Physics. — *"On the Course of the Values of a and b for Hydrogen at Different Temperatures and Volumes"*. II. By Dr. J. J. van Laar. (Communicated by Prof. H. A. Lorentz).

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IX. Influence of the field of force according to Boltzmann.

When we substitute the value

$$dN = 4\pi \, r^2 \, dr \times e^{-\vartheta P_r} \times \tau \times n$$

in the general Virial formula

$$pv = RT - \tfrac{1}{3} \, \Sigma \, r f(r) = RT - \tfrac{1}{6} \, N \int dN \; r \frac{dP_r}{dr}$$

for dN, the number of molecules in the spherical shell between r and $r + dr$ round the molecule under consideration, then pv becomes:

$$pv = RT - \tfrac{2}{3} \, \pi \, Nn \int_s^{r_a} \tau r^3 \frac{dP_r}{dr} e^{-\vartheta P_r} \, dr.$$

In this P_r represents, therefore, the function of force in the points at a distance r from the centre of the considered molecule (thought spherical); so that $f(r) = dP_r : dr$. The integration extends from $r = s$ (the distance of the centres of two molecules — thought incompressible at the collision, so that s represents the diameter of the molecule) as far as the field of force extends outside the molecule ($r = r_a$).

The factor $e^{-\vartheta P_r}$ is the well-known Boltzmann *temperature* "distribution factor" under the influence of the field of force. The parameter ϑ is $= N : RT$, in which N represents the total number of molecules in the volume v, so that $N = nv$, when n represents the number of molecules in the unit of volume.

The other factor τ is the *volume* distribution factor. For $r = s$ (at collision) $\tau_s =$ will be $= \dfrac{b}{b_g} \dfrac{v}{v-b}$ (see further below), which will approach to 1 for $v = \infty$, as this fictitious quantity b then becomes $= b_g$. For $r = \infty$ τ is $= 1$ for all values of v. But already at a short distance from the considered molecule τ can be put $= 1$.

Let us at first only consider the exceedingly rarefied gas state — i. e. the planetary condition of matter — then $\tau = 1$ everywhere, so that we may write:[1])

$$pv = RT - \tfrac{4}{3}\,\pi\,Nn\,s^3\int_{s-\delta}^{s}\frac{dP_r}{dr}\,e^{-\theta P_r}\,dr - \tfrac{2}{3}\,\pi\,Nn\,r_1^3\int_{s}^{r_a}\frac{dP_r}{dr}\,e^{-\theta P_i}\,dr, \quad (a)$$

in which we assume that at the *collision* the distance of the molecules remains $= s$ (no appreciable compression), and that also the *attraction* extends only to a small distance from s, so that a mean value r_1^3 can be brought as a constant factor before the integration sign.

In this r_a is in any case to be supposed *greater* than s. For if this were not so, and if the attraction only worked at an exceedingly short distance $s + \delta$ just before the collision, as is still sometimes supposed, the virial of attraction would, for smaller volumes, be subjected to the *same* volume distribution factor τ_s as the virial of collision — with the consequence that the equation of state would not contain *two* distinct constants a and b, but only one, and would assume the form $p(v-\beta) = RT$.

Critical phenomena — which can be explained theoretically justly by the different behaviour of the two separate virial parts, in this way that the factor τ will have no or hardly any influence on the virial of attraction for smaller volumes (as the middle value τ_1 can then always be assumed to be near 1), whereas it will exert a great influence on the virial of collision (for $v = v_k$, where $v = 3$ or 2 times b, τ_s will already have a value between 1,5 and 2) — these phenomena would *entirely fail* to appear. For then there is no distinction possible at all between the two constants a and b, on account of which the equation of state can be brought in the well-known form $(p + {}^a/_{v^2})(v-b) = RT$ (see also further below).

It is, therefore, almost *completely excluded* that the attraction should not take place until at immediate (or almost immediate) contact of the molecules. For *very small* volumes (smaller than the critical volume), where the centres of the molecules possess e.g. a mean smaller distance (l) than r_a, it may be expected that also the virial of attraction will be somewhat influenced by the factor τ, so that a becomes dependent on v. But then we are already past the critical point — where $l = s \sqrt[3]{4} = 1,6\,s.$ $(r_a$ will appear to be not much greater than about 1,6 s). Hence the quantity a would

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[1]) Cf. also my Article in the Arch. Teyler (2) T VII, Troisième partie, 1901; chiefly chapter X, p. 28—34.

then be able to increase with decreasing v, but on the other hand the value of a can also decrease in consequence of absorption of the lines of force, when v becomes smaller.

X. The Virial of Attraction.

Let us first determine the value of the virial of attraction.

For $r = s$ P, will evidently be $= -M$, the (negative) maximum value of the force function. For $f(r)$ is taken so in the virial formula that attraction becomes *positive*. If e.g. $P_r = -c : r^q$, then $f(r)$ becomes $= dP_r : dr = qc : r^{q+1}$, hence properly positive. Further $P_r = 0$ for $r = r_a$, where the attraction stops or becomes imperceptible, so that the second integral yields:

$$\left(-\frac{e^{-\theta P_r}}{\theta} \right)_{-M}^{0} = \frac{e^{\theta M} - 1}{\theta} = \frac{RT}{N}\left(e^{\frac{MN}{RT}} - 1 \right)$$

And as $N \times \frac{2}{3}\pi s^3$ is evidently $= N \times 4m = (b_q)_\infty$ ($m =$ volume molecule; the index g refers to infinitely large volume; the index ∞ to infinitely high temperature), we may write $(b_q)_\infty \times \left(\frac{r_1}{s} \right)^3 = v\,(b_g)_\infty$ for $N \times \frac{2}{3}\pi r_1^3$, and the value of the virial of attraction, as $n : N = 1 : v$, becomes:

$$V_a = -\frac{v\,(b_q)_\infty}{v} RT\left(e^{\frac{MN}{RT}} - 1 \right).$$

Let us now put

$$v\,(b_q)_\infty\, RT\left(e^{\frac{MN}{RT}} - 1 \right) = a, \qquad \ldots \ldots (\alpha)$$

then for $T = \infty$:

$$a_\infty = v\,(b_q)_\infty\, RT\left(\frac{MN}{RT} + \frac{1}{2}\left(\frac{MN}{RT}\right)^2 + \ldots \right) = v\,(b_q)_\infty.\,MN. \ldots (\beta)$$

Hence, when we put $MN = \alpha$, we get:

$$a = a_\infty \times \frac{e^{\alpha/RT} - 1}{\alpha/RT} = a_\infty \times f(\alpha), \qquad \ldots \ldots (1)$$

and

$$V_a = -\frac{a}{v} \qquad \ldots \ldots \ldots \ldots (2)$$

The quantity α is therefore determined by

$$\alpha = MN = \frac{a_\infty}{v\,(b_g)_\infty}. \qquad \ldots \ldots \ldots (3)$$

We shall presently consider the temperature function $f(a)$ in the quantity a somewhat more fully.

It may only be remarked already here, that when we generally put the integral of work:

$$\int_s^{r_a} \frac{d\,(NP_r)}{dr}\, e^{-\theta P_r}\, dr = RT\,(e^{\alpha/RT} - 1) = \Sigma\ , \quad \ldots \quad (\gamma)$$

$f(a)$ may be represented by

$$f(a) = \frac{\Sigma}{\alpha} \quad \ldots \ldots \ldots \ldots \quad (4)$$

It is easy to see that (4) will hold generally, whatever be the form of the factor of distribution, provided this be only such a function of θP_r, that it becomes $= 1$ for $P_r = 0$. a_∞ will then always be $= v\,(b_q)_\infty\,\alpha$.

In the special case that the factor should be $constant = 1$, Σ becomes simply $= (NP_i)_s^{r_a} = 0 - (N \times - M_i) = MN = a$. $f(a)$ then also becomes $= 1$, so that the quantity a becomes independent of the temperature.

XI. The Virial of Collision.

Here P_r will assume the value $+ \infty$ for $r = s - \delta$ — at least when the molecule is supposed t obe incompressible — whereas P_r for $r = s$ will evidently again have the value $- M$. This makes the first integral indicated in the expression (a) for pv:

$$\left(- \frac{e^{-\theta P_r}}{\theta}\right)_\infty^{-M} = - \frac{e^{\theta M}}{\theta} = - \frac{RT}{N}\, e^{\alpha/RT},$$

and we find for the virial of repulsion $(n : N$ is again $v)$:

$$V_b = \frac{(b_q)_\infty}{v}\, RT\, e^{\alpha/RT}.$$

Let us then put:

$$(b_g)_\infty \times e^{\alpha/RT} = b_g, \quad \ldots \ldots \ldots \quad (d)$$

then b_g becomes:

$$b_g = (b_g)_\infty \times e^{\alpha/RT} = (b_g)_\infty \times f(b)\ , \quad \ldots \ldots \quad (5)$$

and

$$V_b = RT\frac{b_q}{v}\ . \quad \ldots \ldots \ldots \ldots \quad (6)$$

The temperature function $f(b)$ can evidently generally be represented by the equation

$$f(b) = 1 + \frac{\Sigma}{RT} \qquad \cdots \cdots \quad (7)$$

We now get instead of (a), in relation with (2) and (3):

$$pv = RT + RT\frac{b_q}{v} - \frac{a}{v} = RT + \frac{RT\,b_q - a}{v} = RT + \frac{B}{v}, \quad \cdot \quad (8)$$

in which b_g and a are given by (5) and (1) as functions of the temperature. B represents the so-called "second" virial coefficient, when — as we have supposed — v is $= \infty$ (very great). Otherwise B is still a function of v (through the volume distribution factor τ), and instead of $B : v$ can be written $(B : v) + (C : v^2) +$ etc., in which B, C, etc. are still only functions of the temperature.

When we neglect the possible influence of v on the quantity a — hence when we do not take the volume too small — only the influence of the factor τ_s at the collision remains. When we write for this (see also § 9):

$$\tau_s = \frac{b}{b_q}\frac{v}{v - b}, \qquad \cdots \cdots \quad (9)$$

then b_q in (8) becomes $b_q \times \tau_s$, and we may write:

$$pv = RT\left(1 + \frac{b}{v - b}\right) - \frac{a}{v} = RT\frac{v}{v - b} - \frac{a}{v},$$

i.e.

$$p + \frac{a}{v^2} = \frac{RT}{v - b}, \qquad \cdots \cdots \quad (10)$$

through which Van der Waals' well-known separation of the two constants a and b has been brought about. We repeat once more that this was, therefore, only possible by this, that only for b_q a volume distribution factor with $v : v - b$ appears, and *not* for a, after which the factor RT in the virial of collision can be united with the principal term RT.

We should, however, never forget that the quantity b thus introduced for $v - b$ is an entirely *fictitious* b, and is in no *direct* relation with the real quantity $b_q = (b_g)_\infty \times f(b)$. For b follows namely from (9):

$$b = b_g \times \frac{\tau_s}{1 + \tau_s \frac{b_g}{v}}, \qquad \cdots \cdots \quad (9a)$$

so that b can only be expressed in b_q, when τ_s is known in *another*, *independent* way as function of v, which has not yet

succeeded as yet. For $v = \infty$, however, τ_s is always $= 1$, and b becomes b_g, while for $v = b$, where $\tau_s = \infty$, b is $= v = v_0$. Hence the fictitious quantity b will lie between b_g and v_0, i.e. between

$$(b_g)_\infty \times f(b) = N \times 4\,m \times f(b) \quad \text{for} \quad v = \infty, \quad \text{and about} \quad N \times \frac{6}{\pi}\,m$$

(with cubic distribution) for $v = v_0$. Only at high temperature $f(b) = 1$ may be put, and the upper limit becomes $= N \times 4\,m$. ($m =$ volume of one molecule). [1]

That τ_s becomes infinitely great for $v = v_0$, is clear when we consider that then the molecules (cubically distributed) get to lie close against each other, so that every time a *finite* number of molecule centres will lie inside an *infinitely thin* spherical shell, which causes the number of molecules per volume unity not to have the ordinary middle value n at those places, but to be $= n \times \tau_s = \infty$. Then the middle value n is formed by the alternate values 0 (between two centres) and ∞ (at the place of the centres).

XII. Another Derivation of the Virial Collision.

When objections should be raised against the way in which the distribution factor $e^{-\theta P_r}$ is introduced also for the virial of collision, in view of the circumstance that it may be expected that the density of the molecules will not be modified any further after passage through the sphere of attraction, so that the assumption of $P_r = + \infty$ for the collision (which would render the said factor $= 0$) seems unjustifiable (P_r can, indeed, never become ∞, because just so much work is performed by the quasi-elastic forces till the normal (relative) velocity of the colliding molecule is exhausted) — we can also arrive at the result of (5) and (6) in the following way, which is not open to the same objection.

In the foregoing paper we found for the virial of collision the following expression:

$$V_b = \frac{R T'' (b_g)_\infty}{v}\,[1 - a\,\sqrt{T'} + \tfrac{2}{3}\,(a\,\sqrt{T'})^2 - \tfrac{1}{6}\,(a\,\sqrt{T'})^3],$$

in which a represents a coefficient which is in connection with the atomic forces within the molecule, and determines the degree of

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[1] We draw attention here to this, that whereas from $v = \infty$ to $v = v_0$ the *real* quantity $b_q = (b_q)_\infty \times f(b) \times \tau_s$ *increases* from b_g to ∞ (in consequence of τ_s), the *fictitious* quantity b in $v - b$ will *decrease* from b_g to $b_0 =$ about $6'\pi \times Nm$.

compression. When we put in this $\alpha = 0$ (perfectly hard, incompressible spheres), we obtain:

$$V_b = \frac{RT'\,(b_q)_\infty}{v},$$

which in this case we should also have obtained immediately by supposing ϱ constant under the integral sign (see the first Paper). For then the integral had become (the indices 0 and b refer to the interval of collision; in Communication I ϱ_a was written instead of ϱ_b):

$$2\,\varepsilon n\,(b_q)_\infty \int_{\rho_b}^{\rho_0} (\varrho - \varrho_a)\,d\varrho = -\,\varepsilon n\,(b_q)_\infty\,(\varrho_a - \varrho_b)^2,$$

and as $\varepsilon\,(r_0 - r_b)^2$ is $= \varepsilon\,(\varrho_0 - \varrho_b)^2 = RT' : N$, V_b becomes as above.

We wrote RT' and not RT. This is owing to this that the mean relative normal velocity u_0, with which a molecule strikes against another, is *increased* by a certain amount on account of the traversing of the sphere of attraction, and this in such a way that

$$\tfrac{1}{2}\mu u_n'^2 - \tfrac{1}{2}\mu u_n^2 = \int \frac{dP_r}{dr}\,e^{-\theta P_r}\,dr = \Sigma : N,$$

in which Σ is given by (γ) in § 9. But $\tfrac{1}{2}\mu u_n^2$ being $= RT: N$, also

$$RT' - RT = \Sigma, \quad \ldots \ldots \ldots \quad (11)$$

so that we get:

$$\frac{RT'}{RT} = 1 + \frac{\Sigma}{RT} = e^{\alpha/RT},$$

hence

$$V_b = RT\,\frac{(b_q)_\infty}{v} \times e^{\alpha/RT},$$

through which $f(b)$ becomes $= e^{\alpha/RT}$, in agreement with (5).

XIII. Objections to the Function $e^{-\theta P_r}$. Another Factor of Distribution.

For $f(a)$ and $f(b)$ we find therefore resp. the expressions

$$\left.\begin{aligned} f(a) &= (e^{\alpha/RT} - 1) : \alpha/RT = 1 + \tfrac{1}{2}\frac{\alpha}{RT} + \tfrac{1}{6}\left(\frac{\alpha}{RT}\right)^2 + \cdots \\[2mm] f(b) &= e^{\alpha/RT} \qquad\quad = 1 + \frac{\alpha}{RT} + \tfrac{1}{2}\left(\frac{\alpha}{RT}\right)^2 + \cdots \end{aligned}\right\} \quad . \quad (12)$$

And these two functions of the temperature are *not* the same, as the experimental results (see the foregoing communication) have taught. The difference is such that even a very considerable error

in these results could not have given rise to such a difference. For at the critical temperature $1 : RT = 8,2306$, so that with $a = 0,06426$ (see foregoing Paper, 2nd table) the value of $f(a)$ becomes $= 1,3180$, while at the Boylepoint, where $1 : RT$ is $= 2,545$, the value of this function is $= 1,0864$. That of the temperature function $f(b)$ becomes, however, in the two cases resp. 1,6971 and 1,1777, so that $b_q : a$ would become $= (b_g)_\infty : a_\infty \times (1,697 : 1,318) = 1,288 \ (b_q)_\infty : a_\infty$ in the first case, on the other hand $=$ id $\times 1,178 : 1,086 = 1,084 \ (b_q)_\infty : a_\infty$ in the second case.

Experimentally *the same* value (viz. 2,545) was found for the two relations. With Boltzmann's distribution factor they would *not* be the same, but be in the ratio of $1,288 : 1,084$, i. e. $b_q : a$ would have to be 1,19 times greater than at the Boylepoint, which would require an error of almost $20\,^o/_o$ in one of the two observations. And this is very unlikely, indeed — unless the ratio of $b_q : b_k$, for which we assumed 1,044 (see foregoing Communication, § 2), should have to be about 1,24. But since the value of the fictitious b in $v-b$ at the critical point will certainly not be $20\,^o/_o$ smaller than the limiting value for great volume, this supposition is not particularly probable either [1]).

The same thing applies to a still greater degree with respect to the $f(a)$ and $f(b)$, calculated by Reinganum and Keesom [2]), in which they started from the same distribution factor, but where r in the virial of attraction was taken not almost constant $= r$, (see § 9), but varying between s and ∞. In order to render the integration possible, a definite form, viz. $- c : r_q$, was then used for P, $(q > 3)$. Then $\dfrac{dP_r}{dr} = \dfrac{qc}{r^{q+1}}$, hence $r^2 \dfrac{dP_r}{dr} = \dfrac{qc}{r^{q-2}}$. If q were $=$ or < 3, the integral would become infinitely great (for $q = 3$ logarithmically infinite). For $q =$ or > 4 this difficulty disappears.

From the general formula (42) on p. 32 of Suppl. 24 we can derive

$$a = \frac{q}{q-3} \ (b_q)_\infty \ a \left[1 + \frac{q-3}{2q-3} \frac{a}{RT} + \tfrac{1}{2} \frac{q-3}{3q-3} \left(\frac{a}{RT}\right)^2 + \tfrac{1}{6} \frac{q-3}{4q-3} \left(\frac{a}{RT}\right)^3 + \cdot \right]$$

for the quantity a [after subtraction of

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[1]) For this we should have to assume that the value of r_s in (9a) for a volume corresponding with v_k were much greater at lower temperature than at higher temperature, where the ratio 1,044 is determined. Possibly also the value of a on the critical isotherm is *slighter* for large volume than for smaller volumes, because the factor r_1 could then play a part also in the sphere of attraction. (Cf. also the conclusion of § 9, and the footnote in § 11).

[2]) Suppl. Comm. Leiden No. 24, 25 en 26.

$$b_q = (b_g)_\infty \left(1 + \frac{a}{RT} + \tfrac{1}{2} \left(\frac{a}{RT} \right)^2 + \cdot \cdot \right),$$

and multiplication by RT, as Keesom's B represents $= b_q - (a : RT)$], when $N \times {}^2/_3 \pi s^3 = N \times 4 m = (b_q)_\infty$ is put (Keesom writes n, where we have put N), and for $\frac{R}{k} v$ ($=$ our $N \times M$) a is written (hv is

namely $= \frac{v}{kT} = \frac{R}{k} v : RT$).

For $q = \infty$ this becomes $a = (b_g)_\infty \; a \left(1 + \tfrac{1}{2} \frac{a}{RT} + \tfrac{1}{6} \left(\frac{a}{RT} \right)^2 + \cdots \right),$

in agreement with what we found in § 10, as the sphere of attraction becomes infinitely thin for $q = \infty$, so that $r_a = r_1 = s$, hence $v = 1$.

When with Keesom we assume $q = 4$, the functions of the temperature become therefore : [1])

$$f(a) = 1 + \tfrac{1}{6} \frac{a}{RT} + \tfrac{1}{18} \left(\frac{a}{RT} \right)^2 + \cdots$$

$$f(b) = 1 + \frac{a}{RT} + \tfrac{1}{2} \left(\frac{a}{RT} \right)^2 + \cdots \qquad , \quad \cdots \quad (12a)$$

hence $f(a)$ still less pronounced than ours with the coefficients $\tfrac{1}{2}$, $\tfrac{1}{6}$, etc., so that the difference between the two functions of the temperature $f(b)$ and $f(a)$ would become still greater than ours, and the slow decrease of attraction over a greater region, according to the law $q = 4$, would therefore lead to still *more unfavourable* results with respect to the experimentably found *equality* of the two functions of the temperature (at least for T_k and T_B) than our assumptions.

The only factor of distribution that would yield *equal* expressions for the two functions of the temperature, is

$$(1 + \theta P_r)^{-2}$$

instead of $e^{-\theta P_r}$. For then the integral of work Σ becomes:

$$\Sigma = \int_s^{r_a} \frac{d (NP_r)}{dr} (1 + \theta P_r)^{-2} \, dr = \left(- \frac{N}{\theta} \frac{1}{1 + \theta P_r} \right)_{-M}^0 =$$

$$= RT \left(\frac{1}{1 - \theta M} - 1 \right) = \frac{a}{1 - a/RT},$$

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[1]) With $q = 4$ the factor would become $4 (b_g)_\infty a$, hence $v = 4$, which corresponds with a mean value $r_1 = 1,6 \; s$ (see § 9).

as $\theta = N : RT$ and $MN = \alpha$. For $a_\infty = v(b_g)_\infty \times \Sigma_\infty$ (cf § 10) at $T = \infty$ ($\theta = 0$) we find therefore again $v(b_g)_\infty \times \alpha$, and further for

$$f(a) = \Sigma : \alpha, \text{ and } f(b) = 1 + \frac{\Sigma}{RT} \text{ (See (4) and (7))}:[1]$$

$$f(a) = f(b) = \frac{1}{1 - \alpha/RT} = 1 + \left(\frac{\alpha}{RT}\right)^2 + \cdots \quad . \quad . \quad (12b)$$

, This function of the temperature $f(a)$ is, therefore, the *strongest* of all. It duly gives $f(b) = f(a)$. Then follows ours, viz. (12), derived from BOLTZMANN's function of distribution $e^{-\theta P_r}$, on the assumption of rapidly decreasing attraction, only between s and r_a. It is *weaker* and gives $f(b) > f(a)$. At last comes that of REINGANUM and KEESOM, likewise derived from $e^{-\theta P_r}$, but with attraction from $r = s$ to $r = \infty$, and $q = 4$. This it the *weakest* of all, and gives a still greater difference between $f(b)$ and $f(a)$, which pleads against it:

It is the question whether the proposed distribution factor is theoretically justified. But it has the great disadvantage that the denominator already becomes *infinite* for $RT = \alpha$, and would then become *negative* for smaller values of T, which is of course impossible. The agreement with the values of a calculated experimentally from the *found* values of B (namely by dividing B by $(T : T_B) - 1$, see the foregoing communication) is almost the same as for the function $(e^{\alpha/RT} - 1) : \alpha/RT$, which we considered valid not only for a, but also for b.

In the subjoined table a has been calculated from $a = a_\infty : (1 - \alpha/RT)$. The values of a_∞ and α have this time been determined from the values of a, found for $-252°$ and $20°$ C. For $-252°$ C. a is namely $= -475 . 10^{-6} : -0,808 = 588 . 10^{-6}$, and for $20°$ C. a was $= 380 . 10^{-6}$, so that we find $a_\infty = 370,0 . 10^{-6}$ and $\alpha = 0,02797$.

It is seen that the agreement is pretty satisfactory; only the values between $20°$ C. and the critical temperature are again all too low.

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[1] It is again noteworthy that $f(b)$ can also be obtained by carrying out the integration

$$\int_{s-\delta}^{s} \frac{dP_r}{dr} (1 + \theta P_r)^{-2} dr \text{ between the limits } \infty \text{ and } -M \text{ for } P_r. \text{ We then get namely}$$

$$\left(-\frac{1}{\theta} \frac{1}{1 + \theta P_r}\right)_\infty^{-M} = -\frac{RT}{N} \cdot \frac{1}{1 - \theta M}, \text{ so that again (see also § 11) } f(b)$$

becomes $= (1 - \theta M)^{-1} = (1 - \alpha/RT)^{-1}$.

t	T	$1-\alpha/RT$	$a \cdot 10^6$ calc.	$a \cdot 10^6$ found.
$- 257,10$	15,99	0,5220	709	740
$- 255,32$	17,77	0,5699	649	(599)
$- 252,47$	20,62	0,6293	588	588
$T_k = - 239,91$	33,18	0,7698	481	486
$- 204,62$	68,47	0,8884	417	472
$- 103,54$	169,55	0,9549	388	414
$+ 20$	293,09	0,9739	380	380
$+ 100$	373,09	0.9795	378	376

All the functions of the temperature considered approach ∞ at $T = 0$ or in the neighbourhood of $T = 0$, and become, therefore, very great for low temperature. I. e. in the equation (8), viz.

$$pv = RT - \frac{a - RT\,b_g}{v},$$

p would become negative already for comparatively large values of v at very low temperatures. This is, however, practically no objection, for it only means that the *boundary line* where the saturated vapour cannot exist any longer and condenses to liquid, is shifted more to the right (i. e. to the side of the still greater volumes). The negative values of p then fall within the boundary line in the metastable region as before.

That a becomes very great, might also be interpreted in this way. At very low temperature, where the molecules with exceedingly small velocity pass through the sphere of attraction, the accumulation round a molecule will be very great; these will at last all fall together, which would again mean condensation to liquid.

And as for the increase of b_q to infinite large, this would entail that the fictitious quantity b in $v - b$ would approach v more quickly than otherwise would have been the case. For in (9^a), viz. $b = \tau_s b_g$: $: (1 + (\tau_s b_g : v)$, the fact that b_q becomes great in consequence of the low temperature, has now the *same* effect as otherwise the becoming great of τ_s in consequence of the small volume. I. e. that for a volume v, where else (at high temperatures) the fictitious quantity b would still be near $(b_g)_\infty$, and far from v, this will *now* (viz. at low temperatures) already have drawn much nearer to v. This is again

no practical objection, though the probability to such a behaviour may not be great.

The theory of the factor of distribution $e^{-\theta P_r}$ (or $(1 + \theta P_r)^{-2}$, etc. etc.) rests in my opinion on nothing but a misunderstanding, and the theory of the virial of attraction_and collision should be built up *on entirely new grounds*.

XIV. More Accurate Theory of the Virial of Attraction and Collision.

The method of calculation followed up to now (REINGANUM, VAN LAAR, KEESOM) 'might in a certain sense be called the *"static"* method. In this it is assumed that the molecules are distributed according to a certain law round the considered molecule, in which their motion, resp. velocity and direction, is entirely eliminated (disregarding the mean final velocity at the collision). In the place of this BOLTZMANN's factor of distribution $e^{-\theta P_r}$ is then substituted, which is to set everything right again. But in my opinion BOLTZMANN's considerations are no longer valid for separate *micro-complexes*, as molecules in collision, and immediately before impact, or passing each other at a small distance in the sphere of attraction.

It is easily seen that the effect of the attraction will be *this*, that the at first rectilinear path (at least for large volume) will be *inclined* more or less towards the molecule under the influence of the attraction in the sphere of attraction, and that therefore molecules which would otherwise remain further from the molecule under consideration, will now get into spheres where the attraction is *greater*. And the smaller the velocity with which the molecules will pass, the stronger this enlarging influence will be. If the temperature is exceedingly low, *all* the molecules that pass the border of the sphere of attraction $(r = r_a)$ with their centres, will collide with the molecule under consideration, through which for all the maximum value M is obtained for $-P_r$, and a *maximum* value will therefore be found for a — but not an *exponentially infinitely large one*, as with BOLTZMANN's factor of distribution.

The same thing holds for b. Molecules that would not collide under other circumstances, will now collide under the influence of the attraction that causes them, to deflect, and the number of colliding molecules will therefore be increased, in more or less degree as the temperature will be higher or lower. And it is easy to see that here too the value of b_q will approach to a *maximum* for $T = 0$ (as the radius of the sphere of attraction r_a remains

finite), and *not* to infinite. Also the absurdness of the infinitely great value for P_r at the end of the collision is quite obviated now. Of course the distribution remains *finite*, and *during* the collision there comes no change in this at all. (On the assumption of $e^{-\theta P_r}$ the density would decrease during the interval of collision, thought infinitely small, from $n \times e^{\theta M}$ to $n \times 0$, which is nonsense, because when a molecule has once come to collision, the number of them, as has been said, does not change again during the impact).

Thus we are naturally led to a new method of calculation, which — in opposition to the usual one, the *static* one — might be called the *dynamic* one. What happens to the molecules that pass each other and that collide, will then have to be considered separately — though much can be simplified also with this mode of viewing these things, and much can be brought under a comprehensive point of view.

And thus we have again returned from BOLTZMANN to MAXWELL with the consideration of the separate paths or groups of paths.

XV. The fundamental Path Equations.
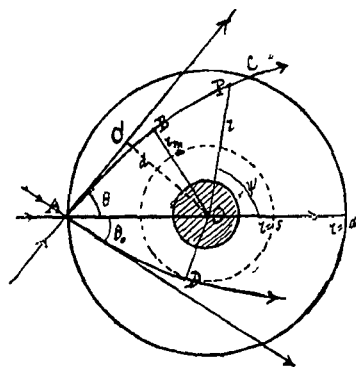
As may be seen from the subjoined figure, the curved path now gets nearer to O (in the point B, with the minimum distance r_m) than the straight path ($u = \infty$, i. e. $T = \infty$) in the point O' with the minimum distance $OO' = d = = a \sin \theta$. The angle, at which the path of the centre of the moving molecule under consideration (O is the stationary centre) comes within the sphere of attraction at A with respect to the joining line AO, is namely indicated by θ. All these angles lie on the circumference of a cone with A as vertex. As the path is still undisturbed at A, the frequency of the angle θ is as usual $= \sin \theta \, d \theta$. Later on we shall have to integrate for all possible angles θ. When the centres of the molecules lie on the circumference of the sphere $r = s$, they collide. The limiting angle θ_0 is that for which the path just touches the circle $r = s$ (in D). All the paths that enter under a smaller angle with respect to AO, give rise to *collision*.

It is self-evident that this limiting angle θ_0 in the limiting case $T = \infty$ (rectilinear paths) is given by $\sin \theta = s : a$, as AD then

becomes the straight tangent. (a is the radius of the sphere of attraction; outside a there is no attraction any more).

If now the attractive force is in the path $= -f(r)$ (hence always directed towards the centre O), then the equation

$$y \frac{d^2 x}{dt^2} - x \frac{d^2 y}{dt^2} = 0, \text{ or } \frac{d}{dt}\left(y \frac{dx}{dt} - x \frac{dy}{dt}\right) = 0, \text{ or } y \frac{dx}{dt} - x \frac{dy}{dt} = \text{const.}$$

follows from $\mu \frac{d^2 x}{dt^2} = - f(r) \cos \psi$ and $\mu \frac{d^2 y}{dt^2} = - f(r) \sin \psi$ with

$x = r \cos \psi$, $y = r \sin \psi$ (r is the radius vector, ψ the amplitude).

But from $\frac{dx}{dt} = \cos \psi \frac{dr}{dt} - r \sin \psi \frac{d\psi}{dt}$, $\frac{dy}{dt} = \sin \psi \frac{dr}{dt} + r \cos \psi \frac{d\varphi}{dt}$

follows immediately $y \frac{dx}{dt} - x \frac{dy}{dt} = - r^2 \frac{d\psi}{dt}$ (which is also immediately seen), hence

$$r^2 \frac{d\psi}{dt} = - c, \quad \ldots \ldots \ldots \ldots \quad (1)$$

in which c is a constant (which is still to be determined more closely). This is the well-known law of sectors.

The square of velocity $u^2 = \left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2$, expressed in pole coordinates, evidently becomes $= \left(\frac{dr}{dt}\right)^2 + r^2 \left(\frac{d\psi}{dt}\right)^2$. But also we have:

$$\frac{d^2 x}{dt^2} \frac{dx}{dt} + \frac{d^2 y}{dt^2} \frac{dy}{dt} = - \frac{f(r)}{\mu}\left[\cos \psi \frac{dx}{dt} + \sin \psi \frac{dy}{dt}\right],$$

i. e. because the expression between [ ] in the second member, in virtue of $r^2 = x^2 + y^2$, is also $= \frac{dr}{dt}$:

$$\tfrac{1}{2} \frac{d}{dt}\left[\left(\frac{dx}{dt}\right)^2 + \left(\frac{dy}{dt}\right)^2\right] = - \frac{f(r)}{\mu} \frac{dr}{dt},$$

hence

$$\tfrac{1}{2} d(u^2) = - \frac{f(r)}{\mu} dr = - \frac{1}{\mu} \frac{dP_r}{dr} dr,$$

when P_r represents the function of force, and μ the mass of a molecule. Integrated between the limits A and P, this gives therefore (in A P_r is $= 0$, and $u = u_o$):

$$\tfrac{1}{2} \mu (u^2 - u_o^2) = 0 - P_r,$$

or

$$u^2 = u_o^2 - 2 \frac{P_r}{\mu}, \quad \ldots \ldots \ldots \ldots \quad (2)$$

the well known law of the vis viva. When now we substitute the above found value in pole coordinates for u^2, we get:

$$\left(\frac{dr}{dt}\right)^2 + \frac{c^2}{r^2} = u_0{}^2 - 2\frac{P_r}{\mu}, \quad \ldots \ldots \quad (3)$$

as $r^2\left(\frac{d\psi}{dt}\right)^2$ is $= c^2 : r^2$ according to (1). This equation (3) is of great importance for our calculations. For the equation of path the following equation follows from this in connection with $\frac{d\psi}{dt} = -\frac{c}{r^2}$:

$$\frac{d\psi}{dr} = \pm \frac{c}{r^2\sqrt{u_0{}^2 - 2\dfrac{P_r}{\mu} - \dfrac{c^2}{r^2}}} \quad \ldots \ldots \quad (4)$$

The upper sign evidently holds for $r = a$ to $r = r_m$ (A to B), the lower sign for all the points beyond B.[1]

We must now first determine the constant c. This can take place in two different ways. The simplest way is to examine the state in the point A, where the path coincides with the tangent AO'. If the considered point P lies in the immediate neighbourhood of A, then evidently $sin (\psi-\theta)$ is $= a \sin \theta : r$ in $\triangle\ OAP$. Differentiation with respect to r gives $cos (\psi-\theta)\dfrac{d\psi}{dr} = -\dfrac{a\sin\theta}{r^2}$, hence because ψ is then $= 180°$ and $r = a$:

$$\left(\frac{d\psi}{dr}\right)_A = \frac{tg\ \theta}{a}.$$

But from (4) follows, because $P_r = 0$ in A, and the positive sign holds:

$$\left(\frac{d\psi}{dr}\right)_A = \frac{c}{a^2\sqrt{u_0{}^2 - \dfrac{c^2}{a^2}}}.$$

From the two expressions follows immediately:

$$c = u_0 \times a \sin \theta.$$

This causes (3) to become:

$$\left(\frac{dr}{dt}\right)^2 = u_0{}^2\left(1 - \frac{a^2\sin^2\theta}{r^2}\right) - 2\frac{P_r}{\mu}, \quad \ldots \ldots \quad (3a)$$

hence we find for the point B, where the radius vector r gets the minimum values r_m, and where therefore $dr : dt = 0$:

[1] We must remark that by differentiation of (3) follows $\dfrac{d^2r}{dt^2} - \dfrac{c^2}{r^3} = -\dfrac{f(r)}{\mu}$.

$$\frac{a^2}{r_m^2} sin^2 \theta = 1 \perp \frac{-P_{r_m}}{\frac{1}{2}\mu u_0^2} \quad \ldots \ldots \ldots \quad (5)$$

, Therefore we find for the limiting angle θ_0, as r_m becomes $= s$ in D, and $-P_{r_m} = M$:

$$\frac{a^2}{s^2} sin^2 \theta_0 = 1 + \frac{M}{\frac{1}{2}\mu u_0^2} \quad \ldots \ldots \ldots \quad (6)$$

XVI. Calculation of the Virial of Attraction.

Now the calculation of the virial of attraction can be carried out in the following way.

As the sum of the radii at the entrance of a molecule with radius $\frac{1}{2}s$ inside the sphere of attraction a is exactly $= a$ (the centre of the entering molecule is then, namely, exactly on the *circumference* of that sphere), the number of entrances per second will be given by the well-known relation

$$N = \pi n a^2 \times u_0 = \omega u_0.$$

The number of entrances for the direction θ is therefore $N_\theta = \omega u_0 \times sin\theta d\theta$, so that the number of molecules that will be found on the element ds of the portion of the path AB, is given by

$$\omega u_0 \, sin \, \theta \, d\theta \times \frac{ds}{u} = \omega u_0 \, sin \, \theta \, d\theta \times dt,$$

when $u = \frac{ds}{dt}$ is the velocity in the element of path in question. But dt is given by (3^a); through which we get for the number in question:

$$\omega u_0 \, sin \, \theta \, d\theta \times \frac{dr}{-u_0 \sqrt{1 - \frac{a^2}{r^2} sin^2 \theta - \frac{2P_r}{\mu u_0^2}}}.$$

As, namely, $dr:dt$ is negative on AB, the negative sign has been taken in the extraction of the root. Let us write:

$$-\frac{2P_r}{\mu u_0^2} = \frac{-P_r}{\frac{1}{2}\mu u_0^2} = \frac{-P_r}{M} \times \frac{M}{\frac{1}{2}\mu u_0^2} = F(r) \times \varphi,$$

in which φ is therefore in connection with the *temperature* through $\frac{1}{2}\mu u_0^2$. (M again represents the maximum value of $-P_r$ for $r = s$).

. Hence we have for the total *virial of attraction* of the considered molecule:

$$\tfrac{1}{3} N \times M\omega \left[\int_{\theta_0}^{90°} \int_{r_m}^{a} \frac{r\left(-F'(r)\right) dr \times \sin\theta \, d\theta}{\sqrt{1 - \frac{a^2}{r^2}\sin^2\theta + \varphi . F(r)}} + \int_0^{\theta_0} \int_s^a \frac{\left(r(-F'(r)\right) dr \times \sin\theta \, d\theta}{\sqrt{id.}} \right], (7)$$

in which the first (double) integration refers to all the entering molecules that do *not* strike against the molecule in question, and where, therefore, a *minimum value* of r is passed through in B (which minimum in the limiting case $\theta = \theta_0$ will get exactly on the circumference of the sphere $r = s$), whereas the second integration refers to all the *colliding* molecules. For the attractive force $\frac{dP_r}{dr} = \frac{d(-P_r)}{dr}$ we have written $- MF(r)$ according to the assumption $- P_r : M = F(r)$. In consequence of the negative sign of the root, the limits of integration are reversed with respect to r.

Besides we still have multiplied by 2 in the above expression, since evidently the second portion of the path from B to C, or from the collision back to the circumference of the sphere of attraction, will yield exactly the same integral value. Everything then takes namely place in the reversed order, the limits of the integrals remaining quite the same. Moreover the summation is extended over *all* the molecules N, which with the virial factor $\tfrac{1}{3}$ yields therefore in all still a pre-factor $\tfrac{1}{3} \times \tfrac{1}{2} N \times 2 = \tfrac{1}{3} N$. (The total number of molecules N has been divided by 2, because else all the pairs of molecules would have been counted double).

We now have to choose a suitable expression for $F(r)$. The accurate law referring to the attraction being unknown, it will not make much difference for the determination of the dependence of the temperature (lying in the quantity φ), which interpolation function is used, provided $F(r)$ become $= 0$ for $r = a$, and $= 1$ for $r = s$. The more so when — as will probably be always the case — a and s do not differ *much*. We can, therefore, choose a function for which the above integrations become *possible*. This cannot be completely reached, as we shall at once see, but through the assumption

$$F(r) = \frac{-P_r}{M} = \frac{\dfrac{1}{r^2} - \dfrac{1}{a^2}}{\dfrac{1}{s^2} - \dfrac{1}{a^2}} \quad \cdots \cdots \quad (8)$$

we can get a long way. In consequence of this we get:

$$-F'(r) = \frac{2}{r^3} : \left(\frac{1}{s^2} - \frac{1}{a^2} \right), \quad \cdots \cdots \quad (8a)$$

and this is indeed not $= 0$ for $r = a$, but no essential objection in principle can be raised against this. It may, namely, be assumed that the molecules will *suddenly* experience an attractive force (proportional to $1 : r^n$) at their entrance inside the sphere of attraction. If only $- P_r$ itself becomes $= 0$ for $r = a$, which is the case on our above assumption.

Fontanivent, Autumn 1917.

(*To be continued*).