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activating one. This effect is the more important as hitherto I have not succeeded in the usual way to demonstrate a favourable influence of zinc.

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

§ 6. It is obvious that the chance that the value of one of the variables p or q lies between specified limits cannot be represented by a normal frequency curve. If however we investigate a region of the spectrum, which is very narrow, but yet contains many elementary vibrations, then we find another probability curve than for one single elementary vibration. If the region is sufficiently small, then the radiation will appear to us to be homogeneous. Only an observation during a long time (i.e. very long compared with one period) will reveal the want of homogeneity by the increase and decrease of the amplitude in consequence of beats. In order to describe the momentaneous condition we can represent one elementary vibration by:

$$a \sin \frac{2\pi t}{T} + b \cos \frac{2\pi t}{T}$$

and the total vibration of the spectral region by:

$$(\sum a) \sin \frac{2\pi t}{T} + (\sum b) \cos \frac{2\pi t}{T}.$$

In this expression the separate a 's and b 's may have all kinds of values. The chance that they lie between specified limits is not represented by a normal frequency curve. But this does not detract from the fact that the chance for a specified value of $(\sum a) = A$, is represented by a normal curve, at least if the sum contains a sufficiently great number of terms.

Let us imagine that the decrease of the amplitude of the vibrators in consequence of the radiation has such a value, that they are perceptibly set vibrating by a great number of elementary vibrations whose period does not differ too much from the fundamental period of the vibrators, then MAXWELL's law will hold for the chance that the velocity of a vibrating particle lies between specified limits. The mean energy of a linear vibrator is probably rightly represented by

the formula of PLANCK:

$$U = \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} \dots \dots \dots (11)$$

so the chance that the velocity of a vibrating particle has the value s will be represented by:

$$C e^{-\frac{1/2 ms^2}{\frac{1}{3} U}} ds \text{ where } \frac{1/2 ms^2}{\frac{1}{3} U} = \frac{1}{2} U = \frac{1}{2} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1}$$

It is true that the formula (11) has been calculated with the aid of an equation of the form. (1) p. 1177 and that such an equation cannot hold good. But here a difference between the theory of PLANCK and the conception indicated in this communication comes to light. For if the quanta-hypothesis is right, the equation (1) cannot even approximately be fulfilled, and it is to be considered as the merest chance if it leads to the exact value for U . According to the here developed conception however, the equation (1) cannot be rigorously satisfied, but it can hold with a rather high degree of approximation, and the sharpness of the lines of the spectra seems to indicate that this is really the case. For this reason it seems to me that we have reason to expect, that we can find the average kinetic energy of rotating particles, or of particles describing paths disturbed by collisions, with the aid of the ordinary fundamental equations of classical mechanics and electromagnetics. For this purpose we have to investigate the motions which those particles would perform according to those equations in an electromagnetic field whose partition of energy is that of the normal spectrum. According to the quanta-hypothesis it would seem doubtful whether such a calculation would yield the right value for the velocity of the particles.

These conclusions would not be justified, if it should appear that the equations of motion of the electrons cannot be approximately represented by equation (1). In this case we should have no reason to expect that the velocities of the vibrating particles are distributed according to MAXWELL's law for the partition of the velocities. It seems probable to me that the normal probability-curve will rather apply to the momenta than to the velocities. If the mass is constant we have no reason to make this difference, but in the case that

the mass of the particles is variable, the fact that the normal probability curve did hold good for the momenta would involve that it could not apply to the velocities. For LORENTZ-electrons the deviations from MAXWELL'S law for the distribution of the velocities, occasioned by the variability of the mass, would remain small for temperatures which are practically reached. The average kinetic energy of electrons of that nature in the normal radiation field can probably be calculated as if the mass were constant.

When we differentiate the value of the kinetic energy which we find in this manner, according to the temperature we find c , as is well known, if only we add to it another term which accounts for the potential energy.

§ 7. *The potential energy. The distribution in space.*

For the distribution in space of particles of mass we have according to classical mechanics the following law: if n represents the number of particles per unit volume and ε the potential energy of one particle, the expression

$$n e^{\frac{\varepsilon}{\theta}} = \text{a constant throughout the space.} \quad (12)$$

For a mixture an expression of the same kind holds good for each of the components. If we wish to take into account the volume of the particles we may write that

$$\frac{1}{V-2b} e^{\frac{\varepsilon}{\theta}} = \text{constant} \quad \dots \quad (12a)$$

where V represents the volume of the molecular weight in grams of the substance, and $V-2b$ the "available space" present in this volume. The logarithm of this expression is, as is well known, equal to the thermodynamical potential ¹⁾ of the component, to which the expression has relation. All thermodynamical equilibria, as well those for simple substances as those for mixtures, and also those in which electrically charged particles play a part, can be derived from the equation (12a), which was for the first time used by BOLTZMANN.

We will now consider the question how the space-distribution must be according to modified mechanics. Will this law of BOLTZMANN hold also according to them? This question must be answered negatively.

Let us imagine two coexisting phases e.g. liquid and vapour. Even if we assume that in each of the two phases MAXWELL'S law for the distribution of the velocities is satisfied, the mean kinetic energy of the molecules in the two phases will be different. Of

¹⁾ Or at least it differs from it only in a function of the temperature which is immaterial for the existence of thermodynamical equilibrium.

course this difference will be exceedingly small at ordinary temperatures and will only get a noticeable value at extremely low temperatures, at which the molecules in the liquid phase which can be regarded as vibrators of a shorter period than those of the vapour, have less kinetic energy than they should have according to the equipartition-law. This will of course have influence on the density of the vapour phase, which will be found to be smaller than we should expect according to classical statistical mechanics.

Corresponding considerations apply to the contact difference of potential at very low temperatures.

Besides the distribution of particles in space there are other problems which may be treated with the aid of considerations of the same kind, e.g. the orientation of the axes of polar particles under the influence of directing forces. The probability that the axis of such a particle, with moment m , in a field of forces, whose intensity is \mathcal{H} , forms an angle α with the direction of this force, is according to classical statistical mechanics equal to

$$e^{-\frac{m\mathcal{H} \cos \alpha}{\theta}} \frac{\sin \alpha}{2} d\alpha \dots \dots \dots (13)$$

According to our considerations the probability that it has a considerable amount will at low temperatures be smaller than is indicated by this formula. Accordingly we find e.g. the CURIE-point at a higher temperature than would be deduced from this formula, at least for those substances, for which this point lies so low, that at the CURIE-temperature the mean kinetic energy of the rotations of the molecules is smaller than it should be according to the equipartition law.

§ 8. It is obvious that the above considerations have an exceedingly provisional character. Many problems are referred to, but not for a single one have we found a sufficiently conclusive solution. I hope to be able to treat some problems more in detail on a later occasion.

In the meantime I think that I have shown that the drawing up of a new system of mechanics as aimed at in my former communication upon this subject is of the highest importance for all thermodynamic questions. I have done this with a view to draw the attention of the mathematicians to the problem and more in particular to the integral equation (5a) or a corresponding equation¹⁾,

¹⁾ I say a corresponding equation because, as I have already remarked on p. 1180 I was not perfectly sure that I was right in leaving the "proper coordinates" of the electron in this equation out of consideration. It is possible that the

the solution of which would bring us an important step nearer to the drawing up of the new system of mechanics.

Some phenomena are at present often considered in connection with the quanta-hypothesis of which it is not clear from the above how they are connected with the new system of mechanics, from which we expect the solution of the question concerning the partition of energy. Specially this is the case with the question of the emission of electrons under the influence of light- or RÖNTGEN rays.

In the thermodynamical applications it appears to me that we may expect from the quanta-hypothesis, that it will yield results which are sometimes quantitatively and always qualitatively accurate. For it has the tendency to lower the kinetic energy of vibrators of short period in agreement with the observations to an amount smaller than would agree with the equipartition law. And it is only this mean energy which is observed in thermodynamics, or the distribution in space which is closely connected with it.

Whether on the other hand the application of the quanta-hypothesis on the emission of electrons is justified seems doubtful to me. From a theoretical point of view it appears to me that no reason for the accuracy of the considerations can be found. And whether the agreement with experiment is sufficient to warrant the validity of the considerations seems to me to be still doubtful.

If in particular we take the theory of SOMMERFELD for these phenomena with the aid of the quanta of "action", then it appears to me that this theory (though perhaps accurate in itself) can be in no way connected with any possible theory for the normal spectrum. Let us imagine e.g. two equal guns with equal projectiles but with unequal charges of gunpowder. The projectile with the greatest gunpowder charge will obtain the greater kinetic energy and that in the smaller time. And so we can assume that the molecular action is of such a nature that always the greater change of energy requires the shorter time in the way as is assumed by SOMMERFELD. This is a question of the law of action of molecular forces; it has nothing to do with the laws of mechanics, and in particular it is not contradictory to the laws of classical mechanics. I at last cannot discover any contradiction. But if indeed the theory of SOMMERFELD can be reconciled with classical mechanics then it can also be reconciled with the spectral formula of RAYLEIGH and leads by no means to the spectral formula of PLANCK.

function φ must depend besides on the p 's and the q 's also on the "proper coordinates" and that we, in connection with this, must add the differentials of the proper coordinates to the product of the differentials $dp_1 \dots dq_n$.