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the viscosimeter was turned round, to drive the remaining liquid out of the capillary. Only one determination was successful. We hope later on to be able to publish more extensive determinations at low temperatures.

Our results are given in the table.

The liquid-densities were measured by a dilatometer.

temp.	time	corrected	density	η
34.5°	235.5	235.2	0.556	0.00163
18.5°	258.5	258.2	0.577	176
0.0	291.8	291.5	0.601	207
-23.6	352.6	352.3	0.631	265

The method of calculation of η from the data is made clear by the following example.

The viscosimeter when filled weighed 16.78 gr. and empty 14.26 gr.

The weight of the butane was therefore 2.52 gr. with a volume of 4.20 cc.

The time of flow of 4.20 cc. water at 0° is 1504.0 sec. (according to table on page 80; of the butane 291.8 sec.

Corrected for capillarity these times become 1499.8 and 291.5.

$$\eta_w = 0.01778 \text{ } ^1) \text{ therefore } \eta_b = 0.01778 \frac{0.601 \times 291.5}{1498.9 \times 0.9999} = 0.00207.$$

THORPE and RODGER (p. 590) give for the viscosity at the boiling point for

normal pentane	$\eta \times 10^5$	200	isopentane	203
„ hexane		204	isohexane	205
„ heptane		199	isoheptane	198
„ octane		198		

As the boiling point of butane is just below 0°, the value we find for η corresponds well with that for the other hydrocarbons.

Physics. — “*On the law of the partition of energy.*” III. By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS Sr.).

§ 9. *The distribution in configuration.*

In § 7 of my preceding note on this subject I have called attention to the deviations of BOLTZMANN's law for the distribution in configuration, but then I did not give a possible formula for it. Nor can I give a formula for the general case now. I will however try for

¹⁾ THORPE and RODGER l. c. p. 449.

a simple special case to draw up a formula here, which is in agreement with what is known concerning the kinetic energy. This special case is the following.

A large number n_0 of particles move in a space V , which has the following properties: the particles can move freely in a part of the space without being subjected to forces. I will call this part the free space. In another part v forces will act which are directed towards a centre; the intensity of these forces will be proportional to the distance from that centre. We will assume that not only one centre of this kind is present in the space, but n_1 , each of them surrounded by a region v . Every region v , however, will be surrounded by a transition region, which is characterised by the property that a particle lying in it has a much higher potential energy than one in the free space. In other words: when the particles come from the free space and penetrate into the transition-regions they are at first repulsed, and not until they have approached towards the centre to within a definite distance R will they experience the forces directed towards the centre, which I will call the quasi-elastic forces. I will assume, that the sum of all the regions v and also of the transition-regions will be small compared with the free space. This latter may therefore also be represented approximately by V .

It is obvious that in each of the regions v particles can move which execute harmonic vibrations. The period of these vibrations will be determined by the mass of the particles and by the intensity of the quasi-elastic forces. We will raise the question, what will be the distribution in velocity and the distribution in configuration of these particles.

I will assume that the component of the velocity in the direction of the radius-vector towards the centre of attraction will show a smaller amount than would agree with the equipartition law; but that the components perpendicular to it will show the normal equipartition amount. I make this assumption in order to account for the energy of di-atomic molecules, which corresponds at ordinary temperatures with five degrees of freedom. In reality, however, the properties of di-atomic molecules will probably be somewhat different from those assumed by me. The average kinetic energy of the component of the velocity in the direction of the radius vector of particles which lie in the regions v will be represented instead of by the normal $\frac{1}{2} \theta$, by the value ascribed to it by PLANCK: $\frac{1}{2} \frac{v h}{e^{\theta} - 1}$.

$$\frac{1}{2} \frac{v h}{e^{\theta} - 1}$$

The supposition would now naturally suggest itself, 1st. that the mean value of the kinetic energy for this degree of freedom would be the same for the different points of the region v ; 2nd. that the partition of the velocities for this component would be represented

by $Ce^{-\frac{1}{2}mv^2/U} dv$. This expression however leads to an untenable formula for the distribution in configuration. I will therefore assume that the radial component of the velocity does not follow MAXWELL's law for the distribution of velocities, and that the mean kinetic energy belonging to it is different for different points of the region v .

For points at a distance r from the centre e.g. it will amount to $F(r)$. This function $F(r)$ is unknown; we only know that its mean value for different values of r will amount to $\frac{1}{2} U$. The components of the velocity perpendicular to the radius vector will be denoted by s' and t' . Their mean kinetic energy will be equal to the normal equipartition-amount.

In a harmonic vibration kinetic and potential energy are periodically converted into one another; therefore the distribution in configuration will follow the same law as the distribution in velocity. We are therefore justified in the following assertions concerning it. Let us take all molecules with a definite velocity v , and investigate their deviations from the position of equilibrium. We will call the component of the deviation in the direction v, r_v , the components normal to this direction r_s and r_t . The mean value of $\frac{1}{2}fr_v^2$ for these molecules will again amount to $F(v)$, which function again is unknown, whereas its average value for different values of v amounts to $\frac{1}{2} U$. The average values of $\frac{1}{2}fr_s^2$ and $\frac{1}{2}fr_t^2$ present the normal equipartition-amount.

In this way we are induced to represent the number of particles whose coordinates and momenta are included between definite limits by:

$$Ne^{-\frac{\epsilon_p + \epsilon_q}{U}} \chi(mr, ms', mt', r_v, r_s, r_t, v) dmr dms' dmt' dr_v ds dr_t \dots \quad (14)$$

Here $\epsilon_p = \frac{1}{2}m(\dot{r}^2 + s'^2 + t'^2)$ and $\epsilon_q =$ the potential energy. In the space V this potential energy has a constant amount ϵ_0 ; in the

¹⁾ These Proc. Vol. XV, p. 1355 I really have expressed the opinion that this partition of velocities would probably exist. I have however written erroneously $\frac{1}{3}U$ in the numerator of the exponent instead of U . If U represented the total kinetic energy of a particle with three degrees of freedom, $\frac{1}{3}U$ would be the right value. U represents however the kinetic energy for one degree of freedom.

regions v it is equal to $\varepsilon_1 + \frac{1}{2}fr^2$, where ε_1 is the energy of a particle lying in a centre of a region v . χ is an unknown function, which for $v=0$ (i. e. in V) assumes the value unity, whereas in the regions v it must satisfy the following equations:

$$\left. \frac{\int \frac{1}{2} mr^2 Ne^{-\frac{\varepsilon_p + \varepsilon_q}{\theta}} \chi() dmr dms' dmt' dr_v dr_s dr_t}{\int Ne^{-\frac{\varepsilon_p + \varepsilon_q}{\theta}} \chi() dmr dms' dmt' dr_v dr_s dr_t} = \frac{\frac{1}{2} \frac{vh}{\theta}}{\frac{vh}{\theta} - 1} \right\} \quad (15a)$$

and a corresponding formula for the mean value of $\frac{1}{2} fr_v^2$; and

$$\left. \frac{\int \frac{1}{2} ms'^2 Ne^{-\frac{\varepsilon_p + \varepsilon_q}{\theta}} \chi() dmr dms' dmt' dr_v dr_s dr_t}{\int Ne^{-\frac{\varepsilon_p + \varepsilon_q}{\theta}} \chi() dmr dms' dmt' dr_v dr_s dr_t} = \frac{\frac{1}{2} \theta}{\theta} \right\} \quad (15b)$$

and three corresponding formulae for the average values of $\frac{1}{2} mt^2$, $\frac{1}{2} fr_s^2$ and $\frac{1}{2} fr_t^2$.

In consequence of the formulae (15b) we no doubt must assume, that χ is independent of s', t', r_s and r_t . If this is so we can divide in (15a)

the numerator and the denominator by $\int_e^{-\frac{\frac{1}{2} ms'^2}{\theta}} dms'$ and by three corresponding integrals. We get therefore, if we add the two equations (15a):

$$\frac{\int (\frac{1}{2} mr^2 + \frac{1}{2} fr_v^2) e^{-\frac{mr^2 + fr_v^2}{2\theta}} \chi(r, r_v, v) dmr dr_v}{\int e^{-\frac{mr^2 + fr_v^2}{2\theta}} \chi(r, r_v, v) dmr dr_v} = \frac{\frac{vh}{\theta}}{\frac{vh}{\theta} - 1} \quad (16)$$

The integrations with respect to v should be extended between 0 and ∞ , properly speaking those with respect to r however only between 0 and R . If R and f are sufficiently great and θ sufficiently small, it will be allowed to introduce also ∞ as superior limit for the integration with respect to r .

If we call the denominator of the left hand member of (16) J , then the numerator may be represented by $\theta^2 \frac{dJ}{d\theta}$. The equation may therefore be written in the following form:

$$\frac{1}{J} \frac{dJ}{d\theta} = \frac{\frac{vh}{\theta^2}}{\frac{vh}{\theta} - 1} = \frac{e^{-\frac{vh}{\theta}} \cdot \frac{vh}{\theta^2}}{1 - e^{-\frac{vh}{\theta}}} \quad (17)$$

from which we deduce:

$$J = \frac{C}{1 - e^{-\frac{vh}{\theta}}} \quad (18)$$

The value of C may be determined, because we know that for $v=0$ the function χ assumes the value 1. Then the integral becomes

$\sqrt{2\pi m\theta} \cdot \sqrt{2\pi \frac{\theta}{f}}$ and the right hand member $C \cdot \frac{vh}{\theta}$. In connection with $v = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$ this yields:

$$C = h.^1)$$

§ 10. Application to chemical equilibrium.

We will apply these results for the derivation of a formula for the dissociation equilibrium of a di-atomic gas. For this purpose we will assume, that n_1 free atoms are present in a unit of volume. Each atom has a region v , whose properties are described in the preceding paragraph. When another atom penetrates into the region v , a di-atomic molecule is formed. According to our considerations in the preceding paragraph we have:

$$n_1 = Ne^{-\frac{\epsilon_0}{\theta}} \int e^{-\frac{\epsilon_p}{\theta}} dm r' dm s' dm t' = Ne^{-\frac{\epsilon_0}{\theta}} (2\pi m\theta)^{3/2} \quad (19)$$

χ being unity for free space. The number of particles in one region v amounts to:

$$\begin{aligned} n_v &= Ne^{-\frac{\epsilon_1}{\theta}} \int e^{-\frac{\epsilon_p + 1/2 f (r_v'^2 + r_s'^2 + r_t'^2)}{\theta}} \chi(r, r_v) dm r' dm s' dm t' dr_v dr_s dr_t = \\ &= Ne^{-\frac{\epsilon_1}{\theta}} \cdot 2\pi m\theta \cdot 2\pi \frac{\theta}{f} \cdot \frac{h}{1 - e^{-\frac{vh}{\theta}}} \end{aligned}$$

¹⁾ Properly speaking C can be a function of v , and therefore we should write for $C = h \times F(v)$, where $F(v)$ is a function of v , which for $v=0$ is unity. In the following, however, we will use the simple solution $C = h$.

So the total number of associated molecules is:

$$n_g = n_1 \times n_v = n_1^2 e^{\frac{\epsilon_0 - \epsilon_1}{\theta}} (2\pi\theta)^{1/2} \frac{1}{fV_m} \frac{h}{1 - e^{-\frac{vh}{\theta}}}$$

or

$$n_g = n_1^2 e^{\frac{\epsilon_0 - \epsilon_1}{\theta}} \sqrt{\frac{\theta}{8\pi^3 m^3}} \frac{\frac{h}{v^2}}{1 - e^{-\frac{vh}{\theta}}} \dots \dots \dots (20)$$

So we have found a general formula for the dissociation of di-atomic molecules. I hope to discuss this formula later more fully. At present I will only observe, that it shows a certain analogy with the results of NERNST's "Wärme-theorem". This analogy consists in the circumstance, that the equilibrium-constant is determined by $\epsilon_0 - \epsilon_1$ (i. e. the heat developed by the reaction at the absolute zero of temperature) and by r , which quantity is closely connected with the store of energy and the specific heat. Besides the molecular weight occurs in the formula. The chemical volumes (i. e. BOLTZMANN's "kritische Raume") to which we should be inclined to ascribe an influence on the equilibrium-constant do *not* occur in the formula. The cause of this is that in equation (16) we have extended the integrations with respect to r between 0 and ∞ instead of between 0 and R . If the conditions on which we thought we were justified in doing so are not satisfied, then the formula would of course have to be modified in such a way that the chemical volumes would occur in it. In this case, however, the number of molecules dissociating in one second would be so large, that we should be in circumstances in which we consider the substance to be totally dissociated. We should no longer have occasion to speak of chemical combination, but only of grouping or quasi-association.

A difference with the considerations of NERNST constitutes the circumstance that we started in the usual way from gasreactions, whereas NERNST takes reactions in solid condition as starting-point. Whether this is only a difference of method, or whether it leads to different results is a question which I hope to investigate on a later occasion.

I will still make one single remark in connection with equation (20), namely that it agrees with the law of the equilibrium change.

If namely we put $\frac{n_g}{n_1^2} = K$, then we get:

$$\frac{dK}{d\theta} = \frac{1}{\theta^2} \left\{ \varepsilon_1 - \varepsilon_0 + \frac{1}{2} \theta + U \right\} \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The expression between braces represents the thermal value of the reaction. For in the free space the potential energy is ε_0 and the mean kinetic energy $\frac{3}{2} \theta$. In associated condition the potential energy would be ε_1 , if the particles were always in the centres of the regions v . For the average potential energy of the deviation from that position of equilibrium in the direction v we have found $\frac{1}{2} U$ and for the two components of the deviation normal to v each $\frac{1}{2} \theta$. For the kinetic energy we assumed in the same way $\frac{1}{2} U + \theta$. So we get for the thermal value of the reaction:

$$\varepsilon_1 + 2 \theta + U - \left(\varepsilon_0 + \frac{3}{2} \theta \right) = \varepsilon_1 - \varepsilon_0 + \frac{1}{2} \theta + U.$$

It is by no means superfluous to investigate whether this law is satisfied. If e.g. we had assumed MAXWELL's law for the distribution

$-\frac{1}{2} f r_v^2$

of r and if in connection with this we had written $C e^{\frac{U}{d r_v^2}}$ for the probability of a deviation r_v in the direction v then we should have found a formula for K which in general would not satisfy the law of the equilibrium change. Artificial additional suppositions would be required if we wished this law to be satisfied.

§ 11. *The distribution in configuration in arbitrary fields of force.*

The above considerations only refer to particles subjected to forces, under the influence of which they can execute tautochronic harmonic vibrations. About the question what the formula for the distribution of particles in arbitrary fields of forces will look like, I should not venture to express so much as a supposition, except of course in those cases in which BOLTZMANN's original formula is a sufficient approximation. I will only express the following surmise.

For quasi-elastic forces the energy of the particles is governed by the quantity v , which in its turn is again determined by the quantity f . The conclusion now naturally suggests itself that for an arbitrary field of forces the quantity $\frac{dF}{dx}$ ($F =$ the force that acts on a particle) will be decisive for the energy of the particles. This supposition comes to this, that we assume that the particles, when they get into a very inhomogeneous field of forces, in consequence of this are subjected to changes in properties (shape, mass etc.), which changes are not governed by the laws of classical mechanics, and give rise to the deviations from the equipartition law.