu Zinn reducirt werden. Dies erfordert indessen eine Gewohnheit das Löthrohr zu gebrauchen."⁶⁾ This is in character with C. F. PLATTNER's opinion, who,

¹⁾ Bangka, beschreven in reistochten. Amsterdam 1865, p. 68.

²⁾ On the melting points of minerals. Proceed. R. Irish Acad. of Sc. (3) 4. Dublin 1896—98, p. 413.

³⁾ Beziehungen zwischen Schmelzpunkt und chemischer Zusammensetzung der Mineralien. Tschermaks Miner. petrogr. Mittlg. 22. Wien 1903, p. 399—311.

⁴⁾ C. DOELTER, Handbuch der Mineralchemie 1. 1912, p. 663.

⁵⁾ The above mentioned melting-points are somewhat too low, as the author himself has acknowledged afterwards (Handbuch der Mineralchemie 2. 1. Dresden — Leipzig 1914, p. 579).

⁶⁾ Von der Anwendung der Löthrohrs in der Chemie und Mineralogie. Uebersetzt von H. ROSE. Nürnberg 1821, p. 113—114. At present it is extremely difficult to ascertain whether any writer before BERZELIUS has obtained the same result.

however, adds that in this process a white layer of tin-oxide is formed.¹⁾ W. A. Ross, on the contrary, maintains that the ore does not melt "aber eine weisse *Ausblühung* kommt hervor"²⁾. GIORGIO SPEZIA again believes that the ore changes, but "non par fusione ma par consumo" and he tries to account for the behaviour of the tin-ore by stating that in consequence of the intense heat a reduction takes place indeed, but that it is incontinently followed by an oxidation evolving the white layer.³⁾ Should this interpretation be correct, there cannot possibly be any question about reducing tin-oxide by heat alone. Now which of us is, to quote from Prof. VERMAES, the "metallurgist of Flores" who has indulged in fancies⁴⁾? And when the same writer continues: "WICHMANN ought to have considered that such utterances cannot but be fatal to the upgrowth of a mining concern, of which many experts anticipate great success", I feel urged to say that it is rather disappointing to find that still in the year 1918 one is obliged to appeal to the timeworn maxim that the man of science does not ask whether or no anything is fatal in its effect on a mining concern but that he considers his sole task to be to find the Truth. Apart from this, the effect of science can never be fatal, at all events not for those who know how to study it; on the other hand it is always inspiring, even when an inquiry yields a negative result. If the mining industry had paid more regard to science, they would have been spared many disappointments in the island of Celebes and they could have saved many people's capital. Presumably they will not have become wiser by this time, in spite of all this.

Furthermore, if we reflect that tin foundries in Flores cannot be imagined without charcoal furnaces and agglomerations of tin-slugs of which no trace was ever found, we are safe to say that Prof. VERMAES's endeavours to prove the occurrence of tin-ore on metallurgical grounds have utterly failed.

We shall have to dwell more at large on his arguments derived from ethnography. In estimating his material Prof. VERMAES has entirely neglected to ascertain whether the premiss from which he started was correct, which is a common mistake among ethnologists.

¹⁾ Probirkunst vor dem Löthrohre. 5. Aufl. bearbeitet von TH. RICHTER. Leipzig 1878, p. 136.

²⁾ Das Löthrohr in der Chemie und Mineralogie, übertragen von B. COSMANN. Leipzig 1889, p. 161.

³⁾ Sulla fusibilità dei minerali. Atti R. Accad. delle sc. 22. Torino 1886—87, p. 422.

⁴⁾ l.c. p. 588.

An early illustration of this error was afforded by J. H. CROOCKEWIT, who considered the absence of tin-objects in Billiton — those that were found there had been imported from Banca — to lend support to his hypothesis that *no* tin-ore was to be found in that island.¹⁾ Conversely C. J. v. SCHELLE's whole argumentation rested *only* on the fact that natives of Flores were found in possession of tin objects etc., on which fact also Prof. VERMAES set so high a value. This is the logic of a Papuan, who, judging from the knives and axes he gets from the merchants in exchange for his birds of paradise, believes that Holland is rich in iron-ore.

The truck to which the natives attach great value does not only serve as an ornament, but also as a form of investment, as sometimes occurs in Europe also. There is even among uncivilised nations a liking for capitalization, especially among the more intelligent part. This tendency increases with the degree of personal safety. That is why the government of a Western Power has always encouraged "capitalization". The natives' choice of articles of investment is very limited compared with that of Europeans, who prize stocks and other paper value so highly. Such articles must be proof against the influences of the climate and moreover be gaudy and showy. In districts where Europeans have settled or in not-too insignificant commercial centra coined money, "rijksdaalders",²⁾ and especially gold coins are greatly in favour.

If the soil does not produce the desired objects, as is the case in nearly all the islands of the Timor Archipelago³⁾, the native is obliged to look about for foreign objects. Next to weapons and other iron tools all the native tribes set great value upon the "muti tanah", dirty-coloured orange-red glass beads. They are skilfully wrought, but not beautiful and owe their value rather to being "antique" and to the fact, that they were not imported after the pre-historic period, i. e. after the arrival of the Europeans.

¹⁾ Extract from the report of a journey across the island of Billiton (Natuurk. Tijdschr. Ned. Ind. 3 Batavia 1852, p. 401.

²⁾ Dutch coin worth 4/2.

³⁾ It is true, gold and copper occur in Timor, but by far not sufficiently to meet the demand for those metals. Moreover the occurrence of ores does not prove at all that the natives are skilled in metallurgy. The inhabitants of Billiton e.g. were entirely unacquainted with the art of reducing tin from tin ore, whereas from time immemorial they are quite familiar with the more complicated process of working iron, and it was only recently that F. SARASIN declared: "Die Kunst Metalle zu bearbeiten, haben die Caledonier trotz des enormen Reichtums des Landes an solchen, speziell von Eisen, nie gekannt und auch heute noch nicht gelernt" (Neu-Caledonien. Basel 1917, p. 83).

It is remarkable that in Flores the same legend about their origin prevails as regarding tin, viz. that they have been formed in the soil itself in consequence of the burning of alang-alang; they are accordingly called "muti tanah", that is: earth-beads. About their origin we are still as much in the dark as about that of the glass objects found in the South-Sea islands. Beside a marked concordance in their taste for beads the islanders of the East-Indian Archipelago evince none the less a vast difference respecting the other favourite objects for capitalization. While "moko-moko", peculiar kettledrums made of brass, are in vogue in the Alor-islands, elephants' tusks are generally in favour in the Solor-islands coming next to them in a western direction. In West-Flores there prevails a fancy for tin-ornaments, while the inhabitants of Rotti prefer chains made of gold-wire.

The reasonings of C. J. VAN SCHELLE and of Prof. VERMAES would lead us to conclude that there are coppermines in the Alor-islands, herds of elephants in the Solor-islands and gold-diggings in Rotti. It would be throwing words away to say more about it, but we wish to say a few words more about the tin objects of Flores.

Prof. VERMAES might adduce the argument that there is not a single record extant to support the assertion that tin or tin objects were imported into Flores. But the same argument could apply to the elephants' tusks of the Solor-islands. In the second half of the previous century cast moko-mokos were introduced into Java from Grisse, but the natives soon found out that they were imitations. In Rotti, where not a single grain of gold has ever been found, an old branch of industry has revived in consequence of the sale of horses to Australia, which brought a large number of sovereigns to the island, which were wrought into gold chains¹⁾.

To support his argumentation Prof. VERMAES has added to his memoir not only a number of fine illustrations, but also numerous analyses of the metallic objects found in the island. I hope they will prove most interesting for the ethnography of Flores, but they are not relevant to the origin of the metals.

I can imagine the possibility of establishing through analysis that a table spoon has been procured by such and such a firm, but hundreds of analyses cannot enable us to establish the source of the silver used to make the spoon.

¹⁾ The Rottinese are very superior in civilization to the people in Alor and Flores, who possess but little skill in working metals. J. P. FREYSS says about them: "the art of forging is very little advanced among the inhabitants of West-Flores." (Reizen naar Mangarai Tijdschr. Ind. T. L. en Vk. 9. Batavia 1860, p. 511).

It strikes us that in former times neither export nor import of tin objects was ever thought of¹⁾. In the long run such a trading possibility could not have escaped European enterprise, no more than the trade in "Billiton-axes" and "Tambuku swords". It attracts our attention, however, that the tin objects in this poor island are found in the southwestern part in the possession of the natives. This might be due to the presence of tin-ore in that part; however the conclusion might also be drawn that the population disposes of more truck and consequently obtains possession of such objects as their countrymen in other parts must do without.

According to GODINHO DE EREDIA "cinnamon"²⁾ was exported from these parts already in the time of the Portuguese settlement³⁾ and the fort in Nusa Endeh was certainly not built only for the purpose of protecting the Dominicans. That also this product attracted the notice of the East-Indian Company is borne out by the report of P. A. LEUPE on the discussions at Batavia in 1757, which says: "They had still to contrive a means to get possession of the cinnamon-wood Rokko in Endeh⁴⁾", and according to J. C. M. RADEMACHER it was in the year 1756 that "the Company permitted the natives of Makassar to trade on Endeh and the Mangary *provided no wild cinnamon was* exported, on the penalty of confiscation of ships and cargo"⁵⁾.

Nearly sixty years ago J. P. FREYSS still wrote: The gathering of wax and cinnamon constitutes the chief commercial resource⁶⁾. The natural result of this trade was a comparatively higher degree of prosperity than was enjoyed by their countrymen, whose income, derived from woodproducts, was smaller and who therefore had

¹⁾ As I mentioned before only in 1871 J. A. VAN DER CHIJS made mention of the export of tin arm- and leg-rings from the Rokka district. (Tijdschr. v. Nijverheid en Landbouw in Nederl.-Indië 16. Batavia 1871, pp. 158—159).

²⁾ No doubt *Cassia* was meant. (J. G. F. RIEDEL The island of Flores or Pulau Bunga. Revue colon. internat. 1. Amsterdam 1886, p. 66).

³⁾ ANTONIO LOURENÇO CAMINHA, Ordenações da Índia do Senhor Rei D. Manoel de eterna memoria Informação verdadeira da Aurea Chersoneso feita pelo.... MANOEL GODINHO DE EREDIA. Lisboa 1807, p. 143 (written in 1599).

⁴⁾ Besognes der Hooge Regeering te Batavia gehouden over de commissie van Paravacini naar Timor in 1756. Bijdr. t. de T., L. en Vk. (4) 1. 's Gravenhage 1877, p. 479.

⁵⁾ Korte beschrijving van het eiland Celebes en de eilanden Floris, Sumbawa, Lombok en Baly. Verhandel. van het Batav. Genootsch. van K. en W. 4. Batavia 1786, p. 252.

⁶⁾ Reizen naar Mangarai en Lombok in 1854—1856. Tijdschr. Ind T., L. en Vk. 9. Batavia 1860, p. 512.

to be content with bartering their articles for necessities of life, whereas the Rokkanese could also acquire articles of luxury. What, however, were the events that stopped the import of *muti tanah* and the objects made of tin, will long remain a puzzle, perhaps for ever.

Prof. VERMAES has prefixed to his memoir the following quotation from CROOCKEWIT, as a motto: "I feel justified in concluding from these inquiries, made in three different ways, that the ore found in Billiton does not contain tin oxide"¹). The tendency of this motto was to stigmatize my being mistaken with regard to Flores as CROOCKEWIT had been with regard to Billiton. As appears from the foregoing Prof. VERMAES has not succeeded in demonstrating that tin-ore occurs in Flores; the comparison therefore halts, and was at the very least premature. He has mistaken the persons also in another respect. It was not I, but VAN SCHELLE who, just as CROOCKEWIT, started from faulty premisses; it was not I but VAN SCHELLE whose inquiries, just as CROOCKEWIT's, led to wrong conclusions. No wonder that both failed.

¹) Extract from the report of a journey through the island of Billiton. (Natk. Tijdschr. Ned. Ind. 3. Batavia 1852, p. 401.

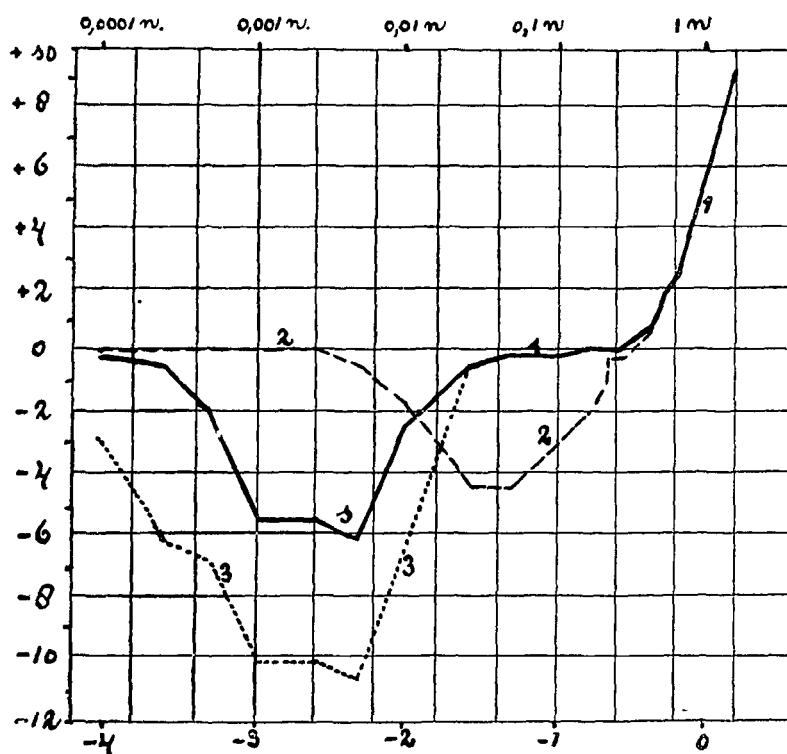
Physiology. — *"On the Sign of the Electrical Phenomenon and the Influence of Lyotrope series observed in this phenomenon".*

By Prof. H. ZWAARDEMAKER and Dr. H. ZEEHUISEN.

(Communicated in the meeting of June 29, 1918).

I. In a previous publication ¹⁾ we have established that the nebulae of salicylic acid salts generated by spraying, owe their electrifying power to the contained anion.

Fig. 1. Influence of 0.1 n NaCl and 6 % canesugar on the charge of *salicylas natricus*.



1. Curve of the Charge of *salicylas natricus* alone.
2. Curve of the Charge of *salicylas natricus* + salt.
3. Curve of the Charge of *salicylas natricus* + sugar.

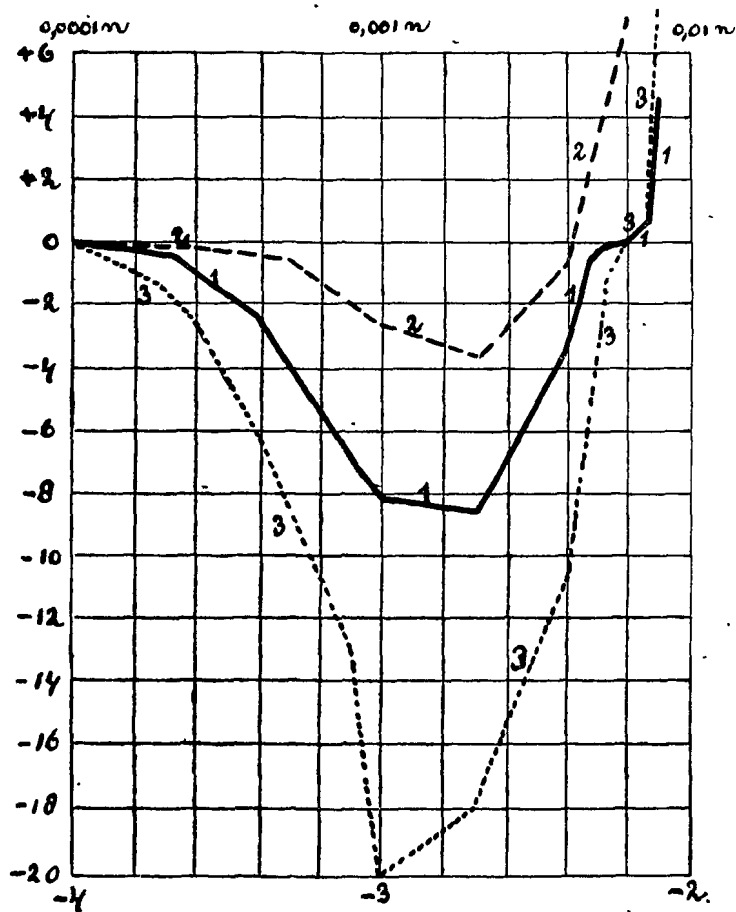
Along the top-abcissa the normal concentrations, along the bottom abcissa the logarithms of the normal concentrations of *salicylas Na.* are given; along the ordinate the deflections of the electroscope in scale-divisions.

¹⁾ These Proceedings Vol. XX, p. 1272, 1918.

As set forth loco citato, the attending cation lessens the negative charge of the nebula of this acid. Consequently salicylic acid and salicylates, in weak concentrations, determine the electrifying power of the nebula in quite the same way and with a negative sign, only with quantitative differences in such a sense that the salt produces a lower charge than the acid, and can be sprayed in higher concentrations on account of greater solubility in water. This also holds good for other salicylates that are soluble in water.

The negative charge of salicylas natricus lessens with the increase of the concentration, so that it gradually approaches the zero-line, and ultimately crosses it. The charge, then, is positive. For a long time there is no charge at all, as is well seen in Fig. 1, which

Fig. 2 Negative and Positive phase of the Charge of salicylic acid and the influence of 0.0025 n. NaCl and of 6% sugar on the charge.



1. Curve of the Charge of Salicylic acid alone.
2. Id of salicylic acid + salt.
3. Id. of " " + sugar.

Division of abscissa and ordinate as in Fig. 1.

also shows the positive part of the charge of salicylas natricus, and gives the logarithms of the strengths of the solutions along the abscissa.

Addition of sodium-chloride to these strong solutions of salicylas natricus had no more influence upon these positive charges than an addition of sugar had. On the other hand, under the influence of the same substances, changes were brought about in the negative charge of weaker solutions, as the figure illustrates.

The charge of the salicylic acid itself also first increases with the rise of the concentration, afterwards it decreases. (Fig. 2), to rise above the zero-line a little before the point of saturation. The effect of salt and sugar upon the charge is very slight at this moment, just as it is with salicylas natricus; after crossing the zero-line, however, it comes forth again, but in a positive sense.

The facts just described or illustrated seem a chaos at first sight. Some order is discovered, when we reflect that in dilute solutions, which are the only solutions we have to deal with in spraying, cations and anions act separately. The effects of cations and anions are superposed. In spraying salicylic acid and caproic acid (fig. 2 and 3) only the anion is of importance. In spraying salicylas natricus there is an action of salicylic acid and sodium; in the combined spraying with salts and sugar there is a combination of effects of all cations and anions present.

It is not possible as yet to account for these phenomena; they belong, indeed, to the field of physics proper. Provisionally we are able to state only that strong solutions of salicylas natricus yield, on spraying, dense nebulae, forming large droplets; the latter are so large that sodium-chloride and sugar particles do not apparently affect them. When the salicylas natricus solution is diluted the charge is affected first by the sodium-chloride and only much later by the sugar.

It is not clear why with sodium-chloride this influence reveals itself first in a negative sense, and, with a weaker salicylas natricus solution in a positive sense, while with sugar that influence manifests itself later and only in a negative sense. This negative sodium-chloride phase is altogether lacking with salicylic acid, while the charge-curves of this acid with and without sugar run together for some time in the neighbourhood of the zero-line (as was the case with salicylas natricus) and after this yield a positive sugar-effect.

Considering these results, it was interesting to ascertain whether there are also other substances presenting charges of opposite signs in different concentrations. We fixed upon the acids of the fatty

acid series, that are soluble in water. The alcohols of fatty acids behave in a remarkably uniform way ¹⁾. With all of them the charge of the solutions, if there is any, is positive. With ethyl- and propyl-alcohol it begins in stronger concentrations than with butyl- and amyl-alcohol ²⁾, as was established before in the physiological laboratory when studying the charges of homologous series; all these charges are raised by sodium-chloride, the more so as the concentration of NaCl was taken higher.

The fatty acids present quite a different electrical phenomenon. Leaving formic acid, which gives only a very low charge, out of consideration, we find that acetic acid always gives a positive charge in all the concentrations in which it gives any charge at all. Propionic acid, butyric acid, valerianic acid, caproic acid on the contrary have a negative sign in those weaker concentrations, in which they produce a charge, as will be seen in fig. 3.

The lowest negative charge occurs with caproic acid; with valerianic acid the curve is less deep, with butyric acid still less, while with propionic acid it is extremely level. The behaviour of the latter acid is very strange indeed; its negative bend keeps very close to the zero-line and proceeds over a considerable distance, the positive line rises suddenly up to a maximum. So the curve of this acid also runs between those of acetic acid and butyric acid; its positive zone is much steeper than that of butyric acid ³⁾, whereas its negative zone is much less deep than that of butyric acid and accounts for the absence of a negative zone with acetic acid. All this may be seen in Fig. 3, without further description. With none of these acids, except with acetic acid, could we find the descending portion of the positive line, because their solubility was less than that of acetic acid.

Taking them all together these various acids present the whole negative and positive phase, with this restriction that practically part of it comes to nothing; of the positive phase with the higher terms of the group on account of too little solubility; of the negative phase with the lower terms for reasons of which we are entirely ignorant.

II. In the second place ⁴⁾ we watched *the influence on the charge*

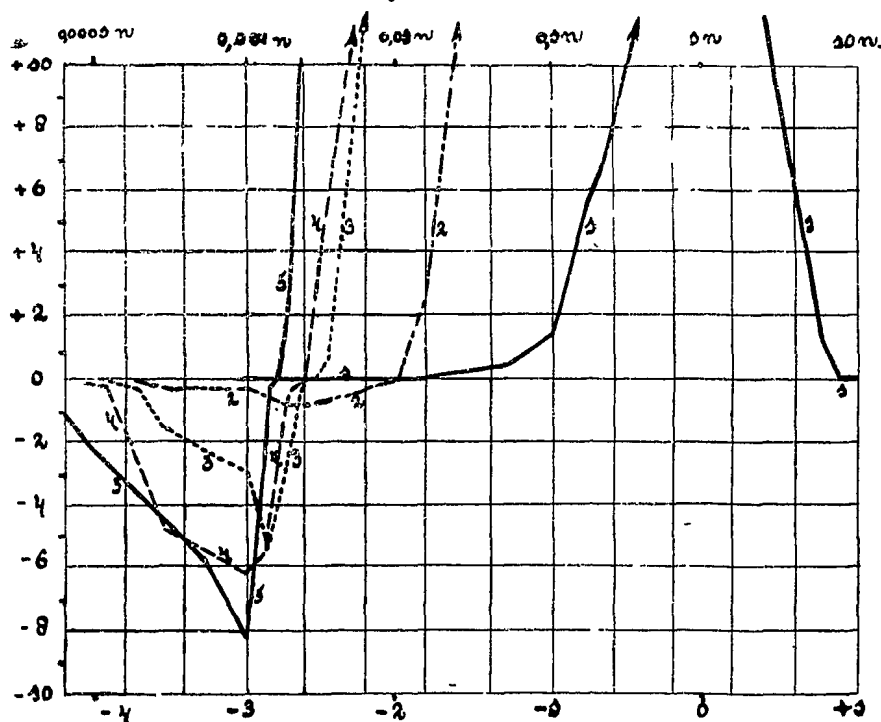
¹⁾ We must perhaps except methylalcohol on account of a probable complication.

²⁾ With ethyl- and propylalcohol in 0.01 n.; with butyl-alcohol in 0.002 n.; with amyl-alkohol in 0.0005 n.

³⁾ This is not noticeable on the (logarithmic) curve.

⁴⁾ These Proc. Vol. XX, p. 1272.

Fig. 3. Phases of negative and positive charges of terms II—VI of the fatty acid series.



1. Acetic acid, 2. Propionic acid, 3. Butyric acid, 4. Valerianic acid, 5. Caproic acid.

Division of abscissa and ordinate as in fig. 1.

of salicylic acid of alkali-cations added in the form of neutral salts. Here it was proved that the inhibitory influence of these cations on the charge of salicylic acid, was effected according to the lyotrope series



We now wished to observe the action of the other cations. The action of alkali-earths on the charge of salicylic acid appeared to fall short of that of the alkalis. This could be established in two concentrations of salicylic acid.

Magnesium marks a transition to some extent, since in weaker concentrations it impedes the charge more than Li, Na, K and Rb, and is second only to caesium, while this inhibition in a higher concentration of the cation does not increase so rapidly as with rubidium, and far less quickly than with the other alkali-metals, so that the inhibitory effect of the latter often exceeds¹⁾ that of Magnesium.

¹⁾ With 0.005 n. salt.

If we take a weak ¹⁾ concentration of salicylic acid, the inhibitory influence of alkali-earths far exceeds that of sodium, and, if we except magnesium, which is now farther removed from the alkalis than calcium, strontium and barium, they form together the lyotrope series more distinctly than in a higher salicylic acid concentration ²⁾, so that the series $\text{Ca, Sr} < \text{Ba}$ is more distinct. Chlorides of zinc, cadmium and lead, all bivalent in this combination, form a progressive series $\text{Zn} < \text{Cd} < \text{Pb}$. Still stronger is the inhibition of bismuth and aluminium-compounds, both trivalent.

The study of the influence of the chlorides of alkali-earths becomes, however, somewhat complicated, because, in a certain concentration, these salts are of themselves able to impart a very weak charge to the nebula.

Still more than by the cation, the action of neutral salts on the electrifying power of salicylic acid is determined by the nature of the anion. This influence has been observed in a series of potassium salts (Table 2). In case no potassium salt was at our disposal, as with tartaric acid, we took sodium-chloride and its action was compared with that of NaCl, acetat Na and KNa tartrate and interpolated in the potassium-series. In this way a distinct lyotrope series is obtained: $\text{CNS, NO}_3 < \text{Id, Cl, Br} < \text{C}_2\text{H}_3\text{O}_2 < \text{Tartr.} < \text{Phosph.} < \text{Cit.} < \text{Sulph.}$

The univalent acids of this series present inter se smaller differences than the bivalent tartrates, the neutral phosphates, the citrates, and the sulphates. Still we can observe in concentrations of 0,001 n, 0,002 n, and 0,005 n more marked differences between the univalent anions themselves. Sulphohydrocyanic acid causes the least inhibition of the charge of salicylic acid; sulphate and citrate act most strongly; the differences between these two extremes are great.

In spraying solutions of salicylic acid, containing neutral salts, the anion is the principal agent in inhibiting the charge of this acid, so that the lyotrope series are much more pronounced for the anion than for the cation; in those of the cations the terms of every group of metals are distinguishable, but there is no regular succession of those groups. In order to estimate the nature of these differences, obtained with a negative sign, we ascertained whether acids, giving a positive sign, such as acetic acid, behave in a similar way. The charge of acetic acid was increased by the addition of neutral salts, so that here, not the factor of inhibition, as was the case with the negative phase of salicylic acid, but that of the increase

¹⁾ At 0.0005 n.

²⁾ 0.001 n.

had to be determined¹⁾ We now tried to find out if the lyotropic series also held for the increase of charge of *acetic acid*. For the cations (Fig. 3) we chose Na, K, Am, Mg, Ca and Ba, because for them *acetic acid* compounds were not at our disposition, so that

TABLE 1. *Influence of cations on the charge of salicylic acid.*
Factor decreasing the deflection of the electroscope, when instead of salicylic acid being sprayed alone, this acid is sprayed with an addition of the chlorides of the subjoined metals.
a. 0.001 n. solution of salicylic acid.

Concentration cation (as chloride)	Li	Na	K	Rb	Cs	Am	Ca	Sr	Ba	Mg	Zn	Cd	Pb	Bi	Al
0.01 n.	8	8	∞				∞	∞	-				18		
0.005 n.	9.6	10.1	∞	∞			5.04	4.94	5.12	4.68	8	7.25	12	8	
0.0025 n.	3.08	3.48	4.9	4.8			2.87	3.15	3.26	4.24	3.6	4.14	4.30	8	
0.002 n.	2.57	2.86	2.69	4.0		∞									
0.0015 n.						6.2									
0.001 n.	1.68	2.27	1.95	2.36	2.90	4.3	1.77	1.85	1.88	2.55	1.8	2.50	2.50	8	16
0.0005 n.	1.35	1.40	1.49	1.67	1.77	2.20	1.52	1.52	1.52	1.95	1.55	1.77	1.80	3.0	16
0.00025 n.	1.05	1.14	1.30	1.40	1.42	1.50	1.16	1.16	1.32	1.46	1.09	1.53		1.4	12
0.000125 n.		1.07		1.20						1.22					
0.0001 n.															2.4
0.00005 n.															1.5
0.000025 n.															1.2
<i>b. 0.0005 normal solution of salicylic acid.</i>															
0.001 n.		2.18					2.54	3.02	3.32	3.86					4.5
0.0005 n.		1.81					2.06	1.93	2.20	2.71					
0.00025 n.		1.31					1.52	1.41	1.55	1.95					
0.000125 n.		1.07					1.17	1.12	1.24	1.69					

N. B. The chlorides of the alkalis do not charge, those of the other metals have only a slight charge (maximum 0.8 with MgCl_2 ; with the others in the solutions used, at most 0.2 scale division).

¹⁾ Not all substances giving a positive charge, give a stronger charge under the influence of neutral salts, as has already been established by BACKMANN from Upsala (for some time at Ulrecht) (Ueber die Verstäubungselektrizität der Riechstoffe,

the influence of the anion was reduced to a minimum; still, besides these acetates also common salt was used as a sodium-salt for purposes of comparison.

TABLE II.

Influence of anions on the charge of salicylic acid (0.001 n.)

Factor decreasing the deflection of the electroscope, when instead of salicylic acid being sprayed alone, this acid is sprayed with an addition of the Potassiumsalts of the subjoined acids.

Concentration anion	KCNS	KNO ₃	KI	KCl	KBr	KC ₂ H ₃ O ₂	KNa tartrate	K phosph.	K citrate	K sulfate
0.01 n.	8	8	8	8	8	8	8	8	8	8
0.005 n.	13.3	13.3	36.5	36.5	36.5	45	8	8	8	8
0.0025 n.	—	15	10	—	10	8	19	8	8	8
0.002 n.	4	4	6.2	6.1	6.2	5.5	12	60	73	8
0.001 n.	2.1	2.2	2.4	2.4	2.4	2.7	2.64	5	3—6	5—6
0.0005 n.	1.5	1.4	1.5	1.4	1.5	1.7	1.61	2.4	2.1—2.5	2.2
0.00025 n.	1.3	1.25	1.3	1.2	1.3	1.2	1.22	1.4	1.4—1.6	—

Plüger's Archiv 168, 351—71, 1917, p. 360, 361) True, this was the case with most of the solutions examined by BACKMANN, with some the charge was decreased under the influence of salts, nay even arrested. This could also be established a new by us for some substances.

A distinct lyotropia $\text{Na} < \text{K} < \text{Am}$ was established; ¹⁾ to a certain extent also $\text{Mg} < \text{Ca} < \text{Ba}$? The increase of charge through alkali-earths was, in lower concentrations, lower than that of alkalis. It was somewhat difficult to determine the charge because the solutions of the acetates of the alkali-earths of themselves impart a weak charge to a screen placed in the nebula. Magnesium again occupied the same peculiar place that it took up in the case of salicylic acid,

TABLE III.

Strengthening influence of Cations on the charge of acetic acid (0.1 normal).

Factor increasing the deflection of the electroscope, when instead of 0.1 n. acetic acid being sprayed alone, 0.1 n. acetic acid is sprayed with addition of the acetate of the subjoined alkalis and alkali-earths.
(NaCl as a control).

Concentration Cation	NaCl	Acetas Na	Acetas K	Acetas Am.	Acetas Mg ¹⁾	Acetas Ca ¹⁾	Acetas Ba ¹⁾
0.01 n.		4.4	5.1	4.85	4.1	4.0	4.6
0.005 n.	2.2	3.1	3.5	4.4	3.12	3.4	3.1
0.0025 n.	2.0	2.15	2.3	3.15	2.12	2.36	2.35
0.002 n.	1.8		2.2	2.7	1.87	1.91	1.95
0.001 n.	1.55	1.4	1.78	2.2	1.37	1.43	1.45
0.0005 n.	1.35	1.3	1.35	1.8	1.08	1.29	1.20
0.00025 n.	1.24	1.1		1.3			
0.0002 n.		1.05		1.05			
0.0001 n.	1.05						

¹⁾ Charge of these acetates: 0.01—0.02 n. charges 0.4—0.7; 0.002 n. charges 0—0.2 scaledivision.

Charge of NaCl and of the alkali acetate = 0. The increase of the charge of the alkali-earths is not greater than that of the alkalis; in weak concentrations (0.002—0.005 n) even smaller.

it was almost equal to sodium, its action was decidedly weaker than that of potassium and ammonium, and it also here constituted the transition from alkalis to alkali-earths. The lyotropia of the anions appeared to be more intense and more general than that of

¹⁾ In another set of experiments with alkali chlorids the series $\text{Li} < \text{Na}, \text{K} < \text{Rb}, < \text{Cs} < \text{Am}$ was obtained.

TABLE IV.

Strengthening influence of anions on the charge of acetic acid (0.1 n).

Factor increasing the deflection of the electroscope, when instead of 0.1 n. acetic acid being sprayed alone, 0.1 n. acetic acid with the additions of the K (and Na) salts of the subjoined acids is sprayed.

Concentration anion	<i>a. Potassium salts.</i>										<i>b. Sodium salts.</i>		
	KCNS	KNO ₃	KI	KCl	KBr	KC ₂ H ₃ O ₂	KNa tartrate	K phosph.	K citrate	K sulphate	NaCl	Acetas Na	Tartrate Na
0.01 n.		5.1				5.39	6.43		> 7			4.85	> 6
0.005 n.	3.85	3.68	3.95	3.63	3.55	4.39	4.43	5.5	5.16	4.56	2.2	4.4	4.75
0.0025 n.	2.70	3.00	3.00	2.70	2.77	2.8	3.07	3.6	3.68	3.56	2.0	3.15	3.3
0.002 n.	2.40	2.50	2.65	2.30	2.37	2.61	2.57	2.93	3.16	2.96	1.8	2.7	3.0
0.001 n.	1.80	2.05	2.20	1.70	1.59	1.8	1.57	2.11	2.21	2.16	1.55	2.2	2.3
0.0005 n.	1.60		1.65	1.4	1.42	1.4	1.36	1.61	1.63	1.92	1.35	1.8	1.7
0.00025 n.	1.35	1.42	1.45	1.2	1.35	—		1.28	1.48	1.45	1.24	1.3	1.5
0.0002 n.		1.32				1.3		1.22	1.32	1.28		1.05	1.15
0.0001 n.											1.05		

the cations (Table 4). It is evident that chloride takes up the lowest place in the series of anions, citrate stands at the top:

$\text{Cl} < \text{CNS}, \text{NO}_3 < \text{Br}, \text{J} < \text{C}_2\text{H}_3\text{O}_2 < \text{Tartr.} < \text{Phosph.} < \text{Sulph.} < \text{Citr.}$

This series of anions differs only very little from that of salicylic acid.

With acetic acid as well as with salicylic acid the differences between the extreme terms of the lyotrope series appear to be larger with the anions than with the cations.

S U M M A R Y.

1. *Salicylic acid*, if not in a completely saturated solution, gives a *negative charge*, that is weakened by cations and anions in a lyotrope-series, in the direction from Li to Cs and from chloride to sulphate.

2. *Acetic acid*, when dissolved in water in a sufficient concentration, gives a *positive charge* increased by cations and anions, for the greater part in a lyotrope-series in the direction from Li to Cs and from Chloride to Sulphate.

3. *Acetic acid* weakens, resp. arrests, the negative charge of salicylic acid. In higher concentrations with a positive electrical phase it prevails, as an acid, over salicylic acid sprayed in weak solutions, which gives a negative charge. As appeared already sub. 1, acetates also have a weakening effect on the charge of salicylic acid, whereas, of themselves — at all events the alkali-acetates (the acetates of the other metals give a very slight charge) — they produce no charge.

Mixtures of salicylic acid showed the electrical property of acetic acid, so long as the latter acid predominates. If the concentration of acetic acid in the salicylic-acid acetic acid mixture decreases to such an extent that such an acetic-acid solution gives of itself hardly any charge at all, the charge of the mixture will at one moment be $= 0$; in still lower concentrations of acetic-acid the charge appears again, this time of a negative sign. There is a moment when the favourable action of the cations on the acetic acid is arrested by the inhibitory effect of these cations on the salicylic acid.

Mathematics. — “*Observations on the development of a function in a series of factorials*”. I. By Dr. H. B. A. BOCKWINKEL.
(Communicated by Prof. H. A. LORENTZ)

(Communicated in the meeting of June 29, 1918).

1. In his book “*Theorie der Gammafunktion*” N. NIELSEN gives the necessary and sufficient conditions for the development of a function in a series of factorials. According to him the following proposition holds:

The necessary and sufficient condition that a function $\Omega(x)$ may be developed in a series of factorials, is that $\Omega(x)$ may be represented as a definite integral of the form

$$\Omega(x) = \int_0^1 g(t) (1-t)^{x-1} dt, \quad (1)$$

where $\varphi(t)$ is a function with the following properties:

1. $\varphi(t)$ is regular within a circle, centre the origin and with a radius no smaller than unity, so that it may be expanded in a power-series:

$$\varphi(t) = a_0 + a_1 t + \dots + a_n t^n + \dots (2)$$

2. If $\varphi^{(p)}(t)$ is the first of the derivatives of $\varphi(t)$ which is infinite for $t=1$, then there is a real number λ such that

$$\lim_{t \rightarrow 1} \varphi^{(p)}(t) \sim (1-t)^{-(\lambda+p+1)} (3)$$

¹⁾ By this notation we mean that $\lim_{t \rightarrow 1} (1-t)^{\lambda+p+\delta} \varphi^{(p)}(t) = 0$ or ∞ , according as $\delta > 0$ or $\delta < 0$. We may express this by saying that $\varphi^{(p)}(t)$ is, for $t=1$, equivalent to $(1-t)^{-(\lambda+p)}$. Since $\varphi^{(p)}(1)$ is supposed infinite, we have $\lambda+p > 0$. Further it follows from a well-known proposition (DINI, Grundlagen für eine Theorie der Funktionen einer reellen Grösse, p. 104) that, if $\varphi(t)$ is itself finite for $t=1$, i.e. if $p \geq 1$, we must have $\lambda+p < 1$. For, if we had $\lambda+p > 1$, then $\varphi^{(p-1)}(t)$ would, according to that proposition, also be infinite, being equivalent to $(1-t)^{-(\lambda+p-1)}$, which is contrary to the hypothesis that $\varphi^{(p)}(t)$ should be the first of the derivatives infinite for $t=1$. We have therefore

$$0 < \lambda+p < 1, \quad \text{for } p \geq 1. (4)$$

from which it follows that λ is never positive in this case. If, on the other hand, $\varphi(t)$ is itself infinite for $t=1$, it is, according to (3), equivalent to $(1-t)^{-\lambda}$, and then λ is not negative.

3. There exists a real number λ' with the property that, corresponding to any assigned number ε , however small, an integer N may be chosen, such that we have, *uniformly* in an interval $0 \leq t \leq \delta$, which, for the rest, we may think as small as we please

$$\left| \frac{\varphi^{(n)}(t) (1-t)^{x+n}}{\Gamma(x+n+1)} \right| < \frac{\varepsilon}{n!} \quad \text{for } n > N \quad (5)$$

according as $R(x) > \lambda'$ or $R(x) < \lambda'$. ($R(x)$ means the real part of x).

The series of factorials corresponding to an integral of the form (1) is

$$\frac{a_0}{x} + \frac{a_1}{x(x+1)} + \frac{2! a_2}{x(x+1)(x+2)} + \dots + \frac{n! a_n}{x(x+1)\dots(x+n)} + \dots \quad (6)$$

where a_0, a_1, \dots are the coefficients of the power-series (2).

This series converges, according to NIELSEN, for the values of x satisfying the two conditions

$$R(x) > \lambda, \quad \text{and} \quad R(x) > \lambda' \quad (7)$$

and if at least one of the two characteristics λ and λ' is not negative, the series (6) will represent the integral (1) for the values of x mentioned¹⁾.

From the first of the inequalities (5), applied for $t=0$, and from the consideration that

$$a_n = \frac{\varphi^{(n)}(0)}{n!}, \quad (9)$$

it may at once be derived that the series (6) converges *absolutely* for $R(x) < \lambda' + 1$. In connection with (7) NIELSEN therefore infers that the number λ is at most equal to $\lambda' + 1$.

The thing to be remarked in the statement of NIELSEN is however

¹⁾ If λ and λ' are both negative, so that $\varphi(t)$ is finite for $t=1$, the integral (1) has in general only a meaning for $R(x) > 0$, and the development in question is valuable for these values of x only. But then we may consider the integral

$$\Omega_p(x) = \int_0^1 \frac{\varphi^{(p)}(t) (1-t)^{x+p-1} dt}{x(x+1)\dots(x+p-1)} \quad (8)$$

which has a meaning for $R(x) > \lambda$. To this integral a certain *remainder* of the series (6), viz.

$$\frac{p! a_p}{x(x+1)\dots(x+p)} + \frac{(p+1)! a_{p+1}}{x(x+1)\dots(x+p+1)} + \dots \quad (8')$$

corresponds and the integral would then be equal to this remainder for the values of x determined by (7).

that, if $\lambda < \lambda' + 1$, there is a certain domain on the left of $R(x) = \lambda' + 1$, where the series (6) converges *conditionally*. If

$$\lambda' < \lambda < \lambda' + 1$$

this convergence takes place in a strip of the plane determined by

$$\lambda < R(x) < \lambda' + 1$$

and if

$$\lambda \geq \lambda'$$

in one determined by

$$\lambda' < R(x) < \lambda' + 1.$$

This is remarkable, because PINCHERLE ¹⁾, who has also published some notes on series of factorials, does not mention the case of *conditional* convergence. And in order to state at once our point of view, we declare not to understand the reasoning of NIELSEN from which the conditional convergence within the domain mentioned would follow; it is even our opinion, as we are going to explain directly, that from his investigations only the validity of his statement follows for the values of x satisfying both the conditions $R(x) > \lambda' + 1$ and $R(x) > \lambda + 1$. The example given by NIELSEN of the development of an integral such as (1) in a *conditionally* converging series is exact, and it is not difficult, as it will be seen, to add others to it. But in reflecting on the subject we have finished to doubt of the general validity of the *special* theorem of NIELSEN. In any case, for the strong proof of it investigations of a farther reaching extent would, in our opinion, be necessary.

2. The mode in which NIELSEN arrives at the development (6) consists in integrating by parts the integral (1): this gives immediately

$$\int_0^1 \varphi(t) (1-t)^{x-1} dt = \frac{a_0}{-x} + \frac{a_1}{x(x+1)} + \dots + \frac{(n-1)! a_{n-1}}{x(x+1) \dots (x+n-1)} + R_n \quad (10)$$

where

$$R_n = \Gamma(x) \int_0^1 \frac{\varphi^{(n)}(t) (1-t)^{x+n-1}}{\Gamma(x+n)} dt \quad \dots \quad (11)$$

From the condition 2° NIELSEN derives that the first of the inequalities of (5) will be valid for an interval $\delta < t < 1$, if $R(x) > \lambda$. Here the quantity δ may be conceived arbitrarily small; it must of course be understood that the choice of the integral number N is influenced by it, and that N will increase indefinitely with $1/\delta$.

¹⁾ Rendic. d. R. Acc. d. Lincei (1903, 2e Sem.).

For this reason NIELSEN has to add the new condition under 3° expressing that the inequality (5) is also valid for an interval $0 \leq t \leq \delta$ for values of x lying in the half-plane on the right of $R(x) = \lambda'$. Then it follows from the reasoning just mentioned, in connection with the condition 3° that the remainder given by (11) certainly approaches to zero for $n = \infty$, if we have at the same time

$$R(x) > \lambda' + 1, \text{ and } R(x) > \lambda + 1 \quad . \quad . \quad . \quad (12)$$

For we may write

$$R_n = \Gamma(x) \int_0^1 \frac{\varphi^{(n)}(t) (1-t)^{x-1+n}}{\Gamma(x-1+n+1)} dt,$$

and since $R(x-1)$ is both greater than λ' and greater than λ , the function under the sign of integration *uniformly* approaches to zero in the interval $0 \leq t \leq 1$, as n becomes indefinitely large. But nothing more can, in our opinion, be derived from the reasoning of NIELSEN.

It is remarkable that in his book the author gives the equality (10) in an erroneous form, in such a manner that under the sign of integration a derivative of $\varphi(t)$ occurs of an order too high by one unity; and it might therefore be supposed that this circumstance has led NIELSEN to his erroneous conclusion. But in a memoir published by him in *Annal. de l'Ecole Normale* (1902) the formula (10) occurs in a right manner, and still NIELSEN draws his conclusion without any further explanation. It would have been of interest, if the author had explained a little more amply how he arrived at it. It seems not impossible that the example given by him, and perhaps others, have led him to the erroneous opinion that his theorem should have been proved by the reasoning he has given.

3. Nevertheless this theorem might be right and then, of course, there is every reason to introduce the characteristic number λ together with λ' . But still it seems not unuseful to show that we may develop the integral (1) in an *absolutely* converging series of factorials under the only conditions 1° and 3°, and then for $R(x) > \lambda' + 1$. We shall even restrict the latter condition a little: not assume that the inequality occurring in it is satisfied for a certain small interval $(0, \delta)$ of t , but only for the endpoint $t = 0$. Since the values of the different derivatives of $\varphi(t)$ in $t = 0$ depend on the coefficients of the power-series of that function by means of the formula

$$a_n = \frac{\varphi^{(n)}(0)}{n!} \quad . \quad . \quad . \quad . \quad . \quad . \quad (13)$$

this supposition amounts to the following as to those coefficients themselves:

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3a°. The coefficients a_n of the power-series for $\varphi(t)$ satisfy the condition

$$\overline{\lim}_{n=\infty} \frac{a_n}{n^{\lambda'+\delta}} = \begin{cases} 0 & \text{for } \delta > 0 \\ \infty & \text{for } \delta < 0 \end{cases} \quad (14)$$

which we shall denote shortly by writing

$$\overline{\lim}_{n=\infty} a_n \sim n^{\lambda'} \quad (14')$$

and by saying that the upper limit of a_n for $n = \infty$ is *equivalent* to $n^{\lambda'}$. We write intentionally the sign of *upper* limit, because this will do for our purpose; it is not necessary to suppose that the coefficients a_n have a "croissance régulière".

From the only supposition 3a° it may already be derived that the part of the earlier condition 3° corresponding to the first of the inequalities (5) is *uniformly* satisfied in the whole interval (0,1) of the variable t , provided we add a factor $(1-t)$. To prove this we compare, for large values of n , the n^{th} derivative of $\varphi(t)$

$$\varphi^{(n)}(t) = \Gamma(n+1) a_n + \frac{\Gamma(n+2)}{1!} a_{n+1} t + \dots + \frac{\Gamma(n+s+1)}{s!} a_{n+s} t^s + \dots \quad (15)$$

with the n^{th} derivative of the function

$$f(t) = \frac{\Gamma(\lambda' + \delta + 1)}{(1-t)^{\lambda'+\delta+1}}$$

that is

$$\begin{aligned} f^{(n)}(t) &= \frac{\Gamma(\lambda' + \delta + n + 1)}{(1-t)^{\lambda'+\delta+n+1}} = \\ &= \Gamma(\lambda' + \delta + n + 1) + \frac{\Gamma(\lambda' + \delta + n + 2)}{1!} t + \dots + \frac{\Gamma(\lambda' + \delta + n + 1 + s)}{s!} t^s + \dots \quad (16) \end{aligned}$$

Here δ is a certain positive number. However small we may choose this, there is always, on account of our condition 3a° corresponding to any arbitrarily small number ε an integer N such that for all values of $s \geq 0$

$$|a_{n+s}| < \varepsilon \frac{\Gamma(\lambda' + \delta + n + s + 1)}{\Gamma(n + s + 1)}$$

Thus we have *uniformly* in the interval $0 < t < 1$

$$\frac{(1-t)^{\lambda'+\delta+n+1} \overline{\varphi}^{(n)}(t)}{\Gamma(\lambda' + \delta + n + 1)} < \varepsilon, \quad \text{for } n > N \quad (17),$$

here $\overline{\varphi}(t)$ means the *natural majorant* of $\varphi(t)$ determined by

$$\overline{\varphi}(t) = |a_0| + |a_1| t + \dots + |a_n| t^n + \dots$$

The same inequality a fortiori holds for $\varphi(t)$ itself, and since δ can be taken arbitrarily small, it follows that the integral (11),

denoting the rest of the series of factorials in question, has zero as a limit for $n = \infty$, if $R(x) > \lambda' + 1$, and thus that for these values of x development of the integral (1) in such a series is possible. That this series for these values of x converges *absolutely*, may, as we had already occasion to remark, as well immediately be derived from $3a^0$.

4. We make the following remarks: 1st. The proposition proved just now may be compared with a result due to CESARÒ¹⁾, according to which it follows from the condition $3a^0$ that the inequality (17), for $\lim t = 1$, is already valid from and after the value $n = 0$.

2nd. In our result, and in that of CESARÒ, is included that the number λ , introduced by NIELSEN, is for the natural majorant of $\varphi(t)$ exactly equal to $\lambda' + 1$ ²⁾, whereas for the function itself it is in any case not greater; thus we have

$$\lambda \leq \lambda' + 1, \text{ and } \bar{\lambda} = \lambda' + 1 \quad . \quad . \quad . \quad (18)$$

if $\bar{\lambda}$ is the number in question for $\bar{\varphi}(t)$. This result, derived by NIELSEN from his theorem, can therefore, if our opinion with regard to the inexactness of NIELSEN's proof is right, no more be regarded as deduced by him.

3rd. We may also easily prove that inversally every series of factorials such as (6), if it converges at all, is equal to an integral of the form (1), where $\varphi(t)$ satisfies the conditions under 1° and $3a^0$. In fact, if such a series converges for a certain value $\alpha + i\beta$ of x , the limit of the terms must be zero for that value. Now we have

$$\lim_{n \rightarrow \infty} \frac{n!}{x(x+1) \dots (x+n)} = \frac{1}{n^\alpha}$$

from which it follows that the coefficients a_n of the series of factorials satisfy the condition

$$\overline{\lim}_{n \rightarrow \infty} a_n \leq n^\lambda,$$

where λ' is a certain real number which is at most equal to α , but may be equal to $-\infty$. If now we form with the coefficients a_n a function $\varphi(t)$ as in (2), this function has the properties expressed in the conditions 1° and $3a^0$, and, as we proved in the foregoing paragraph, the given series of factorials is equal to the integral (1) for $R(x) > \lambda' + 1$; at least, if $\lambda' + 1 > 0$, for if not, we should say

¹⁾ Acc. d. Scienze fisiche e matematiche di Napoli, 1893. See also BOREL, Leçons sur les séries à termes positifs.

²⁾ At least when a_n has a "croissance régulière"; otherwise it may be smaller than $\lambda' + 1$, but no smaller than λ' .

that a certain *remainder* of the given series is equal to an integral of the form (8) in the footnote of p. 429.

4. If the coefficients a_n in the power-series for $\varphi(t)$ are real, we can assign one definite case in which the series converges *conditionally*, for $R(x) > \lambda'$, viz. if all derivatives of an order higher than some definite number have the property of conserving the same sign throughout the interval $0 \leq t < 1$, and this in such a way that always two immediately succeeding derivatives are of *opposite* signs. This result can be deduced from the equality

$$R_n - R_{n+1} = \frac{n! a_n}{x(x+1) \dots (x+n)} \dots \dots \dots (19)$$

where R_n has the meaning given by (11). First let x be equal to a real number α . Then R_n and $-R_{n+1}$ have the same sign throughout the interval of t , so that either of them is smaller, in absolute value, than the series-term in the right-hand member of (19). If therefore the latter has zero for its limit, then also R_n , and this is the case for $\alpha > \lambda'$, since $\lim a_n = n^{\lambda'}$.

If x is complex $= \alpha + i\beta$ and $\alpha > \lambda'$, we have

$$\begin{aligned} |R_n| &< \int_0^1 \left| \frac{\varphi^{(n)}(t) (1-t)^{x+n-1}}{x(x+1) \dots (x+n-1)} \right| dt \\ &< \left| \frac{\alpha(\alpha+1) \dots (\alpha+n-1)}{\alpha+i\beta \dots (\alpha+i\beta+n-1)} \right| \int_0^1 \frac{\varphi^{(n)}(t) (1-t)^{\alpha+n-1}}{\alpha(\alpha+1) \dots (\alpha+n-1)} dt. \end{aligned}$$

The latter integral is equal to R_n for $x = \alpha$ and therefore, as we showed, zero for $n = \infty$; the factor by which this integral has to be multiplied evidently has a modulus smaller than unity; thus R_n approaches to zero as n increases indefinitely.

As an illustration we take the example of NIELSEN

$$a(x) = \int_0^1 \frac{(1-t)^{x-1}}{1+t} dt,$$

where

$$\varphi(t) = \frac{1}{1+t}, \quad \lambda = -\infty, \quad \lambda' = 0.$$

This function $\varphi(t)$ satisfies the special condition mentioned in the present remark, and on account of this circumstance we may deduce the possibility of developing the function $a(x)$ into a series of factorials for $R(x) > \lambda'$, this series converging but *conditionally* if $R(x) < \lambda' + 1$. Other examples to illustrate his theorem, especially such that do not

satisfy the *special* condition mentioned here, are not given by NIELSEN, but may easily be imagined.

5. Finally we want to make a remark on another manner to derive the development (6) from the series (2); a way which has been followed both by PINCHERLE and by NIELSEN. We may write $\varphi(t)(1-t)^{x-1} = a_0(1-t)^{x-1} + a_1 t(1-t)^{x-1} + \dots + a_n t^n(1-t)^{x-1} + \dots$, and thus

$$\int_0^1 \varphi(t)(1-t)^{x-1} dt = \int_0^1 [a_0(1-t)^{x-1} + \dots + a_n t^n(1-t)^{x-1} + \dots] dt.$$

If this series is integrated term by term between the limits 0 and 1, we obtain the series of factorials required. In case the latter converges, NIELSEN (p. 239, Handbuch) derives from it that this series is equal to the integral in the left-hand member of the preceding equation; his reasoning is based upon a certain proposition of DINI (Grundlagen, p. 523). If this reasoning were right, then, besides the special case treated of above, we should have a more general one, in which the integral (1) may be developed into a conditionally converging series of factorials: viz. always when the series of factorials to be derived from that integral, whether by means of integration by parts or in the manner described just now, is a converging one.

But, in our opinion, the proposition of DINI in question has been applied in a wrong manner by NIELSEN. The fact is that, in applying that proposition, we should first integrate the function in question over the interval $0 < t < u$, where $u < 1$. Now it is at once to be seen that *in such an interval* we may integrate the above series term by term (on account of its *uniform* convergence in that interval); in other words we shall have

$$\begin{aligned} & \int_0^u \varphi(t)(1-t)^{x-1} dt = \\ & = a_0 \int_0^u (1-t)^{x-1} dt + a_1 \int_0^u t(1-t)^{x-1} dt + \dots + a_n \int_0^u t^n(1-t)^{x-1} dt + \dots, \end{aligned} \quad (20)$$

this equation being valid, however little u differs from unity. The left-hand member of this equation is *by definition* equal to the integral (1). But the right-hand member is only then equal to the series of limit-integrals, if this member, considered as a function of u , is continuous on the left in the point $u = 1$. This condition is explicitly added by DINI, but seems to have been forgotten by

NIELSEN. There is not any simple indication that it would always be satisfied. Only in the case of *absolute* convergence of the series of integrals for $u = 1$, i. e. when $R(x) > \lambda' + 1$, this is realized, because the series (20) then converges at the same time *uniformly* in the closed interval $0 \leq u \leq 1$, and therefore represents, according to a well-known proposition, a continuous function of u in that interval ¹⁾.

¹⁾ The reasoning of PINCHERLE, who, as already remarked, treats of *absolute* convergence only, seems to be incorrect to us. It is based upon his writing for the separate integrals of the series (20), if we replace u by $1 - \varepsilon$,

$$\int_0^{1-\varepsilon} t^n (1-t)^{x-1} dt = \frac{(1-\varepsilon^n + \varepsilon) n!}{x(x+1) \dots (x+n)},$$

which is wrong. If this could be done, the limit of the series (20) would indeed be equal to the series of the individual limits of its terms, if the latter converged, *even if this convergence took place only conditionally*. It seems therefore not superfluous that, in the last sentence of the present paragraph, we have called attention to the strong way in which the idea of integration term by term may be used to prove the possibility of developing the integral (1) into an *absolutely* converging series of factorials.

Physics. — “*Le tenseur gravifique*”. By TH. DE DONDER. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of June 30, 1918).

Dans une note parue dans ce recueil ¹⁾, j'ai obtenu un tenseur gravifique $t_{\lambda\mu}$ répondant à toutes les exigences de la relativité générale.

Au cours de ses recherches sur le champ gravifique, M. LORENTZ ²⁾ a trouvé le même tenseur gravifique.

Dans ce travail, nous donnons *explicitement* la valeur du tenseur gravifique $t_{\lambda\mu}$, et nous en déduisons la valeur explicite du tenseur $t_{\lambda\mu} + T_{\lambda\mu}$; on remarquera que dans celui-ci *tous les termes de $t_{\lambda\mu}$ renfermant des dérivées secondes des potentiels gravifiques ont disparu.*

Nous montrons ensuite que dans tout champ gravifique et électromagnétique, la *force généralisée* F_{λ} ($\lambda = 1, 2, 3, 4$) *est nulle*. Ce résultat est obtenu aussi au moyen de l'identité de HILBERT; les F_{λ} sont encore nuls dans tout champ gravifique renfermant de la matière; ce résultat est indépendant du tenseur gravifique choisi.

Dans le chapitre suivant, nous étudions divers tenseurs gravifiques, et nous indiquons une correction à effectuer sur le tenseur gravifique d'EINSTEIN ³⁾.

Etant donnée l'importance du champ gravifique d'EINSTEIN—SCHWARZSCHILD, nous avons cru utile de calculer le $t_{\lambda\mu}$ relatif à ce champ.

Nous montrons ensuite que $\sum_{\lambda} t_{\lambda\lambda}$ est indépendant des dérivées secondes des potentiels gravifiques.

Enfin, il résulte de la covariance de $t_{\lambda\mu}$, que celui-ci est *cogrédient* au tenseur électromagnétique $T_{\lambda\mu}$ pour tout changement *linéaire* des variables x_1, x_2, x_3, x_4 .

I. Valeur explicite du tenseur gravifique $t_{\lambda\mu}$.

Rappelons tout d'abord la valeur de ce tenseur gravifique:

¹⁾ TH. DE DONDER. Verslag Koninkl. Akad. v. Wetenschappen. Amsterdam. Deel XXV. 27 Mei 1916.

²⁾ H. A. LORENTZ. Verslag Koninkl. Akad. v. Wetenschappen. Amsterdam. Deel XXV. 24 Juni 1916.

³⁾ A. EINSTEIN. Sitzungsberichte Akad. d. Wissenschaften. Berlin. 26 Oktober 1916

$$t_{\lambda,\mu} \equiv \varepsilon_{\lambda,\mu} l - \sum_{ab} \left[\left(\frac{dl}{dg_{ab,\mu}} - \frac{1}{2} \sum_i \frac{d(1+\varepsilon_{\mu i})}{dx_i} \frac{dl}{dg_{ab,\mu i}} \right) g_{ab,\lambda} + \right. \\ \left. + \frac{1}{2} \sum_i (1+\varepsilon_{\mu i}) \frac{dl}{dg_{ab,\mu i}} g_{ab,\lambda i} \right] \quad (1)$$

où

$$l \equiv kC (-g)^{1/2}$$

$$C \equiv \frac{1}{2} \sum_i \sum_m \sum_j \sum_l g^{jl} g^{im} (ij, lm);$$

C est l'invariant de courbure totale de RIEMANN relatif à la forme quadratique différentielle:

$$\sum_i \sum_k g_{ik} dx_i dx_k. \quad (2)$$

On a aussi posé:

$$g_{ab,\mu} \equiv \frac{dg_{ab}}{dx_\mu}, \quad g_{ab,\mu i} \equiv \frac{d^2 g_{ab}}{dx_\mu dx_i}.$$

D'autre part, on a: $\varepsilon_{\lambda\lambda} \equiv 1$, $\varepsilon_{\lambda\mu} \equiv 0$ ($\lambda \neq \mu$); \sum_{ab} indique une sommation étendue aux 10 combinaisons avec répétition des nombres 1, 2, 3, 4 pris 2 à 2.

En dérivant l par rapport aux $g_{ab,\mu}$ et en permutant les indices, on obtient le résultat suivant:

$$\frac{dl}{dg_{ab,\mu}} = k(-g)^{1/2} \left(1 - \frac{\varepsilon_{ab}}{2} \right) \sum_h \sum_l \sum_\alpha \left[\begin{matrix} h & l \\ & \alpha \end{matrix} \right] \left\{ \begin{matrix} g^{a\alpha} (g^{b\mu} g^{lh} - g^{lb} g^{h\mu}) \\ + g^{b\alpha} (g^{a\mu} g^{lh} - g^{l\mu} g^{ha}) \\ - g^{a\alpha} (g^{ab} g^{lh} - g^{la} g^{hb}) \end{matrix} \right\}.$$

En dérivant de même l par rapport aux $g_{ab,\mu i}$ et en réduisant les termes semblables, on obtient:

$$\frac{dl}{dg_{ab,\mu i}} = k(-g)^{1/2} \left(1 - \frac{\varepsilon_{i\mu}}{2} \right) \left(1 - \frac{\varepsilon_{ab}}{2} \right) (2g^{i\mu} g^{ab} - g^{a\mu} g^{bi} - g^{b\mu} g^{ai}).$$

Substituons ces expressions dans (1), et utilisons la formule:

$$\frac{d(-g)^{1/2}}{dx_i} = \frac{1}{2} (-g)^{1/2} \sum_\alpha \sum_\beta g^{\alpha\beta} g_{\alpha\beta,i} = -\frac{1}{2} (-g)^{1/2} \sum_\alpha \sum_\beta g_{\alpha\beta} g^{\alpha\beta,i}.$$

Après quelques réductions obtenues en permutant les indices, on a enfin:

$$t_{\lambda,\mu} = \varepsilon_{\lambda,\mu} l + \frac{k}{4} (-g)^{1/2} \sum_a \sum_b \sum_i \sum_h \sum_\alpha [2g^{ah,h} g^{\mu b} - g^{ab,h} g^{h\mu} + g_{hi,\alpha} g^{\alpha\alpha} g^{\mu b} g^{hi}] g_{ab,\lambda} - \\ - \frac{k}{2} (-g)^{1/2} \sum_a \sum_b \sum_i [g^{\mu i} g^{ab} - g^{a\mu} g^{bi}] g_{ab,\lambda i} \quad (3)$$

Cette expression de $t_{\lambda\mu}$ se simplifie encore en vertu de l'équation complémentaire $l=0$.

II. Valeur explicite du tenseur $t_{\lambda\mu} + T_{\lambda\mu}$.

Rappelons la valeur du tenseur électromagnétique¹⁾:

$$T_{\lambda\mu} = \sum_i (1 + \varepsilon_i) g^{\mu i} \hat{\Delta}^{\lambda i} l \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

Mais en vertu de l'identité²⁾:

$$(1 + \varepsilon_i) \hat{\Delta}^{\lambda i} l \equiv k(-g)^{1/2} \sum_{h,l} g^{hl} (ih, l\lambda) - k(-g)^{1/2} C g_{\lambda i}.$$

l'expression (4) peut s'écrire:

$$T_{\lambda\mu} = -\varepsilon_{\lambda\mu} l + k(-g)^{1/2} \sum_{h,l,i} g^{\mu i} g^{hl} (ih, l\lambda) \quad . \quad . \quad . \quad (5)$$

Rappelons aussi que la parenthèse à 4 indices de CHRISTOFFEL a la valeur suivante:

$$(ih, l\lambda) \equiv \frac{1}{2}(g_{i\lambda,hl} - g_{hl,il} - g_{il,h\lambda} + g_{hl,\lambda i}) + \sum_{\alpha,\beta} g^{\alpha\beta} \left(\begin{bmatrix} h & l \\ \alpha & \beta \end{bmatrix} \begin{bmatrix} \lambda & i \\ \alpha & \beta \end{bmatrix} - \begin{bmatrix} h & \lambda \\ \alpha & \beta \end{bmatrix} \begin{bmatrix} l & i \\ \alpha & \beta \end{bmatrix} \right).$$

Retournons maintenant à la valeur de $t_{\lambda\mu}$ et utilisons la formule:

$$g^{ab,h} = - \sum_{\sigma,\tau} g_{\sigma\tau,h} g^{\sigma a} g^{\tau b} \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Rapprochons la valeur de $t_{\lambda\mu}$ ainsi obtenue (3,6), et la valeur de $T_{\lambda\mu}$ (5): tous les termes de $t_{\lambda\mu}$ renfermant des dérivées secondes des potentiels gravifiques se retrouvent, changés de signe, dans le tenseur électromagnétique $T_{\lambda\mu}$.

Après quelques réductions provenant de permutations d'indices, on trouve enfin:

$$t_{\lambda\mu} + T_{\lambda\mu} = \frac{1}{2} k(-g)^{1/2} \sum_{h,l,i} \left\{ \begin{aligned} & g_{i\lambda,hl} [g^{\mu i} g^{hl} - g^{\mu h} g^{il}] \\ & + \frac{1}{2} \sum_{\alpha,\beta} g_{\beta i,gh\lambda\alpha} \left[\begin{aligned} & 2g^{\lambda\alpha} (g^{ih} g^{\beta l} - g^{lh} g^{\beta i}) \\ & + 2g^{\lambda i} (g^{lh} g^{\alpha\beta} - g^{\beta h} g^{\alpha l}) \\ & + 2g^{\lambda h} (g^{\alpha l} g^{\beta i} - g^{\alpha i} g^{\beta l}) \end{aligned} \right] \end{aligned} \right\} \quad (7)$$

III. La force généralisée F_λ est nulle.

La force généralisée F_λ ($\lambda = 1, 2, 3, 4$) satisfait aux relations suivantes³⁾:

$$(-g)^{1/2} F_\lambda = \sum \frac{d(t_{\lambda\mu} + T_{\lambda\mu})}{dx_\mu}; \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

$\lambda, \mu = 1, 2, 3, 4.$

¹⁾ TH. DE DONDER. Archives du Musée Teyler. Sér. 2. T. III. 1917 (voir spéc. pages 94 et 99).

²⁾ TH. DE DONDER. Voir ma note citée ci-dessus; équations (10).

Voir aussi mon mémoire, Archives Teyler, Haarlem 1917; équations (347).

Substituons dans (8) les valeurs trouvées (7) pour le tenseur $t_{\mu} + T_{\mu}$. Après dérivation et permutations d'indices, on voit que tous les termes se détruisent deux à deux; on aura donc:

$$F_{\lambda} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

Ce résultat est indépendant de l'expression choisie pour le tenseur gravifique t_{μ} . C'est ce que nous allons démontrer au moyen de l'identité de HILBERT ¹⁾, qui peut s'écrire avec nos notations:

$$\frac{1}{2} \sum_{\mu} \sum_{\nu} (1 + \varepsilon_{\mu\nu}) g^{\mu\nu} \hat{\nabla}^{\nu} l \equiv - \sum_{\mu} \sum_{\nu} \frac{d}{dx_{\nu}} \{ (1 + \varepsilon_{\mu\nu}) g^{\mu\nu} \hat{\nabla}^{\nu} l \} \quad . \quad (10)$$

En vertu du principe généralisé de HAMILTON, les équations différentielles gravifiques sont ²⁾:

$$\hat{\nabla}^{\mu\nu} (L + l) = 0$$

ou

$$\frac{dL}{dg^{\mu\nu}} = - \hat{\nabla}^{\mu\nu} l \quad . \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Or, on a ³⁾:

$$\hat{\nabla}^{\mu\nu} L \equiv \frac{dL}{dg^{\mu\nu}} = \left(\frac{\varepsilon_{\mu\nu}}{2} - 1 \right) \sum_k g_{\mu k} T_{\nu k} \quad . \quad . \quad . \quad . \quad (12)$$

d'où, en vertu de (11):

$$\hat{\nabla}^{\mu\nu} l = \left(1 - \frac{\varepsilon_{\mu\nu}}{2} \right) \sum_k g_{\mu k} T_{\nu k} \quad . \quad . \quad . \quad . \quad (13)$$

et inversement:

$$T_{\sigma\nu} = \sum_{\mu} (1 + \varepsilon_{\mu\sigma}) g^{\mu\nu} \hat{\nabla}^{\mu\sigma} l \quad . \quad . \quad . \quad . \quad (14)$$

En vertu de (11), le premier membre de l'identité de HILBERT (10) peut s'écrire:

$$- \left(\frac{dL}{dx_{\sigma}} \right)_M$$

D'autre part, en vertu de (14), le second membre de cette identité (10) peut s'écrire:

$$- \sum_{\nu} \frac{dT_{\sigma\nu}}{dx_{\nu}}$$

On a donc:

¹⁾ D. HILBERT. Nachrichten Königl. Gesellsch. d. Wiss. Göttingen. Math. phys. Klasse, Heft 3. 1915. (Berlin 1916).

²⁾ TH. DE DONDER. Archives Teyler, Haarlem 1917. (Voir équation 339).

³⁾ Voir équation (353) de mon mémoire, Archives Teyler.

$$K_\sigma \equiv \left(\frac{dL}{dx_\sigma} \right)_M = \sum_\nu \frac{dT_{\sigma\nu}}{dx_\nu}.$$

Or, en vertu de (346)¹⁾:

$$(-g)^{1/2} F_\sigma + K_\sigma = \sum_\nu \frac{dT_{\sigma\nu}}{dx_\nu}$$

d'où

$$F_\sigma = 0,$$

$$\sigma = 1, 2, 3, 4.$$

Remarquons que tout ce qui précède peut être généralisé immédiatement en remplaçant l par une fonction covariante plus générale, par exemple: $l = \frac{1}{4} \varphi(-g)^{1/2}$, où φ est une fonction de x_1, x_2, x_3, x_4 ; on obtiendrait ainsi nos équations généralisées²⁾ du champ gravifique renfermant des masses.

IV. Autres tenseurs gravifiques.

Les seize fonctions $t_{\lambda\mu}$ dont l'ensemble constitue le tenseur gravifique ne devant, jusqu'à présent, satisfaire qu'aux quatre équations aux dérivées partielles³⁾:

$$\sum_\mu \frac{dt_{\lambda\mu}}{dx_\mu} = -K_\lambda,$$

$$\lambda = 1, 2, 3, 4,$$

il en résulte qu'il existe une infinité de tenseurs gravifiques différents. Le développement ultérieur de la théorie de la gravitation montrera probablement que le tenseur gravifique doit être déterminé d'une manière *univoque* par des conditions aux limites et des conditions initiales.

En se reportant aux relations (341 à 345) de mon mémoire⁴⁾ (Archives TEYLER), on verra aisément que les seize fonctions suivantes :

$$t^{\lambda\mu} \equiv \varepsilon_{\lambda\mu} l - \sum_{ab} \left[\left(\frac{dl}{dg^{ab,\mu}} - \frac{1}{2} \sum_i \frac{d(1+\varepsilon_{\mu i})}{dg^{ab,\mu i}} \frac{dl}{dx_i} \right) g^{ab,\lambda} + \frac{1}{2} \sum_i (1+\varepsilon_{\mu i}) \frac{dl}{dg^{ab,\mu i}} g^{ab,\mu i} \right] \quad (15)$$

déterminent un tenseur gravifique.

¹⁾ Voir équation (346) de mon mémoire, Archives Teyler.

²⁾ Voir la dernière page de mon mémoire, Archives Teyler.

³⁾ Voir équation (344) de mon mémoire, Archives Teyler.

⁴⁾ Voir aussi notations (348 à 352) de ce mémoire.

Grâce à la théorie des invariants différentiels, ou par un calcul direct, on trouvera que :

$$t^{\lambda\mu} = t_{\lambda\mu} + \frac{1}{2}(-g)^{1/2} \sum_{\alpha} \sum_{\sigma} \sum_{\tau} g_{\sigma\kappa} \left[\begin{array}{c} g^{\lambda\mu} (g^{\sigma\alpha,\mu} - 2g^{\sigma\alpha,i} + g^{\sigma\alpha,\alpha}) \\ - g^{\alpha i} (g^{\sigma\mu,\mu} - g^{\sigma\mu,i}) \end{array} \right]. \quad (16)$$

On remarquera que ces deux tenseurs gravifiques renferment les mêmes dérivées secondes des potentiels gravifiques. On aura en outre :

$$\sum_{\mu} \frac{d(t^{\lambda\mu} - t_{\lambda\mu})}{dx_{\mu}} = 0.$$

En vertu de nos équations (8) et (9), on pourra introduire le tenseur gravifique $-T_{\lambda\mu}$; M. LORENTZ¹⁾ a rencontré ce tenseur gravifique au cours de ses recherches. Quand on adopte le tenseur gravifique de M. LORENTZ, le tenseur $t_{\lambda\mu} + T_{\lambda\mu}$ est identiquement nul.

Plus récemment, M. EINSTEIN²⁾ a trouvé un tenseur gravifique qui ne renferme aucune dérivée seconde des potentiels gravifiques. Nous allons indiquer une méthode nouvelle pour obtenir ce tenseur gravifique (corrigé).

L'invariant de courbure totale de RIEMANN peut s'écrire :

$$\begin{aligned} C &\equiv \frac{1}{2} \sum_{\alpha} \sum_{\beta} \sum_{\sigma} \sum_{\tau} (\alpha\beta, \sigma\tau) g^{\beta\sigma} g^{\alpha\tau} \\ &\equiv \frac{1}{2} \sum_{\alpha} \sum_{\beta} \sum_{\sigma} \sum_{\tau} g^{\alpha\beta} \left[\begin{array}{c} \frac{d \left\{ \begin{smallmatrix} \alpha\sigma \\ \sigma \end{smallmatrix} \right\}}{dx_{\beta}} - \frac{d \left\{ \begin{smallmatrix} \alpha\beta \\ \sigma \end{smallmatrix} \right\}}{dx_{\sigma}} \\ + \left\{ \begin{smallmatrix} \beta\tau \\ \sigma \end{smallmatrix} \right\} \left\{ \begin{smallmatrix} \alpha\sigma \\ \tau \end{smallmatrix} \right\} - \left\{ \begin{smallmatrix} \sigma\tau \\ \sigma \end{smallmatrix} \right\} \left\{ \begin{smallmatrix} \alpha\beta \\ \tau \end{smallmatrix} \right\} \end{array} \right]. \end{aligned}$$

Il en résulte que $l \equiv kC(-g)^{1/2}$ peut s'écrire :

$$l \equiv \frac{1}{2} k \sum_{\alpha} \sum_{\beta} \sum_{\sigma} \sum_{\tau} \left[\frac{d}{dx_{\beta}} \left((-g)^{1/2} \left\{ \begin{smallmatrix} \alpha\sigma \\ \sigma \end{smallmatrix} \right\} g^{\alpha\beta} \right) - \frac{d}{dx_{\sigma}} \left((-g)^{1/2} \left\{ \begin{smallmatrix} \alpha\beta \\ \sigma \end{smallmatrix} \right\} g^{\alpha\beta} \right) \right] + l^* \quad (17)$$

où nous avons posé :³⁾

$$l^* \equiv \frac{1}{2} k \sum_{\alpha} \sum_{\beta} \sum_{\sigma} \sum_{\tau} \left[\begin{array}{c} - \left\{ \begin{smallmatrix} \alpha\sigma \\ \sigma \end{smallmatrix} \right\} \frac{d}{dx_{\beta}} [(-g)^{1/2} g^{\alpha\beta}] + \left\{ \begin{smallmatrix} \alpha\beta \\ \sigma \end{smallmatrix} \right\} \frac{d}{dx_{\sigma}} [(-g)^{1/2} g^{\alpha\beta}] \\ + (-g)^{1/2} g^{\alpha\beta} \left\{ \begin{smallmatrix} \beta\tau \\ \sigma \end{smallmatrix} \right\} \left\{ \begin{smallmatrix} \alpha\sigma \\ \tau \end{smallmatrix} \right\} - (-g)^{1/2} g^{\alpha\beta} \left\{ \begin{smallmatrix} \sigma\tau \\ \sigma \end{smallmatrix} \right\} \left\{ \begin{smallmatrix} \alpha\beta \\ \tau \end{smallmatrix} \right\} \end{array} \right]. \quad (18)$$

On vérifiera, par un calcul direct, que le lagrangien $\hat{\Delta}^{ab}$ d'une

¹⁾ H. A. LORENTZ. Voir la dernière page du mémoire cité. (Verslag Amsterdam 1916).

²⁾ A. EINSTEIN. Sitzungsberichte Akad. der Wissenschaften Berlin (Séance du 26 octobre 1916).

³⁾ Les termes qui figurent dans la première ligne du second membre de (18) ont été omis par M. EINSTEIN.

En vertu de l'équation complémentaire $l=0$, on voit (30) que $\sum_{\lambda} t_{\lambda\lambda}$ est une *forme quadratique des dérivées premières seules*.

VII. Covariance du tenseur gravifique $t_{\lambda\mu}$.

Effectuons un changement *quelconque* des variables x_1, x_2, x_3, x_4 , et représentons par x'_i ($i=1, 2, 3, 4$) les nouvelles variables. Le tenseur gravifique prendra une nouvelle valeur $t'_{\lambda\mu}$ ($\lambda, \mu=1, 2, 3, 4$) fournie par la relation (1) où toutes les lettres auront été, au préalable, affectées d'un *accent*.

Rappelons que ¹⁾:

$$l' = l \frac{\partial(x_1 \dots x_4)}{\partial(x'_1 \dots x'_4)} \dots \dots \dots (32)$$

Grâce à cette relation (32), il sera aisé de comparer $t'_{\lambda\mu}$ à $t_{\lambda\mu}$; de cette comparaison, il résulte que pour tout changement *linéaire* des variables x_1, x_2, x_3, x_4 , on aura:

$$t'_{\lambda\mu} = \frac{\partial(x_1 \dots x_4)}{\partial(x'_1 \dots x'_4)} \sum_{\sigma} \sum_{\tau} \frac{\partial x_{\sigma}}{\partial x'_{\lambda}} \cdot \frac{\partial x'_{\mu}}{\partial x_{\tau}} \cdot t_{\sigma\tau};$$

autrement dit, pour tout changement *linéaire* des variables x_1, x_2, x_3, x_4 , le tenseur gravifique $t_{\lambda\mu}$ est *cogrédient* au tenseur électromagnétique ²⁾ $T_{\lambda\mu}$.

Il n'en est plus de même pour un changement *quelconque* de variables ³⁾. Un fait analogue se présente pour les forces généralisées ⁴⁾ F_{λ} et K_{λ} : la force généralisée gravifique K_{λ} n'est *cogrédiente* à la force généralisée électromagnétique F_{λ} que pour les changements *linéaires* des variables x_1, x_2, x_3, x_4 .

Le 30 avril 1918.

¹⁾ Voir équation (364) de mon mémoire, Archives TEYLER.

²⁾ Voir l'équation (319) de mon mémoire, Archives TEYLER.

³⁾ M. LORENTZ, avait déjà fait remarquer que $t_{\lambda\mu}$ n'est pas *cogrédient* à $T_{\lambda\mu}$ dans le cas d'un changement quelconque de variables (Verslag Amsterdam, 24 Juni 1916).

⁴⁾ Voir les équations (321) et (323) de mon mémoire, Archives TEYLER.

Mathematics. — “On the evaluation of $\zeta(2n+1)$ ”. By Prof. J. C. KLUYVER.

(Communicated in the meeting of September 28, 1918).

By means of a characteristic and very general method MARKOFF¹⁾ transformed the very slowly convergent series $\sum_1^{\infty} n^{-2}$ and $\sum_1^{\infty} n^{-3}$ into other series, that converge more rapidly, and J. G. VAN DER CORPUT²⁾ described a special method of transformation applicable to the series $\sum_1^{\infty} n^{-(2h+1)}$ for larger values of h . I propose to deal anew with the transformation of these series and to add a few results to those previously obtained. In order to appreciate the increase of convergence resulting from the transformation, I will consider D'ALFMBERT's ratio for the transformed expansion, which I will call its index. For the series given by MARKOFF the index is $\frac{1}{2}\pi$, and I will show that a lower index can be attained.

In the first place I base my deductions on the properties of the function

$$\varphi_k(z) = \sum_{n=1}^{n=\infty} \frac{z^n}{n^k},$$

where k denotes a positive integer. In order to uniformise $\varphi_k(z)$, it is convenient to regard the right line $(+1, +\infty)$ as a cut in the complex z -plane, and with this convention we may enunciate the following properties of $\varphi_1(z)$ in substance deduced by ABEL:

$$\left. \begin{aligned} \varphi_1(z) + \varphi_1(1-z) &= -\log z \log(1-z) + \zeta(2), \\ \varphi_1(z) + \varphi_1\left(\frac{1}{z}\right) &= -\frac{1}{2} \log^2 z + \pi i \log z + 2 \zeta(2) \\ \varphi_1(z) - \varphi_1\left(\frac{z-1}{z}\right) &= \frac{1}{2} \log^2 z - \log z \log(1-z) + \zeta(2) \\ \varphi_1(z) + \varphi_1(-z) &= \frac{1}{2} \varphi_1(z^2) \end{aligned} \right\} \dots (1)$$

Obviously in these formulae we have to take real values for $\log z$ and for $\log(1-z)$, when z itself is real and between 0 and 1.

¹⁾ Comptes rendus, t. 109, p. 934.

²⁾ These Proc. XIX, p. 489.

As in general we have

$$\frac{d}{dz} \varphi_{k+1}(u) = \varphi_k(u) \frac{d \log u}{dz},$$

it is possible to extend partially the above relations to the function $\varphi_k(z)$, and indeed it follows that

$$\left. \begin{aligned} \varphi_1(z) - \varphi_1\left(\frac{1}{z}\right) &= -\frac{1}{6} \log^3 z + \frac{1}{2} \pi i \log^2 z + 2\zeta(2) \log z, \\ \varphi_1\left(\frac{z-1}{z}\right) + \varphi_1(1-z) + \varphi_1(z) &= \frac{1}{6} \log^3 z - \frac{1}{2} \log^2 z \log(1-z) + \\ &\quad + \zeta(2) \log z + \zeta(3), \\ \varphi_1(z) + \varphi_1(-z) &= \frac{1}{4} \varphi_1(z^2). \end{aligned} \right\} \quad (2)$$

For $k > 3$ a linear relation between $\varphi_k(z)$, $\varphi_k(1-z)$ and $\varphi_k\left(\frac{z-1}{z}\right)$ no longer exists, there only remains, besides the relation

$$\varphi_k(z) + \varphi_k(-z) = \frac{1}{2^{k-1}} \varphi_k(z^2)$$

an equation of the form

$$\varphi_k(z) + (-1)^k \varphi_k\left(\frac{1}{z}\right) = -(2\pi i)^k g_k\left(\frac{\log z}{2\pi i}\right),$$

where $g_k(u)$ denotes the differential coefficient of BERNOLLI's polynomial $f_k(u)$.

Another expansion valid for all positive and integer values of k is the following:

$$\begin{aligned} \varphi_k(e^{-y}) &= \frac{(-y)^{k-1}}{(k-1)!} \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{k-1} - \log y \right) + \\ &\quad + \sum_{n=0}^{n=\infty} \frac{(-y)^n}{n!} \zeta(k-n) \quad . \quad . \quad . \quad . \quad . \quad (3) \end{aligned}$$

Here the right line $(0, -\infty)$ must be considered as a barrier in the complex y -plane and $\log y$ is real for positive values of y . The accent in Σ' denotes that the term with the index $n = k-1$ is to be excluded. As for the numerical values that the ζ -function takes for the value zero and for negative integer values of the argument, we have

$$\zeta(0) = -\frac{1}{2}, \quad \zeta(-2h) = 0, \quad \zeta(1-2h) = (-1)^h \frac{B_h}{2h}.$$

Therefore after a certain stage the coefficients in the expansion at the right hand side of (3) are expressible by BERNOLLI's numbers and the radius of convergence of the expansion is evidently 2π ,

as we might expect since equation (3) may be established by integrating repeatedly both sides of the equation

$$\sum_{n=1}^{\infty} \frac{e^{-ny}}{n} = -\log y + \frac{1}{2}y + \sum_{n=1}^{\infty} \frac{(-1)^n B_n}{2n!} \cdot \frac{y^{2n}}{2n} \quad (0 < y < 2\pi).$$

By substituting $z = \frac{1}{2}$ in the formulae (1) and (2) we find

$$\varphi_1\left(\frac{1}{2}\right) = -\frac{1}{2} \log^2 2 + \frac{1}{2} \zeta(2),$$

$$\varphi_1\left(\frac{1}{2}\right) = \frac{1}{6} \log^3 2 - \frac{1}{2} \zeta(2) \log 2 + \frac{7}{8} \zeta(3),$$

and then, remembering that

$$\log \log 2 = -\frac{1}{2} \log 2 + \sum_{n=1}^{\infty} \frac{(-1)^n B_n}{2n!} \cdot \frac{(\log 2)^{2n}}{2n},$$

we deduce from (3) by taking $y = \log 2$

$$\zeta(2) = \frac{1}{2} \log^2 2 + 2 \left\{ \frac{\log 2}{1} + \sum_{n=1}^{\infty} \frac{(-1)^{n-1} B_n}{2n!} \cdot \frac{(\log 2)^{2n+1}}{2n+1} \right\},$$

$$\zeta(3) = \frac{2}{3} \log^3 2 + 4 \left\{ \frac{\log^2 2}{2} + \sum_{n=1}^{\infty} \frac{(-1)^{n-1} B_n}{2n!} \cdot \frac{(\log 2)^{2n+2}}{2n+2} \right\}.$$

The index of these expansions is about $\frac{1}{8^{\frac{1}{2}}}$ and the error involved in neglecting terms beyond the second does not affect the fifth decimal.

It is possible to connect these expansions with the equation

$$\frac{u}{2} \coth \frac{u}{2} = 1 + \sum_{n=1}^{\infty} \frac{(-1)^{n-1} B_n}{2n!} u^{2n}$$

and to deduce in this way definite integrals representing $\zeta(2)$ and $\zeta(3)$. Thus we arrive in the first place at the well-known formula

$$\zeta(2) = 2 \int_0^1 \frac{\log(1+\xi)}{\xi} d\xi,$$

but we get also the less familiar result

$$\zeta(3) = 4 \int_0^1 \frac{\log^2(1+\xi)}{\xi} d\xi = 8 \sum_{n=2}^{\infty} \frac{(-1)^n}{n^2} \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} \dots + \frac{1}{n-1} \right).$$

Further, we may prove EULER's result

$$\zeta(3) = \frac{1}{2} \int_0^1 \frac{\log^2(1-\xi)}{\xi} d\xi = \sum_{n=2}^{\infty} \frac{1}{n^2} \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{n-1} \right),$$

and, finally, we may show that

$$\begin{aligned}\zeta(3) &= -\frac{1}{6} \int_0^1 \frac{\log(1-\xi) \log(1+\xi)}{\xi} d\xi = \\ &= \frac{1}{6} \sum_{n=1}^{\infty} \frac{1}{n^3} \left(\frac{1}{1} - \frac{1}{2} + \frac{1}{3} - \frac{1}{4} + \dots + \frac{1}{2n-1} \right).\end{aligned}$$

Quite other expansions of the quantities $\zeta(2)$ and $\zeta(3)$ are obtained by substituting in (1) and (2)

$$z = \frac{1}{2}(\sqrt{5}-1) = a.$$

As we have

$$1-a=a^2 \text{ and } \frac{a-1}{a} = -a$$

we readily get from (1)

$$\begin{aligned}\varphi_1(a) &= -\log^3 a + \frac{1}{6} \zeta(2) \\ \varphi_1(a^2) &= -\log^3 a + \frac{1}{6} \zeta(2)\end{aligned}$$

and from (2)

$$\varphi_3(a^2) = -\frac{2}{3} \log^3 a + \frac{1}{6} \zeta(2) \log a + \frac{1}{6} \zeta(3).$$

Now writing $-2 \log a = \alpha$, we have

$$\log a = \sum_{n=1}^{\infty} \frac{(-1)^n B_n}{2n!} \cdot \frac{\alpha^{2n}}{2n},$$

and substituting $y = \frac{\alpha}{2}$ and also $y = \alpha$ in (3), in order to obtain expansions of $\varphi_1(a)$, $\varphi_2(a^2)$ and $\varphi_3(a^2)$, we infer that

$$\begin{aligned}\zeta(2) &= \frac{5}{6} \left\{ \left(\frac{\alpha}{2} \right) + \frac{1}{4} \left(\frac{\alpha}{2} \right)^2 + \sum_{n=1}^{\infty} \frac{(-1)^{n-1} B_n}{2n!} \cdot \frac{\left(\frac{\alpha}{2} \right)^{2n+1}}{2n+1} \right\}, \\ \zeta(2) &= \frac{5}{6} \left\{ \alpha + \sum_{n=1}^{\infty} \frac{(-1)^{n-1} B_n}{2n!} \cdot \frac{\alpha^{2n+1}}{2n+1} \right\}, \\ \zeta(3) &= \frac{5}{6} \left\{ \frac{\alpha^2}{2} + \sum_{n=1}^{\infty} \frac{(-1)^{n-1} B_n}{2n!} \cdot \frac{\alpha^{2n+2}}{2n+2} \right\}.\end{aligned}$$

The index of the first series representing $\zeta(2)$ is about $\frac{1}{1+\sqrt{5}}$, for the other two series it is less than $\frac{1}{4\sqrt{5}}$.

Again it is possible to convert the series into definite integrals. From the power-series in α we find

$$\zeta(2) = \frac{1}{3} \int_0^1 \frac{d\xi}{\xi} \log(\xi + \sqrt{1+\xi^2}),$$

$$\zeta(3) = 10 \int_0^1 \frac{d\xi}{\xi} \log^2(\xi + \sqrt{1+\xi^2}).$$

If we wish to expand $\zeta(k)$ for $k > 3$, we must proceed in a different manner. We shall use the general identity

$$\varphi_s(z) + \varphi_s(z\theta) + \varphi_s(z\theta^2) + \dots + \varphi_s(z\theta^{p-1}) = \frac{1}{p^{s-1}} \varphi_s(z^p) \quad (4)$$

where p is an integer and $\theta = e^{\frac{2\pi i}{p}}$
Denoting the series

$$\sum_{n=1}^{\infty} \frac{\cos \frac{mn\pi}{3}}{n^s}$$

by U_m , we get by substituting in (4)

$$p=3, z=e^{\frac{\pi i}{3}}$$

$$p=2, z=1$$

$$2U_1 + U_2 = \frac{1}{3^{s-1}} U_3$$

$$U_0 + U_2 = \frac{1}{2^{s-1}} U_4$$

and hence

$$U_1 = \sum_{n=1}^{\infty} \frac{\cos \frac{n\pi}{3}}{n^s} = \frac{1}{2} \left(1 - \frac{1}{2^{s-1}}\right) \left(1 - \frac{1}{3^{s-1}}\right) \zeta(s).$$

From equation (3) we deduce by taking $k=2h+1, y=iv$

$$\begin{aligned} \sum_{n=1}^{\infty} \frac{\cos nv}{n^{2h+1}} &= \frac{(-1)^h v^{2h}}{2h!} \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{2h} - \log v \right) + \\ &+ \sum_{n=0}^{\infty} \frac{(-1)^n v^{2n}}{2n!} \zeta(2h+1-2n) \quad \dots (5) \end{aligned}$$

hence writing

$$1 - \frac{1}{2} \left(1 - \frac{1}{2^{2h}}\right) \left(1 - \frac{1}{3^{2h}}\right) = A_{2h+1},$$

we may conclude to

$$A_{2h+1} \zeta(2h+1) = \frac{(-1)^{h-1} v^{2h}}{2h!} \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{2h} - \log v \right) +$$

$$+ \sum_{n=1}^{h-1} \frac{(-1)^{n-1} v^{2n}}{2n!} \zeta(2h+1-2n) + (-1)^{h-1} \sum_{n=1}^{\infty} \frac{B_n}{(2n+2h)!} \cdot \frac{v^{2n+2h}}{2n}, \quad (6)$$

where v now stands for $\frac{\pi}{3}$.

By means of this equation $\zeta(2h+1)$ is expressed in terms of $\zeta(3), \zeta(5), \dots, \zeta(2h-1)$ and taking successively $h=1, 2, 3, \dots$, we get $\zeta(3), \zeta(5), \zeta(7), \dots$ expressed by a linear combination of expansions the index of which is $\frac{1}{3^k}$.

A slight transformation of (6) is possible. By using

$$\log v = \sum_{n=1}^{\infty} \frac{B_n}{2n!} \cdot \frac{v^{2n}}{2n},$$

and by effecting some other reductions, it may be shown that (6) can take the form

$$\begin{aligned} A_{2h+1} \zeta(2h+1) &= \left(1 - \frac{A_{2h-1}}{h(2h-1)}\right) \zeta(2h-1) \cdot \frac{v^2}{2} + \\ &+ \sum_{n=2}^{h-1} \frac{(h-n)(2h+2n-1)}{h(2h-1)} \cdot \frac{(-1)^{n-1} v^{2n}}{2n!} \zeta(2h+1-2n) + \\ &+ \frac{(-1)^{h-1} v^{2h}}{2h(2h-1)} \left\{ \frac{4h-1}{2h!} - \sum_{n=1}^{\infty} \frac{B_n}{(2n+2h)!} \cdot (2n+4h-1) v^{2n} \right\}. \end{aligned}$$

($v = \frac{\pi}{3}$).

If we put $h=1$ and $h=2$, it will be seen that

$$\begin{aligned} \zeta(3) &= \frac{3}{4} \left\{ \frac{3}{2!} v^2 - \sum_{n=1}^{\infty} \frac{B_n}{(2n+2)!} (2n+3) v^{2n+2} \right\}, \\ \zeta(5) &= \frac{9}{64} \left\{ \frac{137}{4!} v^4 - \sum_{n=1}^{\infty} \frac{B_n}{(2n+4)!} [4(2n+3)^2(2n+4) - (2n+7)] v^{2n+4} \right\}. \end{aligned}$$

I will now proceed to show that for each of the quantities $\zeta(2h+1)$ there exists a linear combination of expansions with an index less than $\frac{1}{3^k}$. For this purpose I use again the identity (4) and writing

$$w = \frac{\pi}{15}, \quad U_m = \sum_{n=1}^{\infty} \frac{\cos mnw}{n^5}$$

¹⁾ Similar results were deduced by Mr. VAN DER CORPUT in the paper quoted. However, in the fundamental expansion of the quantity $I(n, \alpha)$ on p. 1464 by a slight inadvertence the factor 2^{2k} has been omitted in the general term, hence in all the subsequent expansions the general term should be multiplied by 2^{2k} and the index of the series on p. 1470 is $\frac{1}{3^k}$ and not $\frac{1}{14^k}$.

I make in (4) the substitutions

$$\begin{aligned} p=2 & \quad , \quad z=e^{iw} \quad \text{and} \quad z=e^{3iw}, \\ p=3 & \quad , \quad z=e^{4iw}, \\ p=5 & \quad , \quad z=1. \end{aligned}$$

These substitutions give the four equations

$$\begin{aligned} U_1 + U_{14} &= \frac{1}{2^{s-1}} U_2, \\ U_3 + U_{13} &= \frac{1}{2^{s-1}} U_4, \\ U_4 + U_6 + U_{14} &= \frac{1}{3^{s-1}} U_{12}, \\ U_5 + 2U_6 + 2U_{12} &= \frac{1}{5^{s-1}} U_0. \end{aligned}$$

and eliminating U_6, U_{12}, U_{14} we get

$$\begin{aligned} \left(1 - \frac{1}{5^{s-1}}\right) \left(1 - \frac{1}{6^{s-1}}\right) U_0 + 2 \left(1 + \frac{1}{2^{s-1}}\right) U_1 - \frac{1}{2^{s-2}} \left(1 + \frac{1}{2^{s-1}}\right) U_2 - \\ - 2 \left(1 + \frac{1}{3^{s-1}}\right) U_3 - 2 \left(1 + \frac{1}{2^{s-1}}\right) U_4 = 0. \end{aligned}$$

Now, taking $s=2h+1$, we may expand U_1, U_2, U_3, U_4 by applying equation (5) and we will get $U_0 = \zeta(2h+1)$ expressed in terms of the quantities $\zeta(3), \zeta(5), \dots, \zeta(2h-1)$ and of four power-series in w , the indices of which are respectively $\frac{1}{900}, \frac{1}{225}, \frac{1}{100}, \frac{1}{225}$. Since the formulae become somewhat complicated, I will consider only the simplest case $h=1$. Then we have

$$336 \zeta(3) = -900 U_1 + 225 U_2 + 800 U_3 + 900 U_4$$

and hence

$$\begin{aligned} 689 \zeta(3) = 450w^2(36-24\log w - 33\log 2 - 8\log 3) - 900 \sum_{n=1}^{\infty} \frac{B_n}{(2n+2)!} \cdot \frac{w^{2n+2}}{2n} + \\ + 225 \sum_{n=1}^{\infty} \frac{B_n}{(2n+2)!} \cdot \frac{(2w)^{2n+2}}{2n} + 800 \sum_{n=1}^{\infty} \frac{B_n}{(2n+2)!} \cdot \frac{(3w)^{2n+2}}{2n} + \\ + 900 \sum_{n=1}^{\infty} \frac{B_n}{(2n+2)!} \cdot \frac{(4w)^{2n+2}}{2n}. \end{aligned}$$

I will end with remarking that the calculation of the sum of the series

$$\eta(2h) = \frac{1}{1^{2h}} - \frac{1}{3^{2h}} + \frac{1}{5^{2h}} - \frac{1}{7^{2h}} + \dots$$

may be conducted along similar lines. Equation (3) gives, if we take $k=2h, y=iw$,

$$\sum_{n=1}^{u=\infty} \frac{\sin nu}{n^{2h}} = \frac{(-1)^{h-1} u^{2h-1}}{(2h-1)!} \left(\frac{1}{1} + \frac{1}{2} + \frac{1}{3} + \dots + \frac{1}{2h-1} - \log u \right) + \sum_{n=0}^{n=\infty} \frac{(-1)^n u^{2n+1}}{(2n+1)!} \zeta(2h-1-2n) \dots \dots \dots (7)$$

and it is possible to express $\eta(2h)$ by means of series of the form

$$\sum_{n=1}^{n=\infty} \frac{\sin nu}{n^{2h}}.$$

Indeed, putting

$$V_m = \sum_{n=1}^{n=\infty} \frac{\sin \frac{mnv}{2}}{n^s} \quad \text{and} \quad v = \frac{\pi}{3}$$

we have by substituting in (4)

$$p=2, \quad z = e^{\frac{iv}{2}},$$

$$p=3, \quad z = e^{\frac{iv}{3}},$$

$$V_1 - V_s = \frac{1}{2^{s-1}} V_s,$$

$$V_1 + V_s - V_s = \frac{1}{3^{s-1}} V_s,$$

whence

$$V_s \left(1 + \frac{1}{3^{s-1}} \right) = 2 V_1 - \frac{1}{2^{s-1}} V_s.$$

Now, taking $s=2h$, we have $V_s = \eta(2h)$, and expressing V_1 and V_s by means of equation (7), we get an expansion for $\eta(2h)$. In the simplest case $h=1$, I find in this way

$$\eta(2) = \frac{3}{8} v \left(1 + \log \frac{4}{v} \right) + \frac{3}{8} \sum_{n=1}^{n=\infty} \frac{B_n}{(2n+1)!} \cdot \frac{v^{2n+1}}{2n} \left(\frac{1}{2^{2n-1}} - 1 \right).$$

$$\left(v = \frac{\pi}{3} \right)$$

Again the index of the series is $\frac{1}{3^6}$ and the value of $\eta(2)$ is found to five decimals by taking into account only the first two terms of the expansion.

Mathematics. — “*Ueber die Teilkörper des Kreiskörpers $K\left(e^{\frac{2\pi i}{l^h}}\right)$* ”.
(Erster Teil). By Dr. N. G. W. H. BEEGER. (Communicated
by Prof. W. KAPTEYN).

(Communicated in the meeting of September 28, 1918).

Der Zweck des vorliegenden Aufsatzes ist die Untersuchung aller Teilkörper des Kreiskörpers $K\left(e^{\frac{2\pi i}{l^h}}\right)$ (l eine ungerade Primzahl), und namentlich die Bestimmung ihrer Klassenanzahlen. Ich benütze dabei die Definitionen und Notationen des HILBERT'schen “Bericht über die Theorie der algebraischen Zahlkörper”¹⁾.

KUMMER giebt, ohne Ableitung, die Formel für die Klassenanzahl aller Teilkörper des Kreiskörpers $K\left(e^{\frac{2\pi i}{l}}\right)$ ²⁾ (l prim).

Die Klassenanzahlen aller Teilkörper des Kreiskörpers $K\left(e^{\frac{2\pi i}{l^h}}\right)$ sind bis jetzt noch nicht berechnet worden; und weil im allgemeinen die ganze Ableitung der endgültigen Ausdrücke der Klassenanzahl nur publicirt ist für den Kreiskörper $K\left(e^{\frac{2\pi i}{l}}\right)$ selbst, so gebe ich hier die ganze Herleitung meiner Formeln.

§ 1. Einige Bemerkungen über den Körper $K\left(e^{\frac{2\pi i}{l^h}}\right)$.

Dieser Körper, den ich weiter andeute durch $K(Z)$, ist ein cyclischer Körper³⁾. Es sei γ eine primitive Wurzel von l^h und es sei s die Substitution $(Z:Z')$, so wird die Substitutionsgruppe des Körpers vorgestellt durch

$$s, s^2, \dots, s^{l^{h-1}(l-1)} \dots \dots \dots (1)$$

Die Primzahl l ist im Körper die $l^{h-1}(l-1)$ -te Potenz eines Primideals \mathfrak{f} :

$$l = \mathfrak{f}^{l^{h-1}(l-1)} \quad \mathfrak{f} = (1-Z)$$

¹⁾ Jahresb. d. D. M. V. Band IV. Im folgenden angedeutet durch die Buchstabe H.

²⁾ Crelle Journ. Band 40.

³⁾ H. Satz 128.

\mathfrak{f} ist ein Hauptideal ersten Grades.¹⁾

Satz 1.

Die Zerlegungsgruppe des Primideals \mathfrak{f} ist die ganze Gruppe (1). Ebenso die Trägheitsgruppe. Die Verzweigungsgruppe ist

$$s^{l-1}, s^{2(l-1)}, \dots, s^{l^{h-1}(l-1)}$$

Die einmal-überstrichene Verzweigungsgruppe ist

$$s^{l(l-1)}, s^{2l(l-1)}, \dots, s^{l^{h-2}l(l-1)}.$$

Die h -mal überstrichene Verzweigungsgruppe ist

$$s^{l^{h-1}(l-1)}$$

und besteht also nur aus der identischen Substitution²⁾.

Beweis: Die Zerlegungsgruppe eines Primideals besteht aus allen Substitutionen die das Primideal ungeändert lassen. Nun gilt für jede Substitution der Gruppe (1):

$$s^a \mathfrak{f} = s^a (1 - Z) = (1 - Z^{r^a}) = \mathfrak{f}$$

Hiermit ist der erste Teil des Satzes bewiesen.

Die Trägheitsgruppe eines Primideals besteht aus allen Substitutionen der Zerlegungsgruppe für welche, für alle ganzen Zahlen Ω des Körpers:

$$s^a \Omega \equiv \Omega \pmod{\mathfrak{f}}. \quad (2)$$

Jede ganze Zahl Ω des Körpers hat die Form

$$\Omega = a_0 + a_1 Z + a_2 Z^2 + \dots + a_{n-1} Z^{n-1}$$

wo $n = l^{h-1}(l-1)$.

Es wird also notwendig

$$s^a Z \equiv Z \pmod{\mathfrak{f}}$$

Es ist aber

$$s^a Z - Z = Z(Z^{r^a-1} - 1) \equiv 0 \pmod{\mathfrak{f}}$$

Hiermit ist der zweite Teil des Satzes bewiesen.

Der Grad der Verzweigungsgruppe ist eine Potenz von l , es sei l^b und

$$h' = \frac{r_t}{r_v} = l^{h-b-1}(l-1)$$

musz ein Teiler sein von $l-1$ weil der Grad f von \mathfrak{f} gleich eins ist³⁾. Also ist $b = h-1$, und

¹⁾ H. Satz 120.

²⁾ Dieser Satz ist Satz 129 von HILBERT; enthält aber bei HILBERT einen FELD.

³⁾ H. Satz 71.

$$r_v = l^{h-1}$$

Nun muss noch gezeigt werden, dass für jede ganze Zahl Ω des Körpers

$$s^{b(l-1)} \Omega \equiv \Omega \pmod{\mathfrak{L}^2}.$$

Hieraus geht hervor:

$$s^{b(l-1)} Z \equiv Z \pmod{\mathfrak{L}^2}$$

Es ist $r^{b(l-1)} \equiv 1 \pmod{l}$. Wir können daher setzen $r^{b(l-1)} = 1 + vl$ und es ist also

$$\begin{aligned} s^{b(l-1)} Z - Z &= Z^{r^{b(l-1)}} - Z = Z(Z^{vl} - 1) = \\ &= Z(Z^v - 1)(Z^{v+l^{h-1}} - 1) \dots (Z^{v+(l-1)l^{h-1}} - 1) \dots \quad (3) \end{aligned}$$

Hieraus geht hervor

$$s^{b(l-1)} Z - Z \equiv 0 \pmod{\mathfrak{L}^l}$$

weil jeder Factor rechter Hand von (3) teilbar ist durch $(1 - Z) = \mathfrak{L}$. Hiermit ist der Satz der Verzweigungsgruppe bewiesen.

Wenn wir die einmal überstrichene Verzweigungsgruppe bestimmen wollen, müssen wir den grössten Exponenten L von \mathfrak{L} bestimmen für welchen für jede Substitution der Verzweigungsgruppe gilt:

$$s^{b(l-1)} \Omega \equiv \Omega \pmod{\mathfrak{L}^L} \quad 1)$$

Hieraus ergibt sich

$$s^{b(l-1)} Z - Z \equiv 0 \pmod{\mathfrak{L}^L}.$$

und es sei $r^{b(l-1)} = 1 + vl$

Weil für die Zahlen $b = 1, 2, \dots, l^{h-1}$ nicht alle Zahlen v durch l teilbar sind, kann nicht für jede Zahl b das Product aus (3) noch weiter zerlegt werden. Hieraus folgt

$$L = l.$$

Nur wenn $v \equiv 0 \pmod{l}$ ist, so kann jeder Factor aus (3) wiederum in l -Factoren zerlegt werden. Für diese Werte von b ist also $\overline{L} = l^2$. Die einmal überstrichene Verzweigungsgruppe ist also:

$$s^{l(l-1)}, s^{2l(l-1)}, \dots, s^{l^{h-2}l(l-1)}$$

und

$$r_v = l^{h-2}$$

Die zweimal überstrichene Verzweigungsgruppe ist

$$s^{l^2(l-1)}, s^{2l^2(l-1)}, \dots, s^{l^{h-3}l^2(l-1)}$$

und

$$r_v = l^{h-3}$$

1) H. § 44.

Wenn man auf diese Weise das Product rechter Hand von (3) weiter zerlegt, so findet man den weiteren Beweis des Satzes.

Satz 2.

Ist \mathfrak{P} ein von \mathfrak{f} verschiedenes Primideal von $K(Z)$, dann ist die Zerlegungsgruppe

$$s^e, s^{2e}, \dots, s^{fe}$$

wenn f der Grad des Primideals ist, und $ef = l^{h-1}(l-1)$.

Die Trägheitsgruppe besteht nur aus der identischen Substitution ¹⁾.

Beweis: Es sei p die rationale Primzahl, die durch \mathfrak{P} teilbar ist. In $K(Z)$ gilt:

$$p = \mathfrak{P}_1 \mathfrak{P}_2 \dots \mathfrak{P}_e \quad ^2)$$

wo \mathfrak{P}_i , e verschiedene Primideale sind. Es ist also \mathfrak{P} eins dieser. Hieraus geht hervor, dass es e und nicht mehr als e Substitutionen giebt die das Ideal \mathfrak{P} in ein anderes überführen. Die Zerlegungsgruppe besteht also aus f Substitutionen. Daher ist es die im Theorem angegebene Gruppe.

Es sei nun s^{ae} eine Substitution der Trägheitsgruppe, so musz für alle ganzen Zahlen Ω von $K(Z)$:

$$s^{ae} \Omega \equiv \Omega \pmod{\mathfrak{P}}.$$

also

$$s^{ae} Z \equiv Z \pmod{\mathfrak{P}}.$$

Es ist aber

$$s^{ae} Z - Z = Z^{r^{ae}} - Z = Z(Z-1) \frac{Z^{r^{ae}} - 1}{Z-1}$$

Diese Zahl ist nicht teilbar durch \mathfrak{P} , es sei denn dass $a = 0$ ist; denn $(1-Z) = \mathfrak{f}$ und der Bruch ist eine Einheit ³⁾. Die Trägheitsgruppe besteht also nur aus der identischen Substitution.

§ 2. Die Teilkörper von $K(Z)$.

Es ist K ein cyclischer Körper. Daher ist jede Untergruppe auch cyclisch und jeder Unterkörper ein cyclischer Körper. Ohne Einschränkung der Allgemeinheit können wir uns beschränken auf die Untersuchung Primärer Teilkörper ⁴⁾ das sind solche, die nicht zugleich Teilkörper sind eines Kreiskörpers niedrigeren Grades.

Es sei

$$s^a, s^{2a}, \dots, s^{ba} \quad ab = l^{h-1}(l-1)$$

¹⁾ H. Satz 129.

²⁾ H. Satz 122.

³⁾ H. Beweis des Satzes. 120.

⁴⁾ WEBER, Algebra II pag. 77 etc. (2te Auflage).

eine Untergruppe von (1). Diese ist primär, und nur dann, wenn keine der Zahlen

$$r^a, r^{2a}, \dots, r^{ba}$$

der Einheit congruent ist $(\text{mod } l^{h-1})$. Und dies ist dann und nur dann der Fall, wenn a teilbar ist durch l^{h-1} . Jede primäre Untergruppe hat also die Form

$$s^{al^{h-1}}, s^{2al^{h-1}}, \dots, s^{abl^{h-1}} \quad ab = l-1$$

Den Teilkörper, der zu dieser Gruppe gehört, stelle ich weiter vor durch k .

Der Grad der Körpers ist al^{h-1} .

$$\eta = Z^{r^c} + Z^{r^{2c}} + \dots + Z^{r^{bc}} \quad ; \quad c = al^{h-1}$$

ist eine den Körper bestimmende Zahl¹⁾.

Die Substitutionen des Teilkörpers k sind

$$s, s^2, \dots, s^c.$$

Satz 3. Zerlegungssatz.

Ist p eine von l verschiedene rationale Primzahl und f der kleinste positive Exponent, für welchen $pf \equiv 1 \pmod{l}$ ausfällt, und wird $ef = l^{h-1}(l-1)$ gesetzt, so findet in k die Zerlegung

$$p = \mathfrak{p}_1 \mathfrak{p}_2 \dots \mathfrak{p}_{\frac{v}{e}}$$

statt, wo \mathfrak{p}_i von einander verschiedene Primideale $\frac{v}{e}$ -ten Grades in k sind. v ist das kleinste gemeinsame Vielfache von e und c .

Beweis: Es sei \mathfrak{P} ein in p aufgehendes Primideal des Körpers $K(Z)$. Die Substitutionen, welche die Zerlegungsgruppe von \mathfrak{P} gemeinsam haben mit der Untergruppe (4), sind

$$s^v, s^{2v}, \dots, s^{ef} \dots \dots \dots (5)$$

Diese Substitutionen muss man multipliciren mit den Substitutionen der Gruppe

$$s^c, s^{2c} \dots s^v$$

um die ganze Untergruppe (4) zu bekommen.

Die letzte Substitutionen gehören also nicht zu der Zerlegungsgruppe.

Die Zahlen, welche des Ideal \mathfrak{P} und der Körper k gemeinsam haben, bilden ein Ideal \mathfrak{p} . Nehmen wir an, es sei \mathfrak{p} in k kein Primideal, und in k also $\mathfrak{p} = \mathfrak{q} \cdot \mathfrak{r}$. Es wäre also in k \mathfrak{p} teilbar durch \mathfrak{q} , und in K würde also $\mathfrak{p}\mathfrak{G} = \mathfrak{q}\mathfrak{G} \cdot \mathfrak{r}\mathfrak{G}$ wenn \mathfrak{G} das Ideal aller ganzen

¹⁾ WEBER, pag. 85.

Zahlen von K ist. Während aber $p\mathfrak{G}$ durch \mathfrak{P} teilbar ist, so musz $q\mathfrak{G}$ teilbar sein durch \mathfrak{P} . Also würde in k_1 teilbar sein durch p . Hieraus würde sich ergeben $p = q$, also $r = \mathfrak{G}$ und dies ist nicht angenommen. Also ist p in k ein Primideal.

Nun ist $p\mathfrak{G}$, auszer durch \mathfrak{P} , auch teilbar durch die Primideale

$$s^c \mathfrak{P}, s^{2c} \mathfrak{P}, \dots, s^v \mathfrak{P} \dots \dots \dots (6)$$

Diese sind alle von einander verschieden, weil keine der Substitutionen zu der Zerlegungsgruppe gehört. $p\mathfrak{G}$ ist also teilbar durch ihr Product. Wir werden nun zeigen, dasz p durch kein anderes Primideal \mathfrak{P}' teilbar ist. Nehmen wir an, dasz dies wohl der Fall sei. Es besteht eine Zahl A von K , die teilbar ist durch das Product Π der Ideale (6) aber nicht durch \mathfrak{P}' :

$$A = \Pi \mathfrak{Q}.$$

Es wäre dann

$$s^c A = s^c \Pi \cdot s^c \mathfrak{Q} \text{ oder}$$

$$s^c A = \Pi \cdot s^c \mathfrak{Q}$$

Es sei n_r die relativ-Norm in Beziehung zu k :

$$n_r(A) = \Pi^b \cdot n_r(\mathfrak{Q})$$

Das erste Glied ist eine Zahl von k , die teilbar ist durch \mathfrak{P} , und also auch durch p . Das zweite Glied ist aber nicht teilbar durch \mathfrak{P}' und kann also auch nicht durch p teilbar sein. Dies ist unmöglich. Hieraus geht hervor, dasz p durch kein anderes Primideal \mathfrak{P}' teilbar ist.

Das Primideal p kann weiter nicht teilbar sein durch das Quadrat eines der Primideale (6), denn in diesem Falle würde p in K auch durch ein Quadrat teilbar sein und das ist nicht der Fall. Hiermit ist der erste Zeil des Satzes bewiesen.

Um auch den Grad der Primideale zu bestimmen, bemerke man, dasz aus

$$p = s^c \mathfrak{P} \cdot s^{2c} \mathfrak{P} \cdot \dots \cdot s^v \mathfrak{P} \text{ folgt:}$$

$$N(p\mathfrak{G}) = N(\mathfrak{P})^{\frac{v}{c}} = p^{\frac{f^n}{c-1}}$$

Es ist aber $N(p\mathfrak{G}) = n(p)^b$, wenn n die Norm in k vorstellt. Hieraus ergibt sich

$$n(p)^b = p^{\frac{fv}{e}}$$

$$n(p) = p^{\frac{fv}{bc}} = p^{\frac{v}{e}} \dots$$

Satz 4. Zerlegungssatz.

Die Primzahl l gestattet in k die Zerlegung

¹⁾ H. Satz. 122.

$$l = l^c$$

wo $l = (1-Z)^b g$ ein Primideal ersten Grades in k ist.

Beweis:

Wir wissen, dass in K

$$l = \mathfrak{p}^{h-1(l-1)}$$

wo \mathfrak{p} ein Primideal ersten Grades ist:

$$\mathfrak{p} = (1-Z) \mathfrak{G}.$$

Die Zahlen welche \mathfrak{p} und k gemeinsam haben bilden ein Primideal \mathfrak{f} . Man kann dies auf gleicher Weise beweisen wie im Satz 3. Weiter sind alle Zahlen von \mathfrak{p} die in k liegen, teilbar durch

$$s^c(1-Z) \cdot s^{2c}(1-Z) \cdot \dots \cdot s^{bc}(1-Z)$$

also durch $(1-Z)^b$. Hieraus ergibt sich

$$l = (1-Z)^b \mathfrak{G} = \mathfrak{p}^b$$

und weil

$$l = \mathfrak{p}^{h-1(l-1)}$$

$$l = l^c \quad \text{wo } l = (1-Z)^b.$$

Bestimmung der Discriminante des Körpers k .

Satz 5.

Die Discriminante des Körpers ist

$$\pm l^{\frac{l^{h-1}(lh-h-1)-b+1}{b}}$$

Beweis:

Wir benützen die Beziehungen:

$$D = d^{bn}(\mathfrak{d}_r)^1)$$

$$\mathfrak{d}_r = N_r(\mathfrak{D}_r)^2)$$

$$\mathfrak{D}_r = \mathfrak{G}' \cdot \mathfrak{G}'' \cdot \dots \cdot \mathfrak{G}^{(b-1)^3)}$$

wo D die Discriminante von K ist, d die von k und \mathfrak{d}_r die relativ-Discriminante.

Das Element

$$\mathfrak{G}^{(i)} = \{(Z - Z^{r^{ic}}), (Z^2 - Z^{2r^{ic}}), \dots, (Z^{l^{h-1}(l-1)} - Z^{l^{h-1}(l-1)r^{ic}})\}.$$

Weil D eine Potenz von l ist, ¹⁾ kann die Relativ-Discriminante \mathfrak{d}_r nur teilbar sein durch l und die Relativ-Differente \mathfrak{D}_r nur durch \mathfrak{p} ; also auch $\mathfrak{G}^{(i)}$ nur durch \mathfrak{p} . Aus der Form des Elementes $\mathfrak{G}^{(i)}$ folgt,

¹⁾ H. Satz 39.

²⁾ H. Satz 38.

³⁾ H. pag. 205.

⁴⁾ H. Satz 121.

dasz alle ihre Zahlen teilbar sind durch ℓ und dasz sie nicht alle teilbar sind durch ℓ^2 , also

$$\mathfrak{G}^{(n)} = \mathfrak{g}$$

$$\mathfrak{D}_r = \ell^{b-1} \quad \text{und} \quad \mathfrak{d}_r = \ell^{b-1}$$

$$n(\mathfrak{d}_r) = \ell^{b-1} \pm \ell^{h-1}(\ell h - h - 1) = d \ell^{b-1}$$

Hieraus folgt der Satz.

§ 3. Die Klassenanzahl des Teilkörpers k .

Satz 6.

Wenn die Zahl b gerade ist, und der Teilkörper also reell ist, so hat man für die Klassenanzahl des Teilkörpers den Ausdruck:

$$h = \frac{\Delta}{R}$$

wo

$$\Delta = (-1)^{1/2(a-2)(a-3)} \begin{vmatrix} \log \varepsilon_1 & \log \varepsilon_2 & \dots & \log \varepsilon_{c-1} \\ \log \varepsilon_2 & \log \varepsilon_3 & \dots & \log \varepsilon_c \\ \dots & \dots & \dots & \dots \\ \log \varepsilon_{c-1} & \log \varepsilon_c & \dots & \log \varepsilon_{2c-3} \end{vmatrix}$$

$$c = a \ell^{h-1}$$

$$\varepsilon_g = \sqrt{\frac{(1-Zr^g)(1-Zr^{g+c}) \dots (1-Zr^{g+(b-1)c})}{(1-Zr^{g-1})(1-Zr^{g-1+c}) \dots (1-Zr^{g-1+(b-1)c}}}$$

R ist der Regulator.

Wenn der relative Grad b ungerade ist, wenn also der Teilkörper imaginär ist, ist

$$h = \frac{\prod_u \sum_{t=1}^c e^{\frac{2\pi u t}{c}} (r_t + r_{t+c} + \dots + r_{t+(b-1)c})}{2^{1/2c-1} \ell^{1/2hc}} \frac{\Delta}{R}$$

wo das Product über alle ungerade Werte $u < c$ läuft.

$$\Delta = (-1)^{1/8(a-2)(a-4)} \begin{vmatrix} \log \varepsilon_1 & \log \varepsilon_2 & \dots & \log \varepsilon_{1/2c-1} \\ \log \varepsilon_2 & \log \varepsilon_3 & \dots & \log \varepsilon_{1/2c} \\ \dots & \dots & \dots & \dots \\ \log \varepsilon_{1/2c-1} & \log \varepsilon_{1/2c} & \dots & \log \varepsilon_{c-3} \end{vmatrix}$$

$$\varepsilon_g = \sqrt{\frac{(1-Zr^g)(1-Zr^{g+1/2c}) \dots (1-Zr^{g+(2b-1)/2c})}{(1-Zr^{g-1})(1-Zr^{g-1+1/2c}) \dots (1-Zr^{g-1+(2b-1)/2c}}}$$

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$$R' = \begin{vmatrix} \log \eta_1 & \log \eta_2 & \log \eta_{1/2^c-1} \\ \log \eta_1^{(1)} & \log \eta_2^{(1)} & \log \eta_{1/2^c-1}^{(1)} \\ \cdot & \cdot & \cdot \\ \log \eta_1^{(1/2^c-2)} & \log \eta_2^{(1/2^c-2)} & \log \eta_{1/2^c-1}^{(1/2^c-2)} \end{vmatrix}.$$

η_1, η_2, \dots ist ein System fundamentaler Einheiten und $\eta_i^{(k)}$ sind ihre Conjugierten

Beweis: Um diesen Satz zu beweisen, benützen wir den für alle Körper giltigen Ausdruck

$$h = \frac{1}{n} \lim_{s \rightarrow 1} (s-1) \prod_{\mathfrak{p}} \left(1 - \frac{1}{n(\mathfrak{p})^s}\right)^{-1} \quad (1)$$

und wir beweisen zuerst den Hulfssatz:

$$\prod_{\mathfrak{p}} \left(1 - \frac{1}{n(\mathfrak{p})^s}\right) = \prod_u \left\{1 - \left[\frac{p}{l^h}\right]^{bu} p^{-s}\right\}, p \neq l \quad (2)$$

Das Product linker Hand ist zu erstrecken über alle verschiedenen Primideale, welche in der Primzahl p enthalten sind; das Product rechter Hand über alle Zahlen der Reihe

$$0, 1, \dots, (c-1).$$

Beweis: Das Symbol $\left[\frac{p}{l^h}\right]^u$ wird definirt durch die Gleichung

$$\left[\frac{p}{l^h}\right] = e^{\frac{2\pi p^u}{l^{h-1}(l-1)}}$$

wo p' der kleinste Exponent ist, für welchen $p^{p'} \equiv p \pmod{l^h}$ ausfällt; r ist eine Primitivzahl nach l^h . Es möge d der grösste gemeinsame Theiler von p' und $l^{h-1}(l-1)$ sein, dann folgt aus der letzten Congruenz, dass

$$r^{p' \frac{l^{h-1}(l-1)}{d}} \equiv p \pmod{l^{h-1}(l-1)}$$

oder

$$1 \equiv p \pmod{\frac{l^{h-1}(l-1)}{d}}$$

Hieraus ergibt sich, dass $\frac{l^{h-1}(l-1)}{d}$ der kleinste Exponent ist, für welchen die Potenz von p der Einheit congruent ist. Daher ist

$$\frac{l^{h-1}(l-1)}{d} = f$$

¹⁾ H. Satz 56 en § 27.

²⁾ H. § 116.

und

$$d = e.$$

Das Symbol ist also eine f -te und nicht eine niedere Einheitswurzel. Folglich ist $\left[\frac{p}{l^h}\right]^b$ ein $\frac{f}{g}$ -te und nicht eine niedere Einheitswurzel, wenn g der grösste gemeinsame Teiler ist von f und b ; g ist also der grösste gemeinsame Teiler von

$$\frac{l^{h-1}l-1}{e} \text{ und } \frac{l^{h-1}(l-1)}{al^{h-1}}$$

Es sei q eine Primzahl, die bis zur m -ten Potenz in $l^{h-1}(l-1)$ aufgeht, in e bis zur n -ten Potenz und in al^{h-1} bis zur n' -ten Potenz. Sie geht dann in f und b bis zur $(m-n)$ -ten, resp. zur $(m-n')$ -ten Potenz auf. Hieraus folgt, dass q in g aufgeht in einer Potenz deren Exponent der kleinsten der beiden Zahlen $m-n$ und $m-n'$ gleich ist. Weil dies für alle Primzahlen q gilt, ist

$$g = \frac{l^{h-1}(l-1)}{\text{kleinste gemeinsame Vielfache von } e \text{ und } al^{h-1}}$$

also $g = \frac{l^{h-1}(l-1)}{v}$. Wir haben daher gefunden dass $\left[\frac{p}{l^h}\right]^h$ eine $\frac{fv}{l^{h-1}(l-1)} = \frac{v}{e}$ -te Einheitswurzel ist und keine niedere.

Fassen wir nun das Product rechter Hand aus (2). ins Auge. Weil

$$\left[\frac{p}{l^h}\right]^{b\left(u+\frac{v}{e}\right)} = \left[\frac{p}{l^h}\right]^{bu}$$

so folgt hieraus, dass jede $\frac{v}{e}$ -te Einheitswurzel $al^{h-1} : \frac{v}{e} = \frac{eal^{h-1}}{v}$ Mal in dem Producte auftritt, und da

$$\prod_{u=1}^{u=\frac{v}{e}} \left\{ 1 - \left[\frac{p}{l^h}\right]^{bu} p^{-s} \right\} = 1 - p^{-\frac{v}{e}s},$$

wird das Product rechter Hand von (2) dem Ausdrucke

$$\left(1 - p^{-\frac{v}{e}s}\right)^{\frac{ce}{v}}$$

gleich sein. Hieraus ergibt sich der Hulfssatz, wenn man sich des Satzes 3 § 2 bedient.

Aus (1) folgt nun:

$$h = \frac{1}{x} \lim_{s=1} (s-1) \frac{1}{1 - \frac{1}{n(l)^s}} \prod_p \prod_u \left\{ 1 - \left[\frac{p}{l^h}\right]^{bu} p^{-s} \right\}$$

wo die Producte sich erstrecken über alle früher genannten Werte von u und über alle Primzahlen p , mit Ausnahme von l .

Auf Grund des Satzes 4 ist $n(l) \neq l$ und es ist also

$$h = \frac{1}{\pi} \lim_{s \rightarrow 1} (s-1) \prod_p \frac{1}{1-p^{-s}} \prod_u \prod_{p \neq l} \frac{1}{1 - \left[\frac{p}{lh} \right]^{bu} p^{-s}}$$

Das erste Product erstreckt sich über alle Primzahlen p , wie auch das zweite; denn wiewohl der Wert $p = l$ zuerst ausgeschlossen war, darf man den Factor

$$1 - \left[\frac{l}{lh} \right]^{bu} \text{ für } u \neq 0$$

hinzufügen, weil er den Wert 1 besitzt.

Das dritte Product erstreckt sich über die angegebenen Werte von u , wobei aber der Accent angibt, dass $u = 0$ jetzt ausgeschlossen ist. Wir wissen, dass

$$\lim_{s \rightarrow 1} (s-1) \prod_p \frac{1}{1-p^{-s}} = 1$$

und wir finden schliesslich

$$h = \frac{1}{\pi} \lim_{s \rightarrow 1} \prod_p \prod_u \frac{1}{1 - \left[\frac{p}{lh} \right]^{bu} p^{-s}}$$

Es werden nun die zwei Productzeichen verwechselt:

$$\prod_u \prod_p \frac{1}{1 - \left[\frac{p}{lh} \right]^{bu} p^{-s}}$$

und wir entwickeln jeden Factor in eine DIRICHLET'sche Reihe

$$\prod_u \sum_{n=1}^{\infty} \left[\frac{n}{lh} \right]^{bu} \frac{1}{n^s}.$$

In dieser Reihe setzen wir das Integral ein:

$$\frac{1}{n^s} = \frac{1}{\Gamma(s)} \int_0^{\infty} x^{s-1} e^{-nx} dx$$

$$\sum_{n=1}^{\infty} \left[\frac{n}{lh} \right]^{bu} \frac{1}{n^s} = \frac{1}{\Gamma(s)} \int_0^{\infty} x^{s-1} dx \sum_{n=1}^{\infty} \left[\frac{n}{lh} \right]^{bu} e^{-nx}.$$

Nun ist $\left[\frac{n}{lh} \right] = \left[\frac{n'}{lh} \right]$ wenn $n \equiv n' \pmod{lh}$

also

$$\sum_{n=1}^{\infty} \left[\frac{n}{l^h} \right]^{bu} e^{-nx} = \sum_{n=1}^{l^h-1} + \sum_{n=l^h+1}^{2l^h-1} + \dots = \frac{\sum_{n=1}^{l^h-1} \left[\frac{n}{l^h} \right]^{bu} e^{-nx}}{1 - e^{-l^h x}}$$

Wir haben daher zu betrachten

$$\lim_{s \rightarrow 1} \int_0^{\infty} x^{s-1} \frac{\sum_{n=1}^{l^h-1} \left[\frac{n}{l^h} \right]^{bu} e^{-nx}}{1 - e^{-l^h x}} dx.$$

Weil

$$\sum_{n=1}^{l^h-1} \left[\frac{n}{l^h} \right]^{bu} = 0$$

findet man für diesen Limes, wenn man zugleich setzt $e^{-x} = t$:

$$\int_0^1 \frac{\sum_{n=1}^{l^h-1} \left[\frac{n}{l^h} \right]^{bu} t^n}{t(1-t^{l^h})} dt.$$

Es sei $F(t) = \sum_{n=1}^{l^h-1} \left[\frac{n}{l^h} \right]^{bu} t^n$. Das zu betrachtende Integral wird jetzt

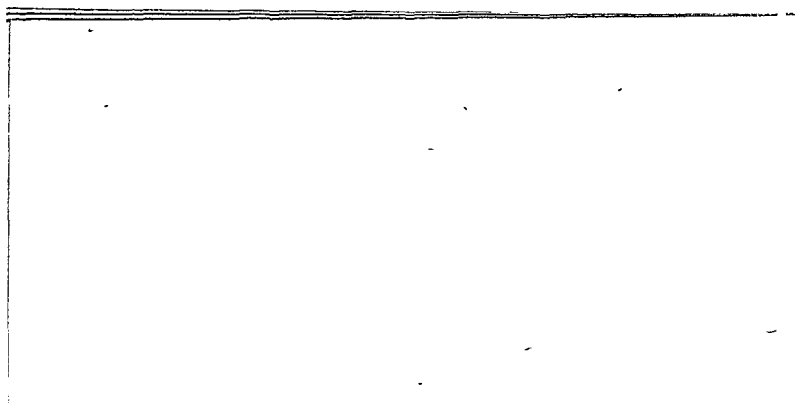
$$\int_0^1 \frac{F(t)}{t(1-t^{l^h})} dt.$$

Die Integration lässt sich durchführen nach Verteilung in rationale Brüche:

$$-\frac{1}{l^h} \sum_{k=1}^{l^h-1} F\left(e^{\frac{2k\pi i}{l^h}}\right) \int_0^1 \frac{dt}{t - e^{\frac{2k\pi i}{l^h}}}$$

und nach der Integration ergibt sich:

$$\begin{aligned} & -\frac{1}{l^h} \left[\sum_{k=1}^{l^h-1} F\left(e^{\frac{2k\pi i}{l^h}}\right) \log \frac{e^{\frac{k\pi i}{l^h}} - e^{-\frac{k\pi i}{l^h}}}{i} + \right. \\ & \left. + \frac{\pi i}{2} \sum_{k=1}^{l^h-1} F\left(e^{\frac{2k\pi i}{l^h}}\right) - \frac{\pi i}{l^h} \sum_{k=1}^{l^h-1} k F\left(e^{\frac{2k\pi i}{l^h}}\right) \right] \quad (4) \end{aligned}$$



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Meteorology. — *"An instrument to be used by the pilot of an aeroplane to measure the vertical velocity of the machine".*

By Dr. C. SCHOUTE, F. A. VAN HEYST, and N. E. GROKNEVELD MEYER. (Communicated by Dr. VAN DER STOK).

(Communicated in the meeting of June 29, 1918).

In many cases it is important that the pilot of an aeroplane should get direct information about the velocity of climbing or falling of his machine, and in the greater part of these cases it is of a higher value that he should know the vertical speed with respect to the medium, the air, than in relation to the earth. The latter especially when he wishes to know the velocity of ascent or descent to be able to judge the effect of his altitude-steering, as well in relation to the safety of flight as where either an extreme quickness or an extreme slowness of the climbing or falling is required.

As a rule the vertical speed is determined by measuring the quickness with which the atmospheric pressure varies. Therefore barometric readings can be executed after certain intervals. In that case however we do not get instantaneous values. The quickness of the changes in the pressure of the air can also be measured by means of the so called variometer, consisting of a vessel that communicates with the outer air by a narrow opening or a capillary tube and is provided with another tube in which a liquid-column can move to and fro when notwithstanding the "leakage" an under-pressure or an over-pressure is generated in the vessel. All these determinations based on pressure-changes give the vertical speed in relation to the earth and not to the medium, and moreover the results are not independent of the height at which they are obtained, so that generally a correction, and often a considerable correction, has to be applied.

This complication does not arise when the determination is made by vertical cup-anemometers. The idea suggests itself, to get indications of the vertical speed electrically by means of a dynamo-armature mounted on the axis of a vertical anemometer. The more so because indications at a distance are wanted, as the anemometer requires to be mounted in undisturbed air, which as a rule is not to be expected immediately in front of the pilot-seat. In such measurements however, the result would be spoiled by the friction, which is unavoidable in the anemometer, and which cannot be slight in this

case, because of the strong lateral pressure on the axis during the rapid motion. The rapport between the vertical speed V_v , and the number of revolutions N can be expressed by the relation

$$V_v = A + B N$$

in which A and B are constant. In the case V_v is smaller than A the anemometer stands still. Further it would already be a difficulty to obtain a permanent vertical position of the axis.

In the instrument the description of which follows and which we have called *scansimeter* the foresaid disadvantages of the vertical anemometer have been avoided without the advantages having been abandoned. Therefore electric currents are measured which are generated in a dynamo-armature, mounted on an axis which has the direction of the line of displacement of the machine instead of being kept vertical. This directing as well as the rotation of the axis are obtained by an airscrew fixed on the hind part of the axis, which is made to rotate by reaction during the rapid motion through the air, and thus gives the correct position to the well-poised axis. Therefore it was practically sufficient to fix the axis pivoting around a line perpendicular to the body of the machine, which line must be horizontal when the aeroplane lies flat in a lateral sense. This simplification was applied for the advantage in the construction only. In what follows this line is always dealt with as a horizontal one, which does not introduce an appreciable error.

The total speed of the machine V_t can, in perfect analogy to what has been said about the vertical velocity be represented by

$$V_t = A + B N$$

In this case the influence of the constant of friction A is much smaller because V_t is always considerable, so that when the axis is made to run lightly between ballbearings the number of revolutions N is approximately proportional to V_t .

In order to generate a current which offers a measure, not of the total speed with respect to the air, but of the vertical component of that quantity, $V_v = V_t \sin \alpha$ (fig. 1), the magnetic field in which

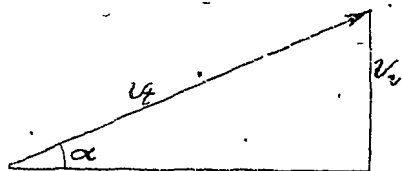


Fig 1

the dynamo-coil rotates is dressed in a special way, viz. in such a way that the direction of the field, which we suppose to be homogeneous for the sake of simplicity, is always kept horizontal and besides that parallel to the vertical plane through the axis of rotation.

In order to realise this in the first model slits have been made in the permanent magnet, which was to procure the magnetic force. This magnet was suspended between horizontal pivots, in such a way that the lines of force were always kept horizontal. By inserting the axis of rotation through the slits, this axis can be made to be parallel to the lines of force when the direction of the flight is horizontal, while when the machine climbs or falls the angle between the lines of force and the axis corresponds to α in fig. 1.

The later models had two magnets instead of one, placed parallel to each other on both sides of the axis. In both cases the horizontal axis of suspension of the magnet was made to coincide with the line around which the armature axis pivoted.

If the axis AA (fig. 2) be parallel to the lines of force, no difference of potential will arise between the ends of the rotating

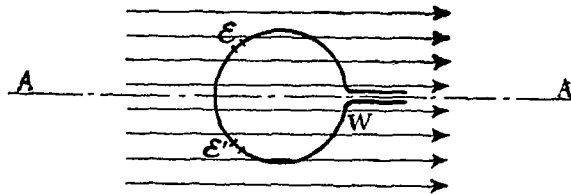


Fig 2

winding W . The electromotive force in an element ϵ of the coil is exactly counteracted by an equivalent E. M. F. in the opposite sense, generated in the element ϵ' lying in the position of a reflected image with respect to the axis.

If the axis AA (fig. 3) makes an angle α with the lines of force, an electromotive force will be generated in W proportional not only

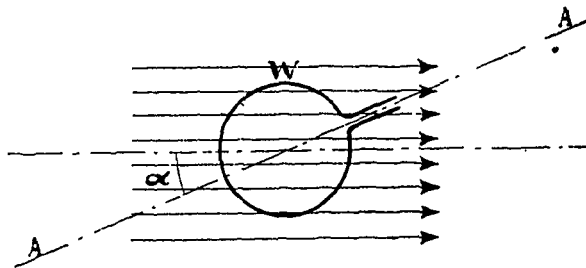


Fig 3

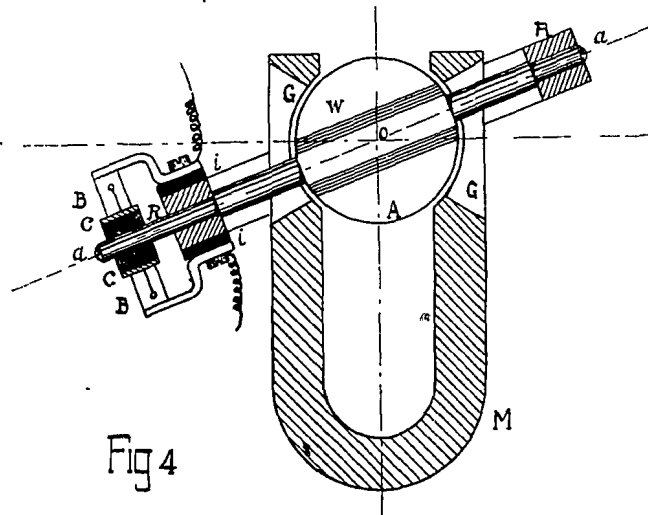
to the speed of rotation and the strength of the field, but *caeteris paribus* also to $\sin \alpha$. The magnetic field can be considered as being

the effect of a cooperation of two fields, one in the direction of the axis of rotation and another parallel to the vertical plane through the axis and perpendicular to the latter, which two fields bear a proportion as for the strength as $\cos \alpha : \sin \alpha$. Of those fields only the latter can generate a current in W .

When the changes in the electromotive force in W in consequence of changes in α shall be proportional to $\sin \alpha$, the condition must be made, that the magnetic field be unvariable when the relative position of axis and lines of force changes. Therefore 1 the material for the axis of rotation must be a non-magnetic one, and 2 if the homogeneity is not to be relied upon, and if a weak iron core shall be used, the form of the core must be globular.

By combining the use of a dynamo axis driven by reaction by an air screw with the *sinusdynamo* described here in principle, a system is obtained by which currents are generated, proportional as well to the total speed V_t of fig. 1, as to the sinus of the angle α under which the machine climbs or falls, (fig. 3) so that the strength of those currents offers a direct measure of the vertical velocity with respect to the medium, which measure is independent of the height of observation and of all quantities connected with the machine, so that no correction whatever has to be applied.

In fig. 4. the mechanism of such a sinusdynamo is illustrated schematically. The armature has been executed in the most simple way: the coil W has been imbedded in two parallel circular grooves on both sides of the axis aa . In the magnet M the slits G allow

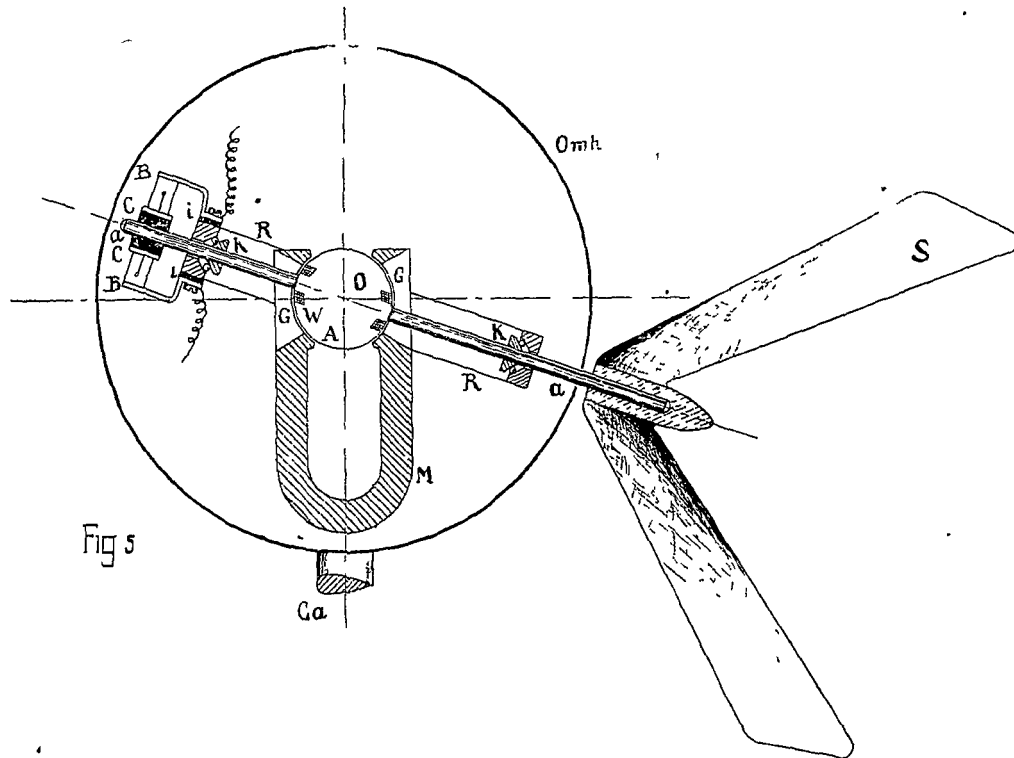


the axis to take different positions with respect to the magnet. The axis pivots around O , the point that at the same time determines

the horizontal axis on which the magnet is suspended. As by continuous currents only the direction of the motion is given, so that it is possible to discriminate between rising and falling, a two parted collector *C* has been made use of, with insulated (*i*) brushes *B*; fixed on the frame *R*.

Fig. 5 represents the scheme of the scansimeter

Besides the parts noted in fig. 4 by analogous symbols this figure shows the screw *S*, the ball-bearings *K* and the circular cover *Omh*.



sideways slightly convex. *Ga* is what is shown of the support in which the common axis of the magnet and of the frame *R* are adjusted.

The currents generated in the dynamo are measured with an instrument, fixed in front of the pilot. It is preferable to choose an instrument of a special form, so that a rising of the hand corresponds to a climbing of the machine and a lowering of the former to a descent of the latter. Meters of the usual Desprez d'Arsonval type are very practical for these determinations.

To avoid the proportionality of the excursion to the speed of rotation from being disturbed by reaction from the armature, it is advisable to keep the current as weak as possible, consequently to give the measurings the character more of determinations of potential

differences than of the strength of currents, and therefore, to take a small resistance for the dynamo-coil in comparison to that of the current meter. On the other hand it is desirable to take a resistance for the dynamo coil of at least some times ten Ohm, in order to exclude a too great influence of transit-resistances.

The following can be recorded about the preparatory experiments carried out with this instrument.

One of the specimens of the scansimeter showed the following unexpected effect, which the others showed less or did not show at all. After the axis of rotation had been carefully placed horizontally in the laboratory, and the position of equilibrium of the magnet had been regulated in such a way that a rotation of the axis did not generate any current, a current could be produced arbitrarily in both directions by changes in the position of the brushes only. This phenomenon, rather startling at first sight, can be explained as follows ¹⁾.

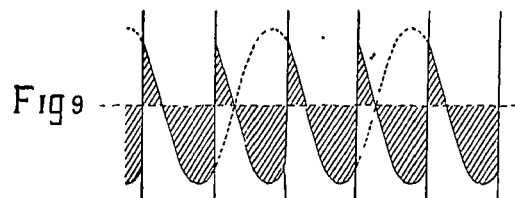
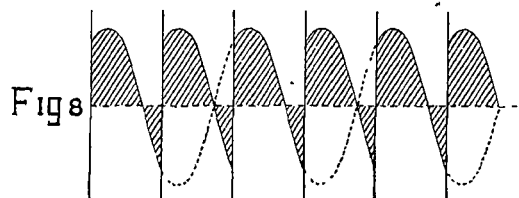
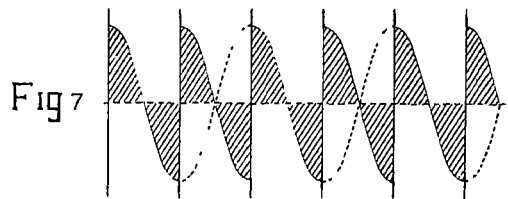
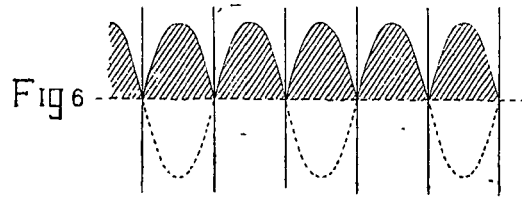
Evidently the magnetic field cannot be considered as resulting from two fields, one after the axis and another perpendicular to the axis, but here a third component has to be accepted, which we can assume to be horizontal and perpendicular to the axis. If the brushes are fixed in such a position, that the component in the vertical plane comes to full development, i. e. that the commutating of the current takes place at the moments the difference of potential is zero (fig. 6), the effect of the horizontal component vertical to the axis is likewise zero, because for this component the commutation comes at the moments the E. M. F. has its maximal value (fig. 7). When the windings are distorted with respect to the collector or the brushes with regard to the magnetic field, then this horizontal component is no longer inactive, so that a current can be produced, at will in either direction (fig. 8 and 9).

The wryness in the field, which this specimen showed, can easily occur, when the centering of the armature between the poles of the magnet resp. the poleshoes, as well sideways as in the direction of the axis, is deficient, which can very well be the case in an air gap of not more than some tenths of a millimeter. This explanation requires, as was confirmed by the experiment, that, when the relative position of collector and coil is the right one, such

¹⁾ We may neglect the armature reaction because it was very small, given the weakness of the currents. Besides, by taking into account this reaction hardly anything changes in the reasoning.

an unsymmetrical distribution of the magnetic force does not cause any error in the determinations.

Some difficulty arose in finding the right form and the right material, that allows the current to be taken off from the collector



uninterruptedly during a long time. In one respect the conditions are not very exigent: fluxions in the strength of the current by changes of the resistance at the collector up to one percent can be allowed in practice without any reserve. On the other hand the reliability of the working must be guaranteed at a minimum of care and looking after. By making the diameter of the collector not to exceed some millimeters and by taking silver both for the collector and for the collector springs a method of transmission of the current was arrived at which gave excellent results during a long time at a stretch, without any greasing or oiling.

A freely suspended magnet cannot be prevented from executing slight oscillations in consequence of incidental accelerations and

retardations in the air, nor the frame which carries the axis of rotation from being set swinging around its pivots. To avoid an inconvenient agility of the hand under influence of such oscillations, care was taken to secure a slow indication of the currentmeter, which was obtained by making the instrument over-deadbeat by damping, the oscillations of the magnet being made as short as possible, besides which a damping by mechanical friction was applied for so far as coexistent with the requirements of an accurate working.

If the instrument was adjusted sideways on the aeroplane out of the "propeller-wind" about halfway between the two decks of a biplane an ascension was indicated when the machine flew at level keel, while an ascending was strongly exaggerated and a descent was not at all or hardly indicated. This shift in the direction of an ascension in the indications, which was observed in a higher or lower degree in a number of places on the aeroplane is caused by air currents generated by reaction from the aeroplane in its quick motion through the air. When fixed at the end of a wing at some distance sideways, the instrument gave undisturbed indications. In this position however the troubles of the oscillations mentioned above were felt more strongly.

It would be a valuable result if by means of this instrument a systematical investigation could be made of the vertical velocities of those reaction currents produced in the neighbourhood of an aeroplane in flight.

It is highly to be regretted that there is no possibility in our country of calibrating the scansimeterscale in an artificial air current. When the electrical resistances, the strength of the magnetic field and the sensitiveness of the currentmeter are known, this calibration consists in the research concerning the number of revolutions the screw makes at various velocities relatively to the air. Since the air-tunnel set up on a small scale by the "Kon. Nederl. Vereeniging voor Luchtvaart" could no longer be used, such a testing cannot be executed in our country.

Physiology. — *“Is there any Relation between the Capacity of Odorous Substances of Absorbing Radiant Heat and their Smell-Intensity?”* By Dr. G. GRIJNS.

(Communicated in the meeting of September 29, 1918).

For a thorough knowledge of the apperception of our senses we must first of all find out the special character of the stimulus to the receiving of which the organ is adapted. The study of light and sound teaches us that the quality is determined by wavelength, and its intensity by amplitude. With regard to smell and taste we do not know as yet what property of the odorous or the gustable substance determines the sensations they arouse.

Many attempts have been made to establish a relation between smell and certain qualities. Up to the present without success.

The chemical properties which, indeed, were thought of first and foremost, appeared to yield no satisfactory interpretation of all the peculiarities. ZWAARDEMAKER¹⁾, therefore, reaches the conclusion in his “Physiologie des Geruchs”, that no direct relation exists between the chemical constitution of a substance and its smell.

LIÉGEOIS²⁾ pointed out that a large number of odorous substances, when put on the surface of clean water, present the same phenomenon as PRÉVOST³⁾ described for camphor and even calls it the “odoroscopic phenomenon”. However, it turned out that a number of inodorous substances also present this phenomenon. So there is no argument for correlating smell with surface-tension phenomena, to which VAN MENSBRUGGE attributes the behaviour of camphor on water.

ZWAARDEMAKER's finding⁴⁾ that a large number of odorous substances evolve an electrically charged vapour, when sprayed in aqueous solution, gave rise to the supposition, that electrical charges come

¹⁾ H. ZWAARDEMAKER, Die Physiologie des Geruchs. Leipzig 1895.

²⁾ LIÉGEOIS: Sur les mouvements de certains corps organiques à la surface de l'eau. Arch. de Physiol. 1868 T. I p. 35.

³⁾ PRÉVOST: Annales de Chimie et de physique XXI p. 254, XXIV p. 31, XL p. 1.

⁴⁾ H. ZWAARDEMAKER, These Proc. XIX p. 44, 334 and 551.

into play here. ZEEHUIZEN¹⁾, however, has detected that also saponins and antipyretica, which do not smell, produce an electrical charge. This, therefore, is not a property peculiar to odorous substances alone.

TYNDALL²⁾ previously observed that several odorous substances possess a great capacity of absorbing obscure rays. We might, therefore, expect a correlation between these two properties, as it is quite possible that odorous substances derive energy from their surroundings to transmit it to the olfactory organ.

If so, we must expect smell-intensity and absorbing capacity in different odorous substances to evince, if not proportionality, at all events parallelism.

On Prof. ZWAARDEMAKER's suggestion I undertook an investigation in this direction.

Since I purposed merely a preliminary orientation with regard to this problem, there was no need of being very accurate, so that many difficulties could be avoided.

I determined the absorptive capacity of dry air that had passed through a slightly curved tube filled with the fluid under examination and compared it with the capacity of pure dry air by a differential method.

On either side of a Nernstlamp a glass tube was placed closed at both ends with a plate of rocksalt. Behind these tubes were arranged MOLL's thermo-piles connected oppositely with a MOLL galvanometer. Air or gas could be sucked through one of the tubes by means of a spirometer. In front of the other tube an irisdiaphragm was mounted, the area of which could be read from a large protractor. The width of the opening, corresponding to every scale-division, was determined by measurement.

The deviation of the galvanometer was measured by the movement of the reflected image of an illumined copperwire on a millimeter-scale. For every determination dry air was first passed through the one tube, and then the diaphragm adjusted so as to make the galvanometer point to zero. - This could readily be done, as the apertures in double screens, interposed between the lamp and the measuring tubes, could be covered or uncovered at the same moment.

Subsequently air was sucked for about ten minutes through the fluid under examination, and through the measuring tube. After this the diaphragm was so adjusted that again removal of the

¹⁾ These Proc. XX p. 1272.

²⁾ J. TYNDALL: Heat as a mode of motion p. 366.

screens did not cause a deflection of the galvanometer. Next the tube was rinsed for a quarter of an hour, or longer if need be, with dry air and the zero-point determined again. If the two zero-points are approximately equal and the determination with the odour-containing air deviates, the ratio of the diaphragm apertures is that of the quantities of light transmitted, from which the absorption can be calculated.

In the same way dry air, sucked through the fluid under examination was led through a glass vessel provided with an opening, which could be closed by a glass plate, or to which ZWAARDEMAKER'S diaphragm odorimeter could be adjusted.

By means of this apparatus, a description of which will soon be published, odour-containing air can be diluted to a known proportion. Into a cylindrical smell-chamber, from which the content is inhaled through a glass tube, the odorous air enters through an irisdiaphragm at the bottom, while free air can enter through lateral adjustable slits.

We estimate the dilution in which the scent almost fails to be recognized. So the absorptive capacity and the smell-intensity of a given mixture of odorous substance and air were known. We now calculated for every examined mixture how many times it had to be diluted to absorb just 1% of the incident light, and from this how many olfacts such a dilution would contain.

The subjoined table shows the results thus obtained:

Substance examined	Number of olfacts	Substance examined	Number of olfacts
Methylic alcohol	12	Bromoform	16°
Ethylic alcohol	7.2	Benzol	72
Ether	> 13 ^{00 1)}	Toluol	16°
Amylic acetate	20 ⁰⁰	Xylol	94
Glacial acet. ac.	36°	Toluidin	51
Propionic acid	22°	Eucalyptol	> 34 ^{00 2)}
Chloroform	14°	Eugenol	> 14 ^{00 2)}

If smell-intensity were related to capacity of absorbing radiant heat the above values might be expected to be approximately equal. Since they are so widely different such a relation must be denied.

¹⁾ The dilution of ether-containing air was beyond the capacity of my measuring instrument.

²⁾ In both these cases the absorption was less than 1/2 perc., consequently so minute as to elude measurement with my equipment.

Botany. — “On the course of the formation of diastase by *Aspergillus niger*”, by Prof. F. A. F. C. WENT.

(Communicated in the meeting of September 29, 1918).

It is already a long time that I have intended to carry out an investigation on the influence which external conditions exercise on the formation of enzymes, more especially in *Aspergillus niger*.

In a certain sense this would be a continuation of an earlier investigation, which however related to another fungus, *Monilia sitophila*¹⁾. That my attention has now been turned to *Aspergillus niger* has its explanation in the fact that KATZ has expressed opinions about the formation of enzymes in this fungus, which seem to me hardly probable, but with regard to which a sure judgment can of course only be formed after a renewed investigation²⁾. Other work has prevented me from carrying out my intention, and seems likely to do so in the near future; moreover in the meantime another investigator, HARALD KYLIN has repeated KATZ' investigation by a better method³⁾. It might thus appear that there is no reason for publishing a paper, if my preliminary experiments had not given some results, which seem to me of sufficient importance to warrant publication even though the investigation is incomplete.

This preliminary inquiry dealt with the question how the formation of diastase by *Aspergillus niger* depends on its age. It seemed to me that in all comparative investigations insufficient attention has been given to this important point, namely the age of the cultures. Generally cultures of differing nutrition were all after the same length of development compared with one another, it being however evident, that the comparison was here made between unlike things, because the nutritive values of the solutions differed widely. It seemed to me that it would be necessary to trace the whole course of the formation of enzymes in successive intervals of time in each nutrient medium.

I have not extended the investigation to this length, but have

¹⁾ F. A. F. C. WENT, Ueber den Einfluss der Nahrung auf die Enzyymbildung durch *Monilia sitophila* (Mont.) Sacc. Jahrb. f. wiss. Botanik. 36 1901.

²⁾ J. KATZ, Die regulatorische Bildung von Diastase durch Pilze. Jahrb. f. wiss. Botanik. 31 1898.

³⁾ HARALD KYLIN, Ueber Enzyymbildung und Enzymregulation bei einigen Schimmelpilzen. Jahrb. f. wiss. Botanik. 53 1914.

only endeavoured to solve the problem in one definite case, how the formation of diastase takes place. For the culture-fluid a solution was always used containing 5 % glucose, 0.5 % NH_4NO_3 , 0.1 % K_2HPO_4 and 0.05 % MgSO_4 . This solution was sterilised by heating it on three successive days for half-an-hour to 100°C .

The inoculation was carried out by means of a platinum loop with fluid containing the conidia of *Aspergillus*. It is known that the latter remain floating on the surface of the fluid and that one cannot keep them submerged. One can take care to get a fairly uniform distribution on the surface of the fluid and then always inoculate the same amount with a loop. Thus one does not indeed obtain a complete uniformity of the number of conidia in the different culture flasks, but the differences are so small as to exercise no influence on the final result, at most a slight difference in development is observable in the first two days. It should be possible to ensure a greater uniformity of inoculation-material, but this would be fraught with so many difficulties that it is not worth while in view of the very small advantage it would yield. It needs no demonstration that the sowing of a single conidium is here wholly impermissible, because then one would have to reckon with great individual differences. These differences can only be compensated for by inoculation with a large number of conidia.

The fungi were grown in glass (Erlenmeyer) flasks and for comparative experiments the same quantity of culture-fluid was always placed in similar flasks. The latter were kept in a room at a constant temperature of 24°C . with variations of 0.5° .

The cultures were in darkness; artificial light only was used for inoculation and observation.

At first daily and later after two, three and more days determinations were made of the amount of enzyme present in the culture-fluid and in the fungus-mass of one of the flasks, but generally this determination was made for 2 or 3 flasks. Then at the same time the fungus-mass formed in one of the flasks was collected on a tared filter and weighed after it had been dried, so that an idea was obtained of the quantity of dry material which had been formed. The other fungus-mass was ground fine in a mortar with the help of a little kieselguhr, and afterwards extracted for one hour with the culture-fluid and subsequently this fluid was filtered off and examined with regard to enzyme: now if we know the quantity of enzyme present in the culture-fluid, which had therefore diffused outwards, then we have only to subtract this from the quantity found in order to ascertain how much enzyme was present in the mycelium.

The quantity of diastase was determined by finding how long it was before the starch had completely disappeared out of a starch-solution of definite strength, which had been mixed with the enzyme-solution, whence the quantity of enzyme must be inversely proportional to the time. The presence or absence of starch was investigated by the aid of an iodine-solution of known strength. Theoretically this is not the best method; it would be better to determine the quantity of sugar which is formed in a definite short time from the starch and then to consider the quantities of diastase proportional to the figures thus found. But this is impossible in the case of the diastase of *Aspergillus niger*, because there is here often such a very small quantity of enzyme, that the sugar could not be determined. For this reason it was thought preferable to divide the enzyme-solution to be examined, into a number of equal parts, and to mix each of these with the same small quantities of very dilute starch-solution and successively to test the mixtures after a definite interval for the presence or absence of starch with the aid of the same very dilute iodine-solution.

Preliminary experiments showed that when a solution is used which contains in 100 gr. water 62.5 mg. iodine and 62.5 mg. potassium iodide, 1 ccm. of this is enough to colour a starch-solution distinctly blue, when this contains 1 mg. soluble starch in 10 c.c. of water, whilst when this amount is only 0.2 mg., a definite red-violet colour still results.

There are formed from starch, before it is completely hydrolysed by the action of the diastatic enzyme of *Aspergillus niger*, erythro-dextrin-like intermediate products, which with iodine are coloured red; so long as such bodies were present it was assumed that the reaction was not ended; it was only when after mixing with the iodine solution, the colour remained yellow, that the starch was considered to have disappeared completely. Naturally all the fluids were under the same condition. For this reason 5 c.c. of the fluid to be investigated was always mixed in test-tubes with 5 c.c. of a solution which contained 0.08 pc. of soluble starch and with some drops of toluene; the latter was for the purpose of preventing any development of fungi or bacteria in the experiments of longer duration. The tubes were then shaken for a short time; and then placed in the dark at a constant temperature of 24° C. After a certain time the fluid was filtered off from one of the test-tubes and 1 cc. of the above mentioned solution of iodine was then added. If the colour was blue or red, this process was repeated some time later, until the colour was decidedly yellow.

The question was whether in this way, by repeated trials, trustworthy results could be obtained. In order to ascertain this, some preliminary experiments were carried out. From a culture of *Aspergillus niger* which was 5 days old, the fluid was filtered off and divided into two equal portions. One half remained unchanged, the other was again divided into two, and one of the halves was boiled for a short time to ensure destruction of the enzyme, and after cooling it was mixed with the unboiled portion, so that there were two fluids of which one must contain double the quantity of the enzyme in the other. 5 cc. of each of the fluids was mixed in a test-tube with 5 c.c. iodine-solution and after certain intervals each tube was tested for the presence of starch. It was found that the undiluted solution after 95 minutes was still coloured somewhat orange yellow by iodine, whilst after 100 minutes the colour was pure yellow, so that the colour-change had taken place after 97.5 minutes. In the twice-diluted solution the change had taken place in the interval between 180 and 190 minutes, therefore in about 185 minutes. The proportion of 97.5:185 is 1:1.9, whilst the quantities of enzyme were to one another as 2:1, so that the error in determination was not more than 5%.

In another case the starch was hydrolysed by the undiluted solution in 495 minutes, by the twice-diluted in 907 minutes and by the 10 times diluted in 4365 minutes. These figures are as 1:1.8:8.8 instead of as 1:2:10.

Lastly there was a third case in which the enzyme-solution had been diluted 2, 4, 8, and 16 times. The result is shown in the following table.

	Still coloured red with I.	Disappearance of starch	Average	Proportion
Undiluted solution	After 1 h. 45 min.	After 2 hours	1 h 52 min.	1.—
Twice diluted "	" 3 " 20 "	" 4 "	3 " 40 "	2.—
4 times " "	" 7 " 30 "	" 8 "	7 " 45 "	4.1
8 " " "	" 13 " 30 "	" 16 "	14 " 45 "	7.9
16 " " "	" 27 " 00 "	" 28 "	27 " 30 "	14.7

When it is remembered how tentative these estimations were then the agreement between the determination and reality must be considered very satisfactory; the difference here amounts to much less than 10% in most cases.

One can therefore conclude that in this way an idea can be obtained of the quantity of enzyme which is present in certain fluids. This only holds good on condition that these fluids have for the rest quite the same composition. Now it has unfortunately to be stated that the culture-fluid of each fungus changes in the course of the development, partly because certain bodies from the fluid are taken up by the developing mycelium, partly also in consequence of secretions by the fungus.

In this respect therefore the cultures of *Aspergillus* at different stages are not quite comparable. The concentration of the H-ions could be made equal, by the addition of acid or alkali, but that would not completely meet the case, because other bodies may certainly be present which hasten or retard the reaction and which, at least at the present time, cannot be determined.

There is indeed another method conceivable which would consist in mixing culture-fluids of different stages with one another, after part of them had been boiled to destroy the enzyme. By this means one would then be able to trace whether in a given solution substances were present which hasten or retard the enzyme-action. From some preparatory experiments it appears that something may perhaps be obtained by such a method. So, for example, the fungus from a culture 7 days old, was finely ground up, and then extracted with its own culture-fluid, and the solution was then diluted with an equal volume of *a.* its own culture-fluid, after this had been boiled to destroy its enzyme, *b.* a culture-fluid similarly boiled from a culture which was 17 days old, and *c.* a like solution of a culture which was 3 days old. On investigation it was found that when 5 c.c. of the above mentioned solutions were mixed with 5 cc. of a solution of soluble starch of 0.08%, 1320 minutes elapsed in the cases of *a* and *b* before all the starch had disappeared, whilst in the case of *c*, this period amounted to 900 minutes. Hence there was in *c* either present an accelerator, or the solutions *a* and *b* contained retarding substances which were wanting in *c*. For the rest this method was not worked out further on account of the condition mentioned at the beginning of this paper, and the figures obtained must therefore be received with a certain reserve. It will, however, be seen that they nevertheless give some idea of the course of the formation of diastase in *Aspergillus niger*.

Before I further mention the results of the investigation I will first indicate by means of an example, exactly how the figures were obtained. Three flasks, each containing 75 c.c. of culture-fluid were investigated, after a culture of *Aspergillus niger* had been in them:

for 3 successive days. From flask 1 the culture-fluid was filtered off, the fungus-mass ground fine in a mortar with kieselguhr, and afterwards extracted with the culture-fluid. Subsequently it was filtered and the filtrate distributed in test-tubes, so that each tube got 5 c.c. of fluid; then to each was added 5 c.c. of a 0.08 % solution of soluble starch. After 60 minutes the fluid of one of the tubes was examined in the manner already described with iodine; the colour was blue. After 180 minutes the second tube gave a pale claret-red, after 225 minutes the colour of a third tube was light-yellow. It may therefore be assumed that the hydrolysis of the starch had taken place in about 200 minutes (1).

A second flask was treated in the same way; the reactions with the iodine solution can be seen in the following table:

After 60 minutes.	blue
„ 180	reddish-violet
„ 220	„
„ 255	pale claret-red
„ 295	reddish-yellow
„ 340	yellow

so that the time taken for hydrolysis was about 315 minutes (2).

The fungus-mass in a third flask was collected on a tared filter, then washed and dried; the dry material weighed 69.5 mg. The culture-fluid alone was examined for enzymes by the method described for the other flasks. The following table shows what reactions were obtained with the iodine-solution.

After 175 minutes	blue
„ 250	blue
„ 335	bluish-violet
„ 485	reddish-violet
„ 1055	reddish-yellow
„ 1130	pale reddish-yellow
„ 1190	yellow

It may therefore be concluded, that the hydrolysis of the starch required about 1160 minutes (3).

If the quantity of enzyme which is necessary to hydrolyse the soluble starch in 10 c.c. of a 0.04 % solution in 100 minutes is put equal to 10 then the quantity in the test-tubes in case (1) is $\frac{100}{200} \times 10$, in (2) $\frac{100}{315} \times 10$, in (3) $\frac{100}{1160} \times 10$, therefore the whole

quantity in the 75 cm. is $\frac{75}{5}$ or 15 times greater.

Therefore the calculation in the case of (1) gives a quantity of diastase of 75.0, in (2) 47.6 and in (3) 12.9. If it is assumed, that in flasks 1 and 2 the same quantity of enzyme was present in the culture-fluid as in flask 3, then there remains for the enzyme in the mycelium for (1) 62, and for (2) 34.7. These figures appear to diverge widely, but nevertheless we shall soon show, that there is a great regularity in the quantity of enzyme found on daily investigation.

The experiment which is here described in detail was the beginning of a whole series of determinations. Altogether 42 similar flasks were inoculated with *Aspergillus*, and after a given number of days three of them were each time examined in the manner described. The result is given in the appended table. In column I the number of days is given, during which the culture lasted, in column II the quantity of enzyme in the mycelium and culture-fluid together, in column III the same for the other flask, in column IV the mean of II and III, in column V the amount of enzyme in the culture-fluid alone of the third flask, in column VI the difference between IV and V, and finally in column VII the dry weight of the crop of fungus in flask 3. Wherever the sign < is found in the table, this indicates that the last test-tube still gave

I	II	III	IV	V	VI	VII
3	75.0	47.6	61.3	12.9	48.4	69.5 mgr.
5	44.1	44.1	44.1	4.2	39.9	319.0 "
7	66.6	41.8	54.2	3.7	50.5	398.0 "
8	21.7	30.3	26.0	3.0	23.0	538.5 "
10	< 6.0	< 6.0	< 6.0	2.3	< 3.7	549.0 "
12	4.1	7.5	5.8	1.8	4.0	699.0 "
15	< 2.8	< 2.8	< 2.8	trace	< 2.8	939.0 "
17	2.3	3.3	2.8	trace	2.8	936.5 "
19	< 1.6	< 1.6	< 1.6	0.5	< 1.1	943.5 "
23	1.0	2.6	1.8	2.0	0.0	899.0 "
26	6.2	10.0	8.1	2.5	5.6	709.0 "
30	16.7	4.5	10.6	3.3	7.3	782.0 "
33	11.1	29.3	20.2	16.7	3.5	742.5 "
37	16.6	50.0	33.3	11.1	22.2	734.5 "

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a reaction with the iodine-solution, so that the limit of hydrolysis had not yet been reached. Wherever "trace" is written, the amount is less than 0.5, although a change in reaction was still clearly observable.

The figures of columns II and III appear at first sight to diverge widely, but on nearer inspection a certain regular course is however noticeable, by which column IV is justified. The amount of enzyme in the culture-fluid is generally very small, so that the course of column VI is scarcely different from that of column IV. There are a few exceptions to this, but I think it better to give the complete observations first and then only to begin a discussion of the figures found.

A second series of figures had reference to a number of cultures which had been made at the same time as those already described, and which only differed from them in that instead of 75, 150 cc. of culture-fluid was used and in larger flasks, in consequence of which the surface of the culture-fluid amounted to 47 square cm. instead of 24 as in the foregoing series. There was indeed the possibility that on this account the development of *Aspergillus* might continue longer,

	Enzyme in fungus and culture-fluid	Enzyme in culture-fluid only
after 3 days	65.2	6.7
" 5 "	75.0	5.4
" 7 "	75.0	3.6
" 8 "	75.0	< 3.0
" 10 "	30.0	2.2
" 12 "	30.0	< 1.9
" 15 "	13.6	1.5
" 17 "	11.0	1.2
" 19 "	1.7	0.0
" 23 "	4.0	0.0
" 26 "	4.2	0.0
" 30 "	11.3	0.0
" 33 "	44.1	0.0
" 37 "	4.5	0.0

and with it also the formation of enzyme. Of these flasks half were directly examined as to enzyme, the others after they had stood for an hour with the finely ground fungus-mass and had then been filtered. The results obtained are shown in the fore-going table.

In order also to trace during a longer period the course of diastase formation, a new experiment was begun with 99 flasks each containing 300 c.c. of nutrient solution and treated exactly in the same way as the first series with this one difference, that this time account was taken of the quantity of liquid which remained when cultivation was over. In consequence of consumption by the fungus and of evaporation this quantity diminishes, a fact that in the above experiment of 37 days could not have so strong an influence on the results as in those lasting no less than 149 days. In consequence of this the calculation was more complicated, but still sufficiently simple, and after what has already been said, it will not be necessary to give the slightly modified calculation here; we may only remark that the figure of column VI is therefore not exactly the difference between IV and V. With this qualification the different columns in the following table, have the same significance as in the first table already given.

The figures of column IV are represented graphically in fig. 1. In this figure the age of the culture (in days) is measured on the axis of

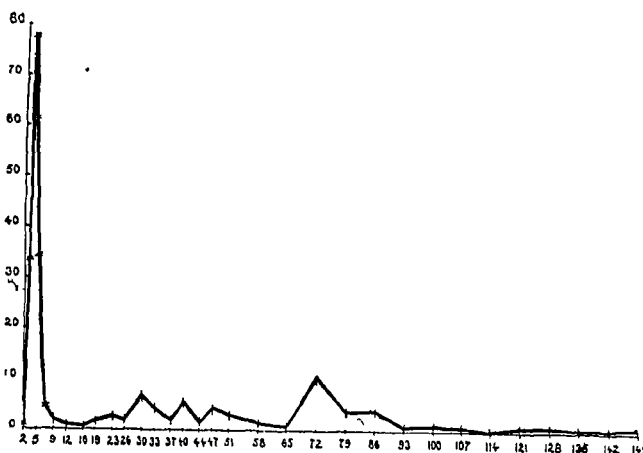


Fig. 1.

the abscissae, whilst the amount of diastase is represented by the ordinates. In figure 2 the figures of column VI are represented in the same way. Valid objections may perhaps be raised against the latter figures, because in these cases the amount of enzyme was deducted, which occurred in the culture-fluid of a culture distinct

I	II	III	IV	V	VI .	VII
2	0.75	0.75	0.75	0.41	0.33	1 mgr.
3	24.19	42.25	33.22	9.71	23.56	85 "
4	44.37	111.11	77.74	10.98	66.64	344 "
5	24.40	43.48	33.94	2.11	31.90	754 "
6	8.00	18.76	13.38	0.76	12.64	952 "
7	2.40	6.34	4.37	0.29	4.09	1236 "
9	1.50	1.50	1.50	0.05	1.45	1577 "
12	1.00	0.50	0.75	0.00	0.75	1562 "
16	0.50	0.50	0.50	0.00	0.50	1259 "
19	1.64	1.00	1.32	0.30	1.01	1117 "
23	1.11	4.45	2.78	0.76	2.04	1095 "
26	3.12	1.24	2.18	1.20	0.97	1080 "
30	4.44	8.70	6.57	4.41	2.11	1025 "
33	4.17	4.17	4.17	0.82	3.46	1073 "
37	1.64	1.50	1.57	1.11	0.57	1087 "
40	6.00	4.44	5.22	4.00	1.10	1031 "
44	1.26	1.12	1.19	1.37	0.00	1040 "
47	4.48	2.00	3.24	3.48	0.00	1034 "
51	1.25	3.13	2.19	7.32	0.00	1035 "
58	0.94	0.94	0.94	1.90	0.00	1039 "
65	1.12	0.72	0.92	0.98	0.00	987 "
72	0.50	20.00	10.25	4.60	5.68	982 "
79	6.40	0.50	3.45	4.56	0.00	1039 "
86	0.38	7.50	3.94	1.08	2.89	1009 "
93	0.04	0.42	0.23	1.71	0.00	966 "
100	0.30	0.42	0.36	0.20	0.16	956 "
107	0.10	0.36	0.23	1.56	0.00	992 "
114	0.10	0.10	0.10	0.08	0.01	933 "
121	0.08	0.44	0.26	0.08	0.17	973 "
128	0.08	0.68	0.38	0.06	0.32	958 "
135	0.00	0.12	0.06	0.57	0.00	917 "
142	0.08	0.00	0.04	0.05	0.00	962 "
149	0.05	0.05	0.05	0.00	0.05	922 "

from that in which the amount of enzyme in the mycelium was

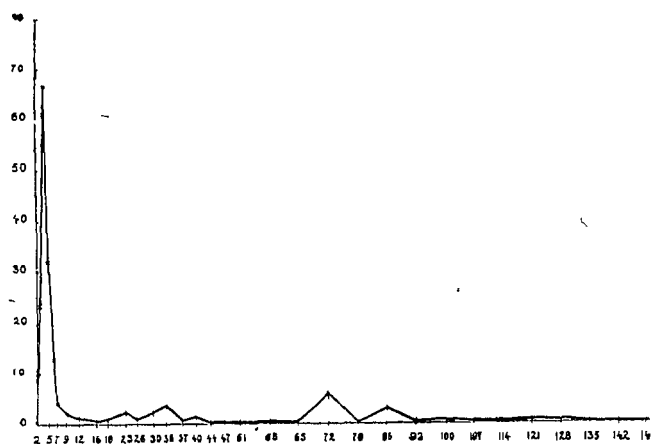


Fig. 2.

determined. To this must be ascribed the fact that such cases occur as that after 79 days, where in the fungus plus fluid an average of 3.45 enzyme occurs, but in the fluid alone 4.56, i. e. more. This is of course absurd, and if its own culture-fluid could have been used, such figures would not have resulted. Nevertheless I have included these figures and represented them in figure 2, in order to show the general course of the presence of diastase in the fungus-mass itself. It is evident that this curve is, generally speaking, exactly identical with that of figure 1. This is easily understood when it is seen from the figures of column V that in general the culture-fluid contains no very appreciable quantity of enzyme; it is only when much enzyme is present in the mycelium, that a quantity can be found in the surrounding fluid, which is not inconsiderable. How it is that the enzyme occurs there, must be left an open question. It might be thought to have arisen from cells already dead, but on the other hand a somewhat greater quantity is only found in very young mycelia.

The enzyme found in the culture-fluid can therefore be left without further consideration in order that attention may be concentrated on the diastase which is found within the mycelium of the fungus. From all the tables and also from figures 1 and 2 it is quite evident that after germination a considerable increase of enzyme is observable, which very quickly reaches a maximum and afterwards shows an almost equally rapid diminution. There will naturally be an inclination to consider this increase in relation to the development of the

mycelium, but the figures for the fungus-crop in the different tables show that this cannot be so. Moreover in figure 3 a representation

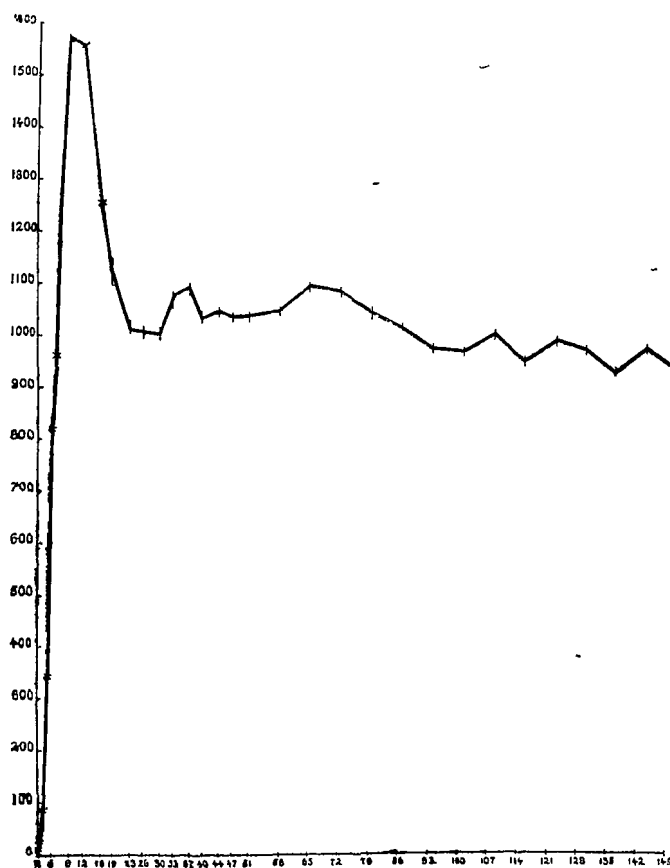


Fig. 3.

is given of the development of the mycelium in the last-mentioned experiment. There the duration of the development, given in days, is measured on the axis of the abscissae, whilst the ordinates give the dry-weight of the fungus-mass. In the first days a strong increase of the crop is evident, which is followed by a decrease, probably caused by the preponderance of the processes of dissimulation over the assimilation. On working up the mycelium for the enzyme a large portion of the older cultures was found to be dead, a phenomenon quite easy to establish, because the hyphae felt soft and flaccid and no longer elastic, as in the young cultures; but this could only with certainty be observed, when the fungi were some months old.

It is however quite clear that no proportion exists between the amount of dry matter of the fungus and the quantity of enzyme.

formed. Moreover it is seen that there is indeed in the beginning of the development an increase in the dry matter as well as in diastase, but that the increase in enzyme comes to a standstill, whilst the fungus-mass continues to increase for many days.

Do the experiments described indeed afford a proof that the amount of diastase in the fungus increases during the first days and then again undergoes a diminution? May it not be that the culture-fluid, which is used for the extraction of the enzyme, undergoes a slow change of such a nature as to accumulate a substance which destroys the enzyme or at least opposes its action? Or conversely may not there be some accelerator which is present at the beginning and first increases, and later diminishes? A decided answer to such questions can only be given when the method has been further worked out which was briefly described at the beginning of this paper. But nevertheless there are facts which make the explanations suggested here very improbable. I therefore point out that in all series of experiments the decrease in the amount of diastase does not take place regularly, but that later again a sudden increase is observed. It is not readily conceivable that the composition of the culture-fluid should suddenly undergo such a change that the sudden change in the figures could be thus explained. One can only think of an increase of the amount of diastase within the cells of the fungus. And when in this case no great influence on the figures for the diastase can be assigned to the culture-fluid, then this cannot be assumed in the other cases either. It may therefore be expected with fairly great certainty that the general course of the curve of figure 1 or 2 gives a picture of the actual quantities of diastase which occur in the mycelium of *Aspergillus niger*.

If we may accept the above conclusion as correct, then there follows more from it. Firstly, if we disregard for a moment the later irregularities of the curve a very quick initial rise is observable, followed by an almost equally strong fall. The former would be explained by the constant formation of more fresh enzyme, but the fall? There hardly remains anything but the conclusion that destruction of enzyme is always going on within the cell; this destruction then in the first days is compensated for and exceeded by the new formation, which latter very quickly comes entirely to a standstill or becomes so slight that it is far from being sufficient to keep the quantity of enzyme at a level.

I now return to the irregularities which are to be seen in the falling part of the curve. It is seen from the first two tables that after about one month the amount of diastase in the fungus suddenly

shows a considerable increase. These experiments did not last long enough to show what the further course would be, and for this very reason the last series of flasks was started, in order to trace for a longer time the behaviour of *Aspergillus niger* in this respect. It was found that here also after about one month the rise of the enzyme-content occurred; thereupon there followed again a decrease and then again a rise, whilst after about three months the decrease became permanent, so that finally practically no diastase remained. The oscillations of this curve are explicable by considering that the great rise in the first 3—4 days coincides with a vigorous development of the young mycelium. The same takes place again later when the fungus has formed new conidia and these, having been shed into the culture-fluid, germinate there; each time that this happens a sudden increase in the quantity of the diastase will be observable. It is self-evident that it cannot always be predicted at what time in the course of the culture this will occur, but we may safely argue that the culture-fluid gradually will become less and less suited for the germination of the conidia, and that therefore this phenomenon will gradually stop altogether. If this explanation is correct it would therefore be possible to make the formation of diastase in *Aspergillus niger* go on for a much greater length of time by renewing the nutrient solution.

The phenomena which have just been described are thus of a secondary character and all study of the formation of enzyme in *Aspergillus niger* must be limited to the first stages of development. One cannot indeed say whether the course of the formation of enzyme would be the same with different nutrition, but this may however be expected. It is therefore not only impermissible to draw conclusions from the quantities of enzyme which occur in cultures which are e.g. some weeks old, but one must try to follow accurately the course of the enzyme-formation during the first days of development of the fungus in the case of each kind of nutrition; then only can conclusions be drawn respecting the influence of a given nutrition on the enzyme-formation of *Aspergillus niger*.

It is evident that these conclusions only concern the formation of diastase in *Aspergillus niger*; but they will nevertheless oblige one to be careful about conclusions as to other enzymes and other fungi; in further investigations the possibility must be borne in mind of similar results occurring.

Summing up, it is found that in *Aspergillus niger* during the first days after germination a great quantity of diastase is formed in the

mycelium (on feeding with glucose as source of carbon and NH_4NO_3 as source of nitrogen), and that in addition, destruction of this enzyme takes place, which at first becomes negligible in comparison with the formation, but which soon makes itself so evident that the total quantity quickly decreases, after it has reached a maximum about 5 days from the commencement of germination. Into the nutrient fluid there passes never more than a very small part of the total quantity of enzyme, occurring in the mycelium; this is perhaps partly derived from dead cells.

Utrecht, August 1918.

Physics. — "*Investigation by means of X-rays of the crystal-structure of white and grey tin. II. The structure of white tin.*" Communication N°. 2a from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht, by A. J. BIJL and N. H. KOLKMEIJER. (Communicated on behalf of Prof. W. H. KEESOM, Director of the Laboratory, by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of September 28, 1918).

In Communication N°. 1 (June 1918) we communicated, that we had taken Röntgenograms of white and grey tin by the method of DEBIJE and SCHERRER and we gave a description of some particulars about the arrangement of these measurements. Moreover we showed in a drawing for both states of tin mentioned the places of the interference-maxima in a plane, perpendicular to the axis of the bars, indicating at the same time the intensities of the interference-lines. The photo of the grey tin indicated, that this material is crystalline, and on comparing the photos for the two states, it was evident, that it possesses a crystal-structure, which differs from that of white tin. We have now determined from those photos the crystal-structure as well of white as of grey tin, and shall communicate in this paper our results for white tin, reserving those for grey tin for communication N°. 2b (these Proceedings).

In table I the intensities of the interference-lines are inserted in the first column: vf means very feeble, f feeble, m moderate, s strong and vs very strong.

In the second column are inserted, expressed in tenths of mm, the distances of the intersections of the interference-lines with a plane through the axis of the incident Röntgen-beam and perpendicular to the axis of the preparation, to the point where that first axis, prolonged, would meet the film, measured on the film when developed on a plane. In the third column the values of $\sin^2 \frac{1}{2} \theta$ are ranged, as computed from the above-mentioned distances and the data of the apparatus, which were given in Comm. N°. 1.

Now the values, given in the third column must undergo a

TABLE I.

Intensity	Half of diameter of interf.-line	$\sin^2 \frac{1}{2} \theta$	$\sin^2 \frac{1}{2} \theta$ correc- ted	corr. $\sin^2 \frac{1}{2} \theta$ $\times \frac{1}{0.01734}$	smoothed	Index-triples with $h_3 = 0$	Index-triples with $h_3 = 1$	Index-triples with $h_3 = 2$	Index-triples with $h_3 = 3$
1	2	3	4	5	6	7	8	9	10
m	168	0.0924	0.0790	4.6	4.5	2.0.0.			
vf	208	0.1393	0.1243	7.2	7		1.0.1.		
vs	228 ^s	0.1663 ^s	0.1502	8.7	9	{3.0.0. 2.2.0.	1.1.1.		
f	280	0.2424	0.2253	13.0	13	3.2.0.			
s	311	0.2928	0.2762	15.9	16	4.0.0.	3.1.1.		
f	322	0.3114	0.2945	17.0	17	4.1.0.			
vf	349 ^s	0.3591	0.3433	19.8	20	4.2.0.			
m	362	0.3813	0.3653	21.1	21				
vs	390	0.4319	0.4173	24.1	24		3.3.1.	0.0.2.	
vf	416	0.4794	0.4666	26.9	27			2.0.2.	
m	438 ^s	0.5208	0.5079	29.3	29.5				
s	464	0.5675	0.5565	32.1	32	4.4.0.	5.1.1.	2.2.2.	
s	500 ^s	0.6332	0.6243	36.0	36	6.0.0.			
vs	538 ^s	0.6990	0.6922	39.9	40	6.2.0.	5.3.1.	4.0.2.	
vf	554	0.7248	0.7182	41.4	41.5				
s	586 ^s	0.7687	0.7640 ^s	44.1	44			4.2.2.	
vf	597	0.7923	0.7878	45.4	45.5				
vs	627	0.8352	0.8325	48.0	48				
f	640	0.8525	0.8499	49.0	49	7.0.0.		{4.3.2. 5.0.2.	
m	690	0.9114	0.9104	52.5	52.5	6.4.0.			
f	721 ^s	0.9415	0.9406	54.2	54				0.0.3.
m	757 ^s	0.9686	0.9686	55.9	56		{5.5.1. 7.1.1.	4.4.2.	1.1.3.
vf	790 ^s	0.9863	0.9863	56.9	57				

correction¹⁾ in connection with the thickness of the preparation. This correction is not needed, when the absorption of the characteristic rays in the preparation can be neglected, which was the case for many of the materials, which were till now examined by the method of DEBIJE and SCHERRER. This does not hold however in our case (*Cu*-radiation), in which the radiation penetrated only to a very small depth, practically not at all in the preparation. The corrected values of $\sin^2 \frac{1}{2} \theta$ are found in the fourth column of the table.

During the computations for the drawing up of a formula for $\sin^2 \frac{1}{2} \theta$ it appeared that the majority of the values in the fourth column, in dividing them by 0,01734, give a quotient, which differs only little from a whole number. These quotients are found in the fifth column. The values of these quotients, smoothed to half a unity, are inserted in the sixth column.

MILLER²⁾ has measured the crystal-form on crystals obtained by electrolysis. It appeared to belong to the tetragonal system with a proportion of axes $a : a : c = 1 : 1 : 0,3857$. So it lay at hand, to try to find agreement of the fourth column with a formula of the form:

$$\sin^2 \frac{1}{2} \theta = A (h_1^2 + h_2^2) + B h_3^2 = A (h_1^2 + h_2^2 + q h_3^2),$$

in which $A = \frac{\lambda^2}{4a^2}$ and $B = Aq = \frac{\lambda^2}{4c^2}$. By a and c is meant now in this the edges of the elementary parallelepiped or of the elementary cell. It lies also very much at hand to choose for A the above-given value 0,01734, and so to seek further agreement of the numbers in the sixth column with an expression $h_1^2 + h_2^2 + q h_3^2$, in which evidently q was then to differ little from a whole number.

By choosing $q = 6$, a proper agreement appears to be obtained. In order to see this, it is advisable to compose a table of the values

¹⁾ Comp. also P. DEBIJE, Phys. Z.S. 18 (1917) p. 5. For the value of this correction we found (to diminish the value of $\sin^2 \frac{1}{2} \theta$ with):

$$\frac{r}{4R} \sin \theta \left\{ \frac{R}{d} + \cos \theta + \sqrt{\frac{R^2}{d^2} + \frac{R}{d} \cos \theta + 1} \right\}$$

Here r means the radius of the circular cross section of the bar, R that of the camera, d the distance of the centre of the camera to the opening of the screen, by which the rays enter. Second and higher powers of r/R are neglected. [Added during translation: The deduction of this formula has in the mean time been inserted in A. J. BIJL Thesis for the Doctorate, Utrecht 1918 p. 22].

²⁾ W. H. MILLER, Ann. d. Phys. u. Ch. 58 (1843), p. 660. See also H. VON FOULLON, Jahrb. d. Kais.-Kön. Geol. Reichsanst. Wien 34 (1884), p. 367.

of $h_1^2 + h_2^2$ for the different combinations of h_1 and h_2 ranged in the succession of increasing values of $h_1^2 + h_2^2$. On comparing this series of values of $h_1^2 + h_2^2$ with the numbers of the sixth column, the index-triples with $h_3 = 0$, given in the seventh column (not printed in italics), are found to satisfy. By adding 6 to all the values of $h_1^2 + h_2^2$ and comparing again with the numbers of the sixth column, in the same manner the index-triples with $h_3 = 1$ of the eighth column are found. In a similar manner the ninth and tenth columns are composed.

Apart from the first four lines, in connection with the deviations which exist for the small values of θ (comp. p. 498), of the remaining 19 lines, there are only 2, which do not belong to index-triples (not printed in italics), of which not all the indices are either even or odd. On considering whether all the lines to be expected, which fulfill this condition, are present, it appears that 5 of them still ought to appear. The index-triples meant here, are collected and printed in italics (columns 7—10) and assigned to those lines, of which the place is nearest to the place expected for these lines.

The difference between the places, where these lines are found and those, where they would be expected, is in all those cases minute, and can for two cases be ascribed to the fact, that the line meant, cannot be seen separated from a neighbouring line and in all cases does not exceed (in connection with the small value of A) the uncertainty of observation.

There is evidently indication enough for accepting a structure that is in accordance with the exclusive occurrence of interference-lines, which must be ascribed to reflections on net-planes with only even or only odd index-triples.

The absence of index-triples of which not all indices are either even or odd, points to centered sides.

From the atomic weight (119,0), the specific weight at 18° C. (7.285), Avogadro's number ($6,06 \cdot 10^{23}$) and the wave-length of $\text{CuK}\alpha$ ($1,541 \cdot 10^{-8}$) follows with $A = 0,01734$ and $q = 6,06^1$) (which value later on appeared still better to satisfy than 6), for the number of atoms per cell the value 3,02.

Now, we come to the number 3 by placing atoms in the corners of the cells and in the centra of the prism-faces.

¹⁾ [Note added during translation]. By a somewhat different method of calculation A. J. BILL, l.c. p. 33 obtained the value 5.988. This fact points to a greater probability of $q = 6$ accurately. In this case the projection of all the net-points on a diagonal-plane through the smallest edge of the elementary cell would be a net of equilateral triangles with side $2,37 \cdot 10^{-8}$ cm. (Comp. A. J. BILL, l.c. p. 34).

This is, so far as we know, the first example, in which atoms are found in the centres of the prism-faces, not however in those of the bases.

In excess of the above-mentioned triples, still other triples must in the case of this structure give occasion to interference-lines. In this case namely the structure-factor becomes $S = 1 + e^{\pi i(h_2 + h_3)} + e^{\pi i(h_1 + h_2)}$. The value of this is 3, when all indices are either even or odd and in the other cases 1 or -1 . So it is evident that planes the indices of which do not fulfill the condition mentioned, will be present as interference-lines, though, under equal circumstances for the rest, with $\frac{1}{9}$ only of the intensity of the other lines. So one cannot wonder that a few of this kind of planes can give sufficient intensity to the interference-lines and that their index-triples are present in columns 7—10 of table I.

In order to be able to judge about the agreement between the place and intensity of the interference-lines, which are to be expected on the basis of the given structure and the observed ones, a table has been drawn up, in which the values of $\sin^2 \frac{1}{2}\theta$, as well for $Cu_{K\alpha}$, as for $Cu_{K\beta}$ -radiations, are collected, as computed for all the index-triples that come into consideration, with their relative intensities. Of this table II forms an extract in which are omitted in the first place all the triples for which the structure-factor not equals 3, and in which for the rest out of each group of index-triples which can be esteemed to produce lines which lie so near to each other that these together will give on our Röntgenogram only a single line, only that triple is noted that is the origin of the most intense line of that group. If such a group contains α - as well as β -lines, then the strongest only of both kinds is given.¹⁾

Deviations between computed and observed values of $\sin^2 \frac{1}{2}\theta$, which are larger than corresponds to the degree of accuracy of the measurements, only occur in table II at the first three lines. About this it must be remarked that these lines are very hazy, which, in connection with the veiling of the film as a consequence of the action of white radiation in the Röntgenbeam makes the reading

¹⁾ During Comm. Nr. 1 being under press we learned, that Dr. SCHERRER and Prof. JOHNSEN had taken a Röntgenogram of white tin and Prof. JOHNSEN proposed to us, to exchange the observed values mutually. The results, then communicated to us cordially by Prof. JOHNSEN, give, especially at lower values, all of them somewhat smaller values of $\sin^2 \frac{1}{2}\theta$ than ours. Perhaps this might be ascribed to the correction applied by us for thickness of bar being somewhat too small. In the notes added to table II a few of the differences between the results of SCHERRER and JOHNSEN and ours are discussed.

TABLE II.

Intensity	$\sin^2 \frac{\theta}{2} \cdot 10^3$ observed	$\sin^2 \frac{\theta}{2} \cdot 10^3$ calculated for $\text{Cu}_K\alpha$	Relative intensity (calculated) of the α -lines	$h_1 h_2 h_3$	$\sin^2 \frac{\theta}{2} \cdot 10^3$ calculated for $\text{Cu}_K\beta$	Relative intensity (calculated) of the β -lines	$h_1 h_2 h_3$
m	79 ¹⁾	69	9.0	200			
vf	124				113	9.0	111
vs	150	140	9.0	111			
f	225				225	9.0	311
s	276	278	9.0	311	280	3.6	420
f	294 ⁵		feeble α -line				
vf	343	347	3.6	420	337	3.0	331
m	365 ²⁾					feeble β -lines	
vs	417 ³⁾	417	3.0	331			
vf	467				449	4.5	511
m	508 ⁴⁾	490	2.6	202	504	1.0	600
s	556 ⁵	556	4.5	511	561	3.6	531
s	624	624	1.0	600	620	3.3	422
vs	692	695	3.6	531			
vf	718				729	1.4	640
s	764	767	3.3	422			
vf	788				785	2.6	711
vs	832 ⁵					feeble β -lines	
f	850 ⁵⁾				844	1.2	602
m	910 ⁶⁾	902	1.4	640	897	2.25	731
					900	2.25	622
					904	2.25	313
f	941				953	1.1	820
m	969	972	2.6	711			
vf	986					feeble β -lines	

¹⁾ In SCHERRER and JOHNSON's results this line is preceded by f 57, which may be considered as 56 9 200 β . The values which S. and J. give for the first three lines, vs 72, m 116 and vs 143 namely, give better agreement with the places of the strongest lines, calculated, than ours.

²⁾ Lines 343 and 365 are almost not to be separated on our film. They are given by S. and J. as one line, s 348.

³⁾ S. and J. give 404⁵, presumably by stronger forthcoming of 202 β (at 396) intensity 2.6.

⁴⁾ s 491 of S. and J.

⁵⁾ At the lines 832⁵ and 850 the film shows almost uninterruptedly points from 819 to 866. S. and J. denote the intensities with s to m and f.

⁶⁾ S. and J. have s 906.

somewhat uncertain, and that further the correction for thickness of preparation brings with it a relatively large uncertainty for these lines.

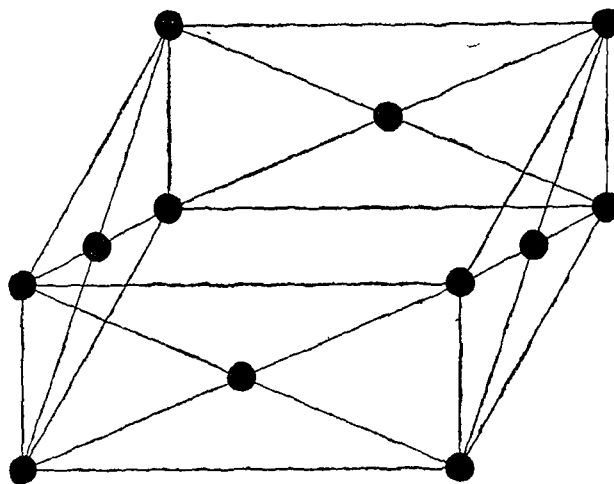


Fig. 1.

From the given values of A and q , there follows for the edges of the elementary-cell: $a = 5,84 \cdot 10^{-8}$ and $c = 0,406 a = 2,37 \cdot 10^{-8}$ cm. In fig. 1 a representation of an elementary-cell is given.

In the space-netting, built of these cells, we see alternating equidistant layers with distance $1,19 \cdot 10^{-8}$ cm. The first layer has a netting of squares with side $5,84 \cdot 10^{-8}$ cm., the next a netting of squares with side $4,13 \cdot 10^{-8}$ cm., which last squares are just above the squares symmetrically inscribed in that of the first layer.

The dense crowding of these planes indicates a strong force-exertion in a direction, perpendicular to the layers; perhaps the occurrence of needle shaped combinations is connected with this fact.

Röntgenometrical investigations teach us to cast a look in the structure of the crystal and may for that reason lead us to a more rational choice for the system of crystallographic axes than the former crystallographic methods. The white tin procures an example of this. So e.g. the bipyramid, accepted by MILLER as (111) (proportion of axes $a:a:c = 1:1:0,3857$) would, conform to the system of axes formed from the edges of the elementary cell proposed by us, be indicated as (403), just so the planes (110), (100), (101) of MILLER by (100), (110), (223) resp. according to us.

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(Communicated in the meeting of September 28, 1918).

In this communication we shall deduce the crystal-structure of grey tin from the Röntgenogram, taken by us and represented by a drawing in Communication N°. 1 (June 1918 p. 408) at the same time as that of white tin. With this aim in the first column of table I are given the distances of the intersections of the interference-lines with a plane, through the axis of the incident beam of X-rays and perpendicular to the lengthdirection of the preparation, to the point where this axis, prolonged, would meet the film, measured on the film when developed on a plane and corrected for thickness of preparation (Comp. Comm. N°. 2a, p. 496). The intensities are denoted by vf very feeble, f feeble, m moderate, s strong, and vs very strong. The second column contains the values of $\sin^2 \frac{\theta}{2}$ deduced therefrom, (radius of camera 27,3 m.m., to be diminished by half the thickness of the film, that is by 0,1 m.m.).

By multiplying these values by 0,808, the square of the proportion of the wave-lengths of $Cu_{K\alpha}$ and $Cu_{K\beta}$, the values which might originate from β -radiation, can be separated, and so a list can be composed which contains α -values exclusively. By using a general method of computation, in which we proceeded from an arbitrary system of axes and on which we shall perhaps publish another paper the grey tin appeared to be regular with great probability. In that case our values must fulfill the equation:

$$\sin^2 \frac{\theta}{2} = A (h_1^2 + h_2^2 + h_3^2) = \frac{\lambda^2}{4a^2} (h_1^2 + h_2^2 + h_3^2),$$

in which A is a constant, h_1, h_2 , and h_3 indices of MILLER, λ wave-length of the Röntgen-radiation, a edge of elementary cube.

So we have only to deduce the constant A and from that the number of atoms in the elementary cube a^3 . A provisional calcu-

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TABLE I.

Distances in 0.1 mm.	$\sin^2 \frac{\theta}{2} \cdot 10^3$	$Cu K_{\alpha}$ -radiation				$Cu K_{\beta}$ -radiation		
		$\sin^2 \frac{\theta}{2} \cdot 10^3$ calculated	Intensity	$h_1 h_2 h_3$	$h_1^2 + h_2^2 + h_3^2$	$\sin^2 \frac{\theta}{2} \cdot 10^3$ calculated	$h_1 h_2 h_3$	$h_1^2 + h_2^2 + h_3^2$
f 112	41					34	1 1 1	3
f 144 ⁵	69	43	1.3	1 1 1	3			
vf 168	92					92	2 2 0	8
m 191	118	114	1.5	2 2 0	8	126	3 1 1	11
m 221	156	156	1.1	3 1 1	11			
vf 239	181					184	4 0 0	16
f 272	230	231	0.4	4 0 0	16			
m 300	274 ⁵	270	0.6	3 3 1	19	275 ⁵	4 2 2	24
s 342	346	341	1.0	4 2 2	24			
m 370	395 ⁵	384	0.6	$\begin{pmatrix} 3 & 3 & 1 \\ 5 & 1 & 1 \end{pmatrix}$	27	402	5 3 1	35
f 406	461	455	0.4	4 4 0	32	459	6 2 0	40
m 426	498	497	0.7	5 3 1	35			
s 464	567	568	0.6	6 2 0	40			
f 488	611	611	0.3	5 3 3	43			
f 509	648					643	6 4 2	56
f 530	684	682	0.2	4 4 4	48	677	$\begin{pmatrix} 5 & 5 & 3 \\ 7 & 3 & 1 \end{pmatrix}$	59
m 554	725	725	0.5	$\begin{pmatrix} 5 & 5 & 1 \\ 7 & 1 & 1 \end{pmatrix}$	51			
vs 596	791	796	0.9	6 4 2	56			
vs 626	834	838	0.6	$\begin{pmatrix} 5 & 5 & 3 \\ 7 & 3 & 1 \end{pmatrix}$	59			
vf 655	871 ⁵					862	$\begin{pmatrix} 5 & 5 & 5 \\ 7 & 5 & 1 \end{pmatrix}$	75
f 678	898	909	0.1	8 0 0	64			
f 694	915					918	8 4 0	80
m 730 ⁵	949	952	0.2	7 3 3	67			

lation pointed to about eight atoms per cube, which suggests the structure of diamond. So we tried to get agreement of our interference-lines with the structure of diamond.

Using the atomic-weight (119,0) and the specific weight of grey tin at 18° C. (5,751), AVOGADRO's number ($6,06 \cdot 10^{23}$) and the wavelength of the K -series of copper-radiation (α $1,541 \cdot 10^{-8}$, β $1,385 \cdot 10^{-8}$) $A_\alpha = 0,0141$ and $A_\beta = 0,0114$ are found. Nearly in agreement with this we find as a mean from the observed lines $A_\alpha = 0,01422$ and $A_\beta = 0,01149$. The third column gives the values of $\sin^2 \frac{1}{2} \theta$, computed with the last-mentioned values of A_α , so far as they give occasion to interference-lines.

From DEBIJE's structure-factor it can be deduced namely, that for the structure of diamond interference-lines can only be got, when h_1, h_2 and h_3 are all even or all odd, and when in case they are even, their sum can be divided by 4. The expression $h_1^2 + h_2^2 + h_3^2$ then becomes 3, 8, 11 and so on, see the sixth column; in the fifth column the corresponding values of h_1, h_2 and h_3 are given.

The intensity, given in the fourth column is found by dividing $64(h_1^2 + h_2^2 + h_3^2)$ in the product of the number of planes and the square of the absolute value of the structure-factor. To this intensity only so much value must be attached that only the intensities of three successive lines must be compared.

The seventh, eighth, and ninth columns relate to β -lines.

On comparing the observed and computed values of $\sin^2 \frac{1}{2} \theta$ a satisfactory agreement appears to exist, also in connection with the intensity.

The two smallest squares of sines are not satisfactory ¹⁾. About this Comm. N°. 2a p. 498 gives information.

When it is examined whether all lines, which must be expected on the ground of the structure mentioned, are present, it appears, that of the expected α -lines not a single is lacking; some of the β -lines however appearingly have too small an intensity, and so are not observed on the Röntgenogram.

From the values of A_α and A_β , deduced from the observations, we found for a , the edge of the elementary cube $6,46 \cdot 10^{-8}$ cm. at 18° C. For the distance of two nearest atoms $2,80 \cdot 10^{-8}$ cm. is thus deduced.

In the grey tin with its diamond-structure, which silicium possesses too, the tetravalency clearly makes its appearance, whilst in the tetragonal modification, in which each atom is surrounded by

¹⁾ Comp. P. DEBIJE, Physik. ZS. 18 (1917), p. 488. Note.

two nearest ones with smaller distances than those of the rest of the surrounding atoms, two valencies especially come to the foreground.

In this connection it might be interesting, to investigate, whether the deviating conduct, observed by GRÜNEISEN¹⁾ in the course of the conductivity at low temperatures for cadmium, tin, and mercury, and which he ascribed to the metals not being regular, is not found with the grey tin, or whether the diamond-structure still causes a deviation in the conductivity at low temperatures from the conduct of the metals crystallising in cubes with centered faces.

We heartily thank Prof. KEESOM for the great interest, which he always showed us.

¹⁾ E. GRÜNEISEN. Verh. D. physik. Ges. 20 (1918); p 36.

Physics. — “On the equivalent of parallel translation in non-Euclidean space and on RIEMANN’s measure of curvature.”
By Dr. A. D. FOKKER. (Communicated by Prof. H. A. LORENTZ.)

(Communicated in the meeting of April 26, 1918).

1. *Introduction.* In the following pages I shall try to give a mental picture of some ideas recently developed by prof. J. A. SCHOUTEN before the Mathematical Society at Amsterdam which will help to illustrate the meaning of a “system of axes moving geodesically”, and the “geodesic differential”, together with a few applications.¹⁾ The great point will be to realise in a new way what kind of displacement in non-Euclidean space must be considered to correspond to a parallel translation, this being an operation indispensable in vector-analysis to compare vectors in different points.

One of the characteristic properties of pure translations is this, that all points of a rigid body are thereby transferred over an equally long distance. This property might be used to define a parallel translation, provided the rigid consists of a number of points exceeding a certain minimum. If, for example, in three-dimensional space, we give a prescribed displacement to one of the points of a rigid system consisting of two or three points, it is not enough to demand an equal displacement for the other point or points to define a translated position without ambiguity. But in a Euclidean space of n dimensions other motions than pure translations are excluded, if for a rigid body of no less than $(2n-2)$ points we want all points to run through equal distances.

This will be our starting-point. We know, however, that in general no body of finite dimensions can move in curved space without changing the mutual distances of its points. In order to retain the idea of a rigid body we shall have to confine ourselves to bodies with dimensions of the order of an infinitesimal ϵ .

Another and more serious difficulty arises from the fact, that we cannot get all points to shift over exactly the same infinitesimal distance Δ . We cannot but leave a margin of the order of $\Delta\epsilon^2$ for the separate distances. Here the question arises whether in a certain

¹⁾ Cf. a treatise offered by Prof. SCHOUTEN to be published in the transactions of the Kon. Akademie: “*Die directe Analysis zur neueren Relativitätstheorie*”.

direction only one displacement can be effected in which this approximation to the exact equality is realised? This, however, cannot be expected, since in the special case of Euclidean space not only pure translations but screw-displacements too are allowed by leaving this margin. Therefore a second property of pure translations is required, fit to exclude these screw-displacements.

This property is found in the fact that the shifts are not only equal, but also parallel to one another. This amounts to a certain reciprocity between translations in different directions. Consider two translations, by which a point P is transferred to neighbouring points Q and R respectively. The first translation will carry point R to the same place where the second translation will carry point Q . This property indeed excludes screw-displacements.

In the following pages we shall first give a summary of the results arrived at in this paper, and afterwards (§ 6) give the analytical formulae. For examples we will mainly take those of three-dimensional space. The results, however, will hold good, independent of whatever number (n) of dimensions we choose to ascribe to our space.

2. *Geodesic displacement.* Let us define an infinitesimal rigid as an aggregate of particles, which keep their mutual distances unchanged during their motions. One of these points we may choose as a central, and imagine the other points defined by the ends of infinitesimal vectors from this central point, these vectors having constant lengths (of the order ϵ) and including constant angles. The number of points must be no less than $(2n-2)$, hence the number of vectors $(2n-3)$, no n of them being situated together in a space of $(n-1)$ dimensions.

We imagine this rigid to execute motions so as to shift the central particle from a starting point P to neighbouring points over distances of the order Δ .

It appears possible (§ 7) to indicate a certain variety of motions in which, firstly *the shifts of all the other points of the rigid*, up to a margin of the order $\Delta\epsilon^2$, *equal the shift of the central point*, and, secondly, there exists a certain *reciprocity* which becomes apparent when we observe *two arbitrarily chosen motions belonging to the variety*, which shift the central particle, let us say, from P to Q and from P to R , and when we notice the displacements of the particles having their starting points in R and Q respectively. *The particle from R in the motion (PQ) will reach the same point attained by the particle from Q in the other motion (PR) .*

The two conditions specified determine without ambiguity a variety

of motions which we may call "*geodesic displacements*" of the infinitesimal rigid. They are the substitutes for parallel displacements¹⁾ in Euclidean extensions. We may assign the name "compass-rigid" to a small rigid body that cannot move but in the geodesic manner defined. It must be understood that a compass-rigid which, after a displacement, returns to its starting-point by the same way, will on arrival be in its starting-position too. If, however, it returns by a circuit, it generally will not be in its starting-position again on arrival.

3. *Geodesic differential.* If we want to compare two vectors in neighbouring points P and Q , we can proceed as follows. We put a compass-rigid with its centre in P and by marking one of its points we delineate the vector in it. Now displacing the compass-rigid to Q it is reasonable to say that the marked point defines the vector displaced geodesically from P to Q . By comparing this vector with the one present in Q we immediately see the meaning of the *geodesic differential* of a vector. If this is known, it is clear what CHRISTOFFEL's covariant differentiation means.

In the same way we can displace our vector-units from P to Q . In general these will differ from the vector-units in Q . A set of geodesically displaced vector-units is what Prof. SCHOUTEN defined as a system of axes moving geodesically.

4. *Geodesic line.* We can easily imagine what we have to do in order to *prolong a given line-element geodesically*. We put the centre of the compass-rigid in the starting-point and mark the end of the line-element by an arrow in the compass-rigid. After the centre has been displaced along the line-element, the arrow will point in another definite direction. This is the geodesic prolongation of the element. Continuing to move the compass-rigid in the direction of the arrow, the centre will gradually describe a geodesic line.

In this case, during displacements along a geodesic line, vectors moving geodesically will continue to include constant angles with the geodesic (cf. LEVI-CIVITA's article), these angles being fixed angles in the compass-rigid.

5. *RIEMANN's measure of curvature.* Let us now suppose that we

¹⁾ Taking another starting-point, T. LEVI-CIVITA arrives at a definition of parallelism which comes to the same thing: "*Nozione di parallelismo in una varietà qualunque, e conseguente specificazione geometrica della curvatura Riemanniana*". Rend. Circ. Mat. Palermo, XLII p. 1, 1917. His geometrical explanation of the measure of curvature, however, is totally different from the one we shall give in section 5.

make a compass-rigid describe a small circuit, e.g. along a vanishing (quasi-)parallelogram. We already pointed out that in general it will *not* return to its starting-position. The difference between the two positions is such as might have been produced by an infinitesimal rotation around the starting-point. The amount of this rotation is proportional to the area of the circuit described, the orientation of the "axis" of rotation (which in higher extensions is of $(n-2)$ dimensions) being determined by the orientation of the plane of the circuit. The rotation is intimately connected with the curvature of space. When this *rotation of curvature*, as it may be called, vanishes in all points for every arbitrary circuit, then the space is Euclidean.¹⁾

The components of the operator by which from the data of the area included by the circuit the rotation of curvature for the compass-rigid can be derived, are RIEMANN'S four-index-symbols, of the second kind.

Further — to confine ourselves to three-dimensional space — if we take the length of the axis of rotation equal to the amount of the angle of rotation, and construct a parallelepiped with this axis and the parallelogram of the circuit, we can consider the ratio of its volume to the square of the parallelogram as a measure for the curvature of space. Indeed, in the limit, for a vanishing circuit, this ratio is just the number indicated by RIEMANN as *the measure of curvature of the space with respect to the plane of the circuit considered*.

6. Now we shall proceed to give the required formulae. We take the length of a line-element as defined by

$$ds^2 = \sum (ab) g_{ab} dx^a dx^b,$$

$dx^a dx^b$ representing increments of the coordinates along the line-element $d\mathbf{x}$, $g_{ab} (= g_{ba})$ being regular functions of the coordinates of the starting-point, each index in the sum going through all the values from 1 to n , where n is the number of dimensions of space. The algebraical complements of g_{ab} will be denoted by g^{ab} , so that

¹⁾ The fundamental idea of a recent article by H. WEYL (*Gravitation und Elektrizität*, Berl. Sitz. Ber. May, 1918) may be considered the hypothesis that a small rigid (= "Vektorraum") after turning about an infinitesimal circuit of "translations" (of a somewhat more general kind) not only will have got in a changed position, but in general will have *changed its dimensions* as well. In four-dimensional space-time the linear dilatation of the (4-dimensional) rigid would be half the scalar product of the alternating electromagnetic tensor and the area included by the circuit. (Note added during the revisal of the proofs).

$$\Sigma(b)g_{ab}g^{nb} = \begin{cases} 1 & \text{for } n = a, \\ 0 & \text{for } n \neq a \end{cases}$$

For the sake of brevity we shall write g for the determinant formed of the g^{ab} . Further we shall avail ourselves of CHRISTOFFEL'S well-known symbols:

$$\left[\begin{matrix} lm \\ a \end{matrix} \right] = \frac{1}{2} \left[\frac{\partial g_{am}}{\partial x^l} + \frac{\partial g_{la}}{\partial x^m} - \frac{\partial g_{lm}}{\partial x^a} \right], \quad \left\{ \begin{matrix} lm \\ b \end{matrix} \right\} = \Sigma(a)g^{ab} \left[\begin{matrix} lm \\ a \end{matrix} \right].$$

The definition of the line-element entails the definition of the length of a vector \mathbf{v} , with components v^a :

$$v^2 = \Sigma(ab)g_{ab}v^av^b,$$

and the definition of the angle between two vectors \mathbf{v} and \mathbf{w} :

$$vw \cos(vw) = \Sigma(ab)g_{ab}v^av^bw^b.$$

7. Let the points of a small rigid be given by their coordinates relative to the centre: $u^a, v^a, w^a \dots$ ($a = 1, 2, 3, n$), these being the components of vectors $\mathbf{u}, \mathbf{v}, \mathbf{w} \dots$ which are of the order of a vanishing quantity ϵ . If the centre shifts from P to a neighbouring point Q , determined by the infinitesimal increments in the coordinates dx^a (of the order Δ), then we require the new coordinates of the points of the rigid relative to Q in order to satisfy the definition and first condition of section 2: the points are to be points of a rigid, and must each cover an equal distance.

Denoting the new relative coordinates by $u^a + du^a, v^a + dv^a \dots$ etc. it is easy to formulate the latter half of the condition. For the increments of the coordinates of the point designed by \mathbf{u} will be $dx^a + du^a$, and the starting point of the line-element through which it runs lies beside P , at a distance defined by \mathbf{u} . So, if this line-element is to be equal to that from P to Q , i.e.

$$ds^2 = \Sigma(ab)g_{ab}dx^adx^b,$$

we necessarily must have

$$0 = \Sigma(abm) \frac{\partial g_{ab}}{\partial x^m} u^m dx^a dx^b + \Sigma(ab) 2g_{ab} dx^a du^b \quad . \quad (1)$$

If the aggregate of points is to form a rigid, both the lengths of the relative vectors $\mathbf{u}, \mathbf{v}, \mathbf{w} \dots$ and the included angles must be constant, and expressions such as

$$u^2 = \Sigma(ab)g_{ab}u^au^b, \quad uv \cos(uv) = \Sigma(am)g_{am}u^av^m,$$

must have the same value in P and Q . This implies

$$0 = \Sigma(aml) \frac{\partial g_{am}}{\partial x^l} dx^l u^a u^m + \Sigma(am) 2g_{am} u^a du^m, \quad . \quad (2)$$

and

$$0 = \Sigma (a m l) \frac{\partial g_{am}}{\partial x^l} dx^l u^a v^m + \Sigma (am) g_{am} \{u^a dv^m + v^m du^a\} \quad (3)$$

These are the equations which must be applicable to du^a , dv^a ... etc. in the translations mentioned. It is not difficult to find expressions satisfying the equations. We can add to (1) the identity

$$0 \equiv \Sigma (a l m) \left(\frac{\partial g_{am}}{\partial x^l} - \frac{\partial g_{lm}}{\partial x^a} \right) dx^a dx^l u^m,$$

and a similar identity to (2):

$$0 \equiv \Sigma (a l m) \left(\frac{\partial g_{al}}{\partial x^m} - \frac{\partial g_{lm}}{\partial x^a} \right) u^a dx^l u^m.$$

Replace at the same time the index b in the first term, right-hand side of (1) by l , and m in the second term, right-hand side of (2), by b , and we get

$$0 = \Sigma (a) \left[\Sigma (lm) \left(\frac{\partial g_{am}}{\partial x^l} + \frac{\partial g_{al}}{\partial x^m} - \frac{\partial g_{lm}}{\partial x^a} \right) dx^l u^m + \Sigma (b) 2g_{ab} du^b \right] dx^a,$$

and

$$0 = \Sigma (a) \left[\Sigma (lm) \left(\frac{\partial g_{am}}{\partial x^l} + \frac{\partial g_{al}}{\partial x^m} - \frac{\partial g_{lm}}{\partial x^a} \right) dx^l u^m + \Sigma (b) 2g_{ab} du^b \right] u^a.$$

Dividing by 2 we can reduce the equations to the form

$$0 = \Sigma (ab) g_{ab} dx^a \left[du^b + \Sigma (lm) \left\{ \begin{matrix} lm \\ b \end{matrix} \right\} dx^l u^m \right], \quad (1')$$

$$0 = \Sigma (ab) g_{ab} u^a \left[du^b + \Sigma (lm) \left\{ \begin{matrix} lm \\ b \end{matrix} \right\} dx^l u^m \right], \quad (2')$$

Similarly, we can put for the third equation

$$0 = \Sigma (ab) g_{ab} \left[u^a [dv^b + \Sigma \left\{ \begin{matrix} lm \\ b \end{matrix} \right\} dx^l v^m] + v^a [du^b + \Sigma \left\{ \begin{matrix} lm \\ b \end{matrix} \right\} dx^l u^m] \right] \quad (3')$$

So we can satisfy the imposed condition by taking

$$du^b = - \Sigma (lm) \left\{ \begin{matrix} lm \\ b \end{matrix} \right\} dx^l u^m. \quad (4)$$

and similar expressions for dv^b , dw^b ...

The equation (4) is covariant. It will retain its form whatever be the choice of coordinates.

It defines the position of the points of the small rigid when, by a first approximation, they have all covered the same infinitesimal distance.

It is seen, from (1), that in developing g_{ab} into a series we have neglected terms with products $u^m u^n$. The squares of the distances covered therefore can differ from PQ by an amount of the order $\epsilon^2 \Delta^2$, so that the distances may only be taken as equal up to an amount of the order $\epsilon^2 \Delta$, which we shall neglect.

8. The "corrections" given by eq. (4) are of the order $\Delta\varepsilon$. In order to see if the solution defined by them is the only one, we may ask if we can satisfy the equations by "corrections" differing from du^a , such as $du^a + \delta u^a$, where δu^a is of the same order as du^a .

If these are to satisfy eq. (1), (2), (3), we must evidently have.

$$\begin{aligned} 0 &= \Sigma(ab) g_{ab} dx^a \delta u^b, \\ 0 &= \Sigma(ab) g_{ab} u^a \delta u^b, \\ 0 &= \Sigma(ab) g_{ab} u^a \delta v^b + g_{ab} v^a \delta u^b, \text{ etc.} \end{aligned}$$

If the rigid, besides the centre, consists of p points, we shall have $2p + \frac{1}{2}p(p-1)$ equations for pn variables $du^a, \delta v^a, \dots$ etc. For $p = 2n-3$ we have as many homogeneous linear equations as there are variables. If no set of n vectors $\mathbf{u}, \mathbf{v}, \mathbf{w}, \dots$ are situated together in an $(n-1)$ -dimensional space, then these equations only permit a solution of the form (e.g. for $n = 3$):

$$\delta u^a = \frac{\omega}{\sqrt{g}} \Sigma(ij) \begin{vmatrix} g_{bi} & g_{ci} \\ g_{bj} & g_{cj} \end{vmatrix} dx^i u^j = \frac{\omega}{\sqrt{g}} \begin{vmatrix} dx_b & dx_c \\ u_b & u_c \end{vmatrix}, \quad (5)$$

where ω is an arbitrary number, and by b, c, a , we mean a set of three indices which form an even permutation of 1, 2, 3. We denote by dx_b and u_b with lowered index the covariant combinations:

$$dx_b = \Sigma(i) g_{bi} dx^i, \quad u_b = \Sigma(j) g_{bj} u^j.$$

It can easily be ascertained that the expression given for δu^a , together with similar expressions for $\delta v^a, \delta w^a, \dots$ satisfy the equations. They must define the displacements in the case of an infinitesimal rotation about \mathbf{dx} as an axis¹⁾. For all vectors $\mathbf{u}, \mathbf{v}, \mathbf{w}, \dots$ keep their lengths unchanged and both the angles included with \mathbf{dx} and the mutual angles remain unaltered.

Since the condition imposed thus far appears not to be sufficient to define a displacement without ambiguity, we must recur to the condition of reciprocity of section 2.

Shifting the centre of the compass-rigid from P to Q the particle designed by \mathbf{u} might come from a position R into the position defined by the coordinates

$$x_P^a + dx^a + u^a + du^a + \delta u^a,$$

or,

$$x_P^a + dx^a + u^a = \Sigma(lm) \begin{Bmatrix} lm \\ a \end{Bmatrix} dx^l u^m + \frac{\omega}{\sqrt{g}} \begin{vmatrix} dx_b & dx_c \\ u_b & u_c \end{vmatrix}.$$

If we now shift the centre from P to R , and we then wish to find what will be the new position for the particle from Q according

¹⁾ Through an angle $\omega|\mathbf{dx}|$.

to the same displacement-law, we only have to interchange the vectors \mathbf{dx} and \mathbf{u}

Now we see, the determinant changing its sign, that this position will never be the same as that reached by the former particle from R , unless $\omega = 0$.

So the application of the condition of reciprocity excludes screw-movements¹⁾.

9. Now in the following way we can see that the condition of the body's rigidity and the equality of the covered distances together with the condition of reciprocity are sufficient to define the variety of geodesic displacements without ambiguity.

From eq. (1) and (2) we learn that the required "corrections" du^a must be proportional both to the components of the displacement \mathbf{dx} and of the vector \mathbf{u} . Therefore let us put

$$du^a = \sum h_{st}^a dx^s u^t \quad . \quad . \quad . \quad . \quad . \quad . \quad (4')$$

Now, according to the condition of reciprocity we must apparently have

$$h_{st}^a = h_{ts}^a.$$

Substitute (4') in (3), and we get

$$0 = \sum (alm) \frac{\partial g_{am}}{\partial x^l} dx^l u^a v^m + \sum (amst) g_{am} \{ h_{st}^m u^a dx^s v^t + h_{st}^a v^m dx^s u_t \}.$$

Taking other indices and putting

$$h_{a,lm} = \sum (b) g_{ab} h_{lm}^b, \quad (h_{a,lm} = h_{a,ml}),$$

we get

$$0 = \sum (alm) dx^l u^a v^m \left\{ \frac{\partial g_{am}}{\partial x^l} + h_{a,lm} + h_{m,la} \right\}.$$

In this equation we may regard the forms in brackets as unknown variables. Because of the symmetry in the indices a and m there are $\frac{1}{2} n^2 (n-1)$ of them. As the equation is to hold for an arbitrary combination

¹⁾ Dr. DROSTE remarked to me that a screw-motion might be excluded in a different manner. Let PQ be part of a geodesic. In P and in Q take two infinitesimal planes perpendicular to the geodesic. Draw the geodesics perpendicular to the first plane and intersecting it in a line-element PR . These together form a "geodesic strip", which will intersect the second plane in an element QR' . PR and QR' can be called "parallel" and in the same way each pair of elements in the same geodesic strip including equal angles with the geodesic PQ .

In our chain of thought, however, geodesic lines are defined by making use of the idea of geodesic displacements (see section 10), and so we cannot avail ourselves of the above suggestion.

of three vectors \mathbf{dx} , \mathbf{u} , \mathbf{v} , we conclude that the variables must vanish. Thus

$$0 = \frac{\partial g_{am}}{\partial x^l} + h_{a,lm} + h_{m,la}.$$

Similarly

$$0 = \frac{\partial g_{la}}{\partial x^m} + h_{l,ma} + h_{a,ml}$$

$$0 = \frac{\partial g_{lm}}{\partial x^a} + h_{m,al} + h_{l,am}.$$

By adding the first two, and subtracting the last, and considering that $h_{l,am} = h_{l,ma}$ etc. we find

$$h_{a,lm} = - \left[\begin{matrix} lm \\ a \end{matrix} \right].$$

Now we know

$$h_{lm}^b = \Sigma g^{ab} h_{a,lm} = - \Sigma g^{ab} \left[\begin{matrix} lm \\ a \end{matrix} \right] = - \left\{ \begin{matrix} lm \\ b \end{matrix} \right\},$$

and so from (4') we see that our values for du^b :

$$du^b = - \Sigma (lm) \left\{ \begin{matrix} lm \\ b \end{matrix} \right\} dx^l u^m \dots \dots \dots (4)$$

constitute the only solution consistent with all conditions.

10. To explain the applications of sections 3 and 4 we proceed as follows. Suppose a vector \mathbf{V} , in point P , be marked in the compass-rigid. After a geodesical displacement to Q the marked vector will have got the components

$$V^a - \Sigma \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} dx^l V^m.$$

Now if we have in Q a vector with components $V^a + dV^a$, where dV^a now represents some increment of the component V^a , then obviously the components of the *geodesic differential* are

$$dV^a + \Sigma (lm) \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} dx^l V^m.$$

This geodesic differential will be a vector itself, being the difference of two vectors, while dV^a are no vector-components.

If the line-element PQ itself is drawn in the compass-rigid as a vector with components dx^a , and displaced geodesically, then in Q the arrow will have got components

$$dx^a - \Sigma (lm) \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} dx^l dx^m.$$

This arrow we have called the *geodesic prolongation* of the

element. It is easily seen that this entails for the geodesic the equation

$$0 = d^2 x^a + \Sigma(lm) \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} dx^l dx^m.$$

This (covariant) equation coincides with what we get from the familiar definition of a geodesic as the shortest line between two points.

11. We shall now displace geodesically a particle P' , which, with relation to P , is defined by a vector u , to a point S' near T , by shifting the compass rigid in two steps from P to T , along PQ and QT . Then, a second time, we displace the particle to S'' near T , taking the steps along PK and KT , the quadrilateral $PQTK$ being a (quasi-) parallelogram with sides dx (PQ and KT) and δx (PK and QT).

After the displacement along PQ the coordinates of the particle considered relative to Q have become

$$u^a - \Sigma(lm) \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} dx^l u^m.$$

At the second step we must be careful to take the values of CRISTOFFEL's symbols at point Q , so that after the displacements along PQ and QT the coordinates relative to T are

$$u^a - \Sigma \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} dx^l u^m - \Sigma \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} \delta x^l \left[u^m - \Sigma \left\{ \begin{matrix} pq \\ m \end{matrix} \right\} dx^p u^q \right] - \Sigma \frac{\partial}{\partial x^p} \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} dx^p dx^l u^m.$$

If the displacements had been performed along PK and KT , the coordinates relative to T would have been

$$u^a - \Sigma \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} \delta x^l u^m - \Sigma \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} dx^l \left[u^m - \Sigma \left\{ \begin{matrix} pq \\ m \end{matrix} \right\} \delta x^p u^q \right] - \Sigma \frac{\partial}{\partial x^p} \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} \delta x^p dx^l u^m.$$

Taking the difference we find

$$\zeta^a = \Sigma(lmp) \left[\frac{\partial}{\partial x^p} \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} - \Sigma(n) \left\{ \begin{matrix} ln \\ a \end{matrix} \right\} \left\{ \begin{matrix} pm \\ n \end{matrix} \right\} \right] (dx^l \delta x^p - \delta x^p dx^l) u^m;$$

or

$$\zeta^a = \frac{1}{2} \Sigma(lmp) \left[\frac{\partial}{\partial x^p} \left\{ \begin{matrix} lm \\ a \end{matrix} \right\} - \frac{\partial}{\partial x^l} \left\{ \begin{matrix} pm \\ a \end{matrix} \right\} + \Sigma \left\{ \begin{matrix} pn \\ -a \end{matrix} \right\} \left\{ \begin{matrix} lm \\ n \end{matrix} \right\} - \Sigma \left\{ \begin{matrix} ln \\ a \end{matrix} \right\} \left\{ \begin{matrix} pm \\ n \end{matrix} \right\} \right] \times \\ \times (dx^l \delta x^p - \delta x^p dx^l) u^m \quad \dots \quad (6)$$

The first factor is seen to be a RIEMANN's four-index-symbol, of the second kind. Availing ourselves of his notation we can put

$$\zeta^a = \frac{1}{2} \Sigma(lmp) \left\{ \begin{matrix} ma, lp \end{matrix} \right\} (dx^l \delta x^p - \delta x^p dx^l) u^m \quad \dots \quad (6)$$

The ζ^a ($a = 1, 2, \dots, n$) are the components of the displacement-

vectors which would become manifest after a geodesical displacement of the compass-rigid about the circuit $TKPQT$. The displacement cannot be anything else but a rotation, the lengths and angles remaining the same. We see how RIEMANN's symbols determine the rotation in terms of the components of the area of the circuit. This rotation is characteristic of the curvature of space.

12. It now remains to prove the statement of section 5 as to the interpretation of RIEMANN's measure of curvature.

The measure of curvature with respect to the plane of \mathbf{dx} and $\delta\mathbf{x}$ is defined to be¹⁾

$$K = \frac{\Sigma(a\,lp\,mq)\,g_{aq}\{ma,\,lp\}(dx^l\delta x^p - dx^p\delta x^l)(dx^m\delta x^q - dx^q\delta x^m)}{\Sigma(lp\,mq)(g_{ln}g_{pq} - g_{lq}g_{pn})(dx^l\delta x^p - dx^p\delta x^l)(dx^m\delta x^q - dx^q\delta x^m)}.$$

The denominator is four times the square of the area of the parallelogram formed by \mathbf{dx} and $\delta\mathbf{x}$. For by changing indices without changing the sum we get four times

$$\Sigma(lp\,mq) \begin{vmatrix} g_{ln} & g_{lq} \\ g_{pm} & g_{pq} \end{vmatrix} dx^l dx^m \delta x^p \delta x^q.$$

Writing d for the length of \mathbf{dx} , and δ for the length of $\delta\mathbf{x}$, we find for the denominator

$$4 \begin{vmatrix} d^2 & d\delta \cos(d\delta) \\ d\delta \cos(d\delta) & \delta^2 \end{vmatrix},$$

this being four times the square of the area of the parallelogram.

We shall discuss the numerator for the case of three-dimensional space and show that it represents four times the volume of the parallelepiped formed by the axis of rotation and the parallelogram.

Proceeding with some caution, the analogon in more-dimensional cases is readily found in the same way. We will put for the numerator

$$2 \Sigma(am\,q)\,g_{aq}\,R_m^a(dx^m\delta x^q - dx^q\delta x^m) \dots \dots \dots (7)$$

denoting by R_m^a the coefficients of the rotation of curvature (6):

$$\zeta^a = \Sigma(m)\,R_m^a\,u^m.$$

or,

$$\zeta^c = \Sigma(j)\,R_j^c\,u.$$

How are the numbers R_j^c related to the components of the axis of rotation? If we suppose the components of the latter equal to \bar{l} , then the rotation is represented, as will be presently shown, by

$$\zeta^c = \frac{1}{\sqrt{g}} \Sigma(ij) \begin{vmatrix} g_{ai} & g_{bi} \\ g_{aj} & g_{bj} \end{vmatrix} \bar{l}^i u^j \dots \dots \dots (8)$$

¹⁾ Cf. for example BIANCHI, Lect. on Diff. Geometry, section 319.

Here we mean by c that index, which with a and b forms an even permutation of 1 2 3. By pqr we shall denote a similar set:

$$abc(=)pqr(=)123.$$

We already saw that displacements of this kind constitute a rotation. To inquire whether the angular amount of the rotation is equal to the length of \mathbf{l} , we must observe the displacement of the end of a vector \mathbf{u} which is perpendicular to \mathbf{l} , so that

$$\sum (ab) g_{ab} u^a l^b = 0. \quad (9)$$

This displacement ought to be $|\mathbf{u}|$ multiplied by $|\mathbf{l}|$. Let us calculate $|\zeta|^2$:

$$\begin{aligned} \zeta^2 &= \sum (cr) g_{cr} \zeta^c \zeta^r, \\ &= \frac{1}{g} (rijv w) \begin{vmatrix} g_{ai} & g_{bi} & g_{ci} \\ g_{aj} & g_{bj} & g_{cj} \\ g_{ar} & g_{br} & g_{cr} \end{vmatrix} l^i u^j \begin{vmatrix} g_{\mu v} & g_{qv} \\ g_{\mu w} & g_{qw} \end{vmatrix} l^\mu u^w. \end{aligned}$$

The summation with respect to c has been effected by writing in full the first determinant. If we want to sum up with respect to r , we notice that the determinant vanishes but for one special value of r , which is different both from i and j . If $i = p$, $j = q$, then the determinant becomes $+g$, if $i = q$, $j = p$, then we get $-g$. In both cases we may write

$$\zeta^2 = \sum (pqvw) \begin{vmatrix} g_{\mu v} & g_{qv} \\ g_{\mu w} & g_{qw} \end{vmatrix} l^\mu l^r u^q u^w,$$

and, by (9):

$$\zeta^2 = u^2 l^2,$$

So the correctness of formula (8) has been shown.

But then we are justified in putting

$$R_j^c = \frac{1}{\sqrt{g}} \sum (i) \begin{vmatrix} g_{ai} & g_{bi} \\ g_{aj} & g_{bj} \end{vmatrix} l^i,$$

and we can subsequently show that (7) represents four times the parallelepiped mentioned. We write (7) with a slight alteration of indices and we get:

$$\begin{aligned} &2 \sum (cjk) g_{ck} R_j^c (dx^j dx^k - dx^k dx^j) = \\ &= \frac{2}{\sqrt{g}} \sum (ijk) \begin{vmatrix} g_{ai} & g_{bi} & g_{ci} \\ g_{aj} & g_{bj} & g_{cj} \\ g_{ak} & g_{bk} & g_{ck} \end{vmatrix} l^i (dx^j dx^k - dx^k dx^j). \end{aligned}$$

Now if j and k assume all values, a set j, k furnishes just as much as a set k, j , the determinant taking the value $+g$ or $-g$ according to the combination i, j, k being an even or odd permutation

of 1 2 3, and vanishing for other combinations. So we get for the numerator

$$4 \sqrt{g} \begin{vmatrix} l^i & l^j & l^k \\ dx^i & dx^j & dx^k \\ \delta x^i & \delta x^j & \delta x^k \end{vmatrix}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

this being four times the volume of the parallelepiped formed by \mathbf{l} , $d\mathbf{x}$ and $\delta\mathbf{x}$.

This sufficiently explains section 5. We may remark that formula (8) for the displacements of rotation implies a convention as to the direction in which the axis of rotation has to be drawn. The axis of rotation must be orientated in a manner to ensure that the direction of ξ is correlated to the directions of \mathbf{l} and \mathbf{u} , i.e. a parallelepiped constructed from \mathbf{l} , \mathbf{u} and ξ , in the order thus specified, must have a positive volume:

$$\sqrt{g} \begin{vmatrix} l^a & l^b & l^c \\ u^a & u^b & u^c \\ \xi^a & \xi^b & \xi^c \end{vmatrix} = \text{positive}.$$

This amounts to the same relation which exists between the directions of the positive axes of X, Y, Z .

One sees from (10) that the measure of curvature will be positive if the direction of the axis of the rotation of curvature bears the above-mentioned correlation to the directions of $d\mathbf{x}$ and $\delta\mathbf{x}$.

Similarly, in four dimensions, if the axis of a rotation in a special case be a parallelogram on the vectors \mathbf{l} and \mathbf{m} , then the rotation is given by

$$\xi^d = \frac{1}{\sqrt{g}} \Sigma (i j k) \begin{vmatrix} g_{ai} & g_{bi} & g_{ci} \\ g_{aj} & g_{bj} & g_{cj} \\ g_{ak} & g_{bk} & g_{ck} \end{vmatrix} l^i m^j u^k.$$

where $a b c d (==) 1 2 3 4$, and the direction of ξ is correlated to the directions of \mathbf{l} , \mathbf{m} and \mathbf{u} , i.e.

$$\sqrt{g} \begin{vmatrix} l^a & l^b & l^c & l^d \\ m^a & m^b & m^c & m^d \\ u^a & u^b & u^c & u^d \\ \xi^a & \xi^b & \xi^c & \xi^d \end{vmatrix} = \text{positive}$$

My thanks are due to prof. J. A. SCHOUTEN for his kindness in allowing me to read his treatise on Direct Analysis, which is to be published soon in the Transactions of the Kon. Akademie.

Astronomy. — “*The Distribution of the absolute Magnitudes among the Stars in and about the Milky Way.*” (First Communication).
By Dr. W. J. A. SCHOUTEN. (Communicated by Prof. J. C. KAPTEYN).

(Communicated in the meeting of October 26, 1918).

1. *Introduction.*

One of the most important problems of statistical astronomy is to examine, how in each part of space the stars with bright and faint absolute magnitudes are mixed and of which percentage of stars the luminosity lies between definite limits. Luminosity means the apparent brightness, which a star would have at the unit of distance, and for this unit we will take, in imitation of Professor KAPTEYN, the distance corresponding to an annual parallax $\pi = 0''.1$.

The first determination of the luminosity law was performed by Professor KAPTEYN and published in *Publ. Groningen* N^o. 11¹⁾. Afterwards several astronomers, employing different methods, have repeated this investigation. Besides the studies of COMSTOCK and WALKER, who availed themselves of measured parallaxes, and whose results therefore are not much to be relied upon, unless great cautiousness is used, the researches of SEELIGER and SCHWARZSCHILD are well-known. In our dissertation²⁾ we have discussed the three methods mentioned, and we have compared the results that were found. It appeared that serious objections may be raised against SEELIGER's investigation, so that we cannot attach much value to the frequency-function of absolute magnitudes found by him. We think we have also demonstrated in our work just cited that the method of KAPTEYN is for various reasons greatly to be preferred to that of SCHWARZSCHILD.

After we had finished this inquiry an earnest wish arose in us to establish the luminosity law according to the method which we think the best. It was known to us, that such a determination had been

¹⁾ Also in these Proceedings, Vol. III, p. 658.

²⁾ On the Determination of the Principal Laws of Statistical Astronomy. Amsterdam, Kirchner 1918.

in course of preparation at the Astronomical Laboratory at Groningen for a long time already.

In this preparation are included the countings of stars of determined magnitude which are published in *Publ. Groningen* Nos. 18 and 27, and the mean parallaxes of stars of determined magnitude and galactic latitude, which will soon be published and have been kindly lent us for our use by Prof. KAPTEYN and Dr. VAN RHIJN.

It is a matter of course that the preliminary results obtained by us, should be replaced by those of the definitive solution as soon as these are available. Yet we thought we might publish our results as they are partly based on other data, because they give a notion of the exactness that is to be obtained now already, and our preliminary results might be of some service perhaps until the time that the definitive shall have appeared.

In this communication we mention the results that we found, when we tried to determine the luminosity law according to KAPTEYN's method for the whole sky and for five zones of different galactic latitude.

We intend to publish in a second communication the results that are found, when SCHWARZSCHILD's method is applied to the same data. At the same time we hope to compare our results with those of other investigators.

In this article we also gratefully tender our sincere thanks to Prof. KAPTEYN for his kind help, which favoured our investigation.

2. The Data of Observation.

In applying KAPTEYN's method we have to take from the observations the following data:

1. the numbers $N_{m,\mu}$ i.e. the numbers of stars of determined apparent magnitude and proper motion,
2. the mean parallaxes $\pi_{m,\mu}$ of stars of determined magnitude and proper motion,
3. the value of ϱ , the probable error of the error curve $\log. \pi/\pi_0$ in which π is the real and π_0 the probable parallax.

In our investigation we divided the sky into 5 zones. The galactic latitude we shall indicate by b .

Zone I	=	part of the sky	between	$b = -10^\circ$	and	$b = +10^\circ$.
Zone II	=	" " " "	with b from	-10° to -30°	and	$+10^\circ$ to $+30^\circ$.
Zone III	=	" " " "	" b "	-30° " -50°	"	$+30^\circ$ " $+50^\circ$.
Zone IV	=	" " " "	" b "	-50° " -70°	"	$+50^\circ$ " $+70^\circ$.
Zone V	=	" " " "	" b "	-70° " -90°	"	$+70^\circ$ " $+90^\circ$.

We have derived the numbers $N_{m,\mu}$ from the numbers of stars of determined magnitude and galactic latitude by performing countings in catalogues of stars with known proper motions. We have computed these numbers N_m for the different zones from the tables in *Publ. Groningen* N°. 18, as these have been corrected in *Publ. Groningen* N°. 27.

The results that VAN RHIJN published in the work last-mentioned, are very reliable, as they were confirmed by several independent studies. The results of NORT and SEARES, indeed, agree fairly well with those of VAN RHIJN and the numbers of CHAPMAN and MELOTTE too correspond to the Groningen countings as soon as they shall have been corrected for a mistake in the method of reduction which has been pointed out by VAN RHIJN.

In our countings the stars were divided according to their magnitudes into groups of 1—2.9, 3.0—3.9, 4.0—4.9, 12.0—12.9. According to their proper motions they were counted between the limits 0—2".9, 3".0—4".9, 5".0—7".9, 8".0—9".9, 10".0—14".9, 15".0—19".9, 20".0—29".9, 30".0—49".9 and $>49".9$.

The following catalogues have been used.

1. L. BOSS. Preliminary Catalogue of 6188 Stars, 1910.
2. A. AUWERS. Catalog der Astronomischen Gesellschaft, Zone $+15^\circ$ bis $+20^\circ$, 1896.
3. W. G. THACKERAY. Greenwich 1910 Catalogue of Stars, Zone $+24^\circ 0'$ to $+32^\circ 0'$. Analysis of Number and Percentages of Proper Motions. *Monthly Notices* **77**, 204—212, 1917.

F. W. DYSON and W. G. THACKERAY. The Systematic Motions of the Stars between Dec. $+24^\circ$ and Dec. $+32^\circ$. *Monthly Notices* **77**, 581—596, 1917.

4. F. W. DYSON and W. G. THACKERAY. New Reduction of GROOMBRIDGE's Catalogue of Circumpolar Stars, 1905.

5. J. C. KAPTEYN and W. DE SITTER. The Proper Motions of 3300 Stars of different Galactic Latitudes, derived from photographic plates, prepared by Prof. ANDERS DONNER. *Publ. Groningen* N°. 19, 1908.

6. J. C. KAPTEYN. The Proper Motions of 3714 Stars derived from plates taken at the observatories of Helsingfors and the Cape of Good Hope. With the co-operation of Dr. H. A. WEERSMA. *Publ. Groningen* N°. 25, 1914.

7. Dr. A. A. RAMBAUT. A photographic Determination of the Proper Motion of 250 Stars in the Neighbourhood of Σ 443. *Monthly Notices* **73**, 616—630, 1913.

8. A. VAN MAANEN. Remarks on the Motion of the Stars in and near the double Cluster in Perseus. *Report of the Nineteenth Meeting*

of the American Astronomical Society. *Popular Astronomy* **25**, 108—110, 1917.

9. W. G. THACKERAY. Notes on some Proper Motions derived from a Comparison of CARRINGTON's Catalogue with the Greenwich Places for 1900. *Monthly Notices* **67**, 146—148, 1906.

Boss' catalogue was only used for stars brighter than $5^m.8$.

AUWERS' catalogue was only used to determine $N_{m,\mu}$ for the whole sky.

The proper motions that have been derived from the Cape plates in *Publ. Groningen* N°. 25, are not very accurate. The plates had not been originally destined for deriving proper motions from them, and they had been measured absolutely. We have, therefore, in determining the mean values attached but very little weight to them.

No corrections have been applied in order to reduce our results for the different catalogues to the same scale of magnitudes or to one fundamental system or in order to correct the proper motions for errors of observation. These corrections may in our opinion be neglected, considering the comparative inaccuracy of the numbers. Moreover, we have always expressed the numbers $N_{m,\mu}$ for every magnitude in percentages of the numbers N_m and these percentages appeared to vary only little with the magnitudes.

Our countings in determining $N_{m,\mu}$ for the whole sky include 38818 proper motions, while moreover in the five zones resp. 8273, 10857, 6981, 3144 and 1488 stars were counted.

Now we are able to determine the numbers of stars of determined magnitude and proper motion. The results we found for the whole sky, are mentioned in table 1.

In our further research we did not use the numbers of stars with $\mu > 50''$. It is very difficult to determine these with sufficient accuracy from the data of known proper motions, so scanty as yet. It will appear that in consequence of this limitation we could not extend the luminosity curve found by us to the faintest stars.

The numbers $N_{m,\mu}$ now being known for the different zones, we may also examine how the stars with determined proper motions are distributed over the sky with reference to the Milky Way. In order to do so we have calculated the numbers of stars with P.M. resp. $> 10''$, $5''$, $3''$ and $0''$ for every magnitude per 100 square degrees. It appeared that the numbers of stars with $\mu > 5''$ do not evince any galactic condensation, except perhaps for stars, fainter than $9^m.0$. The numbers with $\mu > 3''$ very clearly show a condensation for all magnitudes in the direction of the Milky Way, although to a less high degree than the numbers of stars with $\mu > 0''$.

TABLE 1. The numbers of stars of determined magnitude and proper motion for the whole sky.

$m \backslash \mu$	0—2.9	3.0—4.9	5.0—7.9	8.0—9.9	10.0—14.9	15.0—19.9	20.0—29.9	30.0—49.9	> 49.9	Total
1—2.9	31	26	13	8	14	6	13	10	11	132
3.0—3.9	48	41	39	19	39	18	28	14	17	263
4.0—4.9	303	167	128	50	113	57	39	29	21	907
5.0—5.9	1090	665	575	222	329	140	117	72	52	3262
6.0—6.9	4019	2675	1528	564	728	349	185	123	82	10253
7.0—7.9	14664	8268	4150	1092	1716	530	374	281	125	31200
8.0—8.9	44996	27517	11992	2417	3718	930	744	464	186	92964
9.0—9.9	108257	78185	32478	8420	9142	2165	1203	480	241	240571
10.0—10.9	270748	172763	136019	29009	29653	2579	2579	645	645	644640
11.0—11.9	705391	436968	288711	74909	43697	4681	3121	1561	1561	1560600

This result agrees with that found by KAPTEYN in 1893 and with the conclusions, which DYSON and THACKERAY found lately from a discussion of the Greenwich 1910 catalogue.

The mean parallaxes $\pi_{m,\mu}$ for the whole sky and for the different galactic zones have not been determined by us directly. In our opinion they may be reduced for our investigation, preliminary as it is, with sufficient accuracy from former researches.

KAPTEYN found in *Publ. Groningen* N°. 8 for these mean parallaxes

$$\pi_{m,\mu} = a \mu^b \varepsilon^{m-5.0}$$

in which $a = 0''.0038$, $b = 0.71$ and $\varepsilon = 0.905$.

Use was made of the value 16.7 Kilometers a second for the velocity of the sun. If we accept the modern value, 19.5 Kilometers a second, the mean parallaxes π_m , used by KAPTEYN in deducing his formula, are lessened by 14%. If we now suppose — as VAN RHIJN also does ¹⁾ — that this correction for the mean parallaxes π_m changes only the value of a in $\pi_{m,\mu}$, we find $a = 0''.0032^5$.

KAPTEYN's parallaxes corrected in this way agree with the values, deduced by Dr. VAN RHIJN in his dissertation in an investigation, based on other and more modern data than those used by KAPTEYN, in which he partly also applied another method. Hence it follows that the parallaxes $\pi_{m,\mu}$, as given in *Publ. Groningen* N°. 8, are very reliable.

In order to derive from the parallaxes which may be applied to the whole sky, the $\pi_{m,\mu}$ for the different zones, we have assumed, that the $\pi_{m,\mu}$ of the various galactic zones are related in the same way as the π_m of these zones.

This assumption is rather arbitrary. Most probably it cannot be proved to be correct in all respects. There is reason to believe, however, that the error, made in this way, is not very great. Therefore we thought we might use this hypothesis in our preliminary research. We have already mentioned that we were able to use, thanks to the great kindness of Professor KAPTEYN and Dr. VAN RHIJN, the mean parallaxes of stars of determined magnitude and galactic latitude, which will soon be published in *Publ. Groningen* N°. 29. These parallaxes may be respresented by the following formulae:

Zone I	$\log. \pi_m = 8.883 - 0.142 m$
II	$= 8.904 - 0.142 m$
III	$= 8.957 - 0.142 m$
IV	$= 9.024 - 0.142 m$
V	$= 9.066 - 0.142 m$
Whole sky	$= 8.943 - 0.142 m$

¹⁾ Diss. Groningen 1915, p. 35.

We have calculated — if we call the parallaxes, used formerly by KAPTEYN, $\pi_{m, \text{KAPTEYN}}$, and if for convenience' sake we indicate those meant above by $\pi_{m, \text{VAN RUYN}}$ — the $\pi_{m, \mu}$ for the whole sky and for the 5 zones by multiplying the numbers of table G of *Publ.*

TABLE 2.

The mean parallaxes of stars of determined magnitude and proper motion for the whole sky.

$\mu \backslash m$	1.5	4.0	6.5	9.0	12.5	17.5	25	40
2.6	0".0065	0".0132	0".0187	0".0237	0".030	0".037	0".049	0".068
3.6	.0057	.0115	.0163	.0206	.026	.033	.042	.059
4.6	.0049	.0100	.0142	.0178	.023	.029	.037	.051
5.6	.0043	.0087	.0123	.0155	.020	.025	.033	.045
6.6	.0037	.0076	.0107	.0135	.017	.022	.028	.039
7.6	.0033	.0066	.0093	.0117	.014	.019	.025	.034
8.6	.0029	.0057	.0081	.0103	.012	.016	.022	.029
9.6	.0025	.0050	.0071	.0090	.011	.014	.019	.026
10.6	.0022	.0043	.0061	.0077	.009	.012	.016	.023
11.6	.0019	.0036	.0051	.0065	.008	.010	.014	.020

Groningen N°. 8 by a factor $\frac{\pi_m^{\text{VAN RHIJN}}}{\pi_m^{\text{KAPTEYN}}}$. The parallaxes, which may be applied to the whole sky, are given in table 2.

We ourselves have not tried to determine once more the probable deviation of the error curve $\log. \pi/\pi_0$. Moreover we have supposed that ϱ does not vary with the galactic latitude. We made use of the value 0.19, found by KAPTEYN both in our solution for the whole sky and in that for the 5 galactic zones. It has, however, been proved in *Publ. Groningen* N°. 11 that the value of ϱ has only little influence on the result.

3. Applying KAPTEYN's Method.

We have applied KAPTEYN's method without any modification. For a description in detail of this method we refer to his treatise in *Publ. Groningen* N°. 11, which we cited already above. We shall limit ourselves to a short discussion of the hypotheses that have been made and an explanation of the tables mentioned in this essay.

The hypotheses, made in KAPTEYN's investigations, are three in number:

- 1stly the density is only a function of r ;
- 2ndly the luminosity curve is independent of the distance from the sun and there is no absorption of light in space;
- 3^dly the quantities $z = \log. \pi/\pi_0$ are distributed according to the law of errors.

The first hypothesis is necessary if we want to derive frequency-functions that may be applied to the whole sky. We seek for mean values for the unknown quantities and so we cannot take into account the variations in the values with the galactic latitude and longitude. KAPTEYN's method may, however, be used just as well, if we want to reckon with the influence of the galactic latitude by making separate solutions for the different galactic zones.

The second hypothesis can hardly be dispensed with. If we have certainty that the frequency-function of absolute magnitudes is everywhere the same in space, KAPTEYN's method offers the means to examine, whether there is a perceptible extinction of light and, on the other hand, when we know that there is no absorption we can examine if the luminosity curve varies with the distance from the sun. As neither one thing nor the other, however, is certain, we are obliged for the time being to make the supposition in question.

If we establish the frequency-function for the different galactic

zones separately, this difficulty is diminished considerably. We can then compare the luminosity curves, found for the various zones. If now, it appears that these curves correspond, it is highly improbable that the distribution of luminosities varies with the distance to the sun. If the luminosity law depends on r and not on b , we should find a fan-shaped composition of the sidereal system, which is not inconceivable, but highly improbable all the same.

If we may assume that the distribution of the luminosity is independent of the distance to the sun, KAPTEYN's method enables us to determine the absorption, or at least to examine if it has any influence on the distribution of stars in space which we found.

The third hypothesis was, indeed, when KAPTEYN made it for the first time a rather arbitrary assumption, and it must be conceded that other results would have been found, if another hypothesis had been made. The hypothesis was made, because at that time there were still too few measured parallaxes, to enable us to deduce the form of the frequency curve $\log. \pi/\pi_0$ directly from the data. Perhaps this will be possible when applying the method once more. It is, however, of little importance to discuss in the present stage the question whether this hypothesis could be justified or not, as SCHWARZSCHILD has proved that the above-mentioned relation exists for a special form of the density law and the luminosity law, which form obtained a great amount of probability owing also to his investigations.

We have deduced the luminosity law from the data of observation mentioned in § 2. Space was divided into a number of shells the radii of which had been selected for convenience' sake in such a way that $\log. r$ increases with 0.2. Afterwards the mean parallax was determined for each of the numbers $N_{m,\mu}$ that had been found by means of the formula for $\pi_{m,\mu}$. Then with the aid of the value found for the probable deviation of the error curve $\log. \pi/\pi_0$, it was calculated which part of the numbers found occur in every shell.

The numbers $N_{m,\mu}$ which we found for the whole sky are given in table 1, and the corresponding parallaxes $\pi_{m,\mu}$ in table 2. In table 3 we have mentioned, how these numbers of stars are divided over the various shells. Tables in accordance with this we have calculated for the five zones.

Now we have derived from these tables others, indicating the numbers of stars of every absolute magnitude per unit of volume in the different shells. For the whole sky we communicated our results in table 4. Between the fat-faced lines the numbers

TABLE 3.

The number of parallaxes for the whole sky.

π	Mag. $\frac{1}{\pi}$	2.6	3.6	4.6	5.6	6.6	7.6	8.6	9.6	10.6	11.6	Total
0".00000—0".00100		0	1	6	33	228	83	4325	17045	55568	212210	289499
.00100— .00158	0".00118	1	2	20	94	469	3339	9806	28249	90900	245902	378782
.00158— .00251	.00187	3	6	55	247	1170	4603	15720	45170	112684	341132	520790
.00251— .00398	.00296	7	14	99	435	1781	6153	20643	52073	119250	328492	528947
.00398— .00631	.00469	14	25	147	579	1957	6700	18139	46380	139905	234121	447967
.00631— .0100	.00743	16	38	150	597	1780	4721	12972	28374	77002	133400	259050
.0100 — .0158	.0118	24	47	146	503	1430	3155	6896	15180	34288	43900	105569
.0158 — .0251	.0187	21	46	121	389	806	1030	2715	5702	11082	17370	39282
.0251 — .0398	.0296	15	26	65	171	358	678	1222	1752	2806	2247	9340
.0398 — .0631	.0469	11	28	56	117	147	553	267	347	465	202	2193
.0631 — .1000	.0743	6	10	17	27	37	47	62	53	45	47	351
.1000 — .158	.118	2	2	4	7	7	10	11	5	0	16	64
> .158	.204	1	1	0	1	1	3	0	0	0	0	7
		121	246	886	3200	10171	31075	92778	240330	643995	1559039	2581841

TABLE 4.

The log. of the number of stars per unit of volume.

$\frac{M}{\pi}$	-7.0	-6.0	-5.0	-4.0	-3.0	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0
0".00118	3.503	3.804	4.804	5.476	6.274	7.027	7.494	7.954	8.462	8.894										
.00187		4.580	4.881	5.843	6.496	7.171	7.766	8.299	8.758	9.145	9.636									
.00296			5.548	5.849	6.703	7.341	7.954	8.492	9.018	9.420	9.779	0.220								
.00469				6.449	6.701	7.470	8.066	8.595	9.129	9.562	9.969	0.449	0.672							
.00743					7.107	7.483	8.079	8.679	9.153	9.577	0.016	0.356	0.797	1.028						
.0118						7.883	8.175	8.667	9.205	9.658	0.002	0.342	0.684	1.038	1.145					
.0187							8.425	8.766	9.186	9.693	0.009	0.116	0.537	0.859	1.148	1.343				
.0296								8.879	9.118	9.516	9.936	0.257	0.534	0.790	0.947	1.151	1.055			
.0469									9.344	9.750	0.051	0.371	0.470	1.046	0.730	0.843	0.970	0.608		
.0743										9.681	9.903	0.133	0.334	0.471	0.575	0.695	0.627	0.556	0.575	
.118											9.804	0.804	0.105	0.348	0.348	0.503	0.544	0.202	—	0.707
.204												9.979	9.979	—	9.979	9.979	0.456	—	—	—

of stars of the apparent magnitudes 3.0 to 10.0 are found. These are most reliable.

The densities in the different shells were determined by comparing each time in two successive shells the numbers of stars of a determined absolute magnitude. The relative density of two successive shells was found as the average of three determinations, based respectively on the stars of the apparent magnitudes from 3.0 to 8.0, 3.0 to 9.0 and 3.0 to 10.0. The density in the fifth shell, *viz.* the one for which the mean parallax is $0''.0296$, was supposed to be *one*, after which the density at every distance from the sun, expressed in this unity, is known.

The average density for the whole sky varies about in the same way with the distance to the sun as KAPTEYN found. In zone I the density at great distances is considerably more than the average, in zones III, IV and V on the other hand it is much less.

By means of the densities found we now calculated from table 4 and the similar ones for the galactic zones the number of stars per unit of volume, after the density had been reduced to the one for $\pi = 0''.0296$. In order to do so each number in the last-mentioned tables was diminished by the logarithm of the density of the shell pertaining to it. In this way for instance table 5 has been calculated from table 4.

From the tables that were found last of all, the luminosity curves for the whole sky and the 5 zones may be deduced at once. The numbers, standing between the fat lines in each column, correspond pretty well.

In table 5 we took the averages of these numbers (not of the logarithms), and noted down the logarithm of these averages in the last line of each table. In taking the mean equal weight was ascribed to all numbers, except to those of the first four shells. These numbers are not very reliable, because they are small, but especially because we were obliged to exclude from our investigation stars with a proper motion $> 50''$ per century. Consequently the luminosity curves that have been found are only of value up to $M = 5.0$.

It is of interest to point out that our result for the whole sky corresponds beautifully to KAPTEYN's found in *Publ. Groningen* N°. 11.

Furthermore it is remarkable that the curves found for the various zones differ only a little. We already observed that from this we may conclude with a certain probability that the luminosity curve does not change with the distance to the sun either.

In table 5 and the corresponding tables for the 5 galactic zones

TABLE 5.

The log. of the number of stars per unit of volume, reduced to $\pi = 0''.0296$.

$\frac{M}{\pi}$	-7.0	-6.0	-5.0	-4.0	-3.0	-2.0	-1.0	0.0	1.0	2.0	3.0	4.0	5.0	6.0	7.0	8.0	9.0	10.0	11.0	12.0
0''.00118	4.141	4.442	5.442	6.114	6.912	7.665	8.132	8.592	9.100	9.532										
.00187		4.976	5.277	6.239	6.892	7.567	8.162	8.695	9.154	9.541	0.032									
.00296			5.741	6.042	6.896	7.534	8.147	8.685	9.211	9.613	9.972	0.413								
.00469				6.527	6.779	7.548	8.144	8.573	9.207	9.634	0.047	0.527	0.750							
.00743					7.153	7.529	8.125	8.725	9.159	9.623	0.062	0.402	0.843	1.074						
.0118						7.902	8.194	8.686	9.224	9.677	0.021	0.361	0.703	1.057	1.164					
.0187							8.426	8.767	9.187	9.694	0.010	0.117	0.538	0.860	1.149	1.344				
.0296								8.879	9.118	9.516	9.936	0.257	0.534	0.790	0.947	1.151	1.055			
.0469									9.269	9.675	9.976	0.296	0.395	0.971	0.655	0.768	0.895	0.533		
.0743										9.932	9.846	0.384	0.585	0.722	0.826	0.946	0.878	0.807	0.826	
.118											0.249	0.249	0.650	0.793	0.793	0.948	0.989	0.647	—	1.152
.204												0.712	0.712	—	0.712	0.712	1.189	—	—	—
Mean	4.141	4.442	5.367	6.140	6.873	7.572	8.146	8.679	9.182	9.629	0.017	0.299	0.600	0.827	0.947	0.870	1.038	0.647		



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the numbers in each column, as has been already observed, agree with each other. If our conclusion that the frequency curve of the absolute magnitudes does not vary with r , is right, we may derive from the agreement of the luminosity curves in the different shells that there is no perceptible absorption of light in space.

In figure 1 the frequency curves that were found have been drawn. The six lines in the lowest part of the figure refer to the determination of the luminosity curve, discussed in this essay. The six lines in the upper part refer to an application of SCHWARZSCHILD's method to the same data, which will be explained in a following communication.

The line representing our determination of the luminosity curve for the whole sky, indicates the logarithm of the number of stars of every M per unit of volume in the neighbourhood of the sun. For the other curves we added, in order to make comparison possible, a constant amount to each number.

Amsterdam, June 1918.

Mathematics. — “On the arising of a precession-motion owing to the non-euclidian linear element of the space in the vicinity of the sun”. By Prof. J. A. SCHOUTEN. (Communicated by Prof. LORENTZ).

(Communicated in the meeting of June 29, 1918).

If k be an curve in an n dimensional space X_n of arbitrary form, there will be in the euclidian space of $\frac{n(n+1)}{2}$ dimensions, into which X_n can always be placed without changing its linear element, a euclidian space Y_n , i. e. a space Y_n developable on a plane space tangent to X_n along k . If in the euclidian space Y_n a system of n mutual \perp directions be moved with its origin along k parallel to itself, we find that these directions in X_n define a “geodesically moving system”¹⁾. If two arbitrary spaces are tangent to each other in a curve k , it follows from this definition, that a system geodesically moving along k for one space, will geodesically move for the other space too. A volume-element covered with mass can move in X_n as a solid body, but for some infinitesimals of a higher order. If a suchlike element always remains at rest with regard to a geodesically co-moving system of directions we will call it *compassbody*. Hence the compassbody mechanically realizes the geodesically moving system.

If k be a closed curve, the initial position will as a rule not coincide with the final position, if X_n is non-euclidian. Thus the position of the compassbody is changed with every rotation. Now according to the investigations of K. SCHWARZSCHILD²⁾ the space in the vicinity of the sun is not euclidian, but very slightly curved. The linear element is of the form

$$ds^2 = dR^2 + R^2 d\theta^2 + R^2 \sin^2 \theta d\varphi^2 \dots \dots \dots (1)$$

¹⁾ Cf. for a more detailed exposition of the geodesically moving system: “Die direkte Analysis der neueren Relativitätstheorie”. Verh. of the Kon. Akad. v. Wet. Vol. 12. No. 6 and “On the number of degrees of freedom of the geodesically moving system and the enclosing euclidian space with the least possible number of dimensions”. Proc. of the Kon. Akad. v. Wet. May 25, 1918.

²⁾ Ueber das Gravitationsfeld eines Massenpunktes nach der Einstein'schen Theorie, Berl. Sitzungsber. 1916, p. 189—196.

L. FLAMM¹⁾ has indicated how a space with that linear element can be realized. The parabola situated in the xz plane:

$$z^2 = 4a(x - \alpha) \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

has the linear element:

$$ds = \frac{dx}{\sqrt{1 - \frac{a}{x}}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

If this parabola is rotated about the z axis, in the xyz space, there arises a rotation-surface with the linear element:

$$ds^2 = \frac{dR^2}{1 - \frac{a}{R}} + R^2 d\varphi^2 \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

φ being the rotation-angle, measured from the yz plane (fig. 1).

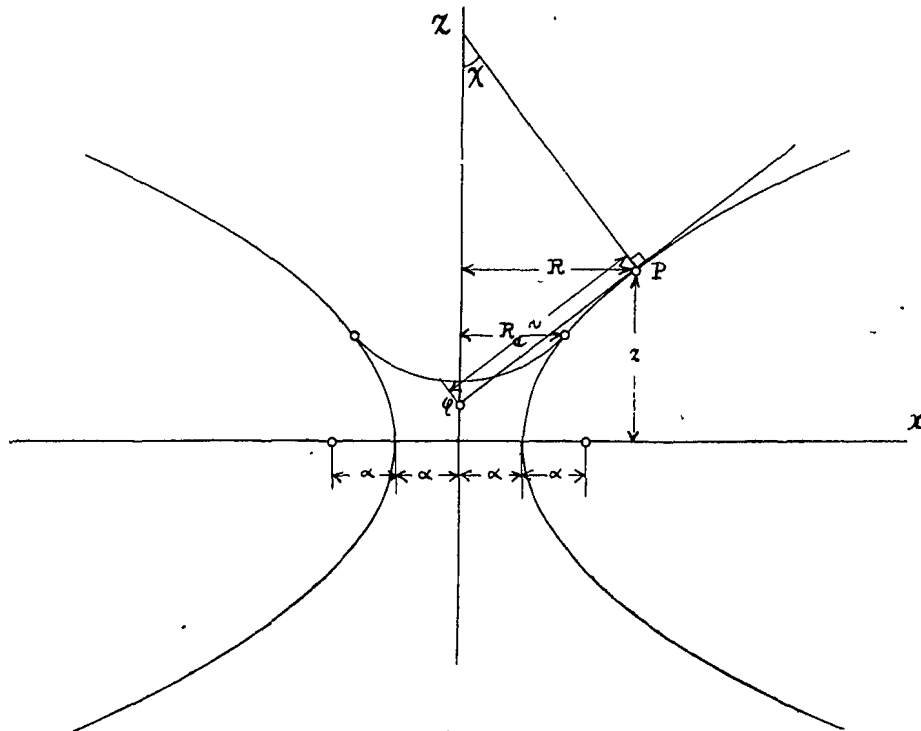


Fig. 1.

A fan of directions in the centre of the sun determines a system of ∞^1 geodesic lines, together forming a diametral surface. Such a diametral surface can as regards the parts beyond the surface of the sun be developed on the rotation-surface (4) without changing its linear element. R may approximately be equalized with the

¹⁾ Beiträge zur Einstein'schen Gravitationstheorie 17 (16) 448—454.

naturally measured distance relative to the centre of the sun, while $\alpha = 2.945 \cdot 10^{15}$ cm. The circle described by a definite point P :

$$\left. \begin{aligned} x^2 + y^2 &= R^2 \\ z &= 2\sqrt{\alpha(R-\alpha)} \end{aligned} \right\} \dots \dots \dots (5)$$

consequently represents a circle in the diametral surface, having the same centre as the sun. If the sun be looked upon as a globe, filled with an incompressible liquid, a diametral surface within the sun will have the same linear element as the globe-surface, which touches the described rotation-surface in a parallel-circle with a radius R_a . This radius R_a too may approximately be equalized with the astronomically measured radius of the sun. If the described rotation-surface (4) is rotated in the four-dimensional $xyzu$ space around the yz plane, there arises a curved three-dimensional space with the linear element (1) when θ is the angle of rotation, measured from the yzu space.

We shall now investigate the motion of a compassbody moving in the circle (5) around the sun. For this purpose it is sufficient to find a space, tangent to (1) in (5), and in which the geodesic motion can conveniently be indicated. We now make the tangent line PQ rotate with the parabola. That tangent line describes a cone with the linear element:

$$ds^2 = \frac{dR^2}{\cos^2 \chi} + R^2 d\varphi^2 \dots \dots \dots (6)$$

in which equation χ only depends on the definitely selected point P , and therefore is a constant. With the second rotation there arises from this cone a space with a linear element:

$$ds^2 = \frac{dR^2}{\cos^2 \chi} + R^2 d\theta^2 + R^2 \sin^2 \theta d\varphi^2 \dots \dots \dots (7)$$

in which χ is once more a constant. The linear element of a euclidian space may be expressed (in polar-coordinates) R' , φ' , θ' :

$$ds^2 = dR'^2 + R'^2 d\theta'^2 + R'^2 \sin^2 \theta' d\varphi'^2 \dots \dots \dots (8)$$

and by the substitution:

$$\left. \begin{aligned} R &= R' \cos \chi \\ \varphi &= \frac{\varphi'}{\cos \chi} \\ \theta &= \frac{\theta'}{\cos \chi} \end{aligned} \right\} \dots \dots \dots (9)$$

(7) passes into:

$$ds^2 = dR'^2 + R'^2 d\theta'^2 + R'^2 \sin^2 \frac{\theta'}{\cos \chi} d\varphi'^2 \dots \dots \dots (10)$$

On the curve (5) we have $\cos \theta = 0$. With the exception of quantities of the order χ^4 the tangent space (7) behaves along the curve (5) as the euclidian space (8). Hence we need only trace the movement of the geodesically moving system in (8) along the curve corresponding to (5). As the coordinates φ and θ have obtained a factor $\cos \chi$ according to (9), (8) can be realized by the part of the euclidian space $x y u$ that remains, when a rotation-cone having for axis the y -axis and a top-angle of $2\pi (1 - \cos \chi)$ is taken away. (fig. 2).

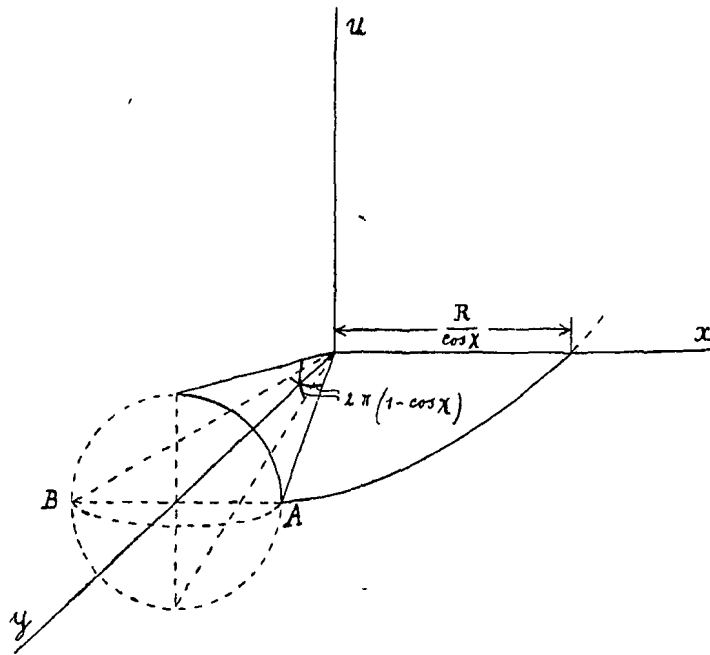


Fig. 2.

The part of the circle :

$$\left. \begin{aligned} x^2 + y^2 &= \frac{R^2}{\cos^2 \chi} \\ u &= 0 \end{aligned} \right\} \dots \dots \dots (11)$$

situated within this space viz. the part extending in fig. 2 from A via a point in the negative part of the y -axis to B , will then correspond with the entire curve (5).

This result may also be obtained by replacing the cone (6) by its unfolded mantle, laid down in the yx plane symmetrically to the y axis, being a sector with an angle $2\pi \cos \chi$. The curve (5) will then coincide with (11). During the revolution about the yz

plane the circle-sector describes the space-section described. By this method it does not at once become obvious that now the obtained euclidian space may indeed replace the originally existent non-euclidian tangent-space along (5). The motion of the compassbody can now be easily traced. In the euclidian space xyu the compassbody always moves parallel to itself. If a constant direction in A in this body has the direction of the radius, then that direction in B forms with the radius an angle $2\pi(1 - \cos \chi)$ situated in a plane // at the xy -plane. Now $\frac{\alpha}{R}$ is very small, hence:

$$\cos \chi = 1 - \frac{\alpha}{2R} \dots \dots \dots (12)$$

so that the total deviation δ in one revolution amounts to:

$$\delta = \pi \frac{\alpha}{R} \dots \dots \dots (13)$$

A compassbody moving around the sun, as its central point, in a circle with a radius equal to the average distance from the earth to the sun will show according to this formula after one revolution a deviation of $0.013''$. If the radius is equal to the average distance from Mercury to the sun, the deviation amounts to $0.0328''$. If the radius is equal to the radius of the sun, the deviation amounts to $2.73''$. If, from another cause, the compassbody already has a revolution around an axis, which is oblique relatively to the plane of the orbit, there will set in, merely on account of the deviation described, a precession-motion, which in the first of the above-mentioned cases would result in a complete revolution of the equinoxes after $\pm 100.000.000$ years. It is noteworthy that the effect described is of the same order as the deviation of a ray, passing the sun at a distance R from the central point. According to EINSTEIN this deviation indeed amounts approximately to $\frac{2a}{R}$.

Whether the deviation computed of the precession motion for the earth will indeed set in, depends on the question to what extent and to what approximation a mass of the quantity and the composition of the earth has the properties of a compassbody. In order to answer this question it is necessary to make definite suppositions as regards the physical qualities of the earth, in particular the mutual attraction of her parts, and starting from these suppositions, to integrate the four-dimensional dynamical equations of motion.

ADDENDUM.

Prof. DE SITTER, to whom I have communicated the above, writes:

A precession of $0''.013$ per annum of course comes well within the reach of observations, since the observed value of the precessional constant is trustworthy to about $0''.0010$. The point is therefore with what accuracy the theoretical value can be computed. Now the lunisolar precession (the planetary precession can be taken as completely known) is given by a formula of the form

$$p_1 = (P + Q\mu).H. \quad (1)$$

where P and Q are known numbers and μ is the mass of the moon (expressed in that of earth + moon as unit) and $H = \frac{C-A}{C}$ depends on the moments of inertia of the earth. The uncertainty of μ causes in p_1 an uncertainty of about $1/2000$ of its amount, thus, if H was exactly known, p_1 would be uncertain to the extent of $\pm 0''.025$ or twice the new precession. A better determination of μ may be expected from the opposition of Eros in 1931¹⁾. However the uncertainty of H is of much greater importance. In 1915²⁾ I have with the aid of the hypothesis of isostasy, derived the ellipticity ϵ of the earth from H , this latter being determined from p_1 by (1). To invert this order it would be necessary, in order to get a p.e. of $\pm 0''.005$ in p_1 , to know ϵ to about $1/20000$ of its amount. The direct determinations of ϵ at present do not go beyond about $1/100$. To increase this accuracy seventyfold would in my opinion be beyond the forces of geodetical science, at least in the near future.

We can determine H with greater accuracy from the constant of nutation, which is given by

$$N = R.\mu.H. \quad (2)$$

where R is again a known number. From (1) and (2) we derive

$$p_1 = \left(S + \frac{T}{\mu}\right).N \quad (3)$$

where S and T are also practically exactly known. The uncertainty of the multiplier owing to the uncertainty of μ is now about $1/4000$ or $1/5000$, and it will probably be reduced to $1/10000$ by the new determination of μ in 1931.

¹⁾ The figure of the earth and some related astronomical constants. The Observatory Aug. 1915, page 322.

²⁾ On Isostasy, the moments of inertia, and the compression of the earth. These Proceedings April 1915, Vol XVII, p. 1291.

The result of NEWCOMB's discussion in 1891 of all available determinations of the constant of nutation has determined its value to about $1/11000$ of its amount. To get a p.e. of $\pm 0''.005$ in p this accuracy must be increased nine- or tenfold. This certainly is no easy task, but it would be preposterous to say that it exceeded the forces of astronomy. It will of course require very refined and prolonged observations and discussions.

I may be allowed to remark that it still remains to be investigated whether the new precession is the only effect of the new gravitational theory, and the equations (1) and (2) are not affected, i.e. whether EINSTEIN's theory gives exactly the same equations for the motion of the axis of rotation of the earth with reference to the geodetically transported system of coordinates, as are found in NEWTON's theory relatively to a "fixed" system. This cannot be asserted without a special investigation, which so far as I know has not been undertaken, and it might even happen that the precession of the geodetically transported system of coordinates was exactly cancelled by a small change in the precession of the earth relatively to that system.

Physiology. — "*Effects of the Rays of Radium on the Oögenesis of Daphnia pulex*". By Miss M. A. VAN HERVERDEN. M. D.
(Communicated by Prof. C. A. PEKELHARING.)

(Communicated in the meeting of Sept. 29, 1918).

For a considerable time I have been prosecuting the effects of radium radiation on a race of *Daphnia pulex* bred in the laboratory, with whose method of reproduction I had become thoroughly acquainted during a study of rather more than 8 years. My original purpose was to evolve, if possible, parthenogenesis in the sexual period, or conversely, to impart to the parthenogenetic females the faculty of producing a sexual offspring. The importance of this experimentation was sufficiently borne in upon me in connection with the view adopted by many researchers that by radiating the organism with radium, enzymic actions are accelerated or diverted. A short or a prolonged radiation with 0,7 mgrs or 3,1 mgrs of radiumbromide, at my disposal, never resulted in any effect upon the sexual or the parthenogenetic stage, whereas after a radiation with a stronger preparation the animals succumb.¹⁾ Nevertheless I considered it a point of importance to continue the experiments, since they throw a peculiar light upon the resistance of the protoplasm in the several phases of the oögenesis and of the embryonic development under the influence of radium rays.

Daphnia pulex affords extremely fit material for such experiments. Besides being fairly transparent and easy to watch under the microscope, it also enables us not only to follow in the living animal the development of the parthenogenetic eggs located in the broodpouch, but also to determine the degree of maturation of the eggs in the ovary. Sometimes the amount of yolk in the maturing eggs enables us to foretell correctly to a few hours, when they will leave the ovary. There is always plenty of material for control, as several young ones can be expected at every parturition. Over and above, the rapid succession of generations grants a comprehensive survey not only of the animals under examination, but also of a large progeny.

¹⁾ Verslag "Koninklijke Akad. v. Wetenschappen" Deel XX p. 20.

In the experiment I placed *Daphnia pulex*, embedded in a drop of ditchwater, immediately on the micaplate of the radium-preparation. In the following descriptions I shall designate the preparations used, containing 0,7 and 3,1 mgrs. of radium-bromide respectively as capsule A and capsule B.

Animals belonging to different age-periods were radiated separately. It immediately appeared that the adult *Daphnia* is much less responsive to the radium rays than the new-born animal. An exposure of 18 hours on capsule A did not affect the animals so as to kill them. If the animal kept alive after this prolonged radiation, it was sometimes seen to succumb later on at the periodical ecdysis of the chitin shell, which was often attended by an abnormal chitin-formation. This then pointed to some injury to the ectoderm. Still, even when the animal remained perfectly healthy, it had become sterile for the rest of its life. In the case of only a few hours radiation without any yolk-rich mature eggs being noticeable in the ovary the reproductive faculty is not interfered with: the eggs leaving the ovary later on develop normally and the young generating from these eggs reach sexual maturity in the regular way and produce a healthy offspring.

However, when radiation takes place, while the ovary bears large yolk-rich eggs, or when the eggs have only just entered the broodpouch, a radiation of 25 minutes on capsule A, or of some minutes on capsule B, will suffice to cause the eggs to develop abnormally, so that they are destroyed already in the blastula-stage and are resorbed in the mother. Susceptibility varies individually, without any apparent connection with the age of the mature females. Whereas the eggs that have only just entered the broodpouch are as susceptible as, or more susceptible than before leaving the ovary (abortus sometimes occurs already after 1½ minutes' sojourn on capsule B), the resisting power of the embryos is seen to increase during the development. Viable young were developed even after a three hours' radiation on capsule A in the gastrula-stage. Yet in these cases the brood did not seem to be always in good condition, since one of the young emerging from such a radiated gastrula — the only one of this lot that reached sexual maturity — produced a brood of an anomalous morphological structure. It appears then, that the future germ-cells of the gastrula in this case must have been injured already during the radiation.

A greater resisting power is displayed by the almost viable young, as they can stand a 20 hours' radiation on capsule A, without any prejudice to their future fecundity. If, however, these young ones

leave the brood-pouch during the radiation, they invariably perish, every one of them; a sojourn on capsule *A* of a couple of hours only will kill them. After an hour's radiation the cardiac action is weakened and irregular and they die soon after. In the brood-pouch they are presumably walled off by the chitin shell of the mother and by the fluid in which they are swimming, which protection, however, is not sufficient for the young embryos, which are so much more susceptible to the radium rays.

A short radiation of a female with maturing egg-cells in the ovary, leads indeed to destruction of the eggs; but it leaves the mother unhurt. Afterwards it even causes sometimes a more numerous offspring, which phenomenon is analogous to that seen in the action of various poisons on *Daphnia pulex*¹⁾, on which a small dosage of the poison acts as a stimulus. The resistance of eggs from one and the same lot sometimes differs very much, as among the eggs that are being destroyed occasionally a single normal young may be seen that does not appear to have suffered at all from the noxious influences that threatened it before the embryonic stage, and later on may possibly possess a normal faculty of reproduction. An anomaly in the structure of such a young occurs only rarely. It cannot be said to be typical for radium-radiation. Generally these monstra (with abnormal profile or defective intestine) are few and far between. As a rule, therefore, radiation yields a normal embryonic development or none at all. This is the reason why I never succeeded yet in breeding mutations of *Daphnia pulex* by radiation with radium, as MORGAN achieved on a large scale with the *Drosophila* fly. The few abnormal specimens never reached maturity, one excepted, which recovered completely and produced a normal offspring that was still healthy after four months. Indeed my eight years' experience with *Daphnia pulex* have convinced me that this race though highly modifiable, shows only slight mutability.

Other researches in experimental embryology also show that eggs from the same lot vary as to their resisting power to noxious effects. I here call attention to the researches of PEARL²⁾ on the difference in degree of resistance evinced by embryos of the domestic fowl to intoxication with alcohol, in which case also the eggs, liable to reach full development bring forth normal chickens.

It might be objected that in the radiation experiments the eggs are differently exposed. This may occur with a numerous brood, in which the inner eggs are shielded from the noxious rays by the

¹⁾ l.c. p. 1.

²⁾ Proceedings of the National Acad. of sciences. U. S. A., Vol. II, p. 380.

external eggs. But the exposure will presumably be the same for the *Daphnia* moving about freely in the waterdrop on the radium capsule, when, as in our case, there are only 4 or 5 eggs located in the brood-pouch.

What is the cause of this unequal resistance of the *Daphnia* eggs? A reduction-division of the chromosomes, which might be responsible for the unequal distribution of paternal and maternal hereditary units does not occur in this parthenogenetic development; the egg retains the number of chromosomes of the mother. A similar difference in the reaction of the eggs to the noxious influences I previously detected, when treating the *Daphniae* with phenyl-urethan ¹⁾.

Whereas with a short radiation of a female with mature egg-cells only the first brood succumbs, and the succeeding broods are normal (even very abundant), with a longer radiation also the eggs in a younger stage of development are seen to be damaged, until ultimately the *Daphnia* becomes completely sterile. After one single radiation a *Daphnia* may, after many abortus, produce quite unexpectedly normal young again, if namely the younger oögonia are not damaged. Such an after-effect I observed up to the 6th of January 1917 of a radiation for some hours on capsule A on the 23^d of November 1916. After the first date again young were born that were completely normal.

My experience that eggs of *Daphnia pulex* in the last stage of maturation are most susceptible to radium rays, and that only after a prolonged radiation also the younger egg-cells and at last the oögonia are injured, accounts for PACKARD's ²⁾ experience that after radiation of the *Drosophila* larvae, the young flies become sterile for some weeks, and afterwards become fertile again. If we bear in mind that results with mammals also favour the theory that especially the mature egg-cells are very susceptible, we are justified in presuming that this holds for the whole animal kingdom.

How to account for the fact that the maturing eggs are more susceptible to the radium rays than the immature and the remaining cells of embryonic and maternal organism? Again, what molecular transformations occur in the protoplasm under the influence of radium radiation? The view adopted by several researchers that enzymic actions are accelerated or diverted, prompted me to compare the embryonic development of radiated and non-radiated sisters, which as to temperature and diet had been bred under the same conditions.

¹⁾ *l.c.* page 1.

²⁾ Journal of exp. Zoology. XIX, p. 332.

Up to the moment the eggs left the ovary these sisters were kept in the same culture glass, animals being selected for this experiment whose eggs entered the brood-pouch in the same hour. As soon as the eggs began to develop one *Daphnia* was radiated for fifteen minutes on capsule A.

After this the conditions were made equal for either animal. In case a normal brood was developed after this radiation, embryogeny was neither retarded, nor accelerated. At the same hour the heart's pulsation became visible in the brood of the two animals; at the same time the development of the limbs commenced and the first eye-pigment developed itself; in the same hour the young left the parental organism. A similar observation was made at a second radiation. If only the radium action does not pass the physiological boundary there is neither acceleration nor retardation of development.

Is it the alpha-, the beta-, or the gamma-rays to which the egg-cells of the *Daphnia* are particularly responsive. In radiating on the capsule with radium-bromide the alpha-rays are screened out by the mica-plate of the capsule, which they cannot penetrate and consequently they do not reach the animal. When separating the *Daphnia* from the radium-preparation by a leaden platelet of 3 m.m. thickness, the beta-rays do not reach the *Daphnia*, while the secondary beta-rays are allowed to resorb through a mica-platelet of 50 μ thickness on which the *Daphnia* is placed. In this way *Daphniae* with maturing eggs in the ovary could stand a radiation with the gamma-rays from 0,7 mgrs. of radium-bromide for 24 hours, without abortus, which proves the harmlessness of the gamma-rays. When applying the radiumpreparation of 3,1 mgr., which, as has been seen, will destroy the eggs within a few minutes, a radiation of 24 hours with the exclusion of the beta-rays, could be borne without deleterious influences. In a few of the latter experiments, however, the first brood is aborted. It is, therefore, possible that to a stronger concentration of the gamma-rays (not obtainable with these preparations) the *Daphnia* egg-cells prove to be sensitive, a sensitivity, however, that is not to be compared with that to the beta-rays.

The antagonistic action between uranium and radium, demonstrated by ZWAARDEMAKER¹⁾ for the frog's heart, induced me to radiate *Daphnia pulex* in a drop of uranyl nitrate and to determine whether resorption of the eggs stayed away in this process. A concentration of 600 mgrs. of uranyl nitrate pro L. is tolerated for some hours without inhibiting the development of the brood; with

¹⁾ These Proc. XIX p. 1043.

a higher concentration the *Daphnia* itself succumbs in less time. When a *Daphnia* with maturing eggs in the ovary is placed in a solution of 500 mgrms of uranyl nitrate pro I. and after half an hour again in a drop of the same fluid on the radium capsule of 3,1 mgrs, the radiation may be continued for $\frac{1}{2}$ to 4 hours in a series of experiments without causing the brood to abort, while, under the same circumstances, the eggs, when placed in water, are fatally injured already after some minutes. Sometimes, however, the protecting influence of uranyl nitrate was not at all discernible. Up to the present I have not been in a position to account for these various results. This also applies to the lower concentration of uranyl nitrate.

More than fifty *Daphniae* were examined in microscopic sections and compared with non-radiated specimens. *Normal* maturation of eggs in *Daphniae* has already been described by KÜHN¹⁾. Broadly speaking my findings for the normal eggs are in agreement with his. A prolonged radiation did not enable me to detect in the maturing eggs any change either in the chromosomes, or in the nuclear body, or in the egg-plasma. Only in one polar spindle (for the formation of the first polar body) was the number of chromatin rods larger than could be anticipated with twice the number of chromosomes. Any possible alteration in the shape of the chromosomes is difficult to detect owing to the small dimensions.

Not before the blastula-stage, that is about the time when also in the living animal under the low-power microscope the embryos are seen to succumb, well-marked alterations take place in the nuclei, characterised by a collapse of the chromatin into coarse granules. The injury to the eggs, however, has been done long before the aided eye can detect it.

Though microscopic examination did not put us in a position to ascertain whether the noxious action of radium-rays has initially affected the nucleus, the cell-plasma or both, the high degree of susceptibility of the egg in a period when also considerable evolutions take place in the nucleus (formation of the polar spindle and decomposition of the large nuclear body) is indicative of a noxious effect of the beta-rays, especially on the nucleus. The fact that the first cleavage proceeds regularly and only at the close of it degeneration manifests itself, may be explained, when we call to mind BOVERI's²⁾ investigations, which demonstrated that with the Sea-

¹⁾ Arch. f. Zellforschung, Vol. I, p. 538.

²⁾ Jenaische Zeitschr. Vol. 43, 1907.

urchin it is only at the close of the blastula-stage that the various properties of the chromosomes manifest themselves.

The period of maturation, in which the egg is so extremely susceptible to the radium rays, also proves to be the critical period for a poison as phenylurethan in a certain concentration, as discussed by me in an earlier paper ¹⁾.

Just as some eggs of the brood sometimes escape death after radiation with radium, and develop into perfectly normal young, a *Daphnia* was occasionally developed after treatment with $\frac{1}{12000}$ n phenylurethan.

When transmitted to water it produced a normal offspring. This again proves that the resisting power of the eggs to the danger, threatening them from the outer world, was occasionally very different, even with these parthenogenetic animals. But if they succumb in the struggle, the method of reaction in the two series of experiments is widely different. Whereas with a treatment with radium radiation this reaction leads irrevocably to degeneration at the close of the blastula-period, a treatment with phenylurethan evolves fully developed monstra, in consequence of a deleterious influence, exerted in the same period of susceptibility. These monstra, however, are not viable after birth; they are not resorbed, but are expelled from the parental organism.

Summary.

The egg-cells of *Daphnia-pulex* are most susceptible to radium radiation in the last stage of maturation. The resisting power increases in the embryonic stage.

In one and the same brood individual differences of susceptibility to the rays of radium is frequently noted. The egg that resists the deleterious influence often develops into a perfectly normal animal, which itself becomes fertile. The rare samples with morphological abnormalities seldom become adults. Only once did we succeed in breeding from such an abnormal young a stock without morphological anomalies.

A long-continued radiation from 0,7 mgrs of radium-bromide does not endanger the life of the sexually mature *Daphnia*, but only its fertility. It depends on the duration of radiation whether only the maturing eggs, the oöcytes, or also the oögonia are injured. Large progenies being easy of observation afford an opportunity to study this in every special case.

¹⁾ L. c. p. 1.

Prior to maturity *Daphniae* resist radium radiation for a long time. Only after a sojourn of many hours on the capsule with 0,7 mgrs of radium bromide the future ripening of the oögonia is also endangered.

A microscopic examination of the ovary and the embryos reveals that the deleterious effect of radium manifests itself only towards the close of the blastula-stage by an abnormal behaviour of the chromatin, also when the egg-cells were affected when lying still in the ovary.

If the beta-rays are eliminated through filtration the deleterious effect of radium is arrested or highly diminished, which proves the beta-rays to be mainly responsible for the destruction of the eggs.

Physiology. — “*The conduct of the kidneys towards some isomeric sugars (Glucose, Fructose, Galactose, Mannose and Saccharose, Maltose, Lactose).*” By Prof. H. J. HAMBURGER and Dr. R. BRINKMAN.

(Communicated in the meeting of September 28, 1918).

It has been proved by former researches¹⁾, that the glomerulus epithelium of the kidney of the frog is able to hold back glucose if the solution which is passed through the vascular system has a suitable composition. If one passes through the arteria renalis of the frog the following Ringer's solution: NaCl 0,7 %, KCl 0,01 %, CaCl₂ 0,0075 %, NaHCO₃ 0,02 %, in which 0,1 % glucose has been dissolved, then an artificial urine is excreted containing 0,07 % glucose; 0,03 % glucose has thus been retained by the glomerulus epithelium. If however the Ringer's solution contains 0,285 %, i.e. a quantity that corresponds to the titrational alkalinity of the serum of the frog, then much more sugar than 0,03 % is held back and not seldom the urine is free from sugar.

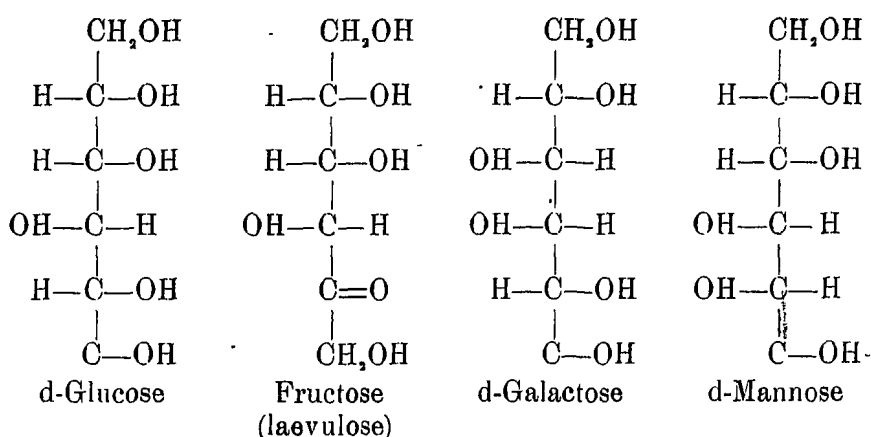
This phenomenon proves that the glomerus membrane, which is permeable to salts, is under physiological conditions impermeable to the also crystalline glucose.

In order to come to an explanation of this remarkable and useful contrast it seemed interesting to investigate how the glomerulus membrane would behave towards laevulose, galactose and mannose, all isomeric to glucose, and also towards the mutually isomeric saccharose, lactose and mannose.

Let us begin with the four first-named.

As is well known, the structural formula of the monosaccharides (C₆H₁₂O₆) can be represented in the following way:

¹⁾ HAMBURGER and BRINKMAN: Proceedings of the Royal Acad. of Sciences Section of Jan. 27, and Sept. 29, 1917. Also: Biochem. Zeitschr. 88, 97, 1918.



The experiments were made in exactly the same way as was described in the articles cited above. The perfusion liquid was of the following composition: NaCl 0,5 %, NaHCO₃ 0,285 %, KCl 0,01 %, CaCl₂ 0,2 %. This solution was prepared by mixing

50 ccm. NaCl 10 %,
50 ccm. NaHCO₃ 5,7 %,
10 ccm. KCl 1 % and
40 ccm. CaCl₂ 5 %

and adding boiled distilled water up to 1 Liter. Certain quantities of the sugars¹⁾ were dissolved in this solution, but still the reductive capability was estimated before each experiment. This was done in view of the possible errors in weighing or unknown differences in the amount of water contained in the sugars. BANG's method (1916) was used for estimating the reductive capability of the perfusion liquid as well as that of the urine excreted. The reductive power of the various sugars was *expressed in the percentage of glucose contained*.

As is well known the final titration is an estimation of Iodine with the aid of amyllum; the amount of glucose contained is then computed from the quantity of Iodine necessary, by means of the formula $(a-0,12) : 4$, in which "a" is the number of c.c. solution of Iodine used.

A. Laevulose (Fructose).

Experiment 1 (July 11, 1918)

The perfusion liquid contains 0,1 % laevulose.

The reduction, expressed in glucose, amounts to 0,21 %.

0,1 ccm. urine from the right kidney needs 0,87 ccm. Iodine solution, which

corresponds to $\frac{0,87-0,12}{4} = 0,0875\%$ glucose.

¹⁾ We are indebted to Jhr. W. ALBERDA VAN EKENSTEIN, Director of the laboratory of the ministry of Finance and by Prof. H. J. BACKER, for several of the sugars.

0,1 ccm. urine from the left kidney needs 0,88 ccm. Iodine solution which corresponds to $\frac{0,88-0,12}{4} = 0,19\%$ glucose.

Retained by the right kidney $0,21-0,1875 = 0,0225\%$.

Retained by the left kidney $0,21-0,19 = 0,02\%$.

These quantities are so small that one may say that practically all the laevulose is allowed to pass by the glomerulus epithelium. The following experiments affirm this result.

Experiment 2 (July 12).

The same solution as used in experiment 1.

Reduction (0,1 c.c.) urine of right kidney $0,2125\%$.

Reduction (0,1 c.c.) urine of left kidney $0,215\%$.

Retained by right kidney $0,21-0,2125 = 0$.

Retained by left kidney $0,21-0,215 = 0$.

Result: *No* laevulose retained by the glomerulus epithelium.

Experiment 3 (July 13).

Experiments 1 and 2 were repeated with fresh solution.

Reduction 0,1 c.c. of solution passed $0,18\%$.

Reduction 0,1 c.c. urine of right kidney $0,18\%$.

Reduction 0,1 c.c. urine of left kidney $0,18\%$.

Result: *No* laevulose retained.

Experiment 4 (July 14).

The same solution passed as in experiment 3.

Reduction 0,1 c.c. urine of right kidney $0,1825\%$.

Reduction 0,1 c.c. urine of left kidney $0,1825\%$.

Result: *No* laevulose retained.

It has probably not escaped attention that the laevulose solution used above causes about twice as strong a reduction as a glucose solution of 0.1% viz. 0.18% on an average. Where it could be possible that a solution with a so much larger reductive capability could, just in connection with that fact, be allowed to pass by the glomerulus epithelium, we experimented with a solution in which there was 0.05% laevulose instead of 0.1% .

Experiment 5 (July 15).

RINGER's solution in which $0,05\%$ laevulose has been dissolved.

Reduction 0,1 c.c. of perfusion liquid $0,095\%$.

0,1 c.c. urine of right kidney: 0,5 c.c. Iodine solution; reduction $0,095\%$.

0,1 c.c. urine of left kidney: 0,52 c.c. Iodine solution; reduction $0,1\%$.

0,1 c.c. urine of right kidney: 0,52 c.c. Iodine solution; reduction $0,1\%$.

Retained by right kidney $0,095-0,095 = 0$.

Retained by left kidney $0,095-0,1 = 0$.

Retained by right kidney $0,095-0,1 = 0$.

Result: The diluted laevulose solution also passes completely through the glomerulus epithelium.

It seemed interesting to investigate whether laevulose could influence the retention of glucose.

In order to ascertain whether the circumstances, as regards the manner in which we had formerly worked with glucose, had indeed remained unaltered, several experiments were made with glucose alone.

B. Glucose and a mixture of Glucose and Laevulose.

Experiment 6. (July 18).

Perfusion liquid in which there was 0,1% glucose.

0,1 c.c. of solution, reduction 0,0975%.

0,1 c.c. urine of right kidney: 0,3 c.c. Iodine solution; reduction 0,045%.

0,1 c.c. urine of left kidney: 0,31 c.c. Iodine solution; reduction 0,0475%.

Retained by right kidney: $0,0975 - 0,045 = 0,0525\%$

Retained by left kidney: $0,0975 - 0,0475 = 0,05\%$.

Experiment 7 (July 18).

The same perfusion liquid as in experiment 6.

0,1 c.c. urine of right kidney: 0,26 c.c. Iodine solution; reduction 0,035%.

0,1 c.c. urine of left kidney: 0,29 c.c. Iodine solution; reduction 0,0425%.

Retained by right kidney: $0,0975 - 0,035 = 0,0625\%$.

Retained by left kidney: $0,0975 - 0,0425 = 0,0550\%$.

Experiment 8 (July 20).

Perfusion liquid contains 0,07% glucose.

Reduction by 0,1 c.c. of solution passed 0,065%

0,1 c.c. urine of right kidney: 0,22 c.c. Iodine solution; reduction 0,025%

0,1 c.c. urine of left kidney: 0,22 c.c. Iodine solution; reduction 0,025%.

Retained by each kidney: $0,065 - 0,025 = 0,04\%$.

Experiment 9 (Sept 20).

At the same time an experiment was made in which the perfusion liquid contained 0,2% glucose.

Reduction 0,1 c.c. of this solution 0,22%.

Reduction by 0,1 c.c. urine of right kidney 0,095%.

Reduction by 0,1 c.c. urine of left kidney 0,1125%.

Retained by right kidney: $0,22 - 0,095 = 0,1250\%$.

Retained by left kidney: $0,22 - 0,1125 = 0,1075\%$.

From these experiments it follows that now, as formerly, a quantity of glucose is retained, which is physiologically present in the blood of the frog. A remarkable contrast thus exists between the permeability of the kidney to glucose and to laevulose.

With this marked difference it appeared to be of importance to ascertain whether laevulose was perhaps capable of altering the permeability to glucose.

Both these substances were therefore dissolved in the perfusion liquid.

Experiment 10 (Sept. 20).

The perfusion liquid contains 0,1% glucose and 0,05% laevulose.

Reduction 0,1 c.c. of solution passed 0,205%.

0,1 c.c. urine of right kidney: 0,58 c.c. Iodine solution; reduction 0,1175%.

0,1 c.c. urine of left kidney: 0,60 c.c. Iodine solution: reduction 0,12%.

Retained by right kidney: $0,205 - 0,1175 = 0,0875\%$.

Retained by left kidney: $0,205 - 0,12 = 0,085\%$.

Experiment 11 (Sept. 20).

The same perfusion liquid as in experiment 9.

Reduction 0,1 c.c. urine of right kidney 0,155%.

Reduction 0,1 c.c. urine of left kidney 0,1575%.

Retained by right kidney: $0,205 - 0,155 = 0,05\%$.

Retained by left kidney: $0,205 - 0,1575 = 0,0475\%$.

Experiment 12 (Sept. 20).

The perfusion liquid contains a mixture of glucose and laevulose

Reduction of solution passed 0,205%.

Reduction 0,1 c.c. urine of right kidney 0,115%.

Reduction 0,1 c.c. urine of left kidney 0,12%.

Retained by right kidney: $0,205 - 0,115 = 0,09\%$.

Retained by left kidney: $0,205 - 0,12 = 0,085\%$.

Experiment 13 (Sept. 21).

The perfusion liquid contains 0,07% glucose and 0,05% laevulose.

Reduction 0,1 c.c. of this solution 0,175% (average of 3 homonymous experiments).

0,1 c.c. urine of right kidney: 0,63 c.c. Iodine solution; reduction 0,1275%.

0,1 c.c. urine of right kidney: 0,62 c.c. Iodine solution; reduction 0,125%.

0,1 c.c. urine of left kidney: 0,65 c.c. Iodine solution; reduction 0,1325%.

Retained by right kidney: $0,175 - 0,1275 = 0,0475\%$.

Retained by right kidney: $0,175 - 0,125 = 0,05\%$.

Retained by left kidney: $0,175 - 0,1325 = 0,0425\%$.

Experiment 14 (Sept. 21)

The same perfusion liquid as in experiment 13.

0,1 c.c. urine of right kidney: 0,64 c.c. Iodine solution; reduction 0,13%.

0,1 c.c. urine of left kidney: 0,64 c.c. Iodine solution; reduction 0,1275%.

Retained by right kidney: $0,175 - 0,13 = 0,045\%$.

Retained by left kidney: $0,175 - 0,1275 = 0,0475\%$.

It is apparent from these experiments that the glomerulus epithelium which, as we have seen, is completely permeable to laevulose, has held back a quantity of glucose, which was also retained when the solution perfused contained glucose alone. The laevulose while passing itself does not or hardly influence the retention of glucose. With a little exaggeration one might say that *the kidney separates the glucose from the laevulose by means of filtration.*

C. Galactose.

Experiment 15 (July 18).

The perfusion liquid contains 0,09% galactose.

Reduction (0,1 c.c.) of solution passed 0,07%.

0,1 c.c. urine of right kidney: 0,35 c.c. Iodine solution; reduction 0,055%.

0,1 c.c. urine of left kidney: 0,33 c.c. Iodine solution; reduction 0,052%.

Retained by right kidney: $0,07 - 0,055 = 0,015\%$.

Retained by left kidney: $0,07 - 0,052 = 0,018\%$.

Experiment 16 (Aug. 22).

The perfusion liquid contains 0,1% galactose.

Reduction 0,1 c.c. of solution passed 0,07%.

0,1 c.c. urine of right kidney: 0,3 c.c. Iodine solution: reduction 0,045%.

0,1 c.c. urine of left kidney: 0,28 c.c. Iodine solution; reduction 0,04%.

Retained by right kidney: $0,07 - 0,045 = 0,025\%$.

Retained by left kidney: $0,07 - 0,04 = 0,03\%$.

Experiment 17 (Aug. 23).

Reduction 0,1 c.c. of perfusion liquid 0,055%.

0,1 c.c. urine of right kidney: 0,25 c.c. Iodine solution; reduction 0,0325%.

0,1 c.c. urine of left kidney: 0,15 c.c. Iodine solution; reduction 0,0325%.

Retained by each kidney $0,055 - 0,0325 = 0,0225\%$.

Experiment 18 (Aug. 23).

The same perfusion liquid as in experiment 17.

0,1 c.c. urine of right kidney: 0,25 c.c. Iodine solution; reduction 0,0325%.

0,1 c.c. urine of left kidney: 0,25 c.c. Iodine solution; reduction 0,0325%.

Retained by each kidney: $0,055 - 0,0325 = 0,0225\%$.

All these experiments show that the kidney retains a slight quantity of galactose.

We shall now record a few experiments with a perfusion liquid the reduction of which approximately agrees with that of 0.1% glucose.

Experiment 19 (Aug. 23).

The perfusion liquid contains 0,15% galactose.

Reduction 0,1 c.c. of perfusion liquid 0,0975%.

0,1 c.c. urine of right kidney: 0,4 c.c. Iodine solution; reduction 0,07%.

0,1 c.c. urine of left kidney: 0,4 c.c. Iodine solution: reduction 0,07%.

Retained by each kidney: $0,0975 - 0,07 = 0,0275\%$.

Experiment 20 (Aug. 23).

The same perfusion liquid as in experiment 19.

0,1 c.c. urine of right kidney: 0,33 c.c. Iodine solution; reduction 0,0525%.

0,1 c.c. urine of left kidney: 0,32 c.c. Iodine solution; reduction 0,05%.

Retained by right kidney: $0,0975 - 0,0525 = 0,045\%$.

Retained by left kidney: $0,0975 - 0,05 = 0,0475\%$.

Here again it becomes clear that some galactose is retained. In the last experiment (20) the quantity is even comparatively large.

That galactose is retained is efficient in the same way as is the case with glucose. While glucose is a source of energy for muscular contraction; *galactose helps in the formation of the cerebrosides.*

As has been remarked earlier, frogs often present not inconsiderable differences in their capacity for retaining glucose. The time of year also has some influence. Therefore experiments were again made with frogs that had lived under the same circumstances as those of the experiments described above.

Experiment 21 (Aug. 24).

The perfusion liquid contains 0,1% glucose.

Reduction 0,1 c.c. of perfusion liquid 0,10%.

0,1 c.c. urine of right kidney: 0,24 c.c. Iodine solution; reduction 0,03%.

0,1 c.c. urine of left kidney: 0,22 c.c. Iodine solution; reduction 0,025%.

Retained by right kidney: $0,10 - 0,03 = 0,07\%$.

Retained by left kidney: $0,10 - 0,025 = 0,075\%$.

Experiment 22 (Aug. 24).

The same perfusion liquid as in experiment 21.

0,1 c.c. urine of right kidney: 0,25 c.c. Iodine solution; reduction 0,0325%.

0,1 c.c. urine of left kidney: 0,22 c.c. Iodine solution; reduction 0,025%.

Retained by right kidney: $0,10 - 0,0325 = 0,0675\%$.

Retained by left kidney: $0,10 - 0,025 = 0,075\%$.

It is clear that these frogs, which were placed in the same circumstances as those of experiments 16—20, retained a much larger quantity of glucose than of galactose.

It now seemed desirable to investigate whether the retention of galactose although this occurred in a much smaller degree than was the case with glucose, was governed by the same conditions as regards the composition of the Ringer-solution, as had formerly been found to apply to glucose. For this reason the following Ringer's solution was used: NaCl 0,7%, **NaHCO₃** 0,02%, KCl 0,01%, CaCl₂ 0,0075%. With the application of this solution glucose was at the time retained to a maximum of 0,03%. Only when the quantity of NaHCO₃ was increased above 0,09% on account of which the urine was no longer acid, there could be retained much more sugar; the urine could then even be free from sugar.

What would now be the result with galactose if the Ringer's solution also in this case contained 0,02% NaHCO₃ only?

Experiment 23 (Sept. 14).

The perfusion liquid with only 0,02% NaHCO₃ contains 0,1% galactose.

Reduction of 0,1 c.c. of perfusion liquid 0,08%.

0,1 cc. urine of right kidney: 0,42 c.c. Iodine solution; reduction 0,075%.

0,1 c.c. urine of left kidney: 0,43 c.c. Iodine solution; reduction 0,0775%.

Retained by right kidney: $0,08 - 0,075 = 0,005\%$.

Retained by left kidney: $0,08 - 0,0775 = 0,0025\%$.

Experiment 24 (Sept. 14).

The same perfusion liquid as in experiment 23.

0,1 c.c. urine of right kidney: 0,43 c.c. Iodine solution; reduction 0,0775‰.

0,1 c.c. urine of left kidney: 0,44 c.c. Iodine solution; reduction 0,08‰.

Retained by right kidney: $0,08 - 0,0775 = 0,0025‰$

Retained by left kidney: $0,08 - 0,08 = 0$.

We see thus that with galactose as well as with glucose, the quantity of NaHCO_3 in the perfusion liquid is of great importance for the permeability of the glomerulus epithelium. A solution containing a small quantity of NaHCO_3 causes galactose to pass in toto; if the perfusion liquid contains a physiological quantity of NaHCO_3 (0,285 ‰) then on an average 0.025 ‰ galactose is retained. We say on an average, as frogs present individual differences.

Here follows a table which gives a summary of a series of other experiments with galactose in which however the quantity of NaHCO_3 was, accidentally, 0.2 ‰ instead of 0.285 ‰. As had also formerly been found with glucose such a modification was of very little importance.

Retention capability of kidney for galactose.

Reduction perfusion liquid, containing \pm 0.1 ‰ galactose	Reduction urine of right kidney	Retained by right kidney	Reduction urine of left kidney	Retained by left kidney
0.0825 ‰	A $\begin{matrix} 0.05 \\ 0.0475 \end{matrix} \} 0.049$	0.033 ‰	A $\begin{matrix} 0.0525 \\ 0.0475 \end{matrix} \} 0.050$	0.0325 ‰
	B $\begin{matrix} 0.0775 \\ 0.08 \end{matrix} \} 0.078$	0.038 "	B $\begin{matrix} 0.0825 \\ 0.0825 \end{matrix} \} 0.0825$	0 "
	C $\begin{matrix} 0.0675 \\ 0.065 \end{matrix} \} 0.0663$	0.0163 "	C $\begin{matrix} 0.0675 \\ 0.0675 \end{matrix} \} 0.0675$	0.015 "
0.0725 "	D 0.05	0.0225 "	D 0.0525	0.02 "
	E 0.045	0.0275 "	E 0.048	0.0245 "
	F 0.047	0.0250 "	F 0.045	0.0275 "

When we make a study of this table it becomes clear;

1. that there is a difference in the power for retaining galactose in the various frogs A, B, C, D, E, and F.

2. that the individual differences range between 0 and 0,033‰.

3. that the power of retention is more or less the same for the right and the left kidney of the same frog.

Here again as in the former experiments it is clear that galactose

does not, like *brevulose*, pass through the kidney altogether, but is generally retained to a slight degree.

This indicates in any case that galactose is used in the body. We know indeed that lactose is built up from dextrose and galactose and an article of ELSE HIRSCHBERG ¹⁾ from WINTERSTEIN's laboratory has just appeared in which a certain affinity, that is wanting in *laevulose*, becomes clear between glucose and galactose in connection with the spinal cord.

We repeat, that the amount of galactose retained is in all the experiments expressed in the percentage of glucose. This is also the case with other sugars.

D. Mannose.

Experiment 25 (Aug. 20).

In the suitable perfusion liquid consisting of NaCl 0,5%, NaHCO₃ 0,285%, KCl 0,01% and CaCl₂ 0,02%, 0,1% mannose is dissolved.

0,1 c.c. perfusion liquid: 0,45 c.c. Iodine solution; reduction 0,0825%.

0,1 c.c. urine of right kidney: 0,48 c.c. Iodine solution; reduction 0,09%.

0,1 c.c. urine of left kidney: 0,46 c.c. Iodine solution; reduction 0,085%.

Retained by right kidney: $0,0825 - 0,09 = 0$.

Retained by left kidney: $0,0825 - 0,085 = 0$.

Experiment 26 (Aug. 20).

The same perfusion liquid as in exp. 25.

0,1 c.c. urine of right kidney: 0,45 c.c. Iodine solution; reduction 0,0825%.

0,1 c.c. urine of left kidney: 0,44 c.c. Iodine solution; reduction 0,08%.

Retained by right kidney: $0,0825 - 0,0825 = 0$.

Retained by left kidney: $0,0825 - 0,08 = 0,0025\%$.

Thus also in this experiment no mannose was retained.

Experiment 27 (Aug. 21).

0,1 c.c. perfusion liquid: 0,35 c.c. Iodine solution; reduction 0,0575%.

0,1 c.c. urine of right kidney: 0,37 c.c. Iodine solution; reduction 0,0625%.

0,1 c.c. urine of left kidney: 0,35 c.c. Iodine solution; reduction 0,0575%.

0,1 c.c. urine of right kidney: 0,35 c.c. Iodine solution; reduction 0,0575%.

In this exp. also no mannose is retained.

Experiment 28 (Aug. 21).

The same perfusion liquid as in exp. 27.

0,1 c.c. urine of right kidney: 0,36 c.c. Iodine solution; reduction 0,06%.

0,1 c.c. urine of left kidney: 0,36 c.c. Iodine solution; reduction 0,06%.

Retained by each kidney: $0,0575 - 0,06 = 0$.

In this experiment the Kidneys have also passed all the mannose.

From these experiments we may draw the conclusion that the glomerulus epithelium is totally permeable to mannose.

We shall now report some experiments made with mutually isomeric disaccharides: saccharose, maltose and lactose.

¹⁾ ELSE HIRSCHBERG. Zeitschr. f. physiol. Chemie, 100, (1918).

These experiments seemed of importance because, amongst other reasons, their molecules are larger than those of the monosaccharides already considered. If the permeability was in connection with this size it would probably appear that the glomerulus epithelium was impermeable to the disaccharides.

E. Saccharose.

To estimate the quantity of saccharose in the perfusion liquid and in the urine, 0.1 cc. of the liquid was heated to 37° C. during 1½ hours with 0.15 cc. hydrochloric acid 1:1 and the reduction of the solution thus obtained determined.

Experiment 29 (July 17).

The perfusion liquid contains 0.1% cane sugar.

After inversion it causes a reduction of 0.1275%.

0.1 c.c. urine of right kidney after inversion causes 0.13% reduction.

0.1 c.c. urine of left kidney after inversion causes 0.1325% reduction.

Retained by right kidney: $0.1275 - 0.13 = 0$.

Retained by left kidney: $0.1275 - 0.1325 = 0$

Result: all the cane sugar has passed through.

Experiment 30 (July 17).

The same perfusion liquid as in exp. 29.

Reduction 0.1 c.c. urine of right kidney after inversion 0.1125%.

Reduction 0.1 c.c. urine of left kidney after inversion 0.095%.

Retained by right kidney: $0.1275 - 0.1125 = 0.015\%$.

Retained by left kidney: $0.1275 - 0.095 = 0.032\%$.

Here follows a table in which several experiments are summarised.

There can be no doubt that the glomerulus epithelium has retained saccharose, either as such or in the form of glucose which has then been formed through the splitting of saccharose in the glomerulus epithelium, while the laevulose has passed into the urine. This latter alternative is of no great probability.

F. Maltose.

Experiment 35 (July 16).

In the suitable perfusion liquid with 0.285% NaHCO_3 , 0.15% maltose is dissolved.

0.1 c.c. perfusion liquid: reduction 0.0825%.

0.1 c.c. urine of right kidney: reduction 0.07%.

0.1 c.c. urine of left kidney: reduction 0.07%.

Retained by each kidney: $0.0825 - 0.07 = 0.0125\%$, thus hardly any at all.

Experiment 36 (July 16).

The same perfusion liquid as in exp. 35.

0.1 c.c. urine of right kidney: reduction 0.0875%.

0.1 c.c. urine of left kidney: reduction 0.0625%.

Retained by right kidney: $0.0825 - 0.0675 = 0.015\%$.

Retained by left kidney: $0.0825 - 0.0625 = 0.02\%$.

Retention capability of kidney for saccharose.
Experiments of September 17—23 1918.

Reduction perfusion liquid containing $\pm 0.1\%$ saccharose		Reduction urine of right kidney		Retained by right kidney	Reduction urine of left kidney		Retained by left kidney
Previous to inversion	after inversion	Previous to inversion	after inversion		Previous to inversion	after inversion	
Frog A 0.01 %	0.13 %	0.0325 %	0.09 %	0.043 %	0.025 %	0.0825 %	0.0475 %
" B "			0.08	0.05		0.0775	0.0525
Frog A 0.015	0.125	0.02	0.0925	0.0325	0.02	0.0925	0.0325
" B "		0.04	0.0925	0.0325	0.03	0.0925	0.0325
Frog A 0.025	0.14	0.03	0.1025	0.0325	0.03	0.10	0.04
" B "	"		0.0875	0.0525		0.0825	0.0575
" C "	"		0.09	0.05		—	—

Experiment 37 (Sept. 26).

The perfusion liquid contains 0.15% maltose.
0.1 c.c. perfusion liquid: reduction 0.095%.
0.1 c.c. urine of right kidney: reduction 0.105%.
0.1 c.c. urine of left kidney: reduction 0.11%.
Retained by each kidney: *nothing*.

Experiment 38 (Sept. 26).

The same perfusion liquid as in exp. 37.
0.1 c.c. urine of right kidney: reduction 0.1%.
0.1 c.c. urine of left kidney: reduction 0.105%.
Retained by each kidney: *nothing*.

Experiment 39 (Sept. 26).

The same perfusion liquid as in exps. 37 and 38.
0.1 c.c. urine of right kidney: reduction 0.0625%.
0.1 c.c. urine of left kidney: reduction 0.0625%
Retained by each kidney: 0.095—0.0625 = **0.0325%**.

Experiment 40 (Sept. 27).

0.1 c.c. perfusion liquid: reduction 0.08%.
0.1 c.c. urine of right kidney: reduction 0.065%.
0.1 c.c. urine of left kidney: reduction 0.0625%.
Retained by right kidney: 0.08—0.065 = **0.015%**.
Retained by left kidney: 0.08—0.0625 = **0.0157%**.

It is clear from all these experiments that the quantity of maltose retained is in any case extremely small, notwithstanding the fact that

this dissaccharide is built up from two molecules of glucose, and that the glomerulus epithelium is permeable to glucose to a very slight degree.

G. Lactose and a mixture of glucose and lactose.

Experiment 41 (July 3).

0,20% Lactose is dissolved in the perfusion liquid.

0,1 c.c. of perfusion liquid: reduction 0,14%.

0,1 c.c. urine of right kidney: reduction 0,1375%.

0,1 c.c. urine of left kidney: reduction 0,14%.

Retained by right kidney: $0,14 - 0,1375 = 0,0025\%$.

Retained by left kidney: $0,14 - 0,14 = 0$.

Experiment 42 (July 3).

0,1 c.c. perfusion liquid: reduction 0,11%.

0,1 c.c. urine of right kidney: reduction 0,11%.

0,1 c.c. urine of left kidney: reduction 0,1075%.

Retained by right kidney: $0,11 - 0,11 = 0$.

Retained by left kidney: $0,11 - 0,1075 = 0,0025\%$.

Here again the kidney has retained no, or very little, lactose.

Experiment 43 (July 3).

The same perfusion liquid as in exp. 42.

0,1 c.c. urine of right kidney: reduction 0,1075%.

0,1 c.c. urine of left kidney: reduction 0,1075%.

Retained by each kidney: $0,11 - 0,1075 = 0,0025\%$.

Here again neither of the kidneys retained lactose.

Experiment 44 (July 4).

0,1 c.c. perfusion liquid: reduction 0,14%.

0,1 c.c. urine of right kidney: reduction 0,1450%.

0,1 c.c. urine of left kidney: reduction 0,1325%.

Retained by right kidney: $0,14 - 0,1450 = 0$.

Retained by left kidney: $0,14 - 0,1325 = 0,0075\%$.

Lactose has thus been retained by neither of the kidneys.

From this we may draw the conclusion that the glomerulus epithelium allows the lactose to pass altogether, although it is built up from glucose and galactose, of which compounds the former is retained to a large degree, and galactose as well, although less.

From a theoretical as well as from a clinical point of view it seemed of importance to investigate how the kidney would behave towards a mixture of lactose and glucose.

From these experiments we learn that the retention of glucose by the kidney is not influenced by lactose. The latter is passed while glucose is retained to the same degree as when there was no lactose present.

This result is in accordance with the use which for a

Retention capability of kidney for a mixture of 0.1 % glucose and 0.1 %
sacch. lactis (lactose).

Experiments of September 24—26.

Reduction perfusion liquid	Reduction urine of right kidney	Retained by right kidney	Reduction urine of left kidney	Retained by left kidney
Frog A 0.1575 } 0.16 }	0.0825 } 0.0825 }	0.0765 %	0.0825 } 0.0825 }	0.076 %
Frog B " "	0.09 } 0.095 } 0.0925	0.065 "	0.095 } 0.095 } 0.095	0.065 "
Frog C " "	0.09	0.0675 "	0.0925	0.065 "
Frog D " "	0.1	0.06 "	—	—
Frog A 0.16 %	0.096	0.064 "	0.104	0.056 "
Frog B " "	0.10	0.06 "	0.10	0.056 "
Frog C " "	0.104	0.056 "	0.094	0.066 "
Frog D " "	0.096	0.064 "	0.10	0.060 "

considerable time has been made of lactose for clinical use to estimate the validity of kidneys and which is founded on the consideration that the healthy kidney easily passes lactose.

We thank Mr. R. ROELINK for his able assistance during this research.

Summary and Conclusion.

1. The fact, now again affirmed, that, when we pass a RINGER's solution to which glucose has been added, through the kidney, this is retained by the glomerulus membrane, while salts, which are also crystalloids, are allowed to pass, has raised the question to what this contrast must be attributed.

2. In the first place we can think of the circumstance that glucose possesses a so much larger molecule, which could then impede the passage. If this hypothesis be correct then the disaccharides such as saccharose, maltose and lactose, which possess a still larger molecule ($C_{12}H_{22}O_{11}$) than glucose ($C_6H_{12}O_6$), would certainly not pass through. Experiments have however proved that the glomerulus epithelium is permeable to a large degree to these sugars, even to raffinose ($C_{18}H_{32}O_{16}$).

The permeability to lactose is perfect.

3. *Where the cause for the retention of glucose cannot be ascribed to the size of its molecule, we are bound to consider its structure or configuration.* There is the more occasion for doing this because its isomerics, laevulose and mannose, are allowed to pass altogether and galactose to a large degree, as has been proved by the experiments under discussion.

4. Glucose therefore occupies a unique position among the monosaccharides in regard to the glomerulus membrane. In other words *the glomerulus membrane can distinguish glucose from the other monosaccharides in a manner that reminds of the relation of sugars and ferments*, in connection with which EMIL FISCHER used the well-known simile of a *lock and key*.

In any case these experiments are again *a new illustration of the doctrine of stereoisometrics*, but now not as has thus far been the case, through facts of chemical but of *physiological nature*, belonging to permeability.

5. Not without theoretical and clinical importance seems the fact that the capability for retention of glucose is not modified when glucose and laevulose are simultaneously present in the perfusion liquid. The two sugars are simply separated as by a filter: the glucose remains behind, the laevulose is passed. This also appears to be the case with a mixture of lactose and glucose: the lactose passes completely into the urine and the glucose is retained by the glomerulus epithelium to the same degree as when there was no lactose present.

Groningen, September 1918.

Physiological Laboratory.

Chemistry. — “*On the Significance of the Volta-Effect in Measurements of Electromotive Equilibria*”. By Prof. A. SMITS and J. M. BIJVOET. (Communicated by Prof. P. ZEEMAN).

(Communicated in the meeting of Sept 28, 1918).

Introduction.

Many physicists are of opinion that the Volta effect amounts to only a few milli volts, and that the electromotive force of an electrical cell resides practically exclusively in the potential differences metal-electrolyte, so that these alone need be taken into consideration; there are even those who think that the Volta-effect is theoretically zero. It is chiefly the German school that assumes that the Volta-effect may be neglected with respect to the potential difference metal-electrolyte. On the other hand a great number of investigators think they have found that the Volta-effect can constitute $\frac{1}{2}$, $\frac{3}{4}$ and even a still larger fraction of the electromotive force of a cell, and can accordingly amount to as much as 1 Volt.

The opinions concerning the value of the Volta-effect are therefore greatly divided, which is owing to the great difficulties which attend the determination of the Volta-effect.

In the application of the recent views about the electromotive equilibria¹⁾ to the Volta-effect it appears, that even though this effect should be small for metals in the state of internal equilibrium, it must become great for phenomena of polarisation, so that we may certainly not neglect the Volta-effect for these cases.

2. *The variation of the Volta-effect on polarization and passivation.*

The following equation holds for the potential difference of a metal in active state with respect to an electrolyte:

$$\Delta_{M \text{ active} \rightarrow L} = - \frac{0,058}{v} \log \frac{K' M^{v'} (M_S^{v'})_{\text{active}}}{M_L^{v'}}$$

and thus we get for the passive state:

$$\Delta_{M \text{ passive} \rightarrow L} = - \frac{0,058}{v} \log \frac{K' M^{v'} (M_S^{v'})_{\text{passive}}}{(M_L^{v'})}$$

from which follows.

¹⁾ Zeitschr. f. physik. Chemie **88**, 743 (1914).

“ ” ” ” **90**, 723 (1915).

$$\Delta_{M_{active}-L} - \Delta_{M_{passive}-L} = - \frac{0,058}{v} \log \frac{(M_S^{'})_{active}}{(M_S^{'})_{passive}}$$

For the Volta-effect holds the relation:

$$\Delta_{M_1-M_2} = \frac{\theta_{M_1} - \theta_{M_2}}{F}$$

from which follows in the same way as we have derived this for the potential difference metal-liquid, that the following equation holds for the Volta-effect:

$$\Delta_{M_1-M_2} = 0,058 \log \frac{K'_\theta(\theta_{M_1})}{(\theta_{M_2})}$$

so that:

$$\Delta_{M_1 active-M_2} - \Delta_{M_1 passive-M_2} = 0,058 \log \frac{(\theta_{M_1})_{active}}{(\theta_{M_1})_{passive}}$$

When we call:

$$\frac{(M_{1s}^{'})_{active}}{(M_{1s}^{'})_{passive}} = n$$

then also

$$\frac{(\theta_{M_1})_{active}}{(\theta_{M_1})_{passive}} = n$$

It follows from this that when on polarisation or passivation the change of the potential difference metal-electrolyte is:

$$\frac{0,058}{v} \log n$$

that of the Volta-effect amounts to:

$$0,058 \log n$$

hence v times the value.

What we measure is the sum of these two changes:

$$\frac{v+1}{v} 0,058 \log n.$$

Hence the part $\frac{v}{v+1}$ of this total change is due to the Volta-effect. This is, therefore, $\frac{1}{2}$ for a uni-valent metal, and $\frac{2}{3}$ for a bi-valent one etc.

When it is now borne in mind that on passivation through anodic solution the potential difference metal-electrolyte, as it is found by measurement, can change by an amount of 1 or 2 Volt. (e.g. 1.7 Volt, is found for iron), it follows from this that according to these considerations also the Volta-effect is subjected to a great change¹⁾.

¹⁾ It must still be pointed out that the case iron is certainly more intricate than the case considered above, because iron contains ions of different valency.

This throws, indeed, a peculiar light on the Volta-effect, for it now appears clearly that when really the Volta-effect for metals in the state of internal equilibrium should be zero or very small, which comes to the same thing as equality or nearly equality of the molecular thermodynamic potential of the electrons in those metals, this would be a special characteristic property according to the theory of electrons for metals in the state of internal equilibrium.

But apart from the value of the Volta-effect, in the logical development of the given theory of the electromotive equilibrium, the Volta-effect cannot be neglected.¹⁾

¹⁾ In this we will also point out that when the new views about the rôle of the electrons and the electromotive equilibrium are consistently applied to an arbitrary electrical circuit, we arrive at the result that everywhere where a potential difference occurs, a reaction takes place on passage of the current, in which the change in free energy of the reaction proceeding at that place, determines the value of the potential difference. It is known that according to the given theory at the places of contact metal-electrolyte this reaction consists: 1. of the splitting up of metal ions into ions and electrons; resp. of the formation of metal atoms from the electrically charged dissociation products mentioned here and 2 of the transition of ions and electrons from the metal phase into the electrolyte or vice versa. In this transition from one phase into the other the ions take a preponderant part.

When we consider the contact metal-metal, the just-mentioned transition consists to by far the greater part of the displacement of electrons from the metal M_1 to the metal M_2 .

This view differs accordingly from that which is particularly met with in German handbooks, in which the opinion is embraced that the reactions during passage of the current exclusively take place at the places of contact metal-electrolyte.

It is clear that on application of the relation:

$$E = A - T \frac{dA}{dT}$$

to the transition of electricity from one metal into the other we may only conclude to:

$$A = T \frac{dA}{dT}$$

when in the process mentioned here no change of the thermo-dynamic energy takes place ($E = 0$).

LEBLANC does so in his handbook p. 227 (1914), and thus comes to the conclusion that the Volta-effect must be small, because $\frac{dA}{dT}$ is small.

According to the theory of electrons the difference in solubility heat of the electrons in the two metals will, however, have to be taken into account. In the isotherm transition of electricity between the two metals the free energy of the electrons will change, and be converted into electrical energy in case of a reversible process, the occurring change of the bound energy becoming manifest through the latent heat, which heat is the heat of PELTIER.

It is this quantity, the heat of PELTIER which, is represented by $T \frac{dA}{dT}$, and not the Volta-effect.

3. *The experimental electrical potential.*

When we measure the potential difference metal-electrolyte, we do so by the aid of an auxiliary electrode, e.g. a calomel or hydrogen electrode, in other words, we then make an electrical circuit, which is closed during the measurement. The electro-motive force of this circuit, in which we suppose the diffusion potential between L_1 and L_2 annulled, then becomes:

$$E = \Delta_{M_1-L_1} - \Delta_{M_2-L_2} - \Delta_{M_1-M_2}$$

in which $\Delta_{M_1-M_2}$ is a Volta-effect.

When in this we put $\Delta_{M_2-L_2} = \text{zero}$ (N. hydrogen-electrode), we get:

$$E = \Delta_{M_1-L_1} - \Delta_{M_1-M_2},$$

in which we shall call E the *experimental electrical potential*.

This expression, therefore, always contains the Volta-effect, and until this quantity is known, and until we introduce further suppositions about its value, we can of course not determine the difference $\Delta_{M_1-L_1}$ alone in this way, and consequently not the saturation concentration of the metal-ions either (which quantity is equivalent with NERNST's "Lösungstension"), which was calculated from:

$$E = -\frac{RT}{v_1 F} \ln \frac{K_{M''}}{(M_L'')} \quad (1)$$

in which $\Delta_{M_1-M_2}$ has been neglected.

Nor can we draw conclusions about the order of the saturation concentrations of the metal-ions from the so-called tension series, until the Volta-effect shall be known. From the fact that the metal M_1 immersed in a normal solution of one of its salts appears on measurement to be more negative than the metal M_2 , immersed in a 1 norm.-solution of a corresponding salt, we conclude namely that:

$$\Delta_{M_1-L_1} \text{ is more negative than } \Delta_{M_2-L_2},$$

but strictly speaking this conclusion is not permissible, because the measurement only says that $\Delta_{M_1-L_1} - \Delta_{M_1-M_2}$ is more strongly negative than $\Delta_{M_2-L_2}$.

We demonstrated that the equations for the exp. elec. potential in the form in which they contain the saturation-concentration of the ions or the "Lösungstension", have the drawback that the unknown Volta-effect occurs in them. It is entirely different with the new already before given equation, in which the *solubility product* of the metal or the *solubility quotient* of the metalloid occurs, and the same thing may be said of the electron equation.¹⁾

¹⁾ Zeitschr. f. physik. Chemie **92**, 1 (1916).

Thus the following equation was namely derived:

$$\Delta_{M_1-L_1} - \Delta_{M_2-L_2} = \frac{RT}{v_1 F} \ln \frac{(M_1' L)}{L_{M_1}} - \frac{RT}{v_2 F} \ln \frac{(M_2' L)}{L_{M_2}} + \frac{\mu_{M_1} - \mu_{M_2}}{F} \quad (2)$$

we measure, however,

$$E = \Delta_{M_1-L_2} - \Delta_{M_2-L_2} - \Delta_{M_1-M_2} \quad (3)$$

and the Volta-effect being:

$$\Delta_{M_1-M_2} = \frac{\mu_{M_1} - \mu_{M_2}}{F}$$

it follows from this that:

$$E = \frac{RT}{v_1 F} \ln \frac{(M_1' L)}{L_{M_1}} - \frac{RT}{v_2 F} \ln \frac{(M_2' L)}{L_{M_2}} \quad (4)$$

in which the Volta-effect has been eliminated.

This equation enables us, therefore, to find the ratio of the solubility-products from the electromotive forces.

In the practical application the hydrogen electrode may be taken for the metal M_2 , and for L_{H_2} the value may be substituted which had already been given before, viz. $10^{2 \times -48.1}$;

in this case we get:

$$E = \frac{0.058}{v} \log \frac{(M_L')}{L_M} - 2.8 \quad (5)$$

When equation (4) is compared with the expression for E , which contains the saturation-concentrations of the metal-ions found by substituting the values of $\Delta_{M_1-L_1}$ and $\Delta_{M_2-L_2}$ given by equation (1) in equation (3), which gives:

$$E = - \frac{RT}{v_1 F} \ln \frac{K_{M_1' }}{(M_1' L)} + \frac{RT}{v_2 F} \ln \frac{K_{M_2' }}{(M_2' L)} - \Delta_{M_1-M_2} \quad (6)$$

the great advantage which equation (4) resp. (5) have over equation (6) is very apparent, for the latter equation contains a still unknown Volta-effect. While the construction of a series of the potential differences metal-electrolyte is not yet possible, on account of our ignorance of the Volta-effect, equation (5) enables us to draw up a series for the solubility-products of the metals, and from such a relation there may be found a series for the solubility-quotients of the metalloids, as has been done already²⁾.

The determination and order of this series is of course the same as that of the so-called tension-series, which gives the order in which

¹⁾ Zeitschr. f. physik. Chemie **92**, 1 (1916).

²⁾ SMITS and LOBRY DE BRUYN. Verslag Kon. Ak. **26**, 270.

the metals oust each other from equally concentrated solution. We demonstrated, however, that in a theory which assumes the existence of Volta-effects, the quantities derived from the electromotive equilibria should not be considered as the saturation-concentrations of the metal-ions or as the "Lösungstensionen".

The electron equation gives a relation that agrees with equation (2), viz.:

$$\Delta_{M_1-L_1} - \Delta_{M_2-L_2} = -\frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})} + \frac{\mu_{\theta_{M_1}} - \mu_{\theta_{M_2}}}{F},$$

so that

$$E = -\frac{RT}{F} \ln \frac{(\theta_{L_1})}{(\theta_{L_2})}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Of course the Volta-effect does not occur in this relation either, so that when a definite value is assumed for the electron conc. (θ_{L_2}) in the electrolyte in which the hydrogen electrode is found, the electron-concentration (θ_{L_1}) , which belongs to the other electromotive equilibrium, can be found. •

Equations (4) and (7) are, therefore, not approximate, but perfectly rigorous, which also appears from the consideration that equation (7),

from which (4) is found by substitution of $\frac{L_M}{(M_L^v)}$ for $(\theta_L)^v$, follows immediately from the condition for electron equilibrium between the liquids E_1 and L_2 . The derivation of this electromotive force as sum of the potential differences occurring in the circuit was accordingly only followed here in order to keep in agreement with the derivation given before.

•

4. As appears from a previous communication¹⁾, the experimental elec. potential of a Ni-electrode, immersed in an electrolyte through which hydrogen was led, was found equal to the hydrogen potential. In order to account for this fact that the electromotive force E of the closed circuit nickel-electrode-electrolyte-hydrogen-electrode is zero according to our considerations we must show, as follows directly from equation (7), in what way the electron concentration of the nickel equilibrium has become equal to that of the hydrogen equilibrium.

This phenomenon is already explained in a very simple way²⁾ by the assumption that the nickel-electrode is, at least superficially,

¹⁾ SMITS and LOBRY DE BRUYN loc. cit.

²⁾ SMITS and LOBRY DE BRUYN loc. cit.

disturbed, which disturbance for a very inert metal will go so far till the electron concentration of the nickel equilibrium in the electrolyte has conformed to the electron concentration of the hydrogen equilibrium, and has become almost equal to it.

For the limiting case of an ideal inert metal this equality will become perfect, as is also required by E becoming zero in this case.

In a former discussion of these phenomena the neglect of the Volta-effect led on the other hand to the conclusion that the electromotive force of the circuit, in case of equal electron-concentrations in the electrolyte of the two metal equilibria, would be zero *only in approximation*.

It will have become clear through what precedes that while up to now the Volta-effect has been neglected in the Δ, X -figure, it is better to draw the experimental potential E (e.g. with respect to hydrogen) as ordinate instead of the potential difference metal-liquid; then the thus obtained E, X -figures are perfectly rigorous. They then indicate that for the three-phase equilibrium the two electrodes possess the same experimental potential; the difference between their potential differences with the electrolyte then being equal to the Volta-effect between the two metals.

In this point the following equation then holds:

$$\Delta = \frac{0.058}{v_1} \log \frac{(M_1^v)_L}{L_{M_1}} = \frac{0.058}{v_2} \log \frac{(M_2^v)_L}{L_{M_2}}$$

or

$$\frac{L_{M_2^v}}{L_{M_1^v}} = \frac{(M_2^v)_L}{(M_1^v)_L}$$

so that from the ratio of the solubility-products the situation of the coexisting electrolyte immediately follows. Though this has been shown already before, this circumstance is once more pointed out here, to make clear that equation (6) is of no use to us here, for this equation gives for the three-phase equilibrium:

$$-\frac{0.058}{v_1} \log \frac{K_{M_1^v}}{(M_1^v)_L} = -\frac{0.058}{v_2} \log \frac{K_{M_2^v}}{(M_2^v)_L} + \Delta_{M_1-M_2}$$

In this form the equation contains, however, the unknown Volta-effect and the unknown saturation-concentrations, so that a calculation as above is not possible.

Summary.

By application of the more recent views on the electromotive

equilibria to the Volta-effect the result was obtained that on polarisation and passivation the *change* in the Volta-effect must be great according to this theory, and that in these phenomena the Volta-effect would even constitute the greatest part of the total change in the electromotive force. It was further pointed out that if the Volta-effects between metals in which the state of internal equilibrium prevails, should be really very small, on which the opinions are still divided, but which has, indeed, become probable by the experiments made of late, this would have to be considered according to the theory as a very characteristic property for metals in the state of internal equilibrium.

As in principle the Volta-effect at any rate in the given theory of the electromotive equilibria may not be neglected, it was here taken into account. The quantities that are found on measurement of potential differences metal-electrolyte, and which are here called *experimental electrical potentials*, always contain an unknown Volta-effect; which is the cause that from the said potentials the saturation concentrations of the metal ions (resp. the "Lösungstensionen") cannot be calculated.

The newly derived relations, in which the *solubility product* of the metal, the *solubility quotient* of the non-metal resp. the electron concentration in the electrolyte occurs, do not contain the Volta-effect, however, and enable us to draw up a *solubility-product-series* of metals, and a *solubility-quotient-series* of metalloids, as has indeed already been done, from which conclusions can be drawn about the chemical and electrochemical behaviour of the elements.

Amsterdam,
Sept. 1918.

General and Anorg. Chem. Laboratory
of the University.

Zoology. — "*Androgenic origin of Horns and Antlers.*" By Prof.
J. F. VAN BEMMELLEN.

(Communicated in the meeting of September 29, 1918).

In his excellent work "die Saugetiere", MAX WEBER gives as his opinion about the origin of the cephalic armament of numerous Ungulates, that horns and antlers originally started in both sexes as defensive weapons against enemies, but later on more and more came to be used as instruments of offence by the males in their fights for the females, and so either have grown an exclusive attribute of the male sex, or at least have developed much more strongly than in the female sex.

In this instance therefore WEBER evidently shares the opinion pronounced by TANDLER and GROSS in their paper: Die biologischen Grundlagen der sekundären Geschlechtscharaktere, where they say: "All secondary sexual features were originally specific features, properties therefore, characteristic of a certain species, even of a whole order of Vertebrates, without their primarily having any connection with the genital sphere."

In their commentary on this proposition they remark: "Hitherto in the morphology of the sexual characteristics too little attention has been paid to the question, how much of them is peculiar not for the sex, but for the species." As a special example they cite the case of the horns of Cavicornia, "which do not constitute a sexual characteristic in themselves, but only in their shape, which differs for males and females, whereas on the contrary it is identical in masculine and feminine castrates."

"The same is the case with the hairiness in man. We have been able to show that such an eminently secondary sexual feature of the male sex, as the beard, is also found in old castrates, but there in form and extension resembles that of old women."

According to TANDLER and GROSS the question should not be formulated "Is an organ a secondary sexual feature", but: "How much in the development of an organ is specific, how much sexual."

Though this assertion might be granted, yet I believe to be justified in opposing to it another view: viz. that the evolution has been just the reverse; the cephalic armament arising in males as a means of attack in their duels for the females, and afterwards passing to

the latter in a more or less reduced form and only in some of the species (according to the well-known rules of monosexual transgressive heredity), the result being that the horns now could be used in both sexes as means of defence.

As arguments in favour of this opinion may be cited:

1. In Deer the antlers are absent in all females except those of the Reindeer, and precisely in this species a useful application of the horns, not connected with any sexual function, and alike for both male and female may be conceived, viz. the digging up of food from under the snow, though some authorities (e.g. BREHM) deny this function.

2. Among Antilopes, besides genera in which both sexes are horned, others occur in which only the male possesses these attributes, and in the majority of cases the horns of the females are smaller than those of the males. The latter moreover show a tendency to hypertrophic growth, just as is the case with deer, leading to unwieldy size or to sundry strange shapes (e.g. screwlike contortions) which seem to stand in direct contradiction with the requirements of practical use.

3. The same is the case with Cattle, Sheep and Goats, as shown by the four-horned goat, or the excessive development of the horns in the carabou and other buffaloes.

4. Even in Giraffes, whose minute pedicles with their small os cornu may probably be considered as rudiments of formerly better differentiated antlers (compare *Ocapia* and *Sivatherium*) the males possess higher and stronger hornstumps than the females, and moreover the unpaired nasal knob. In *Ocapia* on the other hand the horns are primarily absent in the female, and the same was probably the case during their whole life in those of *Siva*-, *Hellado*- and *Samotherium*.

5. The more original kinds of Ruminants: the Tragulidae and Camelidae, are destitute of horns, and so were the oldest and primitive extinct Artiodactyla (*Pantolestidae*, *Anoplotheridae*) as well as all Nonruminantia amongst them. The oldest fossil deer likewise did not yet possess antlers, as the muskdeer does up to this day, though the miocene *Palaeomeryx* according to RÜTIMEYER and SCHLOSSER was already provided with them. Perhaps this might be considered as an indication that the tendency to the formation of antlers arose independently in the tribe of the Cervidae, but also as the manifestation of a far older hereditary inclination to the production of bony frontal appendages of the male. This tendency then must have been in abeyance in the tribe of the Artiodactyla in general; in Deer

it probably reappeared, and from thence continually increased in potency and complication.

This conception according to my view is strengthened by the fact, that also among the Suidae a tendency to the formation of bony protuberances on the dorsal side of the skull undoubtedly occurs and appears in stronger manifestation in the male sex than in the female, as is shown by the monstrous skull of the male African wart-hog.

6. In Protoceratinae likewise the skull of the male only was provided at its upper side with a complete set of paired bony excrescences.

7. According to MARSH both sexes of the Dinoceratidae possessed these bony protuberances (and the large dagger-like tusks besides), yet in the male they grew unto a larger size than in the females. We might conclude from this that the tendency to the production of bony knobs on the skull is even older than the separation of Ungulates into Artio- and Perissodactyles.

8. The annual shedding of the antlers and their regeneration in Cervinae is apparently connected with the rut. The same appears to be the case in Antilocapra.

9. The abovementioned bony processes on the head of Giraffidae, (sensu latiori) Suidae, Protoceratinae and Dinoceratidae, cannot reasonably be considered as really practical weapons, as they are far too cumbersome and hypertrophic for that. Neither can this be the case with the antlers of most Deer or the horns of numerous Antilopes, Cattle, Sheep, and Goats.

On the other hand they wear to a very high degree the character of sexual attributes, in their exuberance, unpractical build, curious complication, obviousness and variability.

10. In the first (primitive) members of the Ruminantia antlers and horns apparently arose at a relatively late stage, though this may be further removed in the geological past than is generally supposed. In any case the appearance or return of this feature is younger than the remaining peculiarities of Artiodactyla.

As I consulted the literature on the subject, I found that in considering horns and antlers as sexual attributes, I had come to a similar conclusion as the well-known popular author on questions of evolution in Zoology, BÖLSCHÉ, has set forth in his Tierbuch IV, der Hirsch. Yet on the first cause of the origin of frontal appendages our opinions disagree, for BÖLSCHÉ sees in the excrescences on the roof of the skull of so many Ruminants nothing more than originally purely ornamental attributes, and ascribes their birth to a periodical exuberance of energy of growth, manifesting

itself in exostoses of the bones of the cranial roof, especially and at last exclusively of the frontal bones. In his opinion the periodicity of this surplus of growth-energy keeps time with the rut of the males, but its presence should be ascribed to the regression of another differential feature of the male sex, viz. the ensiform tusks, as they still occur in Suidae, Tragulidae and the unhorned muskdeer.

The strongest expression of this opinion is given by Bölsche in the words (p. 88) "The pedicle is no weapon." On p. 89 he continues: "As we saw, the idea "weapon" cannot be applied without reserve to the beam, although it may occasionally be used as such. Far exceeding that application and evidently its real nature, this beam is an ornamental product, a somatical arabesk, abstract from all usefulness, rhythmic in structure, with an inherent connection with the erotic side of life. The pedicle, in principle a product of the skull like the beam, cannot by any means be considered as a weapon, at the same time however it does not want erotic connections."

Against these views I think objections may be raised in two respects. In the first place there is no plausible reason, why the origin of horns and antlers should not be connected with single combats between males belonging to the same species, in which the more primitive mode of fighting with tusks (as still found among hogs) was gradually replaced by knocking of the foreheads against each other.

The question, whether this new custom was the immediate or the indirect cause of the exostotic hypertrophic process (Lamarckism versus Darwinism) may be passed over in silence here as in all similar cases. Nor do I want to deny that exuberant growth, in cooperation with periodical sexual maturity, exerted an important influence on their development, as it still does every time the antlers are shed and renewed: we need only remember how profoundly this renewal is disturbed by every injury to the male sexual glands.

In the same way, Bölsche's verdict: "The pedicle is no weapon", seems to me to be liable to serious doubt. Already in itself, the comparison of the long pedicle in the Muntjac-deer with the shorter ones of the remaining Cervidae leads to the conception, that the pedicle should be considered as an organ in a state of regression. To the same consideration leads a survey of the extinct Deer: in the middle-miocene *Palaeomeryx*-species no separation exists between pedicle and beam, they only show a long bony outgrowth of their frontal bones, slightly forked at its top. This excrescence therefore might be considered as a pedicle of extraordinary length. In the

first fossil deer showing a separate pedicle, the latter is very long, like that of the existing Muntjac.

In accordance with this observation is the fact that in Sivatherinae no rose can be detected near the base of their gigantic and ramified antlers, which therefore as a whole might be considered as pedicles.

Starting from the fact that in recent Giraffes the small hornstumps permanently retain their covering of hairy skin, the same may have occurred in their extinct allies: the Sivatherinae, and perhaps likewise in the first antlered ancestors of Deer. The separation of the latter's antlers into pedicle and beam, combined with the phenomena of yearly shedding and regeneration, the "rubbing" of the "velvet", in short the entire process of the renovation of the antlers, so inconvenient and dangerous for the stag, might then have developed from a similar primitive condition as that in Sivatherinae, where the frontal bony outgrowths, clad with hairy skin, must gradually have increased in size and complication. If one applies to the latter the designation "pedicle", it follows that for them just the contrary might be true of what is implied in BÖLSCHÉ's assertion: viz. the pedicle would have originated as a weapon and only lost this function in the Giraffes proper.

In the second place I cannot see sufficient reason for accepting such an intimate and strict connection between the regression of the tusks in the upper jaw of the stag and the progression of their antlers, as necessarily follows from the supposition that a surplus of growing energy should pass from those tusks to the frontal bones.

Against this hypothesis it may be objected that the male Protoceratinae as well as the Dinoceratidae were provided with powerful tusks, largely protruding from their mouths, and yet had a whole range of paired and single bony knobs and projections on the roof of their skulls, somewhat like those still found in the (male) warthogs. Among deer the male Muntjac still possesses strong tusks projecting downward and outward out of the mouth from under its upper lip, and yet carries well-developed, though simple antlers.

There is moreover little reason for the assumption that in Cavi-cornia the same course of events should have taken place as in Cervicornia, viz. a regression of large tusks, going hand in hand with an increased growth and a higher complication of frontal appendages, and yet the origin of these excrescences may be attributed to similar causes in all Horn- and Antlerbearing Ungulates.

On the other hand there is nothing incomprehensible in the fact that the upper tusks of Deer should have been reduced, as soon as they were no longer used as weapons, because the male Deer got accus-

tomed to a new mode of fighting which made them acquire antlers.

This vicariating development can be understood, without taking refuge to such an intricate correlation between upper tusks and antlers, as BÖLSCHKE does, where he speaks of a surplus of energy of growth, set free by retardation in the development of tusks, and manifesting itself in hypertrophic excrescences on the frontal bones.

When we proceed in this course of thought, the question unvoluntarily arises, if the far higher development of tusks in the male sex of so many species of mammals might not be considered as a support for the abovementioned hypothesis about the androgenic origin of frontal appendages. The difference between the two phenomena lies especially in the fact, that with canines modified to tusks or incisors prolonged into darts, only their stronger development and differentiation need be ascribed to influences of sexual, especially male nature, while for horns and antlers also their first appearance had to be traced to this same cause. But this does not exclude that the tusks of Elephants and Cetacea, the canines of so many Apes, Carnivores and Ungulates etc. find their most plausible explanation in the assumption, that in so far as they are larger than the other teeth and also differ in shape and position from the incisors and molars, they may be considered as an acquisition of the male sex, which afterwards passed to the female, but in reduced proportion, and so to a certain extent again lost its monosexual character. Especially the growth far over the limits of practical fitness may be adduced as an argument for this hypothesis; we should only remember the tusks of the Mammoth curled up in a complete circle, the gigantic canines of the male walrus or the usually unilateral dart of the male Narwhal.

In this connection I should like to move the question whether the uncouth tusks of the extinct Sabretoothed tiger (*Machairodus*), might not have formed a special attribute of the male sex, as beyond doubt they were far from practical in defence as well as offence. With certainty this is the case with the Walrus. Also the upper canines of the Babirussa, which perforate the upper lip, and are curled up dorsally and backwards, give us a good example of hypertrophic growth far beyond the limits of real usefulness.

Groningen, September 1918.

Chemistry. — "*On the estimation of the geraniol content of citronella oil*". By Dr. A. W. K. DE JONG. (Communicated by Prof. VAN ROMBURGH).

(Communicated in the meeting of September 29, 1918).

The chemists of the firm of SCHIMMEL & Co. have a method for the estimation of geraniol in citronella oil which in the "Bericht" of this firm of October 1899, 20 and also in that of October 1912, 39, is described as follows: "Etwa 2 g Phthalsäureanhydrid und 2 g des zu untersuchenden Oels werden mit 2 ccm Benzol zwei Stunden in einem Kolben, wie er zu Acetylierungen benutzt wird, auf dem Wasserbad erwärmt, dann erkalten gelassen und mit 60 ccm wässriger Halbnormal-Kalilauge 10 Minuten geschüttelt. Der Kolben ist hierbei mit einem eingeschlifften Glasstopfen verschlossen. Nach dieser Zeit ist alles Anhydrid in neutrales phthalsaures Kali und der saure Geraniolester in sein Kalisalz übergeführt worden. Nun wird das überschüssige Alkali mit Halbnormal-Schwefelsäure zurücktitriert. Zieht man dann von der Menge Alkali, die der eingewogenen Phthalsäure entspricht, die für den Versuch verbrauchte Menge ab, so erfährt man, wieviel Alkali dem an Phthalsäure gegangenen Geraniol äquivalent ist, woraus der Prozentgehalt an Geraniol zu berechnen ist".

This method is at the outset subject to suspicion, since it is based on the assumption that geraniol is quantitatively esterified by phthalic anhydride, whereas this is not even the case with acetic anhydride (98.5 p.c. was found to be esterified).

For the following experiments a very pure phthalic anhydride was prepared; 1 gram. was neutralised by 135 c.c. $\frac{1}{10}$ n KOH, whereas 135.1 c.c. was calculated for the pure substance.

The citronellal used was isolated from citronella oil by means of the bisulphite compound. The sp. gr. at 26° was 0.8526; $[\alpha]_D^{26} = +10.21^\circ$. It was faintly acidic; 1 gram. was neutralized by 0.2 c.c. $\frac{1}{10}$ n KOH.

The geraniol was isolated from Palmarosa oil by means of the calcium chloride method. The sp. gr. at 26° was 0.8752.

To the mixture of anhydride, citronellal or geraniol 4 c.c. of benzene was added. After heating, the flask was cooled rapidly, so

that the crystals which separated remained small and dissolved readily in $\frac{1}{2}$ n KOH. The phenolphthalein was added as powder.

Duration of heating: 2 hours.

Temperature of the water bath in degrees C.	Quantity of phthalic anhydride used	Quantity of citronellal used	c.c. N/10 KOH		Difference
			found	calculated	
85	1.2600 gm.	0.4450 gm.	169.9	170.1	0.2
85	0.9480 "	0.5120 "	127.6	127.95	0.35

At this temperature citronellal is not attacked by the anhydride, or scarcely so.

Temperature of the water bath in degrees C.	Duration of heating	Quantity of phthalic anhydride gm.	Quantity of geraniol used gm	Quantity of geraniol found	
				gm.	%
99	2 hours	2.1740	0.4645	0.4158	89.5
88	2 "	2.1810	0.4960	0.4575	92.2
84	2 "	2.1300	0.4860	0.4481	92.2
77	2 "	2.1160	0.4950	0.4527	91.5
88	2 "	1.0550	0.4490	0.4073	90.7
82	3 "	1.6930	0.4515	0.4173	91.4

This showed clearly that the esterification of the geraniol had not been complete. The mixture does not boil, however, and I thought that this might possibly be the cause of the shortage. Hence a few further estimations were made in which the heating was done with a small flame.

Duration of heating: 2 hours.

Quantity of phthalic anhydride used in gm.	Quantity of geraniol used in gm.	Quantity of geraniol found	
		gm.	%
2.0540	0.8890	0.8193	92.2
2.0495	0.4970	0.4497	90.5

Nor did an increase in the benzene from 4 c.c. to 8 c.c. change the result. Found: 90.6 %.

With this way of heating the citronellal is also attacked more extensively.

Quantity of phthalic anhydride used in grm.	Quantity of citronellal used in grm.	Number of c.c N/10 KOH		
		found	calculated	difference
0.9490	0.5950	126.5	128.1	1.6
1.2850	0.5050	171.15	173.45	2.3

Evidently the scientific investigators of the firm of SCHIMMEL & Co only worked with mixtures of geraniol, citronellal and limonene. As the following estimations show, results are obtained with mixtures of geraniol and citronellal which differ but little from the true values.

Temperature of the water bath in degrees C.	Quantity of phthalic anhydride used in grm.	Quantity of geraniol used in grm.	Quantity of citronellal used in grm.	Quantity of geraniol found	
				grm.	%
88	2.4883	0.5610	1.3602	0.5480	97.7
82	2.1090	1.0115	0.8120	1.0255	101.4
86	2.3600	1.3745	0.7560	1.3883	101.0

That the presence of the citronellal should lead to better esterification of the geraniol is very improbable; since in the previous experiments about 92 % of the geraniol was esterified, the amount of citronellal esterified in the last three estimations would be 0.032 grm., 0.095 grm. and 0.123 grm. respectively.

It would appear from this that the amount of citronellal esterified increases with that of the geraniol. The cause for the esterification of citronellal in the presence of geraniol must be sought in the formation of the acid phthalic ester of geraniol. Phthalic acid itself has little effect because it is only slightly soluble in benzene. It is well known that citronellal is very sensitive to acids, being converted by them into isopulegol.

In acetylating citronellal without sodium acetate the same phenomenon is observable when working with mixtures of acetic acid and acetic anhydride.

An indirect method was employed corresponding to the way in which the geraniol was estimated by phthalic anhydride. The apparatus consisted of a small flask with long neck to which a ground in U-tube was attached. Into the flask there was always weighed 2 c.c. of citronellal and 2 c.c. of the acetic anhydride mixture. 5 c.c. of $\frac{1}{2}$ n KOH were placed in the U-tube, which was fitted with a soda-lime tube.

Acetic anhydride content of the mixture %	Quantity of citronellal esterified in %		Mean
	A	B	
95.0	28.3	32.0	30.2
75.9	51.9	55.8	53.9
53.6	70.0	68.8	69.4
31.2	59.4	—	59.4
15.25	43.7	41.8	42.5
Acetic acid of 97.2 %	30.9	30.9	30.9

When the duration of heating was increased from 2 hours to 3 hours, the amount of citronellal esterified was also increased. On using 95 % acetic anhydride, 40.1 % and with 52.9 % anhydride, 76.7 % of the citronellal was esterified.

Clearly the presence of acetic acid in the mixture favours the esterification of the citronellal. It might be concluded, that the citronellal which is not esterified, is nevertheless transformed in some other way, for instance into a terpene or similar body. In order to investigate this point larger quantities of the various products were prepared in the manner in which the estimation of the so called total geraniol content is carried out (Bericht of SCHIMMEL & Co April 1910, 155).

A portion of each product was examined by means of phthalic anhydride for the presence of alcohols, of another portion the saponification number was determined in the ordinary way and a third portion was acetylated by the indirect method, by heating 2 c.c. of the product with 2 c.c. of acetic anhydride of 95 % and 0.2 grm. of sodium acetate for 3 hours.

Acetic anhydride content of the mixture %	Number of c.c. of N/10 phthalic acid esterified	Saponification number	% acetylated according to indirect method
95.0	1.6	124.3 ¹⁾	67.7
53.6	—	219.0	13.4
31.2	1.0	180.3	19.8
15.25	—	129.0	28.4
Acetic acid of 97.2 %	1.3	98.0	38.6

Altogether the following amounts of citronellal were therefore acetylated.

95.0 %	$37.7 + 74.6 = 112.3$
53.6	$72.0 + 16.0 = 88.0$
31.2	$57.3 + 22.9 = 80.2$
15.25	$39.2 + 31.6 = 70.8$
Acetic acid of 97.2 %	$29.1 + 41.6 = 70.7$

The original use of 95 % anhydride therefore leads to partial formation of a diacetate, while the other acetic anhydride mixtures do not yield 100 %, which would indicate that these cause, in addition, the formation of hydrocarbons terpenes.

The presence of geraniol, like that of acetic acid, leads to a better esterification of the citronellal, as was the case in the estimations with phthalic anhydride.

While according to the indirect method with acetic anhydride of 95 % in two hours only 30.2 % of citronellal was esterified, mixtures with geraniol gave the following result:

Quantity of geraniol grm.	Quantity of citronellal grm.	Quantity esterified grm.
0.4940	1.1365	0.9478
0.8275	0.9465	1.3195
1.3390	0.8260	1.8740

Assuming that in the mixture 98.5 % of the geraniol is esterified,

¹⁾ This higher figure is most probably due to increased absorption of water, when working on a large scale.

as was found in the experiment with the pure substance, we can calculate that the following quantities of citronellal were esterified: 40.6, 53.3 and 67.2.

It further follows that no complete esterification is possible without the use of sodium acetate. Even by increasing the duration of heating to 10 hours only 93.3 % of the geraniol-citronellal mixture (1 c.c. to 4 c.c.) was esterified

Finally some estimations were made in which for every 2 c.c. of citronellal 0.2 grm. of sodium acetate (previously melted) was employed.

Acetic anhydride content of the mixture %	Citronellal esterified in %		Mean
	A	B	
95.0	95.0	95.3	95.1
88.3	93.5	—	93.5
75.9	90.0	92.4	91.2
52.9	84.4	—	84.4
31.2	54.5	—	54.5
15.25	40.2	—	40.2
Acetic acid of 97.2 %	30.3	31.4	30.8

Hence the presence of sodium acetate increased the quantity of acetylated citronellal in those mixtures which contained 53—95 % of anhydride, and did not affect the others. The rise of temperature due to the addition of the sodium acetate is not the cause of the improved acetylation in the former mixtures, since heating the mixture in a sealed tube without sodium acetate to the same temperature (about 149°) did not result in better esterification. The curve shows, however, that when sodium acetate is used, the presence of acetic acid is harmful, whereas, in the absence of sodium acetate, the acid has a favourable effect up to a certain concentration. It follows therefore that in using sodium acetate we induce a different reaction from that which occurs in the absence of this salt.

Buitenzorg, 27 May 1918.

Mathematics. — "*Observations on the expansion of a function in a series of factorials.*" II. By Dr. H. B. A. BOCKWINKEL.
(Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of September 29, 1918).

5. We now consider another example of NIELSEN's theorem, not belonging to the cases mentioned under N°. 4 of the remarks made in the preceding paragraph. We choose

$$\varphi(t) = \frac{1}{e^{i\theta} - t}$$

where θ is a number between 0 and 2π , not equal to one of these numbers. For this function we have

$$\lambda = -\infty, \quad \lambda' = 0,$$

the first of these equations resulting from the fact that $t=1$ is an ordinary point of the function. It is further easily found that the n^{th} derivative of $\varphi(t)$ satisfies the equation

$$\frac{\varphi^{(n)}(t)(1-t)^{\delta+n-1}}{\Gamma(\delta+n)} = \frac{n\Gamma(n)}{\Gamma(\delta+n)} \left(\frac{1-t}{e^{i\theta}-t} \right)^n \times \frac{(1-t)^{\delta-1}}{e^{i\theta}-t} \quad (21)$$

The modulus of the expression $\frac{1-t}{e^{i\theta}-t}$ is given by the relation

$$\left| \frac{1-t}{e^{i\theta}-t} \right| = 1 - \frac{2t(1-\cos\theta)}{1-t+\sqrt{1-2t\cos\theta+t^2}} \quad (22)$$

and it is not very difficult to see that it increases monotonously from the value 0 to 1, if t decreases from 1 to 0.

We divide the interval (0,1) of t into two parts, (0, ν) and (ν , 1), where ν is a number given by

$$\nu = n^{\delta_1-1} \quad (0 < \delta_1 < 1) \quad (23)$$

so that ν depends on n and approaches to zero as a limit when n becomes indefinitely large. The positive number δ_1 is at our disposal and will be fixed immediately. The maximum value of the modulus (22) then differs from unity by a quantity greater than

$$kn^{\delta_1-1}$$

if t lies in the second interval, k being a certain positive number, which is independent of n and t ; thus we have in this interval

$$\left| \frac{1-t}{e^{i\theta}-t} \right|^n < e^{-kn\delta_1}$$

so that the left-hand member of (21) for these values of t approaches *uniformly* to zero for $n = \infty$ (the factor $n \Gamma(n) : \Gamma(\delta + n)$ is only equivalent to $n^{1-\delta}$ and does therefore not affect this statement). The integral

$$\int_0^1 \frac{n \Gamma(n)}{\Gamma(\delta + n)} \left(\frac{1-t}{e^{i\theta}-t} \right)^n \frac{(1-t)^{\delta-1}}{e^{i\theta}-t} dt$$

consequently has zero for its limit if n increases indefinitely, however small the value of δ may be fixed.

For the interval $(0, \nu)$ we have, independently of t and n ,

$$\left| \frac{n \Gamma(n)}{\Gamma(\delta + n)} \left(\frac{1-t}{e^{i\theta}-t} \right)^n \frac{(1-t)^{\delta-1}}{e^{i\theta}-t} \right| < \frac{kn \Gamma(n)}{\Gamma(\delta + n)} < kn^{1-\delta},$$

where k is again a positive number not depending on n and t .¹⁾ Thus, considering (23), it follows

$$\left| \int_0^\nu \frac{n \Gamma(n)}{\Gamma(\delta + n)} \left(\frac{1-t}{e^{i\theta}-t} \right)^n \frac{(1-t)^{\delta-1}}{e^{i\theta}-t} dt \right| < kn^{1-\delta} \times \nu < kn^{-(\delta-\delta_1)}$$

We therefore need only choose δ_1 less than δ , to see that also the integral over the interval $(0, \nu)$ is zero for $n = \infty$. Thus the whole remainder (11) is zero for $n = \infty$, if only $R(x) > 0$, i.e., since $\lambda = -\infty$ and $\lambda' = 0$, if $R(x) > \lambda'$ and $R(x) > \lambda$. For these values of x the integral

$$\int_0^1 \frac{(1-t)^{x-1}}{e^{i\theta}-t} dt$$

can therefore be expanded into a series of factorials; and the theorem of NIELSEN holds in this case.

Again we take the example

$$\varphi(t) = \frac{1}{e^{i\theta}-t} + \frac{1}{(1-t)^\mu}, \quad \left(\begin{matrix} 0 < \theta < 2\pi \\ 0 < \mu < 1 \end{matrix} \right).$$

Here $\lambda' = 0$, on account of the first term, and $\lambda = \mu$, on account

¹⁾ We shall always, in future, denote by k a finite positive number, without always meaning the *same* number by this letter. This will not cause any ambiguity, because the exact value of k is of no importance in our reasonings. For the sake of clearness, however, we shall often mention the quantities on which k does *not* depend.

of the second. If $\varphi(t)$ were equal to the second term only, the integral (1) could be expanded into a series of factorials for $R(x) > \mu$ only, and this series would be *absolutely* converging for these values of x . Thus the *whole* function may also be represented by such a series for $R(x) > \mu$, i.e. for $R(x) > \lambda$ and $R(x) > \lambda'$, but the convergence is, on account of the first term, only *conditional* for $\lambda < R(x) < \lambda' + 1$. This, again, is exactly the proposition of NIELSEN.

6. If, in the first example of the foregoing paragraph, we account for the reason of the validity of this proposition, we infer that it is a consequence of the fact that the expression

$$\left| \frac{1-t}{e^{it} - t} \right|^n,$$

for a fixed value of $t > 0$, decreases with $1/n$ as the n -th power of a number less than 1, which causes that, in the integral (11), only an interval has to be considered which, in a proper manner, approaches to zero as n becomes infinite, so that the value of $R(x)$ for which expansion is possible can be depressed by unity. This suggests the idea that something of the kind might occur *as a rule*, if $\varphi(t)$ has $t=1$ for an *ordinary* point. The truth of this presumption is proved by the following investigation.

We again divide the interval (0,1) of t into two partial intervals, with the point $t=v$ as a common end-point, which is to approach ultimately to zero as n becomes indefinitely large; and we assume, as in the preceding paragraph, for v the value (23). Consider the circle, with centre v and passing through two fixed points C and C' lying on the circumference of the circle of convergence (0,1) of $\varphi(t)$, symmetrically with regard to the axis of real quantities, and in the interior of an arc $DA D'$ of the latter circle, which does not contain a singular point of $\varphi(t)$, D and D' being also conjugate points, whereas A is the point with the affix $t=1$. Then, from and after some value of n the value of v will be so small that the circle with centre v does not contain any singular point of $\varphi(t)$ in its interior and on its circumference; and at all points of the latter between the radii OD and OD' , including an arc EBE' of it (B being the point on that arc with argument zero), the modulus of $\varphi(t)$ will remain under a finite quantity K , independent of n and t . As regards points of the supplementary arc EFE' of circle (v), F being the point opposite to B , we may remark that $\varphi(t)$ there has a modulus no greater than

$$\overline{\varphi(1-v'')},$$

$\bar{\varphi}(t)$ means the natural majorant of $\varphi(t)$, and v'' the distance of the points D and E .

We further remark that the radius of the circle (v) is greater than $1 - v$, say $1 - v + v'$. It is evident that the numbers v' and v'' both approach to zero together with v , but that their ratios to the latter number remain finite and *different from zero*.

At a point P of the interval $(v, 1)$ we have, according to a well-known proposition

$$\left| \frac{\varphi^{(n)}(t)}{n!} \right| < \frac{M}{(1-t+v')^n},$$

if M is the greater of the numbers K and $\bar{\varphi}(1-v'')$. Instead of this inequality we may write

$$\left| \frac{(1-t)^{n-1} \varphi^{(n)}(t)}{n!} \right| < \left(\frac{1-t}{1-t+v'} \right)^{n-1} M v'^{-1},$$

or, since for $0 < t < 1$, $\frac{1-t}{1-t+v'} < \frac{1}{1+v'}$,

$$\left| \frac{(1-t)^{n-1} \varphi^{(n)}(t)}{n!} \right| < \frac{M v'^{-1}}{(1+v')^n} \quad \dots \quad (24)$$

With regard to $\bar{\varphi}(1-v'')$ the following remarks may be made. If, in the equivalence-equation

$$\lim a_n = n^{\lambda'}$$

the quantity λ' is no less than -1 , we have, according to the proposition of Cesàro, for any fixed $\delta > 0$,

$$\lim_{v''=0} (v'')'^{1+\delta} \bar{\varphi}(1-v'') = 0,$$

and hence, in virtue of the remark made above on the relation between v'' and v ,

$$\lim_{v=0} v^{\lambda'+1+\delta} \bar{\varphi}(1-v'') = 0$$

and further

$$\lim_{v=0} v^{\lambda'+1+\delta} \times M = 0$$

since, as a matter of course, the expression $K \times v^{\lambda'+1+\delta}$ has, too, zero for its limit.

Thus we may write for (24), in connection with the assumption (23) and the finite, not disappearing ratio between v and v'

$$\begin{aligned} \left| \frac{(1-t)^{n-1} \varphi^{(n)}(t)}{\Gamma(n-1)} \right| &< \frac{kn^k}{(1+kn^{\delta_1}-1)^n} \\ &< kn^k e^{-n^{\delta_1}}, \end{aligned}$$

where k is again a positive number not depending on n and t . Hence, corresponding to any fixed positive quantity ε chosen arbitrarily small, there is an integral number N , such that the left-hand member of the latter inequality is less in value than ε , for every value of t in the interval $(v, 1)$, if only $n > N$. For these values of n we have therefore

$$\left| \int_0^1 \frac{(1-t)^{x+n-1} \varphi^{(n)}(t)}{\Gamma(x+n)} dt \right| < k\varepsilon \int_0^1 (1-t)^{R(x)} dt < k\varepsilon$$

if $R(x) > -1$. For any such value of x , i.e. a fortiori for $R(x) > \lambda'$, since λ' was supposed greater than -1 , the part of the integral (11) taken over the interval $(v, 1)$ has zero for its limit for $n = \infty$.

For the integration over the remaining interval $(0, v)$ we apply the mode of treatment of § 3 and the inequality (17). According to the latter there is, corresponding to any fixed σ and ε , chosen as small as we please, an integer N such that we have *uniformly* in the interval $(0, 1)$, and hence in $(0, v)$,

$$\left| \frac{\varphi^{(n)}(t) (1-t)^{\lambda'+\sigma+n+1}}{\Gamma(\lambda'+\sigma+n+1)} \right| < \varepsilon, \text{ if } n > N.$$

For the interval $(0, v)$ it follows from this that, for $n > N$

$$\left| \frac{\varphi^{(n)}(t) (1-t)^{x+n-1}}{\Gamma(x+n)} \right| < k\varepsilon n^{1-R(x)+\lambda'+\sigma}$$

thus

$$\left| \int_0^v \frac{\varphi^{(n)}(t) (1-t)^{x+n-1}}{\Gamma(x+n)} dt \right| < k\varepsilon n^{-R(x)+\lambda'+\sigma+\sigma_1}$$

If now $R(x) > \lambda'$, we can have chosen the numbers σ and σ_1 so small that $R(x)$ is also greater than $\lambda' + \sigma + \sigma_1$, and in this case we infer from the latter inequality that the integral over the interval $(0, v)$, too, has zero as a limit for $n = \infty$, if $R(x) > \lambda'$. Thus the theorem of NIELSEN has been proved, in case $t = 0$ is an ordinary point of the function $\varphi(t)$.

If a function $\varphi(t)$ has the point $t = 1$ for its only singular point on the circumference of the circle of convergence $(0, 1)$, and if, moreover, it satisfies the conditions of HADAMARD, i.e. if it is continuous and "à écart fini" on that circumference, or if a certain derivative of negative order $-\omega$ has this property, then we always have

$$\omega = \lambda = \lambda' + 1,$$

and the theorem of NIELSEN has ceased having anything particular.

known truth that the convergence of (25) is a consequence of these two facts. The same thing would hold with regard to the series

$$\sum \frac{a_n}{\varphi(n)}$$

if

$$\lim_{n \rightarrow \infty} \varphi(n) = n^{\lambda' + \theta}, \text{ and } \lim_{n \rightarrow \infty} \Delta \varphi(n) = n^{\lambda' + \theta - 1}.$$

Therefore, in the statement of the above theorem such a series may be chosen as well. We further remark that λ' , which was hitherto supposed to be greater than -1 , may also be *less* than the latter number: the theorem of NIELSEN, in the particular case demonstrated in § 6, keeps its validity for those values of λ' , though we should have to apply our reasonings to an integral of the form (8) (in a footnote of § 1) in the latter case.

By substituting $t = t' e^{i\varphi}$ in the power-series for $\varphi(t)$ we obtain the more general theorem:

If the coefficients a_n of a power-series in the letter t are equivalent to $n^{\lambda'}$ for $n = \infty$, the function $\varphi(t)$ represented by that series has, on the circumference of its circle of convergence (being the circle (0,1), singularities at all points where the series

$$\sum \frac{a_n t^n}{n^{\lambda' + \theta}} \quad (0 < \theta < 1)$$

diverges. We may add that this theorem already holds, if only the *upper limit* of the coefficients a_n is, in the sense of equation (14'), equivalent to $n^{\lambda'}$ for $n = \infty$.

Finally we observe that the reverse of the proposition does not hold: if the series (25) converges, the point $t = 1$ need not be an ordinary point. To make this clear we need only think of the case that the coefficients a_n differ from zero only for values of n lying at a certain distance from each other; it may happen then that the series (25) converges absolutely, but the function $\varphi(t)$ has its whole circle of convergence as a singular line.

8. As already remarked, we doubt of the *general* validity of NIELSEN's theorem, though we are not in a position to furnish a case of the non-validity. It is our opinion that, if $\lambda' < \lambda < \lambda' + 1$, there will be cases in which the integral (1) cannot, for all values of $R(x) > \lambda$, be expanded into a series of factorials. On the other hand we can prove that such an expansion is not possible for any value of $R(x) < \lambda$, which is a thing not immediately evident if λ lies between λ' and $\lambda' + 1$.¹⁾

¹⁾ If $R(x) < \lambda'$, the impossibility is at once evident, since the series-terms have not zero for their limits then.

Suppose the series (25) to converge for $\theta > \theta_1$ and to diverge for $\theta < \theta_1$, and, consequently, the series (26) to converge for $R(x) > \lambda' + \theta_1$, and to diverge for $R(x) < \lambda' + \theta_1$, then the integral (1) will, at any case, not admit an expansion into a series of factorials for any value of $R(x) < \lambda' + \theta_1$. We now shall prove that for any positive δ , taken as small as we please,

$$\lim_{t=1} (1-t)^{\lambda'+\theta_1+\delta} \varphi(t) = 0^+)$$

so that $\lambda < \lambda' + \theta_1$; by this the required proof will have been established.

For the sake of brevity we write

$$\lambda' + \theta_1 + \delta = \alpha.$$

Consider the derivative of negative order $-\alpha$ of $\varphi(t)$, which according to the definition of RIEMANN²⁾, is given by

$$D^{-\alpha} \varphi(t) = \frac{1}{\Gamma(\alpha)} \int_0^t (t-u)^{\alpha-1} \varphi(u) du = t^\alpha \psi(t),$$

then $\psi(t)$ is a function regular at $t=0$ with the same circle of convergence (0,1) as $\varphi(t)$ has; its expansion into a power-series is

$$\psi(t) = \sum_{n=0}^{\infty} \frac{n! a_n t^n}{\Gamma(\alpha+n+1)} \quad \dots \quad (27)$$

From this formula it may be derived that $\psi(t)$ remains finite for $t=1$, in virtue of the initial hypothesis.

Conversely we have

$$\varphi(t) = D^\alpha [t^\alpha \psi(t)].$$

First, let

$$\lambda' + \theta_1 < 1.$$

Then we may choose δ so small that also $\alpha < 1$ and write

$$\begin{aligned} \varphi(t) &= D^{\alpha-1} D[t^\alpha \psi(t)]^3) = D^{\alpha-1} [\alpha t^{\alpha-1} \psi(t) + t^\alpha \psi'(t)] = \\ &= \frac{1}{\Gamma(1-\alpha)} \int_0^t (t-u)^{-\alpha} [\alpha \psi(u) u^{\alpha-1} + \psi'(u) u^\alpha] du \end{aligned} \quad (28)$$

Now $\psi(u)$ is, in the range $0 < u < 1$, finite and thus less than a certain number g . Hence

¹⁾ Or for negative values of $\lambda' + \theta_1$, $\lim_{t=1} (1-t)^{\lambda'+\theta_1+n+\delta} \varphi^{(n)}(t) = 0$, if n is such that $\lambda' + \theta_1 + n > 0$.

²⁾ See among others BOREL, *Leçons sur les séries à termes positifs*, p. 75.

³⁾ Properly speaking it should be $D \cdot D^{\alpha-1}$, but this operation, in the present case, is equal to $D^{\alpha-1} \cdot D$, since the subject of the operation is zero for $t=0$.

$$\left| \int_0^t \psi(u) u^{\alpha-1} (t-u)^{-\alpha} du \right| < g \int_0^t u^{\alpha-1} (t-u)^{-\alpha} du$$

or, substituting $u = tv$

$$\left| \int_0^1 \psi(u) u^{\alpha-1} (t-u)^{-\alpha} du \right| < g \int_0^1 v^{\alpha-1} (1-v)^{-\alpha} dv,$$

so that the integral in the left-hand member of this inequality remains finite for all values of t in the closed interval $(0,1)$. Further we divide the second integral on the right-hand side of (28) as follows, supposing $t > \frac{1}{2}$,

$$\int_0^t \psi'(u) u^{\alpha} (t-u)^{-\alpha} du = \int_0^{t-(1-t)} + \int_{t-(1-t)}^t$$

To the first of these two integrals we apply the second mean value theorem, which is allowed, because the expression $u^{\alpha} (t-u)^{-\alpha}$ increases monotonously in the interval in question. We obtain

$$\int_0^{t-(1-t)} \psi'(u) u^{\alpha} (t-u)^{-\alpha} du = (2t-1)^{\alpha} (1-t)^{-\alpha} [\psi(2t-1) - \psi(\beta)]$$

where β is a number in the interval $(0, 2t-1)$. This part of the integral, as $\varphi(t)$ remains within finite limits, is therefore for $t=1$ at most equivalent to $(1-t)^{-\alpha}$. In order to infer the same thing with regard to the second integral, we make use of the fact that

$$\lim_{t \rightarrow 1} (1-t)^n \psi^{(n)}(t) = 0, \quad (n = 1, 2, \dots) \quad (29)$$

We shall prove this at once; it should not be thought that it is a consequence of the proposition mentioned in a footnote of § 1: it follows solely from the convergence of the series (27) for $t=1$.

If we assume, for a moment, the formula to be true, we have for the whole interval $0 < \alpha < 1$, if K is a certain positive number, not depending on u ,

$$\psi'(u) < \frac{K}{1-u},$$

and so, in the interval of integration $2t-1 < u < t$

$$\psi'(u) < \frac{K}{1-t},$$

from which it follows

$$\left| \int_{2t-1}^t \psi(u) u^{\alpha} (t-u)^{-\alpha} du \right| < \frac{K}{1-t} \int_{2t-1}^t (t-u)^{-\alpha} du = K(1-t)^{-\alpha},$$

so that this integral, too, is for $t=1$ at most of order $(1-t)^{-\alpha}$. The same holds therefore for the function $\varphi(t)$, and since α may be supposed arbitrarily little greater than $\lambda' + \theta_1$, we have certainly for every $\delta > 0$

$$\lim_{t=1} (1-t)^{\lambda'+\theta_1+\delta} \varphi(t) = 0$$

and thus, as we proposed to show

$$\lambda < \lambda' + \theta_1.$$

Secondly, let $\lambda' + \theta_1$ lie between the integers $p-1$ and p ; we may choose δ so small that the same holds for $\lambda' + \theta_1 + \delta = \alpha$. We write

$$\alpha = p-1 + \alpha' \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

so that

$$0 < \alpha' < 1 \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

In this case we have the following reduction

$$\begin{aligned} \varphi(t) &= D^{\alpha'-1} D^p [t^{\alpha} \psi(t)]^1) \\ &= D^{\alpha'-1} \left[\Gamma(\alpha' + p) \sum_m^p \frac{p_m t^{\alpha'+m-1} \psi^{(m)}(t)}{\Gamma(\alpha' + m)} \right] \end{aligned}$$

Owing to (31) we may, as in the former case, using here the inequality (29) for $n=m$, prove that the expression

$$D^{\alpha'-1} [t^{\alpha'+m-1} \psi^{(m)}(t)]$$

is at most equivalent to $(1-t)^{-(\alpha'+m-1)}$ and thus $\varphi(t)$, as m is no greater than p , is of an order no higher than that of $(1-t)^{-(\alpha'+p-1)}$, that is, according to (30), of the order $(1-t)^{-\alpha}$. Thus the required result is obtained completely.

9. We now give a proof of the proposition used in the preceding paragraph. It may be stated as follows:

If the expansion in a power-series of a function $\varphi(t)$ converges at the point $t=1$ of the circle of convergence $(0,1)$, we have for all positive integral values of n

$$\lim_{t=1} (1-t)^n \varphi^{(n)}(t) = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad (32)$$

This proposition, of course, ceases to have a particular meaning,

¹⁾ Properly speaking it should be $D^p D^{\alpha'-1}$, but this comes to the same thing as $D^{\alpha'-1} D^p$, because $t^{-(p-1)}$ -times the subject of operation is zero for $t=0$

if $t = 1$ is not a singular point of $\varphi(t)$, but if it is, the proposition is not a matter of course.

Since, if the coefficients of the power-series in question are complex, the two series formed separately by means of the real and of the imaginary parts of those coefficients must both converge, we may without loss of generality suppose the coefficients to be real quantities. We then consider, together with the function

$$\varphi(t) = a_0 + a_1 t + \dots + a_n t^n + \dots$$

the function

$$f(t) = \frac{\varphi(t)}{1-t} = \sum_{n=0}^{\infty} s_n t^n \quad \dots \quad (33)$$

where

$$s_n = \sum_{p=0}^n a_p$$

Since s_n , as n becomes indefinitely large, approaches to a definite limit s , the series (33) behaves, so far as regards its terms for large values of n , as the power-series of the function

$$\frac{s}{1-t},$$

and according to the reasoning of CESARO we have not only

$$\lim_{t \rightarrow 1} \left[f(t) : \frac{1}{1-t} \right] = s,$$

but also

$$\lim_{t \rightarrow 1} \left[f^{(n)}(t) : \frac{n!}{(1-t)^{n+1}} \right] = s. \quad \dots \quad (34)$$

Further, from n -fold differentiation of the identity

$$\varphi(t) = (1-t)f(t)$$

we obtain the new one

$$\frac{(1-t)^n \varphi^{(n)}(t)}{n!} = \frac{(1-t)^{n+1} f^{(n)}(t)}{n!} - \frac{(1-t)^n f^{(n-1)}(t)}{(n-1)!}.$$

The limit of the right-hand side of the latter equation for $t = 1$, is, by (34), equal to zero for all positive integral n -values, and the required formula (32) has thus been proved.

By substituting $t = t' e^{\epsilon}$ we obtain: *If the expansion in a power-series of a function $\varphi(t)$ converges at the point $t = e^{\epsilon}$ of its circle of convergence $(0,1)$, then, for all positive integral values of n and for real values of t' , we have*

$$\lim_{\epsilon \rightarrow 0} \frac{(1-t')^n \varphi^{(n)}(t' e^{\epsilon})}{n!} = 0$$

Physics. - "*Deduction of the third virial coefficient for material points (eventually for rigid spheres), which exert central forces on each other*". By Prof. W. H. KEESOM and Mrs. C. NORDSTRÖM-VAN LEEUWEN. (Communication N°. 3a from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of September 29, 1918).

§ 1. *Introduction.* This paper contains a continuation of the research, started in Supplement N°. 24a of the communications from the physical laboratory at Leiden (These Proceed., June 1912), in which the existing data on the virial coefficients B and C in KAMERLINGH ONNES' ¹⁾ empirical equation of state ²⁾

$$pv = A \left\{ 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5} \right\} \quad . \quad . \quad . \quad (1)$$

were compared with formulae, which can be derived for those virial coefficients starting from different hypotheses on the structure and mutual actions of the molecules.

In the preceding ³⁾ papers on this subject especially the second virial coefficient B was considered. In the present communication the third virial coefficient C will be treated. To that purpose there will be derived in § 2 a general expression for this third virial-coefficient for material points (eventually rigid spheres) which exert central forces on each other. In § 3 C is calculated for the case that the molecules (rigid spheres) do not attract each other. The thus obtained value is at the same time the first term of a series of ascending powers of T^{-1} , in which C can be developed for the case that the attraction between the molecules varies with the distance according to a law $r^{-(q+1)}$ (potential energy proportional to r^{-q}). In Comm. N°. 3b the development will be given for the next two terms of this series for the laws of force r^{-5} and r^{-6} .

These calculations had already been started, when the importance

¹⁾ H. KAMERLINGH ONNES. Comm. Leiden N°. 71; These Proceed. June 1901. Comm. N°. 74; Arch. Néerl. (2) 6 (1901), p. 874.

²⁾ Comp. H. KAMERLINGH ONNES and W. H. KEESOM. Die Zustandsgleichung. Math. Enz. V 10, Leiden Suppl. N°. 23 (1912), § 36.

³⁾ W. H. KEESOM. Comm. Leiden Suppl. N°. 24b (These Proc. June 1912), 25 (Sept. 1912), 26 (Oct. 1912), 39a (Sept. 1915), 39b (Oct. 1915), W. H. KEESOM and Miss C. VAN LEEUWEN, Leiden Suppl. N°. 39c (March 1916).

of the theoretical investigation of C was increased by a remark of HOLST¹⁾, who concluded from the investigations on the compressibility, that for substances as water and ammonia the molecules of which possess an electric moment such as that of a doublet, C is negative in the considered temperature interval, while for normal substances C is found positive. A calculation of C for molecules whose attraction is equivalent to that of a doublet at their centre and a comparison of this result e.g. with that for molecules like those considered in this communication or with that for quadruplets will have to prove whether really the deviating behaviour of C for the substances mentioned must be ascribed to the molecule possessing an electric moment such as that of a doublet. The calculation of C for doublets and quadruplets must however be postponed till later.

§ 2. *Deduction of a general expression for the third virial coefficient for material points which exert central forces on each other.* This deduction is analogous to that of the second virial coefficient for this case given in Suppl. Leiden N°. 24b § 5, which paper may be referred to with respect to the method and the notations already used there.

Definition of the macro-complexion.

Generalizing (23) l.c., the n_{11} molecules in $dv_1 dv_1$ will now be distinguished in:

n_{11a} single molecules (with no other molecule within their sphere of action),

n_{11b_1} molecules belonging to pairs with a mutual distance between r_1 and $r_1 + dr_1$,

n_{11b_2} molecules belonging to pairs with a mutual distance between r_2 and $r_2 + dr_2$

etc.

$n_{11c_{1,1}}$ molecules belonging to sets of three, the mutual distances of which are resp. lying between r_1 and $r_1 + dr_1$, r_2 and $r_2 + dr_2$, r_3 and $r_3 + dr_3$,

etc.

(2)

We define the group macro-complexion²⁾ by giving the numbers $n_{11a} \dots$ without attending to any individuality of the molecules.

The individual macro-complexion²⁾ is defined as follows:

n_{11a} definitely indicated molecules are single,

.....

¹⁾ G. HOLST. Leiden Suppl. N°. 41f. These Proceed. Jan. 1917, HOLST points there also to the importance of the knowledge of the behaviour of C for the determination of the molecular weight from the gas density, comp. also H. KAMERLINGH ONNES and W. H. KEESOM. Die Zustandsgleichung. Leiden Suppl. N°. 23 §§ 77—80.

²⁾ Comp. Leiden Suppl. N°. 24a § 2 (These Proceed. June 1912).

n_{11c123} definitely indicated molecules belong to sets of three, the mutual distances of which are r_1 (dr_1), r_2 (dr_2), r_3 (dr_3), etc.

Here we have not yet fixed in what way these n_{11c123} molecules are divided into sets of three, and which two molecules of each set of three have the distance r_1 (dr_1) and which that r_2 (dr_2).

The number of individual macro-complexions contained in the group macro-complexion is:

$$\frac{n!}{n_{11a}! n_{11b}! \dots n_{11c123}! \dots} \quad (3)$$

The micro-complexion is defined in the way mentioned Suppl. Leiden N^o. 24b § 5.

Number of micro-complexions in the individual macro-complexion:

In dv_1 n_1 molecules are to be placed. First we place the n_{1a} single molecules. There are at the disposal of the

$$\begin{aligned} 1^{\text{st}} \text{ molecule:} & \quad \kappa \text{ places} \\ 2^{\text{nd}} \text{ ,,} & \quad \kappa \left\{ 1 - \frac{b}{dv_1} \right\} \text{ ,,} \end{aligned} \quad \text{where} \quad b = \frac{4}{3} \pi r^3 \quad (4)$$

has been written for the volume of the sphere of action,

$$3^{\text{rd}} \text{ molecule:} \quad \kappa \left\{ 1 - 2 \frac{b - \beta}{dv_1} \right\} \text{ places:}$$

(here an amount β has been subtracted from b because of the occurrence of a certain number of cases in which the spheres of action of the molecules 1 and 2 partially overlap each other);

$$4^{\text{th}} \text{ molecule:} \quad \kappa \left\{ 1 - 3 \frac{b - 2\beta}{dv_1} \right\} \text{ places, etc.}$$

Thus the distribution of the n_{1a} molecules gives for the number in question the factor:

$$\kappa^{n_{1a}} \left\{ 1 - \frac{b}{dv_1} \right\} \left\{ 1 - 2 \frac{b - \beta}{dv_1} \right\} \left\{ 1 - 3 \frac{b - 2\beta}{dv_1} \right\} \dots \left\{ 1 - (n_{1a} - 1) \frac{b - (n_{1a} - 2)\beta}{dv_1} \right\}. \quad (5)$$

Calculation of β : Call the hatched spherical segment $s(r_{12})$.

Probability that molecule 2 has a distance r_{12} from 1:

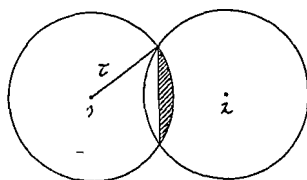


Fig. 1.

$$\frac{4\pi r^2 dr_{12}}{dv_1}$$

From this we find:

$$\beta = \int_0^{2r} \frac{4\pi r^2 dr_{12}}{dv_1} s(r_{12}).$$

As

$$s(r_{12}) = \frac{2\pi}{3} \left\{ \tau^2 - \frac{3}{4} \tau^2 r_{12} + \frac{1}{16} r_{12}^3 \right\},$$

we get

$$\beta = \frac{1}{64} \frac{b^2}{dv_1} \dots \dots \dots (6)$$

Then we place the n_{1b1} molecules:

At the disposal of the first molecule are:

$$\kappa \left\{ 1 - n_{1a} \frac{b}{dv_1} \right\} \text{ places,}$$

where a term with β has been omitted, being negligible for the order of magnitude wanted;

of the 2nd molecule:

here we must take into consideration that of the space at the disposal of this molecule in the mean a certain part is occupied by one of the n_{1a} molecules; doing this we find for the number of places at the disposal of the 2nd molecule:

$$\kappa \frac{4\pi r_1^2 dr_1}{dv_1} \left\{ 1 - n_{1a} \frac{\pi r_1 (\tau^2 - \frac{1}{12} r_1^2)}{dv_1} \right\} \text{ places;}$$

of the 3rd molecule:

$$\kappa \left\{ 1 - (n_{1a} + 2) \frac{b}{dv_1} \right\} \text{ places,}$$

etc.

Thus the placing of all the n_{1b} molecules (comp. Suppl. Leiden N^o. 24b § 5) gives us the factor:

$$\kappa^{n_{1b}} \prod_{dr} \frac{n_{1b1}!}{\frac{n_{1b1}}{2} \left(\frac{n_{1b1}}{2} \right)!} \left\{ 1 - n_{1a} \frac{b}{dv_1} \right\} \left\{ 1 - (n_{1a} + 2) \frac{b}{dv_1} \right\} \dots \dots \dots (7)$$

$$\left(\frac{4\pi r_1^2 dr_1}{dv_1} \right)^{\frac{n_{1b1}}{2}} \left\{ 1 - n_{1a} \frac{\pi r_1 (\tau^2 - \frac{1}{12} r_1^2)}{dv_1} \right\}^{\frac{n_{1b1}}{2}}$$

Now we are going to place the n_{1c123} definitely fixed molecules, belonging to sets of three, with the mutual distances r_1 (dr_1), r_2 (dr_2), r_3 (dr_3). In $\frac{n_{1c123}!}{\left(\frac{n_{1c123}}{3} \right)!}$ ways these molecules can be combined to such

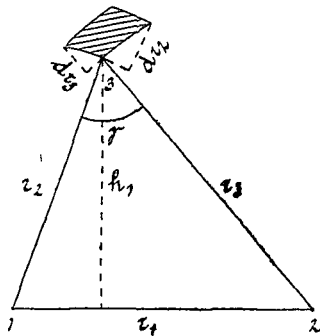
sets, where it has been taken into consideration that 3 fixed molecules can form such a set in 3! different ways viz. 1st with distance from molecule 1 to molecule 2 = r_1 , distance 2 to 3 = r_2 , distance 1 to 3 = r_3 ; 2nd distance 1 to 2 = r_1 , distance 2 to 3 = r_2 , distance 1 to 3 = r_3 ; etc.

Now we calculate the number of places at the disposal of a definite set of three, going only until the required order of magnitude:

molecule 1: \propto places

molecule 2: $\propto \frac{4\pi r_1^2 dr_1}{dv_1}$ "

molecule 3: at the disposal of this molecule is the space described by the hatched parallelogram in revolving about the line 1, 2.



Contents: $\frac{dr_2 dr_3}{\sin \gamma} \cdot 2\pi h_1$.

The number of places in question is

therefore $\frac{\propto \cdot 2\pi \frac{r_2 r_3}{r_1} dr_2 dr_3}{dv_1}$, where the relation $r_1 h_1 = r_2 r_3 \sin \gamma$

Fig. 2.

has been used.

The n_{1c} molecules thus give the factor:

$$\propto n_{1c} \prod_{dr_1 dr_2 dr_3} \frac{n_{1c123}}{\left(\frac{n_{1c123}}{3}\right)!} \left(\frac{8\pi^2 r_1 r_2 r_3 dr_1 dr_2 dr_3}{dv_1^2} \right)^{\frac{n_{1c123}}{3}} \quad (8)$$

where the sign of multiplication has to be extended over all possible combinations r_1, r_2, r_3 .

The number of micro-complexions in the group macro-complexion, W , is now obtained by multiplication of (3) by the product of the factors (5), (7), and (8), taken for each of the volume elements dv_1, dv_2 , etc.

From this we derive

$$\begin{aligned} \ln W = & -n_{11a} \ln n_{11a} \dots - n_{11b1} \ln n_{11b1} \dots - n_{11c123} \ln n_{11c123} \\ & - \sum_{dv} \frac{1}{2} n_{1a}^2 \frac{b}{dv_1} - \sum_{dv} \frac{1}{2} n_{1a} n_{1b} \frac{b}{dv_1} + \sum_{dv} \frac{1}{8} n_{1a}^3 \frac{\beta}{dv_1} - \\ & - \sum_{dv} \frac{1}{6} n_{1a}^2 \frac{b^2}{dv_1^2} + \sum_{dv} \sum_{dr} \left[\frac{n_{1b1}}{2} \ln n_{1b1} - \frac{n_{1b1}}{2} + \right. \\ & \left. + \frac{n_{1b1}}{2} \ln \frac{4\pi r_1^2 dr_1}{dv_1} - \frac{n_{1b1} n_{1a}}{2 dv_1} \pi r_1 (r^2 - \frac{1}{2} r_1^2) \right] + \\ & + \sum_{dv} \sum_{d_1 d_2 d_3} \left[\frac{2}{3} n_{1c123} \ln n_{1c123} - \frac{2}{3} n_{1c123} + \right. \\ & \left. + \frac{n_{1c123}}{3} \ln \frac{24\pi^2 r_1 r_2 r_3 dr_1 dr_2 dr_3}{dv_1^2} \right]. \end{aligned} \quad (9)$$

The state of equilibrium:

As in Suppl. Leiden N°. 24b § 5: — $\varphi(r_1)$ may represent the potential energy with respect to the mutual forces for a pair of molecules with the mutual distance r_1 , where for $r_1 > \tau$ $\varphi(r_1) = 0$. For a set of three molecules the total potential energy is:

$$-\Phi(r_1, r_2, r_3) = -\{\varphi(r_1) + \varphi(r_2) + \varphi(r_3)\}, \quad (10)$$

where we assume, that the attraction between two molecules is not changed by the presence of a third molecule.

The condition for the energy is then:

$$u = \sum_{dv} \sum_{dw} n_{11} u_{11} - \frac{1}{2} \sum_{dv} \sum_{di} n_{1i} \varphi(r_1) - \frac{1}{3} \sum_{dv} \sum_{dr_1 dr_2 dr_3} n_{123} \Phi(r_1, r_2, r_3) = \text{const.} \quad (11)$$

For the state of equilibrium we then find after some reductions e.g. for the distribution of the molecules into single molecules, into molecules belonging to pairs, into molecules belonging to sets of three, with the required degree of approximation:

$$\left. \begin{aligned} n_a &= n \left\{ 1 - \frac{n}{v} P + \frac{n^2}{v^2} (-bP + 2P^2 + R - S) \right\}, \\ n_b &= \frac{n^2}{v} \left\{ P + \frac{n}{v} (bP - 2P^2 - R) \right\}, \\ n_c &= \frac{n^3}{v^2} S, \end{aligned} \right\} \quad (12)$$

where passing from summations to integrals:

$$\left. \begin{aligned} P &= \int_0^\tau e^{h\varphi(r)} 4\pi r^2 dr, \\ R &= \int_0^\tau e^{h\varphi(r)} (\tau^2 - \frac{1}{12} r^2) 4\pi^2 r^3 dr, \\ S &= \iiint e^{h\Phi(r_1, r_2, r_3)} 24\pi^3 r_1 r_2 r_3 dr_1 dr_2 dr_3. \end{aligned} \right\} \quad (13)$$

Deducing further the entropy, then the free energy ψ and from this the pressure, we finally find for the second virial coefficient:

$$B = \frac{1}{2} n(b - P), \quad (14)$$

analogous with Suppl. Leiden N°. 24b equation (40), and for the third:

$$C = \frac{1}{3} n^2 \left(\frac{1}{3} b^2 - 3bP + 3P^2 + 3R - 2S \right) \quad (15)$$

§ 3 *Development for rigid spheres without attraction.* As first

case for the development of C according to (15) and (13) we put

$$\varphi(r) = -\infty \quad \text{for } r < \sigma \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\varphi(r) = 0 \quad \text{for } \tau > r > \sigma \quad . \quad . \quad . \quad . \quad . \quad (17)$$

with which case we have to do when we consider rigid spheres with diameter σ which do not attract each other. We must then obtain the same result found for the first time in another way by JÄGER ¹⁾ as a second volume correction in VAN DER WAALS' equation of state. Notwithstanding this the calculation based upon the general expression (15) we have derived above, will be discussed here rather in details, because the term obtained here may be considered as the first of the development of C in ascending powers of h for $\varphi(r) = cr^{-q}$. The calculation of the following in the next communication may then be discussed more shortly.

As also for $r > \tau$ $\varphi(r) = 0$, the quantity τ must evidently vanish from the result.

We easily find that for $\varphi(r)$ according to (16) and (17):

$$\left. \begin{aligned} P_1 &= \frac{4}{3} \pi (\tau^3 - \sigma^3) \\ R_1 &= \frac{17}{18} \pi^2 \tau^6 - \pi^2 \tau^2 \sigma^4 + \frac{1}{18} \pi^2 \sigma^6 \end{aligned} \right\} \quad . \quad . \quad . \quad . \quad . \quad (18)$$

where the quantities P and R have been marked with an index 1 in order to indicate that these values are the first terms in the development in ascending powers of h for $\varphi(r) = cr^{-q}$.

For the calculation of $S_1 = \iiint 24\pi^2 r_1 r_2 r_3 dr_1 dr_2 dr_3$ it may be useful that $2\pi \iint \frac{r_2 r_3}{r_1} dr_2 dr_3$ represents the space at the disposal of molecule 3, when of the set of three the molecules 1 and 2 have already taken their places.

The mutual distances may be thus numbered that

$$r_1 \geq r_2 \geq r_3.$$

Now two parts of the domain of integration must be distinguished:

1. $2\tau > r_1 > \tau$.

The sets of three belonging to this part must still be subdivided into:

a. $r_1 - \tau > \sigma$,

b. $r_1 - \tau < \sigma$.

We suppose namely $\tau > 2\sigma$, so that the case $r_1 < 2\sigma$ need not be considered here.

Let us consider in details case a:

¹⁾ G. JÄGER. Wien Sitz.-Ber. [2a] 105 (1896), p. 15, 97. For further literature see H. KAMERLINGH ONNES and W. H. KEESOM. Die Zustandsgleichung § 40a.

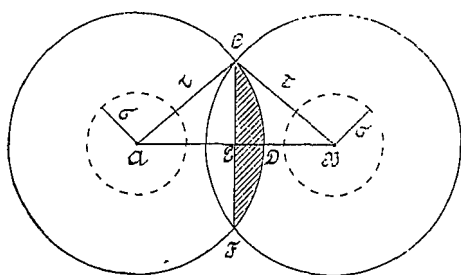


Fig. 3.

Multiplication by $12 \pi r_1^2 dr_1$ and integration between $\tau + \sigma$ and 2τ gives for the contribution to S_1 :

$$\frac{\pi^2}{12} \{17\tau^6 - 30\tau^5\sigma - 3\tau^4\sigma^2 + 20\tau^3\sigma^3 + 3\tau^2\sigma^4 - 6\tau\sigma^5 - \sigma^6\}.$$

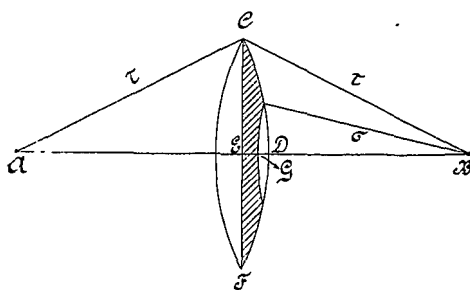


Fig. 4.

to r_1 between τ and $\tau + \sigma$ this gives:

$$\frac{\pi^2}{12} \{30\tau^5\sigma + 3\tau^4\sigma^2 - 20\tau^3\sigma^3 - 39\tau^2\sigma^4 + 6\tau\sigma^5 + 3\sigma^6\}.$$

2. $\tau > r_1 > \sigma$.

This part too must again be subdivided, this time into:

a. $\tau > r_1 > 2\sigma$,

b. $2\sigma > r_1 > \sigma$.

a. The space disposable for molecule 3 (the hatched part in Fig. 5) is now bounded by: sphere AB with radius r_1 (as $r_2 \leq r_1$), plane CDG (as $r_2 \leq r_1$), and sphere BF with radius σ (sphere of distance of molecule 2). Contribution to S_1 after integration with respect to r_1 between 2σ and τ :

$$\frac{\pi^2}{12} \{5\tau^6 - 32\tau^5\sigma + 18\tau^4\sigma^2 - 136\sigma^6\}.$$

b. Space at the disposal of molecule 3 bounded in the same way as sub a; now sphere BF cuts, however, the plane CDE , so that only an annular space (hatched) is left.

¹⁾ In drawing this figure the supposition $\tau < 2\sigma$ has been neglected.

Contribution to S_1 after integration between σ and 2σ :

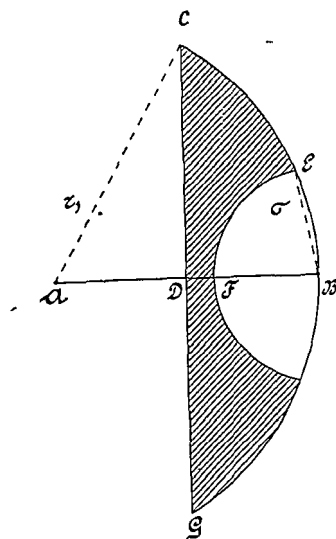


Fig. 5.

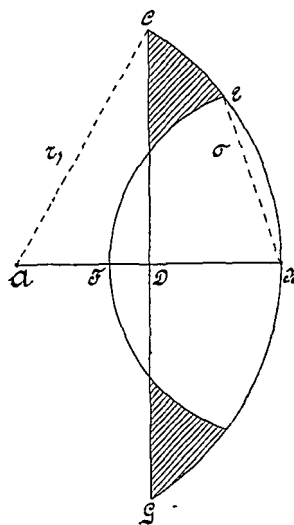


Fig. 6.

$$\frac{\pi^2}{12} \cdot 162 \sigma^6.$$

Adding the four contributions we find:

$$S_1 = \frac{\pi^2}{6} \{11\tau^6 - 16\tau^3\sigma^3 - 9\tau^2\sigma^4 + 14\sigma^6\}. \quad (19)$$

From (14) we see that (ascribing to the index 1 the same significance as above):

$$\begin{aligned} C_1 &= \frac{1}{3} n^2 \cdot \frac{5}{6} \pi^2 \sigma^6 \\ &= \frac{5}{8} n^2 \cdot \left(\frac{4}{3} \pi \sigma^3\right)^2. \end{aligned} \quad (20)$$

This result agrees with that first found by JÄGER l.c. Introducing namely the quantity b_w from the equation of state of VAN DER WAALS:

$$b_w = n \cdot \frac{1}{2} \cdot \frac{4}{3} \pi \sigma^3,$$

we find for (20): $C_1 = \frac{5}{8} b_w^2$, the agreement of which result with that of JÄGER is e.g. evident by comparison with Die Zustandsgleichung l.c. § 40a.

Physics. — “*Development of the third virial coefficient for material points (eventually rigid spheres), which exert central attracting forces on each other proportional with r^{-5} or r^{-6} .*” By Prof. W. H. KEESOM and Mrs C. NORDSTRÖM-VAN LEEUWEN. (Communication N°. 3b from the Laboratory of Physics and Physical Chemistry of the Veterinary College at Utrecht). (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of September 29, 1918).

§ 1. In Comm. N°. 3a a general expression was found for the third virial coefficient for material points (eventually rigid spheres), which exert central forces on each other, while as a special case the value of C was derived from that formula for spheres without attraction. As has been remarked already there the value of C found for this case may at the same time be considered as the first term in the development of C according to ascending powers of T^{-1} for a law of force $r^{-(q+1)}$ (potential energy proportional with r^{-q}). In this communication some of the next terms of that development into a series will be calculated for $q=4$ (§ 2) and $q=5$ (§ 3).

§ 2. *Development for rigid spheres with attraction proportional with r^{-5} .* Instead of (17) of the preceding communication we now put:

$$\varphi(r) = \frac{e}{r^4} \quad \text{for } \tau > r > \sigma, \quad . \quad . \quad . \quad . \quad . \quad (21)^1)$$

and develop the exponential factor in P , R , and S according to (13) according to ascending powers of h , indicating the succeeding terms by indices.

In the same way C splits up into:

$$C = C_1 + C_2 + C_3 \quad . \quad . \quad . \quad . \quad . \quad (22)$$

C_1 has been calculated already in Comm. N°. 3a § 3, see equ. (20).

With a view to C_2 we must calculate:

$$S_2 = 24 \pi^2 h c \iiint \left\{ \frac{r_1 r_2}{r_{12}^5} + \frac{r_1 r_3}{r_{13}^5} + \frac{r_2 r_3}{r_{23}^5} \right\} dr_1 dr_2 dr_3.$$

The domain of integration is divided in the same way as in § 3

¹⁾ The equations have been numbered in continuation of those of Comm. N°. 3a.

of Comm. N°. 3a. For the domain sub 1, for which $r_1 > \tau$ and thus $\varphi(r_1) = 0$, the last term in the brackets of S_2 must be omitted.

As to the integrations with respect to r_1 and r_2 in the domain 1b we must still discern between:

$$\alpha: \tau > r_2 > r_1 - \sigma$$

and

$$\beta: r_1 - \sigma > r_2 > \frac{r_1}{2},$$

in the same way in 2a between:

$$\alpha: r_1 > r_2 > r_1 - \sigma$$

and

$$\beta: r_1 - \sigma > r_2 > \frac{r_1}{2}.$$

In the following table the different integration limits have been collected for the succeeding integrations with respect to r_1 , r_2 , and r_3 :

Integration with respect to	1			2		
	a	b		a		b
		α	β	α	β	
r_3	$r_1 - r_2, r_2$	σ, r_2	$r_1 - r_2, r_2$	σ, r_2	$r_1 - r_2, r_2$	σ, r_2
r_2	$\frac{r_1}{2}, \tau$	$r_1 - \sigma, \tau$	$\frac{r_1}{2}, r_1 - \tau$	$r_1 - \sigma, r_1$	$\frac{r_1}{2}, r_1 - \sigma$	σ, r_1
r_1	$\tau + \sigma, 2\tau$	$\tau, \tau + \sigma$		$2\sigma, \tau$		$\sigma, 2\sigma$

Finally we find:

$$S_2 = \pi^2 hc \left\{ 8 \frac{\tau^3}{\sigma} - \frac{33}{4} \tau^2 - (11 + 6 \ln 2) \sigma^2 + 16 \frac{\sigma^3}{\tau} + 6\tau^2 \ln \frac{\tau}{\sigma} \right\}. \quad (23)$$

Further we have

$$\left. \begin{aligned} P_2 &= 4\pi hc \left\{ \frac{1}{\sigma} - \frac{1}{\tau} \right\} \\ R_2 &= \pi^2 hc \left\{ 4\tau^2 \ln \frac{\tau}{\sigma} - \frac{1}{6} \tau^3 + \frac{1}{6} \sigma^3 \right\} \end{aligned} \right\} \quad (24)$$

Using the value of P_1 found in (18) we find:

$$C_2 = \frac{1}{3} n^2 \cdot \pi^2 hc (12 \ln 2 - \frac{19}{2}) \sigma^2 \quad (25)$$

C_3 follows from

$$S_3 = 12 \pi^2 h^2 c^3 \iiint \left\{ \frac{r_1 r_2}{r_3^7} + \frac{r_1 r_2}{r_2^7} + \frac{r_2 r_2}{r_1^7} + \frac{2r_1}{r_1^3 r_2^3} + \frac{2r_2}{r_1^3 r_2^3} + \frac{2r_3}{r_1^3 r_2^3} \right\} dr_1 dr_2 dr_3,$$

where for domain 1 the 3rd, 5th, and 6th terms between the brackets must be omitted. Performing the calculation in the same way as for C_2 we find:

$$S_1 = \pi^2 h^2 c^2 \left\{ \frac{\tau^3}{6\sigma^4} + \frac{3}{4} \frac{\tau^2}{\sigma^4} + \left(\frac{9581}{320} - 12 \ln 2 \right) \frac{1}{\sigma^2} - \frac{66}{\sigma\tau} + \frac{543}{40} \frac{1}{\tau^2} - \right. \\ \left. \frac{5}{2} \frac{\sigma^2}{\tau^4} + \frac{8}{5} \frac{\sigma^3}{\tau^5} + \frac{18}{\sigma^2} \ln \frac{\tau}{\tau-\sigma} - \frac{6}{\tau^2} \ln \frac{\tau}{\tau-\sigma} \right\} \quad (26)$$

while

$$P_1 = \frac{2}{5} \pi h^2 c^2 \left\{ \frac{1}{\sigma^5} - \frac{1}{\tau^5} \right\} \\ R_1 = \pi^2 h^2 c^2 \left\{ \frac{1}{2} \frac{\tau^2}{\sigma^4} - \frac{1}{12} \frac{1}{\sigma^2} - \frac{5}{12} \frac{1}{\tau^2} \right\} \quad (27)$$

so that finally

$$C_1 = \frac{1}{3} n^2 \cdot \pi^2 h^2 c^2 \left\{ \left(24 \ln 2 - \frac{2453}{160} \right) \frac{1}{\sigma^2} + \frac{36}{\sigma\tau} + \frac{18}{\tau^2} + \right. \\ \left. + \frac{3\sigma^3}{\tau^4} - \frac{36}{\sigma^2} \ln \frac{\tau}{\tau-\sigma} + \frac{12}{\tau^2} \ln \frac{\tau}{\tau-\sigma} \right\} \quad (28)$$

Remarkable is that the radius τ of the sphere of action does no longer occur in C_1 . Developing the logarithmic terms in (28) according to ascending powers of $\frac{\sigma}{\tau}$ we obtain

$$C_1 = \frac{1}{3} n^2 \cdot \pi^2 h^2 c^2 \frac{1}{\sigma^2} \left\{ (24 \ln 2 - \frac{2453}{160}) - \frac{15}{5} \frac{\sigma^5}{\tau^5} \dots \right\} \quad (29)$$

so that evidently the attractive forces excited by the molecules on each other over mutual distances greater than a certain distance τ , furnish a contribution to C_1 , the ratio of which to the total term is of the same order of magnitude as that in which the forces decrease at an increase of the mutual distance from σ to τ .

If now we put $\tau = \infty$, we find, adding (20), (25) and (29) and introducing the potential energy at contact

$$v = \frac{c}{\sigma^4},$$

$$C = \frac{5}{32} \cdot n^2 \left(\frac{4}{3} \pi \sigma^3 \right)^2 \left\{ 1 - \frac{3}{5} (19 - 24 \ln 2) h v + \frac{3}{400} (3840 \ln 2 - 2453) (h v)^2 \dots \right\} \\ \text{or}$$

$$C = \frac{5}{32} n^2 \left(\frac{4}{3} \pi \sigma^3 \right)^2 \{ 1 - 1,418 h v + 1,566 (h v)^2 \dots \} \quad (30)$$

As $h = \frac{1}{k_P T}$, k_P being the well known constant of PLANCK, this gives us the first term in the development of C according to ascending powers of T^{-1} .

§ 3. *Development for rigid spheres with attraction proportional with r^{-6} .* Performing the calculation as in § 2, but now with

$$\varphi(r) = \frac{c}{r^6} \quad \text{for } \tau > r > \sigma. \quad (31)$$

we find:

$$\begin{aligned} C_2 &= -\frac{1}{3} n^2 \cdot \pi^2 h c \sigma \\ C_3 &= \frac{1}{3} n^2 \pi^2 h^2 c^2 \left\{ \left(\frac{76339}{2688} - 40 \ln 2 \right) \frac{1}{\sigma^4} - \frac{32}{\sigma^3 \tau} - \frac{12}{\sigma^2 \tau^2} - \right. \\ &\quad \left. - \frac{16}{3 \sigma \tau^3} - \frac{2}{\tau^4} + \frac{4}{3} \frac{\sigma^2}{\tau^6} - \frac{8}{\sigma^3 (\tau - \sigma)} - \frac{40}{\sigma^4} \ln \frac{\tau - \sigma}{\tau} \right\} \end{aligned} \quad (32)$$

The radius of the sphere of action neither occurs here in C_2 , while the development of C_3 according to ascending powers of $\frac{\sigma}{\tau}$ induces the same remark as was made in § 2 concerning the contribution furnished by the attractive forces for greater mutual distances.

For $\tau = \infty$ we obtain:

$$\begin{aligned} C &= \frac{5}{32} n^2 \left(\frac{4}{3} \pi \sigma^3 \right)^2 \left\{ 1 - \frac{6}{5} h v + \left(\frac{76339}{26880} - 48 \ln 2 \right) (h v)^2 \dots \right\} \\ \text{or} \\ C &= \frac{5}{32} n^2 \left(\frac{4}{3} \pi \sigma^3 \right)^2 \left\{ 1 - 1,2 h v + 0,809 (h v)^2 \dots \right\} \end{aligned} \quad (33)$$

§ 4. In order to represent the dependency of C on the temperature more in details and to compare this for the two laws of force discussed in this paper, we shall introduce a temperature characteristic of each gas as a reduction temperature¹⁾. As the series for B found Suppl. Leiden N°. 24b § 3 eq. (42) converges still sufficiently rapidly at the BOYLE-point, this point suggests itself as reduction temperature.

For $\varphi(r) = cr^{-4}$ equation (42) Suppl. Leiden N°. 24b becomes:

$$B = B_\infty \left\{ 1 - 3 h v - \frac{3}{16} (h v)^2 - \frac{1}{18} (h v)^3 \dots \right\} \quad (34)$$

where B_∞ represents the value of B for $h = 0$, viz. for $T = \infty$.

From (34) we find for the BOYLE-point for which $B = 0$:

$$(h v)_B = 0,3223.$$

Writing now $t_{(B)}$ for $\frac{T}{T_B}$, where T_B is the BOYLE-temperature, so that $t_{(B)}$ represents the reduced temperature with respect to the BOYLE-point as reduction-temperature, we find for (34)

$$B = B_\infty \left\{ 1 - 0,9669 t_{(B)}^{-1} - 0,0312 t_{(B)}^{-2} - 0,0019 t_{(B)}^{-3} \dots \right\} \quad (35)$$

¹⁾ Comp. H. KAMERLINGH ONNES and W. H. KEESOM. Die Zustandsgleichung. Leiden Suppl. N°. 23 § 38b.

while (30) becomes:

$$C = C_{\infty} \{ 1 - 0,457 t_{(B)}^{-1} + 0,163 t_{(B)}^{-2} \dots \} \quad (36)$$

b. For $\varphi(r) = cr^{-5}$ we obtain:

$$B = B_{\infty} \{ 1 - \frac{3}{2} hv - \frac{3}{14} (hv)^2 - \frac{1}{24} (hv)^3 - \frac{1}{136} (hv)^4 \dots \}, \quad (37)$$

$$(hv)_B = 0,6070$$

$$B = B_{\infty} \{ 1 - 0,9105 t_{(B)}^{-1} - 0,0789 t_{(B)}^{-2} - 0,0093 t_{(B)}^{-3} - 0,0010 t_{(B)}^{-4} \dots \}. \quad (38)$$

$$C = C_{\infty} \{ 1 - 0,728 t_{(B)}^{-1} + 0,298 t_{(B)}^{-2} \dots \}. \quad (39)$$

c. In fig. 1 B and C have been represented as functions of $t_{(B)}$ according to the above formulae, while B_{∞} , resp. C_{∞} have been taken = 1.

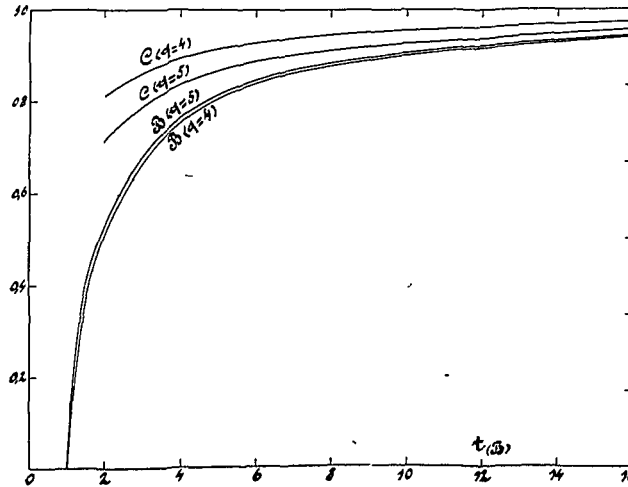


Fig. 1.

We see that within the represented range of temperature C is positive. C decreases with rising temperature, in a considerably less degree however than B .

How the behaviour will be towards lower temperatures it is impossible to say before more terms of the developments into series will have been calculated. When following terms do not change this result, the terms here calculated would cause a minimum of C ,¹⁾ after which C would rise again, so that it is not improbable that C remains positive up to a domain of considerably lower temperatures than those to which fig. 1 refers.

While for the two laws of force considered the curves of B are nearly the same above the BOYLE-point, the coefficient C decreases with the temperature for $q = 5$ much more rapidly than for $q = 4$, at least in the beginning.

¹⁾ Comp. the representation of the values of C for helium in H. KAMERLINGH ONNES and W. H. KEESOM, Die Zustandsgleichung, Leiden. Suppl. N° 23, § 38, Fig. 15.

Mathematics. — “On the number of degrees of freedom of the geodetically moving system and the enclosing euclidian space with the least possible number of dimensions”. By Prof. J. A. SCHOUTEN. (Communicated by Prof. J. CARDINAAL).

(Communicated in the meeting of May 25, 1918).

Suppose k to be a non-special curve in a finite part X_n of a general space of n dimensions, containing no singular points and where only one geodetic line exists between two arbitrary points. Assuming in a point O on k a system of n mutually independent directions, we can move this system *geodetically* along k .

This geodetic moving can be geometrically defined in the following way. X_n can always be placed in a euclidian space of $\frac{n(n+1)}{2}$

dimensions, without changing its linear element. There exists in this space a space Y_n developable on a euclidian space of n dimensions, tangent to X_n in k . The geodetically moving directions will now coincide at any moment with the directions moving parallel to themselves in the euclidian space Y_n . It appears analytically that the known *covariant* differential of a directed quantity e.g. a vector is a *common* differential judged from a geodetically moving system of directions. Hence if \mathbf{v} is a vector stationary with respect to this system, \mathbf{v} satisfies the differential-equation:

$$d\mathbf{v} = 0,$$

or in co-ordinates:

$$dv^\mu + \left\{ \begin{matrix} \mu \nu \\ \lambda \end{matrix} \right\} v^\lambda dx^\nu = 0,$$

and this equation then gives the analytical definition of the notion geodetic moving.¹⁾ A geodetic line is characterised by the property that its linear element forms at every point the same angles with a system moving geodetically along the line.

¹⁾ The covariant notations in this paper are the customary ones, but the contravariant characteristic numbers of the linear element $d\mathbf{x}$ are written contravariant agreeing to G. HESSENBERG, but contrary to G. RICCI and T. LEVI CIVITA. For the invariant notations, the here used direct analysis, cf. “Ueber die direkte Analysis der neueren Relativitätstheorie”, a paper presented to the “Koninkl. Akademie v. W.” together with this note. (Verh. Vol. 12 N°. 6).

Starting from a point O a system of directions is now geodetically moved along a closed curve. On returning to O the system will generally appear to have rotated. Dependent on the choice of the curve it is generally possible to obtain in this manner $\infty^{\frac{n(n-1)}{2}}$ positions of the system. If this number is for one point and hence for every point of the area ∞^N , we call N the *number of degrees of freedom* of the geodetically moving system. Now the following theorem exists:

I. *The number of dimensions of the euclidian space, in which a given space X_n may be placed, without changing its linear element, is at most equal to the number of degrees of freedom belonging to the geodetically moving system increased with n .*

We will prove this theorem. If the number of degrees of freedom is smaller than $\frac{n(n-1)}{2}$, there will remain invariant r mutually perfectly perpendicular directions of p_1, p_2, p_3, \dots dimensions $p_1 + \dots + p_r = n$ (by direction of two dimensions or 2-direction we mean a plane direction, etc.). The number of possibilities exactly corresponds to the number of manners, in which n can be written as the sum of whole positive numbers. We imagine the r invariant directions marked once for all in O . The system then may be brought in every point of X_n , always by geodetically moving. The invariant p_j -direction, $j = 1, \dots, r$, will then define at every point a p_j -direction, and it is the question whether these directions will compose a system of ∞^{n-p_j} curved spaces P_j of p_j dimensions. This is a PFAFFIAN problem in a general space.

We select a definite invariant direction, say the p_j -direction, and for convenience, sake we shall write p for p_j . If we now define the p -direction belonging to this direction at every point by the simple p -vectors,

${}_p\mathbf{v} = \mathbf{v}_1 \wedge \dots \wedge \mathbf{v}_p$, which all pass into one another by geodetically moving and likewise the perfectly perpendicular $(n-p)$ -direction to this,

by ${}_q\mathbf{w} = \mathbf{w}_1 \wedge \dots \wedge \mathbf{w}_q$, $q = n-p$, then:

$$d_{{}_p\mathbf{v}} = 0 \quad , \quad d_{{}_q\mathbf{w}} = 0,$$

hence:

$$\nabla_{{}_p\mathbf{v}} = 0 \quad , \quad \nabla_{{}_q\mathbf{w}} = 0.$$

It is worth mentioning, that the vectors \mathbf{v}_k , $k = 1, \dots, p$, do not pass into each other by geodetically moving and hence $d\mathbf{v}_k \neq 0$. The same holds good for \mathbf{w}_l , $l = 1, \dots, q$. If now the linear element

be $d\mathbf{x}$, the usual formulation of a problem as under consideration, is as follows.¹⁾

Given the pn functions of x^1, \dots, x^n :

$$v_k^1, \dots, v_k^n \quad ; \quad k = 1, \dots, p$$

(the contravariant characteristic numbers of the vectors \mathbf{v}), and the qn functions:

$$w_l^1, \dots, w_l^n \quad ; \quad l = 1, \dots, q$$

(the covariant characteristic numbers of the vectors \mathbf{w}), satisfying the relation:

$$\sum_{k=1}^{1, \dots, n} v_k^j w_{lj} = 0$$

equivalent to

$$v_k \cdot w_l = 0,$$

we ask, when the system of the total differential-equations

$$\left\| \begin{array}{cccc} dx^1 & \dots & dx^n \\ v_1^1 & \dots & v_1^n \\ \vdots & & \vdots \\ v_p^1 & \dots & v_p^n \end{array} \right\| = 0$$

equivalent to

$$dx \cdot v_1 \wedge \dots \wedge v_p = 0$$

is perfectly integrable.

If \mathbf{r} and \mathbf{s} are two vectors, lying in the p -vector ${}_p\mathbf{v}$, and consequently satisfying the relations:

$$w_l \cdot \mathbf{r} = 0 \quad , \quad w_l \cdot \mathbf{s} = 0 \quad , \quad l = 1, \dots, q$$

which is equivalent to:

$$\sum_{\lambda}^{1, \dots, n} w_{l\lambda} r^\lambda = 0 \quad , \quad \sum_{\lambda}^{1, \dots, n} w_{l\lambda} s^\lambda = 0 \quad , \quad l = 1, \dots, q,$$

but being otherwise arbitrary, the conditions of integrability are, as known:

$$\sum_{\mu, \nu}^{1, \dots, n} \left(\frac{\partial w_{l\mu}}{\partial x^\nu} - \frac{\partial w_{l\nu}}{\partial x^\mu} \right) r^\mu s^\nu = 0; \quad l = 1, \dots, q.$$

These equations are generally covariant²⁾ and are equivalent to:

$$\mathbf{r} \wedge \mathbf{s} \wedge \nabla \wedge \mathbf{w}_l = 0; \quad l = 1, \dots, q$$

¹⁾ Cf. e.g. E. von WEBER, Vorlesungen über das PFAFF'sche Problem, pages 93 and f.f.

²⁾ Owing to the circumstance that the expression $\frac{\partial w_{l\mu}}{\partial x^\nu} - \frac{\partial w_{l\nu}}{\partial x^\mu}$ is generally covariant.

Now it follows from this mode of notation that they may be replaced by the invariant equation:

$$r \frown s^2 \nabla \frown (w_1 \cdot \dots \cdot w_q) = r \frown s^2 \nabla \frown q w = 0,$$

or, as follows from the preceding, still more simplified without making use of two auxiliary vectors:

$${}_p v^2 \nabla \frown q w = 0. {}^1)$$

But this equation is identically true, $\nabla \frown q w$ being a multiple-sum of isomers of $\nabla q w$, and $\nabla q w$ being zero.

As the plane tangent-spaces of p_j dimensions, in the various points of the spaces P_j have p_j -directions, which by means of geodetic motion pass into each other and in the invariant p_j -direction in O , but never in any other direction, two spaces P_j can therefore never intersect. A geodetic line in X_n , which has a linear element in common with a definite space P_j , is apparently altogether contained in that space and in that space it is geodetic too. Hence two different spaces P_j can never be tangent to one another. Therefore we call the spaces P_j parallel ones. As any geodetic line having two points in common with a P_j space, falls completely within that space, which will be proved later on, we call a P_j space geodetic. The r obtained systems of parallel geodetic spaces P_1, \dots, P_r are at every point of X_n perfectly perpendicular to each other.

We shall first contemplate the case $r=2$, $p_1=p$, $p_2=q$. The parameter-spaces of $n-1$ dimensions of the primitive variables x^1, \dots, x_p are placed thus that each of them contains ∞^{n-p-1} spaces P , those of x^{p+1}, \dots, x^n likewise with regard to the spaces Q . At every point we place the mutually perfectly perpendicular p - resp. q -vectors ${}_p v$ and ${}_q w$. The measure-vectors \mathbf{e}'_κ , $\kappa=1, \dots, p$ are then situated in ${}_p v$ and for the measure-vectors \mathbf{e}'_μ , $\mu=p+1, \dots, n$ the same holds good with regard to ${}_q w$. Because $\mathbf{e}'_\kappa \perp \mathbf{e}'_\mu$ we have

$$g_{\kappa\mu} = \mathbf{e}'_\kappa \cdot \mathbf{e}'_\mu = 0; \quad \begin{matrix} \kappa=1, \dots, p \\ \mu=p+1, \dots, n \end{matrix}$$

hence the quadratic form ds^2 may be written thus:

$$ds^2 = \sum_{\kappa, \lambda}^{1, \dots, p} g_{\kappa\lambda} dx^\kappa dx^\lambda + \sum_{\mu, \nu}^{p+1, \dots, n} g_{\mu\nu} dx^\mu dx^\nu$$

Now may be demonstrated, that $g_{\kappa\lambda}$ is independent of x^{p+1}, \dots, x^n , and likewise $g_{\mu\nu}$ is independent of x^1, \dots, x^p . It is always possible to choose a scalar k as function of x^1, \dots, x^n , so that:

¹⁾ This equation can also be obtained very easily by means of the direct analysis used here. Another form of the same equation is:

$${}_q w^1 (\nabla^1 {}_p v) = 0.$$

$${}_p v = k e_1' \cdot \dots \cdot e_p'$$

Consequently:

$$\nabla k e_1' \cdot \dots \cdot e_p' = (\nabla k) (e_1' \cdot \dots \cdot e_p') + k \sum_{\kappa}^{1, \dots, p} \nabla (a \cdot e_{\kappa}') (e_1' \cdot \dots \cdot e_{\kappa-1}' \cdot a e_{\kappa+1}' \cdot \dots \cdot e_p') = 0.$$

By complete transvection with:

$e_p' \cdot \dots \cdot e_{\nu+1}' e_{\mu}' e_{\kappa-1}' \cdot \dots \cdot e_1' e_{\nu}'$
all the terms except the $(\kappa + 1)$ -th give zero, hence:

$$\left(\frac{\partial}{\partial x^{\nu}} a_{\nu} \right) a_{\mu} = 0 \quad \begin{matrix} \kappa = 1, \dots, p \\ \mu, \nu = p + 1, \dots, n. \end{matrix}$$

Now:

$$\bar{g}_{\mu\nu} = a_{\mu} a_{\nu},$$

and

$$\left(\frac{\partial}{\partial x^{\nu}} a_{\nu} \right) a_{\mu} = a_{\nu\mu} a_{\nu} = \left[\begin{matrix} \kappa \nu \\ \mu \end{matrix} \right] = a_{\nu\mu} a_{\mu},$$

thus

$$\frac{\partial g_{\mu\nu}}{\partial x^{\kappa}} = a_{\mu\kappa} a_{\nu} + a_{\nu\kappa} a_{\mu} = 0.$$

Hence the linear element in the Q spaces is independent of x^1, \dots, x^p ; the corresponding property of the P spaces relative to x^{p+1}, \dots, x^n is similarly demonstrated.

This property can also be expressed in the following manner.

II. If in a general space X_n is placed a system of ∞^{n-p} parallel geodetical spaces of p dimensions P , having perfectly perpendicular to it a system of ∞^p similar spaces Q of $n-p$ dimensions, a figure in a definite P -space will be congruently projected by the Q -spaces on all the other P -spaces.

For $p=1$ this is the well-known property that the distance of two definite Q -spaces measured along the P -lines is constant. So we can here introduce in this case for primitive variable x^1 the curve length measured along these lines from a definite space, the spaces remaining parameter-spaces. Hence the linear element may then be expressed in the following way:

$$ds^2 = dx^1{}^2 + \sum_{\mu, \nu}^{2, \dots, n} g_{\mu\nu} dx^{\mu} dx^{\nu}$$

in which the $g_{\mu\nu}$ do not depend on x^1 .¹⁾

As, however, a quadratic differential form in $n-1$ variables can

¹⁾ This formula has already been derived by T. LEVI CIVITA. Nozione di parallelismo in una varietà qualunque e conseguente specificazione geometrica della curvatura Riemanniana. Rend. di Pal. 42 (17).

always be written as a sum of $\frac{n(n-1)}{2}$ quadrates of complete differentials, ds^2 can be reduced to a sum of $\frac{n(n-1)}{2} + 1$ similar quadrates. Hence the space X_n can be placed in this case in a euclidian space of

$$\frac{n(n-1)}{2} + 1 = \frac{(n-1)(n-2)}{2} + n$$

dimensions. As the number of degrees of freedom of the geodetic moving system amounts exactly to

$$\frac{(n-1)(n-2)}{2},$$

the required proof has been furnished.

If we now return to the case $r=2$, $p_1=p$, $q_2=q$, the number of degrees of freedom is $\frac{p(p-1)}{2} + \frac{q(q-1)}{2}$. The quadratic form breaks up into two forms, which may be written as a sum of $\frac{q(q+1)}{2}$ resp. $\frac{p(p+1)}{2}$ quadrates. Therefore the space X_n can be placed within a euclidian space of

$$\frac{p(p+1)}{2} + \frac{q(q+1)}{2} = \frac{p(p-1)}{2} + \frac{q(q-1)}{2} + n$$

dimensions, and here again the required proof has been furnished.

The case $q > 2$ may be reduced to the preceding one. For this purpose the differential form is divided into two. The spaces of one of the systems, say P_2 , then again contain themselves at least two perfectly perpendicular systems of parallel geodetic spaces. Then the second part of the differential form is once more divided etc.

If owing to the existence of the P_j -system the division of the differential form is:

$$ds^2 = \overset{2}{a} \overset{2}{dx} = \overset{2}{a_p} \overset{2}{dx} + \overset{2}{a_q} \overset{2}{dx},$$

in which \mathbf{a}_p and \mathbf{a}_q are the ideal radices of the two parts of the fundamental tensor \mathbf{a}^2 , the differential equation of a geodetic line will be:

$$d \frac{d\mathbf{x}}{ds} = d \left(\mathbf{a} \cdot \frac{d\mathbf{x}}{ds} \right) \mathbf{a} = d \left(\mathbf{a}_p \cdot \frac{d\mathbf{x}}{ds} \right) \mathbf{a}_p + d \left(\mathbf{a}_q \cdot \frac{d\mathbf{x}}{ds} \right) \mathbf{a}_q = 0.$$

\mathbf{a}_p compossing itself only of the measure vectors $\mathbf{e}'_1, \dots, \mathbf{e}'_p$ and \mathbf{a}_q only of $\mathbf{e}'_{p+1}, \dots, \mathbf{e}'_n$, we have:

$$d \left(a_p \cdot \frac{dx}{ds} \right) a_p = 0 \quad , \quad d \left(a_q \cdot \frac{dx}{ds} \right) a_q = 0,$$

from which the property is inferred :

III. *In the proposition made in formulating II the projection of a geodetic line by means of Q spaces on a P space, or vice versa, is, as far as existent, a geodetic one itself.*

If two points A and B are situated in a P space P_1 , the projections of these points on all spaces coincide. Hence the projections on a Q space of the line AB geodetic in X_n passes twice through the same point, being at the same time geodetic in Q , which is only possible when that projection has degenerated into a point. But then the geodetic line AB must be situated altogether in a P space, e.g. in the present case in P_1 .

Hence any geodetic line, having two points in common with a P -space, is entirely contained in that space.

Mechanics. — „Bemerkungen über die Beziehungen des DE SITTER'schen Koordinatensystems B zu der allgemeinen Welt konstanter positiver Krümmung.“ By Prof. FELIX KLEIN.

(Communicated in the meeting of September 29, 1918).

1. Ich gehe zunächst von dem sphärischem Falle aus und setze:

$$\xi^2 + \eta^2 + \zeta^2 - v^2 + \omega^2 = R^2,$$

$$ds^2 = \pm (d\xi^2 + d\eta^2 + d\zeta^2 - dv^2 + d\omega^2),$$

wo das $+$ oder $-$ Zeichen gelten soll, je nachdem wir einen „Raumlichen“ oder „Zeitlichen“ Vector messen. Der Uebergang zum elliptischem Falle erfolgt am einfachsten, indem wir setzen:

$$x = \frac{R\xi}{\omega}, \quad y = \frac{R\eta}{\omega}, \quad z = \frac{R\zeta}{\omega}, \quad u = \frac{Rv}{\omega}.$$

2. Dann will ich von vorn herein betonen, daß die so definierte Welt bei 10^{10} homogenen linearen Substitutionen der $\xi, \eta, \zeta, v, \omega$ — also bei ∞^{10} Kollineationen der x, y, z, u (welche $x^2 + y^2 + z^2 - u^2 + R^2 = 0$ in sich überführen) — in sich übergeht.

3. Den Uebergang zum DE SITTER'schen ds^2 mache ich nun so, daß ich setze:

$$\xi = R \sin \vartheta \cos \varphi,$$

$$\eta = R \sin \vartheta \sin \varphi \cos \psi,$$

$$\zeta = R \sin \vartheta \sin \varphi \sin \psi,$$

$$v = R \cos \vartheta \sin h \frac{ct}{R},$$

$$\omega = R \cos \vartheta \cos h \frac{ct}{R},$$

(unter $\sin h, \cos h$ gewöhnliche hyperbolische Funktionen verstanden).

4. Weiter wird also

$$\tan h \frac{ct}{R} = \frac{v}{\omega} = \frac{u}{R},$$

woraus

$$\frac{ct}{R} = \log \left(\frac{\omega + v}{\omega - v} \right) = \log \left(\frac{R + u}{R - u} \right).$$

Dabei sind $\omega + v = 0$, $\omega - v = 0$ irgend zwei Tangential-ebenen, welche man durch den Koordinatenanfangspunkt an dem Gebilde $\xi^2 + \eta^2 + \zeta^2 - v^2 + \omega^2 = 0$ legen kann; t ist der in geeigneter Maasseinheit gemessene „projektive Winkel“ im Büschel

$$\lambda(\omega + v) + \mu(\omega - v) = 0.$$

5. In Uebereinstimmung damit wird $t = -\infty$, bzw. $t = +\infty$, wenn $\omega + v = 0$ oder $\omega - v = 0$; verschwinden beide Ausdrücke, so wird t unbestimmt¹⁾. t ist nur in dem Ausschnitte der vierdimensionalen Welt reell, für den $\frac{\omega + v}{\omega - v}$ positiv ist; jenseits wird es imaginär.

6. ds^2 behält seine Form bei ∞^4 Transformationen, nämlich wenn man

a) ξ, η, ζ beliebig orthogonal substituiert,

b) t durch $t + \text{const.}$ ersetzt.

Mit Rücksicht auf 2 gibt es also in der Welt (1) ∞^4 „DE SITTER'schen Uhren“.

7. Da ist es nun sehr amüsant sich auszumalen, wie sich zwei Beobachter unterhalten würden, die mit zwei verschiedenen DE SITTER'schen Uhren ausgestattet sind. Ereignisse, die für den einen in der Ewigkeit liegen, sind für den anderen zugänglich, und umgekehrt, ja der eine erlebt Ereignisse, welche der andere für imaginär halt.

8. Dies alles sind zunächst selbstverständlich nur mathematische Spekulationen, ob der Physiker sie aufnehmen will steht auf einem anderem Blatte.

¹⁾ Dies ist aber nur eine Singularität der Koordinate t , nicht der zu Grunde liegenden Mannigfaltigkeit (1).

Physics. — “*On friction in connexion with Brownian movement*”.

By Dr. O. POSTMA. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of September 29, 1918).

§ 1. The different deductions of the mean displacement of a suspended particle caused by the Brownian movement in a certain time, can be divided into two groups. In the deductions of the *first* kind the forces acting on the particle are divided into accelerating and retarding forces, in those of the *second* kind this difference is not made.

To the deductions of the first group belongs that of EINSTEIN, the second one of VON SMOLUCHOWSKI, that of LANGEVIN and that of DE HAAS—LORENTZ (by the method of EINSTEIN and HOPF). To those of the second group belongs the first deduction of VON SMOLUCHOWSKI, that of VAN DER WAALS and SNETHLAGE and that of SNETHLAGE (given in her dissertation)^{1) 2)}.

In the theories first mentioned a retarding force (friction) has been assumed proportional to the radius of the particle, which is considered as a sphere and has the velocity v . The applied formula $W = 6\tau\zeta av$ is deduced in hydrodynamics on the supposition that at the surface of the particle the fluid has the same velocity as this. All theories of the first kind come to the result that the mean square of the displacement ($\overline{\Delta^2}$) is inversely proportional to t and proportional to a .

The theories of the second kind give the result: $\overline{\Delta^2}$ proportional to t and inversely proportional to a^2 and to the density ρ ³⁾.

It is however not to the resolution of the forces into accelerating

¹⁾ See: G. L. DE HAAS—LORENTZ “Die Brownsche Bewegung”, die Wissenschaft 1913, J. D. VAN DER WAALS JR. and MISS A. SNETHLAGE “The theory of the Brownian movement”. These Proceedings Vol. XVIII, p. 1322 and A. SNETHLAGE: ‘Molecular-kinetic phenomena in gases, especially the Brownian movement’. Amsterdam 1917.

²⁾ Recently VAN DER WAALS JR. gave still a theory in which, though in a somewhat different form, the two kinds of forces are found back. (These Proc. XX p. 1254.

³⁾ The first result gives the best agreement with the investigations of SNETHLAGE.

and retarding ones that these different results must be ascribed. This is evident from considerations of VON SMOLUCHOWSKI, who, though assuming such a resistance proportional to v , obtained the second results by simply taking this resistance proportional to a^2 and ρ .

The reason of the difference lies in the assumptions on the sliding at the surface. Without sliding the resistance is found proportional to a , and not to a^2 and ρ . As long as the velocities of the molecules may be considered as independent of those of the particle, the assumption W proportional to $\rho a^2 v$ is the more natural one.

The number of collisions is then proportional to the surface of the particle and the density, while the total force is also proportional to v by the added opposite influences of the forces on the fore-and back-side, each of which is proportional to the square of the relative velocity. This resistance has been calculated by CUNNINGHAM ¹⁾,

who found: $\frac{2}{3} a^2 v n \sqrt{\frac{\pi M m}{(M+m)h}}$.

When however the velocity of the molecules depends on that of the particle the relative velocity v can again depend on a , so that the dependency on a becomes different from that in the preceding formula.

It is therefore evidently not true that the assumption of a resisting force, represented by $w = pv$ should be connected with the supposition that there is no sliding.

It is the last assumption that is of importance here.

VAN DER WAALS and SMETHLAGE have objections to this assumption. When the molecules of the fluid participate in the motion of the particle, the velocities of the molecule are no longer independent of the velocity of the particle, which should however be the case in the here existing state of statistic equilibrium. This participation of the motion would e.g. be possible in the case of the fall of a particle under the influence of gravitation, but not here in that of the BROWNIAN movement.

Here it may be remarked however, that just by the resolution of the forces into accelerating and retarding ones an analogous case has been created. The accelerating forces take the place of gravitation. The action of the molecules on the particle is resolved into an accidental, irregular one, which may be regarded as the cause of the motion and a regular, resisting one which represents the friction.

When we consider a *long time* there is statistical equilibrium. There is however a continual transformation of energy of the

¹⁾ E. CUNNINGHAM: "On the Velocity of Steady Fall of Spherical Particles through Fluid Medium". Proc. Roy. Soc. Ser. A. Vol. 83 p. 357. 1910.

molecules by the irregular, accelerating forces into molar energy of the particle, and of this again by the resisting forces into molecular energy.

Also the molecular velocities are *as a whole* independent of those of the particle, but the molecules can be divided into a large majority the mean velocity of which differs too little from that of the particle, and into smaller complexes whose velocities differ too much from that. The first group joins the motion of the particle, the second causes the accelerating forces. These forces, however, are not only caused by accidental deviations of the velocity, but also by accidental deviations of density. The relative dimensions of the molecules, the particles and the free path agree with the above considerations. While the order of magnitude of the molecules is 10^{-7} , we generally find for that of the particles about 10^{-5} , the free path in the fluid being of the order 10^{-6} . We thus can represent the dimensions of the molecules and the particles on a scale by 1 mm and 1 dm, while then the free path would become 1 cm. As a rough approximation we may assume that in a fluid 10^4 molecules are acting at the same time on the particle (of the same order of magnitude as the number that can cover the whole surface) and in a gas 10^2 . The collisions which keep the particle in motion are therefore due to accidentally arising complexes of these molecules.

§ 2. Now we find for the mean distance travelled by a particle

EINSTEIN'S formula $\bar{\Delta}^2 = \frac{RT}{N} \frac{1}{3\pi\zeta a} \cdot t$, when we take for the frictional

resistance $W = 6\pi\zeta av$. This value has been deduced by STOKES on the assumption that the fluid is incompressible and that there is not any sliding at the surface, while the velocity may not be too great. It is however questionable, whether it is allowed to assume this absence of sliding.

CUNNINGHAM has tried the supposition that the velocity of the fluid at the surface of the particle is kv , so that the relative velocity of the particle with respect to the adjoining fluid would be $v - kv$. STOKES' formula would then give for the resistance $W = 6\pi\zeta a kv$. CUNNINGHAM now calculated this k in the following way.

As has been mentioned above he found for the resistance by purely kinetic considerations the value $\frac{8}{3} a^2 v n \sqrt{\frac{\pi M m}{(M + m) h}}$; where v represents the relative velocity. This would now become

$\frac{8}{3}\alpha^2(v-kv)\sqrt{\frac{\pi m}{h}}$ (when at the same time m is neglected with respect to M). He now equalizes this value to the value $6\pi\zeta akv$ derived from phenomenological considerations, and thus finds an equation from which k can be calculated.

In my opinion, however, there are several objections to this way of calculation. The assumptions on which the deductions of the two expressions are based are not the same; the results refer therefore to different cases and need not be equal. In his kinetic considerations CUNNINGHAM supposed namely, that the colliding molecules possess MAXWELL's partition of velocities, viz. in the gas or the fluid there is no internal friction (this depends on the deviations from MAXWELL's partition), while moreover colliding molecules exert only normal forces on the particles viz. there is no external friction.

In the case of STOKES' formula on the contrary there is an internal friction and the fluid exerts also lateral forces on the body. In my opinion it is therefore impossible by equalization of the two results to obtain a relation which has any significance. Moreover there is still the inner contradiction in the kinetic deduction between a uniform transformation of velocity kv and the assumption of a purely elastic collision. For this reason no great importance may be ascribed to the final result: $W = 6\pi\zeta av \left(1 + 1.63 \frac{l}{a}\right)^{-1}$.

Instead of assuming a uniform motion of the fluid with the sphere to an amount kv it might be preferable to suppose the normal velocity of the fluid to be equal to that of the particle, the tangential one being different and a friction existing proportional to the relative tangential velocity.

The resistance of a sphere under this assumption has been calculated by LAMB and by BASSET¹⁾. The first of these uses in his deduction the dissipation function (with the aid of the property: in a fluid the energy transformed into heat = the work of the forces necessary to entertain the motion); the other one follows a direct method by calculating the pressure at the surface. The two results however

do not agree exactly. LAMB finds: $W = 6\pi\zeta av \frac{1 + 4\frac{\zeta}{\beta a} + 6\left(\frac{\zeta}{\beta a}\right)^2}{\left(1 + 3\frac{\zeta}{\beta a}\right)^2}$,

¹⁾ See: HORACE LAMB "A Treatise on the Math. Theory of the Motion of Fluids". Cambr. 1879 p. 230 (not reprinted in the later issues) and A. B. BASSET, "A Treatise on Hydrodynamics" Cambr. 1888 II p. 270.

and BASSET. $W = 6\pi\zeta av \frac{1 + \frac{2\zeta}{\beta a}}{1 + \frac{3\zeta}{\beta a}}$, where β is the coefficient of external

friction. The second expression is also equal to: $6\pi\zeta av \frac{1 + 5\frac{\zeta}{\beta a} + 6\left(\frac{\zeta}{\beta a}\right)^2}{\left(1 + 3\frac{\zeta}{\beta a}\right)^2}$,

so that the difference between the results is: $6\pi\zeta v \frac{\frac{\zeta}{\beta a}}{\left(1 + 3\frac{\zeta}{\beta a}\right)^2}$.

A mistake suggests itself in the indirect method and seeking for it we are led by the remark that the two values become equal when $\beta = 0$ and when $\beta = \infty$ viz. when there is no friction and when there is no sliding.

In both cases the friction does no work: in the first case because the force becomes zero, in the second because the way becomes zero.

Probably we shall therefore have to add the work of the friction at the surface to the heat, calculated from the dissipation-function with the formula $\iiint F dx dy dz$, where $F = -\frac{2}{3}\zeta(a+b+c)^2 + 2\zeta(a^2 + b^2 + c^2 + 2f^2 + 2g^2 + 2h^2)^{1/2}$. This proves indeed to give the right result.

At a point determined by the angle θ the force of friction is:

$$U = \beta \left\{ \frac{A}{a^2} - \frac{B}{a} + v \right\} \sin \vartheta, \text{ where } A = \frac{-\frac{1}{2}va^2}{1 + 3\frac{\zeta}{\beta a}} \text{ and } B = \frac{\frac{2}{3}va \left(1 + \frac{2\zeta}{\beta a}\right)}{1 + 3\frac{\zeta}{\beta a}}$$

so that $U = \beta \frac{\frac{3\zeta v}{2\beta a}}{1 + \frac{3\zeta}{\beta a}} \sin \vartheta$. This friction is exerted on the surface

$2\pi a^2 \sin \vartheta d\vartheta$, while the relative velocity, opposite to the force, is

$$\frac{\frac{3\zeta v}{2\beta a}}{1 + \frac{3\zeta}{\beta a}} \sin \vartheta.$$

¹⁾ Notation of LAMB.

²⁾ See LAMB p. 230 and BASSET p. 270.

We thus find for the numerical value of the work of the friction per second:

$$\int_0^\pi 2\pi a^2 \sin \vartheta \, d\vartheta \beta \left[\frac{\frac{3\zeta v}{2\beta a}}{1 + \frac{3\zeta}{\beta a}} \sin \vartheta \right]^2 = \int_0^\pi 2\pi a^2 \sin^3 \vartheta \frac{\frac{9\zeta^2 v^2}{4\beta^2 a^2}}{\left(1 + \frac{3\zeta}{\beta a}\right)^2} d\vartheta =$$

$$= 6\pi \zeta v^2 a \frac{\frac{\zeta}{\beta a}}{\left(1 + \frac{3\zeta}{\beta a}\right)^2}.$$

When to this term the heat calculated from the dissipation-function is added, the force, necessary to entertain the motion, and therefore also the friction in question, is just increased by the missing term.

With the aid of this last formula for the resistance we find for the mean deviation of the particles:

$$\overline{\Delta^2} = \frac{RT}{N} \cdot \frac{1}{3\pi \zeta a} \cdot \frac{1 + \frac{2\zeta}{\beta a}}{1 + \frac{3\zeta}{\beta a}} \cdot t.$$

§ 3. That, when the above mentioned work of the resistance is taken into consideration, the dissipation function can give the resistance to which the particle is submitted, may be made evident in the following way.

We think the incompressible fluid enclosed by a surface S , part of which is formed by the surface of a body of arbitrary form, which moves through the fluid. Now we consider the kinetic energy

$T = \frac{1}{2} \iiint \rho q^2 \, dx \, dy \, dz$ (the molar energy only, not the heat) and deduce from the equation of motion an energy equation which indicates how the kinetic energy changes with the time. We then find¹⁾:

$$\frac{dT}{dt} = \iiint \rho (Xu + Yv + Zw) \, du \, dy \, dz - \frac{1}{2} \iint \rho q^2 (lu + mu + nw) \, dS +$$

$$+ \iint (X_1 u + Y_1 v + Z_1 w) \, dS - \iint F \, dx \, dy \, dz. \quad . \quad . \quad . \quad (1)$$

Here X, Y, Z represent the components of the external force acting on the fluid, pro unit of mass, X_1, Y_1, Z_1 the pressure components

¹⁾ See BASSET II l.c. p. 252 and HELMHOLTZ "Wissenschaftl. Abhandlungen" Lpzg. 1882 p. 225.

pro unit of surface acting at the surface of the fluid, F the-dissipation function. The first term on the right hand side represents thus the increase of the kinetic energy by the action of external forces, the second term the increase by the flow inwards of the fluid, the third term the increase by the action of the pressure forces, the fourth the decrease by the transformation of the kinetic energy by the inner resistance. This last integral is always positive, the other ones can be positive or negative.

When we suppose the surface S to be quite formed by solid bodies, at the boundaries of which the friction is neglected except along the moving body, the second term falls away, while the third term has to be taken over this body only. When further the state is stationary, equation (1) becomes:

$$0 = \iint (X_1 u + Y_1 v + Z_1 w) dS - \iiint F dx dy dz \quad (2)$$

For the moving body we have in this case the equation:

$$\Sigma (X' u + Y' v + Z' w) dt + \iint (-X_1 u - Y_1 v - Z_1 w) dS dt = 0 \quad (3)$$

The summation has to be extended over the points, where the external forces (X' etc.) act, the integration over the surface. This notation expresses that the forces acting on the surface layer are equal and opposite to those acting there on the fluid.

In the case of sliding however the components of velocity are not equal as far as they refer to the body. on one hand, and to the fluid on the other hand. Calling the components in the fluid u_o etc. those in the body u_l etc. then $u_o = u_l + u$, etc. (4), when u is written for the component of the relative velocity.

Now equation (2) becomes:

$$\iint (X_1 u_o + Y_1 v_o + Z_1 w_o) dS - \iiint F dx dy dz = 0$$

and equation (3):

$$\Sigma (X' u + Y' v + Z' w) - \iint (X_1 u_l + Y_1 v_l + Z_1 w_l) dS = 0.$$

Summation gives us:

$$\Sigma (X' u + Y' v + Z' w) + \iint [X_1 (u_o - u_l) + Y_1 (v_o - v_l) + Z_1 (w_o - w_l)] dS - \iiint F dx dy dz = 0$$

so, using (4):

$$\Sigma (X' u + Y' v + Z' w) = \iiint F dx dy dz - \iint (X_1 u_l + Y_1 v_l + Z_1 w_l) dS.$$

As the normal forces at the surface are perpendicular to the relative velocity they do not contribute to the last integral; this term represents therefore the work of the friction. The result is thus: the work done per unit of time by the external forces that act on the body is equal to the heat generated in the fluid increased by the absolute value of the work of the external friction¹⁾.

Taking now as the body a sphere with the velocity v , which is kept in a state of uniform motion by a force K in the centre, the work per unit of time is Kv . This K being equal to the resistance W that has to be overcome, it is also equal to

$Wv = \iiint F dx dy dz +$ the work done by the friction along the surface. From this formula we can calculate W .

1) "Absolute" value, as X_1 and u_r referring both to the fluid are oppositely directed, so that finally the form becomes positive. The result says therefore only: external work = total generated heat. It must be remarked, that RAYLEYGH, who first introduced the dissipation function, did not mean the above mentioned F , but the total generated heat. (Proc. Lond. Math. Soc. 1873 p. 363).

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Physiology. — "*Our equilibrium-organ*". By Dr. D. J. HULSHOFF
POL. (Communicated by Prof. C. WINKLER.)

(Communicated in the meeting of November 24, 1917).

When studying the functions of the cerebellum¹⁾ I always halted before the difficulty of interpretation of the observed phenomena. It is not easy to deduce whether they are dependent on the organ in itself, or resulted from the interruption of tracts in the cerebellum, which took origin in other parts of the central nervous system.

Therefore it seemed to me desirable, before continuing my investigations on the cerebellum, to trace in the first place the connection between those influences which are lying outside of this organ and the cerebellum itself.

As experiments on this subject have often been made, it was clear that repetition of the former investigations would not bring a nearer solution of this problem.

Therefore I resolved not to start by experimenting on animals, but to examine the suffering people and especially to pay full attention to ataxia.

As this phenomenon is often observed by disturbances of the central nervous system and as it is known, that according to the illness, also the decomposition of the movement can show a different type, I thought, that perhaps it could be possible by putting together the different types to get a more distinct insight into the nosology of the cerebellum.

Now it is in general accepted that cerebellar ataxia is caused by a disturbance in efferent paths, and thus could be a motor disturbance, but as this kind of conducting fibres is not well imaginable without afferent tracts, one may accept that these too, interrupted in the cerebellum, will show disturbance in movement.

As my former investigations were exclusively restricted to the motor functions, I thought it now wise to draw attention to the afferent tracts.

¹⁾ *Cerebellar ataxia*. Psych. Neurol. bladen 1909 N^o. 4.

Cerebellar functions in correlation to their localisation. Psych.-Neurol. bl. 1915 N^o. 3.

Of the sensory and sensorial stimuli which reach the cerebellum along centripetally conducting paths and which are well-known to us, we may mention in the first place the functions of the deep sensation and of the sense for the muscle tone and the equilibrium.

The first pass with the posterior nerve-roots into spinal cord and run partially uncrossed, with the Column of Clark as mid-station, to the tractus spino-cerebellaris dorsalis (FOVILLE-FLECHSIG), while another part, with the area nuclei intermedii as mid-station, run also for more than the greater part uncrossed to the tractus spino-cerebellaris ventralis (GOWER), while a smaller part goes to the same column of the crossed side. This bundle is therefore partially composed of crossed, partially of uncrossed fibres.

The tracts of FLECHSIG and GOWER lie in a long but narrow strip at the lateral edge of the spinal cord and run centripetally.

The tract of FLECHSIG goes through the restiforme body and the inferior brachium conjunctivum towards the vermis of the cerebellum, without coming in contact with the dentate nucleus.

The tract of GOWER does not pass into the restiforme body after having reached the medulla oblongata, but runs on in longitudinal direction. On the level of the nervus trigeminus it bends round in latero-dorsal direction and passes along the brachium conjunctivum cerebelli into the vermis superior and the nuclei tecti cerebelli.

From the posterior columns of the spinal cord however, there are along other paths also tracts connected with the cerebellum, e.g., through the nuclei of GOLL and BURDACH, along the fibrae arcuatae externae and anteriores to the restiforme body and from here to the cerebellum.

As the influence of these latter fibres is far from known, I will leave them in the further discussion out of the question.

Now the experiments of MARBURG and BING¹⁾ have taught, that the lesion of the spino-cerebellar tracts provokes a very serious disturbance of the statotonus. Partial or total destruction of these bundles from the entrance in the spinal-cord to the cerebellum, will therefore show disturbance of the equilibrium.

If the connection between the tracts of FLECHSIG and GOWER with the cerebellum are well-known, this is less the case with those between the vestibular organ and the cerebellum.

LANGELAAN²⁾ writes that the end-arborisation in the oblongata of

¹⁾ EDINGER. Zeitschr. f. Nerv. Heilk. V. 45, 1912 p. 303.

²⁾ J. W. LANGELAAN. Bouw van het centrale zenuwstelsel. Amsterdam. VERSLUYS. 1910.

the vestibular nerve is T-shaped, of which the ascending fibres continue into the cerebellum. They unite into bundles, between which is found gray matter, belonging to the nucleus of DEITERS. These bundles form the greater part of the corpus juxta-restiforme and pass with the fibres of the corpus restiforme into the cerebellum, where they end in the dentate nucleus and in the nucleus tecti. JELGERSMA ¹⁾ too points out (p. 217) the fibres of the nervus vestibularis as thick bundles running through and along the brachium conjunctivum inferius towards the cerebellum, being everywhere visible as distinct bundles. WINKLER is of a different opinion and thinks from sections, which he possesses, he can make out that the nervus vestibularis does not stand in direct connection with the cerebellum, but that the fibres all end in the corpus juxta-restiforme, around cells of the nucleus of DEITERS, the nucleus triangularis, of the proper nucleus of the radix descendens N. VIII. Cells of middle size, lying in the regions of these nuclei, carry the impulses through the corpus juxta-restiforme towards the cerebellum. It does not receive direct nerve-roots of the N. VIII.

In this case therefore the connection has to take place by means of an interjacent link.

As to the physiological function, the investigators of this region are almost of the same opinion, that the vestibular organ will be *an organ for the muscle tone and for the equilibrium*.

Its great importance for our equilibrium has gradually and regularly come to the foreground, even so, that GOLTZ made a sixth organ of it. ²⁾

We may say, therefore, recapitulating in short the above mentioned that from the spinal cord as well as from the vestibular organ, strong tracts run to the cerebellum and that interruption of these disturbs the equilibrium.

In my investigations I thought I was allowed to start from the standpoint, even although from both organs paths go to the cerebellum, yet the difference between the stimuli which they conduct, is so great, that it could perhaps show me the way in the intricate mass of the cerebellar phenomena.

Thus, as the spinal path, taking its origin in the peripheral nervous system, enters the spinal cord through the posterior nerve roots and i.a. as the thick posterior fibres of the roots send their collateral fibres to the column of CLARK and the area nuclei intermedii, I thought I could best study the disturbance in the equilibrium when

¹⁾ G. JELGERSMA. De functie van het cerebellum. Psych. en Neur. bl. 1915.

²⁾ H. ZWAARDEMAKER. Physiologie. De Erven F. BOHN. Haarlem 1915. bl. 286.

the centripetal impulses along the tractus spino-cerebellares were fallen away, as happens in cases, affecting the posterior funiculi, e.g. in *tabes dorsalis*.

For disturbances of the vestibular organ I had best limit myself to those cases, in which the equilibrium organ had lost its functions, *inter alia* after scarlatina, cerebro-spinal meningitis etc.

In working out these investigations I tried in the first place to devise a scheme, which could serve as well in lesions of the posterior funiculi, as in those of the vestibular organ and in alterations of the cerebellum.

I thought I had found one in letting the patients perform walking-tests, which were registered on paper. For this purpose a line was drawn in the middle of large pieces of paper, on which the patients walked after blacking their footsoles.

When in this paper I leave the results, which I found in cerebellar alterations out of account, and when I limit myself to those which are correlated to lesions of the posterior funiculi and the vestibular organ, I find what follows:

1. If a patient, who suffers from *tabes* in a rather far advanced state, walks on the paper, then the reproduction of figure 1¹⁾ appears:

The patient tries to fulfil the task of walking on the line (foot print 1—2 and 3), but sways to and fro, as in the *ROMBERG* syndrome and he is obliged to put down the right foot lateralwards, (4). Still worse the swaying becomes in the following right footstep (6) when he replaces the foot three times to keep his equilibrium.

The deviation in the line of equilibrium is most distinct with the footsteps 8 to 11, which he had to put down close to each other and during which it was impossible to him to remain on the line. He therefore leaves off trying it and walks on rather well along a broad gait-path.

2. When that which is ordered sub I, is repeated, but with eyes shut, then the deviations of the gaitpath are still more distinctly visible.

3. If one lets the patient repeat the same walking exercises as sub 1 and 2, but allows him at the same time to touch our hands²⁾, then one sees a gaitpath nearly as normal (fig. 2).

¹⁾ The cross on the photo indicates the moment when I thickened the contours of the foot prints with ink, because otherwise the footsteps do not come out well enough on the photograph.

²⁾ While walking the patient, who is standing on the middle of the paper, stretches his arms to the left and to the right and lays his hands on the dorsal plane of those, which are tended to him from the side. The persons, who help to

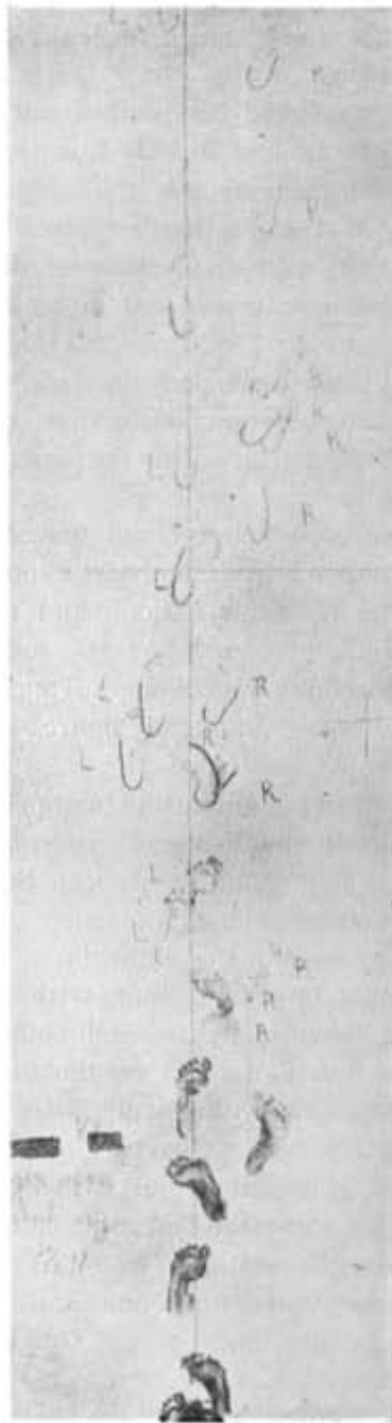


Fig. 1.
Tabes no contact-sensation.



Fig. 2.
Tabes contact-sensation.



Fig. 3.
Vestibular affection no
contact sensation.



Fig. 4.
Vestibular affection
contact-sensation.

4. If one reproduces of a patient, suffering from a vestibular inflection, a gait-path, then distinct deviations will be visible (fig. 3).

5. If we repeat the experiment, but with eyes shut, then the deviations sub 4 are more distinctly visible.

6. If we allow the vestibular suffering patient to touch our hands, then one gets a very important amelioration, even a nearly abolished ataxia (fig. 4).

If the symptoms which these patients show are put together, then we have three types:

- a. distinct deviation while walking with open eyes, while the hands do not find contact.
- b. increasing of these deviations, when the eyes are shut.
- c. gait nearly normal, at least important improvement of it, when the hands find contact.

If one wants to comprehend these three differences well, then it is necessary to bring to the foreground that our movement equilibrium, as it were, is principally regulated by the eyes, the vestibular organ and the equilibrium sensation¹⁾ of the trunk and the lower limbs.

Of these three factors the eyes are the least important, which is easily tested by the fact that a person can walk very well with his eyes shut, but directly shows disturbances, when the vestibular organ or the equilibrium sensation are suffering. This can also be explained, because the last two factors give proprioceptive stimuli, according to the particular conception of SHERRINGTON, which do not affect consciousness, while the eyes convey exteroceptive stimuli, with regard to the gait. We could describe it best in this way, that the equilibrium is governed by the vestibular organ, also by the equilibrium sensation of the trunk and the limbs, while the eyes only regulate the intended direction of the movements.

Therefore when a patient suffering from tabes walks, he does not wholly dispose of the three above mentioned factors, but he walks, if we are allowed to express it thus, by his eyes, by the vestibular organ and the rests of the equilibrium sensation of the trunk and the legs. The result is, that the movements become uncertain. If such a person shuts his eyes, then the exteroceptive stimuli, moreover,

do this and *who walk along the edge of the paper*, are asked *not to support* the patient, but to give way as it were in vertical direction to the movements, which the patient makes. Their hands therefore have to balance too. The patient has no support, but only contact sensation with the persons who walk alongside of him, and by which his equilibrium sensation can orientate itself.

¹⁾ Equilibrium sensation has to be interpreted as an independent subdivision of that, which till now is brought together in conception of "deep-sensation".

fall out, because the eyes cannot give direction to the intended movements and therefore it is comprehensible that the uncertainty of the gait augments.

However on the other hand it can be said that as the equilibrium in particular is only regulated by proprioceptive stimuli, disturbances in gait will occur, when a part of those fall out, but the disturbances will be partially improved by the exteroceptive stimuli, which by means of the eyes can convey their stimuli.

The above mentioned is known, but it is most important, that when to such a tabes patient, either with opened, or shut eyes, *contact* is given through persons walking alongside of him, the gait greatly improves, even so, that the ataxia nearly altogether disappears.

As such a patient is *not supported*, but as he has only *contact* with persons walking alongside of him, I think it may be assumed that the equilibrium sensation of the upper limbs is put into action. The equilibrium-sensation orientates itself along this new path, brings in this way new afferent proprioceptive impulses towards the central nervous system and therefore it can better control the movements of the lower limbs. The equilibrium sensation of the arms, in the tabes patient, thus takes over the function of the equilibrium sensation of the lower limbs and trunk (this only of course when the tabes is present in the caudal part of the spinal cord), which for a great part has disappeared.

Therefore we can say the following:

- a.* a tabes patient walks by his eyes, by the vestibular organ and the *rests* of the equilibrium sensation of the trunk and the legs.
- b.* if such a patient has contact-sensation with persons walking alongside of him, then he *moreover* walks by the equilibrium sensation of the arms.

In case *a* he lacks afferent equilibrium impulses on a great scale and therefore he walks atactic, in case *b* the amount of these equilibrium-impulses is very considerably augmented and the ataxia therefore is improved, nay it even has entirely or almost disappeared.

If we have a patient suffering from a vestibular affection, then we see on the whole the same effect.

In this sort of patients the central nervous system too receives the exteroceptive impulses by way of the eyes, and moreover the proprioceptive ones of the trunk and the legs, through the posterior roots of the spinal cord, but none or only partially from the proprioceptive ones of the vestibular organ.

The result of this is, that the amount of equilibrium impulses is not sufficient, therefore the patient walks atactic.

For these cases too it is important, that when the patients, by means of their arms, receive equilibrium contact through persons walking at their side, then the ataxia either very importantly improves or it entirely is abolished.

Here too we see, that the equilibrium contact of the arms replaces totally, or for a very large amount the proprioceptive impulses from the vestibular organ.

Therefore we can say for this case:

a: a vestibular patient walks by his eyes, by the equilibrium sensation of the trunk and the legs, and the afferent-proprioceptive stimuli from the vestibular organ, which is left to him.

b: if such a patient has equilibrium contact with persons leading him, then he *moreover* walks by the equilibrium sensation of the arms.

In case *a* he lacks afferent equilibrium stimuli and the patient walks atactic. In case *b* the ataxia totally or partially disappears, because his lack is supplied.

Now the peculiarity of the results found is, in tabes as well as in vestibular affection, *that the equilibrium sensation of the arms can compensate the equilibrium sensation of the trunk and legs as well as the impulses from our vestibular organ.*

On account of this the question arises whether it is possible, that in our equilibrium different organs can replace each other.

This question deserves to be answered in the affirmative to a certain extent.

If e.g. we close the eyes of a person, who is then asked to walk straight on, there will be many, who deviate to the right or to the left. The reason of it will depend among other things on the fact, that the proprioceptive equilibrium stimuli, which arise from both the halves of the body, are not of the same strength; the result is that one half predominates and that the gait will not be totally straight. If we place, however, at a distance a person, who counts, then the blindfolded person will be able, guided by the sound, to walk straight on towards the counting person. The extero-ceptive stimuli, which pass from the ears towards the cerebrum, complete the others, through which the straight gait is made possible. The sense of hearing comes to the aid of the equilibrium sensation. It is also well-known that the eye sense can give direction to our movements.

It is comprehensible that as these two senses are already able to give assistance under normal circumstances to the equilibrium sensation, they can help the suffering person in yet higher degree after practice.

It is also a well-known fact that e.g. the ataxia in tabes patients, who can still walk straight with their eyes opened, comes to the

foreground, when the same movements are performed with eyes shut, or when they are walking in the dark and cannot make use of their eyes.

This help may be rather sufficient in light cases of tabes, but it will not be possible to totally improve the disturbance, if the illness has become of a rather serious nature. If we give to this kind of patients contact-sensation by the arms, there will yet be an important improvement. (Fig. 2).

Consequently from this follows as is moreover near at hand, that the equilibrium sensation of the arms, being of the same sort as of the trunk and limbs, compensates in reality, while the other senses can only correct to a certain degree.

I have pointed out in the preceding pages, that one finds the same facts back in lesions of the vestibular organ. Here too the ataxia improves, when the patient uses his eyes (Fig. 3), but here too one finds, that *when the eyes cannot sufficiently correct any more, the ataxia totally or nearly totally vanishes, when through the arms equilibrium-sensation is obtained with the surrounding world.* Here too we find, that the equilibrium sensation of the arms acts totally or nearly totally compensatory. (Fig. 4).

The question arises how we can explain this.

I think that I may except as easy to comprehend, *that the proprioceptive stimuli of the equilibrium sensation of the trunk and the limbs and those of the vestibular organ are to be considered of the same sort.*

Referring to our equilibrium, no difference should be made between the afferent-proprioceptive stimuli, which from the vestibular organ are conducted to the central nervous system and those which come there from the trunk and the limbs. It is a large system of equilibrium fibres that is spread over our whole body and its aim is to regulate the equilibrium.

The sixth sense, the one for our equilibrium, has therefore not only to be looked for in the vestibular organ, but it is, as I explained, spread over the whole of our body. The vestibular organ is but a part of it.

Now probably one might ask, why does that organ form a whole while in the other equilibrium paths very little independency is found. The reason for this, according to my view, has to be found in the extraordinary relation of the head, in comparison to the rest of the body.

To make this clear, one has to keep in mind, that the equilibrium sensation of the different parts of our body is not everywhere the same, or otherwise expressed, is no everywhere equivalent. E.g. the equilibrium sensation for the trunk, which can only move

moderately, is but little developed. For the lower limbs it must be already higher, because the movements which they perform are already much more complicated.

In yet higher degree this is the case with our arms. So it is known, that as soon as our equilibrium gets in any danger, we do not only immediately put our arms into function, but that we trust even more to our arms, which are weaker concerning our muscle strength than to our much more muscular legs. If the equilibrium sensation of our arms has already reached a high degree, this will be yet more so with our head, which is above all designed to bring to our knowledge our attitude in space. It speaks for itself that without this knowledge no equilibrium is possible. Moreover, with exception of the lower jaw, the different parts of the head are not linked together by joints, but they are tightly grown together. That this puts the head into an extraordinary relation is comprehensible. The trunk and the limbs are in opposition to the head composed of movable parts, which are joined together by tendons and sinews. All the changes in attitude, therefore also those which are of importance for our equilibrium, come to our consciousness. This is not the case with our head.

By means of the neck and all that is connected with it, it can, however, fix its own *posture* with relation to our body, but it will not be of any use for the determination of the equilibrium.

The equilibrium organ of the head has, on account of what was above reported, to be not only much more highly developed, but it must be differently composed from the equilibrium paths for the trunk and the limbs. Therefore too the vestibular organ is built up in a different way. As the joints in our head, necessary for the equilibrium, are all missing, it is most probable, that the statoliths through movements during the changes of attitude stimulate the equilibrium fibres and thus put into action the necessary afferent-proprioceptive impulses. The central nervous system is immediately warned of any danger that threatens our equilibrium and can take the necessary steps against it.

CONCLUSIONS.

- a. The sixth equilibrium sense is not placed in the vestibular organ only, but has its tracts spread over the whole body.
 - b. The vestibular organ is, as far as it refers to our equilibrium only to be considered as a part of the equilibrium sense.
 - c. The different parts of this sense can compensate each other reciprocally.
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Physiology. — "*Cerebellar ataxia as disturbance of the equilibrium-sensation.*" By Dr. D. J. HULSHOFF POL. (Communicated by Prof. C. WINKLER.)

(Communicated in the meeting of Jan. 26, 1918).

In a former paper¹⁾ I explained, that the ataxia which a patient, suffering from tabes, shows, while walking, is nearly quite abolished when he has by means of his hands contact-sensation with the persons walking to his right as well as to his left side.

The reason for this improved walking has to be looked for in the fact, that as long as the affliction resides in the lower part of the spinal cord, it enables him to make use of the equilibrium-sensation of the upper limbs (afferent-proprioceptive stimuli), and in this way he can orientate himself better in space.

If this latter happens to be, then all the efferent impulses, necessary for the regulated movements, can run down along the motor paths to the trunk and the lower limbs, through which the ataxia becomes abolished, respectively ameliorated.

I expressed myself thus, that where an ordinary person walks by his eyes and the equilibrium-sensation of the vestibular apparatus, the trunk and the lower limbs, a tabes-patient does it by the equilibrium-sensation of the vestibular apparatus and the rests of that which is still left in the trunk and lower limbs.

If such a person therefore has contact-sensation with people walking alongside of him, he moreover walks by the equilibrium-sensation of the upper limbs.

If one examines, not a tabes-patient, but a sufferer from the vestibular organ, then, as I wrote, such a patient will walk by his eyes, the equilibrium sensation of the trunk and legs and the rests of the equilibrium impulses which are obtained through the vestibular apparatus. If one therefore gives to such a patient contact sensation through persons walking alongside of him, then it also appears that he is enabled to walk normally again or at least nearly normally.

As the ataxia, which both these patients show, are both almost totally abolished through the same influence, viz. contact sensation

¹⁾ Our equilibrium-organ. These Proceedings p. 626.

by means of the upper limbs, I thought I had to accept the involved afferent-proprioceptive impulses in those cases as being of the same sort.

The vestibular apparatus therefore has to be considered, *as far as our walking function is concerned*, as a modified and higher developed organ for the equilibrium-sensation of the head.

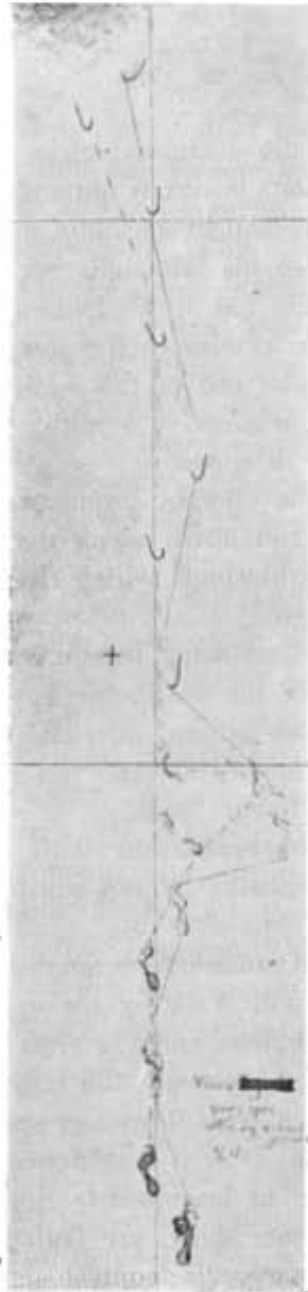


Fig. 1.

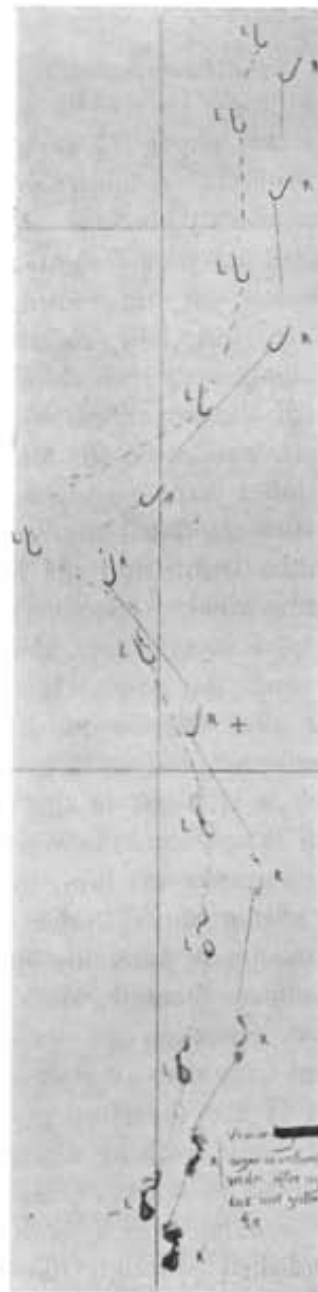


Fig. 2.

It would take me too long in this paper to enter more in particular into this hypothesis; I refer the interested reader to the original communication. The one thing to which I will draw attention, is, that according to this view, considering our equilibrium, there should be made no principal difference between the afferent-proprioceptive stimuli which are conducted from the cerebellar tracts of the lateral column and those from the vestibular apparatus to the cerebellum. All these stimuli are related to the equilibrium-sensation and therefore regulate our gait. These different afferent tracts thus form a whole and they are to be considered as a subdivision of the same equilibrium system.

Now it is important to trace, whether they change, and if so, what alterations these afferent stimuli undergo, when they arrive in the cerebellum.

If, investigating this, one makes patients, suffering from e.g. cerebellar tumors, perform the same walking-tests, as I did with sufferers from tabes or vestibular affliction, then the results prove to be totally the same.

For instance I will report the following case, in which during life the diagnosis was made of a tumor, which was located at the left side, where it pressed as well on the cerebellum as on the nervus octavus. During the operation and also post-mortem the diagnosis could be confirmed.

If one had the patient walk totally unsupported with open eyes, then the part of her gait was obtained as reproduced in fig. 1. The ataxia is distinctly visible. If her eyes were shut, then the path of her gait became as in fig. 2.

When comparing the two the ataxia proves to be considerably augmented. This is comprehensible, because in the latter case the afferent-extero-ceptive stimuli from the eyes are missing. The difference between these two paths of gait results from the influence of the eyes on the performed movements.

It is important to point out once more (see preceding paper) that, when by abnormalities of the static organ a second organ comes to his aid, the latter only can partially replace the deficiencies of the former, if these are of rather severe nature.

This is distinctly visible in fig. 1, because notwithstanding the aid of the eyes, the ataxia however is far from gone.

If we now let such a patient walk quite free with eyes open, but giving her contact sensation through persons next to her, then *although also the neck-equilibrium-impulses are shut out* by means of a bandage, the gait path in fig. 3 is reproduced, in which the

ataxia proves to be totally gone. The equilibrium sensation which is augmented through the contact-sensation of the arms is enabled to compensate all that is missing. What the eyes could not do, the afferent-proprioceptive stimuli of the upper limbs could do. They compensated, thus abolishing the ataxia.



Fig. 3.



Fig. 4.

As one could oppose against this important amelioration that the result had been due for the greater part to the help of the eyes, I repeated the test in precisely the same way, but now with eyes closed. The produced gait path is found in fig. 4. Now too no sign of ataxia is seen. The only deviation is, that the patient walks to the right instead of walking straight on. As this deviation takes place gradually and the gait-path remains straight, the circus gait must be excluded; it seems to me, that in this case one cannot speak of a deviation to the right. It is most probable that the patient did not stand straight in front of the line, but somewhat in oblique direction and therefore walked in that way.

The 4th fig. proves that the contact sensation through the arms is yet able to abolish the ataxia, even if the patient misses the afferent-extero-ceptive impulses from the eyes.

One thus sees here exactly the same phenomenon as with the ataxia in tabes and in vestibular affliction.

Therefore it lies at hand to assume that cerebellar sensory ataxia arises when in the cerebellum the equilibrium paths are being interrupted which from the spinal cord and the nervus octavus pass into it.

This would confirm JELGERSMA's¹⁾ view (pg. 217): "The supposition that the cerebellum is a central place of innervation for both these organs²⁾, is therefore probable."

Should my view be right, then cerebellar sensory ataxia will occur, when the process of the disease arises in those parts of the cerebellum, in which the equilibrium-paths pass.

In connection with the above a few questions arise.

The first is whether the cerebellum exclusively dominates the equilibrium.

This question is answered in negative sense by many investigators, because e.g. experiments on animals have taught that experimentally obtained cerebellar ataxia can totally pass away after a certain time, which proves that the afferent equilibrium impulses can arrive at the cerebrum also along other paths.

The second question is whether the cerebellar ataxia always shows the same image.

Should I, as regards the experiments on animals, confine myself to the well-known investigations of LUCIANI³⁾, then he too made a

¹⁾ JELGERSMA, G. The function of the cerebellum. Psych. Neur. bl. 1915.

²⁾ Meant are: tonus- and equilibrium organ and the deep sensation.

³⁾ LUCIANI, L. Das Kleinhirn. Georg. Thieme. Leipzig 1893.

difference between the ordinary atactive movements and those which were indicated by him as "dysmetria".

When one wishes to see these differences reproduced distinctly I refer to my photographs in my communication on "cerebellar ataxia". Plate VIII, X to XIV ¹⁾.

In man, where the phenomenon cannot be localized as sure as in animal-experiment, a conclusion is drawn with more difficulty. Yet I will quote some writers, who showed that the deviations in gait do not always give the same aspect.

JELGERSMA (l. c. p. 227) e. g. writes that the occurrence of the cerebellar ataxia is due to the fact that the trunk sways over the legs: "a gait, which greatly resembles the walking of drunken men."

He only describes one type of deviation of the gait. OPPENHEIM, however, differentiates in his hand-book two forms of cerebellar ataxia, 1. "auf (Schwindel und) Gleichgewichtsstörung beruhende, "die grosse Aehnlichkeit mit der Gangweise des Betrunkenen "zeigt," and 2. "eine auf Bewegungsataxie beruhende. Patient "geht breitbeinig und stampfend, aber ohne dass ein ubermässiges "Schlendern eintritt. . . . Eine scharfe Unterscheidung dieser Gehstörung "von der spinalataktischen ist wohl nur möglich, wenn sich die unter "1^e beschriebene Abart mit ihr verbindet."

OPPENHEIM therefore thinks the cerebella ataxia e. g. also dependent on the spinal cord.

DÉGÉRINE on the other hand writes in his work "Traité de Pathologie générale" 1901, on page 643 "b. Ataxie labyrinthique. Les affections "de l'oreille interne produisent quelquefois des troubles de la marche "et de l'équilibre, qui ressemblent jusqu'à un certain point aux "disordres de l'ataxie cerebelleuse." DÉGÉRINE points out in this case the connection of the cerebellar ataxia with the phenomena which are found in vestibular disturbances.

Now the question arises to interpret the difference in the atactic aspect.

In my former communication I explained that even although the equilibrium-impulses, originating from the vestibular organ may be considered as to belong to the same which come from the spinal cord, yet there exists a great difference in their results, owing to the higher development of that organ.

The consequence of this is, that according to the afferent equilibrium path suffering more in the one case than in the other, the complex of atactic symptoms will also appear differently.

If the spinal tracts have suffered most, then the type as described

¹⁾ Psych. Neur. Bl. 1909 N^o. 4.

by OPPENHEIM will be found in general, viz. his second form of cerebellar ataxia.

Should the vestibular tract be hurt, then the description of DÉGÉRINE comes right. If there is an interruption of both the paths or if the disturbance of the paths from the right and from the left side commences more or less simultaneously, then perhaps the gait of the drunken man will become more prominent.

If the results of the animal experiment are compared with those found in man, then we may say that the cerebellar ataxia does not always show the same aspect and that this can be explained by the fact, that the cerebellum possesses more than one afferent tract, whose interruption causes disturbance in its course and that according to the suffering of the one or the other or more paths, the aspect will change.

The *third* question is to explain in cerebellar disturbance the fact how the equilibrium sensation of the upper limbs can totally compensate the ataxia, because one may accept that its equilibrium paths, just as those of the lower limbs, pass into the cerebellum and therefore will also be broken off by the process of the illness.

I must acknowledge that I cannot very well give an explanation of this fact, if not the possibility should be accepted of a better connection of the equilibrium sensation of the arms (apart from the cerebellum) with the cerebrum, than is the case with the legs. Later experiments will have to give a decision on this point.

CONCLUSION.

1. By interruption in the cerebellum of afferent cerebellar tracts, originating from the vestibular organ and the tractus spino-cerebellares, ataxia appears.

2. According as these tracts suffer more or less, whether alone, or together, the aspect of the cerebellar ataxia will present a different type.

Physics. — “On the Heat of Dissociation of Di-atomic Gases in Connection with the Increased Valency-Attractions \sqrt{A} of the Free Atoms”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of October 27, 1918).

Introduction.

1. In a series of Treatises in these Proceedings¹⁾ on the additivity of the values of b and \sqrt{a} of the equation of state, and on the fundamental values of these quantities for different elements in connection with the periodic system, I determined the following values of $b \cdot 10^5$ and $\sqrt{a} \cdot 10^2$, expressed in so-called “normal” units.

The values of $b_k \cdot 10^5$ (per Gr. atom), determined up to now, are found collected in Table I.

TABLE I. (Values of $b_k \cdot 10^5$).

H = 59 (34; 14)						He = 105
Li = 145		C = 100 (75)	N = 85 (60)	O = 70 (50)	F = 55	Ne = 76
Na = 270		Si = 155	P = 144	S = 125	Cl = 110 à 115	Ar = 144
K = 480		Ti = 180				
Cu = 110		Ge = 210	As = 195	Se = 180	Br = 165	Kr = 177
Rb = 580		Zr = 235				
Ag = 150		Sn = 265	Sb = 250	Te = 235	I = 220	X = 228
Cs = 710		Ce = 290				
Au = 150	Hg = 150	Pb = 320 à 375	Bi = 305			Nt = 277
		Th = 400				

It will be remembered that these fundamental values present a great regularity. Starting from the carbon group the decrease in every

¹⁾ These Proceed. 18, 1220 and 1235; 19, 2, 287 and 295 (1916); 20, 138, 492 and 505 (1917). Cf. also Journ. de Chim. Phys. 14, 3 (1916), and Zeitschr. f. anorg. u. allg. Chem. 104, 56—156 (1918).

horizontal row of the periodic system towards the right is 15 *units*, in every vertical row the increase downward 55 *units*. The elements of the valence-less Helium group evidently fit in with the elements of the preceding Halogen group in a natural way.

In this Helium group the values of b_k are directly calculated from those of T_k and p_k ; also the value 59 for H from that of H, ¹⁾. The other values have been calculated from the *compounds* of the different elements (for Cl the value 115 seems to be more satisfactory than 110). From T_k and p_k we can directly calculate for N, P, O, Cl from N₂, P₄, O₂ and Cl₂: $b = 86, 135, 71$ and 113 to 125 (according as for Cl₂ the data of DEWAR or the more recent ones of PELLATON are used).

All the values of b can now be built up *additively* by the aid of these fundamental values for the most divergent compounds. In this also the "condensed" values 34 and 14 are valid for H; for C, N, and O the condensed values 75, resp. 60 and 50. The rules holding for this are found in the two cited principal papers of 1916 in These Proceedings and in the Journ. de Ch. Ph.

No exceptions have been found to this additive law, those that still existed for a few organic substances (e.g. the *amines*) have now all disappeared, owing to the later determinations of T_k and p_k by BERTHOUD ²⁾ at Neuchâtel, undertaken expressly in connection with these deviations. The critical pressures determined earlier by VINCENT and CHAPPUIS appeared to be all faulty to a high degree ³⁾. It is to be foreseen that this will also be the case with other earlier determinations.

We will also state that the values of b for H, Li, Na, K, Rb and Cs are to each other in the ratio $1/2 : 1 1/4 : 2 1/8 : 4 : 5 : 6$.

The values of b found are *entirely independent* of the state in which the atom is: whether as *free* atom e.g. in metallic tin, or as part of a molecule as in SnCl₄. It will presently appear that this is *not* the case with the fundamental values of \sqrt{a} .

2. For the values of $10^3 \sqrt{a_k}$ per Gr. atom, again expressed in "normal" units, were found up to now the values recorded in table

¹⁾ Of course the latest data were used for this; for H₂ and Ne the values found very recently by K. ONNES, CROMMELIN and CATH.

²⁾ Journ. de Chim. Phys. 15, 3 (1917).

³⁾ Thus p_k appeared to be = 55,5 for NH₃.C₂H₅, whereas V. and Ch. found 66; for NH(C₂H₅)₂ the value 36.6 was found, against 40 by V. and Ch.; etc. Also for C₃H₇Cl BERTHOUD found 45,2, whereas V. and Ch. found 49. Errors therefore from 10 to 20%!

II; the values printed in bold type refer to the *increased* values of the *free atoms*, the others to those which are found in *compounds*: hence the *rest-values*.

TABLE II. (Values of $\sqrt{a_k} \cdot 10^2$).

H = 1,1 (3,2; 1,6)						He = 0,8
Li = ? 23		C = 3,1 32	N = 2,9	O = 2,7	F = 2,9	Ne = 2,1
Na = ? 27		Si = ? 34	P = 6,4	S = 6,3	Cl = 5,4	Ar = 5,2
K = ? 33		Ti = ? 35				
		Ge = ? 36	As = 7	Se = 7	Br = 6,9	Kr = 6,9
Rb = ? 35		Zr = ? 37				
		Sn = ? 38	Sb = 8,9 33	Te = 9,8	I = 8,8	X = 9,1
Cs = ? 38		Ce = ? 39				
	Hg = 10,7	Pb = ? 40	Bi = 11 36			Nt = 11,5
		Th = ? 41				

Not from the fundamental values of a can the values of a of all possible compounds be built up additively — but those of \sqrt{a} from the fundamental values of \sqrt{a} given in the above table. Here too no important deviations were found; those for the amines have again disappeared for the greater part through the later determinations of BERTHOUD (loc. cit.).

The values of $\sqrt{a_k}$ for the noble gases (calculated directly from those of T_k and p_k) fit in again perfectly with the values holding for every horizontal row. It may be said of them that (starting from the carbon group) the values of $\sqrt{a_k}$ in *compounds* are *about the same* for every horizontal row of the periodic system, and can be represented in approximation by the whole numbers 1. 3. 5. 7. 9. 11 from the 0. to the 5. row (inclusive).

The values of $\sqrt{a_k}$ calculated for N, P, O, and Cl directly from N_2 , P_4 , O_2 , and Cl_2 are resp. 2,6, 6,4, 2,6 and 5,4 to 5,8 (DEWAR or PELLATON).

For H in compounds only the values 3,2 and chiefly 1,6 hold. The value 1,1 calculated directly from T_k and p_k of H_2 is only found for H_2 itself.

3. However — what is self-evidently *not* found for b — it should be taken into account that for the fundamental values of \sqrt{a} the indicated attractions can be entirely or partly *destroyed* by an interception of the rays of attraction. Thus the value of \sqrt{a} of a central atom surrounded on all sides by atoms or atom groups — as e.g. C in CH_4 , C_2H_6 etc., Si in $SiCl_4$, Sn and Ge in $SnCl_4$ and $GeCl_4$, N and P in NH_3 and PH_3 — is found $= 0$ everywhere, so that these enclosed atoms do not exert *any attractive action towards the outside*¹⁾.

But as soon as the C-atom gets *partly free* again, by *double bindings* e.g. as in C_2H_4 (only imagine the position of the C-atom stereo-chemical), the value of $\sqrt{a_k}$ rises immediately from 0 to 1,55, hence half the fundamental value 3,1. And when the C-atom gets *entirely free*, for *triple bindings* e.g. as in C_2H_2 , the full value 3,1 is accordingly at once found.

This rule holds everywhere. An interesting example is the *isomylene*. Here there are three singly bound and two doubly bound C-atoms. Hence the value $3 \times 0 + 2 \times 1,55 + 10 \times 1,6 = 19,1$ is calculated for $\sqrt{a_k}$. From T_k and p_k 19,2 was found. Indeed, an exceedingly remarkable confirmation of the rule.

The same thing holds for benzene and naphthalene. But for the singly bound C-atoms in the *substitution groups* the old value 0 is again valid. Thus for Toluene $= C_6H_5.CH_3$ the value of $\sqrt{a_k}$ is $= 6 \times 1,55 + 1 \times 0 + 8 \times 1,6 = 22,1$, while 22,2 is found; for O-Xylene $= C_6H_4(CH_3)_2$ we calculate $6 \times 1,55 + 2 \times 0 + 10 \times 1,6 = 25,3$, quite identical with the value 25,3 found from T_k and p_k . We might add numerous others to these examples, but we refer for this to the earlier principal papers.

We have now reached the *main question*: what happens when the atoms no longer occur in compounds, as N in N_2 , Cl in Cl_2 , etc. — but can occur *entirely free*, as for the *metals*, or for the *free atoms* Cl, Br and I in Cl_2 , Br_2 , I_2 , which get decomposed at

¹⁾ Accordingly in consequence of this (see the table) we were not able to give the values of $\sqrt{a_k}$ for Si, Ti, Ge and Sn in compounds, though compounds of them are known, of which T_k and p_k have been determined. But it is exactly in *these* compounds ($SiCl_4$, $GeCl_4$ etc.) that the attraction of the central atom Si, Ti, Ge, Sn is eliminated.

high temperatures, or for H, N and O in the gases H_2 , N_2 , O_2 , which also dissociate at very high temperatures?

Then — and this is perhaps the most remarkable of our results, which is fully confirmed by what follows presently with respect to the heats of dissociation — the values of \sqrt{a} rise at once to the greatly increased values from **30** to **40** (instead of from 1 to 11). These increased values are therefore the real *valency-attractions*, whereas the values found in compounds represent only the so-called *rest-values*: what still remains for action outside, after the chief valencies are saturate, and have therefore become inactive towards the outside.

That for the elements of the helium group only the ordinary rest values are found in spite of their atomistic behaviour is of course owing to this that these elements are *valence-less*.

For arsenic only a partially increased value was found, pointing to a dissociation of As_4 at T_k to an amount of 20%, whereas phosphorus appeared to be still perfectly normal = P_4 at T_k . For Se and Te we found amounts of dissociation (always at T_k) of 30% resp. 80%. In the halogen group only a very slight degree of dissociation (5 and 10%) was observed for Br_2 and I_2 . As the atoms occur more and more as *free atoms*, the *metal character* asserts itself more and more in a group: $As \rightarrow Sb \rightarrow Bi$, $Se \rightarrow Te$; etc.

Besides the rise from 0 to 1.55 and 3.1 for *carbon* — according as the C-atom is entirely or only partially shadowed by surrounding atoms or atom groups, to which it is *bound* — another rise of \sqrt{a} takes place, up to 32, the ten-fold value, when the C-atom has also got released from these bindings, and can occur *quite independent* as *atomistic* carbon. Hence the enormously high value of the critical temperature, viz. 6500 abs., which would only have amounted to 120° abs. in the case of C_2 , as is easy to calculate. The carbon would have become comparable with N_2 , O_2 etc., whereas it is now on a line with a metal that is exceedingly difficult to melt.

For *Tellurium* the peculiarity is still found that the normal rest-attraction 9, which is among others found for $TeCl_4$ ¹⁾, has already

¹⁾ That for $TeCl_4$ the central Te atom does not exert an intercepting influence like C in CCl_4 , Ge in $GeCl_4$, etc. is owing to the configuration of the molecule. While for CCl_4 the four chlorine atoms are regularly situated in the *space* round the C-atom (in the direction of the four angular points of a tetrahedron), it should be supposed that for $TeCl_4$ the Cl atoms lie in one plane round the central Te-atom. Nor do we find a complete intercepting influence for PCl_5 and $POCl_3$, AsH_3 and $AsCl_3$, SbH_3 and $SbCl_3$, which for these substances is probably owing to the comparatively greater extension of the central atom. For $SbCl_3$ we find even again the full rest value 9 (Cf. the cited papers in these Proceedings).

risen to 13 for TeCl_2 — where two valencies have been liberated. For entirely free metallic Te \sqrt{a} will rise still further, namely to about 30.

What consequences this behaviour of molecules and atoms with regard to the attraction exercised by them can have for the properties of many substances (volatility, surface tension, etc.), has been set forth at length by me elsewhere.¹⁾

4. The heat of dissociation of di-atomic gases.

After these introductory remarks we may now proceed to the real subject of this Paper, viz. the calculation of the *heats of dissociation* Q from the values of the increased valency attractions \sqrt{A} , which were mentioned above, and which are recorded in table II (the values printed in bold type under the elements), for so far as they are now known.

Let us take hydrogen as an example. For the internal energy of the not dissociated gas H_2 we may write:

$$E_{\text{H}_2} = (E_0 - Q_0) - \frac{a}{v} + c_{\text{H}_2} T, \quad (a)$$

in which E_0 represents the so-called *constant of Energy* of the *unbound* H-atoms, hence $E_0 - Q_0$ that of the *bound* H_2 -atoms in H_2 . Hence Q_0 is the absorbed (internal) heat of dissociation (in units of energy e.g.) in the dissociation $\text{H}_2 \rightarrow 2\text{H}$, at $T = 0$ — i.e. the chemical energy (at $T = 0$), which is liberated in the formation of 1 Gr. mol. H_2 from the separate H-atoms.

For the dissociated $\text{H} + \text{H}$ we have evidently:

$$2E_{\text{H}} = E_0 - \frac{4A}{v} + 2c_{\text{H}} T. \quad (b)$$

While, namely, for H_2 the quantity a represented the ordinary rest attraction (per Gr. mol.) between the *molecules*, A now represents the increased attraction of valency between the separate, now free *atoms* per Gr. atom, hence $4A$ per Gr. mol. = 2 Gr. atoms.

In the *ideal gasstate*, where v is very great, we shall simply have:

$$E_{\text{H}_2} = (E_0 - Q_0) + c_{\text{H}_2} T \quad ; \quad 2E_{\text{H}} = E_0 + 2c_{\text{H}} T,$$

and as these two quantities of energy will just differ the *total* (internal) heat of dissociation Q , we have then:

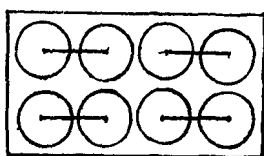
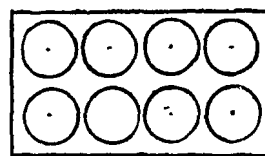
$$Q = 2E_{\text{H}} - E_{\text{H}_2} = Q_0 + (2c_{\text{H}} - c_{\text{H}_2}) T, \quad (c)$$

the well-known expression for Q in the function of T , when c_{H} represents the limiting value of the specific heat at constant (large)

¹⁾ Cf. Chemisch Weekblad, Sept. 14, 1918, N^o. 37 (p. 1124—1137).

volume of 1 Gr. atom H, and c_{H_2} the same quantity for H_2 . As c_{H_2} is = 5, and $c_H = 3$ (in Gr. cal.), $Q = Q_0 + T'$ may be written in the case of $H_2 \rightarrow 2H$ for Q .

When, however, the volume becomes smaller and smaller, and the quantities $\frac{a}{v}$ and $\frac{A}{v}$ larger and larger, at last a (fictitious) volume will arise, in which the difference of the two energies has become = 0, in consequence of the fact that with respect to the internal energy it will then have become quite indifferent whether the atoms are separately present in that small space, or combined to molecules — i.e. when also the energies of translation do not differ, hence at $T' = 0$.

 H_2  $H + H$

For the difference $Q' = 2E'_H - E'_{H_2}$ we have in this case.

$$Q' = Q_0 - \frac{4A}{v_1} + \frac{a}{v_1} + (2c_H - c_{H_2})T', \quad \dots \quad (d)$$

in which v_1 represents the above mentioned small volume, which we shall have to define more closely. Now it follows immediately from (d) at $T' = 0$, in which case Q' must be = 0, that

$$Q_0 = \frac{4A}{v_1} - \frac{a}{v_1}, \quad \dots \quad (1)$$

and this is the simple relation between the heat of dissociation Q_0 at $T' = 0$ and the two attractions A and a , which we have sought.

We must now determine the small volume v_1 . This will evidently be of the order of the limiting volume, which the molecules themselves (see the above figure) occupy in the *natural* state in *unconstrained* condition, i.e. the volume expressed by b_g — and not e.g. the smaller volume b_l in the liquid state, where the molecules will be *compressed* in consequence of the smaller space, and which therefore denotes a *constrained*, and no free, no natural condition ¹⁾. Now b_g is about = b_k , so that we may put:

$$v_1 = \gamma b_g = \gamma b_k,$$

¹⁾ In this it has also been supposed that b_g is not = $4m$, when m denotes the *real* volume of the molecules, but simply = m itself. According to recent views the latter supposition is theoretically at least as well justified as the former $b_g = 4m$, which refers specially to collisions of *mathematical spheres*, and not of *real*

in which $\gamma(>1)$ will not be far from unity. When we put $4A = na$, (1) becomes:

$$Q_0 = \frac{(n-1)a_1}{v_1} = \frac{(n-1)\varepsilon a_k}{\gamma b_k},$$

in which we put a_1 , the attraction in the small volume $v_1 = \varepsilon a_k$. In this $\varepsilon(>1)$ will differ somewhat more from unity than γ , so that ε will be $>\gamma$. For $a_k : b_k$ we may now write $\frac{27}{8\lambda} RT_k$, in which γ is only little smaller than 1, so that we finally get, when $\gamma\lambda : \varepsilon = \theta$ is put:

$$Q_0 = (n-1) \frac{27}{8\theta} RT_k, \quad . \quad . \quad . \quad . \quad . \quad . \quad (1a)$$

which enables us to calculate Q_0 , when A and a , and in consequence of which also n and T_k are known. But as we do not know the values of A for H_2 , N_2 , O_2 , but as we on the other hand *do* know those of Q_0 in approximation, we shall follow the *reversed* course, and calculate n from Q_0 . We can then see whether the values of \sqrt{A} calculated in this way are really of the expected order of magnitude, compared with the already known values of \sqrt{A} for elements of the periodic system lying near (cf. Table II). We then get:

$$n = 1 + \frac{4}{27} \theta \frac{Q_0}{T_k},$$

hence:

$$4A = a \left(1 + \frac{4}{27} \theta \frac{Q_0}{T_k} \right),$$

when 2, the value in Gr. cal., is put for R , which renders it possible to leave also Q_0 expressed in Gr. cal. The value of a refers to 1 Gr.mol. H_2 . When therefore a' represents the value of one *gram-atom* (these values are recorded in table II), then $a = 4a'$, and we get finally:

$$\sqrt{A_k} = \sqrt{a'_k} \times \sqrt{1 + \frac{4}{27} \theta \frac{Q_0}{T_k}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

when we take A and a' both at the critical temperature. Accordingly these two quantities now duly refer to 1 Gr.atom. Under the root sign, however, Q_0 refers to 1 Gr.mol. according to the derivation of the formula. As ε will always be $>\gamma\lambda$, $\theta = \gamma\lambda : \varepsilon$ will be *somewhat smaller* than unity, also when we take into account that R is not

molecules (which can differ considerably from the spherical shape, e.g. the elongated molecules of the hydro-carbons). Moreover, when the real size of the molecules is calculated by another method, we also find values that are in concordance with b_k ($\sim b_q$), calculated from T_k and p_k , and *not* with $\frac{1}{4} b_k$. Cf. among others my Article in These Proc. of Oct. 1914 (Vol. 17), especially p 883 and the Note on the same page.

exactly = 2, but somewhat smaller. The values of $\sqrt{A_k}$ calculated from (2) will, therefore, be sooner *too large* than too small, when we shall take for the present $\theta = 1$ in what follows.

5. Calculation of the values of $\sqrt{A_k}$ from Q_0 .

Let us begin with *hydrogen*. ISNARDY (1915) determined $Q_0 = 95000$ Gr. cal., whereas LANGMUIR (well-known method) gave 132000 Gr. cal. in 1912. But the latter found from 70000 to 80000 Gr. cal. in 1914.

We are therefore not very far from the truth, when for H_2 we put the value of Q_0 at round 90000 Gr. cal. With $T_k = 33,18$ (K. ONNES, CROMMELIN, CATH, 1917) $Q_0 : T_k$ becomes therefore = 2700, hence $^{1/27}Q_0 : T_k = 402$. And as $\sqrt{a'_k} = 1,1$ (see table II), we get (all the values of $\sqrt{a'_k}$ and $\sqrt{A_k}$ are still to be multiplied by 10^{-2}):

$$\sqrt{A_k} = 1,1 \times \sqrt{403} = 2,08 = \mathbf{22},$$

which is in very good harmony with what we have found for Li (23) and Na (27) (see table II).

For *nitrogen* BRINER¹⁾ calculates $Q_0 =$ at least 150000 Gr. cal. from a single value given by LANGMUIR. This value of BRINER's seems too high to me considering the values for H_2 and for O_2 , and in my opinion 130000 Gr. cal. will be nearer the truth. When we calculate $\sqrt{A_k}$ from the two values of Q_0 , we get $^{1/27}Q_0 : T_k = ^{1/27} \times \times \left(\frac{150000}{130000} : 126 \right) = ^{1/27} \times \left(\frac{1190}{1032} \right) = 176$ to 153. And $\sqrt{a'_k}$ being = 2,6, we get:

$$\sqrt{A_k} = 2,6 \times \sqrt{\frac{177}{154}} = 34,6 \text{ or } 32,3 = \mathbf{35} \text{ or } \mathbf{32}.$$

As in connection with C = 32 also a value in the neighbourhood of 32 can be expected for N, the result is also here a confirmation of our formula (1) or (1a), the more so when we bear in mind that the result may possibly be slightly too high in consequence of our having put $\theta = 1$.

For *Oxygen* SIEGEL²⁾ has found $Q_0 = 160000$ Gr. cal. Hence $^{1/27}Q_0 : T_k$ here becomes = $^{1/27} \times (160000 : 154.25) = ^{1/27} \times 1040 = 154$. With $\sqrt{a'_k} = 2,6$ we find further:

$$\sqrt{A_k} = 2,6 \times \sqrt{155} = 32,4 = \mathbf{32},$$

which is again in excellent agreement.

In the second place we shall examine the *Halogens*.

First of all *Chlorine*. PIER³⁾ found the value 113000 Gr. cal. for

¹⁾ Journal de Chem. Phys. 12, 119 (1914) and 13, 219 and 465 (1915).

²⁾ Zeitschr. f. physik. Chem 87, 642 (1914). Cf. also BRINER, l.c.

³⁾ Ibid 62, 385 (1908).

Q_0 . According to PELLATON the critical temperature is $144^\circ \text{C} = 417^\circ,1$ abs., so that ${}^{1/27} Q_0 : T_k$ becomes $= {}^{1/27} \times 271 = 40,2$. Hence with $\sqrt{a'_k} = 5,6$ we shall get about (from the critical data of DEWAR would namely follow 5,43, from those of PELLATON 5,75)

$$\sqrt{A_k} = 5,6 \times \sqrt{41,2} = 35,0 = 35.$$

Though this seems somewhat too high to us, as from 32 to 30 may be expected, the order of magnitude is yet again in agreement with what was found for it for \sqrt{A} with other elements. Possibly Q_0 is somewhat too high, or also $\sqrt{a'_k} < 5,6$; and perhaps in this case — where $a_k : a_1$ will be further from unity than for H_2 , N_2 and O_2 , which have so much lower critical temperatures — θ will also be so much smaller than 1, that the found value 35 will have to be lowered to ± 32 .

With regard to *Bromine* PERMAN and ATKINSON¹⁾ found for Q_0 the value 57000 Gr.cal. With $T_k = 302^\circ,2 \text{ C} = 575,3$ abs. we have ${}^{1/27} Q_0 : T_k = {}^{1/27} \times 99 = 14,7$. We calculate with $\sqrt{a'_k} = 7$:

$$\sqrt{A_k} = 7 \times \sqrt{15,7} = 27,7 = 28,$$

a value that is very plausible.

In conclusion *Iodine*. STARK and BODENSTEIN (1910) found for it $Q_0 = 35500$ Gr.cal., so that with $T_k = 512^\circ \text{C} = 785^\circ,1$ abs. we find ${}^{1/27} \times 45,2 = 6,7$ for ${}^{1/27} Q_0 : T_k$. With $\sqrt{a'_k} = 9$ this gives: accordingly:

$$\sqrt{A_k} = 9 \times \sqrt{7,7} = 25,0 = 25.$$

Nor is this value, though somewhat small, at all impossible.

6. Conclusion.

It has, indeed, appeared very clearly from the above, that the heats of dissociation Q_0 , on the decomposition of the molecules H_2 , N_2 , O_2 , Cl_2 , etc. into their atoms, are perfectly accounted for by the increased valence attractions \sqrt{A} of the separate atoms found by us in earlier papers.

By means of (1) or (1^a) we are henceforth able to calculate Q_0 , when \sqrt{a} and \sqrt{A} are known or reversely to compute \sqrt{A} according to (2), when Q_0 is known.

In GIBBS-PLANCK's well-known formula for the dissociation of gases²⁾

¹⁾ Ibid. 33, 215 (1900).

²⁾ Of course this formula has *nothing* to do with the so-called theorem of heat of NERNST, as many pupils and followers of this scientist erroneously think (cf. many articles in many periodics). The formula was already given in nuce by GIBBS in 1878, and was later frequently elaborated by PLANCK (1887), v. D. WAALS (1891), myself (1892), DUHEM (1893) and many others for different cases. [Cf.

$$\log K = -\frac{Q_0}{RT} + \Sigma \left[\nu_1 \left(\frac{c_1}{R} + 1 \right) \right] \log T + (\Sigma \nu_1) \log p + \Sigma (\nu_1 C_1), \quad (3)$$

in which K represents the constant of dissociation in the relation $\frac{k_2'^2}{k_1'^2} = K$ (for di-atomic gases, where $k_2 = \frac{2x}{1+x}$, $k_1 = \frac{1-x}{1+x}$, $\frac{4x^2}{1-x^2}$ will be therefore $= K$, when x represents the so-called degree of dissociation and k_1 etc. the so-called molecular concentrations), we cannot only theoretically get nearer to the constants C_1 etc. (the so-called *chemical constants* of the components), and so also to $\Sigma (\nu_1 C_1) = C$ — this has been of late done by LORENTZ, PLANCK, SACKUR, TETRODE and others in virtue of considerations of probability in connection with the so-called theorem of heat of NERNST and PLANCK's theory of quanta — but we can also calculate the heats of reaction Q_0 for $T=0$. Up to now we had to be satisfied with determining Q_0 , just as $C = \Sigma (\nu_1 C_1)$, experimentally from a few values of x , but now we should be able to calculate the value of $\log K$ at given temperature and pressure accurately for every gas reaction, as soon as only the values of the chemical constants and of \sqrt{A} and \sqrt{a} are accurately known for *every element separately*.

This must henceforth be the task of physicists: to get to know *these* values completely. They are essential for the knowledge of the behaviour of the chemical substances reacting on each other. When we are further acquainted with all the values of b for the different elements, then T_k and p_k are known of every simple or compound substance, hence also their further thermal behaviour.

among others my *Lehrbuch der math. Chemie* (BARTH, 1901), p. 1—13, 25—28, and the "Sechs Vorträge" (VIEWEG, 1906), p. 64 et seq. These latter appeared originally in the Chem. Weekbl. 1905].

NERNST has only said something about the constant $\Sigma (\nu_1 C_1) = C$ — which is in connection with the constants of entropy — *in reference with his theorem*. This enabled him namely to bring the said quantities C_1 (the "chemical constants") in connection with the constants of the equations of the vapour pressure at very low temperature. But all this has of course nothing to do with formula (3) itself, which is *quite independent* of the theorem of heat. The latter says only something concerning the approach to Θ of entropy, specific heat etc. in condensed systems, in connection also with PLANCK's theory of quanta.

When formula (3) (p constant) is differentiated with respect to T , we get:

$$\left(\frac{d \log K}{dT} \right)_p = \frac{Q_0}{RT^2} + \frac{\Sigma \{ \nu_1 (c_1/R + 1) \}}{T}.$$

And as $\left(\frac{d \log K}{dT} \right)_p = \frac{Q}{RT^2}$, $Q_{p=const.} = Q_0 + \Sigma [\nu_1 (c_1 + R)]T$, hence $Q_{v=const.} = Q_0 + \Sigma (\nu_1 c_1) T$, in perfect agreement with (c) of § 4.

As regards the values of b , and of $\sqrt{\alpha}$ and \sqrt{A} , I have already started an examination of them, and I hope I shall be able to continue this work.

Whether after all a substance as H_2 or Na at ordinary temperatures and pressures will occur in the form of *molecules*, e.g. H_2 , or in that of *free atoms*, as Na, depends entirely on the values of C and Q_0 (hence on $\sqrt{\alpha}$ and \sqrt{A}). The greater Q_0 will be and the smaller C , the smaller will be the value of K , hence of x — the sooner therefore the substance under consideration will occur in the state of molecules, and *not* in that of atoms.

I will still point out that the coefficient of $\log T$, viz. $\Sigma \left[v_1 \left(\frac{c_1}{R} + 1 \right) \right]$, is erroneously stereotypically put $= 1,75$ by NERNST, POLLITZER and many pupils of NERNST. For $2HI \rightarrow H_2 + I_2$ this coefficient will be $= -2 \times \frac{1}{2} + 1 \times \frac{1}{2} + 1 \times \frac{1}{2} = 0$ (as is, indeed, sufficiently known), hence not $= 1,75$. For $H_2 \rightarrow 2H$ it will be $= -1 \times \frac{1}{2} + 2 \times \frac{1}{2} = 1,5$, which again is not $= 1,75$! The same thing applies to many other reactions. It will, therefore, be advisable to determine the value of the coefficient under consideration separately for every reaction. The same thing applies to the constant C . It will not do to assume the chemical constants C_i all in the neighbourhood of 3; these will, indeed, also no doubt be different according to whether we have to do with a mon-atomic or a di-atomic substance, which theory indeed confirms.

Many values of Q_0 are inaccurate because they have been calculated from experiments by means of a formula with faulty coefficients (1,75 and wrong values of C); it will, therefore, deserve recommendation to calculate for a reaction not only the values of Q_0 , but also those of the coefficient in question and of the constant $C = \Sigma(v_1 C_1)$ from the *experiments themselves*. Only in this way is it possible to obtain accurate experimental values of Q_0 .

Since in the computations of § 5 we could not always reckon with perfectly reliable values of Q_0 , the values found for \sqrt{A} are of course not *perfectly* accurate. Also in connection with our putting $\theta = 1$, which will also not be perfectly true, the agreement between the found values of \sqrt{A} , and those which we could expect (see table II) in virtue of the values found already (in an entirely independent way) may be considered very remarkable indeed.

La Tour près de Vevey. August 1918.

Physics. — “*On the measurement of very low temperatures. XXIX. — Vapour-pressures of oxygen and nitrogen for obtaining fixed points on the temperature-scale below 0° C.*” By P. G. CATH. Communication N°. 152*d* from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of Oct. 26, 1918). ¹⁾

§ 1. *Introduction.* The measurements of Comm. Nos. 152*a* and *b* (1917) conducted in conjunction with Prof. KAMERLINGH ONNES (these Proc. XX pp. 991, 1155, 1160) and those of Comm. N°. 152*c* carried out with Prof. KAMERLINGH ONNES and J. M. BURGERS (these Proc. XX p. 1663) offered the welcome opportunity of making some determinations of vapour-pressures of oxygen and nitrogen using the apparatus and measuring instruments which had been fitted up and used for obtaining and measuring constant temperatures. KAMERLINGH ONNES and BRAAK (1908) (Comm. N°. 107*a*, these Proc. XI (1) p. 333) had added to the available fixed points on the temperature-scale the boiling point of oxygen and a couple of lower points, determined under sufficient guarantees as to accuracy. The determinations mentioned above were intended to supplement the latter and might serve to obtain an independent calibration of the oxygen-²⁾ and nitrogen vapour-pressure thermometers, founded directly ³⁾ on the temperature-scale of KAMERLINGH ONNES and his collaborators.

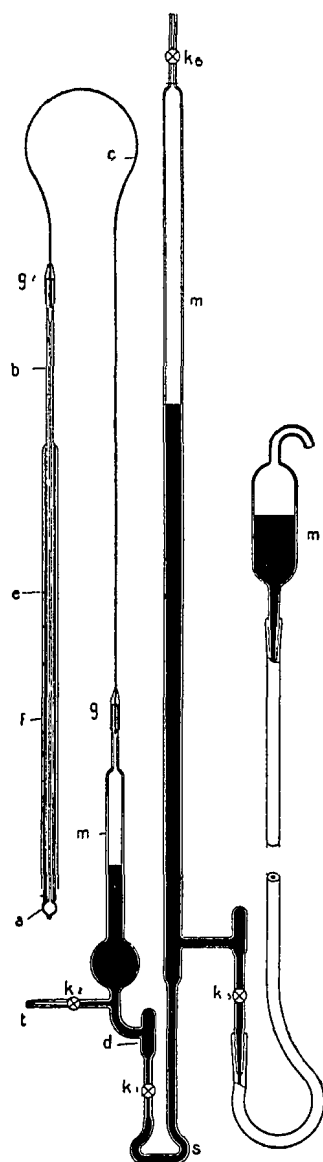
Prof. KAMERLINGH ONNES was good enough to invite me to avail

¹⁾ This paper was originally presented in the meeting of June 1917; in being prepared for the press it underwent some slight modifications on points of secondary importance.

²⁾ The oxygen vapour-pressure thermometer is often used in the form given to it by STOCK and NIELSEN (Ber. d. D. Chem. Ges. 2 (1906) p. 2066) and is then usually simply called STOCK's thermometer. For accurate measurements it is necessary to resort to more suitable forms of the instrument, such as the one described in this paper. The scale given by STOCK and NIELSEN is in need of very considerable corrections (Comp. G. HOLST, Comm. N°. 148*a*; these Proc. XVIII (1) p. 829).

³⁾ VON SIEMENS (vid. G. HOLST Comm. N°. 148*a*) determined the temperatures at which he observed the vapour-pressures by means of a platinum-thermometer, whose readings were reduced to those of *Pt'* of KAMERLINGH ONNES and his collaborators, chiefly by means of four calibration-points, in such a manner that the scales were made to coincide at the boiling point of oxygen as determined by KAMERLINGH ONNES and BRAAK.

myself of this opportunity. I am happy to express my sincere thanks to him on this occasion for his assistance in the investigation.¹⁾



§ 2. *Details of the determinations.* The temperatures were measured with the helium thermometer described in Comm. N^o. 152a and were reduced in the same way as on that occasion to a scale which approaches the absolute scale as closely as possible (Avogadro-scale of helium according to a future communication by CATH and KAMERLINGH ONNES).

The vapour-pressure apparatus agreed in its main features with model A used by KAMERLINGH ONNES and BRAAK (Comm. N^o. 107a), in particular I adhered to the use of the copper tube the purpose of which is to prevent a lower temperature existing anywhere in the apparatus but in the bulb where the liquefied gas collects, at which spot the temperature of the bath is measured. As in the previous experiments mentioned use was made of the advantage offered by the apparatus of allowing different quantities of gas to be condensed in the bulb. As regards the manometer the modification was adopted which HOLST introduced in his vapour-pressure measurements of methyl chloride (Comm. N^o. 144b Sept. 1913): the moveable tube connected to the fixed tube by a rubber tube is replaced (see fig. 1²⁾

by a fixed manometric tube³⁾ to which a mercury vessel is attached by means of a rubber tube. This fixed tube can be exhausted or it

¹⁾ Part of the present paper is embodied in P. G. CATH, Dissertation Leiden 1917, which appeared a few months after the presentation of this communication (see also note 1).

²⁾ The letters are for the greater part the same as in fig. A Comm N^o. 107a, to which we may refer for the further description; a more complete explanation than that given above seems unnecessary.

³⁾ The protection from temperature-changes was obtained by packing in wool. The temperature of the mercury column was determined by means of thermometers suspended beside the tube at the upper and lower ends of the mercury column.

can be connected to a space of constant pressure and a barometer through the stopcock k_0 . The ground joint t may be used for exhaustion, for drying with the aid of a moisture-catcher placed in liquid air and for filling.

The oxygen was prepared from potassium-permanganate in an apparatus which could be evacuated by means of a Toepler-pump and dried by freezing with liquid air. The gas was condensed in a small bulb which was attached to the apparatus and cooled in liquid air, whence it was conveyed to the vapour-pressure apparatus by means of the air-pump ¹⁾.

The nitrogen was prepared by Dr. LEMKES under supervision of Prof. VAN ITALLIE, to whom I express my sincere thanks.

§ 3. *Results.* The results for oxygen were as follows:

TABLE I. Vapour-pressures of oxygen.						
	θ	T	p in int.c.m. ²⁾	p in int. atm.	p calculated	$\angle T$ O—C
I	— 182.62 C.	90.47 K.	78.663	1.0350	1.0351	0.00 deg.
II	182.88	90.21	76.560	1.0074	1.0093	+ 0.02
III	183.22	89.87	73.867	0.9719	0.9725	+ 0.01
IV	183.91	89.18	68.776	0.9050	0.9053	0.00
V	186.91	86.18	49.330	0.6491	0.6491	0.00
VI	192.01	81.08	21.319	0.3463	0.3463	0.00
VII	195.50	77.59	16.215	0.2138	0.2137	0.00
VIII	201.38	71.71	6.401	0.08423	0.08398	— 0.02
IX	204.52	68.57	3.611	0.04752	0.04753	0.00
X	210.72	62.37	0.959	0.01262	0.01286	+ 0.08

¹⁾ One third of the distillate was used for rinsing out the apparatus, the second third for the filling.

²⁾ In order to prevent possible misunderstanding it is mentioned here that the pressure is given in "international centimeters" i.e. in the 76th part of an international atmosphere or in other words as the height of a mercury-column measured not at Leiden itself (local cm), but at a place where one international atmosphere exactly agrees with 76 cms mercury at 0° C, i.e. where $g = g_{\text{Bur.Int}} : 1.0003322$, the value which is taken as g_{norm} and at present is to be put at 980.615. (At Leiden $g = 981.276$ and 1 int. atm. = 75.9488 cms). For the definition of international atmosphere Comp. Leiden Comm. Suppl. 23. Mathem. Enc. V 10. Einh. α . When in these Communications about observations at Leiden an atmosphere pure and simple is mentioned, the international atmosphere is always meant.

The last two columns show, that the observations are very well represented by an equation of the form

$$\lg p = \frac{A}{T} + B + CT \quad (p \text{ in int. atm.})$$

with $A = -419.31$, $B = 5.2365$, $C = -0.00648$, kindly calculated for me by Professor VERSCHAFFELT. According to the equation the normal boiling point of oxygen would be

$$T = 90^{\circ}.13 \text{ K.}, \quad \theta = -182^{\circ}.96 \text{ C.},$$

whereas the observations in the immediate neighbourhood of the boiling point themselves give:

$$T = 90^{\circ}.14 \text{ K.}, \quad \theta = -182^{\circ}.95 \text{ C.}$$

This boiling point was found to be $T = 90^{\circ}.11 \text{ K.}$ ¹⁾ by

TABLE II. Vapour-pressures of oxygen. Comparison with KAMERLINGH ONNES and BRAAK and with v. SIEMENS (corr.).					
T	p (in atm.) (K.O. and B.)	p (in atm.) (v. S. corr.)	p (in atm.) (CATH)	ΔT (K.O., B.—C.)	ΔT (v. S.—C.)
90.69	1.0618		1.0583	—0.03 ⁵ deg.	
90.47		1.036	1.0351		—0.01 deg.
90.21		1.010	1.0093		0.00
90.11	1.0002		0.9975	—0.03	
89.87		0.9742	0.9725		—0.01
89.18		0.9059	0.9053		—0.01
86.56	0.6792		0.6777	—0.02	
86.18		0.6500	0.6491		—0.01
83.66	0.4819		0.4808	—0.02	
81.08		0.3463	0.3463		0.00
77.59		0.2137	0.2137		0.00
71.71		0.08390	0.08398		0.00
68.57		0.04695	0.04753		+0.05
62.37		0.01272	0.01286		+0.04

¹⁾ Comm. N^o. 107a gives $T - T^{\circ}\text{C} = -182^{\circ}.986\text{C}$. In the computation, however, the pressure-coefficient of hydrogen at 1100 mm. freezing point pressure is taken at 0.0036627, whereas, if we put $T^{\circ}\text{C} = 273^{\circ}.09 \text{ K.}$ and adopt the corrections to the absolute scale given by KAMERLINGH ONNES and BRAAK, the correct value is 0.0036628, which leads to -182.98 and $T = 90^{\circ}.11 \text{ K.}$

KAMERLINGH ONNES and BRAAK and $T = 90^{\circ}.12$ K by HENNING.¹⁾

In Table II the results of KAMERLINGH ONNES and BRAAK and those of v. SIEMENS, the latter after the reduction of his temperature-measurements to those of KAMERLINGH ONNES and his collaborators has been corrected according to HOLST²⁾, are compared with the formula which represents my observations³⁾.

The results show that except for the lowest points HOLST's reduction of v. SIEMENS' observations has been very successful.

The results for *nitrogen* are given in Table III.

TABLE III. Vapour-pressures of nitrogen.						
Nº.	θ	T	p (in int. cm.)	p (in atm.)	p (calc.)	ΔT (O—C)
I	— 188° 88 C.	84° 21 K.	159.11	2.0942	2.0948	0.00 deg.
II	190.66	82.43	133.44	1.7558	1.7539	0.00
III	193.91	79.18	93.86	1.2350	1.2382	0.02
IV	195.84	77.25	75.19	0.9893	0.9904	0.01
V	198.26	74.83	56.13	0.7385	0.7366	— 0.02
VI	201.55	71.54	36.16	0.4758	0.4756	0.00
VII	204.69	68.40	22.837	0.30049	0.30031	0.00
VIII	208.58	64.51	12.090	0.15908	0.15882	— 0.01
IX	213.14	59.95	4.695	0.06178		
X	215.20	57.89	2.1882	0.03792		

¹⁾ Ann. d. Phys. (4) 40 (1913) p. 635. The theoretical correction to the readings on the scale of the hydrogen-thermometer given by BERTHELOT which HENNING applies, does not differ appreciably in this region of low temperatures from the experimental correction found by KAMERLINGH ONNES and BRAAK. All the same it is doubtful whether HENNING's value may be looked upon as a final confirmation of the boiling point found by KAMERLINGH ONNES and BRAAK, since his measurement contains an uncertainty to which attention was drawn in note 1 to p. 998 of these Proc. XX (2) (Comm. N°. 152a).

²⁾ In this correction HOLST puts the temperatures at the higher points 0.02 and at the lowest point 0.01 of a degree higher than KAMERLINGH ONNES and BRAAK, which is due to the fact that in the reduction he uses his own formula of interpolation instead of the observations themselves. This explains the difference of the deviations at the top of the two columns for coinciding points, although v. SIEMENS in his determinations takes those of KAMERLINGH ONNES and BRAAK as his starting point.

³⁾ As observed in Comm. N°. 107a, there is a systematic difference of 0.10 degree at the boiling point and 0.13 degree at the lower points between the observations

The observations I to VIII refer to liquid nitrogen, the last two to solid nitrogen. The last two columns show that for liquid nitrogen the relation between vapour-pressure and temperature can be successfully represented by an equation of the same form as for oxygen, with

$A = -334.64$, $B = 4.6969$, $C = -0.00476$ (p in int. atm.); according to this equation the normal boiling point of nitrogen is
 $T = 77^{\circ}.31$ K. $\theta = -195^{\circ}.78$ C.

FISCHER and ALT¹⁾ give -195.67 on the hydrogen scale, on the basis of $\alpha = 0.0036625$. With $\alpha = 0.0036627$ the result changes to $-195^{\circ}.66$, whence $\theta = -195^{\circ}.61$ C. With the smaller dimensions of their thermometer a smaller accuracy was to be expected. They give their accuracy as being $\pm .05$ of a degree²⁾.

T	p in atm. (v. S. corr.)	p in atm. (H. en H.)	p in atm. (CATH)	ΔT (v. S.—C.)	ΔT (H.H.—C.)
$84^{\circ}.21$ K.	2.099		2.0948	-0.02 deg.	
82.43	1.756		1.7539	0.00	
80.93*		1.4983	1.4894		-0.06 deg.
79.18	1.236		1.2382	$+0.01$	
78.55*	1.1561	1.1561	1.1460		-0.03
77.25	0.9895		0.9904	0.01	
74.83	0.7331		0.7366	0.04	
72.15*		0.5222	0.5143		-0.06
71.54	0.4706		0.4756	0.09	
69.34*		0.3484	0.3439		-0.02^5
68.40	0.2952		0.30031	0.10	
64.51	0.1546		0.15882	0.14	
59.95	0.05958		0.06178	0.17	
57.89	0.03618		0.03792	0.19	

by TRAVERS, SENTER and JAQUEROD (London Phil. Trans. A. 200 (1902)) and those of KAMERLINGH ONNES and BRAAK, the latter being lower. The former are therefore now only of importance historically.

¹⁾ Ann. d. Phys. (4) 9 (1902) p. 1149.

²⁾ The uncertainty in their determination seems to have been larger, for as

The two measurements for solid nitrogen give the relation

$$\log p = -\frac{358.73}{T} + 4.7769;$$

as holding near the triple-point; this combined with the equation for liquid nitrogen gives for the triple point (i.e. the point of intersection of the two vapour-pressure curves).

$$T = 63^{\circ}.23 \text{ K}, \quad p = 0.1269 \text{ int. atm.} = 9.64 \text{ int. cm.}$$

whereas v. SIEMENS, account being taken of HOLST's corrections, found

$$T = 63^{\circ}.25 \text{ K.} \quad p = 9.35 \text{ cm.}$$

In Table IV v. SIEMENS' results — after correction according to HOLST of the reduction to the scale of KAMERLINGH ONNES c.s. — and those of HAMBURGER and HOLST to which I have applied a small correction¹⁾ are compared with the equation which represents my observations.

Finally I have tried to connect my results to CROMMELIN's measurements between the boiling point and the critical point²⁾. The latter may be represented satisfactorily³⁾ by the equation⁴⁾

regards my measurements it seems improbable that the uncertainty in the determination of the temperature, independently of systematical errors, has been larger than about 0.01 of a degree (cf. table III), and — in view of the recent determinations with the instrument, which will be published in the next communications — the systematical error of the Leiden gasthermometer (apart from the effect of errors in the expansion of the glass and in the constant for the capillary depression of the mercury) also may be put at about 0.01 of a degree.

With regard to the differences in Table IV it should be borne in mind, that the observations of v. SIEMENS as well as those of HAMBURGER and HOLST are based on the readings of a platinum thermometer, which has not been compared directly with the gasthermometer. They cannot serve therefore to estimate the systematical error in the temperature-determination. [This note has been somewhat modified in the translation].

¹⁾ HAMBURGER and HOLST (these Proc. XVIII 1 (1915) p. 872) obtained their results by reducing the readings of their platinum-thermometer to the vapour-pressures as found by KAMERLINGH ONNES and BRAAK (comp. note 2 page 660). As the authors also give the temperatures at the oxygen-pressures observed by them and as at 78° 42 K. their temperature is 0.05 degrees higher than my results for oxygen which are at present the only direct measurements of sufficient accuracy in that region, I have applied a correction of that amount to their temperatures. These are marked with an asterisk.

²⁾ Comm. N^o. 145d, these Proc. XVII (2) p. 959.

³⁾ We leave out of account the reading at 81° 21 K., which CROMMELIN himself marked as inaccurate by placing it in square brackets.

⁴⁾ The agreement with this formula containing two terms of the expansion of $T \log p$ in powers of $1/T$ is not inferior to what is obtained by means of three terms of the expansion in $1/T$ as given by CROMMELIN. The latter formula, however,

$$T \log p = A + B(T - T_k) + C(T - T_k)^2$$

where $A = 190.86$, $B = 3.9649$, $C = 0.00100$ for p in int. atm. This equation is again due to the kindness of Prof VERSCHAFFELT.

Table V gives the comparison between observation and calculation.

For $T = 81^\circ.87$ K. the equation gives $p = 1.6363$ (CROMMELIN),
 whereas $p = 1.6584$ (CATH)
 is found from the equation which represents my observations. The

TABLE V. Vapour-pressures of nitrogen (CROMMELIN).

T	p (in atm.)	p calc. II.	$\Delta T(O-CII)$
125.96 K.	33.49	32.728	-0.09 deg.
124.24	30.364	30.219	0.00
120.98	25.889	25.892	0.06
117.62	21.820	21.906	0.04
111.78	15.949	15.993	-0.01
99.51	7.3705	7.3652	0.04
93.91	4.8278	4.8467	-0.06
90.62	3.7248	3.7043	-0.02
86.21	2.5067	2.5016	

difference between these two values (corresponding to $\Delta T_{C_1-C_2} = .10$ of a degree) is so large, that for the present it seems impossible to combine the observations above the boiling point with those below it in one and the same equation.

satisfies the condition of giving the correct critical pressure at the critical point. The present formula gives $p_k = 32.728$ atm. instead of the observed value $p_k = 33.49$.

Chemistry. — "*On Phenyl Carbaminic Acid and its Homologues*".

By Prof. F. E. C. SCHEFFER. (Communicated by Prof. BÖESEKEN.)

(Communicated in the meeting of September 29, 1918).

1. *Introduction.*

It was observed by DITTE in 1887 that under high pressure and at temperatures lower than room temperature aniline with carbonic acid can react under formation of a solid compound which consists of equal molecular quantities of aniline and carbonic acid ¹⁾. It may besides be inferred from his paper that unmixing takes place at ordinary temperature. Some years ago Dr. J. J. POLAK carried out a number of experiments with the same system of substances in the organic chemical Laboratory of the Amsterdam University ²⁾; he too succeeded in ascertaining the existence of a compound, and the result of his analysis pointed to the same composition as was given by DITTE. It further appeared in his researches that the compound melts on being heated in the presence of a liquid and a vapour rich in carbonic acid, before the meniscus liquid-vapour disappears, with formation of a second liquid layer; this suggested the thought to me that the system aniline-carbonic acid would present an analogy in its behaviour with BAKHUIS ROOZEBOOM's gas-hydrate systems and with the system sulphuretted hydrogen-water, the phenomena of which I have fully described in These Proceedings ³⁾. It will appear from the below-mentioned observations that the compound, which in my opinion is to be considered as a carbaminic acid, gives rise in the P-T diagram to the appearance of a quadruple point, where solid compound, two liquid layers, and gas coexist, and that the three-phase lines which intersect in this quadruple point, can be determined with sufficient accuracy. This system also furnishes a new application of the quadruple point rule, drawn up by me in 1912 ⁴⁾, which was described by SCHREINEMAKERS in the Zeitschrift für physikalische Chemie almost at the same time ⁵⁾.

¹⁾ Compt. rend **105**. 612. (1887).

²⁾ Not published. The results of his research have been kindly put at my disposal by Dr. POLAK, for which I gladly express my indebtedness to him here.

³⁾ These Proc. **13**. 829 (1910/11) and **14**. 195 (1911/12)

⁴⁾ These Proc. **15**. 389 (1912/13).

⁵⁾ Zeitschr. f. physik. Chem. **82**. 59 (1913).

I further extended this investigation to the three toluidines, and I have succeeded in determining the limits of existence of three compounds. I have determined the composition of two of these compounds by analysis; the composition of the third had already

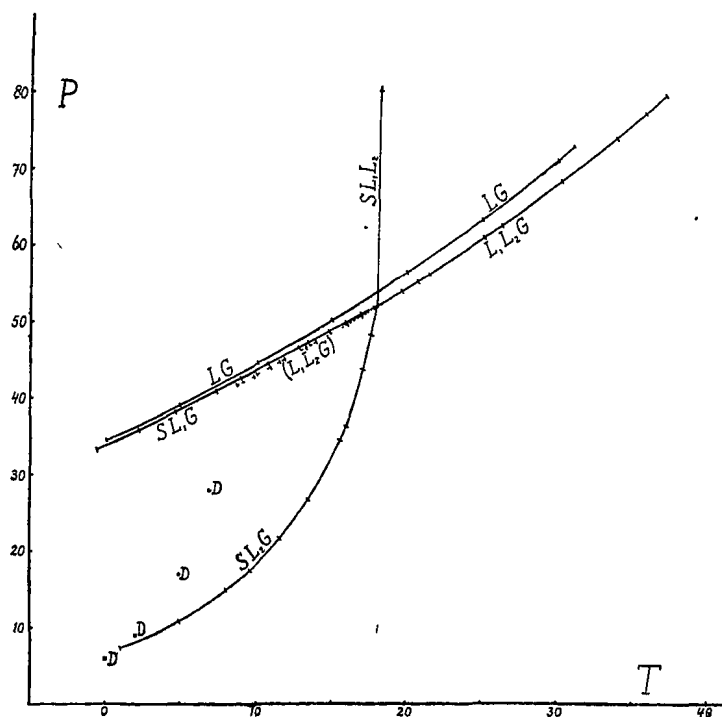


Fig. 1.

been found by DITTE. The great analogy between the three systems will probably justify the conclusion that these compounds are the three isomer tolyl carbaminic acids.

2. The system aniline-carbonic acid; the phenyl carbaminic acid.

From "anilin purissimum" of MERCK coloured red by contact with the air a middle fraction was separated by fractionation; a slight quantity of this was put into the Cailletet tube by the aid of a long glass capillary. As a test tube I used a tube with a widened upper end of the same shape as in my researches on the systems ether-water and hexane-water¹⁾. For the filling with carbonic acid the test tube was connected with a ground piece to an apparatus consisting of a generating apparatus for carbonic acid, which was obtained from diluted sulphuric acid and sodium bicarbonate, and was dried with phosphorus pentoxide,

¹⁾ These Proc. **15**. 380 (1912/13),

²⁾ These Proc. **16**. 404 (1213 14).

an apparatus for a high vacuum, consisting of a vessel with cocoa-nut carbon and a GEISSLER tube, a tube for condensation of the carbonic acid (by the aid of liquid air) and a vessel of about $\frac{1}{2}$ liter capacity as carbonic acid reservoir¹⁾. As it was exclusively my purpose in these experiments to determine three-phase pressures, a determination of the concentration of the mixtures used was superfluous. For the first observation I used a mixture with great excess of carbonic acid. When the test tube had been screwed on to the pressure cylinder after the filling, and the mixture had been heated to the ordinary temperature, it appeared that the solid substance could be kept at ordinary temperature only under high pressure. When the available volume was so small that there was only a small quantity of gas present, then a three-phase equilibrium of compound by the side of a thinly liquid layer (rich in carbonic acid) and gas occurred at the ordinary temperature at a pressure of about 50 atmospheres. When the pressure was diminished, the liquid vanished with violent boiling, and solid remained by the side of gas. Below 30 atmospheres the solid substance decomposed with formation of a liquid rich in aniline, a strong generation of gas being perceptible in this layer. Accordingly the solid compound is decomposed into liquid and gas on decrease of pressure. It is clear that the pressure at which this decomposition just sets in indicates the three-phase coexistence of compound, liquid rich in aniline, and gas. On increasing enlargement of the volume there remains coexistence of liquid by the side of gas. At the ordinary temperature the existence of phenyl carbaminic acid is, therefore, only possible at pressures above about 30 atmospheres. Hence in perfect analogy with the gas hydrates the dissociation tensions of this compound are three phase equilibria. This applies also to the determinations which DITTE carried out by observation of the pressure at which gas begins to form from the crystals, or of the pressure at which this generation ceases, which are of course theoretically the same, but practically different according to DITTE²⁾. DITTE ascribes the latter to inaccuracies of the temperature determination, in my opinion the slowness of the transformation $S \rightarrow L + G$ is undoubtedly responsible for this. In my former researches on the system sulphuretted hydrogen-water I have also been able to observe such a slow transformation³⁾.

In order to be able to determine the three-phase pressures

¹⁾ Cf. also These Proc. 13. 830 (1910/11).

²⁾ loc. cit.

³⁾ loc. cit.

accurately, I have adjusted a wide cylindrical vessel narrowed at the lower end round the test tube, in which vessel alcohol was stirred by means of vertically moving leaden plates; the heating took place electrically; cooling was effected by introduction of solid carbonic acid. In the observations with small volume it now appeared that the maximum temperature at which the compound can exist by the side of gas, is about 18° . The quadruple point lies at this temperature; the pressure is about 52 atmospheres. In this point there is intersection of the three-phase lines S (compound), L_1 (liquid rich in carbonic acid), and G (gas), which is stable at temperatures below the quadruple point, and cannot be prolonged above the quadruple point, $S + L_1 + G$, which exhibits a value of $\frac{dp}{dT}$ which rapidly increases with the temperature in the neighbourhood of the quadruple point, $L_1 + L_2 + G$, which indicates stable equilibria above the quadruple point, but can also be easily determined below the quadruple point; then these equilibria are, however, metastable with respect to the solid phase. The fourth three-phase line $S + L_1 + L_2$ rapidly moves from the quadruple point to higher pressure. The situation of the three-phase lines is indicated in fig. 1 by the letters given above; the quantitative data have been collected in table 1; they have been obtained with two mixtures; one contained a great, the second a small excess of carbonic acid; the determinations carried out with the two mixtures, are in good agreement. When the figure is consulted the phenomena described in the beginning of this paragraph will be clear. As long as gas is present, the solid compound can only exist for pressures which are higher than the three-phase line SL_1G . DITTE's determinations, which are indicated both in the figure and in the table by the symbol D, appear to depart perceptibly from mine; only in the neighbourhood of 0° do the observations agree fairly well. It makes the impression that DITTE has determined the points where solid substance is formed on increase of pressure, and that the pressures have been found much too high through the retardation of the transformation $L + G \rightarrow S$, though DITTE mentions that he observed the pressures at which the generation of gas ceased. In this respect the phenomena are again in perfect analogy with the system sulphuretted hydrogen-water, where CAILLETET and BORDET's observations present analogous deviations with mine. ¹⁾ DITTE does not lay claim, however, to great accuracy for his observations; he states that his determinations give

¹⁾ These Proc. 13. 833, fig. 2 and table on p. 834. (1910/11).

only rough values, but that they may yet give an impression of the way in which "aniline carbonate" dissociates.

TABLE 1.

LG(CO ₂)		L ₁ L ₂ G		SL ₂ G	
T	P	T	P	T	P
0	34.4	8.7	41.8	0	6 D
5.0	39.0	9.8 ⁵	42.8	0.9 ⁵	7.4
10.1	44.6	10.0	43.2	2	9 D
15.0	50.2	10.9	43.9	5.0	10.9
20.0	56.6	11.5	44.8	5	17 D
25.0	63.4	11.8 ⁵	45.1	7	28 D
30.0	71.1	13.2 ⁵	46.6	8.1	15.0
31.1	72.9	13.9 ⁵	47.4	9.7	17.5
SL ₁ G		16.0	49.7	11.6	21.7
		16.9 ⁵	50.8	13.5	26.7
T	P	17.8	51.8	15.5	34.6
		19.7	54.1	15.9	36.4
-0.6	33.3	20.7	55.4	17.1	43.8
+2.2	35.7	21.5	56.3	17.6	48.3
4.7	38.1	25.1 ⁵	61.1	SL ₁ L ₂	
7.4	40.8	26.3	62.7		
9.0	42.5	30.2 ⁵	68.4	T	P
10.8	44.4	33.9	74.0		
12.8	46.5	35.8	77.1	18.0	52
13.4	47.3	37.1 ⁵	79.5	18.2	80
14.8	48.6	Quadruple point		18.0° 52.0 atm.	
15.9	49.8				
16.9 ⁵	50.9				

When we pursue the three-phase line L₁L₂G towards higher temperature, the fluidity of the upper layer becomes greater and greater, and at 37° the critical phenomenon presents itself; the critical end-point lies 6° and about 7 atmospheres higher than the critical point of carbonic acid. We further derive from the figure that the three-

phase tension L_1L_2G begins to depart more from the carbonic acid tension with increasing temperature; at the quadruple point the deviation amounts almost to 2 atmospheres; at the critical point of carbonic acid to about $3\frac{1}{2}$ atmospheres.

It follows from the already mentioned quadruple rule, which I formulated before as follows: *The region that does not possess metastable prolongations of threephase lines in the P.-T.-projection, is that of coexistences of phases of consecutive concentration*¹⁾, that the region between SL_1G and SL_2L_1 satisfies the above mentioned condition. In this region, which besides by the two mentioned three-phase equilibria is also bounded by SL_1G and L_1L_2G resp. by SL_1L_2 and SL_2G , the coexistences occur of the two phases which the adjoining three-phase equilibria have in common, hence in this case $S + L_1$, $L_1 + G$, and $S + L_2$. As these coexistences according to the rule mentioned must refer to phases which succeed each other in concentration, the succession is GL_1SL_2 ; the concentration of the compound lies, therefore, between that of the two coexisting liquid layers. Hence the transformation $S \rightleftharpoons L_1 + L_2$ takes place on the three-phase line SL_1L_2 in the neighbourhood of the quadruple point.

3. In order to get acquainted with the concentration of the compound Dr. POLAK has caused a weighed quantity of aniline to act on an excess of carbonic acid in a fused-to tube at the ordinary temperature. After the compound had been formed the tube was opened again at -80° , and placed in a bath of about -60° ; after half an hour the tube was again fused to, and weighed after having been heated to the ordinary temperature. This analysis yielded the concentration $C_6H_5NH_2 \cdot 1.01 CO_2$.

I have carried out three analyses in a way that differs but little from that described here; the method of investigation was the same as that which I have described in my second paper on the system sulphuretted hydrogen-water²⁾; the excess of carbonic acid was sucked off at -80° by means of a waterjet pump. For the quantity of carbonic acid in gramme-molecules which combines with one mol. of aniline, was found successively 0.98, 0.99, and 0.98. The compound consists, therefore, of an equal number of molecules of aniline and carbonic acid.

4. *The system o-toluidin-carbonic acid; the o-tolyl-carbaminic acid.*

Also in the system o-toluidine-carbonic acid I have been able to ascertain the formation of a compound; the quadruple point lies here,

¹⁾ loc. cit.

²⁾ loc. cit.

however, at lower temperature. As the inquiry into the equilibria

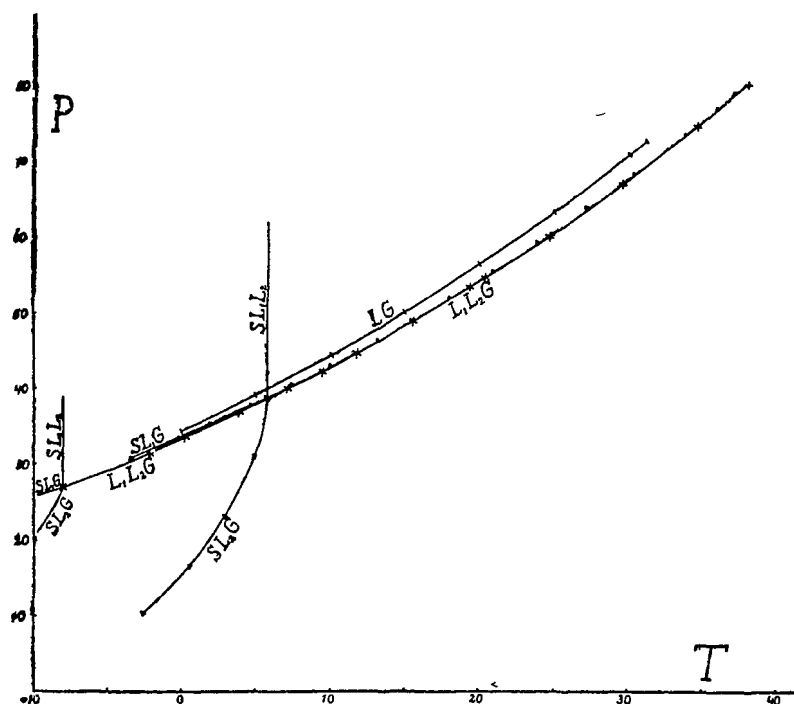


Fig. 2.

at low temperatures is attended with experimental difficulties, I have rested satisfied with the determination of the quadruple point and of the three-phase line L_1L_2G with the critical end point. The found three-phase pressures are recorded in table 2 and indicated in fig. 2

TABLE 2.

L_1L_2G			
T	P	T	P
-2.1	31.5	19.4	53.5
+0.3	33.6	20.4	54.8
3.9	36.8	24.7	60.1
7.3	40.1	29.6	67.1
9.5	42.3	34.5	74.9
11.8	44.7	38.1	80.8
15.6	49.0		
Quadruple point		-7.5°	27.5 atm.

by crosses. At temperatures below the quadruple point a compound again occurs, which has also already been observed by DITTE, and which according to him consists of equal molecular quantities of o-toluidine and carbonic acid. I myself have not determined the concentration of this compound; the application of the above described method of analysis is accompanied with pretty great difficulties at the low temperatures. The possibility that the solid substance should be pure o-toluidine is excluded, because the quadruple point lies at higher temperature than the melting-point of the pure substance. (Cf. table 5).

5. *The system m-toluidine-carbonic acid, the m-tolyl carbaminic-acid.*

There occurs a quadruple point SL_1L_2G in the system m-toluidine-carbonic acid at a temperature which lies between that of o-toluidine-carbonic acid and that of aniline-carbonic acid. The three-phase lines have again the same relative situation as was described above. The observations referring to the three-phase lines L_1L_2G , SL_1G and SL_2G are recorded in table 3 and indicated in figure 2 by triangles. In this figure are also found the vapour tensions of pure carbonic acid (see table 1).

6. The analysis of the compound according to the method

TABLE 3.

L_1L_2G		SL_2G		SL_1G	
T	P	T	P	T	P
7.5	40.5	- 2.6	10.4	- 3.4	30.8
10.0	43.1	+ 0.6	16.5	- 0.2	33.4
13.2	46.4	2.9	23.1	+ 1.9	35.3
15.5	49.2	5.0	31.5	2.9	36.2
18.0	52.1			4.7	37.7
20.9	55.7			5.7	38.6
23.9	59.5	Quadruple point			
27.3 ⁵	64.2				
30.3	68.5				
33.7	73.8				
35.8 ⁵	77.4				
37.2	79.6				
				6.3°	39.2 atm.

mentioned in § 3 yielded varying values in contrast to those of aniline and of p-toluidine, as will appear in § 8. For the quantity of carbonic acid which combines with one molecule of m-toluidine, was found successively 0.76, 0.79, 0.85, 0.86, 0.88, 0.88, 0.93, 0.89, 0.86, 0.92, and 0.89 mol. These values for the carbonic acid content are most probably all too small. The cause of this deviation is in my opinion the following: Liquid carbonic acid and m-toluidine are little miscible. Accordingly the formation of the compound on cooling takes chiefly place on the boundary of the two layers. In consequence of this a partition of solid substance is continually formed, separating the two layers. Part of the toluidine can, therefore, be withdrawn from the action of carbonic acid. It is clear that after the excess of carbonic acid has been sucked off, the quantity of bound carbonic acid is found too small. In order to render the formation as complete as possible, the tubes were kept in ice for several days; in the successive determinations this period increases from 2 to 10 days. It appears, therefore, that the time has not much influence on the result of the analysis. In the last determination the tube was cooled for 7 hours with ice and salt (-15 to -20°); it also yields too low a result. The supposition that the m-toluidine should be impure, appeared erroneous, as the correct value of 65° was found for the melting-point of the acetate compound. I think I am justified in concluding from the above-mentioned determinations that the compound likewise consists of equal molecular quantities of toluidine and carbonic acid.

7. *The system p-toluidine-carbonic acid; the p-tolyl carbaminic acid.*

In the P-T-diagram the system p-toluidine-carbonic acid yields a three-phase line L_1L_2G , which deviates little from that of the said systems. (Cf. fig. 3). The quadruple point SL_1L_2G lies here at higher temperature; the four three-phase lines which intersect in this quadruple point, are indicated in fig. 3; the quantitative data in table 4. The relative situation of the four phases is the same here as in the preceding systems. The stable part of the three-phase line SL_2G terminates at lower temperature in a second quadruple point SS_BL_2G (S_B is solid p-toluidine). In the preceding systems the corresponding quadruple point lies at lower temperature and pressure; in this system the temperature of the two quadruple points differs little from the critical temperature of carbonic acid. The three-phase lines SL_2G and S_BL_2G are easy to determine, when we heat at constant pressure and read the temperature at which liquid is formed. Without further examination we may state about the three-phase

line $SS_B L$, that the slope will be steep. Of three of the three-phase lines that pass through the quadruple point $SS_B L_2 G$ the situation

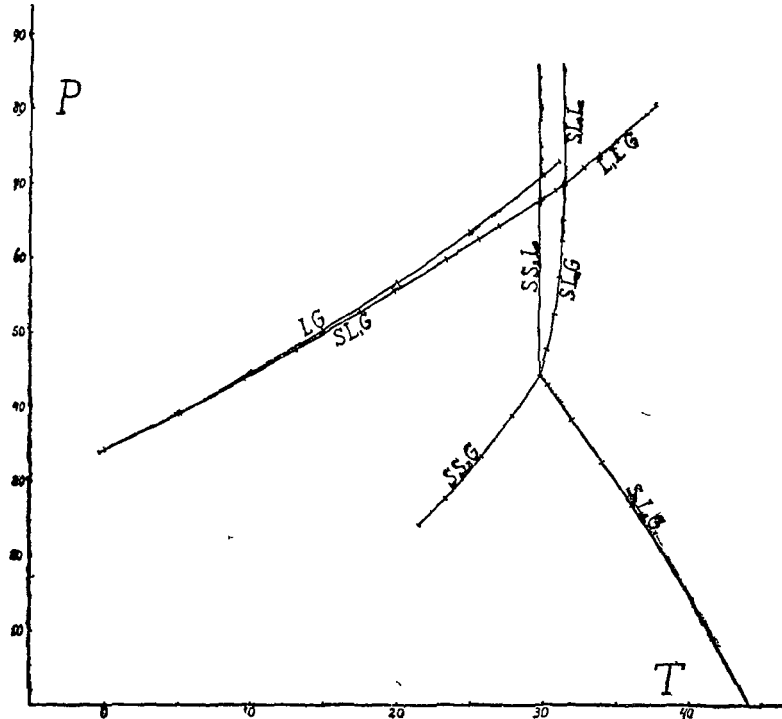


Fig. 3.

could, therefore, easily be given. The fourth three-phase line $SS_B G$ was, however, difficult to find. The quadruple point rule mentioned, however, gave me an indication where it was to be found. There exist two possibilities for the situation of this fourth three-phase line, which are represented by fig. 4a and b. The three-phase line

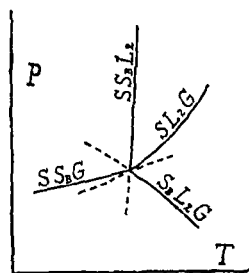


Fig. 4a.

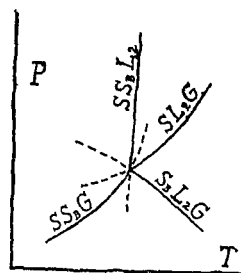


Fig. 4b.

$SS_B G$ must namely lie between the metastable prolongations of $SL_2 G$ and $S_B L_2 G$ (fig. 4a) or between those of $SL_2 G$ and $SS_B L_2$ (fig. 4b). Other situations are impossible, because else two-phase coexistences

would occur with an angle larger than 180° ; I have set forth in the mentioned paper that this is impossible. When with the aid of the quadruple point rule we examine what succession of the phases would appear according to fig. 4a, it appears that no metastable prolongations occur between $SS_B L_2$ and $SL_2 G$, that the two-phase coexistences in this region are: $G + S$, $S + L_2$ and $L_2 + S_B$ and that the succession of the phases is given by $GSL_2 S_B$.

In an analogous way it would follow from fig. 4b that the order of the phases would be $SGL_2 S_B$. This order indicates diminishing carbonic acid content, because S_B represents solid p-toluidine. That the compound S would be richer in carbonic acid than the gas phase, which practically consists of pure carbonic acid, is excluded; p-toluidine has a very slight vapour tension (b.pt. 200°) at this temperature, and the content of p-toluidine in the vapour is, therefore, very small. The only possibility is, therefore, given by fig. 4a. I have, therefore,

TABLE 4.

$SL_1 G$		$L_1 L_2 G$		$SL_2 G$	
T	P	T	P	T	P
-0.4	33.9	32.8	72.0	30.2	47.7
+5.1	39.1	33.9	73.9	30.8	52.5
9.6	43.6	35.0 ^s	75.7	31.1	57.3
13.1	47.6	37.7 ^s	80.4	31.3	62.2
17.5	52.7	$SS_B G$		31.4	65.0
19.8	55.5			$S_B L_2 G$	
23.3	59.8	T	P		
25.6	62.4			T	P
27.0	64.3	21.5	24.2		
29.7	67.7	23.3	27.6	30.3	43.0
30.8	69.0	25.8	33.4	32.0	38.2
		27.9	38.8	34.0	32.5
				36.2	26.8
Quadruple point		$SL_1 L_2 G$		31.5°	70 atm.
		$SS_B L_2 G$		29.7°	44 atm.

tried to find the required three-phase equilibrium in the region between

the metastable prolongations of SL_2G and $S_B L_2G$. The determinations were difficult; the only way to find the equilibria was by examining whether rise of pressure or descent of pressure takes place at constant temperature after some lapse of time. It is clear that below the three-phase line $SS_B G$ (fig. 4a) the two-phase coexistence $S_B + G$ is found, and above it $S + G$ and $S + S_B$, because S with regard to its concentration lies between G and S_B , and the coexistence of the two solid substances will extend towards higher pressure¹⁾. Hence the transformation $S_B + G \rightleftharpoons S$ occurs on the three-phase line. The upper arrow indicates the conversion on diminution of volume, the lower one on expansion. When at a definite temperature a fall of the pressure takes place, we are above $SS_B G$; when the pressure increases, we are below $SS_B G$. In this way an upper and a lower limit was found, which were no further apart than one atmosphere, sometimes some tenths of an atmosphere. The slowness of the transformation rendered this method of working necessary; the lower limit was found to yield values which were better reproducible than the upper one. The explanation of this is in my opinion to be found in the fact that the transformation $S \rightarrow S_B + G$ takes place more easily than the opposite one. This is self-evident, as the action of G on S_B can exclusively take place on the boundary of the two phases, and formation of a phase S can stop the action. Accordingly the values of the lower limit are recorded in table 4; besides, the upper limit often differs no more than a fraction of an atmosphere from the lower one, as has been said. The relative situation of the three-phase lines is actually that which was predicted with the aid of the quadruple point rule.

8. The analysis of the compound did not present any difficulties. The results of the analyses were resp. 1.00, 0.97, and 0.99 mol. CO_2 to 1 mol. p-toluidine. Hence the compound contains equal molecular quantities of the two components.

9. *Summary of the results.*

The four examined systems yield pretty well coinciding three-phase lines $L_1 L_2 G$. The critical end-points lie close together. The great difference between the systems consists only in the situation of the quadruple points. In table 5 the four systems are arranged

¹⁾ This can also be immediately derived from the relative situation of the three-phase lines in fig. 4a.

according to ascending quadruple point temperatures. The order in temperature is the same as that in pressure.

TABLE 5.
Quadruple points SL_1L_2G .

o-toluidine		m-toluidine		aniline		p-toluidine	
T	P	T	P	T	P	T	P
-7.5	27.5	6.3	39.2	18.0	52.0	31.5	70
Melting points.							
m-toluidine		o-toluidine		aniline		p-toluidine	
-30		-15		-7		44	

This is indeed also necessary on account of the coincidence of the L_1L_2G lines.

The order of the melting-points of the pure components deviates from this only in so far that *m*-toluidine and *o*-toluidine have exchanged places. I have determined the four melting-points given in table 5 myself. That of *m*-toluidine was not known, as far as I could find out; that of *o*-toluidine agrees with the observation by KNOEVENAGEL ¹⁾. For the melting-point of aniline we find -8° given; my value lies somewhat higher; TIMMERMANS' value lies again higher than mine ²⁾. I think, however, that I may conclude from the small melting-range presented by my preparation, that the substance was pure. We find 45° for the melting-point of *p*-toluidine in the handbooks; my value is lower, and agrees with HULETT's very carefully executed determination ($43, 9^\circ$) ³⁾.

The compounds that occur in these systems, contain the components in the ratio 1: 1. I think, therefore, that I have to consider them as carbaminic acids. These compounds were still unknown, only DITTE has evidently observed two of them in his experiments. It is clear from the limits of stability of the compounds, why they have not been found; at ordinary temperature only two of these compounds are possible (phenyl- and *p*-tolylcarbaminic acid). The first decomposes directly into liquid and gas, the second into solid *p*-toluidine and gas, when the tubes are opened.

¹⁾ Ber 40. 517. (1907). KNOEVENAGEL finds besides the melting-point of -15.5° another belonging to a metastable modification (-21°). TIMMERMANS' determination (-24.4°) may refer to this metastable modification.

²⁾ TIMMERMANS. Bull. Soc. Chim. Belg. 27. 334. (1914).

³⁾ HULETT. Zeitschr. physik. Chem. 28. 650. (1899).

At low temperature they can all exist at ordinary pressure, but the formation will be hampered by the afore-said reason that the compound can put a stop to the action of the two phases (gas and solid) on each other by separation.

It is worthy of note that evidently through the action of aromatic amines on carbonic acids free acids are formed in contrast with ammoniac and the aliphatic amines, which form salts.

Of the said carbaminic acids a few salts are known. When it is tried to obtain the free acids by double conversion with acid, they split up into carbonic acid and the free amines; only at high pressure or low temperature could the free carbaminic acids be formed. Yet it is possible, and even probable that these acids, though they are durable at the ordinary temperature only under increased pressure, occur in the liquids L_1 . The assumption that for certain reactions the carbaminic acids can act as intermediate product, is therefore certainly not to be deemed impossible.

It appears from the P-T-diagrams that the quadruple point of p-tolylcarbaminic acid lies higher than that of phenylcarbaminic acid. Possibly the quadruple point of one of the xylylcarbaminic acids lies at still higher temperature. The as-o-xylidine certainly invites to further investigation, the quadruple point will probably have shifted here to higher temperature, as the melting-point lies higher than that of p-toluidine. It is possible that for this system the quadruple point has already disappeared; we should then pass to another type of binary systems; in this case the behaviour will become analogous to that of sulphuretted hydrogen-ammoniac, the particulars of which I described on an earlier occasion.¹⁾

When we think the quadruple point gradually removed to higher temperature, it will disappear when it coincides with the critical end-point. A gradual change is not to be realized, as the change in constitution takes place discontinuously. It is here, however, possible that by suitable choice of the homologues the displacement takes place in small leaps, and the transition of the type presented by these systems into that of sulphuretted hydrogen-ammoniac appears very clearly.

In his thesis for the doctorate BUCHNER already pointed out the existence of such a transition for systems without compound. I shall describe the phenomena which present themselves in these transformations in a later treatise.

Delft, August 30th 1918.

Technical University.

¹⁾ Thesis for the Doctorate (1909). Zeitschr. physik. Chemie. 71. 214 and 671. 1910).

Physics. — *“Experimental Inquiry into the Nature of the Surface-Layers in the Reflection by Mercury, and into the Difference in the Optical Behaviour of Liquid and Solid Mercury”.*
By Dr. J. J. HAAK and Prof. R. SISSINGH. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of September 29, 1918).

1. *Introduction.* Since in 1850 L. LORENTZ¹⁾ advanced the supposition, that the elliptical polarisation on reflection by transparent bodies is the consequence of a gradual transition between the two adjoining media and elaborated this view theoretically, the influence of these surface layers has been more than once theoretically investigated, both in case of the reflection by transparent bodies and by metals²⁾. There have, however, been made only few experimental investigations into the nature of these surface-layers and our knowledge of it is confined to more or less plausible suppositions. Great influence is always assigned to the grinding and polishing and also to the grinding and polishing material itself, with which these operations are made. An investigation by RAYLEIGH shows, however, that it is not yet possible to state in what way this influence arises³⁾. Besides, an influence of the condensed gas layers has often been supposed and examined⁴⁾. Up to now however, attempts to demonstrate the influence of a condensed gas layer have not yet succeeded.

2. *Purpose of the research.* In order to obtain the optical constants of a metal, quite independent of the grinding and polishing and the material used for this purpose, mercury was chosen for this investigation. Both the liquid mercury and a mirror of solid mercury can be examined. It becomes then also evident, whether at the transition from liquid to solid mercury the optical constants are subjected to a modification. In the investigation of liquid mercury the impression,

¹⁾ L. LORENTZ, Pogg. Ann., **111**, 460, 1860; **114**, 238, 1861.

²⁾ C. A. VAN RIJN VAN ALKEMADE, Thesis for the doctorate, Leiden, 1882; Wied. Ann., **20**, 22, 1883. P. DRUDE, Wied. Ann., **43**, 126, 1891; R. C. MAC LAURIN, Proc. Roy. Soc., (A), **76**, 49, 1905.

³⁾ RAYLEIGH, Proc. Roy. Inst., **16**, 563, 1901.

⁴⁾ J. J. SEEBECK, Pogg. Ann., **20**, 35, 1830; P. GLAN, Wied. Ann., **11**, 464, 1880; R. SISSINGH, Thesis for the doctorate, Leiden, 1885; Arch. Néerl., **20**, 171, 1886.

however, gained ground, that the layers of air, which are condensed on the surface, exert an appreciable influence on the elliptical polarisation at the reflection, so that in the first place this influence has been more closely examined.

3. *The used monochromator.* The determination of the optical constants took place in an entirely analogous way, as has been described by one of us ¹⁾. For the investigation a goniometer has been used, the graduated circle of which can be placed vertical. Before the goniometer there is a monochromator of a very simple structure, which was constructed from material, present in the laboratory. The monochromator consists of a collimator with an aperture 1 : 6, a flint-glass prism of STEINHEIL with an angle of refraction of 60°, and a second collimator, which will be referred to in future as the collimator of the goniometer. The illumination takes place by means of an arc-lamp of 18 Ampères. A lens of 7 dioptrics forms an image of the crater on the slit of the collimator of the monochromator. Behind the prism a lens of 11 dioptrics forms a spectrum on the collimator of the goniometer. The axes of the two collimators are placed horizontal, the slits and the edge of the refracting angle of the prism vertical. Care has always been taken, that the image of the crater and the spectrum fall on the middle of the collimator slits. A silvered glass mirror is adjusted to the collimator of the goniometer; it can revolve round an horizontal axis and throws a monochromatic, cylindrical beam of light at the required angle of incidence on the mirror in the middle of the goniometer. The wave-length of the incident rays lies between 5790 and 5990 Ångström-units. During the observations the invariability of this colour-sifting of the incident beam of light is repeatedly examined. The fringes in the BABINET compensator are always uncoloured. Monochromator and goniometer are mounted on a firm foundation, erected free from the floor in the room, in which the observations have been made. The three levelling-screws of the legs of the goniometer stand each on two thick pieces of india-rubber, in order to prevent as much as possible the influence of vibrations on the liquid mercury surface.

4. *The goniometer.* For the adjustment and the centring of the parts of the goniometer we refer to the investigation of one of us ²⁾. Only a few points are briefly mentioned here.

¹⁾ R. SISSINGH, loc. cit.

²⁾ R. SISSINGH, loc. cit.

The following expedient proved very convenient in the mutual adjustment of the parts of the goniometer. The sledge on which the silver mirror stands, which served for these adjustments, was fastened to a socket, which fits over a conical pivot in the middle of the goniometer circle. This pivot can be levelled with three adjusting screws. The mirror with the socket can in this way easily be placed on the goniometer and can be removed from it ¹⁾.

As polarizer a nicol is used with pretty large oblique end-planes, which only gives a small deviation to the rays of light, which pass through it. This amounts to 2'.5.

For the adjustment of the compensator we refer again to the investigation of one of us ²⁾.

The polarisation planes of *each* of the two compensator wedges are placed in the required position, i. e. parallel to the plane of incidence and normal to it ³⁾.

To bring the movable wedge in the required position, we make use of the images of the collimator slit, which are formed in the eye-piece behind the goniometer. There are formed three pairs of images. The images of each pair coincide, if the planes of the wedges are parallel. The principal positions of the nicols, in which their planes of polarisation are parallel to the plane of incidence or normal to it, have been determined both in the vertical and in the horizontal position of the goniometer circle. The azimuth of the polarizer is called 0, when the light, that the polarizer transmits, vibrates normal to the plane of incidence, that of the analyzer, when the direction of vibration of the transmitted light is parallel to the plane of incidence. We obtained successively in the horizontal and vertical position of the goniometer circle: mean

Polarizer in azimuth 0° 81°57', 81°43'; 81°50'

Analyzer „ „ 0° 86°33', 86°35'; 86°34' ⁴⁾.

Considering the inevitable errors of observation, the agreement may be called satisfactory.

¹⁾ For fuller details compare J. J. HAAK, Thesis for the doctorate, Amsterdam, 1918.

²⁾ R. SISSINGH, loc. cit.

³⁾ It is noteworthy, that it is *supposed* both in the investigation of R. HENNIG, Gött. Nachr., **13**, 365, 1887, as in that of P. DRUDE, Wien. Ann., **34**, 489, 1888; **36**, 532, 1889; **39**, 481, 1890, that the principal sections of the wedges are normal to each other and only the angle between the principal section of one of the wedges and the plane of incidence is determined and taken into account. Cf. SISSINGH in BOSSCHA's Textbook of physics, Light, II, p. 555, note 2.

⁴⁾ All the experiments have been made by J. J. HAAK. Compare for further details Mr. HAAK's thesis for the doctorate, Amsterdam, 1918.

The positions of the movable compensator wedge, in which the difference of phase for the narrow beam of light, which passes between the threads before the fixed wedge, amounts successively to $-\frac{1}{2}$, 0, $+\frac{1}{2}$, are:

63.86; 49.52; 35.10.

As the displacements of the wedge are always reduced to those between 49.52 and 63.86, a displacement of 14.34 mm. corresponds with a phase-difference of $\frac{1}{2}$ or π .¹⁾

The angle of incidence on the mercury surface is derived from the position, in which the line of sight of the telescope of the goniometer is horizontal. This position is found halfway between the positions, in which that line of sight runs successively parallel to that of an incident beam of light and of the corresponding beam of light, which is reflected by a liquid surface in the centre of the goniometer. These positions are $81^{\circ}36'$ and $104^{\circ}24'$, so that the axis of the telescope of the goniometer runs horizontal in the position $81^{\circ}36' + (104^{\circ}24' - 81^{\circ}36') : 2 = 93^{\circ}0'$. As reflecting surface is used that of thick machine oil, because this gives rise to a pure image of the slit, which is not the case with mercury.²⁾ The goniometer circle is vertical, when the axis of the incident beam coincides with that of the tube in which later the polarizer is placed and after reflection with the axis of the telescope.

5. *Preliminary investigation of the optical influence of a condensed layer of air.* When, as was already communicated in § 2, it became evident from the observations, that the layer of air condensed on the mercury surface was optically active, the angles of principal incidence I and the principal azimuth H were determined on the mirror of pure mercury, immediately after the formation. This took place by the determination of the phase-difference and the restored azimuth for two angles on both sides of the angle of principal incidence from extensive series of observations. From these values those of I and H were obtained by interpolation.³⁾

It was found that $I = 79^{\circ}18'$, $H = 35^{\circ}45'$.

This determination could be made within three hours.

On an earlier occasion we obtained $I = 78^{\circ}23'$, $H = 36^{\circ}18'$, in which the mercury surface was exposed to the air for some days,

¹⁾ The phase-differences are given as phase-retardations with respect to the light vector in the reflected light, perpendicular to the plane of incidence.

²⁾ For the mercury surface the compensator fringes remain however straight, only slightly less sharply defined. The accuracy of the adjustment of this fringe is somewhat less than with a solid surface, viz. 0.03 instead of 0.02

³⁾ R. SISSINGH, loc. cit.

but protected against contact with dust, before the observations took place. In both cases the mercury had been distilled in vacuum.

With mercury that had been purified by being shaken with potassium hydroxide and nitric acid and had then been dried, we found in the same way some days after the formation of the mercury surface:

$$I = 78^{\circ}14' \quad , \quad H = 36^{\circ}12',$$

which is in satisfactory agreement with the second determination. The sign of the difference between the values of I and H in the two first determinations is the same as is to be derived from the theoretical research by DRUDE. A surface layer greatly diminishes the angle of principal incidence and enlarges the principal azimuth but little¹⁾.

The following observations show the influence of the layer of air very clearly. The pure mercury is in a well cleaned receptacle of LEYBOLD with plane parallel side walls, as is very often used for light-filters. The observations have been made at an angle of incidence of 78° , with the analyzer at an azimuth of 45° ²⁾.

Adjustment of the	
Compensator	Polarizer
56.46 ³⁾	43°33'

Two days later, during which time the mercury was protected from dust,

56.71	43°47'
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After the mercury in the receptacle had been shaken and a new surface had been formed:

	56.44	43°33'
After one day	56.64	43°44'
After shaking	56.42	43°34'

In a following set of observations, in which a pure surface was obtained by means of the method of overflowing of RÖNTGEN⁴⁾, which has also been used by RAYLEIGH, the observations yielded:

	Adjustment of the Compensator	Polarizer
	56.43	43°44'
After two days	56.74	43°41'

¹⁾ P. DRUDE, Wied. Ann., **36**, 532, 865, 1889; **43**, 126, 1891.

²⁾ At this azimuth the error in the determination of the phase-difference introduced by the metallic reflexion and of the azimuth of the restored plane polarisation, which henceforth will be referred to as restored azimuth, is a minimum. Cf. R. SISSINGH, Thesis for the doctorate, p. 57; Arch. Néerl., **20**, p. 188.

³⁾ These and all the further values are every time the mean of four readings.

⁴⁾ RÖNTGEN, Wied. Ann., **46**, 152, 1892; RAYLEIGH, Phil. Mag., (5), **30**, 398, 1890.

After overflowing	56.45	43°37'
After one day	56.68	43°44'
After overflowing	56.45	43°50'

The polarizing action of the side walls of the glass receptacles not having been examined, these values have no absolute value, but they represent the change by the adsorbed air layer no doubt very accurately.

6. *Change of the thickness and the influence of the layer with the time.*

There is no doubt but the thickness of the adsorbed layer of air and so also its optical influence increases with the time. In order to examine this influence the adjustments must be effected in a short time. Those of the polarizer have been omitted, because it appears from § 5, that the influence of the layer of air on the restored azimuth is very small and about of the order of magnitude of the errors of observation. In order to be able to execute the observations in a short time, only observations at one angle of incidence, viz. the angle 79°46', which is very near the angle of principal incidence, were made, the analyzer also always being set in the same quadrant. The determination of the phase-difference, that arises at metallic reflection between the components vibrating perpendicular to and in the plane of incidence, took place only by annulling this phase difference¹⁾.

The shifting of the movable compensator wedge was therefore exclusively from 49.52 → 63.86 (see § 4). In this way the errors in consequence of the deviation of the light in the polarizer and the inaccurate position of the planes of polarization of the compensator wedges continue to exist, but their influence on the slight change in the phase-difference, that is to be determined, may be considered as of the second order of magnitude. Care should, however, be particularly taken, that the incident beam of light consists always of the same part of the spectrum and keeps the same direction, i. e. always falls on the middle of the slit of the collimator of the goniometer. A slight shifting of the spectrum, which was not even so much as the height of the spectrum, already modified the compensator-reading by 0.06. This is to be ascribed to the change in the angle of incidence. In the observations the mercury was placed in a shallow iron dish, attached to the bottom of a bronze cylinder. Two side-tubes, closed by plane parallel glass plates, the axes of which lie in a same meridian plane

¹⁾ SISSINGH, Thesis for the doctorate, p. 79: Arch. Néerl., 20, 196, 1886.

of the cylinder, enable us to make the light strike the mercury at the required angle of incidence. The mercury is conveyed into the dish by a tube in the upper surface of the cylinder. This bronze cylinder is attached to the middle of the goniometer circle. A vertical sledge makes it possible to place the mercury surface so, that the axis of the goniometer lies in it. By means of an horizontal sledge the dish may be placed so, that the axes of the incident and the reflected beam of light pass through the middle of the glass windows. The cylinder can be exhausted and filled with air, that has been dried with calcium-chloride, sulphuric acid, potassium-hydroxide and phosphor-pentoxide.

When the position of the movable prism of the compensator, immediately after the formation of the mercury surface is called c_0 , that t seconds later c , and the final position c_∞ , a very plausible supposition on the increase of the thickness of the layer of air and its optical influence leads to the differential equation:

$$\frac{d(c-c_0)}{dt} = k(c_\infty - c)$$

So that

$$c - c_0 = (c_\infty - c_0)(1 - e^{-kt}).$$

In this k will be proportional to the pressure of the air. This supposition is confirmed by series of observations, made at a pressure of one and of half an atmosphere, which are graphically represented in fig. 1. There have been traced six curves for different values of k . It appears clearly from the traced lines within what limits the value of k lies for the two series of observations. As value of $c_\infty - c_0$ has been taken 0.25, viz. the change of the readings in dry air after 24 hours. When the cylinder is exhausted, no change in the compensator-readings can be demonstrated even after 8 hours. Compare the line . . ., which indicates the observations in the exhausted cylinder. Here follow the means of three series of observations in dry air for a pressure of an atmosphere.

Time	Angle of Incidence 79°46'	
0	$C_0 = 56.84$	$C - C_0$
$\frac{1}{2}$ hour	$C = 56.863$	0.023
1 „	56.89	0.05
$1\frac{1}{2}$ hours	56.92	0.08
2 „	56.918	0.078
$2\frac{1}{2}$ „	56.94	0.10
3 „	56.965	0.125
$3\frac{1}{2}$ „	56.975	0.135
4 „	56.972	0.132

4½ hours	56.97	0.13
5 „	56.992	0.152
5½ „	56.99	0.15
6 „	57.00	0.16
6½ „	57.01	0.17
7 „	57.013	0.173
7½ „	57.03	0.19
8 „	57.03	0.19

$$\Delta = C - C_0$$

$$\frac{1}{0.001 M}$$

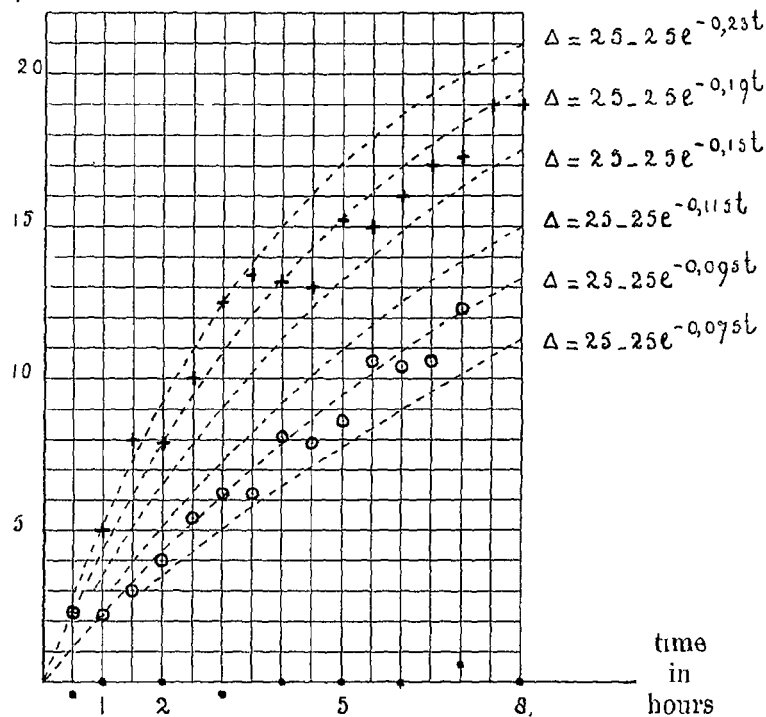


Fig. 1.

When it is borne in mind, that the error in the readings of the compensator amounts to 0.03, the agreement of the observations with the curves traced may be considered as very satisfactory. As according to § 4 a displacement of 14.34 of the movable compensator wedge corresponds to a difference of phase of π in circular measure, $c_\infty - c_0$ denotes a difference of phase of $0.25 : 28.68 = 0.0087$. In the following way the change in the angle of principal incidence I , corresponding with this, could be obtained.

The measurements on pure mercury, immediately after the formation of the mirror, gave

Angle of Incidence	Compensator	Angle of Principal Incidence
78°38'	56.24	79°18'

Observations made at the same angle of incidence on the mirror with an adsorbed layer of air yielded:

78°38'	56.90	78°19'
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It follows from this, that if the compensator-reading in the neighbourhood of the angle of principal incidence diminishes by 0.66, the angle of principal incidence increases by 59', so that it follows from the observed value $c_{\infty} - c_0 = 0.25$, that the adsorbed layer of air decreases the angle of principal incidence by 22'.5. It is to be doubted very much whether the change, which has been observed for crystals on natural cleavage surfaces, shortly after the splitting, in the phase difference between the components of the reflected light, which vibrate normal to and in the plane of incidence, should be attributed to layers of air. DRUDE found this change for fresh cleavages surfaces of antimony glance, calcspar, and rock-salt.¹⁾ For rock-salt the cause is not to be looked for in a layer of water on the hygroscopical crystal. The observed change in the phase difference is greatest for antimony glance at the angle of principal incidence. According as the optical axis of the crystal is parallel to the angle of incidence or normal to it, this change amounts successively to 0.01 and 0.06. This value is many times greater than has been observed for mercury. Besides the greater part of the change has already taken place in 2 hours and the retardation in the increment of the ellipticity on standing is much more considerable than for mercury. DRUDE considers fresh cleavage-planes as unsaturated and thinks that also a greater condensation of the gas layers would have to result from this. Experiment should decide, however, whether gas layers play a part also here. Fresh cleavage-planes of lead glance do not exhibit a change in the elliptical polarisation with the time.

7. *On the changes in the phase-difference obtained in a previous investigation.*

It appears from the observations mentioned in § 5, that changes of nearly 1° in the angle of principal incidence caused by surface-layers were observed. Hence the question is, what gives rise to these greater changes? Very probably these occur in consequence of liquid layers, which are enveloped by the dust falling on the mercury. When

¹⁾ DRUDE, Wied. Ann., 34, 489, 1888; 36, 532, 1889.

some dust is swept up from the floor and some of it is strewn over the mercury, the displacement of the compensator fringe can immediately be observed without any adjustment. No liquid is, however, to be observed on the mercury either with the naked eye or with a telescope. When the dust is taken from a place, where oil has been spilt, the compensator-fringe assumes a tortuous form and liquid streaks are to be observed on the surface by means of the telescope. The sinuous compensator-fringe indicates, that not everywhere an equal quantity of liquid is spread over the mercury.

That in this case really a liquid is spread over the mercury surface, is also in agreement with the fact, that the mercury surface is smoother, so that an image may be observed in the telescope of the thread, stretched across the centre of the slit of the collimator of the goniometer. This does not succeed with a clean mercury surface in consequence of the vibrations caused by the traffic in the streets.

8. *On the values of I and H for mercury without surface layer.* It follows from § 6 that for a pressure of air of one atmosphere, the curve for $k = 0.79$ best represents the observations, so that the compensator reading successively increases by 0.045, 0.08, and 0.11 in 1, 2, and 3 hours or on an average by 0.04 an hour. As the determinations of I and H , mentioned in § 5, took up three hours, I has been diminished by 6' on an average in this time, the principal azimuth H has, however, remained unchanged. The change in H lies namely within the errors of observation. From this follows, that for mercury without adsorbed layer of air:

$$I = 79^{\circ}24' \quad H = 35^{\circ}45'$$

We subjoin the values obtained by other investigators:

BREWSTER ¹⁾	78°27'	34°46'
QUINCKE ²⁾	77° 3'	33°47'
DES COUDRES ³⁾	79° 3'	33°30'
DRUDE ⁴⁾	79°34'	35°43'
MEYER ⁵⁾	78°23'	35°17'
MESE ⁶⁾	79°22'	36° 7'

In this the following points are noteworthy. BREWSTER gives 26°0' as restored azimuth after two reflections under the angle of principal incidence. From this the above given value of the principal azimuth

¹⁾ BREWSTER, Phil. Trans., 287, 1880.

²⁾ QUINCKE, Pogg. Ann., 142, 202, 1871

³⁾ DES COUDRES, Thesis for the doctorate, Berlin, 1887.

⁴⁾ DRUDE, Wied. Ann., 39, 511, 1890.

⁵⁾ MEYER, Ann. d. Phys., 81, 1017, 1913.

⁶⁾ MESE, Gött. Nachr., 530, 1913.

has been calculated. It cannot be inferred from BREWSTER's records, whether his observations have been made on a free mercury surface or on mercury against glass. In the latter case scratches in the glass may be responsible for the too low value of the principal azimuth. Also the too low value of the principal azimuth determined by QUINCKE should be attributed to scratches¹⁾. DES COUDRES' observations have been made on a free surface. The deviations seem to be owing to inaccuracies in the observations. DRUDE obtains a clean mercury surface by the aid of two funnels. No further particulars are given about this. The method is probably similar to RONTGEN's method of overflowing. The observations were made within two hours after the formation of the mercury mirror. QUINCKE and MEYER used a mercury surface against glass. A surface layer between mercury and glass has undoubtedly caused the too low value of the angle of principal incidence. MEESE also made observations on mercury against glass and demonstrates the existence of surface layers, that are then present. The values of I and H given here, have been calculated from his observations. In how far a condensed layer of air has also exerted an influence cannot be ascertained. From the values determined by us and those of DRUDE, MEESE, and MEYER, whose value for I , which is certainly too low, has not been taken into account, the following values of the optical constants for mercury may be assumed as the most probable:

$$I = 79^{\circ}27' \quad H = 35^{\circ}43'.$$

§ 9. *The thickness of the adsorbed layer of air.* Both VAN RIJN VAN ALKEMADE (see § 1) and DRUDE have given equations, from which the thickness of the surface layer may be derived. According to DRUDE²⁾ the change in the phase-difference between the components of the reflected light, parallel to and normal to the plane of incidence, brought about by the surface layer is:

$$\Delta' - \Delta = \frac{4\pi \cos\varphi \sin^2\varphi (a - \cos^2\varphi)}{\lambda (a - \cos^2\varphi)^2 + a^2} \int_0^L \left(1 - \frac{1}{n^2}\right) dl$$

In this φ is the angle of incidence, L the thickness of the surface layer, n the index of refraction in this layer at the distance l of the reflecting metal surface:

$$a = \frac{\cos 4H}{\sin^2 I \tan^2 I}, \quad a_1 = \frac{\sin 4H}{\sin^2 I \tan^2 I}.$$

¹⁾ J. J. HAAK, Thesis for the doctorate, Amsterdam, 1918, p. 47.

²⁾ DRUDE, Wied. Ann., **39**. 481, 1890.

The index of refraction n of the surface layer will increase on approaching the reflecting metal surface. When for n a mean value is taken, viz. that between n_{an} and the value for the greatly condensed air, immediately adjoining the metal and when with QUINCKE¹⁾ it is supposed, that the density of this is equal to that of the mercury, $n = 4.048$ is found for this by the aid of the relation: $(n-1):d = \text{constant}$ ²⁾. Hence the mean value of n is $(4.048 + 1.003):2 = 2.52$. As $\Delta' - \Delta$, the phase difference for the absorbed layer of air, amounts to 0.0087 (see § 6) and $\varphi = 79^\circ 46'$ (see § 6), we find with the values of I and H mentioned in § 8:

$$L = 1.6 \mu\mu.$$

This value is in agreement with that for the transition layer liquid-vapour, for which BAKKER³⁾ gives $1-2 \mu\mu$.

When in the same way the thickness of a layer of oil ($n = 1.5$, $d = 0.9$) is calculated, which according to § 5 can modify the angle of principal incidence by 1° , the compensator-reading by 0.50 and more, we find, introducing the value 0.50, $L = 3 \mu\mu$. This is in accordance with RAYLEIGH's and FISCHER's⁴⁾ determinations. RAYLEIGH found, namely, for the thickness of the thinnest layer of oil, that stops the movements of the camphor particles on water, $2\mu\mu$. FISCHER found for liquid layers, which spread over mercury, thicknesses smaller than $5\mu\mu$.

As the adsorbed layer of air of a thickness of $1.6 \mu\mu$ changes the compensator-reading by 0.25 and the mean error in the reading amounts to 0.02, a layer of a thickness of $0.13 \mu\mu$ can still be demonstrated in this way by this optical method. Such a layer is of the thickness of a molecule. It is not possible to prove the existence of such thin layers by the aid of the capillary phenomena.

It is not possible to remove the once adsorbed layer of air by means of a very far exhausted vacuum, as the mercury airpump of GAERDE can bring about. After eight hours' pumping no displacement of the compensator reading could be demonstrated⁵⁾.

¹⁾ QUINCKE, Pogg. Ann., **108**, 326, 1859.

²⁾ L. LORENZ—H. A. LORENTZ's formula cannot be applied here, as n^2 would become negative. Let $\frac{n_1^2 + 2}{n_1^2 - 1} d_1$ be $= \frac{n^2 + 2}{n^2 - 1} d$, then $\frac{n^2 + 2}{n^2 - 1} \frac{d}{d_1}$ must be > 1 , if n_1^2 is to be positive. In the case considered here $\frac{d_1}{d} = 10^4$, $\frac{n^2 + 2}{n^2 - 1} = 5.10^3$, so that the condition is not fulfilled.

³⁾ G. BAKKER, Z. f. Phys. Chem., **91**, 571, 1916.

⁴⁾ RAYLEIGH, Phil. Mag., (5), **30**, 396, 1890; FISCHER, Wied. Ann., **68**, 436, 1899.

⁵⁾ This result is in agreement with other experiments, which show with how

10. *Testing of the obtained results by means of a mercury mirror got by distillation of pure mercury.* According to § 6 the phase-difference was measured with the compensator by annulling this phase-difference, in order to determine the influence exerted by the adsorbed layer of air. From the values given in § 4 it appears, that the lowest compensator-reading corresponds with the smallest phase-difference. As according to DRUDE every surface layer diminishes the angle of principal incidence, hence increases the phase-difference for every angle of incidence, the mercury surface is the better, i.e. less contaminated by surface layers, as the compensator-reading is smaller. For an angle, somewhat greater than I , this smallest reading was 56.84¹⁾. Mercury, distilled in vacuum, which was conveyed into a dish after being filtered through a paper funnel, yields the reading 56.84. This dish had been placed free in the air and was not surrounded by a case (see § 6), so that the rays of light need not pass through glass windows. Mercury purified by being shaken with potassium hydroxide and nitric acid, but not distilled in vacuum, yields the reading 56.85. The difference with the preceding value falls within the errors of observation. Mercury, conveyed into the dish through a drawn-out glass tube, yields 57.00, if the tube has not been very well cleaned. For a thorough cleaning heating to a dull red glow is generally sufficient. Touched by a piece of cloth, which is not clean, the mercury gives the adjustment 57.20. When breathed upon, the mercury yields a reading increased by 0.04 or 0.05.

In order to prove by another way, that 56.84 is the reading for pure mercury without surface layer, pure mercury was distilled in vacuum into the iron dish, which is situated in the bronze cylinder. It was previously ascertained, that the glass windows — carefully cooled glass plates of a thickness of 3 mm. — did not modify the compensator-reading, even though the cylinder was exhausted of air. For this purpose an iron mirror was placed in the dish and the compensator-reading was observed before and after the exhaustion. The pure mercury was heated in a glass globe. The vapour was condensed in the spiral windings of a glass cooler and received in a glass bottle, from which it flows out into the iron vessel through a glass tube with drawn-out point. All the junctions of this apparatus consist of sealed glass. The air-tight connection of the glass tube with

great a force these adsorbed layers of air are attached to the surfaces. Cf. among others VOIGT, Wied. Ann., 19, 39, 1884. Likewise it is in agreement with the fact, that the layer of air cannot be removed by means of carbon powder, which has been heated just before to a red glow. Cf. among others SISSINGH, Thesis for the doctorate, p. 162; Arch. Néerl. 20, 228, 1886.

¹⁾ The values recorded here are again the means of four readings.

drawn-out point, which passes through the short tube in the upper wall of the bronze cylinder, with this short tube was effected by means of an airpump tube and a little collodion. A GAEBE mercury airpump exhausts the space. The compensator-adjustment was 56.84, hence exactly the same as that which prevails for mercury without adhering layer of air, according to the observations communicated in this §.

11: *Inquiry into a difference in the optical constants of liquid and solid mercury.* At first the air in the bronze cylinder was very carefully dried. The cooling of the cylinder and the dish with mercury in it took place by putting a mixture of solid carbonic acid and ether on a tin plate screwed on to the bottom of the cylindrical case. By means of ebonite as heat-insulator the conduction of heat from the metallic parts of the goniometer to the cylinder is prevented. In order to prevent the cooling of the glass windows in the side tubes, because no water vapour from the air may settle on them, these windows are cemented to ebonite tubes, which are screwed on to the side tubes of the bronze cylinder. The air-tight closure was effected by means of very tough Ramsay-grease. As it appeared that in spite of this precaution some water-vapour deposits on the glasses, a current of dry air was blown along them by means of a GAEBE box pump, which quite remedied this evil.

During the cooling the following phenomena are observed. When during the cooling the compensator is adjusted for the dark compensator-fringe, this winds, while the mercury is still liquid and becomes less dark, after which it disappears altogether. At last the fringe, which has then become black again, jumps back to its original position. When the telescope, which is placed behind the analyzer, is then adjusted on the mercury, ice crystals appear to float on the mercury. From this it is evident, that the explanation of the observed phenomenon is the following. In spite of the careful drying the air contains traces of water vapour, which are deposited on the mercury surface during the cooling and spread over it as a liquid ¹⁾. The compensator-fringe is probably sinuous, when the water layer consists of incoherent patches and is very thin. When the water forms a coherent layer and this layer has become so thick, that the reflection takes place on water, the fringe disappears, as at the chosen angle of incidence of $79^{\circ} 46'$ water does not perceptibly polarize the light elliptically on reflection. As soon as the tempera-

¹⁾ These phenomena are not observed on an iron mirror during the cooling, so that the condensed water vapour does not seem to spread over this mirror.

ture falls below 0° , the water freezes and contracts to a few ice crystals, which lie spread with large interstices on the mercury. Then we have again a mercury surface and the normal adjustment of the compensator-fringe. In the meantime the mercury is still liquid.

Attempts to prevent this deposition of the water vapour by careful drying of the air proved unsuccessful. This was done thoroughly however by exhausting the bronze cylinder. When an iron mirror is placed in the cylinder, it appears, that the glasses on the side-tubes do not become bi-refringent when the case is exhausted, but that they do so through the one-sided cooling during the fall of the temperature of the bronze cylinder by solid carbonic acid and ether. Then the adjustment of the compensator-fringe changes by the constant amount 0.08. During the cooling of the mercury in vacuum no sudden change in the position of the compensator-fringe is observed at the moment of the freezing. The reading of the compensator-fringe diminishes gradually, till this change reaches an amount of 0.08. It appears from this that only the slight double refraction of the glasses plays a part here and that neither during the freezing of the mercury, nor during the further cooling down to -80° the phase-difference, hence also the angle of principal incidence of the mercury changes perceptibly.

At first the position of the polarizer presented a change during the freezing, which could amount to as much as 3° . This, however, must be attributed to the influence of wrinkles, which make their appearance with the freezing in consequence of inevitable vibrations caused by the traffic in the streets or by tram cars. This is in agreement with the observations of FIZEAU, DRUDE, and HAAK¹⁾ on the diminution of the restored azimuth through grooves or scratches in various directions on the reflecting surface. In order to prevent these wrinkles as much as possible, the iron dish is filled brimful with mercury and then the temperature is slowly lowered. When the traffic in the streets is not too great, it is then sometimes possible to get such a smooth mercury mirror, that a pure image of the collimator slit can be observed. In this case the adjustment of the polarizer does not change. It appears from this, that on freezing and cooling of the solid mercury to -80° neither the angle of principal incidence nor the principal azimuth are subjected to any change. Optically liquid and solid mercury behave in the same way²⁾,

¹⁾ FIZEAU, *Ann. de Chim. et de Phys.*, **3**, 373, 1861; DRUDE, *Wied. Ann.*, **39**, 497, 1890; J. J. HAAK, Thesis for the doctorate, Amsterdam, 1918.

²⁾ Besides it follows from this that LUMMER and SORGE's supposition (*Ann. der Phys.*, **31**, 325, 1910), according to which internal tensions would give rise to the elliptical polarisation, cannot be valid for solid mercury.

Chemistry. — “Investigations on PASTEUR’s Principle concerning the Relation between Molecular and Crystallonomical Dissymmetry: VIII. On the spontaneous Fission of racemic Potassium-Cobalti-Oxalate into its optically-active Antipodes.” By Prof. F. M. JAEGER and WILLIAM THOMAS. B. Sc.

(Communicated in the meeting of Nov 30, 1918).

§ 1. As a continuation of the fissions, accomplished up to this date, of the racemic complex *trioxalates* of *potassium* and the trivalent metals: *chromium*¹⁾, *rhodium*²⁾, and *iridium*³⁾, — it appeared desirable to make an attempt to separate the analogously built *potassium-cobalti-oxalate*: $K_3\{Co(C_2O_4)_3\} + 3\frac{1}{2}H_2O$, into its optically-active components for the purpose of a comparison of their rotatory dispersion and crystal-forms. The series of the complex *oxalates* investigated, would then be really complete. The proposed separation into its antipodes was, however, hindered till now by a number of difficulties of various kinds, partially caused by the salt being not very resistant towards an increase of temperature, and on the other hand by its particular solubility-relations, when combined with active bases; moreover a troublesome circumstance was its sensitiveness to light-radiation, this causing a rapid decomposition of these salts in solution, under formation of a pale pink, hardly soluble precipitate, — a reaction, the study of which is now started in our laboratory.

The racemic salt: $K_3\{Co(C_2O_4)_3\} + 3\frac{1}{2}H_2O$ has been studied by COPAUX⁴⁾. It has, like the corresponding salts of the other metals, triclinic symmetry, but it is *not* isomorphous with them, as follows already from the deviating content of water of crystallisation: while the *iridium*- and *rhodium*-salts contain $4\frac{1}{2}$ molecules of water, the corresponding *chromi*-salt has *three*, the *cobalti*-salt $3\frac{1}{2}$ molecules of it. The salt was prepared in the following way in greater quantities.

A mixture of 25 grammes of *cobalti-carbonate*, 250 ccm of a satu-

¹⁾ A. WERNER, Ber. d. d. Chem. Ges. 45. 3061. (1912).

²⁾ A. WERNER, Ber. d. d. Chem. Ges. 47. 1954 (1914); F. M. JAEGER, Proceed. Ak. v. Wet. Amsterdam, 20. 263. (1917).

³⁾ F. M. JAEGER, Proceed. Kon. Akad. v. Wet. Amsterdam, 20. 273. (1917); 21. 203. (1918).

⁴⁾ H. COPAUX, Bull. de la Soc Min. 29. 75. (1906); Ann. de Chim. et Phys. (8). 6. 508. (1905).

rated solution of *potassium-oxalate*, and 230 ccm of a saturated solution of *oxalic acid*, was heated on the waterbath under continuous stirring, till all the carbonate had entered into solution. The liquid thus obtained was cooled to 40° C, and then 30 grammes of finely pulverised *lead-peroxide*: PbO_2 , were added. After some time 50 ccm of a 50 % solution of *acetic acid* were slowly added to the rigorously cooled solution under continuous stirring. Then the liquid was filtered and precipitated by 400 ccm of 97 % alcohol; the green precipitate was sucked off, and several times washed with absolute alcohol. In this way 80 grammes of the dark green *potassium-cobalti-oxalate* were readily collected.

§ 2. The *silver*-, and the *barium*-salts being both only slightly soluble, we used the *potassium*-salt itself for the preparation of the corresponding *strychnine*-compound, thus avoiding the troublesome use of large volumes of solution; this is of advantage, because also at lower temperatures the solutions are partially decomposed under development of carbondioxide. The *strychnine*-salt ¹⁾ is for the greater part precipitated, if the calculated amount of *strychnine-sulphate* is added to the solution of the *potassium*-salt, and only so much cold water is consequently added as to dissolve the precipitate formed. All these experiments were executed in a dark room, where the solution is left standing in an open vessel for several weeks, at a temperature of about 16° C; the fractions successively deposited from the mother-liquor are collected separately.

The crystals obtained are treated, in the same way as described on former occasions, with an excess of *potassium-iodide*, the *strychnine-iodide* is sucked off, and the filtrate precipitated by means of 97 % alcohol. The salt obtained is purified by repeated crystallisations from a small quantity of water.

The first fractions of the *strychnine*-salt in this way gave crystals of the *laevogyratory* antipode, containing 1 molecule of water of crystallisation. The determination of the water-content cannot be made at 120° C, because of the decomposibility of the substance; it was therefore made by passing a current of dry air at 20° C over the finely powdered substance during a very long time, and a loss of weight corresponding to 0,8 molecules of water was finally observed.

With respect to the light-absorption by the dark green solutions,

¹⁾ Originally the separation of the racemic salt was tried by the aid of *cinchonine*, but without success. Afterwards we repeated these experiments under somewhat varied conditions, but they gave no positive results either.

it was found that in layers of 20 cm., a solution of 0.41 percentages by weight showed a pronounced absorption-band in the yellow and blue part of the spectrum between the wavelengths of 5510 and 6520 A.U. For concentrations of 0.82% and 1%, no light was transmitted; but the solution just mentioned allowed the light to come through between 4850 and 5515 A.U. With a solution of 0.31%, these limits were: 4770 to 5670 A.U., and 6480 A.U.; with one of 0.27%: 4720 to 5750, and 6450 A.U.; etc. Determinations corresponding to wave-lengths within these limits can only be made with extremely diluted solutions, and the incertitude of the readings caused thereby may explain the deviations of the values obtained in the case of the laevo-, and dextrogyratory components, in so far as these values are observed in the immediate vicinity of the deep minimum in the dispersion-curve. But notwithstanding this incertitude, the characteristic slope of the dispersion-curve is in all cases fixed with full certainty.

For the salt from the first fractions, we found values of the rotation in good agreement with each other, which are suited to elucidate the strange form of the dispersion-curve (fig. 1) immediately:

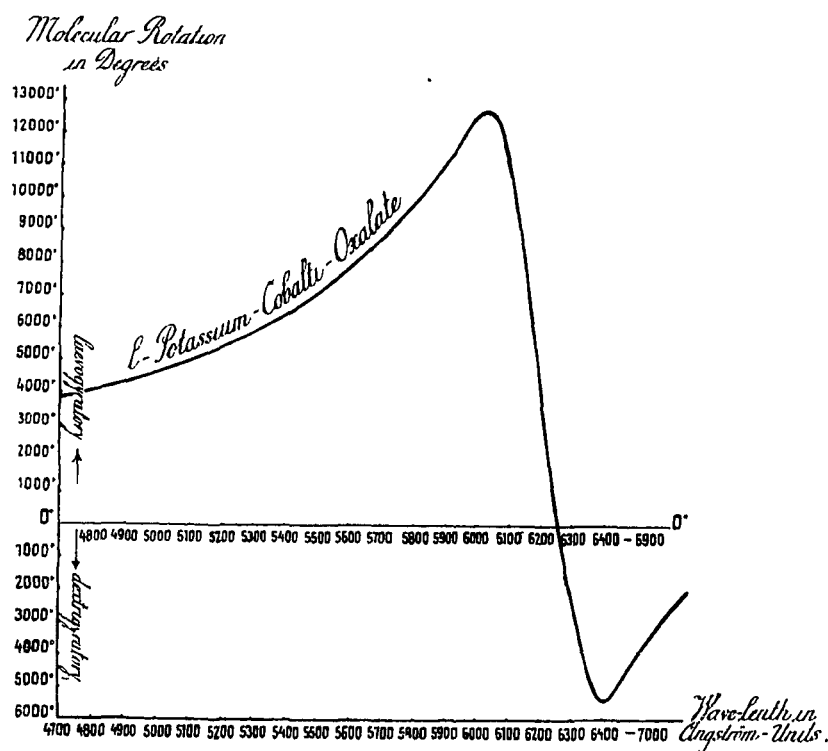


Fig 1. Molecular Rotatory Dispersion of Laevogyratory Potassium Cobalti-Oxalate (+ 1 H₂O).

MOLECULAR ROTATION OF LAEVOGYRATORY POTASSIUM-COBALT-OXALATE (+ 1 H ₂ O).	
Wave-length in Angström-Units:	Molecular Rotation in Degrees:
4730	- 3913°
4780	4031
4870	4196
4945	4399
5020	4619
5105	4916
5180	5123
5260	5487
5340	5900
5420	6387
5515	7086
5610	7805
5700	8682
5800	9708
5910	11327
6020	12508
6140	- 8506
6260	+ 263
6380	5391
6520	4126
6660	1799
6800	+ 160

This curve therefore appears to possess the peculiarity, that the rotation at first rapidly increases for greater wave-lengths, but decreases then very steeply in the vicinity of the absorption-band, to assume the opposite algebraic sign at circa 6260 A.U. The right-handed rotation now reached, shows a minimum at about 6400 A.U., and decreases at first rapidly, afterwards more slowly, so that the

curve approaches more and more the axis of the *zero*-value. The dispersion has therefore, properly speaking, only a really "normal" character between 6240 A.U., and 6400 A.U. The maximum of the laevogyrotory rotation is situated at about 6000 A.U.

On comparing the magnitude of the rotations for corresponding wave-lengths, in the cases of the complex *oxalates* of *chromium*, *cobaltum*, *rhodium*, and *iridium*, — the influence of the specific nature of the central metallic atom on the whole character, as well as on the absolute values of the rotation, is immediately evident. The figures 2 and 3 will show this clearly; in fig. 2 the curves of the *cobalti*-, *rhodium*- and *iridium*-salts are drawn, in fig. 3 those of the *chromium*-, and *cobalti*-salts. While the complex *rhodium*-, and *iridium*-oxalates show an analogous dispersion, the *cobalti*-salt seems to have a

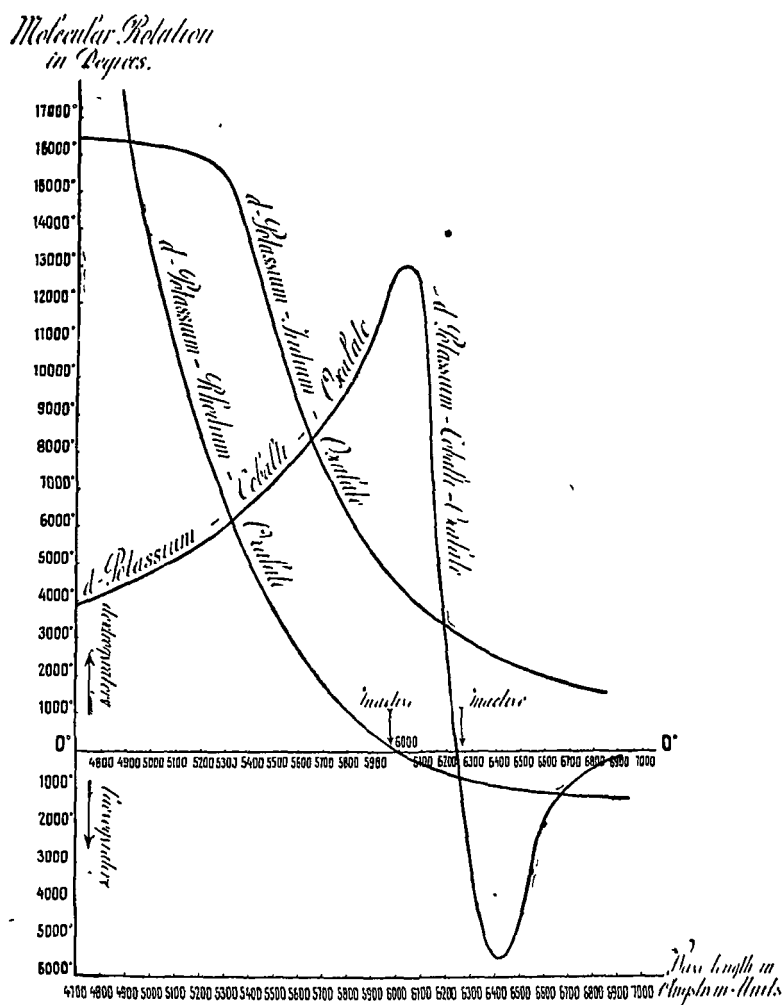


Fig. 2.

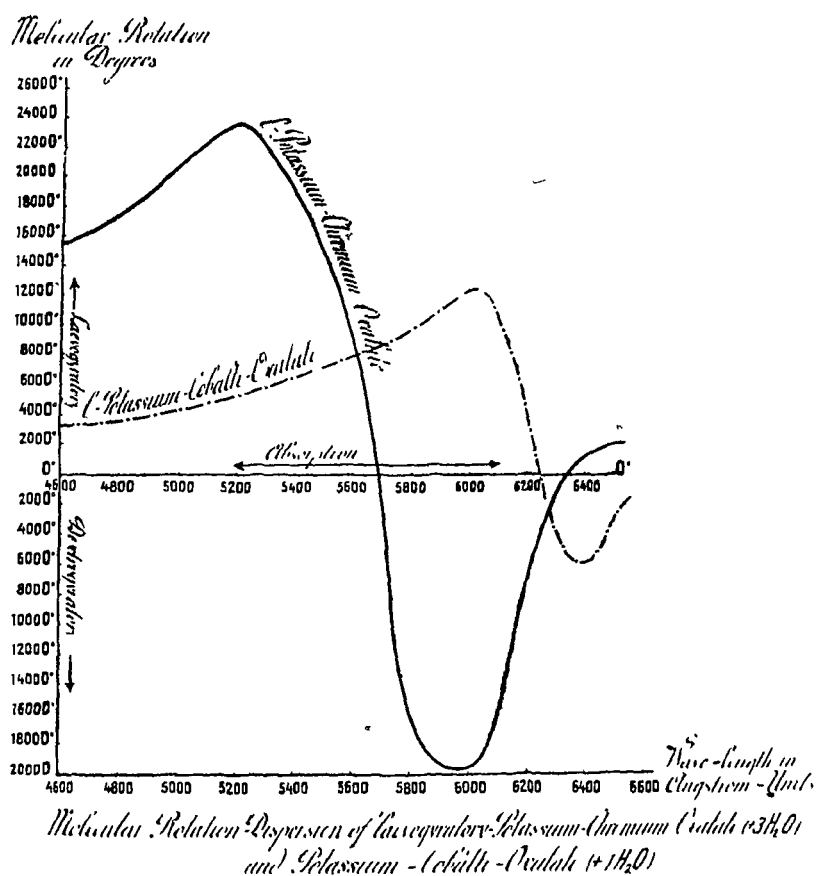


Fig.3.

deviating position amongst them. ¹⁾ However, this salt shows a complete analogy in this respect with the corresponding *chromium*-salt, as may be easily seen from the measurements made in this laboratory by Mr. P. J. BECKER with the *potassium-chromi-oxalate*: $K_2\{Cr(C_2O_4)_3\} + 3H_2O$, which was separated into its antipodes after WERNER's method²⁾. On comparing the rotation of this salt with that of the *cobalti*-salt at corresponding wave-lengths, it may be seen that the rotations of the *chromium*-salt are, up to 5640 A.U., and above

¹⁾ According to an investigation of G. BRUHAT (Bull. de la Soc. Chim. (4), 17, 226 (1915), there is also a maximum in the dispersion-curve of the complex *iridium*-oxalate at short wave-lengths (about 4930 A.U.). It therefore seems probable, that the character of the anomalous dispersion curves is really very analogous in all these cases, however with a considerable difference in the positions of the maxima.

²⁾ A. WERNER, Ber. d. d. Chem. Ges. 45. 3061 (1912). It is difficult to obtain good crystals of this compound which, moreover, rapidly autoracemises in solution; therefore crystallographic measurements could till now not be made in any way.

6280 A.U., considerably *greater* than those of the *cobalti*-salt; while between 5640 and 6280 A.U. the reverse occurs, and the two salts even show an opposite rotation as a consequence of the shift of their maximum and minimum; this shift is, in its turn, intimately connected with the very different situation of the absorption-bands: for the *chromium*-salt has a very broad band in the orange, yellow, partially in the green and the violet. It must, moreover, be remarked, that our former experience has made it clear, that the *triethylenediamine-chromi*-salts show in general only about half the rotations of the *triethylenediamine-cobalti*-salts for corresponding wave-lengths. From this it is evident how great and unexpected an influence the presence of *basic* groups, or that of *acid* radicles, has, on the magnitude of the rotation when they are dissymmetrically arranged round the central metal-atoms of such complex salts.

§ 3. As was already mentioned before, the racemic *cobalti*-salt has already been investigated by COPAUX, who described it as a *triclinic* substance, but *not* isomorphous with the corresponding *rhodium*-salt. As will be soon demonstrated, COPAUX most probably obtained his crystals from solutions evaporated in the darkness and at low temperatures; for even in diffuse day-light the solution is decomposed with development of carbondioxide and precipitation of *cobalto-oxalate*, — a decomposition which is quite analogous to the photochemical decomposition of the corresponding *ferric*-salt. It must be remarked that in this photochemical reaction, *blue* light decomposes the solutions much more rapidly, than *red* or *green* light, — in full agreement with DRAPER's law. But it is a remarkable fact that *yellow* and *orange* light, which is absorbed also to a considerable amount, has scarcely any stronger influence than the only slightly active green or red rays.

In our experiments the saturated solutions were evaporated in a dark space, the temperature of which differed only slightly from 0° C. In this case we really obtained *triclinic-pinacoidal* crystals of a dark green, almost black colour, and showing in most cases curved faces and rudimentary forms; accurate measurements were therefore very difficult. The angular values obtained really differ not inconsiderably from those published by COPAUX, at least within some zones; but the identity of his crystals and ours need not be doubted in any way, as may appear from the following values:

<i>Angular values:</i>	<i>Observed:</i>		<i>Calculated:</i>
	JAEGER:	COPAUX:	
$m:\nu = (110):(\bar{1}\bar{1}0) =$	60° 37'	60° 36'	—
$c:m = (001):(110) =$	79 22	79 26	—

$q:m = (011):(110) =$	65	10	65	28	—
$a:b = (100):(\bar{0}10) =$	89	2	88	42	88° 40'
$c:q = (001):(011) =$	33	10	32	28	—
$b:c = (010):(001) =$	88	37	88	39	88 32
etc.					

The specific gravity of these crystals, which commonly only showed the combination-forms: $m = \{110\}$, $\mu = \{1\bar{1}0\}$, $c = \{001\}$, $q = \{011\}$, $\omega = \{\bar{1}12\}$, and $\alpha = \{100\}$ and $b = \{010\}$ very narrow, — was at 15° C. determined at: $d_{40} = 1,877$; the molecular volume is therefore: 268,14.

An analogy of form with the corresponding *rhodium*-, and *iridium*-salts is not present; neither is this the case with the monoclinic *chromium*-salt, which possesses $3H_2O$.¹⁾

These facts prove in every case undeniably, that at temperatures in the neighbourhood of 0° C., the saturated solutions deposit crystals of the *racemic* compound. But the stranger therefore appeared to us originally the behaviour of solutions evaporating at room-temperature. For from an also inactive solution, which during the summermonths was slowly evaporated in a dark room at temperatures only slightly differing from 18° C., dark green, almost black needles were obtained, which even on superficial examination appeared to differ appreciably from the triclinic racemate. Crystal-measurements taught us, that they had *trigonal* symmetry, and that their form was identical with that of the laevogyratory antipode. A crop of small crystals of this crystallisation-product, dissolved in water, did however not show any appreciable rotation. Suspicion immediately arose, that the racemic salt might have been split under these circumstances into its antipodes spontaneously, and that no trace of rotation could be detected according to our way of investigation, only because the solution deposes the crystals of the two antipodes besides each other in about equal number, so that a crop of several crystals, which by the lack of hemihedral faces cannot be discerned from each other, contains in general almost an equal number of dextro- and laevogyratory individuals, when collected from the solution at random. It is evident that such a mixture will not exhibit any appreciable optical activity. If this suspicion were true, the optical activity must appear immediately, if only a single crystal at the same time were dissolved. Indeed, experience proved,

¹⁾ The parametres of the *cobalti*-salt are: $a:b:c = 0,5963:1:0,6590$; $\alpha = 91^\circ 42'$; $\beta = 101^\circ 23'$; $\gamma = 88^\circ 22'$. The *chromium* salt is monoclinic, with: $a:b:c = 1,0060:1:1,3989$; $\beta = 86^\circ 0'$. For the *rhodium*- and *iridium*-salts, cf. these Proceedings, 20, p. 270, (1917); and 21, 214, (1918).

that the first crystal thus investigated, showed the full activity of the *dextrogyratory* component, which then had not yet been obtained in the pure state by our fission-experiments; the following numbers can convincingly demonstrate the fact mentioned:

MOLECULAR ROTATION OF THE DEXTROGYRATORY POTASSIUM-COBALT- OXALATE (+ 1 H ₂ O).	
Wave-length in ÅNGSTRÖM- Units:	Molecular Rotation in Degrees:
4730	+ 3876°
4780	4009
4870	4167
4945	4428
5020	4689
5105	4923
5180	5106
5260	5553
5340	6013
5420	6416
5510	7023
5610	7916
5700	8703
5800	9764
5910	11365
6020	12812
6140	+ 8269
6260	- 103
6380	5468
6520	4317
6660	1678
6800	526
6940	- 198

The minimum in the dispersion-curve is here somewhat steeper

than our former measurements with the laevogyrotory component indicate, — a deviation probably caused by the uncertainty of the readings in the interval of the absorption-band. But the correspondence of the curves cannot be doubted any longer. Continued study of the single crystals deposited from the solution, taught, that besides the lefthanded crystals, also those of the laevogyrotory component occur. It is commonly quite impossible to recognise the two kinds of crystals from each other by their outward appearance, and thus to select them, because the facets of the right- or lefthanded trapezohedra or trigonal bipyramids are commonly lacking, so that the aspect of the crystals is in both cases quite the same.

It cannot be doubted therefore any longer, that we have found here a *first instance of a fission into optically active antipodes of such complex metallic compounds, by spontaneous crystallisation*; for the case of *potassium-rhodium-oxalate* formerly indicated by WERNER as an instance of this kind, can no longer be considered as such, as was some time ago proved by us.¹⁾

For the purpose of justifying this view, it was necessary to determine the *temperature of transition* of the racemic compound into its antipodes as accurately as possible. This was done in two ways: by means of the dilatometrical method, and by the study of the

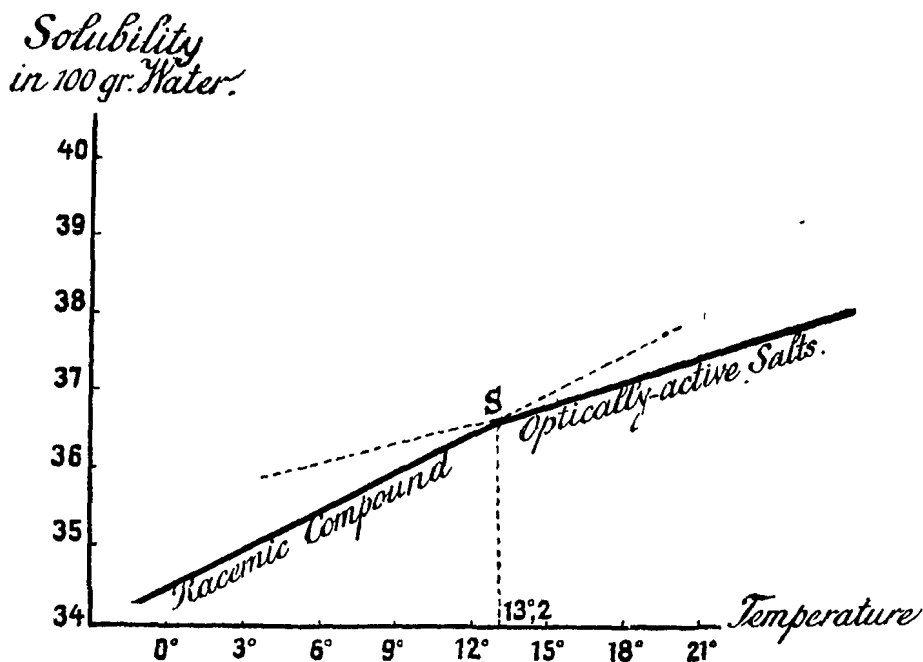
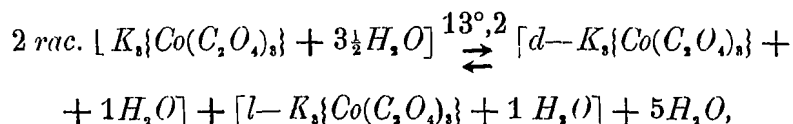


Fig. 4.

¹⁾ F. M. JAEGER, Proceed. Kon. Akad. v. Wet. Amsterdam, 20. 264, 265. (1917).

solubilities of the salts at different temperatures. For we have already formerly drawn attention¹⁾ to the fact, that below and above the transition-temperature, the metastable forms must have, as in all such cases, the greater solubility; and this was exactly one of the arguments used, by us to reject WERNER's conclusions about the occurrence of a spontaneous fission in the case of the *potassium-rhodium-oxalate*.

Indeed, our experiments fully confirmed this view: we were able to demonstrate, that below 14° C. the solubility of the inactive form is really *smaller* than that of the optically-active antipodes, whereas above 14° C. the reverse was the case. Thus 100 grammes of water at 0° C. e.g. appeared to dissolve 34.50 grammes of the racemic salt, at 14° C. 36.81 grammes; etc. On the other hand, 100 grammes of water at 20° C. dissolved 37.40 grammes of the laevogyrotory salt, at 22° C. 37.6 grammes; etc. The fig. 4 shows, that the transitionpoint to be determined, without appreciable error, may be fixed as 13.2° C.; this temperature, at which the reaction:



takes place, is therefore a *minimum*-temperature for the existence of the optically-active salts.

The dilatometrical experiments were rather difficult, because of the tendency of the compound to decompose, when its solution is kept at somewhat higher temperatures for a long time, and because of the inevitable retardation-phenomena. Notwithstanding this, we were able to prove a sharp discontinuity of the volume-temperature-curve, at a temperature between 12° and 16° C. That such retardation-phenomena really occur, cannot be doubted; even in solution, the active salt is transformed just below the transition-temperature into the racemic one, with considerable slowness. Thus we found, that at 12° C, the dilute solution of the laevogyrotory antipode lost in one day about half, in two days two thirds, in three days almost five sixths, and in four days about nine tenths of its original optical activity, while at the said temperature the optical antipodes beyond all doubt are already metastable with respect to the racemic salt.

Crystallisation-experiments made in a thermostate at 22° C gave results in full agreement with our conclusions: the solutions deposited

¹⁾ A. WERNER, Ber. d. d. Chem. Ges. **47**. 1954 (1914).

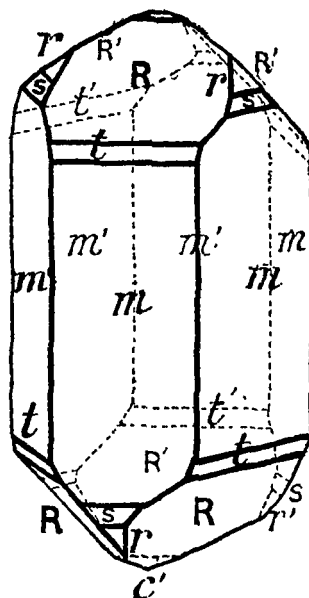
always the trigonal needles of the active components besides each other, but at 0° C we got only the triclinic crystals of the racemate. Therefore complete proof has been given now, that a fission of the *potassium-cobalti-oxalate* by spontaneous crystallisation into its optically active components really occurs at temperatures above 13°,2 C.

§ 4. Crystallographical research taught us, that both the optically active components occur in commonly not distinguishable crystals of *trigonal-trapezohedral* symmetry, which are completely *isomorphous* with those of the optically-active *rhodium*-, and *iridium*-salts.

They have the appearance (fig. 5 and 6) of a prismatic forms of more or less extension; the *dextrogyratory* component hitherto always presented the rhombohedron-like shape of fig. 6.

Trigonal-trapezohedral.

$$a : c = 1 : 0,8968 \text{ (BRAVAIS)}; \alpha = 100^{\circ}27' \text{ (MILLER)}.$$

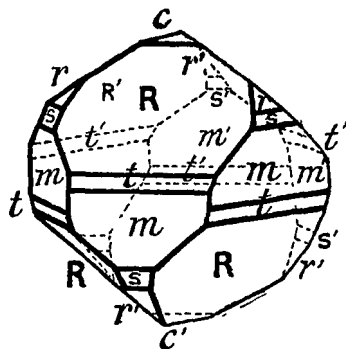


Laevogyratory Potassium-Cobalti-Oxalate (+ 1 H₂O)

Fig 5.

Forms observed: $R = \{10\bar{1}1\} [100]$, large and very brilliant; $c = \{0001\} [111]$, always present, but subordinate; $m = \{10\bar{1}0\} [2\bar{1}1]$, commonly predominant with the lefthanded crystals, and in the case of the dextrogyratory individuals small, but well developed and yielding sharp images; $r = \{01\bar{1}1\} [221]$, and $s = \{02\bar{2}1\} [1\bar{1}1]$, always present, small, but very lustrous; $t = \{20\bar{2}1\} [5\bar{1}1]$, rather large and yielding good reflections. Hemihedral combination-forms were hardly ever

observed; only once a crystal of the *laevogyrotory* antipode presented the *right-handed* trigonal bipyramid $x = \{2\bar{2}41\} [71\bar{5}]$ as an extremely narrow truncation of the edge $R:m$. From this it may be concluded, that in this case too, the substance manifests only a very weak tendency to present hemihedral forms, unregarded the enormous optical activity, which these salts exhibit in aqueous solution; and, moreover, that also in the case of the complex *oxalates*, the same morphological relation between the *cobalti*- and the *rhodium*-salts appears to exist, as between the corresponding *cobalti*- and *rhodium-triethylenediamine nitrates* ¹⁾, in so far, as the *oppositely* rotating *cobalti*- and *rhodium*-salts, which are separated from the less soluble compounds with optically-active bases (*strychnine*) or acids (*tartaric acid*), yet exhibit hemihedral forms of *the same* algebraic sign:



Dextrogyrotory Potassium-Cobalti-Oxalate (+1H, O).

Fig 6.

Substance:	Rotation of the salt separated from the less soluble compound:	Algebraic sign of the hemihedral forms present:
<i>Triethylenediamine-Cobalti-Nitrate.</i>	(<i>Chloro-tartrate</i>): d.	+ sphenoid.
<i>Triethylenediamine-Rhodium-Nitrate.</i>	(<i>Chloro-tartrate</i>): l.	+ sphenoid.
<i>Potassium-Cobalti-Oxalate.</i>	(<i>Strychnine salt</i>): l.	+ bipyramid.
<i>Potassium-Rhodium-Oxalate.</i>	(<i>Strychnine salt</i>): d.	+ bipyramid.
<i>Potassium-Iridium-Oxalate.</i>	(<i>Strychnine salt</i>): d.	+ bipyramid.

At the same time it is evident that the *cobalti*- and *rhodium*-salts

¹⁾ F. M. JAEGER, Proceed. Kon. Akad. v. Wet. Amsterdam, 20. 258, 261 (1917).

set free from the less soluble compounds with optically active bases or acids, in the case of *triethylenediamine*-derivatives exhibit just the *opposite* rotatory power, as is observed in the case of the complex *trioxalates*; a fact, which sustains the view, according to which it is the basic or acid nature of the radicles placed round the central metallic atom, rather than the special nature of the latter, which in the first instance determines the direction of the rotation.

Angular Values:	Observed:	Calculated:
$c:R = (0001):(10\bar{1}1) =$	* 46° 5'	—
$m:t = (10\bar{1}0):(02\bar{2}1) =$	25 43	25° 46½'
$m:m = (10\bar{1}0):(0\bar{1}\bar{1}0) =$	60 0	60 0
$R:R = (10\bar{1}1):(\bar{1}101) =$	77 11	77 12
$c:r = (0001):(0\bar{1}\bar{1}1) =$	46 8	46 5
$r:s = (0\bar{1}\bar{1}1):(02\bar{2}1) =$	18 0	18 8½'
$s:m = (02\bar{2}1):(0\bar{1}\bar{1}0) =$	25 55	25 46½'
$s:R = (02\bar{2}1):(10\bar{1}1) =$	51 13	51 5
$R:t = (0\bar{1}\bar{1}1):(02\bar{2}1) =$	17 58	18 8½'
$R:m = (10\bar{1}1):(10\bar{1}0) =$	43 55	43 55
$x:R = (2241):(0\bar{1}\bar{1}1) =$	78 13	78 9

No distinct cleavage was observed.

The specific gravity of these crystals was at 15° C. determined at: $d_4 = 1.8893$; the molecular volume is therefore: 242.57, and the topical parameters become: $\chi:\omega = 7,4676:6,6971$; or $\chi' = 6,3789$. The values of χ of the *Co*-, *Rho*-, and *Ir*-compounds appear to decrease therefore continuously with increasing atomic weight of the metallic atom, while ω reaches a minimum in the case of the *Rho*-salt.

Groningen, November 1918.

Laboratory for Inorganic and Physical
Chemistry of the University.

Mathematics. — “*Ueber eineindeutige, stetige Transformationen von Flächen in sich*” (sechste Mitteilung¹⁾). By Prof. L. E. J. BROUWER.

(Communicated in the meeting of November 30, 1918).

§ 1. In einem in 1912 in den Göttinger Nachrichten (S. 603—606²⁾) in Auszug abgedruckten Briefe an R. FRICKE habe ich (S. 605, Fussnote³⁾) kurz skizziert, wie das von HURWITZ herrührende analytische Theorem, dass *birationale Transformationen einer Riemannschen Fläche vom Geschlechte $p > 1$ in sich unmöglich ein vollständiges kanonisches Schnittsystem der Fläche in ein äquivalentes kanonisches Schnittsystem überführen können*, mittels der Analysis Situs bewiesen werden kann, wobei sich seine Gültigkeit herausstellt für *alle periodischen, eineindeutigen und stetigen Transformationen*. Die damalige Andeutung wird im folgenden näher präzisiert und gerechtfertigt werden.

Sei O die gegebene zweiseitige Fläche, I die Menge der bei der n -periodischen, eineindeutigen und stetigen, die Ränder invariant lassenden Transformation t von O invarianten Punkte. Wir nehmen an, dass jedes von I in O bestimmte Gebiet von t in sich transformiert wird (was, wenn t die Indikatrix von O invariant lässt, stets der Fall ist), und unterziehen die Wirkung von t auf eines dieser Gebiete, welches wir mit ω bezeichnen werden, einer näheren Betrachtung. Dabei ziehen wir im Falle, dass t die Indikatrix von O umkehrt, jeden eventuellen für t *nicht* invarianten Rand von ω

¹⁾ Vgl. diese Proceedings, XI, S. 788; XII, S. 286; XIII, S. 767; XIV, S. 300; XV, S. 352.

²⁾ Das daselbst S. 604 auf künftige Publikationen von P. KOEBE (der Neujahr 1912 im Besitze einer Abschrift meines Briefes an R. FRICKE war) hinweisende Zitat ist nach der Erledigung der Korrekturen von einer mir unbekannten Hand, ohne meine Mitwirkung oder Vorkenntnis eingefügt worden; die bezüglichen Noten sind mir erst nach ihrem Erscheinen bekannt geworden.

In engem Zusammenhang mit dem Inhalte meines (Anfang März 1912 gedruckten) Briefes an R. FRICKE stehen die Karlsruher Verhandlungen über automorphe Funktionen vom Jahre 1911; der über dieselben erstattete Bericht (Jahresber. d. D. M. V. XXI), ist, ebenso wie die in Gött. Nachr. 1912 erschienene KOEBE'sche Mitteilung über den Kontinuitätsbeweis, im Sommer 1912 gedruckt worden. Das in diesem Berichte enthaltene Referat über den Vortrag von P. KOEBE (insbesondere die auf S. 162 befindliche Anmerkung⁴⁾) ist insofern irreführend, dass im wirklichen KOEBE'schen Vortrage, nach der ihm vorangegangenen, S. 156—157 wiedergegebenen kurzen Diskussion mit mir, vom Kontinuitätsbeweise überhaupt nicht wieder die Rede gewesen ist.

in einen Punkt zusammen und fügen diesen Punkt zu ω hinzu. Sei R die Menge der übrig bleibenden (für t invarianten) Ränder r_α von ω und seien $(a_1, b_1), (a_2, b_2), (a_3, b_3), \dots$ die Rückkehrschnittpaare einer *vollständigen* kanonischen Zerschneidung von ω . Wir nehmen an, dass innerhalb jedes dieser Rückkehrschnittpaare ein a , so gewählt werden kann, dass nicht nur a , selbst, sondern auch seine beiden Seiten von t ungeachtet der Ränder äquivalent abgebildet werden (was, wenn t jeden Rückkehrschnitt der kanonischen Zerschneidung ungeachtet der Ränder äquivalent abbildet und die Indikatrix von O umkehrt, stets der Fall ist). Weiter schliessen wir den Fall aus, dass entweder kein Rückkehrschnittpaar (a_ν, b_ν) und höchstens zwei Ränder r_α , oder kein Rand r_α und nur ein einziges Rückkehrschnittpaar (a, b) existiert.

§ 2. Im Falle, dass in ω wenigstens zwei Rückkehrschnittpaare (a_ν, b_ν) existieren, verstehen wir unter Ω diejenige (kein Rückkehrschnittpaar mehr aufweisende) Schottkysche Ueberlagerungsfläche von ω , welche die a_ν als blättertrennende Ufer besitzt, unter L die Menge derjenigen Ränder l_α von Ω , welche durch eine unendliche Zahl von Ueberschreitungen der a_ν auf ω erzeugt werden, unter ${}_1a_\nu, {}_2a_\nu, \dots$ die Ueberlagerungsbilder von a_ν auf Ω , unter a'_ν das durch t auf ω bestimmte Bild von a_ν , unter ${}_1a'_\nu, {}_2a'_\nu, \dots$ die Ueberlagerungsbilder von a'_ν auf Ω . Wenn wir jedem ${}_p a_\nu$ dasjenige ${}_p a'_\nu$ zuordnen, dessen Umlaufkoeffizienten zwischen den l_α die gleichen absoluten Werte besitzen, wie die entsprechenden Umlaufkoeffizienten von ${}_p a_\nu$, so ist in Anschluss daran eine durch die Ueberlagerung von Ω über ω in t übergehende, eindeutige und stetige Transformation t' von Ω in sich bestimmt, welche, ebenso wie t , n -periodisch sein muss und jeden Rand l_α invariant lässt. Ob *alle* Ränder von Ω für t' invariant sind, lassen wir dahingestellt, ziehen aber jeden eventuellen für t' *nicht* invarianten Rand in einen Punkt zusammen und fügen diesen Punkt zu Ω hinzu.

Im Falle, dass in ω nur ein einziges Rückkehrschnittpaar (a, b) existiert, verstehen wir unter Ω diejenige (kein Rückkehrschnittpaar mehr aufweisende) Schottkysche Ueberlagerungsfläche von ω , welche a als blättertrennendes Ufer besitzt, unter l_1 und l_2 diejenigen Ränder von Ω , welche durch eine unendliche Zahl von Ueberschreitungen von a auf ω erzeugt werden, unter ${}_1r, {}_2r, \dots$ die Ueberlagerungsbilder auf Ω eines (für t der Annahme gemäss invarianten) Randes r von ω . Alsdann existiert eine durch die Ueberlagerung von Ω über ω in t übergehende, eindeutige und stetige Transformation t' von Ω in sich, welche ${}_1r$ (mithin auch ${}_2r, {}_3r, \dots$) invariant lässt,

so dass sie, ebenso wie t , n -periodisch sein muss. Ob *alle* Ränder von Ω für t' invariant sind, lassen wir wieder dahingestellt und ziehen jeden eventuellen für t' *nicht* invarianten Rand in einen Punkt zusammen, den wir zu Ω hinzufügen.

Im Falle, dass in ω kein Rückkehrschnittpaar (a, b) existiert, verstehen wir unter Ω die Fläche ω selbst und unter t' die Transformation t selbst.

In jedem der drei Fälle besitzt die Fläche Ω *wenigstens drei* Ränder und ist sie eineindeutiges stetiges Bild eines Teilgebietes der Kugel, während t' eine n -periodische, eineindeutige und stetige Transformation von Ω in sich darstellt, welche jeden Rand, aber keinen Punkt invariant lässt.

Wir dürfen annehmen, dass von den Rändern von Ω *wenigstens einer isoliert* ist. Im entgegengesetzten Falle können wir nämlich in Ω ein Gebiet g bestimmen, zu dessen Grenze kein Grenzpunkt von Rändern von Ω gehört, und welches, ebenso wie seine Komplementärmenge, Ränder von Ω enthält. Die Vereinigung von g und seinen Bildern für t', t'', \dots, t'^{n-1} bildet eine Fläche, welche, ebenso wie Ω , wenigstens drei Ränder besitzt und von t' mit invarianten Rändern und ohne invariante Punkte in sich transformiert wird, überdies aber einen isolierten Rand besitzt.

§ 3. Seien P_1, P_2, \dots, P_{n-1} die Punkte, in welche ein in Ω willkürlich gewählter Punkt P von t', t'', \dots, t'^{n-1} der Reihe nach übergeführt wird. Ein P und P_1 verbindender stetiger Kurvenbogen j_P bildet mit seinen von t', t'', \dots, t'^{n-1} bestimmten Bildern eine geschlossene stetige Kurve k_P . Die Menge R' der Ränder r'_α von Ω lässt sich in solcher Weise in eine endliche Zahl ≥ 3 von voneinander isolierten Teilmengen $R'_1(k_P), R'_2(k_P), \dots, R'_m(k_P)$ zerlegen, dass der Umlaufkoeffizient von k_P zwischen einem zu $R'_\nu(k_P)$ und einem zu $R'_\lambda(k_P)$ gehörigen Rand modulo n gleich einem durch ν und λ bestimmten, für $\nu = \lambda$ fortfallenden Wert $c_{\nu\lambda}(k_P) \geq 0$ und $< n$ ist. Diese $R'_\nu(k_P)$ behalten ihre Brauchbarkeit und die zugehörigen $c_{\nu\lambda}(k_P)$ ihre Gültigkeit bei, wenn für festes P der Bogen j_P diskontinuierlich geändert wird. Mittels gleichzeitiger stetiger Variierung von P und j_P sieht man weiter ein, dass auch durch Änderung des Punktes P die Rolle der $R'_\nu(k_P)$ und $c_{\nu\lambda}(k_P)$ nicht gestört wird. Indem wir aber P in hinreichender Nähe von R'_h und j_P in passender Weise wählen, können wir dafür sorgen, dass der Umlaufkoeffizient von k_P zwischen einem zu $R'_\nu(k_P)$ und einem zu $R'_\lambda(k_P)$ gehörigen Rand, für ν und λ beide von h verschieden, fortfällt und

hieraus folgern wir unmittelbar, dass $c_{\nu}(k_P) = 0$ für jedes ν , jedes λ , jedes P und jedes j_P .

§ 4. Wir bezeichnen einen willkürlich gewählten isolierten Rand von Ω mit ϱ , die Menge der übrigen Ränder von Ω mit R' , und betrachten die sich um R' aperiodisch herumwindende Ueberlagerungsfläche S von Ω . Diese Fläche S ist eineindeutiges und stetiges Bild der Cartesischen Ebene; ihr Rand R'' enthält einen aus ϱ hervorgegangenen Teil R_1'' und einen aus R' hervorgegangenen Teil R_2'' ; diese beiden Teile sind voneinander isoliert.

Sei P ein Punkt von Ω in der Umgebung von ϱ , P_1 sein von t' bestimmtes Bild. Wir verbinden P und P_1 in der Umgebung von ϱ durch einen solchen stetigen Kurvenbogen j_P , welche mit seinen von $t', t'^2, \dots, t'^{n-1}$ bestimmten Bildern eine geschlossene stetige Kurve k_P erzeugt, deren Umlaufkoeffizient zwischen zwei willkürlichen Rändern von Ω fortfällt. Die Möglichkeit, einen derartigen Kurvenbogen j_P herzustellen, folgt aus § 3. Sei P_m der Anfangspunkt, P_{1m} der Endpunkt eines Ueberlagerungsbildes von j_P auf S , so existiert eine durch die Ueberlagerung von S über Ω in t' übergehende, eineindeutige und stetige Transformation t'' von S in sich, welche P_m in P_{1m} überführt. Alsdann lässt die Transformation t''^n den Punkt P_m invariant, so dass t'' , ebenso wie t' , n -periodisch sein muss. Hiermit sind wir aber zu einem Widerspruch gelangt, weil eine periodische, eineindeutige und stetige Transformation der Cartesischen Ebene in sich ohne invariante Punkte nicht existieren kann.

§ 5. Im Falle, dass t die Indikatrix von O invariant lässt und von einer vollständigen kanonischen Zerschneidung von O jeden Rückkehrschnitt samt seinen beiden Seiten ungeachtet der Ränder äquivalent abbildet, besitzt t dieselbe Eigenschaft in bezug auf ω (was unmittelbar wie folgt eingesehen werden kann: Sei s ein Rückkehrschnitt von ω , der ω nicht zerlegt, so entspricht einer stetigen Variierung von s in O , wenn die Ränder von ω je in einen zu ω hinzuzufügenden Punkt zusammengezogen werden, eine stetige Variierung von s in ω). Wäre nun ω samt seiner Grenze nicht identisch mit O , so besäße ω einen durch eine zusammenhängende perfekte Menge von für t invarianten Punkten abgeschlossenen Rand und würde, auf Grund davon die in den §§ 3 und 4 hinsichtlich der Transformation t' von Ω angestellte, auf einen Widerspruch führende Ueberlegung auch im Falle, dass in ω kein Rückkehrschnittpaar (a, b) und nur zwei Ränder existieren, in Kraft bleiben. Mithin ist in diesem Falle ω samt seiner Grenze mit O identisch und O entweder eine Kugel, oder ein Zylinder, oder eine Cartesische Ebene, oder ein Torus.

Physiology. — “*The Significance of the Size of the Neurone and its Parts.*” By Prof. EUG. DUBOIS. (Communicated by Prof. H. ZWAARDEMAKER.)

(Communicated in the meeting of October 26, 1918).

The existence of definite relations of quantity of the neurone and its parts to the weight of the body is no longer open to doubt.¹⁾ For homoneuric species of mammals (species with the same organization of nervous system), whose body weights are to each other in the ratio of $P:1$, the volume of homologous neurones — as the volume (or the weight) of the brain — varies proportionally to $P^{0.56}$; the volume of their central part, the cell body proportionally to $P^{0.28}$. It may be assumed that the ideal values are $P^{0.55}$ and $P^{0.277}$.

These relations can best be verified by a study of the peripheral nerve fiber. As this constitutes by far the greater part of the neurone to which it belongs, also the volume of the homologous peripheral nerve fibers varies pretty accurately proportionally to $P^{0.56}$ for homoneuric species. And given that the length of the nerve fiber, for *perfectly uniform* homoneuric species, must vary proportionally to the longitudinal dimension of the animal, i.e. to $P^{0.33}$, the conclusion follows naturally that both, the area of the section and the length of the homologous peripheral nerves of homoneuric species, which in reality — for physiological reasons — cannot be *perfectly uniform*, varies *about* proportionally to the longitudinal dimension of the animal.

For perfect uniformity, the area of the section would have to increase proportionally to $P^{0.66}$ and the volume proportionally to P , when the nerve length increases proportionally to $P^{0.33}$. This now, is physiologically impossible, as may appear in what follows. The available numerical data, considered physiologically, really lead to the conclusion that *the length and the area of the section of a nerve increase uniformly*, i.e. both proportionally to $P^{0.28}$, hence in the same ratio as the cell-body becomes more voluminous. This holds both for the neurones with peripheral nerve fibers, which conduct the influxions centripetally, the sensitive nerve fibers, and for the neurones with peripheral nerve fibers, through which influxions are

¹⁾ These Proceedings. Vol. XX. (1918), p. 1328—1337.

transmitted from the center outward, the motor nerve fibers chiefly. Thus the volume of homologous neurones increases proportionally to $P^{0.56}$.

Also for the volume of homologous neurones in the brain (certainly to be compared, if not morphologically, yet as functional units with the peripheral neurones), the same proportionality may be assumed as for the neurones with peripheral nerve fibers, as appears from the equal relations of quantity holding for brain-weight.

Direct data concerning the relative areas of the sections of homologous nerve fibers, are, however, at our disposal only to a very limited degree as yet. Most of them refer to the eye, more particularly to nerve ends, where the retinal area marks the total area of the receptive terminations of a very important group of centripetally conducting nerves. Many of these data have been furnished to us by LAPICQUE, in collaboration with LAUGIER and WATERLOT ¹⁾ through measurements of the diameter of the eye in a number of Mammals, Birds, Reptiles, and Amphibians; from these we can derive the relative size of the retina in approximation. Though at first (1908) LAPICQUE, in virtue of these measurements, assumed that the diameters of the eye vary pretty nearly proportionally to the power $1/8$ of the body weight, he later on (1910) considered as more accurate proportionality the power $1/7$ of the body weight. According to the first estimation of LAPICQUE the retinal area would have to vary about proportionally to $P^{2/8}$ or $P^{0.25}$, on the other hand proportionally to $P^{2/7}$ or $P^{0.2857}$ according to his last estimation. The data as such allow, indeed, only estimation of the general result.

Some examples may suffice here, derived in the first place from the tables of LAPICQUE and his collaborators. For the exponent of relation in question, which I shall denote by r_o in the formula

$$\left(\frac{P}{p}\right)^{r_o} = \frac{O}{o},$$

and

$$r_o = \frac{\log O - \log o}{\log P - \log p},$$

where P and p denote the body weights, and O and o the retinal areas (more accurately here the areas of section of the eye-ball proportional to these in approximation) I find the following values.

In comparison of the area of section of the eye, computed from the diameter of the eye, of *Equus caballus* and *Antelope (dorcass?)* 0.2643, of *Canis lupus* and *Canis vulpes* 0.2668, of *Felis pardus* and

¹⁾ These Proceedings Vol. XX. (1918), p. 1337, Note 1).

Felis domestica 0.2390, of *Mustela putorius* and *Mustela erminea* 0.3004; as a mean of these three pair of Carnivores 0.2687.

Of the Reptiles examined by WATERLOT the gigantic Lizard *Varanus niloticus*, with a body weight of 7500 grams and a diameter of the eye of 5.8 mm., compared with the small Gecko *Hemidactylus Brooki* (3 indiv.), which weighs only 4.9 grams and has a diameter of the eye of 4.25 mm. on an average, gives the value 0.2942 for r_0 . Comparing the same Varan or Monitor with a Green Lizard, *Lacerta viridis* (examined by LAPICQUE) of a weight of 16.8 grams and a diameter of the eye of 5.8 mm., I find $r_0 = 0.2517$. The mean of these two values is 0.2730.

Among Amphibians I mention (again examined by LAPICQUE) *Rana fusca* with a body weight of 53.0 grams and a diameter of the eye of 6.6 mm., and *Hyla arborea*, with a body weight of 4.8 grams and a diameter of 4.6 mm. They give $r_0 = 0.3006$.

Two species of Fishes according to WELCKER¹⁾, *Cyprinus carpio* and *Gobio fluviatilis* (2 indiv.), of resp. 1817.3 grams and 42.2 grams body weight, and 1550 and 238 milligrams weight of the eye (from which here the sectional area is calculated) give $r_0 = 0.3290$.

Records of *retinal* areas of some adult species of aquatic mammals, accurately computed from direct measurements, of which some differ very much in the size of their bodies, may be found in PÜTTER's extensive treatise²⁾.

The most homoneuric species, *Phoca barbata* and *Phoca vitulina*, whose body lengths were in a ratio of 3 : 1.75 to each other, had retinal areas of 2543 and 1980 square millimeters. Assuming uniformity of these animals, we find, for a ratio of weight of only a little more than 5 : 1, $r_0 = 0.2972$.

Of two Toothed Whales, which are, indeed, not so closely akin, but with much greater difference of weight, *Hyperoodon rostratus* and *Phocaena communis*, the ratio of length was 6 : 1, and the areas of the retina 5000 and 1225 square millimeters. Assuming again uniformity, we find for the ratio of the body weights 216 : 1 and then $r_0 = 0.2617$. As however the body of *Hyperoodon* is somewhat slenderer than *Phocaena*, the real ratio of weight must have been somewhat smaller; the real value of r_0 was, therefore, somewhat higher.

¹⁾ H. WELCKER—A. BRANDT, Gewichtswerthe der Körperorgane bei dem Menschen und den Thieren. Archiv für Anthropologie, Bd. 28 (1902), p. 60.

²⁾ A. PÜTTER, Die Augen der Wassersäugetiere. Zoologische Jahrbücher, Abteilung für Anatomie und Ontogenie der Tiere. Jena 1903, p. 167, 174, 198, 209, 239, 243, 272, 280. The calculations of the areas of the retinae, not immediately comparable, were made by A. LERCH.

Comparing the gigantic *Balaenoptera physalus*, which is likewise somewhat slenderer than *Phocaena communis*, with the latter, of still more distant relationship, but which it exceeds 5323 times in weight calculated according to the length, we find $r_0 = 0.2610$ for a ratio of the retinal areas of 11500 : 1225 square-millimeters. This value, too, would certainly become somewhat larger, if the real weight could have been taken into account, instead of what has been found from the length.

The deviations of the found exponents of the value 0.277.. are not very important if it is considered that:

1. The compared species are not all perfectly homoneuric,
2. also the specimens are not always typical for their species,
3. the retinal area can only be calculated from the diameter of the eye (in one case the weight of the eye) in approximation,
4. in other cases the body weight was not directly determined.

In virtue of these and many other data, considered in the light of their physiological significance, I think I may assume that the area of the retina really varies on an average proportionally to $P^{0.28}$ or more accurately $P^{0.277}$ for homoneuric species of Vertebrates, and that the same proportionality is of general application for the area of the section of the homologous nerve fibers.

About these relations for individuals within a species hardly any direct data are available. LAPICQUE¹⁾ states that for *Canis familiaris* the diameter of the eye only varies from 20 to 23 mm., whereas the body weight varies from 5 to 40 kilograms, i.e. about as the fifteenth power root of this weight. For r_0 we find here 0.1344, which means the individual ocular exponent of relation has decreased in the same ratio (taking the degree of accuracy of these measurements into account), with respect to what is observed between different species, as the encephalic exponent of relation. That the found value lies nearer half 0.28 than half 0.22 may be remarked in passing.

Measurements of the thickness of homologous nerve fibers in individuals of different weight of one species, to form an opinion of the ratio considered here, are entirely wanting, but I think I may deem it probable that the area of the section of the peripheral nerve fibers remains the same, and that on the other hand the white nerve fibers of the brain vary both in length and in section proportionally to $P^{0.14}$ (or $P^{0.11}$?), which is in connection with the absence of the

¹⁾ L. LAPICQUE, La grandeur relative de l'oeil et l'appréciation du poids encéphalique. Comptes rendus des séances de l'Académie des Sciences. Paris 1908 (2). Tome 147, p. 210.

nodes of Ranvier at those nerve fibers in the brain, and with the fact that the number of nodes at the peripheral nerve fibers remains the same for large and small individuals of the same species, whereas between different species this number varies proportionally to the length of the peripheral nerve fiber.¹⁾

The meaning of the term $P^{0.28}$ must be looked for in the physiological function of the nerve fiber and the retina, namely the conduction of the impulsions or influxions. Likewise of the same relation between the body weight and the volume of the ganglion cell, which volume must undoubtedly be in relation with the quantity of the impulsions which it can receive and emit.

GÖTHLIN (in 1907) was the first to pronounce the idea that the rate of conduction of the nerve influxion in an axis cylinder seems to be in a definite relation to the diameter of the axis cylinder and to the thickness of the medullary sheath, when he tried to apply WILLIAM THOMSON's cable formulae to the white nerve fiber²⁾. Ten years later GÖTHLIN justly considers the data enabling us to judge about this relation, deplorably few³⁾. He reminds (in 1917) of the fact that according to the exceedingly important researches by CHAUVÉAU in 1878, the conduction in the motor nerve fibers of the larynx of the Horse is about 8 times more rapid than in the motor nerve fibers of the oesophagus of this animal⁴⁾, and he brings this difference in rate of conduction of the "influx nerveux" in connection with the very different thickness of the nerve fibers in question⁵⁾. In the very thin and at the same time non-medullated fibers of the splenic nerve of the Ox the rate of conduction, according

¹⁾ A. E. BOYCOT, On the Number of Nodes of Ranvier in Different Stages of the Growth of Nerve Fibres in the Frog. *Journal of Physiology*. Vol. 30 (1904). London, p. 370—380. At this place we find also a comparison of *Cavia porcellus* and *Mus musculus*.

²⁾ G. F. GÖTHLIN, *Experimentella Undersökningar af Ledningens Natur i den Hvita Nervsubstansen*. Uppsala 1907, p. 120 seq.

³⁾ Relation entre le fonctionnement et la structure des éléments nerveux. Upsala 1917, p. 15.

⁴⁾ A. CHAUVÉAU, Vitesse de propagation des excitations dans les nerfs moteurs des muscles rouges de faisceaux striés, soustraits à l'empire de la volonté. *Comptes rendus de l'Académie des Sciences*. Tome 87. Paris 1878, p. 238—242. There, p. 138—142, also: Vitesse de propagation des excitations dans les nerfs moteurs des muscles de la vie animale, chez les animaux mammifères.

⁵⁾ A. VAN GEHUCHTEN and M. MOLHANT, (Contribution à l'étude anatomique du nerf pneumogastrique chez l'Homme. *Le Névrase*, Vol. 13. Louvain 1912, p. 96) for the Rabbit.

to A. FISCHER¹⁾ is only $\frac{1}{11}$ of that in those slow oesophagus nerves of the Horse. GÖTHLIN adds to this (p. 16) that only by assuming the influxion to be conducted in the same way in the nerve fiber as electricity in a cable, it is to be understood why the velocity of conduction varies according to the dimensions of the fibers. With the thickening of the medullary sheath, which serves as "relative isolator", the capacity of the cable evidently diminishes, and with the enlargement of the area of section of the "conducting" axis cylinder, the resistance of the cable diminishes. In fact then they equally enhance the conductivity of the nerve fiber, and thus it becomes comprehensible that (as DONALDSON and HOKE and also others found) the mean area of section of the medullary sheath in all vertebrates remains equal to that of the axis cylinder, which it envelops. However, GÖTHLIN again justly points this out, the nerve fiber should by no means be imagined as an equally passive conductor as e.g. a telegraph wire. On the contrary, many circumstances render it necessary to assume that in all long nerve fibers which are rapid conductors, the influxion is regenerated in some way or other during its conduction, and thus compensates for the losses of energy during the propagation in an ever enlarged space²⁾.

CHAUVEAU evidently supposed a relation between the greater or smaller rate of conduction of the "excitations" in the nerves, and the voluntary or involuntary character of the movements they excite. It is pretty firmly established now that we have to think here of more tangible causes.

Our knowledge took an important step forward by CARLSON's researches (in 1904 and 1906)³⁾. He demonstrated that for Reptiles (Snakes), Amphibians (Frog), Fishes (the Californian Hagfish *Bdellostoma*), Cephalopods (Octopus, Loligo), Gastropods (Slug *Limax*, *Ariolimax*, Sea hare *Pleurobranchaea*) and Crustaceans (Spider Crab, Lobster, *Limulus*) there exists proportionality between the rate of propagation of the impulses in the motor nerve and the contraction

¹⁾ A. FISCHER, Ein Beitrag zur Kenntnis des Ablaufs der Erregungsvorgänge im marklosen Warmblüternerven. Giessen 1911. cf. Göthlin, p. 15.

²⁾ Cf: J. B. JOHNSTON, On the Significance of the Caliber of the Parts of the Neurone in Vertebrates. *Journal of Comparative Neurology and Psychology*. Vol. 18. Philadelphia 1908, p. 609—618.

³⁾ A. J. CARLSON, The Rate of the Nervous Impulse in the Spinal Cord and in the Vagus and the Hypoglossal Nerves of the Californian Hagfish (*Bdellostoma Dombeyi*). *American Journal of Physiology*. Vol. X. Boston 1904, p. 401—418.

—, Further evidence of the direct relation between the Rate of Conduction in a Motor Nerve and the Rapidity of Contraction in the Muscle. *Ibid.* Vol. XV. Boston 1906, p. 136—143.

time of the muscle. In every animal "the swifter the action of the muscle, the greater the rate of propagation of the impulse in the motor nerve supplying the muscle". All the nerves are, so to say, tuned to the muscle they supply.

This relation having been established, LAPICQUE and LEGENDRE¹⁾ examined which anatomic characteristic of the nerve fibers answers to those physiological properties. They found for the common Frog (*Rana esculenta*) that the thickness of the nerve fibers regularly increases with the rate of conduction of the influxion, to be measured by the rapidity of contraction in the muscle. It may be derived from the values communicated by them that the rapidity in question in the nerve fiber varies in geometrical ratio with the *area of the section* of the nerve fiber. They also found with regard to the Rabbit, that among others the nerve fibers for the rapid adductor magnus muscle are thicker than those for the semitendinosus, which is a slow muscle. These data make it highly probable that the principle holds good universally: "Les fibres nerveuses sont d'autant plus rapides qu'elles sont plus grosses."

LAPICQUE demonstrated further that the movements of different Amphibians are the quicker or the slower as the rate of propagation of influxions in the nerves of the hind-legs is greater or smaller.²⁾ For the slow Common Toad (*Bufo vulgaris*) the rate of conduction in the nerve for the musculus gastrocnemius is only about half so great as for the common Frog (*Rana esculenta*), which jumps quickly and far. The Frog-toad (*Pelobates fuscus*), far exceeds the Toads proper in the rapidity of its movements, and has, in agreement with this, equally rapid nerves in its hind-legs as the Frog. But also the Green Toad (*Bufo viridis*), which is more agile and quicker than the Common Toad, which makes comparatively big jumps, and swims and climbs well, is on a par with the Frog as far as the rate of conduction in the nerves is concerned. Though the Walking Toad (*Bufo calamita*) does not, indeed, jump like the Frog, it runs almost as fast as a mouse (hence its other name *cursor*), it swims nimbly and rapidly, climbs better than any other Toad

¹⁾ L. LAPICQUE et R. LEGENDRE, Relation entre le diamètre des fibres nerveuses et leur rapidité fonctionnelle. Comptes rendus de l'Académie des Sciences. Paris 1913 (2). Tome 157, p. 1163—1166. Also: La rapidité fonctionnelle des fibres nerveuses mesurée par la chronaxie et son substratum anatomique. Bulletin du Muséum d'histoire naturelle. Année 1914, N^o. 4, Paris 1914, p. 248—252.

²⁾ LOUIS LAPICQUE, Rapidité nerveuse des membres postérieurs chez divers Batraciens anoures. Bulletin du Muséum d'histoire naturelle, Année 1914, N^o. 6, p. 363—366.

and easily digs holes, (casting out the earth with its hind-legs); it has about the same rate of conduction in the nerve as the Frog. The same thing is the case with the Tree-Frog (*Hyla arborea*), which pounces upon winged insects as its prey.

Now, for a slow American Toad (*Bufo lentiginosus*), which has the same size as our Common Toad, the mean diameter of the fibers of the nervus ischiadicus is, according to DONALDSON and HOKE, 11.2 micra, as against 14.7 for a frog specimen of about the same weight, belonging to *Rana virescens*. In a common American Lizard (*Sceloporus undulatus*) of a body weight of 8.2 grams, the mean diameter of the nerve fibers in the plexus brachialis was 9.8 micra, on the other hand only 6.2 micra in the Horned Toad (*Phrynosoma cornutum*), which is at least six times heavier, and owes its name to the fact that it moves more like a toad than as the proverbially quick lizard, to the family of which it belongs. For an equally great rapidity as the said Lizard the nerve fiber of the so much heavier Horned Toad would have to double its diameter (to 12.7 micra). The American Turtle *Chrysemys marginata*, though probably weighing scarcely less than a kilogram, i.e. certainly as much as a hundred times more than the said small Lizard, has nerve fibers of a mean diameter of no more than 12.4 micra, in its plexus brachialis.¹⁾ It would have to amount to 18.7 micra for equal rapidity as that Lizard.

GÖTHLIN also points out that Shrimps of the genera *Crangon*, *Palaemon* and others, which are among the quickest animal species, possess thick nerve fibers provided with medullary sheaths.²⁾ L. and M. LAPICQUE found the greatest rapidity of nerves and muscles of all the Invertebrates which they examined, in the tail of *Palaemon*.³⁾

ALCOCK was the first to inquire into the possible influence of the *size of the body* on the rate of propagation of the influxion in nerves, by experiments on the nervus ischiadicus of the Frog, and, externally, in the nervus medianus of Man.⁴⁾ He finds for Man, as

¹⁾ Cf. these diameters of nerve fibers in H.H. DONALDSON and G. W. HOKE, On the Areas of the Axis Cylinder and Medullary Sheath as seen in Cross Sections of the Spinal Nerves in Vertebrates. *Journal of Comparative Neurology and Psychology*. Vol. 15, Philadelphia 1905, p. 9—11.

²⁾ G. F. GÖTHLIN, Die doppelbrechenden Eigenschaften des Nervengewebes. *Kungl. Svenska Vetenskapsakademiens Handlingar*, Ny Följd, Bd. 51 (1913), p. 84.

³⁾ LOUIS et MARCELLE LAPICQUE, Quelques chronaxies chez les Mollusques et Crustacés marins. *Comptes rendus de la Société de Biologie*. Année 1910. Vol. 2 (69). Paris 1910, p. 280.

⁴⁾ N. H. ALCOCK, On the Rapidity of the Nervous Impulse in Tall and Short Individuals. *Proceed. Roy. Society*, Vol. 72 (1903). London 1904, p. 414—418.

well as for the Frog, that in all the examined individuals, of one species and in the same nerve, the rate (per unity of length) is the same, hence independent of the size of the body. Small differences in the values of the rate, viz. of on an average 67.5 m. per second for two men of a mean height of 1887 mm. and on an average 65.9 m. for two men of a mean height of 1721 mm., are neglected, evidently considered as experimental errors. The mean body weights of these men may be put at 85 and 67 kg. according to HASSING's tables,¹⁾ and by means of this an exponent of relation for the velocity of impulsion of 0.1007 can be calculated, to which, however, in itself, not much significance should be ascribed.

Of greater importance, for the study of the influence of the size of the body on the rate of propagation of impulses in homologous nerves are MÜNNICH's experiments.²⁾ The rate (66 m. in the nervus medianus) found by him for Man is in good concordance with the mean rate according to ALCOCK and the latest determination by HELMHOLTZ and BAXT (64.56 m., in 1870), which speaks, indeed, for the reliability of the method. The greatest importance for our subject have, however, the determinations of the rapidity in the nervus ischiadicus of some mammals, viz. three dogs of different sizes and breeds, two cats, and a rabbit. MÜNNICH justly lays stress on the fact that the reliability of the results of his experiments on animals must be greater than those of experiments on Man, where the nerve cannot be laid bare. Besides, it is of importance for a judgment of the influence of the dimension of the nerve on the rate of conduction of the nerve influxions that among MÜNNICH's dogs a large and a small specimen was examined, the body weights of which inter se differed more than six times as much as those of the tall and the short individuals examined by ALCOCK. MÜNNICH found not inconsiderable deviations between a large and a small dog, with which the breed had nothing to do, and a particularly important deviation in a representative of the so remarkable breed of Dachshunds. Also the rapidities found for cats are of great importance. Though MÜNNICH himself, not realizing that the found numerical differences could have any meaning, leaves undecided whether they rest on different rates of conduction or are only caused by the defectiveness of the method, it has now been raised above doubt,

¹⁾ H. VIERORDT, Anatomische, physiologische und physische Daten und Tabellen. 3 Aufl. 1906, p. 589.

²⁾ FERDINAND MUNNICH, Ueber die Leitungsgeschwindigkeit im motorischen Nerven bei Warmblütern. Zeitschrift für Biologie. Bd. 66. München und Berlin 1916, p. 1—22.

that they have a real meaning. In this connection the much smaller deviation found by ALCOCK between tall and short men, does not even seem to be *entirely* devoid of interest, now that it appears to run parallel with that between the dogs of a much more considerable difference of weight, and these results are in accordance with what was forced on our attention about the significance of the dimensions of the nerves.

For a dog, "brauner Bastard von der Grösse eines Foxterriers," which must have weighed about 7 or 8 kg., MÜNNICH finds a rate of 61 m. per second, equal to that for the Rabbit, which can only have had about one fourth of this body weight. Hence the rapidity for the Rabbit is comparatively great, and we accordingly find for this burrowing Rodent thicker nerve fibers than for the Dog. As mean diameter in the plexus brachialis DONALDSON and HOKE found 13.3 micra for a Rabbit and 11.6 micra for a Shepherd's Dog (probably 8 times heavier). A definite ratio between the rapidity and the area of the section can, however, not be derived from this, because different nerves and different breeds of dogs are compared here.

For his largest cat MÜNNICH found a rate of 81 meters per second, for another specimen, of which he feels it necessary to state that it is adult, and for which he experimented on a shorter length of nerve, which specimen will therefore have been smaller, the rate was 75 meters. As even the largest cat can hardly have reached half the weight of a middle-sized Foxterrier, the rapidity is certainly relatively very large for the Cat. Undoubtedly the considerable thickness of the nerve fibers in the Cat is in connection with this, on an average in the plexus brachialis a diameter of 16 micra, as against 11.6 micra for a dog 5 times heavier according to DONALDSON and HOKE.¹⁾ Besides, the Cat is also distinguished by particularly large ganglion cells (a peculiarity of all the *Felis* species). The muscle fibers of the extremities, too, seem to be particularly thick. Already CAVAZZANI had found that the cells of the cervical and of the lumbar ganglia spinalia are particularly large, and equal to the corresponding cells of dogs which are 5 times heavier²⁾. Also LEVI found the cells of the fifth cervical ganglion spinale in the cat much larger than in an about equally heavy dog (diameter 81 as against 65.6 micra). They only reached an almost equal diameter (79.7 micra)³⁾ in a dog of 7 times the weight (of 23 kg.). According to

¹⁾ Loc. cit.

²⁾ E. CAVAZZANI, Sur les ganglions spinaux. Archives Italiennes de Biologie. Tome 28. Turin 1897, p. 52. Shepherd's Dogs, Pointers, and adult cat.

³⁾ G. LEVI, I gangli cerebrospinali Supplemento al Vol. VII dell' Archivio

LEVI the Cat has also larger ganglion cells in the columnae anteriores of the intumescencia lumbalis of the spinal cord than the Fox, and of all the Mammals examined by him, among which the Ox, the largest pyramid cells in the cerebral cortex ¹⁾. It has appeared, from particularly comparable measurements of HARDESTY, that the mean diameter of homologous cells of the intumescencia cervicalis in the Cat is not much smaller than in the Foxhound, which is 6 times heavier (53.5 micra as against 58.7 micra) ²⁾. The muscle fibers in the rectus femoris were thicker in the Cat than in any other Mammal that LEVI examined, with the exception only of the Horse; while the mean diameter in the Cat amounted to 55 micra, he found it only 36.2 micra in a dog of about twice the weight (of 6.3 kg.) ³⁾.

It appears, therefore, very clearly that the quick muscles of the Cat's leg receive rapid impulsions from large ganglion cells through thick nerve fibers.

Something similar holds for the mole-footed Dachshund. Still somewhat more rapidly than in the nervus ischiadicus of a 9 times heavier butcher's dog "von der Grösse einer Deutschen Dogge" did the impulsions propagate in this nerve of a dachshund (at a rate of 88 meters a second as against 85 meters for the butcher's dog).

From the rate of conduction (given by MÜNNICH) of the influxion of 61 meters a second in the nervus ischiadicus of the mongrel dog of the size of a foxterrier and 85 meters a second for the butcher's dog, likewise of a mixed breed, which had the size of a German Boarhound, and must therefore have had about 8 times the weight of the smaller dog of the same species, an interindividual exponent of relation for the rate at which the influxions are conducted in the nervus ischiadicus of 0.1595 can be calculated. This is in satisfactory agreement with the exponent 0.1344 derived above from a record by LAPICQUE for the area of section of the eye-ball within the species *Canis familiaris*, and the deviations from the value 0.28 are so great, as to justify for both cases the conclusion that here the same relation of the homoneuric species is not valid, but the other relation, the interindividual, which is expressed by an exponent of half the value of that of the species. It does, however, not follow from this that the *area of the section* of the nerve fiber varies in the same ratio as that of the retinal area, for as the

Italiano di Anatomia e di Embriologia. Firenze 1908, p. 177, and: Studi sulla grandezza delle cellule. I. Ibid. Vol. V. Firenze 1906, p. 332.

¹⁾ Ibid. (1906), p. 334 and 337. Cf. also: K. BRODMANN, Vergleichende Lokalisationslehre der Grosshirnrinde. Leipzig 1909, p. 81.

²⁾ Journal of Comp. Neurology. Philadelphia 1902. Vol. 12, N^o. 2. p. 160.

³⁾ Loc. cit., (1906), p. 327.

length of the nerve fiber varies, from one individual to another within a species, without change of the number of the nodes of RANVIER, where the resistance for the nerve influxion must be much larger than in the internodia, the resistance in the larger animal becomes slighter in inverse ratio to the length of the nerve fiber. I imagine that in this way the nerve fiber, from individual to individual within a species, does not actually become thicker, only longer. This is different for homoneuric species; there the number of internodia, hence also of the nodes, increases in direct ratio to the length of the nerve fiber, which does not bring about a change in the rapidity of the influxion (per unit of length); this is, therefore, directly dependent on the area of the section.

When the propagation of the influxions in the nerve fiber is compared with the motion of electricity in a circuit, in which the resistance (the reciprocal value of the conductivity) is in inverse ratio to the section, and in direct ratio to the length, much becomes clear in the relations of the size in the nervous system that would otherwise remain unaccountable. Then the ganglion cell may, in a certain sense, be compared with an electric condensator or storage battery, which is charged and discharged.

In the first place it becomes clear that only on comparison of homoneuric species the regular quantitative relations of the neurone and its parts to the body weight are found. For the exponent of relation for the volume of the largest ganglion cells of the columnae anteriores in the intumescentia cervicalis the value 0,2387 is found between Horse and Mouse, according to HARDESTY's records, the value 0.3931, on the other hand, between Cat and Mouse; the exponent is only 0.0851 between Horse and Cat. A Cat that had the weight of the Horse, would have a ganglion cell for the motor nerve fiber of the claw muscles 2.763 times as voluminous as the cell belonging to the longest motor nerve fiber of the Horse. HARDESTY points out (p. 166) that the American Hoary Bat (*Atalapha cinerea* Pal.), which is considerably smaller than the House Mouse, possesses somewhat larger cell bodies in the columnae anteriores of the intumescentia cervicalis than the latter, which he brings in connection with the innervation of the wings. OBERSTEINER also sees a connection between this great functional importance of the fore-legs as wings in the Bats and the fact that, while for most Mammals the cells of the intumescentia lumbalis are appreciably larger than those in the intumescentia cervicalis, the reverse is true for Bats.¹⁾

¹⁾ H. OBERSTEINER, Bemerkungen zur Bedeutung der wechselnden Grösse von Nervenzellen. (Del Volume Jubilare in onore L. BIANCHI. Catania 1913), p. 4.

From the much older records of KAISER it may be derived that the exponent of relation for the volume of the largest ganglion cells of the cervical medulla of the much larger Bat *Plecotus auritus* is only 0.1568 in comparison with the Mole¹⁾. This Bat has, accordingly, a much larger ganglion cell than the Mole, in ratio of equal body weight. OBERSTEINER points out that Man and the Orang-outang have strikingly small cells in their cervical medulla²⁾.

According to HARDESTY's measurements homologous cells of the cervical intumescencia of Man are actually somewhat smaller than in the Foxhound, which he exceeds four times in body weight³⁾, and not much larger than those of the Cat, which he exceeds more than twenty times in body weight. As well for *Macacus*, *Cynocephalus*, *Ateles* as for Man, the nerve fibers of the plexus brachialis are thin, in comparison with those of other Mammals, the size of the body being taken into consideration.

Evidently the slight quickness of the muscles, but comparative delicacy of the muscle fibers for the hand and the fingers, as necessary factor for their finely regulated collaboration, may be imputed to the slight thickness of the nerve fibers and the comparatively small volume of the ganglion cells, with which they are connected.

The dimensions of the peripheral "conductors" and of the central "accumulators", connected with them, can become of great importance for the quantity of the brain. Where they are to supply muscles which are both strong and quick, the nerve fibers become particularly thick, the cell-bodies large, and thus the neurones voluminous, to which also voluminous brain neurones must answer. Of the problems of the Elephant having a more voluminous brain than the Anthropoid Apes, to which it was thought that an extraordinary mental height had to be attributed for this reason, of the *Ateles* and *Cebus*, equally high above the Anthropoids with respect to their quantity of brain, of the aquatic Mammals, among which the *Mysticetes* possess comparatively larger brain than the Dogs, of the *Denticetes*, which like the Seals can almost be put on a line with the Anthro-

¹⁾ O. KAISER, Die Funktionen der Ganglienzellen des Halsmarkes. Haag 1891, p. 63.

²⁾ L. c. p. 4. The same property may be assumed for the Gorilla, whose spinal cord was examined by W. WALDEYER (Das Gorilla-Rückenmark. Abhandlungen der Kön. Preus. Akademie der Wissenschaften Berlin. Jahr 1888. Physikalisch-mathematische Classe. Abt. III, S. 1—147). Cf. HARDESTY, l.c., p. 168.

³⁾ CAVAZZANI (l. c., p. 52 and 53) had already found that the ganglion cells in Man are smaller than in Shepherd's Dogs and Pointers, smaller even than in the Cat.

poids, in this respect¹), — facts that have led to speculations about uncommonly great intelligence of the Whales — of the comparatively highly cephalised Crocodiles, and of the class of the Fishes, which in general are not inferior to the Reptiles, as far as the quantity of brain is concerned, of all these problems the solution is now obvious²). The proboscis of the Elephant, which plays a prominent part in the animal's life, is not only strong and agile, but also provided with very voluminous muscles. That of the Asiatic Elephant measures 2 meters for a length of the body of $3\frac{1}{2}$ meters. Quick strong muscles move the long tail of the American Apes mentioned, which muscles are of still greater service to these animals than those of their hands and feet. But also their arms and legs are very long in comparison with the body, especially for Ateles, which owes its popular name of Spider-Monkey to this, and they consequently contain a large mass of muscles. The Whales have an exceedingly quick and strong motor apparatus in their long body for the tail, which admirably like a ship's screw propels the gigantic

¹) Judging from not yet full-grown animals, some investigators have assumed somewhat too great cephalisation. Thus the Seal is not full grown with $12\frac{1}{2}$ kg. body weight (LOUIS LAPICQUE, Sur le poids encéphalique des Mammifères amphibies. Bulletin du Muséum d'histoire naturelle. 1912, N^o. 1 p. 2). An adult female, examined many years ago by E. H. WEBER (Ueber den Bau des Seehunds, Phoca vitulina. Verhandlungen der Kön. Sächsischen Gesellschaft der Wissenschaften zu Leipzig. Math.-Phys. Classe. Jahrgang 1850, p. 108), however somewhat emaciated in captivity, weighed as much as 4311 kg. The animal possessed 266.5 grams of brain, from which a coefficient of cephalisation $k = 0.6766$ can be calculated. Of a female Otaria californiana, which had lived in the Amsterdam Zoological Gardens since 1902, and was already fully adult at the time, the body weight was 74 kg., the weight of the brain 374.5 grams, at its death in Nov. 1913, from which $k = 0.7025$ may be calculated. The weight of the body of this animal, too, must, indeed, have been somewhat higher in its healthy state. Accordingly the calculated coefficients of cephalisation are decidedly somewhat higher than normal for both Pinnipeds.

As regards the Whales, we may refer to the weight of a Balaenoptera sulfurea, 22.5 meters long, viz. 63 Am. tons, i. e. 64000 kg. (according to determinations by LUCAS inaccessible to me), which is mentioned in Vol. 12, p. 503 of the fourth edition (1915) of BREHM's Tierleben. The brain, freshly removed, of a Balaenoptera musculus, 18.8 m. (= 60 Norwegian feet) long, weighed 6700 grams, according to G. A. GULDBERG (Forhandlingar i Videnskabs Selskabet i Christiania. Aar 1885. Christiania 1886, p. 128). Assuming uniformity with the other Balaenoptera species, a body weight of 37385 kg. is found for the latter, and in connection with this a cephalisation coefficient of 0.3841.

²) The significance of the influence of the organs of hearing, touch and other organs of sense on the quantity of the brain of these Vertebrates is, however, not slight either.

mass with great velocity, and skilfully steers it. The flipper-like hind-limbs of the Seals (*Phoca*), which form a kind of tail, move the body along through pretty intricate but nimble movements; in other cases (*Otaria*) very large pectoral fins render such services to the animal, the feet, directed backwards here too, acting more like a helm, worked by powerful muscles. For the Fishes it is again the tail which derives its propelling force from the muscles of the hind part of the body. The Crocodiles have a strong propelling tail. For all these vertebrate aquatic mammals the locomotor muscles must not only be quick, but also particularly voluminous and strong, because of the great density of the medium, in which the movements take place; hence they must consist of thick, but also of numerous muscle fibers. Hence very voluminous and at the same time very numerous neurones. In fact LEGENDRE demonstrated that the nerve fibers of the medulla and the roots of the Dolphin (*Delphinus delphis* L) are among others much thicker than in Man, the Stag, the Dog, the Rabbit, and the Mouse. He partly accounts for the high cephalisation of this aquatic Mammal by the thickness of its nerve fibers ¹⁾.

Though I do not enter more fully into the discussion of the mutual relation of the dimensions of muscle- and nerve fibers here, I will, however, point out that between homoneuric species the variations of the dimensions of the neurones and their parts, in function of the body weight, *entirely* account for the variations of the weight of the brain, in function of the body weight; hence that the *number* of the neurones (differently from what I thought possible at first) remains the same. This must also apply to the sarco-neurones, hence to the muscle fibers.

That the cell-body of the neurone must become more voluminous, for homoneuric species, in ratio to the arithmetical longitudinal dimension of the body, is a consequence of the already long known dynamic proportion that the weight (the mass) of similar animals augments according to the *cube* of the homologous longitudinal dimensions, the muscular force, on the other hand, proportional to the area of the section of homologous muscles or the *square* of the homologous longitudinal dimensions. Already ninety years ago STRAUS-DÜCKHEIM ²⁾ set forth clearly that thus, for similar animals, consequently having the same organization, but of different sizes, the time of every movement must be nearly proportionate to the longitudinal dimen-

¹⁾ R. LEGENDRE, Notes sur le système nerveux central d'un Dauphin (*Delphinus delphis*). Bulletin du Muséum d'histoire naturelle, 1912, N^o. 1, p. 6—7. Pl. I.

²⁾ H. STRAUS DÜCKHEIM, Considérations générales sur l'anatomie comparée des animaux articulés Paris 1828, p. 189 et seq.

sions, although the rate of the locomotion is equal. For this, increase of the accumulated influxion in the cell-body of the neurone is required, and hence of its volume, in the ratio of about $\sqrt[3]{P}$ or $P^{0.33}$. In about the same ratio the lengths of the nerve fibers of homoneuric animal species necessarily increase, these lengths being nearly proportionate to the longitudinal dimensions of the animals. At the same time, it may be assumed, as a matter of course, that there is a tendency for the homologous nerve fiber to increase with the least possible deformation. Without any deformation its area of section should increase in the ratio of $P^{0.22}$, while its length increases in the ratio of $P^{0.33}$.

On the other hand, the mode of propagation of nervous influxions being similar in homoneuric species of animals, the only possibility to obtain this similarity, i.e. physiological homoneury, under the given conditions, is that *the area of section of the nerve fiber should increase proportionally with its length*. Therefore the area of the section of the fiber has become somewhat greater and its length less than for uniformity of the homologous nerve fibers, both in the ratio of $P^{0.055}$. Hence the ratio $P^{0.277} : 1$, as was discussed in the outset.

$$P^{0.277} = P^{0.333} : P^{0.055} = P^{0.222} \times P^{0.055} = P^{0.277}.$$

Thus the accumulated influxion, the time and the rate of propagation increase, as they ought to do, in the same ratio.

Through this way of viewing the matter, which starts from the relations of quantity existing in the nervous system, many imponderabilia, such as the mental height, the intelligence, and not seldom also the degree of brain evolution may be eliminated from the foreground of our considerations of the relation between structure and functions of the nervous system, which can only promote the fruitfulness of researches in this region, among others and particularly with regard to the cortex of the brain.

A striking proof for this is furnished by OTTO MAYER's researches on the density in which the cells occur in the cortex of the brain of Apes¹⁾. He namely determined, for seven genera, the mean number of cells per 0.01 cubic millimeter, in 10 fields (according to BRODMANN), throughout the whole thickness of the cortex. His results induced him to point out emphatically that the densities by no means run parallel with the order of the examined animals in the zoological system, their degree of brain organization or their intel-

¹⁾ OTTO MAYER, Mikrometrische Untersuchungen über die Zelldichtigkeit der Grosshirnrinde bei den Affen. Journal für Psychologie und Neurologie. Band 19. Leipzig 1912, p. 233—251. 2 Tafeln.

ligence. A result which strongly reminds of the absence of systematical order in the "relative brain weights".

I have, therefore, treated the densities in a similar way as the brain weights, namely by considering them in connection with the weights of the body. For this purpose calculating the mean densities of the whole cortex (over those ten important fields), from MAYER's records, I find a mean density of cell of 1765,4 for the Chimpanzee (*Anthropopithecus troglodytes*), of 3160 for the Gibbon (*Hylobates syndactylus*), of 3580.9 for the Capuchin-Monkey (*Cebus capucinus*), of 3603.4 for the Saimiri or Squirrel-Monkey (*Chrysothrix sciurea*), and of 3448.1 for the Marmoset (*Hapale jacchus*), which mean values no more show systematic order than the densities in the separate fields, from which they are computed.

This disorder is replaced by regularity, as soon as the size of the animals is taken into account.

The ratio of the density of cells between the Chimpanzee and the Siamang is as 1:1.79. The Chimpanzee has 8 times the weight of this Gibbon-species, and now it is very remarkable that, between these homoneuric species, according to the proportionality demonstrated in my former paper, homologous cells must be more voluminous to a ratio of $8^{0.28} = 1.79$ for the Chimpanzee than for this Gibbon. Between these homoneuric species the density of cells is, therefore, accurately in inverse ratio with the volume of every cell. In other words: for a Gibbon that had the size of a Chimpanzee, the density of cells in the cortex of the cerebrum would be equal to that of the Chimpanzee. It may, therefore, be assumed that these Anthropoids of equal cephalisation (equal quantity of the brain in function of the body weight) are also equal in the organisation of their cortex of the brain. The cells of these two species must be uniform, both as far as the dendrites and the other interstitium is concerned, and with regard to the cell-body.

When *Cebus* is compared with *Hapale*, which he exceeds 6 times in body weight (these weights are on an average 1300 and 215 grams; the brain weight of *Cebus* is 125, that of *Hapale* is about 8 grams), the cortical density of cells for *Cebus* is found 1.7 times greater than for a *Hapale* of equal body weight. In about the same ratio, viz. 1.8:1 the cephalisation is, however, also greater for *Cebus* than for *Hapale*, a very fair agreement when it is borne in mind that different specimens were compared. Compared with *Chrysothrix* (*Saimiri*), (whose body weight amounts to about 400 grams, and which possesses 24 grams of brain) *Cebus* has 1.5 times higher cephalisation, and a *Saimiri* of equal body weight as *Cebus* would

have almost 1.4 times greater density of cells. For these allied American Monkeys the density of cells, in function of the body weight, is, therefore, proportionate to the cephalisation: the greater the quantity of brain, in function of the body weight, the greater the density of cells.

A Cebus, however, of the same body weight as *Hylobates syndactylus*, would have only two thirds of the density of cells of this long-armed ape, though the latter has three fifths of the weight of the brain of the large Cebus-species in question. Here the density of cells is about in inverse ratio to the cephalisation.

Of special interest is the comparison of the density of the cells of the Chimpanzee with that of Man, both having about the same body weight. HAMMARBERG ¹⁾ determined the density of cells, in normal human brains, through the whole thickness of the cortex, per 0.001 cubic millimeter, i. e. $\frac{1}{10}$ of MAYER's unit of volume, in different cortical areas, some of which may be compared with the areas according to BRODMANN. Thus in the lobus occipitalis the area striata or field 17 of BRODMANN. Calculated to the same unit of volume as that of MAYER we find here 386 cells, whereas MAYER's chimpanzee has 2888, i. e. 7.5 times as many. Thus 152 in the area gigantopyramidalis or BRODMANN's field 4, as against a density for that chimpanzee of 1172, i. e. 7.7 times as many. In the area frontalis agranularis or field 6 the density for Man is only 111, as against 1136 or 10.2 times as much for the chimpanzee examined by MAYER ²⁾.

As, according to BRODMANN's ³⁾ measurements, the entire surface of the cortex in the Chimpanzee is about a third of that in Man, the regio

¹⁾ C. HAMMARBERG, Studien über Klinik und Pathologie der Idiotie, nebst Untersuchungen über die normale Anatomie der Hirnrinde. Upsala 1895.

²⁾ In the part of the gyrus frontalis superior, which belongs to the area frontalis agranularis or BRODMANN's sixth field I have *estimated* the density of cells in the deepest half of the third layer, and likewise in the deepest half of the fourth layer of the part of the lobus occipitalis, which corresponds to the area striata or BRODMANN's seventeenth field, from drawings (Table I, Fig. 2 and Table II, Fig. 4), namely according to the ratio of the other densities drawn and also calculated by HAMMARBERG. Thus was also evaluated the density of cells of the insignificant first layer in the part of the gyrus centralis anterior, which belongs to the area gigantopyramidalis or BRODMANN's fourth field.

HAMMARBERG calculated the number of cells per unity of volume from 10 successive sections, each of a thickness of 0.01 mm., or 5 sections of a thickness of 0.02 mm., MAYER on the other hand from only a single section of a thickness of 0.01 mm. As also parts of cells are counted, the number must be slightly greater according to the latter method. Judging by HAMMARBERG's drawings the difference can, however, not be considerable.

³⁾ K. BRODMANN, Neue Forschungsergebnisse der Grosshirnrinden-anatomie, mit

praecentralis (the fourth and the sixth field) of the Chimpanzee, about two thirds of that in Man, the area striata about equal to that of Man, it must be assumed, according to these determinations, that the absolute number of the nerve cells in the cerebral cortex of Man is much smaller than in the Chimpanzee; greatest is the value of the ratio in the area striata (7, against 6 in the regio praecentralis). The human brain being, however, certainly more complicated functionally, (which is generally called highly developed), it would appear that not the number of neurones, but the multiplication of the contiguities of their dendritic processes, which principally constitute the interstitium, corresponds to more complicated (higher) functions.

besonderer Berücksichtigung anthropologischer Fragen. Gesellsch. Deutscher Naturforscher und Aerzte. Verhandlungen 1913. Leipzig 1913, p 9, 22 and 25.

The brain weight of the examined chimpanzee amounted only to 295 grams; the average in full-grown state may be estimated at about 400 grams. The ratio of the surface of the cortex to that of Man may, therefore, become somewhat more favourable. With greater brain weight the density of cells in the cortex of the chimpanzee would have become proportionally less, hence the number of cells would have remained the same. The cortex of Man is, indeed, somewhat thicker, in consequence of which the actual values of the ratio must be proportionately smaller than those calculated.

Astronomy. — "*Expansion of a cosmic-gassphere, the new stars and the Cepheids*". By Dr. A. PANNEKOEK. (Communicated by Prof. W. DE SITTER).

(Communicated in the meeting of October 1918).

I.

The new stars which are most fully known in their changes of intensity are of two distinct types. The sudden quick flaming up is common to both; but they differ in their further changes of light. To the one class belong the two brightest Novae of this century, Nova Persei 1901 and Nova Aquilae 1918, as well as Nova Coronae 1866. Immediately after attaining the greatest brilliance the light begins to decrease quickly; then the diminution becomes slower, while a periodicity sets in. In the other class, of which Nova Aurigae 1892 is the best known example — and to which Tycho's star Nova Cassiopeiae 1572 belongs — the star retains its brilliance for a long time, fluctuates irregularly, and finally loses its brilliance rather rapidly. These two types of change of light show a certain correspondence with the two types of light-maximum, long and short, which are observed, alternately in the same star, in the Antalgol stars such as SS Cygni. Whether this analogy is more than an accidental correspondence, or that a real relationship exists, cannot yet be ascertained.

In connection with the appearance of Nova Aurigae SEELIGER has given an explanation which fits the phenomena of this type very well; when a star enters a nebulous mass, thereby being brought to a high temperature, as long as it flies through denser and thinner parts, its temperature will fluctuate up and down. This theory fits the other type less well. Here there is obviously an enormous rise of temperature, caused by a momentary event, of which all the further processes are merely the consequences.

The cause from which this sudden heating arises need not be discussed here. We only put the question of what may be deduced concerning the further events, from simple hypotheses. A cosmic body, suddenly brought to such a high temperature, will not be in equilibrium. It will expand adiabatically, and as a consequence it

will cool down. Usually the loss of heat by radiation is given as the principal cause of the cooling of a star; but the cooling from adiabatic expansion is of much more importance. In a first approximation, therefore, radiation may be neglected. The force of gravity is also left out of account, which to some extent diminishes the force of expansion; this may be done the more legitimately as it is to a greater or less extent compensated by the radiation-pressure. We assume that all changes take place homocentrically.

A volume-element at a distance r_0 from the centre is found by expansion after a time t at a distance $r = r_0 + \Delta$. We must then have the relation

$$\frac{d^2 \Delta}{dt^2} = -\frac{1}{\varrho} \frac{dp}{dr}.$$

A volume-element $r_0^2 dr_0 dw$ shifts to the distance r and becomes $r^2 dr dw$. By this the density changes according to:

$$\frac{\varrho}{\varrho_0} = \frac{r_0^3}{r^3} \frac{dr}{dr_0}.$$

As the change takes place adiabatically, $p\varrho^{-1/7}$ remains constant, or $\varrho = \text{Const.} \times p^{5/7}$, therefore:

$$\frac{d^2 \Delta}{dt^2} = -\frac{p_0^{5/7}}{\varrho_0} p^{-5/7} \frac{dp}{dr} = -\frac{7}{2} \left(\frac{p_0^{5/7}}{\varrho_0} \right) \frac{dp^{2/7}}{dr}.$$

The index 0 specifies the conditions at the time 0, which thus remain a function of r . We shall indicate by the index 00 the condition for $t=0$ and $r=0$, at the centre therefore; putting

$$\left(\frac{p}{p_0} \right)^{2/7} = y, \quad \frac{p_{00}}{\varrho_{00}} = \alpha, \quad \frac{p_0}{p_{00}} \frac{\varrho_{00}}{\varrho_0} = \beta;$$

we find

$$\frac{d^2 \Delta}{dt^2} = -\frac{7}{2} \frac{p_0}{\varrho_0} \frac{dy}{dr}.$$

Then α is a constant for this gas ball, of the dimension $L^2 T^{-2}$: it is according to $p = \varrho HT$ ($H = \text{gas-constant}$) proportional to the temperature at the centre, and has the physical meaning of the square of the speed of propagation of isothermic disturbances of equilibrium at the centre. β is a number without dimensions, which at the centre is $=1$, a function of r , which gives the course of α from the centre outwards in the initial condition. The equation of motion now becomes:

$$\frac{d^2 \Delta}{dt^2} = -\frac{7}{2} \alpha \beta \frac{dy}{dr} \quad (1)$$

where y is determined by

$$y = \left(\frac{p}{p_0}\right)^{2/7} = \left(\frac{\rho}{\rho_0}\right)^{2/5} = \left(\frac{r_0^2}{r^2} \frac{dr}{dr_0}\right)^{2/5}.$$

or

$$y = \left\{ \left(\frac{r}{r_0}\right)^2 \frac{dr}{dr_0} \right\}^{-2/5} \quad (2)$$

y gives the change of the temperature.

By the formulae (1) and (2) the change of Δ with the time is determined, when the quantity β , which determines the original condition, is known as a function of r . We may, for instance, assume a density distribution such as EMDEN has calculated for a gaseous sphere in equilibrium, but supposing a much higher temperature at each point than belongs to an equilibrium form of this kind. The original conditions must be such that Δ continually increases, owing to the strong force of expansion which is working all the time towards the outside in consequence of the high temperature. This will cause the temperature of each layer to fall in a ratio which is given by the quantity y , and in consequence the luminosity will decrease. The most external coldest layers, which absorb the light of the central parts, will move towards us with great rapidity; *this explains why in all new stars, as soon as the light begins to decrease, the dark absorption-lines are displaced strongly towards the violet* — a phenomenon which it has been attempted in vain to explain by a rapid approach of the whole star, or by differences of pressure.

Even when the initial conditions are simple, the equations (1) and (2) are difficult to integrate. An attempt to find the course of the change by mechanical quadrature failed through the fact that small variations in y come out greatly increased in $\frac{dy}{dr}$, and therefore also in the Δ that is found and the subsequent values for y , so that each step gives an increasing inaccuracy, which, after integration through a few units of time, makes the results quite unreliable. On this account we have not succeeded in explaining the periodic variation in brightness — which both in Nova Persei and Nova Aquilae began to appear after the star had decreased 4 classes of magnitude — by special initial conditions.

On the other hand the general mean course of the process may be calculated. The question may be asked: is it possible for the

or

$$= 2x^{-5/6} (1-x)^{1/2} \left\{ 1 - \frac{2}{9} (1-x) - \frac{2.4}{9.15} (1-x)^2 - \frac{2.4.10}{9.15.21} (1-x)^3 - \dots \right\} + \text{const.}$$

whence

$$At = \sqrt{\frac{3}{5}} f \sqrt{1-f^{-6/5}} \left\{ 1 - \frac{2}{1} x - \frac{2.4}{1.7} x^2 - \frac{2.4.10}{1.7.13} x^3 - \dots \right\} + 1.881$$

or

$$= \sqrt{\frac{5}{3}} f \sqrt{1-f^{-6/5}} \left\{ 1 - \frac{2}{9} (1-x) - \frac{2.4}{9.15} (1-x)^2 - \frac{2.4.10}{9.15.21} (1-x)^3 - \dots \right\} \quad (5)$$

The former series may be used when x is small, or f very large, the latter holds for small f , x being near unity. The additive constant in the second series must be equal to 0, since for $t=0$ x and f are both equal to 1. For the first series the constant cannot be determined by this condition: it was found by computing the value of At for one and the same value of x from both series.

By means of these series the time-function At was calculated for a number of values of the expansion-factor f . The temperature is connected with f by the relation

$$T = T_0 f^{-6/5}$$

Since the temperature changes according to this law throughout the entire star, we are entitled to assume that the same law holds for the effective temperature; the radiation per unit area then changes proportionally to T^4 , i. e. to $f^{-24/5}$. The surface itself changes as f^2 , and thus the luminosity as $f^{-14/5}$, hence

$$\log L - \log L_0 = -14/5 \log f.$$

or expressed in terms of classes of magnitude

$$m - m_0 = 7 \log f. \quad (6)$$

The following table contains for a number of values of f the corresponding At and $m - m_0$.

f	At	$m - m_0$
1.0	0.0	0.0
1.1	0.455	0.290.
1.2	0.655	0.554
1.3	0.815	0.798
1.4	0.956	1.023
1.5	1.086	1.233
1.6	1.207	1.429
1.7	1.322	1.613
1.8	1.433	1.787
1.9	1.541	1.951
2.0	1.645	2.107

f	At	$m - m_0$
2.5	2.137	2.786
	2.135	
3.	2.599	3.340
4.	3.479	4.214
5.	4.327	4.893
10	8.397	7.000
20	16.307	9.107 ¹⁾

The intensity thus diminishes slowly at first and then faster and faster, but the velocity soon reaches a maximum, when the star has fallen rather more than 1 magnitude below the original intensity. The velocity of decrease then becomes slower once more and finally approaches a logarithmic curve.

The slow decrease in the beginning is not observed in the new stars, as the process of blazing up has not yet worked out then. Both Nova Persei and Nova Aquilae had their maximum one day after they had reached the first magnitude, and Nova Persei one day before that had already attained the 3rd magnitude. As the starting-point $t = 0$ we must not therefore take the moment of maximum luminosity, but one or two days earlier. Then follows a rapid decrease which, however, soon becomes slower and is then accompanied by periodical variations. On comparing the observed light-curve and the one here calculated they are found not to agree during the further course of the change; the mean observed intensity decreases much more slowly than according to the above calculation. Evidently other influences are at work here, lying outside the simple theory here given. It is therefore only for the first period of rapid decrease of luminosity that agreement may be looked for.

For Nova Persei we shall take 0,0 as the ideal maximum intensity, a little higher than the greatest brightness observed, because for it the final stage of the blazing up overlaps the beginning of the expansion, and for the ideal starting-point the 21st of February. The following values of At are then found from the values of $m - m_0$ on the smoothed observational light-curve.

Date	m obs.	At	t	quotient	A
Febr. 25	1.00	0.97	4 ^d	0.24	2,8.10 ⁻⁶
„ 27	1.62	1.35	6	0.22	2,6 „
Mrch. 1	2.07	1.62	8	0.20	2,3 „

¹⁾ From 1.0 to 2.5 equation 5b has been used, from 2.5 to 20 equation 5a.

Date	<i>m</i> obs.	<i>A</i> <i>t</i>	<i>t</i>	quotient	<i>A</i>
Mrch 3	2.42	1.85	10	0.18	2,2.10 ⁻⁶
„ 5	2.73	2.07	12	0.17	2,0 „
„ 7	3.02	2.30	14	0.16	1,9 „
„ 9	3.27	2.53	16	0.16	1,8 „
„ 11	3.48	2.71	18	0.15	1,7 „
„ 13	3.65	2.88	20	0.14	1,7 „

The diminution of the quotient shows that those influences which later on retard the decrease to a higher degree than the theory requires, begin to manifest themselves even in the first stage. However that may be, the order of magnitude of *A* as found here cannot but be correct, and from it conclusions may be drawn as to the constitution of the Novae.

When all quantities are expressed in the absolute system, *t* is measured in seconds; taking 0.21 as a mean value of the quotient in the above table we have

$$A = 0,21 : 86400 = 2,5 \cdot 10^{-6}.$$

For Nova Aquilae about the same value is found.

II.

The distribution of pressure and temperature for $t = 0$, which is required for a uniform expansion, and the dependence of *A* on this distribution are determined by equation (3) in which we shall now leave out the indices 0:

$$-\frac{1}{rQ} \frac{dp}{dr} = A^2$$

or

$$\frac{dp}{dr} = -A^2 rQ$$

or

$$p = + A^2 \int_R^r Qr dr.$$

where *R* is the radius of the external surface, where $p = 0$. If a definite density-distribution is assumed as existing at the moment of flaring up, the latter equation determines the pressure as a function of *r*, and therefore also the temperature:

$$T = \frac{A^2}{H_0} \int_R^r Qr dr. \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

For the density the values have been assumed which EMDEN

has calculated for the equilibrium-forms of spherical cosmic gaseous masses (for $n = 2\frac{1}{2}$, $k = 1.4$); the integration has been performed by mechanical quadrature. The integration-intervals were taken four times smaller than the unit of r_1 as used by EMDEN; expressed in our unit the radius of the external surface is 21.67. The result of the integration was as follows:

r	$\log \varrho$	$21.67^2 \int_R^r \frac{\varrho}{\varrho_0} \frac{r dr}{R^2}$	$I = \frac{21.67^2 \varrho_0}{\varrho} \int_R^r \frac{\varrho}{\varrho_0} \frac{r dr}{R^2}$
0	0.00000	22,5274	22.53
2	9.95523	20,6746	22.92
4	9.82604	16.0941	24.02
6	9.62544	10.8138	25.62
8	9.36944	6.3898	27.30
10	9.06954	3.3527	28.56
12	8.72945	1.5525	28.94
14	8.34375	0.6148	26.61
16	7.88832	0.1922	24.84
18	7.29284	0.03928	20.04
20	6.32566	0.00315	15.12

The integral I is proportional to the temperature. The result therefore shows, that *the uniform expansion requires a distribution of temperature which differs very little from an even temperature throughout the mass*. If the original process is not a rise of temperature at the surface by friction in a nebulous mass, but if through some catastrophe the entire mass becomes hot throughout, an approximately equal temperature through the whole mass might be expected and in that case, as was here shown, an approximately uniform expansion would take place.

Now for

$$I = \frac{21.67^2 \varrho_0}{\varrho} \int_R^r \frac{\varrho}{\varrho_0} \frac{r dr}{R^2} \quad . \quad . \quad . \quad . \quad . \quad (8)$$

we have

$$T = \frac{IR^3 A^2}{21,67^2 H} = \frac{IR^3 A^2 \mu}{21,67^2 \cdot 8,3 \cdot 10^7}$$

if μ is the molecular weight of the gas of which the star consists. Substituting the value of A found above, the mean temperature (taking $I = 25$) becomes:

$$T = \frac{25 \times 6.25 \cdot 10^{-12}}{21,67^2 \times 8,3 \cdot 10^7} R^3 \mu = 4 \cdot 10^{-21} R^3 \mu \quad . \quad . \quad . \quad . \quad (9)$$

With $T = 10^4$ degrees this gives:

$$R^2\mu = 2,5 \cdot 10^{11} \text{ hence for } \mu = 1 \text{ (dissoc. } H) \quad \mu = 50 \text{ (metals)}$$

$$R = 1,6 \times 10^{12} \quad 2,3 \times 10^{11}$$

$$= 23 \text{ times the sun} \quad 3,5 \text{ times the sun}$$

and with $T = 10^5$ degrees

$$R^2\mu = 2,5 \cdot 10^{25} \text{ hence } R = 5 \times 10^{12} \quad 7 \times 10^{11}$$

$$= 71 \text{ times the sun} \quad 10 \text{ times the sun}$$

Considering that at this high degree of heat the mass will be highly dissociated, the first values are probably nearer the truth than those corresponding to $\mu = 50$. It shows that *a Nova at the moment of greatest brightness is a body much more gigantic than the sun, not only in luminosity but also in radius and volume*. The theory, that a new star arises when a dark body of the size of our sun, i.e. an ordinary cooled-down dwarf star, suddenly rises to a colossal temperature, is in contradiction with the above calculations; for $R = 7 \times 10^{10}$, the radius of our sun, with $\mu = 50$ and A as observed, the temperature would only rise to 1000° ; for $T = 10^5$ A would be 10 times larger, that is: the time in which the star loses its light would be 10 times smaller.

This result is in accordance with the value of $0''.011$ for the parallax of Nova Persei, derived by KAPTEYN from the supposition that the nebulous rings which were photographed half a year later arose from reflected star-light. This leads to a luminosity 10000 times that of the sun; since the intensity of the surface-radiation was not much different from what it is in an ordinary white star — HERTZSPRUNG found a similar distribution of light in the spectrum of Nova Aquilae as in α Aquilae¹⁾ — the radius of the Nova must have been 30 to 50 times the radius of the sun.

Supposing our interpretation of the dark lines which always accompany the bright lines on the violet side being correct, this also leads us to a high value of R . The velocity with which the outermost particles move towards us is R^{df}/dt . At the moment when the light has fallen by two magnitudes, we have $df/Adt = 1$, hence $R^{df}/dt = AR = 2,5 \times 10^{-6} R$. For $R =$ the radius of the sun this would become 1.7 km. per second. On the other hand the observed displacement of the dark lines was as much as would correspond to 700 km. per second. The real velocity must have been smaller, however, since the absorption-line is partly effaced by the broad adjoining emission-line; on the assumption that the velocity may have been about 100 or 200 km./sec. R is found equal to 60 or

¹⁾ Astronomische Nachrichten Bd. 207. Nr. 4950.

120 times the radius of the sun, therefore again a value of the same order of magnitude.

The Novae in the first stage of their brightness thus possess the characteristics of the giant-stars; in order that their mass may not become too exceptionally large, their density must be small even before the expansion. The relation found here between T , R , and A cannot teach us anything on this point, as it does not contain the density. A further indication for a small density may be found, however, in the fact that after a decrease of 4 magnitudes the spectrum at the minima of the light-variations more and more approached the character of a nebula-spectrum, and after another few months the star had become a nebula. At this stage the density has become so small that the visible emission is derived from the whole body including even the hindmost layers and still gives but a feeble surface-brightness; the fact that this condition sets in, when the expansion factor has become something like 10 or 20, proves that the original density must also have been far below unity.

III.

The original equation of motion (1) may also be written in such a form that it does not contain any dimensions.

Let us put

$$r = \gamma s \quad \Delta = \gamma \sigma \quad t = dz \quad . \quad . \quad . \quad (10)$$

where γ is a linear measure, σ a length of time and s , x , and z are numerical values. The equations then become

$$\left. \begin{aligned} \frac{d^2 x}{dz^2} &= -\frac{7}{2} \alpha \beta \frac{\sigma^2}{\gamma^3} \frac{dy}{ds} = -B \frac{dy}{ds} \\ s &= s_0 + x; \quad y = \left(\left(\frac{s}{s_0} \right)^2 \frac{ds}{ds_0} \right)^{2/5} \end{aligned} \right\} \quad . \quad . \quad . \quad (11)$$

where β is a function of the coördinate s_0 . The function β and the constants α , γ , σ which determine the special constitution and size of the star are united in the one coefficient B . The law of change of x with z is solely dependent on this coefficient, and is the same for all bodies with the same B . Equations (11) determine all possible movements — progressive, irregular or periodical, which may occur in a cosmic gaseous mass, in so far as they are a function of r only and as gravitation may be left out of account. Without calculating these movements themselves, a relation of similarity may be derived from the formulæ which establishes a connection between the changes in different stars. If for different

cosmic gas-spheres the distribution of β along the radius is the same, the expression

$$x = \frac{\Delta}{\gamma} = f\left(\frac{r}{\gamma}, \frac{t}{\sigma}\right)$$

must be the same function for them, provided B i. e. $\alpha\beta\frac{\sigma^2}{\gamma^2}$ for them is the same number. If for each of them a suitable time- and distance-scale is assumed, the motions and variations expressed on this scale are for all these bodies identical.

Assuming that a periodical solution of the equations (11) exists in which the particles move radially to and fro and the density periodically becomes adiabatically larger and smaller, this condition of motion will be valid for all such bodies provided the periods of the variations are expressed in σ as unit and the dimensions of the bodies in terms of γ . We must then have the relation

$$\alpha_1 \sigma_1^2 \gamma_1^{-2} = \alpha_2 \sigma_2^2 \gamma_2^{-2}$$

Now $\alpha = HT'_{00}$ (at the centre), therefore proportional to the temperature at the centre. Calling P the period of the variations and R the radius of the gas-sphere, this gives:

$$P_1^2 : P_2^2 = \frac{R_1^2}{T_1} : \frac{R_2^2}{T_2}$$

If we may assume, that similar bodies of this kind have the same temperature, the brightness becomes proportional to R^2 , i. e. to P^2 . Otherwise the temperature will still depend on some power of R and we have the more general relation

$$P^2 \propto L^n$$

or

$$2 \log P = \text{Const.} + n \log L$$

or

$$2 \log P = \text{Const.} - 0,4 n \times M$$

if M represents the absolute magnitude. A relation of that kind was found by Miss LEAVITT for the variable stars of the δ Cephei-type in the small Magellanic-cloud¹⁾. For 25 stars with periods from 1.25 to 127 days she found, that the period increased with the magnitude in such a manner that the logarithm of the period changed by 0.48 per magnitude-class.

The Cepheids are giant-stars, to which our suppositions are in so far applicable, that gravity, small in itself by the small density, must moreover for the greater part be neutralized by the radiation-

¹⁾ Harvard Circular Nr. 173.

pressure. They are all nearly of the same spectral type, hence their temperature cannot differ much. The relation which has been found to hold for them between period and intensity may therefore be explained in a simple manner by assuming that the variation of light arises from a pulsation of the gaseous sphere; not, as is often assumed, a pulsating deformation, but a pulsating expansion and contraction. Hereby the absorbing layers at the front of the star will alternately move away from us and towards us, hence in the spectrum a periodical displacement will take place. This displacement has usually been taken as indicating an orbital movement and for this reason the Cepheids are admitted amongst the spectroscopic double stars. Still amongst these they occupy a very exceptional position. Calculating the mass from the elements of the orbit, very much smaller values are found for the Cepheids than for other spectroscopic double stars, although their volume is much larger than that of the sun. Although an extremely small density is not altogether impossible a priori, still in the relatively small radial velocity an indication may be seen for the assumption, that a different explanation must be given here than for ordinary spectroscopic double stars.

But the question arises: is it possible that from an expansion and contraction a radial velocity arises of such a value as the experiments give — of several times ten kilometers per second?

The luminosity of δ Cephei and η Aquilae was found by ADAMS from the spectrum to be 60 times that of the sun; for a mean Cepheid with a period of 6.6 days HERTZSPRUNG derived from the proper motions 600 times the luminosity of the sun. Assuming on the ground of the accordance as to spectral type and colour an equal radiating power per unit surface, these results give a radius equal to 8 and 24 times respectively that of the sun. Representing the maximum expansion and contraction by the factor $f = 1 + \Delta f$, the maximum radial velocity will be

$$V = \frac{2\pi\Delta f \cdot R}{86400P},$$

where P is the period in days and R the radius. In kilometres R is 8 or $24 \times 7 \times 10^5$. Taking for P 6 days, this gives

$$V = \frac{6,3\Delta f \times 8 \text{ (of } 24) \times 7 \cdot 10^5}{4,3 \times 10^5} = 82 \text{ resp. } 246\Delta f \text{ KM.}$$

Since these Cepheids fluctuate rather less than 1 magnitude visually and rather over 1 magnitude in photographic intensity, we shall assume one magnitude for the variation in complete radiation;

therefore $\log L$ varies by the amount 0.20 above and below the mean. If the radius changes as the number f , the density changes as f^3 , the temperature as $f^{1/5}$ and the radiation as $f^{24/5}$; from $\log L = \pm 0.20$ it then follows that $\log f = \pm 0.04$, hence f fluctuates between 1.1 and 0.9. In the expression for V we must therefore take 0.1 for Δf and the maximum radial velocity becomes 8 or 25 kilometers per second. This value has to be somewhat lowered, since spectrographically the mean velocity of the entire front surface is measured, of which only the central parts have the velocity which we have here calculated. But even then the value found agrees sufficiently with the measured velocities (10 to 20 kilometers per second) to admit the explanation of the light variation and the variation in radial velocity on the ground of contraction and expansion.

There are some other objections to this explanation. The one is the same objection which also holds against the explanation through an orbital movement viz. that the maximum intensity coincides with the highest velocity towards us. The other objection lies in the coefficient 0.48 found by Miss LEAVITT. If, for these Cepheids equality of spectral class and thus of emissive power and of T may be assumed, the brightness becomes proportional to the surface, which gives

$$P^2 \propto L.$$

or

$$\log P = \text{Const.} - 0.2 M.$$

In this case therefore the coefficient should be 0.2, whereas Miss LEAVITT finds a much larger change of the period or a much smaller change of the brightness. It is therefore difficult to explain the deviation by means of a dependence of the temperature T on the linear dimension R ; for in that case T would have to be smaller, the larger the star. Possibly an explanation may be found by assuming, that the mass of the Cepheids is actually small, and therefore the density very low, so low, that the rays emitted from one side of the star may penetrate the complete body without being completely absorbed. If a glowing gas-sphere is so rare, that we observe the emission even from the hindmost layers without any diminution, the total light from the sphere will no longer be proportional to its surface, but to its mass, therefore be the same for two bodies of equal mass and different dimension. Intermediate conditions are conceivable in which the total light will then be proportional to a lower power of R , say to the first power. In the latter case the coefficient of M in the formula for $\log P$ would become about 0.40.

Physics. — “*On the Theory of the Friction of Liquids*”. By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS).

(Communicated in the meeting of November 30, 1918).

§ 1. *Introduction.* The theory of the friction of gases has been made the subject of numerous researches, the theory of friction of liquids on the other hand has met with but scant attention. Yet it is clear that the explanation given to account for the friction of gases — viz. that it is brought about in consequence of this that molecules diffusing from one gas layer to another, at the same time transport an amount of momentum from one layer to another — cannot equally apply to the friction of liquids. For the friction of gases increases at higher temperature. For liquids on the other hand the viscosity becomes slighter at higher temperature. Such a behaviour cannot be accounted for with “friction by means of transport.”

Maxwell calculated that on the supposition of “friction by means of transport” the coefficient of friction η should be proportional to \sqrt{T} if we assume that the molecules are perfectly rigid spheres, which do not attract each other. Other assumptions concerning the nature of the molecules (repulsion in inverse ratio with the fifth power of the distance, MAXWELL, or mutually attracting rigid spheres, SUTHERLAND and REINGANUM) lead to a still more rapid increase of η with T . Nor can the thermal expansion of the liquids explain the sign of the coefficient of temperature of η . For gases η appears to be independent of the volume. For liquids the expansion will promote an increase of η with T , and not a decrease. This has been shown experimentally (except for water, where the reverse takes place), and it is also easy to understand that this is to be expected for friction by means of transport, at least for not associating or dissociating liquids. The expression derived by MAXWELL:

$$\eta = \frac{1}{3} \varphi l s = \frac{1}{3} \frac{m s}{\pi \sigma^2 \sqrt{2}} \quad (1)$$

in which φ represents the density, l the mean length of path, s the mean velocity, m the mass, and σ the diameter of a molecule, will namely have to be corrected for liquids, to:

$$\eta = \frac{1}{3} \frac{ms}{\pi \sigma^2 \sqrt{2}} \frac{v-b}{v} \quad \dots \quad (1a)$$

which quantity increases with v . Other well-known corrections have been left out of consideration.

Accordingly for liquids we shall not principally have to think of transport of momentum by the diffusing molecules, but we shall have to explain the friction by forces which the molecules exert on each other. If at an arbitrary moment we could suddenly check the motion of the molecules, and if we could arrest them in the position which they occupied at that moment, the friction by means of transport would at the same moment be destroyed, so that we should not have any means to study the friction in those resting molecules.

The case is different for "friction through molecular forces". At least when we think the molecular forces independent of the velocity, the frictional forces would continue to exist also after the immobilisation of the molecules. They would be a consequence of the grouping of the molecules in space. It is now the question: of what nature are the molecular forces and what is the grouping of the molecules, which gives rise to the existence of the tensor of tension as we meet with it for the friction of liquids. The following three answers might be given to this question:

1. *Friction through impact forces or through an instantaneous transfer of momentum.* We might assume that the forces that the molecules exert on each other at an impact would furnish the explanation of viscosity. Let us consider the simple case of a liquid in which the current only moves in a single direction, which has been chosen as x -direction of a cartesian system of coordinates, this velocity (u) being a linear function of z , hence:

$$u = az, \text{ (with } a > 0\text{).} \quad \dots \quad (2)$$

Then the layers with greater z will move towards the righthand side with regard to the underlying layers, if the system of axes is orientated in space in the usual way. A consequence will be that the line connecting the centres of two colliding molecules, which I shall call the central line, will be found more often in the second quadrant of the xz -surface than in the first. When the system of coordinates is turned over an angle of 45° , so that the $+x$ -axis moves towards the $+z$ -axis, and when the new axes are called x' and z' , the pressure that the molecules exert on each other will be greater in the z' direction than in the x' direction. It is evident that this agrees with the value of the tensor of tension in this case.

Instead, however, of the calculation of the forces appearing in case of collision, the friction through this cause can also be calculated by means of the momentum that at impact is momentarily conveyed from the centre of one of the colliding molecules to that of the other. This method of calculation seems simpler and will be carried out in § 2.

II. *Friction for double points. Formation of streaks.* We might also assume the molecules to be electrical or magnetical double points. When they were orientated with regard to each other quite arbitrarily, they would equally frequently repel as attract each other, so that the mean force would be zero. Through the couples which they exert on each other, they will, however, turn so that attraction prevails. When we now assume that molecules that approach each other, are still little orientated, whereas this is the case to a higher degree with molecules that have moved past each other, and recede again from each other, the molecules whose central line lies in the x' -direction will be more orientated on an average than those for which it lies in the z' direction, so that a traction in the x' direction will result, greater than in the z' -direction, which can again account for the tensor of tension.

When we consider more than two molecules whose centres lie on the same line in the x -direction, the couples they exert on each other, will strengthen each other, which can give rise to the formation of a kind of streaks, which still more promotes the friction.

It is difficult to compute the accurate amount of this orientation of the molecule axes; it will be different according as one thinks the rotations of the molecules determined by classical mechanics or by the laws of the theory of quanta. Besides there is no occasion in the experimental data to assume that this case actually presents itself. I shall, therefore, not attempt to calculate the friction according to this hypothesis, though possibly it plays a decisive part in the friction of exceedingly viscous liquids, which present themselves as bi-refrangent in case of friction, as likewise in the glassy state.

III. *Friction in consequence of formation of groups.* Finally we can assume the molecules to combine to groups in consequence of their mutual attraction. In liquids at rest these groups will possess spherical symmetry on an average. When, however, a liquid is in a motion for which $u = az$, these spherical groups will be elongated to ellipsoids. This variation of shape will now again give rise to a greater traction in the x' -direction. This cause of friction will probably chiefly make itself felt in the neighbourhood of the critical point. In § 4 and following paragraphs I will make an attempt

to calculate the amount of the friction which is to be ascribed to this cause.

§ 2. *Friction in consequence of impact forces.* For an accurate calculation of the friction through this cause the accurate knowledge of the distribution of the velocities would be required. I shall, however, confine myself here to an approximate method of calculation of about the same nature as the method of calculation of the "friction by means of transport" for gases by MAXWELL in his papers in the Phil. Mag. in 1860. I shall, namely, assume that the distribution of the velocities of the molecules the centres of which lie in a definite layer $z = z_1$ is found by compounding the velocity of the current of the liquid in that layer with a thermal motion for which the unmodified partition of velocities of MAXWELL is thought to hold.

The error that we make on this supposition will probably be smaller for liquids than for gases. The free length of path is namely very small here, and the supposition departs little from MAXWELL's supposition that the molecules have the velocity of current of the layer in which they have collided last. Even when JEANS' correction is taken into account for the persistence of the velocities, we shall have to assign a velocity to the molecules corresponding with the velocity of current of a layer which is only a small fraction of σ removed from the layer in which their centre is situated. I shall disregard this small fraction.

When we now consider a definite horizontal layer, for which we choose $z = 0$, an instantaneous transfer of momentum through this layer takes place at every collision for which the centres of the colliding molecules lie on different sides of this layer. At every impact an instantaneous transfer from above downwards takes place and one in opposite direction. These two quantities are equal and of opposite signs. Hence we may also take into account double the amount of the transfer from above downwards. We shall now first consider the collisions for which the centre of molecule I lies between the planes $z = z_1$ and $z = z_1 + dz_1$ ($0 > z_1 > -\sigma \cos \gamma$), the central line¹⁾ forming an angle between γ and $\gamma + d\gamma$ with the z -axis, and lying in a plane forming an angle between β and $\beta + d\beta$ with the xz -plane. Further the components of velocity of molecule I will lie between u_1 and $u_1 + du_1$, v_1 and $v_1 + dv_1$ and w_1 and $w_1 + dw_1$, those of molecule II lying between u_2 and $u_2 + du_2$ etc. The chance that such components of velocity occur is represented for the two molecules respectively by

¹⁾ Counted in the direction of molecule I towards II.

$$\frac{1}{\pi\sqrt{\pi}} e^{-\frac{1}{\alpha^2}\{(u_1-az_1)^2+v_1^2+w_1^2\}} d\frac{u_1}{\alpha} d\frac{v_1}{\alpha} d\frac{w_1}{\alpha}$$

and

$$\frac{1}{\pi\sqrt{\pi}} e^{-\frac{1}{\alpha^2}\{(u_2-az_2)^2+v_2^2+w_2^2\}} d\frac{u_2}{\alpha} d\frac{v_2}{\alpha} d\frac{w_2}{\alpha}$$

in which $z_2 = z_1 + \sigma \cos \gamma$.

Hence the number of the collisions in question per second and per surface unity of the layer is

$$\frac{n^2}{\pi^3} e^{-\frac{1}{\alpha^2}\{(u_1-az_1)^2+v_1^2+w_1^2+(u_2-az_1-\sigma\gamma\cos\mu)^2+v_2^2+w_2^2\}} v_1 \cos \mu \sigma^2 \sin \gamma d\gamma d\beta dz. \quad (3)$$

in which n denotes the number of molecules per cm^3 , v , the relative velocity of molecule II with respect to molecule I, and μ the angle between the direction of v , and the central line, so that:

$$v_1 \cos \mu = (u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma$$

At each of these collisions the x -component of the quantity of motion, which is instantaneously transferred from above downwards is:

$$m v_1 \cos \mu \sin \gamma \cos \beta. \quad (4)$$

The condition that really transfer of momentum through the chosen plane is to take place is.

$$z_2 > 0 \text{ or } \gamma < Bg \cos \frac{-z_1}{\sigma}$$

Hence η is found by multiplication of (3) by (4), and then by integration with respect to

$$\gamma \text{ between } 0 \text{ and } Bg \cos \frac{-z_1}{\sigma}$$

$$\begin{array}{llll} \beta & ,, & 0 & ,, & 2\pi \\ u_1 \dots w_2 & ,, & -\infty & ,, & +\infty \\ z_1 & ,, & -\sigma & ,, & 0 \end{array}$$

We have then still to multiply the expression by 2 for the transfer from below upwards. We must, however, still pay attention to something else. In the limits set above collisions have been taken into account which are impossible in reality. Only those combinations of values of the independent variables can occur, for which μ is obtuse, hence $\cos \mu < 0$. It is simpler to introduce the condition that $v_1 \cos \mu < 0$. This condition can be introduced in the way of DIRICHLET

by multiplication by $\frac{1}{\pi} \int_{-\infty}^{+\infty} e^{q\varphi} \frac{\sin p\varphi}{\varphi} d\varphi$.

Which integral is 1 for $-p < q < p$

and 0 for $q < -p$ and for $q > +p$.

Now if we put $p = s$ and $q = v, \cos \mu + s$, and if we make s to increase indefinitely, the integral appears to become 1 for $v, \cos \mu < 0$ and 0 for $v, \cos \mu > 0$.

Thus we finally find for the force which the liquid above the plane $z = 0$ exerts per surface unity on that below it:

$$\begin{aligned} \eta a = & -\frac{2n^2 \sigma^2 m}{\pi^4} \int \{ (u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma \}^2 \times \\ & \times e^{-\frac{1}{2\alpha^2} \{ (u_1 - az_1)^2 + v_1^2 + w_1^2 + (u_2 - az_1 - a\sigma \cos \gamma)^2 + v_2^2 + w_2^2 \}} \times \\ & \times e^{+\varphi \{ (u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma + s \}} \times \frac{\sin s \varphi}{\varphi} \times \\ & \times \sin^2 \gamma \cos \beta \, d\gamma \, d\beta \, d\varphi \, \frac{u_1}{\alpha} \dots d \frac{w_2}{\alpha} \, dz_1 \end{aligned} \quad (5a)^1$$

As az_1 and az_2 will be in general very small compared with u_1 and u_2 , we may write for the first exponential factor under the integral sign:

$$\left\{ 1 + \frac{1}{\alpha^2} 2a (u_1 z_1 + u_2 z_1 + u_2 \sigma \cos \gamma) \right\} e^{-\frac{1}{2\alpha^2} (u_1^2 + \dots + w_2^2)}$$

When we substitute this in the integral, the term 1 between the accolades in (6) will furnish 0 after integration: it is the value of the force of friction for $\alpha = 0$. The integrals with $\frac{2a}{\alpha^2} z_1 u_1$ and $\frac{2a}{\alpha^2} z_1 u_2$ will become equal, but of opposite sign, so that they cancel each other, and the integral with $\frac{2a}{\alpha^2} u_2 \sigma \cos \gamma$ only remains.

When we now divide by α , and when we still put $\frac{z_1}{\sigma} = z'_1$ and $\frac{u_1}{\alpha} = u'_1 \dots \dots \frac{w_2}{\alpha} = w'_2$, $a\varphi = \varphi$ and $\frac{s}{\alpha} = s'$, and when we then again omit the accents, we get:

¹⁾ The minus sign has been written for this, because $v \cos \mu$ is negative, while the number of collisions are naturally positive, and the sign of expression (3) should properly speaking be reversed.

$$\eta = \frac{-4n^2\sigma^4 m\alpha}{\pi^4} \int \left\{ (u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma \right\}^2 \times u_2 \times$$

$$\times e^{-(u_1^2 + v_1^2 + w_1^2) + i\varphi \{ (u_2 - u_1) \sin \gamma \cos \beta + (v_2 - v_1) \sin \gamma \sin \beta + (w_2 - w_1) \cos \gamma + s \}} \times \quad (5b)$$

$$\times \frac{\sin s\varphi}{\varphi} \sin^2 \gamma \cos \gamma \cos \beta \, d\gamma \, d\beta \, d\varphi \, du_1 \dots dw_2 \, dz_1$$

If we substitute in this

$$\left. \begin{aligned} u_1 + \frac{1}{2} \varphi \sin \gamma \cos \beta &= \xi_1 & u_2 - \frac{1}{2} \varphi \sin \gamma \cos \beta &= \xi_2 \\ v_1 + \frac{1}{2} \varphi \sin \gamma \sin \beta &= \eta_1 & v_2 - \frac{1}{2} \varphi \sin \gamma \sin \beta &= \eta_2 \\ w_1 + \frac{1}{2} \varphi \cos \gamma &= \zeta_1 & w_2 - \frac{1}{2} \varphi \cos \gamma &= \zeta_2 \end{aligned} \right\} \quad (6)$$

we get:

$$\eta = \frac{-4n^2\sigma^4 m\alpha}{\pi^4} \int \left\{ (\xi_2 - \xi_1) \sin \gamma \cos \beta + (\eta_2 - \eta_1) \sin \gamma \sin \beta + (\zeta_2 - \zeta_1) \cos \gamma + \varphi \right\}^2 \times$$

$$\times (\xi_1 + \frac{1}{2} \varphi \sin \gamma \cos \beta) \times e^{-(\xi_1^2 + \eta_1^2 + \zeta_1^2) - \frac{1}{2} \varphi^2 + \varphi s} \times \frac{\sin s\varphi}{\varphi} \times \quad (5c)$$

$$\times \sin^2 \gamma \cos \gamma \cos \beta \, d\varphi \, d\gamma \, d\beta \, d\xi_1 \dots d\zeta_2 \, dz_1$$

On integration with respect to $\xi_1 \dots \zeta_2$ terms containing odd powers of $\xi_1 \dots \zeta_2$ vanish, so that the only terms left are those with $+ \{ [(\xi_2^2 + \xi_1^2) \sin^2 \gamma \cos^2 \beta + (\eta_2^2 + \eta_1^2) \sin^2 \gamma \sin^2 \beta + (\zeta_2^2 + \zeta_1^2) \cos^2 \gamma] \frac{1}{2} \varphi \sin \gamma \cos \beta + 2 \xi_1^2 \varphi \sin \gamma \cos \beta - \frac{1}{2} \varphi^3 \sin \gamma \cos \beta \}$.

These terms do not change when ξ_2^2 is substituted for ξ_1^2 , η_1^2 , η_2^2 , ζ_1^2 , and ζ_2^2 , so that $+ (3\xi_1^2 \varphi - \frac{1}{2} \varphi^3) \sin \gamma \cos \beta$ may be written for the sum of the remaining terms. After execution of the integrations we find:

$$\eta = -\frac{2}{\pi} n^2 \sigma^4 m \alpha i \int (3 - \varphi^2) \times e^{-\frac{1}{2} \varphi^2 + \varphi s} \times \sin s\varphi \times$$

$$\times \sin^2 \gamma \cos \gamma \cos^2 \beta \, d\varphi \, d\gamma \, d\beta \, dz_1 \dots \quad (5d)$$

Let us now replace $e^{i\varphi s}$ by $\cos \varphi s + i \sin \varphi s$, and execute the integration with respect to φ , bearing in mind that we seek the value of the integral for $\lim. s = \infty$. Then the term with $\sin s\varphi \cos \varphi s$ vanishes, and in the term with $\sin^2 s\varphi$ we may replace this expression by its mean value $\frac{1}{2}$. Thus we find:

$$- \int_{-\infty}^{+\infty} e^{-\frac{1}{2} \varphi^2 + \varphi s} \times \sin s\varphi \times (3 - \varphi^2) \, d\varphi = \sqrt{2\pi}$$

$$\int_0^{2\pi} \cos^2 \beta \, d\beta = \pi$$

$$\begin{aligned}
& \int_0^{Bq \cos(-z_1)} \sin^2 \gamma \cos \gamma d\gamma = \frac{1}{4} [\sin^4 \gamma]_0^{Bq \cos(-z_1)} = \frac{1}{4} (1 - z_1^2)^2 \\
& \int_{-1}^0 (1 - z_1^2)^2 dz_1 = \frac{8}{15} \\
& \eta = \frac{4\sqrt{2\pi}}{15} n^2 \sigma^4 m a \dots \dots \dots (5e)
\end{aligned}$$

In the calculation of the number of collisions we have, however, up to now disregarded the influence of the mutual attraction of the molecules and of their dimension in the direction of the velocity. If for this we introduce the usual corrections, we find:

$$\eta = \frac{4\sqrt{2\pi}}{15} n^2 \sigma^4 m a \frac{v}{v-b} e^{-\frac{z}{RT}} \dots \dots \dots (5)$$

in which z represents the difference between the amount of potential energy that the molecules in the liquid possess on an average, and the amount which they possess at the moment of a collision.

G. JÄGER¹⁾ and M. BRILLOUIN²⁾ had already derived expressions for the friction of liquids; JÄGER considers exclusively "friction in consequence of impact forces", whereas BRILLOUIN takes besides these also the friction by means of transport into consideration. The method of calculation differs somewhat from that followed above. The results at which they arrive, are in somewhat modified notation:

$$\begin{aligned}
\text{JÄGER} \quad \eta &= \frac{\sigma v s}{6 \left(1 - \sqrt[3]{\frac{b}{v}} \right)} \\
\text{BRILLOUIN} \quad \eta &= \frac{1}{3} \rho s \left\{ \alpha D + \beta \frac{\sigma}{2(D-\sigma)} \right\}
\end{aligned}$$

In this ρ represents the density, s the mean velocity of the molecules, and D the mean distance of a pair of adjacent molecules. α and β are two unknown constants, which will not differ much from 1, and which have been introduced, because all kinds of approximations have been introduced into the calculation, which renders the numerical coefficients not entirely certain. The first term of BRILLOUIN's formula refers to transport, the second to impact forces. It seems to me that BRILLOUIN should also have corrected the first term for the "thickness" of the molecules. In his train of

¹⁾ G. JÄGER, Wiener Sitzungsber. CII, p. 253, Anno 1893.

²⁾ M. BRILLOUIN, Leçons sur la Viscosité des Liquides et des Gaz. Paris. GAUTHIER-VILLARS 1907.

thought this might have been done by multiplication by a factor $\frac{D-\sigma}{D}$. That he failed to do so deprives his test of the experimental data of much of its value, in my opinion.

§ 3. *Test of the formulae for liquids not too near the critical point.* Let us call the "coefficient of friction by means of transport" η_1 , that through forces of collision η_2 , and that in consequence of formation of groups η_3 . For liquids not too near the critical point we shall disregard η_3 . We have further:

$$\frac{\eta_2}{\eta_1} = c \frac{b^2}{(v-b)^2}$$

in which c is a numerical coefficient of moderate value. We may no doubt consider this quantity as large compared with 1, so that we shall also neglect η_1 .

When we do so we notice first of all that for constant volume η according to the formula must increase with T proportional to \sqrt{T} . There are only few substances for which the experimental data are available, required to verify whether the sign of $\frac{\partial \eta}{\partial T_v}$ is really positive. It is clear that always $\frac{\partial \eta}{\partial T_p}$ has been measured, and not $\frac{\partial \eta}{\partial T_v}$. Ether and Benzene are the only substances for which I have found records for $\frac{\partial \eta}{\partial p_T}$ ¹⁾, so that $\frac{\partial \eta}{\partial T_v}$ can be found according to the formula

$$\frac{1}{\eta} \frac{\partial \eta}{\partial T_v} = \frac{1}{\eta} \frac{\partial \eta}{\partial T_p} + \frac{1}{\eta} \frac{\partial \eta}{\partial p_T} \frac{\partial p}{\partial T_v} = \frac{1}{\eta} \frac{\partial \eta}{\partial T_p} - \frac{1}{\eta} \frac{\partial \eta}{\partial p_T} \frac{1}{v} \frac{\partial v}{\partial p_T}.$$

We find:

for ether	for benzene
$\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_p} = -0,01075$ ²⁾	$= 0,01853$ ²⁾

¹⁾ Except for water, which will most likely also behave abnormally in this respect, and for CO_2 in the neighbourhood of the critical point, which observations will be discussed later on.

²⁾ These values, like those of $\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_p}$ for other substances given below have

$$\begin{aligned}\frac{1}{\eta_v} \frac{\partial \eta}{\partial p_T} &= 0,00073 \quad ^1) & 0,00093 \quad ^1) \\ \frac{1}{v} \frac{\partial v}{\partial T_p} &= 0,001585 \quad ^2) & 0,0011763 \quad ^3) \\ \frac{1}{v} \frac{\partial v}{\partial p_T} &= -0,000139 \quad ^4) & -0,0000783 \quad ^5)\end{aligned}$$

This yields for ether

$$\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v} = -0,01075 + 0,0088 = -0,00195$$

and for benzene

$$\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v} = -0,01853 + 0,01462 = -0,00391$$

Theoretically we should find according to equation (5):

$$\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v} = \frac{1}{2T} = +0,00183.$$

Accordingly there is not even agreement in the sign of $\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v}$. When we, however, take into consideration that the value found is the difference of two values which are each about five times the value of the amount sought, and that they are very inaccurately known, it is not excluded that $\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_v}$ is in reality negative. Even in the value of $\frac{1}{v} \frac{\partial v}{\partial p_T}$ an error of 4% is by no means excluded, and the error in the determination of $\frac{1}{\eta} \frac{\partial \eta}{\partial p_T}$ will without doubt be many times larger than that in $\frac{1}{v} \frac{\partial v}{\partial p_T}$. On the other hand it is of course

been found by differentiation of the empirical formulae of the form: $\eta = \frac{a}{(b+t)^c}$, in which THORPE and RODGER, Phil. Trans. Royal Soc. of London **185** p. 397, A. 1894 comprise their observations.

¹⁾ According to WARBURG and SACHS, Ann. d. Phys. u. Chem. **22** p. 521. A. 1884. The pressure is expressed in kg. per cm².

²⁾ According to AMAGAT 1893, extrapolated for 0° and 1 atm. from the values given in the Recueil de constantes physiques.

³⁾ According to KOPF, 1847. Borrowed from the "Recueil etc.".

⁴⁾ According to SUCHODSKI 1910, extrapolated for 0° and 1 atm. from the values given in the "Recueil etc.".

⁵⁾ According to RÖNTGEN 1891, extrapolated for 0° and 1 atm. from the values given in the "Recueil etc.".

also possible that even if formula (5) is valid, the value of $\frac{1}{\eta_0} \frac{\partial \eta}{\partial T_p}$ must

be negative, in consequence of the factor $e^{-\frac{\epsilon}{RT}}$, or because σ , hence also b depend on the temperature. The experimental data are not sufficiently accurate to decide this question.

More satisfactory results are furnished by another test, which can be applied on a more extensive scale. It consists in this that we compare the experimental values of $\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}$ with the values following from equation (5).

For this purpose we write:

$$\frac{1}{\eta} \frac{\partial \eta}{\partial T_p} = \frac{1}{\eta} \left(\frac{\partial \eta}{\partial T_v} + \frac{\partial \eta}{\partial v} \frac{\partial v}{\partial T_p} \right)$$

and in this we put:

$$\frac{1}{\eta} \frac{\partial \eta}{\partial T_v} = \frac{1}{2T} \quad \frac{1}{\eta} \frac{\partial \eta}{\partial v} = \frac{1}{v} - \frac{1}{v-b} = \frac{-b}{v(v-b)} = -\frac{b \left(p + \frac{a}{v^2} \right)}{v \cdot RT}.$$

We shall neglect p by the side of $\frac{a}{v^2}$ and roughly assume

$RT_k = \frac{8a}{27b}$ and $p_k = \frac{1}{27} \frac{a}{b^2}$; we then get:

$$\frac{1}{\eta} \frac{\partial \eta}{\partial v} = -\frac{1}{RTv^3} \left(\frac{3}{8} \right)^3 \frac{R^3 T_k^3}{p_k^2}.$$

v is the volume per gram-molecule, hence $v = m \frac{1}{\rho}$, so that we finally find to test:

$$\left(\frac{1}{\eta} \frac{\partial \eta}{\partial T_p} \right)_{exp} = \frac{1}{2T} - \frac{3^3 R^3 \rho^3 T_k^3}{8^3 T m^2 p_k^2} \left(\frac{1}{v} \frac{\partial v}{\partial T_p} \right) \quad \dots \quad (7)$$

Borrowing the values of ρ , p_k , T_k and $\frac{1}{v} \frac{\partial v}{\partial T_p}$ from the "Recueil etc.", we find: (See Table p. 754).

The agreement is on the whole as satisfactory as could be expected in view of the many approximations. Generally the experimental value is somewhat smaller than the theoretical one, for ether more than for other substances, benzene and orthoxylene deviating in the opposite sense. For acetic acid and for the alcohols the agreement is much less than for the normal substances.

¹⁾ See note 1 on pag. 751.

	$\left(\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}\right)_{exp}$	$\left(\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}\right)_{theor.}$	$\sigma \times 10^8$	$\sigma' \times 10^8$
Pentane	0.01019	0.01269	5.486	4.863
Isopentane	1081	1171	5.774	4.838
Hexane	1123	1354	6.716	5.166
Heptane	1214	1353	7.779	5.456
Octane	1394	1574	9.808	5.714
Chloroform	1149	1066	6.515	4.317
Ether	1075	1463	6.578	4.731
Benzolene	1853	1382	9.770	4.559
Toluolene	1462	1524	8.451	4.867
Orthoxylene	1700	1385	10.871	5.170
Metaxylene	1418	1478	7.973	5.223
Paraxylene ¹⁾	1472	1414	6.716	5.187
Acetic acid ¹⁾	1826	2607	4.713	4.382
Methyl alcohol	1634	1988	4.527	3.749
Ethyl "	2086	1250	10.273	4.046
Propyl "	2887	0970	36.103	4.421

So far we have tested the temperature-coefficients of η . We can also test equation (5) directly, namely by for instance calculating σ from it, and by comparing the values obtained thus with the values of σ calculated in another way. When we again omit

the factor $e^{-\frac{\epsilon}{RT}}$ and when we put $\frac{2}{3}\pi\sigma^2 N = b = \frac{RT_k}{8p_k}$ ($N =$ number of molecules per gram-molecule), substituting again $\frac{RT}{p + \frac{a}{v^2}}$ for

$v - b$, and neglecting p by the side of $\frac{a}{v^2}$, we find:

¹⁾ For these substances the values for $\frac{1}{\eta} \frac{\partial \eta}{\partial T_p}$ also for 0° C. have been calculated from the empirical formula of RODGER and THORPE, though they are solid at this temperature.

$$\sigma = \frac{640}{27} \left(\frac{\pi T}{R^3} \right)^{1/2} \frac{m^{5/2} p k^3}{\rho^3 T_k^3} \eta \dots \dots \dots (8)$$

The values thus calculated for σ are recorded in the table on p. 754. With these the values calculated from the critical quantities:

$$\sigma' = \left(\frac{3RT_k}{16\pi N p k} \right)^{1/3} \dots \dots \dots (9)$$

have been compared. $N = 6,08 \times 10^{-23}$ (SOMMERFELD).

They are represented by σ' and recorded in the last column of the table. It appears that equation (8) gives values that are in perfect concordance with those of equation (9) as far as order of magnitude is concerned. It is noteworthy that the values for σ' differ little inter se, those for σ presenting much greater differences between each other. The alcohols show again great deviations.

Anatomy. — "*On two Nerves of Vertebrates agreeing in Structure with the Nerves of Invertebrates.*" By Dr. A. B. DROOGLEEVER FORTUYN. (Communicated by Prof. J. BOEKE).

(Communicated in the meeting of November 30, 1918).

As a well-known fact the olfactory cells in the mucous membrane of the nose of Vertebrates are "Sinnesnervenzellen" or "conducting sense-cells" as I propose to call them, unless they have received already another English name. (The word "sensory nerve-cell" may then be reserved to "sensibele Ganglienzelle"). They are sense-cells which are not surrounded by nerve-fibres, but whose cell-body directly passes into a process with all the characteristics of a nerve-fibre. These nerve-fibres, the fila olfactoria, constitute the nervus olfactorius. So the olfactory nerve deviates in its structure from all the other nerves of the vertebrated animals. The truth of this remark may already be deduced from the fact that in Vertebrates besides in the olfactory mucous membrane conductive sense-cells are only found in the retina (rod- and cone-cells) and perhaps in the pineal organ. So all the nerves of the Vertebrates with exception of the olfactory nerve are devoid of nervous processes of conducting sense-cells. On the contrary the majority of the nerves of invertebrated animals do contain processes of conductive sense-cells, which in these animals are always spread about the whole body in all kinds of sense-organs. Often in Invertebrates nerves are composed exclusively of fascicles of neurites of conducting sense-cells as is the case in the olfactory nerve of the Vertebrates. From this I conclude that we have to look upon the olfactory nerve of the Vertebrates as a nerve constructed in a way which is often met with in Invertebrates, and nowhere else in vertebrated animals.

Another striking difference between the nerves of vertebrated and invertebrated animals is this that in the Invertebrates ganglion-cells are generally dispersed along the whole course of the nerve either separately or in groups, ganglia. In the nerves of Vertebrates, however, they are totally wanting or they are accumulated in very few ganglia (spinal ganglia or those of the nerves of the brain). Now if one reads (e.g. in the review on this subject by Prof. VAN WIJHE in these Proceedings, Vol. XXVI, 1918) that also in the nervus

terminalis of the Vertebrates ganglion-cells are scattered along the whole course of the nerve, then one is compelled to grant to the terminal nerve the character of a nerve of an invertebrated animal. Nevertheless this type of nerve is obviously another than that of the olfactory nerve.

In connection with the preceding remarks I should like to point to the fact that *Amphioxus*, whose nervous system is generally compared with that of vertebrated animals, possesses in its sensory nerves the nerves of a true-Invertebrate. All or most of them contain processes of conducting sense-cells as these cells are scattered about the whole body, and moreover most of the sensory nerves are accompanied by dispersed ganglion-cells. Therefore spinal ganglia are lacking.

Leiden, Anatomical Cabinet.

Mathematics. — “*Ueber die Teilkörper des Kreiskörpers $k\left(e^{\frac{2\pi i}{l^h}}\right)$.*”
(Zweiter Teil). Von Dr. N. G. W. H. BEGER. (Communicated
by Prof. W. KAPTEYN).

(Communicated in the meeting of October 26, 1918).

Wir beweisen zunächst einige Hilfssätze über die Function F
und das Karactersymbol.

Hilfssatz I.

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = (-1)^{bu} F\left(e^{-\frac{2k\pi i}{l^h}}\right).$$

Beweis:

$$\begin{aligned} F\left(e^{\frac{2k\pi i}{l^h}}\right) &= \sum_{n=1}^{l^h-1} \left[\frac{n}{l^h}\right]^{bu} e^{\frac{2k\pi ni}{l^h}} = \\ &= \sum_{n=1}^{l^h-1} \left[\frac{l^h-n}{l^h}\right]^{bu} e^{\frac{2k(l^h-n)i}{l^h}} = \sum_{n=1}^{l^h-1} \left[\frac{-n}{l^h}\right]^{bu} e^{-\frac{2k\pi ni}{l^h}} \\ &= \left[\frac{-1}{l^h}\right]^{bu} \sum_{n=1}^{l^h-1} \left[\frac{n}{l^h}\right]^{bu} e^{-\frac{2k\pi ni}{l^h}} \\ &= e^{\frac{2\pi i l^{h-1} \left(\frac{l-1}{2}\right) bu}{l^{h-1}(l-1)}} F\left(e^{-\frac{2k\pi i}{l^h}}\right) \\ &= (-1)^{bu} F\left(e^{-\frac{2k\pi i}{l^h}}\right). \end{aligned}$$

Hilfssatz II: Es sei $l^{h'}$ die höchste Potenz von l die in u aufgeht.
Dann ist

$$\left[\frac{n+l^{h-h'}}{l^h}\right]^u = \left[\frac{n}{l^h}\right]^u.$$

Beweis: Es sei $n + l^{h-h'} \equiv r^{m'} \pmod{l^h}$
dann ist

$$n \equiv r^{m'} \pmod{l^{h-h'}} \text{ wegen } h' < h$$

Es sei nun

$$n \equiv r^{m'} \pmod{l^h} \text{ also auch } \pmod{l^{h-h'}}$$

dann ist

$$r^{m'} \equiv r^{n'} \pmod{l^{h-h'}}$$

also

$$m' \equiv n' \pmod{l^{h-h'-1}(l-1)}$$

oder

$$n' = m' + l^{h-h'-1}(l-1)v.$$

Hieraus ergibt sich:

$$\begin{aligned} \left[\frac{n + l^{h-h'}}{l^h} \right]^u &= e^{\frac{2\pi m' u i}{l^{h-1}(l-1)}} = e^{\frac{2\pi m' u i}{l^{h-1}(l-1)} + \frac{2\pi l^{h-h'-1}(l-1) u i}{l^{h-1}(l-1)}} \\ &= \left[\frac{n}{l^h} \right]^u \cdot e^{\frac{2\pi u l^{h-h'-1}(l-1) i}{l^{h-1}(l-1)}}. \end{aligned}$$

Der letzte Factor ist = 1 da u teilbar ist durch $l^{h'}$.

Hilfssatz III. Es sei $l^{h'}$ die höchste Potenz von l die auf u teilbar ist, so ist:

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = 0 \text{ wenn die höchste Potenz von } l, \text{ die auf } k \text{ teilbar ist,} \\ = l^{h'} \text{ ist}$$

$$= \left[\frac{k/l^{h'}}{l^h} \right]^{-bu} F\left(e^{\frac{2\pi i}{l^{h-h'}}}\right) \text{ wenn die letzt genannte höchste}$$

Potenz = $l^{h'}$ ist.

Beweis: Es folgt aus Hilfssatz II:

$$\begin{aligned} F\left(e^{\frac{2k\pi i}{l^h}}\right) &= \sum_{n=1}^{l^h-1} \left[\frac{n}{l^h} \right]^{bu} e^{\frac{2kn\pi i}{l^h}} = \sum_{n=1}^{l^h-1} \left[\frac{n + l^{h-h'}}{l^h} \right]^{bu} e^{\frac{2kn\pi i}{l^h}} \\ &= e^{\frac{-2k\pi i}{l^{h'}}} \sum_{n=1}^{l^h-1} \left[\frac{n + l^{h-h'}}{l^h} \right]^{bu} e^{\frac{2k(n+l^{h-h'})\pi i}{l^h}} \\ &= e^{\frac{-2k\pi i}{l^{h'}}} F\left(e^{\frac{2k\pi i}{l^h}}\right) \end{aligned}$$

also ist

$$\left(1 - e^{\frac{2k\pi i}{l^{h'}}}\right) F\left(e^{\frac{2k\pi i}{l^h}}\right) = 0$$

Wenn nun die höchste Potenz von l , welche in k aufgeht, kleiner ist als $l^{h'}$, so ergibt sich hieraus $F=0$. Nehmen wir nun weiter an dass k teilbar ist durch eine höhere Potenz von l , $l^{h'+c}$, $c > 0$, dann ist:

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = \sum_{n=1}^{l^h} \left[\frac{n}{l^h} \right]^{bu} e^{\frac{2kn\pi i}{l^h}} = \sum_{n=1}^{l^{h-h'-c}} + \sum_{n=l^{h-h'-c}+1}^{2l^{h-h'-c}} + \dots + \sum_{n=(l^{h'+c}-1)l^{h-h'-c}+1}^{l^h}$$

Nun ist

$$e^{\frac{2k\pi n i}{l^h}} = e^{\frac{2k'\pi n i}{l^{h-h'-c}}} \text{ wegen } k = l^{h'+c} k'$$

also:

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = \sum_{n=1}^{l^{h-h'-c}} e^{\frac{2k\pi ni}{l^h}} l^{h'+c-1} \left[\frac{n + sl^{h-h'-c}}{lh} \right]^{bu}$$

Es sei

$$n + sl^{h-h'-c} \equiv r^{s'} \pmod{lh} \quad \text{und} \quad n \equiv r^{n'} \pmod{lh}$$

dann ist

$$n \equiv r^{s'} \pmod{lh-h'-c} \quad n \equiv r^{n'} \pmod{lh-h'-c}$$

also

$$r^{s'} \equiv r^{n'} \pmod{lh-h'-c}$$

$$s' \equiv n' \pmod{\varphi(l^{h-h'-c})}$$

und

$$s' = n' + v_s \varphi(l^{h-h'-c}) \cdot \dots \cdot \dots \quad (5)$$

Hieraus folgt:

$$\left[\frac{n + sl^{h-h'-c}}{lh} \right]^{bu} = e^{\frac{2\pi i \frac{n' + v_s \varphi(l^{h-h'-c})}{l^{h-1}(l-1)} bl^{h'} u}{l^{h-1}(l-1)}}$$

(wo $u = l^{h'} u'$)

$$\begin{aligned} &= e^{\frac{2\pi i n' bu}{l^{h-1}(l-1)}} \cdot e^{\frac{2\pi i v_s bu'}{l^c}} \\ &= \left[\frac{n}{lh} \right]^{bu} e^{\frac{2\pi i v_s bu'}{l^c}} \end{aligned}$$

und schliesslich

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = \sum_{n=1}^{l^{h-h'-c}} \left[\frac{n}{lh} \right]^{bu} e^{\frac{2k\pi ni}{l^h}} l^{h'+c-1} \sum_{s=0}^{l^{h'+c}-1} e^{\frac{2\pi i v_s bu'}{l^c}} \cdot \dots \quad (6)$$

Wenn nun in der letzten Summe zwei Werte von $v_s \pmod{l^c}$ mit einander congruent sind, so ergeben diese Werte zwei gleiche Glieder dieser Summe. Nehmen wir an dass:

$$v_{s_1} \equiv v_{s_2} \pmod{l^c}$$

$$v_{s_1} = v_{s_2} + wl^c.$$

und dass weiter

$$s'_1 = n' + v_{s_1} \varphi(l^{h-h'-c}) \quad \text{und} \quad s'_2 = n' + v_{s_2} \varphi(l^{h-h'-c})$$

dann ist auch

$$s'_1 = n' + (v_{s_2} + wl^c) \varphi(l^{h-h'-c})$$

$$s'_1 = n' + v_{s_2} \varphi(l^{h-h'-c}) + wl^c \varphi(l^{h-h'-c})$$

$$s'_1 = s'_2 + wl^c \varphi(l^{h-h'-c}).$$

Weiter ist:

$$n + s_1 l^{h-h'-c} \equiv r^{s'_1} \quad \text{und} \quad n + s_2 l^{h-h'-c} \equiv r^{s'_2} \pmod{lh}$$

und auch ist also:

$$\begin{aligned} n + s_1 l^{h-h'-c} &\equiv r^{s_2'} + v l^c \varphi(l^{h-h'-c}) \\ &\equiv r^{s_2'} + v l^c \varphi(l^{h-h'-e}) \\ &\equiv (n + s_2 l^{h-h'-e}) + v l^c \varphi(l^{h-h'-c}) \end{aligned}$$

und wegen

$$r^{l^c \varphi(l^{h-h'-c})} = r^{l^{h-h'-1}(l-1)} \equiv 1 \pmod{l^{h-h'}},$$

folgt hieraus

$$n + s_1 l^{h-h'-c} \equiv n + s_2 l^{h-h'-c} \pmod{l^{h-h'}}$$

also

$$s_1 \equiv s_2 \pmod{l^c}$$

Schliesslich bemerken wir noch dasz die Werte von v_s , die zu zwei verschiedenen Gliedern der Summe Σ aus (6) gehören, nicht gleich sind; denn, nehmen wir an dasz die zwei Werte von v , die zu s_1 und s_2 gehören, gleich sind, so folgt aus (5) $s_1' = s_2'$, und also würde

$$n + s_1 l^{h-h'-c} \equiv r^{s_1'} \quad \text{en} \quad n + s_2 l^{h-h'-c} \equiv r^{s_2'}$$

also

$$\begin{aligned} s_1 l^{h-h'-c} &\equiv s_2 l^{h-h'-c} \pmod{l^h} \\ s_1 &\equiv s_2 \pmod{l^{h'+c}} \end{aligned}$$

Und dies ist nicht möglich da s in der Summe Σ nur läuft bis $s = l^{h'+c} - 1$.

Hieraus folgt dasz $\sum_s = \frac{l^{h'+c}}{l^c} \times$ die Summe aller l -ten Einheitswurzeln.

Diese letzte Summe ist aber, wie bekannt, gleich Null, so dasz sich ergibt $\sum_s = 0$ und $F = 0$.

Der Beweis des zweiten Teiles gestaltet sich wie folgt:

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = \sum_n \left[\frac{n}{l^h}\right]^{bu} e^{\frac{2kn\pi i}{l^h}} = \left[\frac{k/l^{h'}}{l^h}\right]^{-bu} \sum_n \left[\frac{nk/l^{h'}}{l^h}\right]^{bu} e^{\frac{2kni}{l^h}}$$

da $k/l^{h'}$ nicht teilbar ist durch l . Hieraus ergibt sich weiter

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = \left[\frac{k/l^{h'}}{l^h}\right]^{-bu} \sum_n \left[\frac{nk/l^{h'}}{l^h}\right]^{bu} e^{\frac{2nk/l^{h'} \pi i}{l^{h-h'}}}.$$

Nun durchläuft $nk/l^{h'}$ zugleich mit n ein reducirtes Restsystem $(\text{mod } m)$, folglich ist:

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = \left[\frac{k/l'}{l^h}\right]^{-bu} \sum_n \left[\frac{n}{l^h}\right]^{bu} e^{\frac{2n\pi i}{l^{h-h'}}}$$

Hilfssatz IV.

$$F'\left(e^{\frac{2\pi i}{l^{h-h'}}}\right) F'\left(e^{\frac{2\pi i}{l^{h-h'}}}\right) = l^{h'+h} (-1)^{\frac{u}{l^{h'}}} u = \frac{1}{2} al^{h-1}$$

wo $l^{h'}$ die höchste Potenz von l ist, die in u aufgeht, und F' aus der Function F erhalten wird, wenn in letzterer u durch $-u$ ersetzt wird.

Ist $u = \frac{1}{2} al^{h-1}$, a gerade, so ist $F'(e^{\frac{2\pi i}{l}}) = l^{h-1/2} l^{1/4} (l-1)^2$

Beweis: Es ist

$$F\left(e^{\frac{2\pi i}{l^{h-h'}}}\right) = \sum_{n=1}^{l^h-1} \left[\frac{n}{l^h}\right]^{bu} e^{\frac{2n\pi i}{l^{h-h'}}} = \sum_{n=1}^{l^h-1} \left[\frac{nk}{l^h}\right]^{bu} e^{\frac{2n\pi ki}{l^{h-h'}}}$$

wenn k nicht teilbar ist durch l . Hieraus geht hervor:

$$\left[\frac{k}{l^h}\right]^{-bu} F\left(e^{\frac{2\pi i}{l^{h-h'}}}\right) = \sum_{n=1}^{l^h} \left[\frac{n}{l^h}\right]^{bu} e^{\frac{2\pi kni}{l^{h-h'}}}$$

Wir multipliciren mit $e^{\frac{2\pi ki}{l^{h-h'}}}$ und nehmen die Summe über alle Werte von k , die nicht durch l teilbar sind. Es ergibt sich

$$F'\left(e^{\frac{2\pi i}{l^{h-h'}}}\right) F'\left(e^{\frac{2\pi i}{l^{h-h'}}}\right) = \sum_{n=1}^{l^h} \left[\frac{n}{l^h}\right]^{bu} \sum_k e^{\frac{2\pi kn(n+1)i}{l^{h-h'}}}$$

Wir teilen die letzte Summe in drei Partialsummen:

1°. Die Summe über alle Werte von n für welche $n+1$ teilbar ist durch $l^{h-h'}$.

2°. Die Summe über alle Werte von n für welche $n+1$ teilbar ist durch $l^{h-h'-1}$ und nicht durch eine höhere Potenz von l .

3°. Die Summe über alle Werte von n für welche $n+1$ durch eine niedrigere Potenz von l teilbar ist, inclusiv die nullte-Potenz.

Bei dieser Einteilung haben wir keine Zahl n vergessen. Wir betrachten nun jede dieser drei Summen.

1°. In diesem Falle ist jedes Glied von \sum_k gleich Eins, also $\sum_k = \varphi(l^h)$. Die hierher gehörigen Zahlen $n+1$ sind:

$$l^{h-h'}, 2l^{h-h'}, \dots, l^{h'} \cdot l^{h-h'}$$

Für die Zahlen n ergibt sich hieraus

$$n = -1 + l^{h-h'} v_n \quad v_n = 1, 2, \dots, l^{h'}$$

also:

$$\left[\frac{n}{l^h} \right]^{bu} = e^{\frac{2\pi b u n i}{\varphi(l^h)}} \quad n \equiv r^{h'} \pmod{l^h}. \text{ Dann ist aber}$$

$$-1 \equiv r^{h'} \pmod{l^{h-h'}}$$

und also:

$$n' \equiv 0 \pmod{\frac{1}{2}\varphi(l^{h-h'})}$$

Folglich:

$$\left[\frac{n}{l^h} \right]^{bu} = e^{\frac{2\pi i b l^{h'} u' \cdot \frac{1}{2}\varphi(l^{h-h'}) v_n}{\varphi(l^h)}} = (-1)^{bu'}$$

In der Summe 1°. finden sich $l^{h'}$ Glieder vor.

Infolge dessen ist der Wert dieser Summe:

$$(-1)^{bu' l^{h'}} \varphi(l^h)$$

2°. In diesem Falle ist:

$$\frac{2\pi k(n+1)i}{l^{h-h'}} = \text{einer } l\text{-ten Einheitswurzel.}$$

Die hierher gehörige Summe \sum_k ist also gleich $\frac{\varphi(l^h)}{\varphi(l)} \times$ die Summe

der primitiven l -ten Einheitswurzeln, d.h. gleich $-\frac{\varphi(l^h)}{\varphi(l)}$.

Weiter ist $\left[\frac{n}{l^h} \right]^{bu} =$ einer l -ten Einheitswurzel von ± 1 wegen

$$n = -1 + l^{h-h'-1} v_n$$

wo v_n alle Werte annimmt welche $< l^{h'+1}$ sind und nicht teilbar durch l . Das sind $\varphi(l^{h'+1})$ Werte.

Auf gleiche Weise wie unter 1°. zeigt man dasz $\left[\frac{n}{l^h} \right]^{bu}$ eine l -te Einheitswurzel ist aus 1 oder -1 je nachdem bu' gerade oder ungerade ist, wo $u = l^{h'} u'$. Jede primitive l -te Einheitswurzel tritt in der Summe $\sum_n \frac{\varphi(l^h)}{\varphi(l)} \times$ auf.

Gemäsz diesen Bemerkungen findet man leicht dasz der Wert der hierher gehörigen Partialsumme \sum ist:

$$-\frac{\varphi(l^h)}{\varphi(l)} \times \mp \frac{\varphi(l^{h'+1})}{\varphi(l)} = l^{h'} \cdot l^{h-1} (-1)^{bu'}.$$

3°. Die Summe \sum_k kan man verteilen in einige Male die Summe

der primitiven $l^{h-h'-c}$ -te Einheitswurzeln, wo $c > 1$. Daher ist auch $\Sigma = 0$.

Nach einer kleinen Rechnung findet man nun den ersten Teil des Hilfssatzes.

Beweis des zweiten Teils:

$$\begin{aligned} F\left(e^{\frac{2\pi i}{l}}\right) &= \sum_n \left[\frac{n}{l^h}\right]^{1/2} a b l^{h-1} e^{\frac{2\pi n i}{l}} = \\ &= \sum_n (-1)^{\text{ind } n} e^{\frac{2\pi n i}{l}} = \sum_{t=1}^{l^h} (-1)^t e^{\frac{2\pi r_t i}{l}} \end{aligned}$$

wo r_t den kleinsten positiven Rest bezeichnet von $r^t \pmod{l}$

$$\begin{aligned} F\left(e^{\frac{2\pi i}{l}}\right) &= \sum_{t=1}^{l-1} + \sum_{t=l}^{2(l-1)} + \dots \text{ Nun ist } r_{t+(l-1)} = r_t \text{ also} \\ &= l^{h-1} \cdot \sum_{t=1}^{l-1} (-1)^t e^{\frac{2\pi r_t i}{l}} \end{aligned}$$

Die letzte Summe verteilt man in zwei Teile, n.l. für t gerade und t ungerade. Nun ist r_{2t} immer quadratischer Rest, und r_{2t+1} quadratischer Nichtrest. Man findet leicht dasz die Summe eine sogenannte GAUS'sche ist, deren Wert

$$l^{1/2} i^{1/4} (l-1)^2$$

Es ergibt sich nun aus (3) dasz die Klassenanzahl H (welche im Ersten Teil dieses Aufsatzes durch h angedeutet ist) $\frac{1}{\alpha}$ Mal dem Producte über $u = 1, 2, \dots, al^{h-1}-1$ von (4) gleich ist. Die weitere Herleitung der Formel für die Klassenanzahl, fällt nun sehr verschieden aus, je nachdem der Relativgrad b gerade oder ungerade ist. Es ist ersichtlich dasz im ersteren Falle der Teilkörper reell ist, und im letzteren imaginär.

1°. Die Klassenanzahl für reelle Teilkörper (b gerade).

Aus Hilfssatz I ergibt sich

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = F\left(e^{\frac{-2k\pi i}{l^h}}\right)$$

Weiter ist:

$$\begin{aligned} \sum_{k=1}^{l^h-1} k F\left(e^{\frac{2k\pi i}{l^h}}\right) &= \sum_{k=1}^{l^h-1} (l^h - k) F\left(e^{\frac{2\pi(l^h-k)i}{l^h}}\right) \\ &= \sum_{k=1}^{l^h-1} l^h F\left(e^{\frac{-2\pi k i}{l^h}}\right) - \sum_{k=1}^{l^h-1} k F\left(e^{\frac{-2\pi k i}{l^h}}\right) \end{aligned}$$

$$= l^h \sum_{k=1}^{l^h-1} F\left(e^{\frac{2\pi ki}{l^h}}\right) - \sum_{k=1}^{l^h-1} k F\left(e^{\frac{2\pi ki}{l^h}}\right)$$

Man findet daher:

$$2 \sum_{k=1}^{l^h-1} k F\left(e^{\frac{2\pi ki}{l^h}}\right) = l^h \sum_{k=1}^{l^h-1} F\left(e^{\frac{2\pi ki}{l^h}}\right).$$

Es ist aber:

$$\begin{aligned} \sum_{k=1}^{l^h-1} F\left(e^{\frac{2\pi ki}{l^h}}\right) &= \sum_{k=1}^{l^h-1} \sum_{n=1}^{l^h-1} \left[\frac{n}{l^h}\right]^{bu} \left(e^{\frac{2\pi kni}{l^h}}\right) \\ &= \sum_{n=1}^{l^h-1} \left[\frac{n}{l^h}\right]^{bu} \sum_{k=1}^{l^h-1} e^{\frac{2\pi kni}{l^h}} \\ &= \sum_{n=1}^{l^h-1} \left[\frac{n}{l^h}\right]^{bu} \cdot -1 = 0 \end{aligned}$$

Also ist:

$$\sum_k k F\left(e^{\frac{2\pi ki}{l^h}}\right) = 0.$$

und:

$$H = \frac{1}{x} H'_u - \frac{1}{l^h} \left[\sum_{k=1}^{l^h-1} F\left(e^{\frac{2\pi ki}{l^h}}\right) \log \frac{e^{\frac{k\pi i}{l^h}} - e^{-\frac{k\pi i}{l^h}}}{i} \right]$$

oder

$$H = \frac{(-1)^{c-1}}{2l^h (al^{h-1}-1)} H'_u \sum_{k=1}^{l^h-1} F\left(e^{\frac{2\pi ki}{l^h}}\right) \log A_k$$

wo:

$$A_k = \frac{e^{\frac{k\pi i}{l^h}} - e^{-\frac{k\pi i}{l^h}}}{i} = i e^{-\frac{k\pi i}{l^h}} \left(1 - e^{\frac{2k\pi i}{l^h}}\right)$$

Das Product zerlegen wir in verschiedene andere Producte:

1. Ueber alle Werte von u die nicht durch l teilbar sind,
2. Ueber alle Werte von u die durch l teilbar sind aber nicht durch l^2

schliesslich über alle Werte von u die durch l^{h-1} teilbar sind.

Fassen wir nun ins Auge die Werte von u welche teilbar sind durch l^h und nicht durch l^{h+1} .

Wegen Hilfssatz III finden wir

$$\sum_{k=1}^{l^h-1} F\left(e^{\frac{2\pi ki}{l^h}}\right) \log A_k = F\left(e^{\frac{2\pi i}{l^{h-h'}}}\right) \sum_k \left[\frac{k/l^{h'}}{l^h}\right]^{-ub} \log A_k$$

wo, in der Summe rechter Hand, k alle Zahlen durchläuft $< l^h$, welche teilbar sind durch $l^{h'}$ aber nicht durch $l^{h'+1}$. Diese Summe verändern wir in eine Summe welche sich über alle Werte von k erstreckt, die nicht durch l teilbar sind. Es sei $k = l^{h'} \cdot k'$, so ist

$$\begin{aligned} A_k &= i e^{-\frac{k\pi i}{l^h}} \left(1 - e^{\frac{2k\pi i}{l^h}}\right) = i e^{-\frac{k\pi i}{l^h}} \left(1 - e^{\frac{2\pi k' i}{l^h}}\right) \left(1 - e^{\frac{2\pi(k' + l^{h-h'}) i}{l^h}}\right) \dots \\ &\dots \left(1 - e^{\frac{2\pi(k' + (l^{h'}-1)l^{h-h'}) i}{l^h}}\right) \\ &= i l^{\frac{h'}{h}} e^{-\frac{\pi k' i}{l^h}} \cdot e^{-\frac{\pi(k' + l^{h-h'}) i}{l^h}} \dots e^{-\frac{\pi(k' + (l^{h'}-1)l^{h-h'}) i}{l^h}} \end{aligned}$$

Hieraus folgt:

$$A_k = A_{k'} \cdot A_{k'+l^{h-h'}} \cdot A_{k'+2l^{h-h'}} \dots A_{k'+(l^{h'}-1)l^{h-h'}}$$

Es ist also:

$$\sum_k \left[\frac{k/l^{h'}}{l^h}\right]^{-bu} \log A_k = \sum_{k'} \left[\frac{k'}{l^h}\right]^{-bu} (\log A_{k'} + \log A_{k'+l^{h-h'}} + \dots + \log A_{k'+(l^{h'}-1)l^{h-h'}})$$

und wegen Hilfssatz II:

$$\begin{aligned} &= \sum_{k'} \left[\frac{k'}{l^h}\right]^{-bu} \log A_{k'} + \sum_{k'} \left[\frac{k'+l^{h-h'}}{l^h}\right]^{-bu} \log A_{k'+l^{h-h'}} + \dots \\ &\dots + \sum_{k'} \left[\frac{k'+(l^{h'}-1)l^{h-h'}}{l^h}\right]^{-bu} \log A_{k'+(l^{h'}-1)l^{h-h'}} \end{aligned}$$

Die ursprüngliche Summe dehnt sich aus über $(l-1)l^{h-h'-1}$ Werte wie man leicht findet. Diese Summe ist nun ersetzt durch $l^{h'}$ andere und kann daher aufgefasst werden als eine Summe über

$$l^{h'} \cdot (l-1) l^{h-h'-1} = (l-1) l^{h-1}$$

Zahlen. Und diese Anzahl ist gleich der Anzahl der Zahlen welche $< l^h$ sind und nicht teilbar durch l . Es sind weiter nicht zwei dieser Zahlen $(\text{mod } l^h)$ mit einander congruent; denn wäre z. b.

$$k' + i l^{h-h'} \equiv k' + j l^{h-h'} (\text{mod } l^h)$$

so würde sich ergeben:

$$i \equiv j (\text{mod } l^{h'})$$

und dies ist unmöglich da i und j beide $< l^{h'}$ sind.

Schliesslich ist also:

$$\sum_k \left[\frac{k/l^{h'}}{l^h} \right]^{-hu} \log A_k = \sum_k \left[\frac{k}{l^h} \right]^{-bu} \log A_k$$

wo, in der Summe rechter Hand, die Zahl k alle Werte durchläuft $< l^h$ welche nicht durch l teilbar sind.

Wir haben nun gefunden:

$$H = \frac{(-1)^{c-1}}{\kappa l^{h(al^{h-1}-1)}} \prod_{u_1} F\left(e^{\frac{2\pi i}{l^h}}\right) \cdot \prod_{u_2} F\left(e^{\frac{2\pi i}{l^{h-1}}}\right) \dots \prod_{u_{1/h}} F\left(e^{\frac{2\pi i}{l}}\right) \times \\ \times \prod_u \sum_k \left[\frac{k}{l^h} \right]^{-bu} \log A_k.$$

Das erste Product erstreckt sich über alle Werte von u die auf der vorletzten Seite unter 1^o genannt sind u. s. w. Fassen wir nun insbesondere das Product ins Auge, welches läuft über alle Werte von u welche teilbar sind durch $l^{h'}$ und nicht durch $l^{h'+1}$. Wir nehmen die Factoren zu zweien und gebrauchen Hilfssatz IV. Dies ist möglich wegen

$$\left[\frac{n}{l^h} \right]^{-bu} = \left[\frac{n}{l^h} \right]^{b(al^{h-1}-u)}$$

und da u und $al^{h-1}-u$ beide zugleich durch $l^{h'}$ teilbar sind. Man findet dann für jedes Factorenpaar: $l^{h+h'}$. Die Factorenzahl wird gleich der halben Anzahl der Zahlen welche $< al^{h-1}$ sind, und die durch $l^{h'}$ teilbar sind. Also

$$\frac{1}{2}(l-1)al^{h-h'-2}$$

Das Product, welches wir ins Auge gefasst haben, hat daher den Wert

$$l^{\frac{1}{2}(h+h')(l-1)al^{h-h'-2}}$$

Für $h' = 0, 1, \dots, h-2$.

Im Falle $h' = h-1$ gibt es $a-1$ Factoren, denn es gibt $a-1$ Zahlen $< al^{h-1}-1$ welche durch l^{h-1} teilbar sind. Der Wert dieses Productes ist also

$$l^{\frac{(2h-1)(a-2)}{2}}$$

Der Endwert aller Producte, wird nun

$$\frac{1}{2} h l-1 al^{h-2} + \frac{1}{2} (h+1)(l-1) al^{h-3} + \dots + \frac{1}{2} (2h-2)(l-1)a + (2h-1) \frac{a-1}{2}$$

$$= l^{\frac{1}{2} h al^{h-1} + \frac{1}{2} a \frac{l^{h-1}-1}{l-1} - h + \frac{1}{2}}$$

und für die Klassenanzahl findet man

$$H = \frac{(-1)^{al^{h-1}-1}}{\frac{1}{2}h al^{h-1} - \frac{1}{2}a \frac{l^{h-1}-1}{l-1} - \frac{1}{2}} - \prod'_{u=1}^{lh} \left[\frac{k}{l^h} \right]^{bu} \log A_k$$

Für jeden Körper gilt¹⁾:

$$\frac{1}{\kappa} = \frac{w|\sqrt{D}|}{2r_1+r_2\pi r_2R}$$

In unserem Falle ist $w=2$, denn der Körper ist reell und es sind daher ± 1 die einzigen Einheitswurzeln welche sich im Körper vorfinden. $r_2=0$, $r_1=al^{h-1}$. Die Discriminante D ist bestimmt in Theorem 5. R ist der Regulator. Man findet, indem man dieses alles substituirt, dass die Potenz von l verschwindet und

$$H = \frac{(-1)^{al^{h-1}-1}}{2al^{h-1}-1} \cdot \frac{\prod_{u=1}^{lh} \sum_{k=1}^{lh} \left[\frac{k}{l^h} \right]^{bu} \log A_k}{R} \quad (7)$$

Das Product ist gleich einer Determinante, welche man findet durch ein bekanntes Theorem der Norm einer Algebraischen Zahl²⁾:

$$\sum_k \left[\frac{k}{l^h} \right]^{bu} \log A_k = \sum e^{\frac{2\pi bu \text{ind } k}{l^{h-1}(l-1)}} \log A_k$$

wo k alle Zahlen durchläuft $< l^h$ und die nicht durch l teilbar sind. Es nimmt also $\text{ind } k$ alle Werte an von 1 bis $\varphi(l^h)$. Setzen wir also $\text{ind } k = t$, so ist $rt \equiv k \pmod{l^h}$.

Die letzte Summe nimmt daher folgende Form an:

$$\begin{aligned} & \sum_{t=1}^{\varphi(l^h)} e^{\frac{2\pi buti}{l^{h-1}(l-1)}} \log A_{rt} = \sum_{t=1}^{\varphi(l^h)} e^{\frac{2\pi uti}{al^{h-1}}} \log A_{rt} \\ & = \sum_{t=1}^{al^{h-1}} + \sum_{t=al^{h-1}+1}^{2al^{h-1}} + \dots + \sum_{t=(b-1)al^{h-1}+1}^{bal^{h-1}} \\ & = \sum_{t=1}^{al^{h-1}} + \sum_{t=1}^{al^{h-1}} e^{\frac{2\pi uti}{al^{h-1}}} \log A_{rt+al^{h-1}} + \dots + \sum_{t=1}^{al^{h-1}} e^{\frac{2\pi uti}{al^{h-1}}} \log A_{rt+(b-1)al^{h-1}} \\ & = \sum_{t=1}^{al^{h-1}} e^{\frac{2\pi uti}{al^{h-1}}} \log A_{rt} \cdot A_{rt+al^{h-1}} \dots A_{rt+(b-1)al^{h-1}} \end{aligned}$$

¹⁾ H. Seite 229.

²⁾ BALTZER. Th. u. Anw. der Determinanten. S. 98.

Es sei jetzt:

$$A_t = e^{\frac{\pi i}{l^h} (r^t + \dots + r^{t+(b-1)al^{h-1}})} i^b (1-Z^{r^t})(1-Z^{r^t+al^{h-1}}) \dots (1-Z^{r^t+(b-1)al^{h-1}})$$

$$= i^b \cdot e^{\pi i \cdot r^t \cdot g} \cdot (1-Z^{r^t})(1-Z^{r^t+al^{h-1}}) \dots (1-Z^{r^t+(b-1)al^{h-1}}).$$

So ist: (wo g eine ganze Zahl bedeutet)

$$\prod_{u=1}^{al^{h-1}-1} \sum_{t=1}^{al^{h-1}} e^{\frac{2\pi u t i}{al^{h-1}}} \log A_t = \prod_{u=1}^{al^{h-1}-1} e^{\frac{2\pi u i}{al^{h-1}}} \sum_{t=1}^{al^{h-1}} e^{\frac{2\pi u (t-1) i}{al^{h-1}}} \log A_t =$$

$$= \frac{e^{\frac{2\pi i}{al^{h-1}} (1+2+\dots+al^{h-1}-1)}}{\log A_1 + \dots + \log A_{al^{h-1}}} \begin{vmatrix} \log A_1 & \log A_2 & \dots & \log A_{al^{h-1}} \\ \log A_{al^{h-1}} & \log A_1 & \dots & \log A_{al^{h-1}-1} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \log A_2 & \log A_3 & \dots & \log A_1 \end{vmatrix}.$$

Man kan diese Determinante auf folgende Weise umformen. Von den Elementen einer jeden Colonne werden die entsprechenden Elemente der vorangehenden Colonne subtrahirt, wobei man mit der vorletzten anfängt, und schliesslich von den Elementen der ersten Colonne die entsprechenden Elemente der letzten Colonne subtrahirt. Jetzt addirt man die entsprechenden Elemente einer jeden Zeile zu denen der letzten. Alle Elemente dieser letzten Zeile verschwinden dann, ausgenommen das letzte, welches folgenden Wert annimmt:

$$\log A_1 + \log A_2 + \dots + \log A_{al^{h-1}}.$$

Dies ist auch der Factor der sich im Nenner des Bruches vor der Determinante findet. Er fällt also hinweg. Die Elemente der Determinante haben nun folgende Form erhalten:

$$\log \frac{A_t}{A_{t-1}} = \log e^{\frac{\pi i}{l^h} (r^t + r^{t+c} + \dots + r^{t+(b-1)c} - (r^{t-1} + \dots))} \times$$

$$\times \frac{(1-Z^{r^t})(1-Z^{r^t+c}) \dots (1-Z^{r^t+(b-1)c})}{(1-Z^{r^{t-1}}) \dots (1-Z^{r^{t-1}+(b-1)c})}$$

Man findet leicht dass der Exponent von e gleich

$$(r^t - r^{t-1}) \frac{(1 + r^{al^{h-1}} + \dots + r^{(b-1)al^{h-1}})}{l^h}$$

wird, also eine gerade ganze Zahl ist. Hieraus folgt:

$$\log \frac{A_t}{A_{t-1}} = \log \frac{(1-Z^{r^t})(1-Z^{r^t+c}) \dots (1-Z^{r^t+(b-1)c})}{(1-Z^{r^{t-1}}) \dots (1-Z^{r^{t-1}+(b-1)c})} = \log \epsilon_t$$

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Die Factoren 2, welche sich vor dem Producte aus (7) vorfinden, bringen wir in die Elemente der Determinante. Diese werden dann $\log \varepsilon_i$ anstatt $\log \varepsilon_i^2$ wie sie bis jetzt waren. Nachdem man noch Zeilen verwechselt hat, findet man die ganze, im Theorem dargestellte Form.

2. Die Klassenanzahl für imaginäre Teilkörper (b ungerade).

Der Hülfsatz I ergibt, in diesem Falle

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = (-1)^u F\left(e^{-\frac{2k\pi i}{l^h}}\right)$$

Wir zerlegen das Product, welches von (4) genommen werden muss, in zwei Factoren: 1. das Product über alle geraden Werte von u ; 2. das Product über alle ungeraden Werte von u .

Das erstgenannte Product kann man auf dieselbe Art umformen wie im Falle dass b gerade ist, wegen

$$F\left(e^{\frac{2k\pi i}{l^h}}\right) = F\left(e^{-\frac{2k\pi i}{l^h}}\right)$$

Für dieses Product findet man daher

$$\leq \prod_{u \text{ gerade}} a^{l^{h-1}-1} - \frac{1}{l^h} \sum_{k=1}^{l^{h-1}} F\left(e^{\frac{2k\pi i}{l^h}}\right) \log A_k$$

Fassen wir nun weiter das zweite Product ins Auge. Es ist, ebenso wie früher schon gefunden ist:

$$\sum_{k=1}^{l^{h-1}} F\left(e^{\frac{2k\pi i}{l^h}}\right) = 0$$

und weiter:

$$\begin{aligned} \sum_{k=1}^{l^{h-1}} F\left(e^{\frac{k\pi i}{l^h}}\right) \log A_k &= \sum_{k=1}^{l^{h-1}} F\left(e^{\frac{2(l^{h-1}-k)\pi i}{l^h}}\right) \log A_{l^{h-1}-k} = \\ &= \sum_{k=1}^{l^{h-1}} F\left(e^{-\frac{2k\pi i}{l^h}}\right) \log A_k = - \sum_{k=1}^{l^{h-1}} F\left(e^{\frac{2k\pi i}{l^h}}\right) \log A_k \end{aligned}$$

Hieraus ergibt sich dass diese Summe verschwindet. Wir finden daher für das Product:

$$\leq \prod_{u \text{ ungerade}} a^{l^{h-1}-1} + \frac{\pi i}{l^h} \sum_{k=1}^{l^{h-1}} k F\left(e^{\frac{2k\pi i}{l^h}}\right).$$

Um die Zahl $\frac{1}{\pi}$ zu bestimmen bemerken wir dass der Körper

imaginär ist. Und da es ein GALOIS'scher Körper ist, sind alle conjugirte Körper imaginär, d.h. $r_1 = 0$, $r_2 = \frac{1}{2}al^{h-1}$. Wiederum ist $w = 2$ (als $b \neq 1$ ist). Wir finden, nachdem die Werte substituirt sind:

$$H = \frac{|\sqrt{D}| \cdot \prod_{u \text{ ungerade}} \frac{\pi i}{l^{2h}} \sum_k k F\left(e^{\frac{2\pi ki}{l^h}}\right)}{2^{\frac{1}{2}} al^{h-1} - 1 \cdot \pi^{\frac{1}{2}} al^{h-1}} \cdot \frac{\prod_{u \text{ gerade}} \frac{1}{l^h} \sum_k F\left(e^{\frac{2\pi ki}{l^h}}\right) \log A_k}{R}. \quad (8)$$

Die Factoren der beiden Producten werden auf dieselbe Art umgeformt wie für b gerade. Im ersten Product erscheinen dann die Factoren

$$S = \sum_k \left[\frac{k/l^{h'}}{l^h} \right]^{-bu} k$$

wo u teilbar ist durch $l^{h'}$ und nicht durch $l^{h'+1}$ und die Summe erstreckt sich über alle Werte von k die teilbar sind durch $l^{h'}$ und nicht durch $l^{h'+1}$. Die Summe S formen wir auf folgende Weise um:

$$\begin{aligned} S = l^{h'} \sum_k \left[\frac{k/l^{h'}}{l^h} \right]^{-bu} \frac{k}{l^{h'}} &= \sum_k \left[\frac{k/l^{h'}}{l^h} \right]^{-bu} \frac{k}{l^{h'}} + \sum_k \left[\frac{k/l^{h'}}{l^h} \right]^{-bu} \left(\frac{k}{l^{h'+1}} + l^{h-h'} \right) + \dots + \\ &+ \sum_k \left[\frac{k/l^{h'} + (b^{h'} - 1)l^{h-h'}}{l^h} \right]^{-bu} \left(\frac{k}{l^{h'}} + (l^{h'} - 1)l^{h-h'} \right) - \\ &- \{l^{h-h'} + 2l^{h-h'} + \dots + (l^{h'} - 1)l^{h-h'}\} \sum_k \left[\frac{k/l^{h'}}{l^h} \right]^{-bu} \end{aligned}$$

Uebrigens ist

$$\sum_k \left[\frac{k/l^{h'}}{l^h} \right]^{-bu} = 0$$

da es die Summe aller $(l-1)l^{h-h'-1}$ -ten Einheitswurzeln ist, multipliziert mit einer ganzen Zahl.

Weiter sind nicht zwei der Zahlen $k/l^{h'} - i l^{h-1} \pmod{l^h}$ mit einander congruent. Keine dieser Zahlen ist teilbar durch l und ihre Anzahl ist gleich $\varphi(l^h)$. Man findet also

$$\sum_k k \left[\frac{k/l^{h'}}{l^h} \right]^{-bu} = \sum_k k \left[\frac{k}{l^h} \right]^{-bu}$$

wo in der letzten Summe die Zahl k sich erstreckt über alle Werte $< l^h$ welche nicht durch l teilbar sind.

Nach Umformung aller Factoren findet man sodann, wenn man bemerkt das a gerade ist und dasz das erste Product $\frac{1}{2} al^{h-1}$ Factoren enthält und das zweite $\frac{1}{2} al^{h-1} - 1$:

$$H = \frac{(-1)^r i^b \cdot \prod_{u \text{ ungerade}} \sum_{k=1}^{l^h-1} \left[\frac{k}{l^h} \right]^{bu} k}{2^{\frac{1}{2}} al^{h-1} - 1 \cdot l^{\frac{1}{2}} al^{h-1}} \cdot \frac{\prod_{u \text{ gerade}} \sum_{k=1}^{l^h-1} \left[\frac{k}{l^h} \right]^{bu} \log A_k}{R}$$

Die im ersten Factor auftretenden Summen kan man auf folgende Weise umformen :

$$S = \sum_{k=1}^{l^h} \left[\frac{k}{l^h} \right]^{bu} = \sum_k e^{\frac{2\pi bu \text{ ind } ki}{l^{h-1}(l-1)}}_k$$

Es sei $\text{ind } k = t$ so ist $k \equiv r^t \equiv r_t \pmod{l^h}$ wo r_t den kleinsten positiven Rest bedeutet von $r^t \pmod{l^h}$. Dann wird

$$S = \sum_{k=1}^{l^{h-1}(l-1)} e^{\frac{2\pi uti}{al^{h-1}}} r_t$$

Wenn man diese Summe verteilt in andere die sich erstrecken von $k=1$ bis $k=al^{h-1}$, so ergibt sich :

$$S = \sum_{t=1}^{al^{h-1}} e^{\frac{2\pi uti}{al^{h-1}}} \sum_{j=0}^{b-1} r_{t+j} al^{h-1}$$

Es ist leicht ersichtlich dasz die Summe \sum_j fur jeden Wert von t teilbar ist durch l^h .

Die Summe des zweiten Productes lasst sich wie folgt umformen :

$$\begin{aligned} \sum_{k=1}^{l^h-1} \left[\frac{k}{l^h} \right]^{bu} \log A_k &= \sum e^{\frac{2\pi ui \text{ ind } k}{al^{h-1}}} \log A_k = \\ &= \sum_{t=1}^{\varphi(l^h)} e^{\frac{2\pi uti}{al^{h-1}}} \log A_{r^t} = \sum_{t=1}^{al^{h-1}} e^{\frac{2\pi uti}{al^{h-1}}} \log A_t = \\ &= \sum_{t=1}^{\frac{1}{2}al^{h-1}} + \sum_{t=\frac{1}{2}al^{h-1}+1}^{al^{h-1}} = \sum_{t=1}^{\frac{1}{2}al^{h-1}} e^{\frac{2\pi uti}{al^{h-1}}} \log A_t + \sum_{t=1}^{\frac{1}{2}al^{h-1}} e^{\frac{2\pi uti}{al^{h-1}}} \log A_{t+\frac{1}{2}al^{h-1}} \end{aligned}$$

(weil u gerade ist)

$$= \sum_{t=1}^{\frac{1}{2}al^{h-1}} e^{\frac{2\pi uti}{al^{h-1}}} \log A_t A_{t+\frac{1}{2}al^{h-1}}$$

Auf gleiche Weise, wie im Falle dasz b gerade ist, kann man diese Summe in eine Determinante verwandeln. Wenn man dann die Factoren 2 des Nenners aus (8) in die Elemente der Determinante hinein bringt, so findet man die im Theorem aufgegebene Determinante. Man muss nun noch die Potenzen von -1 beachten, und von i , die entstehen bei der Benutzung des Hulfssatzes IV.

Wenn wir schliesslich noch ein System reeller Grundeinheiten nehmen, so ist

$$\log \eta_i^{(k)} = \frac{1}{2} l_k \cdot (\eta_i)^{1)}$$

Wir müssen also in R substituieren $l_k(\eta_i) = 2 \log \eta_i^{(k)}$ wonach die Potenz von 2 im Nenner verschwindet.

¹⁾ H. Seite 215.

Mathematics. — “Ueber die Teilkörper des Kreiskörpers $k\left(e^{\frac{2\pi i}{l^h}}\right)$.”
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by Prof. W. KAPTEYN).

(Communicated in the meeting of November 1918).

Der Ausdruck für die Klassenanzahl der primären Teilkörper hat die Form eines Productes zweier Brüche, wenn b eine ungerade Zahl ist. Ebenso wie es der Fall ist mit der Klassenanzahl des Kreiskörpers der l^h -ten Einheitswurzeln selbst, sind auch hier die zwei Brüche ganze Zahlen. Ich will dies hier beweisen, und nenne dabei die Brüche den ersten, resp. zweiten, Factor der Klassenanzahl.

Zuerst beweise ich einen Hilfssatz.

Hilfssatz 1.

Jedes System von Grundeinheiten eines primären Teilkörpers, in Bezug auf welches der Kreiskörper selbst den Relativgrad $2b$ hat, ist auch ein System von Grundeinheiten des primären Teilkörpers, in Bezug auf welches der Kreiskörper selbst den Relativgrad b hat, wenn b eine ungerade Zahl ist.

Beweis:

Wir nennen den ersten Teilkörper k und den zweiten K . Es ist dann k ein Teilkörper von K . Der Grad von K ist c ; der von k ist dann $\frac{1}{2}c$ und $bc = \varphi(l^h - 1)$. Wir zeigen erst dasz k in K zu der Substitution

$$s^{1/2bc}, \text{ wo } s = (Z : Z'), \text{ gehört.}$$

(r eine primitive Wurzel von l^h).

Die, den Körper K erzeugende, Zahl ist:

$$\eta_K = Z^{r^c} + Z^{r^{2c}} + \dots + Z^{r^{bc}}$$

Also ist

$$s^{1/2bc} \eta_K = Z^{r^{c+1/2bc}} + Z^{r^{2c+1/2bc}} + \dots + Z^{r^{bc+1/2bc}} \dots \quad (1)$$

Nach einer kleinen Rechnung ergibt sich:

$$s^{1/2bc} \eta_K = Z^{r^{1/2c}} + Z^{r^{3/2c}} + \dots + Z^{r^{(2b-1)/2c}}$$

Die, den Körper k erzeugende, Zahl ist:

$$\eta_k = Z^{r^{1/2c}} + Z^{r^{3/2c}} + \dots + Z^{r^{(2b-1)/2c}}$$

¹⁾ Fortsetzung von „Procéedings“ XXI Seite 454 und Seite 758.

Man schlieszt hieraus dasz die Gleichheit

$$E = -s^{1/2bc} E$$

nicht bestehen kann. Dann musz aber

$$E = s^{1/2bc} E.$$

E ist daher eine Einheit des Körpers k .

Satz 1.

Der zweite Factor der Klassenanzahl von K stellt die Klassenanzahl des Körpers k dar, und ist also eine ganze Zahl.

Beweis: Aus Satz 6 (S. 461) ergibt sich dasz die Δ der beiden Körper einander gleich sind.¹⁾ Aus dem Hülfsatz folgt dasz auch $R = R'$.

Satz 2.

Der erste Factor der Klassenanzahl von K ist eine ganze Zahl.

Beweis: Es ist leicht ersichtlich dasz

$$r_t + r_{t+c} + \dots + r_{t+(b-1)c}$$

teilbar ist durch l^h . Man braucht daher nur noch zu zeigen dasz

$$\prod_{u=1}^c e^{\frac{2\pi u t i}{c}} (r_t + r_{t+c} + \dots + r_{t+(b-1)c})$$

teilbar ist durch $2^{1/2c-1}$. Die Summe teilen wir in zwei Partialsummen:

$$\sum_{t=1}^{1/2c} e^{n \frac{2\pi u t i}{c}} + \sum_{t=1/2c+1}^c e^{n \frac{2\pi u t i}{c}}$$

Für die letzte kann man schreiben:

$$\sum_{t=1}^{1/2c} e^{\frac{2\pi u (t+1/2c) i}{c}} (r_{t+1/2c} + r_{t+3/2c} + \dots + r_{t+(b-1/2)c})$$

Es ist aber:

$$r_{t+n} \equiv r_{t+n} \equiv -r_{t+n \pm 1/2bc} \equiv -r_{t+n \pm 1/2bc} \pmod{l^h}$$

und daher:

$$r_{t+n} = l^h - r_{t+n \pm 1/2bc}.$$

Nach einer kleinen Rechnung findet man dasz die in der letzten Summe auftretende Form zwischen () gleich

$$b \cdot l^h - (r_t + r_{t+c} \dots r_{t+(b-1)c})$$

¹⁾ Im Satz 6 musz, im Falle b ungerade, vor den ersten Factor der Klassenanzahl, $(-1)^{1/2a}$ gesetzt werden. Vor der Determinante soll nicht $(-1)^{1/8(a-2)(a-4)}$ stehen, sondern $(-1)^{1/8(c-4)(c-6)}$.

ist. Da u ungerade ist, ergibt sich nun für die im Producte auftretende Summe:

$$2 \sum_{t=1}^{1/2c} e^{\frac{2\pi u t i}{c}} (r_t + r_{t+c} + \dots + r_{t+(b-1)c}) + 2b \cdot l^h \sum_{t=1}^{1/2c} e^{\frac{2\pi u t i}{c}}$$

Es ist also, nachdem man die letztere dieser beiden Summen berechnet hat:

$$(1 - e^{\frac{-2\pi u i}{c}}) \sum_{t=1}^c e^{\frac{2\pi u t i}{c}} (r_t + r_{t+c} + \dots + r_{t+(b-1)c}) =$$

$$= 2 \left\{ b \cdot l^h + \sum_{t=1}^{1/2c} e^{\frac{2\pi u t i}{c}} (r_t + \dots + r_{t+(b-1)c}) \right\}$$

Met Rücksicht auf die Beziehung

$$\prod_u (1 - e^{\frac{-2\pi u i}{c}}) = 2$$

findet man dasz das Product, welches im Zähler des ersten Factors der Klassenanzahl auftritt, teilbar ist durch $2^{1/2c-1}$.

Man kann den Beweis dieses Satzes auch erbringen auf die nämliche Art wie KUMMER und KRONECKER bewiesen haben dasz der erste Factor der Klassenanzahl eines jeden Kreiskörpers (der m -ten Einheitswurzeln) eine ganze Zahl ist, oder ein Bruch mit Nenner gleich 2. ¹⁾

Verzeichnis einiger Werte des
ersten Factors der Klassenanzahl.

l	h	b	erster Factor.
7	1	3	1
7	2	3	1
11	1	5	1
13	1	3	1
19	1	3	1
23	1	11	3
29	1	7	1
31	1	15	3
37	1	9	1
37	1	3	1
47	1	23	5

¹⁾ Monatsber. Berlin 1863 und Crelle's Journ. Band 40.

Satz 3.

Der erste Factor der Klassenanzahl des Teilkörpers, für welchen die Zahl b ungerade ist, ist ein Teiler der Klassenanzahl des Kreiskörpers (der l^h -ten Einheitswurzeln) selbst.

Beweis: Der erste Factor der Klassenanzahl des Kreiskörpers selbst, ist: ¹⁾

$$\frac{\prod_u \sum_{t=1}^{l^{h-1}(l-1)} e^{\frac{2\pi u t i}{l^{h-1}(l-1)}} r_t}{2^{1/2} \varphi - 1 l^{h(1/2\varphi-1)}}.$$

wo, zur Abkürzung φ den Wert der Function $\varphi(l^h)$ vorstellt, und das Product sich erstreckt über alle Zahlen $1, 3, \dots, \varphi-1$. Man weisz dasz der Bruch einer ganzen Zahl gleich ist. Die im Zähler auftretende Summe bringen wir in die folgende Form

$$\sum_{t=1}^c \left\{ e^{\frac{2\pi u t i}{\varphi}} r_t + e^{\frac{2\pi u(t+c)i}{\varphi}} r_{t+c} + \dots + e^{\frac{2\pi u(t+(b-1)c)i}{\varphi}} r_{t+(b-1)c} \right\}$$

Für die Werte

$$u = bu' \quad u' = 1, 3, \dots, c-1$$

hat diese Summe denselben Wert wie die Summe welche auftritt im Zähler des ersten Factors der Klassenanzahl des Teilkörpers des Relativgrades b . Der letztgenannte Zähler ist daher ein Teiler des Zählers des Kreiskörpers selbst. Der Quotient der beiden ersten Factoren der Klassenanzahlen ist nun

$$\frac{1}{2^{1/2} \varphi - 1/2^c l^{h(1/2\varphi-1/2^c-1)}} \prod_u \sum_{t=1}^{\varphi} e^{\frac{2\pi u t i}{\varphi}} r_t \dots \dots \dots (3)$$

wo u alle ungeraden Zahlen $1, 3, \dots, \varphi-1$ durchläuft die nicht durch b teilbar sind. Es ist weiter:

$$(re \quad \varphi \quad -1) \sum_{t=1}^{\varphi} e^{\frac{2\pi u t i}{\varphi}} r_t = \sum_{t=1}^{\varphi} e^{\frac{2\pi u(t+1)i}{\varphi}} (rr_t - r_{t+1})$$

und $rr_t - r_{t+1} \equiv 0 \pmod{l^h}$.

Auch ist:

$$\prod_u (re \quad \varphi \quad -1) = \frac{\prod_u (re \quad \varphi \quad -1)}{\prod_{u'} (re \quad \varphi \quad -1)} = \frac{r^{\frac{1}{2}\varphi} + 1}{r^{\frac{1}{2}c} + 1}$$

¹⁾ H. Satz 141.

wo, im ersten Product, u alle Werte $1, 3, \dots, p-1$ durchläuft die nicht durch b teilbar sind; im zweiten Product aber, durchläuft u alle Zahlen $1, 3, \dots, p-1$. Der Zähler des letzten Bruches ist teilbar durch l^h ; der Nenner nicht. Man kann die primitive Wurzel r so wählen dasz der Zähler nicht teilbar ist durch l^{h-1} . Hieraus ergibt sich dasz der Zähler aus (3) durch die Potenz von l teilbar ist, die sich im Nenner von (3) vorfindet.

Auf dieselbe Art wie beim Beweise des vorigen Satzes kann man beweisen dasz der Zähler von (3) teilbar ist durch die Potenz von 2 die sich im Nenner vorfindet.

Auf ganz gleiche Art kann man den Satz beweisen:

Wenn ein Teilkörper k Teilkörper ist eines Teilkörpers K , so ist der erste Factor der Klassenanzahl von k ein Teiler des ersten Factors von K . (Der Relativgrad b ist für beide Körper also ungerade anzunehmen).
