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Physics. — “*On the Equation of State for Arbitrary Temperatures and Volumes. Analogy with PLANCK’s Formula*”. By Dr. J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

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§ 1. Introduction.

In four papers¹⁾ I tried more closely to study the dependence on the temperature of the quantities a and b of VAN DER WAALS’s equation of state on the ground of *kinetic* considerations. I then came to the conclusion that the quantity a must steadily increase with descending temperature to a maximum value in the neighbourhood of the absolute zero point, after which it again decreases to the value 0 at $T = 0$. All this with very large volume.

Also with respect to b I carried out similar computations, but the mathematical difficulties become greater and greater, and the results obtained become very complicated. And for small volumes such a treatment of the problem is still less suitable. I, therefore, gave up the idea of publishing what was still found in connection with the said paper, and tried to solve the question by another and simpler way.

The thought had already occurred to me before, to substitute for the three-dimensional problem an analogous problem of one dimension, and then to transform the result in the well-known way to one which would hold for three dimensions. It is clear that so doing the *nature* of the sought dependence on the temperature and the volume of the constants occurring in the equation of state will not be modified; there can only arise some difference in a few *numerical* factors. But these are after all immaterial, when in the result some groups of quantities, the said factors included, are joined to one or more constants.

This method has besides also the advantage that it cannot only be used for large volumes, but also for *small volumes*, and results are, therefore, obtained which are universally valid, not only for arbitrary temperatures, but also for arbitrary *volumes*, from $v = \infty$ up to $v = b$.

¹⁾ These Proceedings XX, p. 750 and 1195; XXI, p. 2 and 16.

When calculating the different **time averages** — which up to now were too much neglected in this problem, the attention being almost exclusively concentrated on all kinds of spacial mean values, which can only modify some numerical values already alluded to above — it already soon appeared that the relation between the mean *Energy* and the *temperature* was the same for small volumes and low temperatures¹⁾ as the relation

$$E = E_0 + \frac{2E_0}{e^{\frac{2}{3}E_0/RT} - 1},$$

which was drawn up by PLANCK on behalf of the theory of radiation on assumption of the so-called hypothesis of quanta, in which only $\frac{2}{3}Nh\nu$ would have to be substituted for E_0 to find back PLANCK's expression²⁾.

By a *purely kinetic* way, on the sole foundation of the ordinary laws of *classical mechanics*, we could therefore derive PLANCK's famous expression, which I think was only possible up to now on the strength of very special suppositions, namely on the supposition that the energy is *emitted* only in entire multiples of the quantity $h\nu$ ("energy quanta"). (The absorption can take place in arbitrary quantities according to the last modification applied by PLANCK in his theory).

§ 2. General Considerations on the Nature of the Attractive and Repulsive Forces.

We shall suppose the molecules to be all arranged along one dimension, and assume every arbitrary molecule M to move continually to and fro between the two adjacent molecules M_1 and M_2 . Let the mean distance between the molecule centres be l (the analogon of the volume v for three dimensions), the radius of the sphere of attraction ρ , the diameter of the molecule s . As M_1 and M_2 may

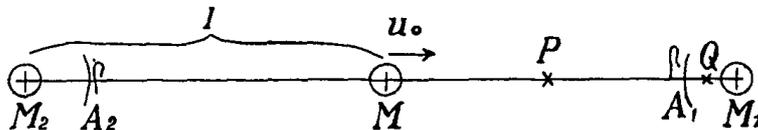


Fig. 1.

be found both on the lefthand side and on the righthand side of the mean places M_1 and M_2 , we may suppose them to be on an average always in M_1 and M_2 ; besides we may assume M_1 and M_2

¹⁾ With the difference only of a small finite term, which may be neglected by the side of the principal term, which becomes logarithmically infinite (see § 6).

²⁾ I.e. multiplied by 3 on transition from a linear to a spacial oscillator.

to be at rest, because their movement may just as well be directed towards the left side as towards the right side (cf. however § 6). Hence M moves steadily to and fro between the molecules M_1 and M_2 , assumed to be fixed. We call u_0 the velocity, which possesses M in the point in the middle between M_1 and M_2 (indicated by M in fig. 1: the so-called dead or neutral point), either to the lefthand side, or to the righthand side.

With this velocity M covers the part MA_1 (e.g. in P), but then it enters the sphere of attraction ρ of the molecule M_1 (e.g. in Q); i.e. we assume that the attractive force does not make itself appreciably felt until the molecule has entered this sphere, and then increases steadily till M touches the molecule M_1 (distance of the middle points = s). Consequently the velocity u has also continually increased from A_1 to a maximum value u_s . Then repulsive forces appear; the two molecules are a little compressed and M is repelled. Between M_1 and M everything takes place in exactly the same way, only in opposite order; and between M and M_2 and back everything is again repeated. Hence we shall only have to consider the fourth part, viz. the portion MM_2 of every movement to and fro.

It is easily seen that three cases are possible. In the *first* place the case represented in fig. 1, in which $l > \rho$, and the molecule M , therefore, passes over a longer or shorter path *outside* the influence of the attraction of M_1 , and *always* outside the sphere of attraction of M_2 .

In the *second* place we have the transition case of fig. 2, viz. $l < \rho$, but $> \frac{1}{2}(\rho + s)$. Then M is *continually within* the sphere of attraction $M_1 A_1$ of M_1 , and besides during a period (from M to A_2 , e.g. in P) also within that ($M_2 A_2$) of M_2 . As soon as M has passed the point A_2 , e.g. in Q , it will be outside the influence of M_2 .

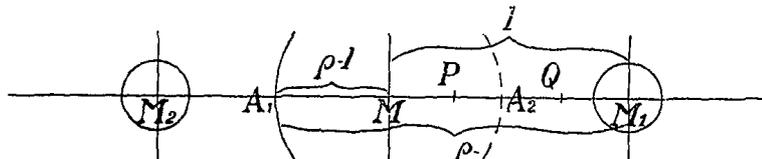


Fig. 2.

In the *third* place M can also be continually within the sphere of attraction of M_2 , as soon as viz. M , on contact with M_1 (distance of the middle points = s), is still just on the edge of the sphere of attraction of M_2 ; i.e. when $A_2 M_1 = 2l - \rho$ has just the value s . Then l is therefore = $\frac{1}{2}(\rho + s)$. Thus in the second (transition) case $l > \frac{1}{2}(\rho + s)$; while for the third case we have simply $l < \frac{1}{2}(\rho + s)$. Now we found before (see the cited papers) ρ to be about 1,7 s .

We should then have: 1st case $l > 1,7 s$; 2nd case $l < 1,7 s > 1,35 s$; 3rd case $l < 1,35 s$.

At the critical temperature $v_k = 3,8 b_0$ (at least for "ordinary" substances), hence $l = s^3 \cdot 3,8 = 1,56 s$ (the molecule thought to be cubical). Hence the *entire solid state and almost all liquid volumes*, starting from the melting point ($l = 1,08 s$ about) to far above the boiling-point, are in the *third* case, every molecule being continually within the sphere of attraction of the neighbouring molecules. Only the volumes quite close to T_k , both the liquid and the vapour volumes, belong to the second (transition) case, and almost all the vapour volumes should be reckoned to the first case (see fig. 1).

When ρ is taken still somewhat greater than $1,7 s$, e.g. $= 2s$, the transition case lies between $2 s$ and $1,5 s$, and then comprises only the smallest vapour volumes in the neighbourhood of the critical point, while (practically) *all* the liquid volumes up to T_k , where $l = 1,56 s$, belong to the third case.

We must now make a plausible supposition about the nature and the way of action of the attractive and repulsive forces, which supposition should also enable us to make the mathematical calculations easy to carry out. Among all the suppositions which I have tried with respect to the attractive forces on different occasions, now and before, the simplest is this that we assume the attraction to increase *from the sphere of attraction ρ linearly* proportionate to the distance to that sphere. If e.g. the molecule is in the point P (fig. 2), the attraction that it undergoes from M would be $= f \times A_1 P$.

Instead, therefore, of supposing the attractive action to *decrease* from the centre of the molecule outwards to the edge of the sphere of attraction (according to a certain reciprocal power of the distance r to the centre, by e.g. putting $T = f : r^6$, or $T = (f : r^2) \times e^{-r/u}$, which renders the integrations always unfeasible or exceedingly complicated, and in consequence of which the attractive action at the edge of the sphere of attraction never becomes $= 0$), the reversed course is taken, and the attractive action is made to *increase* from the edge of the sphere of attraction *inwards*. The results will not differ much, but a great simplification of the calculations is reached. We shall only see quantitative differences appear on different suppositions about the attractive forces (in the numerical coefficients etc.), but the found form of the functions of temperature and volume will remain *qualitatively* unchanged. And it still remains the question whether our supposition, in connection with the assumption that the molecules and atoms are all electron-systems, is not at least as justifiable as the other above-mentioned suppositions.

As regards the *repulsive* forces on contact of the molecules, for them I assume the same thing as before (cf. among others loc. cit. I § 7 p. 856), namely that as soon as the molecule is compressed (the atoms or the electron rings pressed inward from their state of equilibrium), there is excited a quasi-elastic repulsive force, which (for not too great compressions) likewise increases *linearly* with the deviation from the state of equilibrium.

§ 3. Construction of the Fundamental Equations.

Hence in the *first* of the three above indicated cases ($l > \varrho$), the attraction of M through M_1 (when $MQ = x$ is put in fig. 1) may be represented by $F = f \times A_1Q$, i.e. by $f \times (MQ - MA_1)$, or by

$$F = f(x - (l - \varrho)).$$

In the integrations x is then to be taken from $l - \varrho$ to $l - s$.

In the *second* case ($l < \varrho < \frac{1}{2}(\varrho + s)$) in P (fig. 2) the attraction of M by M_1 is $f \times A_1P = f \times (MP + A_1M)$, whereas that which M experiences from M_2 is $= f \times PA_2 = f \times (MA_2 - MP)$. Hence, putting MP again $= x$, we get:

$$F_1 = f(x + (\varrho - l)) \quad ; \quad F_2 = f((\varrho - l) - x).$$

In this x must be taken between 0 and $l - s$ for F_1 ; for F_2 only between 0 and $\varrho - l$. If x becomes $> \varrho - l$, F_2 would become negative, i.e. P gets outside the sphere of attraction of M_2 .

In the *third* case of course the same expressions hold as in the second case, but now x can also be taken between 0 and $l - s$ for F_2 , $l - s$ now being $< \varrho - l$. ($2l < \varrho + s$).

Throughout the *entire* path between $MP = 0$ and $MP = l - s$ we may thus write in this third case for the joint action $F = F_1 - F_2$, i.e.

$$\underline{F = f \times 2x.}$$

It seems, therefore, *as if* the attractive action starts from the point M , and is proportional to double the distance from P to that neutral initial point, where in all the three cases mentioned the total action will, of course, be $= 0$.

We shall treat this last (third) case first, as it is by far the most important. We shall then be able to treat the two first cases in a simple way. The now following considerations, therefore, all refer to *small* volumes ($l < 1,35$ to $1,5s$, i.e. $v < 2,5$ to $3,4 b_0$), both for liquids and for solid bodies.

For the square of velocity w^2 in the point P ($MP = x$) the following equation then holds:

$$u_x^2 = u_0^2 + \frac{2}{m} \int_0^x f \times 2x \, dx = u_0^2 + \frac{2f}{m} x^2 \dots (a)$$

On contact of the two molecules u^2_{l-s} has therefore become $= u_0^2 + \frac{2f}{m} (l-s)^2$, while — in consequence of the appearance of the repulsive force, given by (the quasi-elastic force being represented by 2ε)

$$F' = 2\varepsilon (x - (l-s)),$$

when P is within the distance s (on contact) — the velocity is henceforth represented by

$$u_x^2 = u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2}{m} \int_{l-s}^x 2\varepsilon (x - (l-s)) \, dx,$$

i.e. by

$$u_x^2 = u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (x - (l-s))^2 \dots (b)$$

Hence we have, u being $\frac{dx}{dt}$:

$$dt_1 = \frac{dx}{\sqrt{u_0^2 + \frac{2f}{m} x^2}}; \quad dt_2 = \frac{dx}{\sqrt{u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (x - (l-s))^2}};$$

i.e. for the times t_1 and t_2 resp. between M and the collision, and during the collision up to the culminating point, where u has become $= 0$:

$$t_1 = \int_0^{l-s} \frac{dx}{\sqrt{u_0^2 + \frac{2f}{m} x^2}}; \quad t_2 = \int_{l-s}^{l-s'} \frac{dx}{\sqrt{u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (x - (l-s))^2}}, \dots (c)$$

when s' represents the distance of the molecule centres at the highest point of the compression.

For the mean square of velocity, i.e. the time-average, which also occurs in the *Virial equation*, and to which the *temperature* is proportional, we evidently have now quite generally:

$$\overline{u^2} = \frac{1}{t} \int_0^{l-s'} \left[u_0^2 + \frac{2f}{m} x^2 - \frac{2\varepsilon}{m} (x - (l-s))^2 \right] dt,$$

i.e. with

$$dt = \frac{dx}{\sqrt{u_0^2 + \frac{2f}{m} x^2 - \frac{2\varepsilon}{m} (x - (l-s))^2}},$$

also :

$$\bar{u}^2 = \frac{1}{t} \int_0^{l-s} \sqrt{u_0^2 + \frac{2f}{m} x^2 - \frac{2\varepsilon}{m} (x - (l-s))^2} dx,$$

when the two paths covered $x = 0$ to $l-s$, and $x = l-s$ to $l-s'$ are considered as one. Over the first range ε must be always taken as $= 0$, whereas over the second we must put $f = 0$. The above integration may now also be split up into two parts, and the following equation may be put:

$$\bar{u}^2 = \frac{1}{t} \left[\int_0^{l-s} \sqrt{u_0^2 + \frac{2f}{m} x^2} dx + \int_{l-s}^{l-s'} \sqrt{u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (x - (l-s))^2} dx \right], \quad (d)$$

in which $t = t_1 + t_2$ may be put (see (c)). In the second integral x^2 has become constant and equal to $(l-s)^2$ for the part referring to the attraction, and it does not increase any further in consequence of the elimination of the attractive force. ¹⁾

The importance of this last relation is very great. For if $\frac{1}{2} N m \bar{u}^2$ (N is the total number of molecules, e.g. in 1 Gr. mol.) is a measure for the *temperature* of the system, then $\frac{1}{2} N m u_0^2$ will be a measure for the *Energy* of that system. For only the velocity u_0^2 , with which a molecule passes the neutral position in M , can be arbitrarily increased or decreased by addition or diminution of energy (heat). What is added to $\frac{1}{2} N m u_0^2$, in the term $N f (l-s)^2$ e.g. till the collision, in consequence of the attractive action of the molecules, can never be modified by supply or removal of energy. This

¹⁾ When we assume that the attractive action still continues to exist *during* the collision (which would even be plausible), $\frac{2f}{m} x^2$ should again be substituted for

$\frac{2f}{m} (l-s)^2$ at the second integration in (c) and (d). But then the results become

much more intricate, while the difference is after all exceedingly slight, because ε is so many times greater than f . The already very short period of time of the collision would only become *somewhat* longer, while also the mean square of velocity would be subjected to only a slight modification in its value. Hence we have relinquished the idea of working out this entirely unnecessary complication, the more so as the supposition concerning the mode of action of the attractive forces made by us (i.e. in direct ratio to the distance of the centre of the moving molecule to the edge of the sphere of attraction of one of the two other molecules between which it moves to and fro), should only be esteemed an approximation.

amount is *constant*, and can be represented by E_0 ; i. e. the Energy that remains when $u_0 = 0$ (quite potential in the neutral point M ; quite kinetic at the moment of the impact). Accordingly this quantity is what PLANCK and others have called the so-called *zero-point energy*, which is nothing but the energy of the attractive forces, which is also in connection with the quantity a/v (Cf. also § 5).

Hence the quantities \bar{u}^2 and u_0^2 will always be very different according to (d) (only at high temperatures and large volumes there will practically be no difference), and for years I have already harboured the conviction that in this ¹⁾ we should look for the clue of the remarkable relation between T and E drawn up by PLANCK for low temperatures and small volumes — but which according to him can only be derived on the strength of very particular suppositions (the so-called hypothesis of *quanta*).

§ 4. Calculation of t and \bar{u}^2 .

According to (c) we now find for t_1 , putting $\frac{x}{u_0} \sqrt{\frac{2f}{m}} = y$:

$$t_1 = \int_0^{l-s} \frac{dx}{\sqrt{u_0^2 + \frac{2f}{m} x^2}} = \sqrt{\frac{m}{2f}} \log (y + \sqrt{1 + y^2}) \Big|_{x=0}^{x=l-s},$$

which with

$$\varphi = \frac{l-s}{u_0} \sqrt{\frac{2f}{m}} \dots \dots \dots (1)$$

leads to:

$$t_1 = \sqrt{\frac{m}{2f}} \log (\varphi + \sqrt{1 + \varphi^2}) \dots \dots \dots (2)$$

For $u_0 = \infty$ ($\varphi = 0$) this approaches to $t_1 = \sqrt{\frac{m}{2f}} \log (\varphi + 1) = \varphi \sqrt{\frac{m}{2f}} = \frac{l-s}{u_0}$, as was to be expected. The time is then scarcely shortened by the attractive action. But when u_0 approaches 0 ($\varphi = \infty$), t_1 approaches $\sqrt{\frac{m}{2f}} \log 2\varphi = \sqrt{\frac{m}{2f}} \log \left(\frac{l-s}{u_0} \sqrt{\frac{2f}{m}} \right)$, which thus approaches logarithmically infinite. This is owing to this, that when

¹⁾ Apart of course from the interpretation of the quantity $h\nu$ occurring in PLANCK's formula, in which h is a universal constant — which forms an *entirely separate* problem.

u_0 is exceedingly small, the time in which the very first part of the path close to the neutral point M is passed over will be very great, in spite of the attractive action (which will then, however, be still very small). We shall presently see that it is *this* circumstance which leads to the essential element of PLANCK'S relation, viz. to the logarithmical approach (in direct ratio to $1 : \log \frac{1}{u_0}$) to 0 of \bar{u}^2 (i. e. of T), when u_0^2 (i. e. $E - E_0$) approaches to 0. The time integral $\int u^2 dt$ remains namely *finite* (in consequence of the attractive action the exceedingly slight value of u_0^2 increases to a finite value), notwithstanding t itself approaches (logarithmically) to infinite.

Further we now find for t_2 with

$$y = (x - (l-s)) \sqrt{\frac{2\varepsilon}{m \left(u_0^2 + \frac{2f}{m} (l-s)^2 \right)}}$$

$$t_2 = \int_{l-s}^{l-s'} \frac{dx}{\sqrt{u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (x - (l-s))^2}} = \sqrt{\frac{m}{2\varepsilon}} (Bg \sin y)_{l-s}^{l-s'} =$$

$$= \sqrt{\frac{m}{2\varepsilon}} Bg \sin \left\{ (s-s') \sqrt{\frac{2\varepsilon}{m(u_0^2 + \text{etc})}} \right\}.$$

But in consequence of the relation

$$u^2 = u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (s-s')^2 = 0$$

at the culminating point of the collision (see equation (b)), the quantity under $Bg \sin$ will be exactly = 1, so that:

$$t_2 = \frac{1}{2} \pi \sqrt{\frac{m}{2\varepsilon}}, \dots \dots \dots (3)$$

the known expression for the time of vibration under the influence of the quasi-elastic repulsive action, proportional to the deviation from the state of equilibrium. (That here $\frac{1}{2} \pi$ occurs instead of 2π , is owing to this that only a fourth part of the entire oscillation is considered. (see above)).

We shall now compute the value of \bar{u}^2 according to (d). The first integral within [] gives:

$$I_1 = \int_0^{l-s} \sqrt{u_0^2 + \frac{2f}{m} x^2} dx = u_0^2 \sqrt{\frac{m}{2f}} \int_{x=0}^{x=l-s} \sqrt{1+y^2} dy,$$

when again, like above, $\frac{x}{u_0} \sqrt{\frac{2f}{m}} = y$ is put. Hence we get:

$$I_1 = u_0^2 \sqrt{\frac{m}{2f}} \times \frac{1}{2} \left[\sqrt{1+y^2} - \log(-y + \sqrt{1+y^2}) \right]_{x=0}^{x=l-s}.$$

The lower limit gives 0; for the upper limit y again passes into φ , so that we have:

$$I_1 = \frac{1}{2} u_0^2 \sqrt{\frac{m}{2f}} \left[\varphi \sqrt{1+\varphi^2} - \log(-\varphi + \sqrt{1+\varphi^2}) \right] \dots (4)$$

The second integral becomes:

$$I_2 = \int_{l-s}^{l-s'} \sqrt{u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (x-(l-s))^2} dx =$$

$$= \left\{ u_0^2 + \frac{2f}{m} (l-s)^2 \right\} \sqrt{\frac{m}{2\varepsilon}} \int_{x=l-s}^{x=l-s'} \sqrt{1-y^2} dy,$$

in which now $y = \frac{x-(l-s)}{\sqrt{u_0^2 + \frac{2f}{m} (l-s)^2}} \sqrt{\frac{2\varepsilon}{m}}$. We further find,

therefore:

$$I_2 = \left\{ u_0^2 + \frac{2f}{m} (l-s)^2 \right\} \sqrt{\frac{m}{2\varepsilon}} \times \frac{1}{2} \left[y\sqrt{1-y^2} + Bg \sin y \right]_{x=l-s}^{x=l-s'}.$$

For the lower limit y becomes = 0, and everything disappears, so that we only retain:

$$I_2 = \frac{1}{2} \left\{ u_0^2 + \frac{2f}{m} (l-s)^2 \right\} \sqrt{\frac{m}{2\varepsilon}} \left[\varphi' \sqrt{1-\varphi'^2} + Bg \sin \varphi' \right],$$

when $\frac{s-s'}{\sqrt{u_0^2 + \frac{2f}{m} (l-s)^2}} \sqrt{\frac{2\varepsilon}{m}} = \varphi'$ is put. However, in conse-

quence of the relation

$$u^2 = u_0^2 + \frac{2f}{m} (l-s)^2 - \frac{2\varepsilon}{m} (s-s')^2 = 0$$

at the culminating point of the collision (see above) φ' will evidently be = 1, so that we finally get:

$$I_2 = \frac{1}{2} u_0^2 (1+\varphi'^2) \sqrt{\frac{m}{2\varepsilon}} \times \frac{1}{2} \pi \dots (5)$$

These are, accordingly, the two *time integrals* of the square of velocity u^2 before and during the collision.

Hence we shall have for the mean square of velocity $u^2 = \frac{I}{t} = \frac{I_1 + I_2}{t_1 + t_2}$,

$$\bar{u}^2 = \frac{1}{2} u_0^2 \frac{\sqrt{\frac{m}{2f}} \left[\varphi \sqrt{1+\varphi^2} - \log(-\varphi + \sqrt{1+\varphi^2}) \right] + \frac{1}{2} \pi \sqrt{\frac{m}{2\varepsilon}} (1+\varphi^2)}{\sqrt{\frac{m}{2f}} \log(\varphi + \sqrt{1+\varphi^2}) + \frac{1}{2} \pi \sqrt{\frac{m}{2\varepsilon}}}, \quad (6)$$

being with $\varphi = \frac{l-s}{u_0} \sqrt{\frac{2f}{m}}$ the required expression for u^2 , expressed in u_0^2 , and which will be valid for *small* volumes ($< v_k$) for *all* temperatures.

§ 5. Two Important Limiting Cases.

a. High temperatures.

For $u_0 = \infty$ ($\varphi = 0$) we now get:

$$\bar{u}^2 = \frac{1}{2} u_0^2 \frac{\sqrt{\frac{m}{2f}} \cdot 2\varphi + \frac{1}{2} \pi \sqrt{\frac{m}{2\varepsilon}}}{\sqrt{\frac{m}{2f}} \cdot \varphi + \frac{1}{2} \pi \sqrt{\frac{m}{2\varepsilon}}},$$

as $-\log(-\varphi + \sqrt{1+\varphi^2})$ then approaches to $-\log(1-\varphi) = \varphi$, and likewise $\log(\varphi + \sqrt{1+\varphi^2})$ and $\varphi\sqrt{1+\varphi^2}$. For φ near 0 the first terms will be cancelled by the second, and u^2 will, therefore, approach to

$$(T = \infty) \quad \bar{u}^2 = \frac{1}{2} u_0^2, \quad \dots \dots \dots (7)$$

so that the time average of the square of velocity for small volumes and *high* temperatures amounts to only half the square of velocity in the neutral point. In consequence of the disappearance of the terms with f by the side of those with ε the time average is namely chiefly formed by the *diminution* of velocity *during the collision*, and not by the increase before the impact in consequence of the attraction. This latter increase lasts so short that it may be neglected with respect to the subsequent important diminution of velocity (down to 0).

Now for a linear system $Nm\bar{u}^2$ is not $= 3RT$, but simply $= RT$, and in the general relation

$$\frac{1}{2} Nm u_{l-s}^2 = \frac{1}{2} Nm \left(u_0^2 + \frac{2f}{m} (l-s)^2 \right)$$

for the vis viva at the beginning of the collision, i.e. for the sum

of kinetic and potential energy in the neutral point M (hence in all the points of the path passed over by M) the quantity $\frac{1}{2}Nm u^2$ does not represent the whole spacial Energy E , but only $\frac{1}{2}$ part of it. Likewise $Nf(l-s)^2$ will not represent the whole energy of attraction¹⁾ (zero point energy) E_0 , but again $\frac{1}{2} E_0$ ²⁾. Hence we may put:

$$Nm \bar{u}^2 = RT \quad ; \quad \frac{1}{2} Nm u_0^2 = \frac{1}{2} (E - E_0),$$

so that according to (7) we have at high temperature:

$$(T = \infty) \quad \underline{RT = \frac{1}{2} (E - E_0)} \quad . \quad . \quad . \quad . \quad (8)$$

That this equation is correct, appears from this that it gives for c_v :

$$(T = \infty) \quad c_v = \frac{dE}{dT} = 3R = 6$$

in gr. cal., hence the expected *double* heat capacity, which is only $= 3$ for large volumes (gases) under the same circumstances (i.e. high temperatures) — always on the supposition of *mon-atomic* substances, as otherwise the internal energy of the atoms within the molecules will still be added to E .

We still point out, that when the molecules were *perfectly rigid* systems, hence could not be pressed in, the quantity ϵ in our formula (6) for \bar{u}^2 would be *infinitely great*, and therefore the duration of collision absolutely $= 0$, so that then not the first terms with $\sqrt{\frac{m}{2f}} \cdot \varphi$ would be cancelled by the second with $\frac{1}{2} \pi \sqrt{\frac{m}{2\epsilon}}$, when φ approaches 0, but *just the reverse*. these latter terms would disappear by the side of the former, however small these might be on account of φ . But accordingly then \bar{u}^2 will not become $= \frac{1}{2} u_0^2$, but $= u_0^2$, hence $RT = \frac{2}{3} (E - E_0)$, so that $c_v =$ would become $\frac{3}{2} R = 3$ and not $= 6$. That, therefore, the capacity of heat for condensed systems does not *approach to 3 but to 6*, is a proof that the molecules may *not* be considered as perfectly rigid spheres, but are *elastic* systems, liable to *compression*, in which the *time of*

¹⁾ We point out that for the limiting volume $v = b$ ($l = s$) our $E_0 = 3Nf(l-s)^2$ will approach to 0. In fact, as all movement is then impossible, the energy $\frac{3}{2} Nm u^2$ can in this case not undergo any increase in consequence of the work of attraction. Of course by the side of the E_0 introduced by us, another zero point energy may always be introduced which is in connection with that of the atoms (systems of electrons) *within* the molecule. The formulae are, however, not modified by this in any respect.

²⁾ Division by 3 can also be justified by this that for the linear systems considered by us the velocities are all velocities u_n directed *normally* with respect to the molecules. And now $\bar{u}_n^2 = \frac{1}{3} \bar{u}^2$.

collision is not infinitely small or negligibly small, but will have a certain, though small, yet *finite* value.

It is self-evident that as soon as φ is no longer near 0, but assumes some value (T no longer very high), \bar{u}^2 will very soon rise to higher values than $\frac{1}{2} u_0^2$ in consequence of the increasing influence of the terms with φ , hence c_r will decrease from 6 to lower values.

§ 6. b. Low Temperatures.

At low and very low temperatures u_0 will approach to 0, i.e. φ to ∞ . The general equation (6) then passes into

$$\bar{u}^2 = \frac{1}{2} u_0^2 \frac{\sqrt{\frac{m}{2f}} \left[\varphi^2 - \log \left(-\varphi + \varphi \left(1 + \frac{1}{2\varphi^2} \right) \right) \right] + \frac{1}{2} \pi \sqrt{\frac{m}{2\varepsilon}} \varphi^2}{\sqrt{\frac{m}{2f}} \log \left(2\varphi + \frac{1}{2\varphi} \right)},$$

in which in the denominator the very small time of the collision may be neglected by the side of the time that approaches logarithmically infinite under the influence of the attractive forces. Thus we get with $-\log(1 : 2\varphi) = \log 2\varphi$, and after division in numerator and denominator by $\sqrt{\frac{m}{2f}}$:

$$\bar{u}^2 = \frac{1}{2} u_0^2 \frac{\left(1 + \frac{1}{2} \pi \sqrt{\frac{f}{\varepsilon}} \right) \varphi^2 + \log 2\varphi}{\log \left(2\varphi + \frac{1}{2\varphi} \right)}.$$

But in first approximation also $\frac{1}{2} \pi \sqrt{\frac{f}{\varepsilon}}$ may now be neglected by the side of 1 in the numerator, as ε will then be so many times greater than f . And besides $\log 2\varphi$ may be neglected by the side of φ^2 , when φ approaches ∞ . Hence we finally get:

$$(T = 0) \quad \bar{u}^2 = \frac{1}{2} u_0^2 \frac{\varphi^2}{\log \left(2\varphi + \frac{1}{2\varphi} \right)} = \frac{u_0^2 \varphi^2}{\log (4\varphi^2 + 2)}, \quad \dots \quad (9)$$

in which φ^2 is $= \frac{(l-s)^2}{u_0^2} \cdot \frac{2f}{m}$ (cf. (1) in § 4). From this it already appears that the ratio between \bar{u}^2 and u_0^2 will approach ∞ , i.e. likewise the ratio $RT : (E - E_0)$. For φ^2 is infinitely great with respect to $\log \varphi^2$. However, \bar{u}^2 itself will also approach to 0, as $u_0^2 \varphi^2$ remains *finite* (see also the beginning of § 4). But while the time,

during which the path is covered under the influence of the attraction, approaches logarithmically infinite, \bar{u}^2 does not then approach 0 ordinarily in the same way as u_0^2 , but to a *much slighter degree*, proportionally to $1 \cdot \log \frac{1}{u_0^2}$. I.e. the *temperature* will approach 0

much more slowly than the Energy; when the temperature still has a very small value, the "Energy" (i.e. $E - E_0$) will practically be already = 0. The latter, namely, is only determined by u_0^2 in the neutral point, whereas the temperature is determined by the time average of the square of velocities which has *increased* under the influence of the attraction.

Hence relatively only exceedingly little supply of energy is required to augment the temperature by a certain amount: in other words *the heat capacity will rapidly approach 0 at low temperatures*.

When we substitute its value for φ^2 , $u_0^2 \varphi^2$ becomes = $\frac{2f}{m} (l-s)^2$, so that with $Nf(l-s)^2 = \frac{1}{8} E_0$ and $Nm \bar{u}^2 = RT$ (see above) we get:

$$(T=0) \quad RT = \frac{\frac{2}{8} E}{\log \left(\frac{4E_0}{E-E_0} + 2 \right)}, \quad \dots \quad (10)$$

$$\text{as } \varphi^2 = \frac{2Nf(l-s)^2}{Nm u_0^2} = \frac{\frac{2}{8} E_0}{\frac{2}{8} (E-E_0)} = \frac{E_0}{E-E_0}.$$

Accordingly, by (10) T is expressed in E for the case of small volumes and low temperatures. It is noteworthy that (10) is not *quite* identical with PLANCK's relation, but that the *logarithmically infinite* denominator $\log(4\varphi^2 + 2) = \log \left(\frac{4E_0}{E-E_0} + 2 \right)$ would have to be diminished by the *small finite* quantity $\log 2 = 0,69$, in consequence of which the denominator would become $\log(2\varphi^2 + 1) = \log \left(\frac{2E_0}{E-E_0} + 1 \right)$.

The original denominator $\log \left(2\varphi + \frac{1}{2\varphi} \right)$ would, therefore, have to be diminished by $\frac{1}{2} \log 2 = 0,35$.

Different circumstances might be adduced as an explanation of this exceedingly slight difference, which is for the rest immaterial. First of all possibly an exceedingly small modification in our fundamental suppositions concerning the mode of action of the attractive forces, the logarithmic form of t_1 being retained, might give rise to a modification in this sense that still a constant term is to be applied. And in the second place the taking in account of MAXWELL's distri-

bution-law of velocities in the calculation of t_1 may have a certain influence on the result. Unfortunately the computations referring to this cannot be executed, because they will lead to a definite integral which cannot be determined. In the third place it may be alleged that with respect to the velocity of the moving molecule M it is not quite justifiable to assume the molecules M_1 and M_2 to be *at rest* on the strength of the fact that the movement may be directed equally well towards the left as towards the right. It should be pointed out here that when M_1 , e.g. is on the lefthand side of its mean position, it will exert a stronger attractive action on M than when it is on the righthand side. And there are more similar remarks that might be made.

In virtue of the above considerations we may, therefore, safely apply the said correction, which is exceedingly slight with respect to the logarithmically infinite chief term, and write:

$$RT = \frac{^{2/3} E_0}{\log \left(\frac{2E_0}{E - E_0} + 1 \right)} \dots \dots \dots (10a)$$

When we reverse this relation, we get:

$$E - E_0 = \frac{2E_0}{e^{RT} - 1} \dots \dots \dots (11)$$

Putting in this:

$$E_0 = 3 N f (l-s)^2 = ^{2/3} N . hv \dots \dots \dots (12)$$

we get finally:

$$E = \frac{3}{2} N hv + \frac{3 N hv}{e^{RT} - 1}, \dots \dots \dots (11a)$$

which is in agreement with PLANCK's relation (after multiplication by 3 on account of the transition from a linear to a spacial oscillator).

Hence the quantity hv introduced by PLANCK would have been given by:

$$hv = 2 f (l-s)^2, \dots \dots \dots (11a)$$

from which h could be calculated when v is *determined* (this quantity v would, accordingly, have to contain the factor $(l-s)^2$, hence it would be dependent on the *volume*, as is, indeed, assumed), and when f , the constant of the attractive action introduced by us, is known. We shall return to this *special* problem later on.

We only still point out that our formula (11) or (11a), resp. (10) or (10a) is only valid for *low*, and *not* for high temperatures, whereas

PLANCK is of opinion that the expression (11a) is of general application, for high as well as for low temperatures. According to our derivation the more complicated ¹⁾ formula (6) would represent the generally valid relation, which is only transformed to the form (11a) for very low temperatures.

Christmas 1918.

(To be continued).

¹⁾ Also EINSTEIN, DEBYE and others already derived more complicated relations, which are considered to represent the relations better than PLANCK's simple formula.