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Physics. — “*On the law of partition of energy.*” V. By Prof. J. D. VAN DER WAAALS Jr. (Communicated by Prof. J. D. VAN DER WAAALS)

(Communicated in the meeting of March 28, 1914).

§ 10 bis. In § 10 of this series of communications¹⁾ I have drawn up a formula for the dissociation equilibrium of a di-atomic gas. This formula, however, requires emendation. In the first place, namely, the c_v of the gas would not correspond with 5, but with 7 degrees of freedom on the suppositions introduced l. c. And besides the vibrations of the atom would consist of three equivalent degrees of freedom, and there was no occasion to ascribe the ordinary equipartition amount to two of them (together representing a rotation round the other atom), and the amount U of PLANCK'S formula to the third (the vibration in the direction of the radius vector).

To correct this we shall have to take care that the degrees of freedom do not remain equivalent. Then it will no longer be permissible to consider one atom as a point which moves in the quasi elastic region of the other. We shall then introduce the following suppositions. Every atom will have a point P , which we shall call the pole. The line from the centre M to the pole will be called *axis*. There will be a quasi elastic region G round the pole. Two atoms will now be bound when they lie with their poles in each other's regions G . The potential energy will be minimum when the poles coincide, and when moreover the axes are one another's continuation.

We shall introduce the following coordinates for the diatomic molecules :

1. The three coordinates of the centre of gravity x_z, y_z, z_z . The kinetic energy corresponding to them will be $\frac{3}{2} \theta$.

2. The distance of the centres of the atoms, or rather the displacement in the direction $M_1 M_2$ of the points P_1 and P_2 out of the state of equilibrium (in which they coincided). This displacement will be called r ; it will give rise to vibrations with the frequency ν , in which the potential and the kinetic energy are both equal to $\frac{1}{2} U$.

3. Displacements of P_1 and P_2 with respect to each other normal to $M_1 M_2$, or what comes to the same thing rotations of the axes out of the position $M_1 M_2$. These coordinates will give rise to rotative

¹⁾ These Proc. XVI, p. 88.

vibrations. In agreement with RUTHERFORD, PERRIN, and others I shall assume the moment of inertia of the atom to be very small, even in comparison with $m\alpha^2$ ($m = \text{mass}$, $\alpha = \text{radius of the atom}$). Then the frequency of this rotative vibration will be great compared with ν . In connection with this we shall put the energy of these vibrations equal to zero, and entirely disregard possible atomic rotations.

4. The rotation of the molecule. Of this we may assume for all the cases of equilibrium that have been experimentally investigated that they represent two degrees of freedom, which present the equipartition amount, whereas the rotation round M_1, M_2 practically has an energy zero. We shall represent the position of the axis of the molecule by the aid of the angles α and β indicating the longitude and the latitude.

Instead of equation (19) p. 88 loc. cit. we now find for the number of dissociated pairs of atoms:

$$\begin{aligned} n_1 &= N^2 e^{-\frac{\varepsilon_0}{\theta}} \int e^{-\frac{\varepsilon_0}{\theta}} dx_1 dy_1 dz_1 (m_1)^3 dx_1 dy_1 dz_1 \times \\ &\quad \times dx_2 dy_2 dz_2 (m_2)^3 dx_2 dy_2 dz_2 = \\ &= N^2 e^{-\frac{\varepsilon_0}{\theta}} (2\pi m_1 \theta)^{3/2} \times (2\pi m_2 \theta)^{3/2} \end{aligned} \quad (19a)$$

For the number of bound pairs of atoms we find, representing the moment of inertia of the molecule by M :

$$\begin{aligned} n_v &= N^2 e^{-\frac{\varepsilon_1}{\theta}} \int e^{-\frac{\varepsilon_p + \frac{1}{2} fr^2}{\theta}} \chi(r, v) dx_2 dy_2 dz_2 (m_1 + m_2)^3 dx_2 dy_2 dz_2 \times \\ &\quad \times dr \frac{m_1 m_2}{m_1 + m_2} dr \sin^2 \alpha d\alpha d\beta M^2 d\alpha d\beta = \\ &= N^2 e^{-\frac{\varepsilon_1}{\theta}} \{2\pi (m_1 + m_2) \theta\}^{3/2} \frac{h}{1 - e^{-\frac{h}{v h}}} \times 4\pi \times 2\pi M \theta \end{aligned} \quad (19'a)$$

For ε_p depends on r through the term $\frac{1}{2} \frac{m_1 m_2}{m_1 + m_2} r^2$, which term we shall call ε_p . In connection with this equation (18) loc. cit. must now be written as follows:

$$\int e^{-\frac{\epsilon_p - 1/2 f r^2}{\theta}} \chi(r, r, v) \frac{m_1 m_2}{m_1 + m_2} dr dr = \frac{h}{1 - e^{-\frac{v h}{\theta}}}$$

This gives for the equilibrium constant:

$$\frac{n_1^2}{n_v} = e^{-\frac{\epsilon_1 - \epsilon_0}{\theta}} \left(\frac{m_1 m_2}{m_1 + m_2} \right)^{3/2} \frac{1}{M} \times \frac{1 - e^{-\frac{v h}{\theta}}}{h} \times \frac{1}{2} \sqrt{\frac{\theta}{2\pi}} \quad (20a)$$

§ 13. *Zero point energy and chemical binding.*

In the above given formula PLANCK's later supposition concerning the existence of a zero point energy has not been taken into account. We shall now examine some consequences of this supposition for the chemical phenomena. In the first place we shall show that according to this supposition the entropy of a number of particles does not change at the absolute zero point, when they pass from a binding in which they can vibrate with a definite period into another combined state, in which they have another period. For this purpose we shall make use of BOLTZMANN's quantity H , which we shall represent as follows:

$$H = \int F l(F) m^3 dx dy dz dx dy dz.$$

So we think here again of a three dimensional vibrator with three equivalent degrees of freedom, though this case probably never occurs in reality. If we had taken a linear vibrator, this would have come to the same thing. But then we should have had to speak besides of vibrations, also of rotations of the molecule, which would have rendered the question somewhat less simple.

According to PLANCK's supposition the value of F for $T=0$ is constant for an energy smaller than $v h$, equal to zero for a larger energy. Let us put:

$$m^3 dx dy dz dx dy dz = d\omega,$$

and

$$\int_{\epsilon < v h} m^3 dx dy dz dx dy dz = G$$

then for $T=0$:

$$\int F d\omega = F \int d\omega = FG = N,$$

when N represents the total number of particles, and further:

$$H = l(F) \cdot \int F d\omega = l(F) \cdot N = N \{l(N) - l(G)\}.$$

We may write for G :

$$G = \frac{m^{3/2}}{f^{3/2}} \int_{\epsilon < h} dx_1 dx_2 dx_3 dx_4 dx_5 dx_6$$

when we introduce $x\sqrt{m} = x_1$, $y\sqrt{m} = x_2$, $z\sqrt{m} = x_3$, $x\sqrt{f} = x_4$, $y\sqrt{f} = x_5$ and $z\sqrt{f} = x_6$, so that $\epsilon = x_1^2 + x_2^2 + x_3^2 + x_4^2 + x_5^2 + x_6^2$.

The integral occurring in G , therefore, represents the content of a sixdimensional sphere with a radius $\sqrt{v}h$, and is therefore proportional to $(v h)^3$. Bearing in mind that $v = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$, we see that G and with it also H , becomes an absolute constant.

If we assume for a linear vibrator that besides vibrations with a frequency ν rotations occur with a frequency $\nu' = \frac{h}{2\pi^2 M}$, it appears here in the same way that G and H become absolute constants.

Hence we see that on these simple suppositions PLANCK'S supposition about the zero point energy directly leads to NERNST'S heat theorem.

As known PLANCK formulated NERNST'S theorem by assuming that the entropy remains finite at $T = 0$, and does not become $-\infty$, as it would have to do according to the older theory. According to the older theory, e. g. according to BOLZMANN, one would have to come to the value $-\infty$, because at $T = 0$ the molecules would all have a velocity zero, and there would, therefore, be only one possible distribution of the points of velocity in the diagram of velocity. At every higher temperature there would be ∞ many velocities possible for every molecule; there would therefore be infinitely many possible distributions of the points of velocity. The probability at higher temperature would therefore be ∞ times as great as at $T = 0$, which leads to an ∞ difference of entropy.

It is interesting to observe how the two suppositions introduced by PLANCK into physics evade this difficulty and make the entropy difference finite in the two only ways possible. The infinite entropy difference could namely be evidently evaded in two ways; namely 1. by assuming that there is a finite number of distributions of the points of velocity also at high temperature, and 2. by assuming that there are infinitely many also at $T = 0$. The former hypothesis is that of the energy quanta, the second that of the zero point energy. Each of these two suppositions leads to a finite relation of the number of possible distributions at $T = 0$ and at $T > 0$, and hence to a finite entropy difference.

Let us now examine the distribution of the energy at higher temperature. We shall continue to assume that a number of mole-

cules will possess an energy $< \nu h$, and that for them every value of the energy is equally probable. So in this region the chance that the energy lies between ε and $\varepsilon + d\varepsilon$ will be represented by $F(\theta\nu) d\varepsilon$. In the region where $\varepsilon > \nu h$ I shall continue to assume that the

function is represented by $e^{-\frac{\varepsilon}{\theta}} \chi(\varepsilon\nu) d\varepsilon$ ¹⁾. If we now put:

$$I = \int_0^{\nu h} F(\theta\nu) d\varepsilon + \int_{\nu h}^{\infty} e^{-\frac{\varepsilon}{\theta}} \chi(\varepsilon\nu) d\varepsilon \dots \dots \dots (21)$$

the equilibrium constant of a chemical conversion is represented by:

$$K = e^{-\frac{\Delta\varepsilon}{\theta}} \frac{III}{II I} \dots \dots \dots (20b)$$

In this $\Delta\varepsilon$ represents the difference in potential energy which would occur when the substances passed from the compounds of the lefthand member of the reaction equation into those of the righthand member. In order to obtain the energy amount $\Delta\varepsilon$ then, it would however be necessary that the atoms in the compounds always occupied the positions of minimum potential energy, so in the centres of the quasi elastic regions. *III* represents a fraction with the product of the quantities *I*, referring to substances in the lefthand member in the numerator, and with that in the righthand member in the denominator. The equation is evidently nothing but a generalisation of (20a), in which besides the *I*'s are determined in agreement with the supposition of the zero point energy.

Now

$$\frac{dK}{d\theta} = + \frac{\Delta\varepsilon}{\theta^2} + \sum \frac{1}{I} \frac{dI}{d\theta} \dots \dots \dots (22)$$

On the other hand the law of the equilibrium change requires:

$$\frac{dK}{d\theta} = \frac{Q}{\theta^2} = \frac{Q_0 + \sum \int_0^T C_p dT}{\theta^2} \dots \dots \dots (22a)$$

Further we have:

$$Q_0 = (\Delta\varepsilon + \sum \frac{1}{2} \nu h) \dots \dots \dots (23)$$

¹⁾ Besides in my previous communications this function had already been introduced by EHRENFEST, Ann. d. Phys. IV, 36 p. 91, Ann. 1911, which paper I have not sufficiently taken into account in my previous considerations; the same refers to POINCARÉ's paper, Journal de Physique theor. et appl. V serie II p. 5. Ann. 1912.

$$\Sigma \frac{\theta^2}{I} \frac{dI}{d\theta} = \Sigma \frac{1}{2} \nu h + \Sigma \int_0^I C_\nu dT = \Sigma U. \quad (23a)$$

In all these summations the quantities must have the sign + or — according as they relate to the righthand or the lefthand member of the reaction equation. The equations having to hold for every chemical reaction, independent of the values of the ν 's, we shall be allowed to omit the Σ signs in (23a), and write such an equation for every coordinate separately.

We then get:

$$U = \frac{\int_0^{\nu h} \epsilon F(\theta, \nu) d\epsilon + \int_{\nu h}^{\infty} \epsilon e^{-\frac{\epsilon}{\theta}} \chi(\epsilon, \nu) d\epsilon}{I} = \frac{\theta^2}{I} \frac{dI}{d\theta}$$

or

$$\frac{1}{2} (\nu h)^2 F(\theta, \nu) + \int_{\nu h}^{\infty} \epsilon e^{-\frac{\epsilon}{\theta}} \chi(\epsilon, \nu) d\epsilon = \theta^2 \left\{ \int_0^{\nu h} \frac{dF}{d\theta} d\epsilon + \int_{\nu h}^{\infty} \frac{\epsilon}{\theta^2} e^{-\frac{\epsilon}{\theta}} \chi(\epsilon, \nu) d\epsilon \right\}$$

or

$$\frac{1}{2} (\nu h)^2 F(\theta, \nu) = \frac{dF(\theta, \nu)}{d\theta} \theta^2 \cdot \nu h$$

from which follows:

$$F(\theta \nu) = C \times e^{-\frac{\nu h}{2\theta}} \quad (24)$$

It is evidently not impossible to assign such a value to the C

that $F(\theta, \nu)$ and $e^{-\frac{\epsilon}{\theta}} \chi(\epsilon, \nu)$ continuously pass into each other at more than a single temperature. In general a discontinuity will occur in the function of probability at $\epsilon = \nu h$. I do not know a way to determine C . The value $\chi(\epsilon, \nu)_{\epsilon = \nu h}$ suggests itself most naturally

Then the function of probability becomes continuous, at $\theta = \infty$, which is in accordance with the fact that at high temperatures the deviations from classical mechanics become smaller. With this value of C we see that the number of molecules having an energy slightly smaller than νh , is greater than the number having a some-

what greater energy. The ratio is $e^{\frac{h\nu}{2\theta}}$. This is in harmony with PLANCK'S theory according to which for vibrators which are absorbing energy of radiation, only a part continues to absorb when $\epsilon = \nu h$

is reached, and passes therefore to the group for which $\epsilon > \nu h$, whereas another part emits all the stored energy. For the chance of emission we find another value than PLANCK. This is not astonishing as we assumed that for $\epsilon > \nu h$ the function of probability would be continuous, whereas according to PLANCK it exhibits new discontinuities at $\epsilon = 2\nu h$ etc. At all events we see that PLANCK's hypothesis concerning the zero-point energy can only be reconciled with the thermodynamic law of the equilibrium change, when the function of probability shows a discontinuity at $\epsilon = \nu h$, of entirely the same nature as had already been assumed by PLANCK.

In conclusion we will calculate I , as this quantity occurs in the formula for the equilibrium constant. Integration of (23a) with

$$U = \frac{\nu h}{e^{\frac{\theta}{\nu h}} - 1} + \frac{1}{2} \nu h \text{ yields:}$$

$$I = \frac{h e^{-\frac{1}{2} \frac{\nu h}{\theta}}}{1 - e^{-\frac{\nu h}{\theta}}}$$

This expression differs from the value which we found without zero-point energy, and which we shall call I' by the factor $e^{-\frac{1}{2} \frac{\nu h}{\theta}}$. Hence we may write (20b) in the following form:

$$K = e^{-\frac{\Delta \epsilon}{\theta}} e^{-\frac{1}{2} \sum \frac{\nu h}{\theta}} III'.$$

And Q_0 being $= (\Delta \epsilon + \sum \frac{1}{2} \nu h)$, we find the same expression as without zero point energy, since then $Q_0 = \Delta \epsilon$, and we may, therefore, always write.

$$K = e^{-\frac{Q_0}{\theta}} III'.$$

Chemistry. — “*A new hydrocarbon from the pinacone of methyl-ethylketone*”. By Prof. P. VAN ROMBURGH and Miss D. W. WENSINK.

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When studying the action of formic acid on this pinacone this seemed to take a course quite contrary to expectation. Whereas in this reaction the ordinary pinacone is almost completely converted