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**Physics.** — “On the Course of the Values of  $a$  and  $b$  for Hydrogen at Different Temperatures and Volumes”. III. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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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  $\frac{2}{3} \pi N s^3 = 4m = (b_\eta)_\infty$ ,  $MN = a$ :

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

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

$$a = \omega \times \frac{2a^4}{s(a^2 - s^2)} \left[ \iint_{\theta_0, r_m}^{90, a} \frac{dr \times \sin \theta d\theta}{r^2 \sqrt{1 - \frac{a^2}{r^2} \sin^2 \theta + \varphi \left( \frac{a^2}{r^2} - 1 \right) : \left( \frac{a^2}{s^2} - 1 \right)}} + \iint_{0, s}^{\theta_0, a} \text{ibid.} \right],$$

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  $s^2 \cdot (a^2 - s^2)$ , the above becomes:

$$a = \omega \times \frac{2a^4}{s(a^2 - s^2)} \left[ \iint_{\theta_0, r_m}^{90, a} \frac{dr \times \sin \theta d\theta}{r \sqrt{a^2 \cos^2 \theta - (a^2 - r^2)(1 - k^2 \varphi)}} + \iint_{0, s}^{\theta_0, a} \text{ibid.} \right], \dots (7^a)$$

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

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:

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

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  $\theta_0$  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  $\varphi$  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  $\varphi_0$ , we get therefore

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

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

$\theta_0$  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  $\varphi$  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  $\varphi$  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 rootsign, viz.  $p^2 r^2 - a^2(p^2 - \cos^2 \theta)$  is always  $= 0$ , because then  $dr:dt = 0$  (compare (3<sup>a</sup>)). 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:

1<sup>b</sup>

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

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:

$$a_1 = \omega \times \frac{a^3}{s(a^2 - s^2)} Bg^2 \operatorname{tg} \frac{1}{k} = \omega \times \frac{1}{n(1 - n^2)} Bg^2 \operatorname{tg} \frac{\sqrt{1 - n^2}}{n}. \quad (10)$$

Hence we find for this a value which no longer contains  $\varphi$  (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  $\varphi_0$ ,  $\theta_0$  gets near  $90^\circ$ , so that then the limits of  $I_1$  with respect to  $\theta$  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),  $Bg^2 \operatorname{tg}$  approaches  $\frac{1 - n^2}{n^2}$ , so that then  $a_1$  approaches  $\omega : n^3 = \omega$ . 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 ( $\varphi = \varphi_0$ ).  $\theta_0$  lies, therefore, in both cases in the neighbourhood of  $90^\circ$ , hence the limits of integration of  $I_1$  will almost coincide, viz.  $\theta$  between  $\pm 90^\circ$  and  $90^\circ$  at high temperatures, resp. ( $90^\circ$ ) and  $90^\circ$  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  $\infty$ , 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  $\theta$  will lie between  $\pm 0^\circ$  and  $90^\circ$ , and at low temperatures between  $(90^\circ)$  and  $90^\circ$ . And the limiting value of  $\varphi_0$  is near  $\infty$ , 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<sup>a</sup>). This applies, therefore, to all the molecules that can come in *collision*, as  $\theta$  now remains smaller than the limiting angle  $\theta_0$ . 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:

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

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

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

<sup>1)</sup>  $Bgtg \frac{\sqrt{1-n^2}}{n}$  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:

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

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:

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

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  $\varphi$  (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

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

( $a = s$ ), 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  $\varepsilon$  will lie between  $\frac{1}{8}$  (when  $n = 1$ ) and  $8 : \pi^2 = 0,811$  (when  $n = 0$ ). Accordingly the factor  $\varepsilon$  is little variable. It appears from the expansion into series (see Appendix A), that  $\varepsilon$  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 ( $a \rightarrow s$ ), 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  $\theta$  lies between  $(0^\circ)$  and  $\pm 90^\circ$  at high temperatures, and  $(90^\circ)$  and  $(90^\circ)$  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  $\pm 1$  for  $x_0$  ( $\varphi = 0$ ), resp. (0) at  $\varphi = \varphi_0$ , and (1), resp. (0) for  $p$ ; so that  $\theta$  lies between  $(0^\circ)$  and  $\pm 0^\circ$  at high temperatures, and  $(90^\circ)$  and  $(90^\circ)$  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):

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

According to the above this part comprises the *almost totality* of the angles of incidence, from  $90^\circ$  to near to  $0^\circ$ , at *high* temperatures; and only a *very small part*, from  $90^\circ$  to near to  $90^\circ$  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  $a_\infty$  in (12) lies between  $\omega \times \frac{1-n}{n(1-n^2)^{\frac{1}{4}}} \frac{1}{4} \pi^2 = \omega \times \frac{1}{n(1+n)} \frac{1}{4} \pi^2 = \underline{\omega \times \frac{1}{8} \pi^2}$  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:

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

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:



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

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  $s/a p$  we may also write  $\sqrt{p^2-x_0^2}$ .

The first integral can again be easily integrated.  $d \log$  is namely  $= -\frac{dx}{\sqrt{x^2-p^2}}$ , 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  $\log \sqrt{\frac{1-y}{1+y}} = -Bgtg hyp y$ ,

so that we find with *Bgtg h y* =  $\psi$ :

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

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  $\psi$  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 hyperbolical 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  $\varphi$  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:

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

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

$$= \frac{1}{2} \log \frac{1 + \sqrt{\frac{(1+k^2)\varphi}{1+\varphi}}}{1 - \sqrt{\frac{(1+k^2)\varphi}{1+\varphi}}} = \sqrt{\frac{(1+k^2)\varphi}{1+\varphi}} + \frac{1}{3}(\ )^3 + \text{etc.}$$

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

(a<sub>2</sub>)<sub>2</sub> will evidently at *high* temperature ( $\varphi$  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

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

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

when  $\varphi$  is simply written for  $\varphi : \sqrt{1+\varphi}$ . This becomes therefore properly = 0 for  $T = \infty$ . Then the limits of the original integral ( $I_2$ )<sub>2</sub>, viz.  $p$  and 1, are equal, viz. = 1, which causes the limits of the angle of incidence  $\theta$  to lie between (0°) and 0° (see also the end of § XVII).

For *low* temperatures ( $\varphi$  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:

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

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

When  $n \rightarrow 1$  ( $\alpha \rightarrow s$ ),  $(a_2)_2$  does not become  $= \infty$  in  $13^a$ . For as  $\varphi$  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  $n \rightarrow 0$  ( $\alpha$  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

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

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  $\varepsilon$  (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  $e^\infty$  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  $\varphi$  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  $F(\varphi)$ . 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  $a_\infty$  and  $\gamma$  in (14<sup>a</sup>) 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<sup>a</sup>)  $a_\infty$  then becomes  $= \frac{1}{1,6} \pi^2 \times (b_q)_\infty a$ , 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

$$= \frac{2}{3} \pi N n \int_0^a r^3 \frac{dP_r}{dr} dr. \text{ When } a = s, r^3 = s^3 \text{ can be brought before}$$

the integral sign, and we have  $\frac{2}{3} \pi N n s^3 (P_r)_s^a = \frac{2}{3} \pi N n s^3 (0 - (-M)) = \frac{2}{3} \pi N s^3 \times MN : v$  (as  $n = N : v$ ). Hence we find with  $MN = a$  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  $= \frac{1}{1,6} \pi^2 = 0,617$ , 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  $s \approx 1,55 = 1,16 s$  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  $\varphi$  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:

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

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,

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

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

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

will better answer the purpose, according to (14<sup>b</sup>). In this  $\alpha = k^2 \times \frac{1}{2} \alpha = \frac{n^2}{1-n^2} \times \frac{1}{2} \alpha$ , in which it should be borne in mind that the *log* is now negative, so that the minus sign before  $\lambda$  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 reasons<sup>1)</sup>. To this comes the circumstance that for  $n = 1$  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  $\varphi_0$ , i.e.  $T = \infty$ . And as it has been experimentally found that the said

<sup>1)</sup> 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  $16^\circ$  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.  $14^\circ$  abs.).

Fontanivent, January 1918.

(To be continued).