

to the action of monochromatic light, do not belong to the absorption spectrum of monatomic iodine.

Prof. Joseph Wierusz Kowalski has lent us some apparatus and assisted us in a most generous manner; the same did our colleagues from the different physical laboratories of Warsaw. It may be permitted to express here to those gentlemen our best thanks.

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Warsaw, State Technical School,  
founded by H. Wawelberg and S. Rotwand.  
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XX. *On the Equation of State.* By M. P. APPLEBEY, M.A.,  
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IT has long been known that Clerk Maxwell's law of the equipartition of energy between the degrees of freedom cannot hold for the molecules of gases. The specific heats of solids at low temperatures prove that the translational kinetic energy of the atoms is not subject to the law, and even the energy of free translation of the atoms of helium has been shown to fall below the theoretical value  $3/2R$  at high pressures and low temperatures †. We are therefore no longer justified in assuming that the mean kinetic energy of translation of a molecule is proportional to the temperature. Apparently the dynamical definition of temperature must be abandoned.

The best known equation of state is that of Van der Waals. It does not accurately represent the behaviour of gases; but this was scarcely to be expected, since in its deduction it was assumed that the volume occupied by the molecules is small in comparison with the volume of the gas, and the quantities "a" and "b" were taken as constant, whereas it is probable that these magnitudes vary with the temperature and density of the gas. On theoretical grounds, however, it seems to us that fewer objections can be urged against Van der Waals' equation than might be raised against other equations of state which are in much closer accord with the facts.

Van der Waals in deriving his equation assumed that the

\* Communicated by the Authors.

† Eucken, *Ber. Deutsch phys. Ges.* xviii, p. 4 (1916).

mean kinetic energy of translation of a molecule was proportional to the temperature. Strictly this is not true. We are only justified in concluding that

$$\left(p + \frac{a}{v^2}\right)(v-b) = \frac{2}{3}nmV^2, \quad . . . . \quad (1)$$

where the letters have their usual significance. In other words, the equation relates the pressure and volume of the gas with the total kinetic energy of translation of the molecules, but not with the temperature. If any relation is to be established between the pressure, volume, and thermodynamic temperature of a gas, some assumption will have to be made in order to replace that which is no longer strictly valid.

*We assume that in a closed space which contains a large number of like molecules the ratio of the number of molecules per unit volume whose potential energy is  $\Lambda$  to the number of molecules per unit volume whose potential energy is zero is given by the expression  $e^{-\frac{\Lambda}{kt}}$ ,  $k$  being the gas constant for a single molecule, and  $t$  the thermodynamic temperature.*

It will be observed that the distinction between this assumption and the corresponding proposition deduced from Maxwell's laws of the partition and distribution of energy, is that  $t$  is substituted in the assumption for  $\frac{2}{3}$  of the mean kinetic energy of translation in the corresponding proposition.

Starting from this assumption, a modified form of Van der Waals' equation can be deduced in the following way. Consider a column of gas in a field of force—let us say gravity. Take the axis of  $x$  in the direction of the force. The density of the gas will increase in the direction of increasing  $x$ . The increasing density of the gas will set up a field of cohesive force acting in the same direction as gravity and equal in magnitude to  $\alpha \frac{d\rho}{dx}$ , where  $\rho$  is the density of the gas and  $\alpha$  a constant. Let  $m$  be the mass of a molecule of the gas. The sum of the forces due to gravity and cohesion, acting in the direction of  $x$ , on this molecule will be  $m\left(g + \alpha \frac{d\rho}{dx}\right)$ ,  $g$  being the acceleration of gravity. From this must be subtracted the upthrust due to the fluid displaced by the molecule. Let the volume of fluid displaced be represented by  $b'$ . Then the total downward force acting on the molecule becomes:  $(m - b'\rho)\left(g + \alpha \frac{d\rho}{dx}\right)$ . If the molecule is displaced

through a distance  $dx$  the increase of potential energy is  $-(m-b'\rho)\left(g+\alpha\frac{d\rho}{dx}\right)dx$  or  $-(m-b'\rho)(gdx+\alpha d\rho)$ . Whence, introducing the assumption which relates the temperature, the potential energy, and concentration of the molecules, we obtain

$$\frac{\rho+d\rho}{\rho} = e^{\frac{(m-b'\rho)(gdx+\alpha d\rho)}{kt}};$$

$$\therefore \frac{d\rho}{\rho} = \frac{(m-b'\rho)(gdx+\alpha d\rho)}{kt}.$$

Substituting  $d\rho$  for  $\rho g dx$  and solving the equation, we find

$$p = -\frac{kt}{b'} \log \frac{m-b'\rho}{m} - \frac{\alpha}{2} \rho^2.$$

If in this equation we put  $\rho = \frac{m}{v}$ ,  $v$  being the volume occupied by a molecule, the equation reduces to

$$p = -\frac{kt}{b'} \log \frac{v-b'}{v} - \frac{a^*}{v^2}, \quad \dots \dots (2)$$

where  $a = \frac{\alpha m^2}{2}$ .

If in the above equation (2)  $P$  is substituted for  $p + \frac{a}{v^2}$ , the total internal pressure, the relation expressed by the equation

$$kt \frac{\frac{Pb'}{e^{\frac{kt}{Pb'}}} - 1}{e^{\frac{kt}{Pb'}} - 1} = P(v-b') \quad \dots \dots (3)$$

can easily be shown to hold.

The similarity between the left-hand side of equation (3) and the expression deduced by Planck for the mean energy of a resonator at temperature  $t$  will be immediately recognized, and the similarity suggests that there may be a close relation between the product  $Pb'$  and the quantum  $h\nu$ .

\* If  $a$  and  $b$  are assumed to be constant the above equation has the defects of Van der Waals' equation. For example, it leads to the relation

$$\frac{Rt_c}{v_c^2} \approx 2.6.$$

In this connexion it may be pointed out that when  $v$  is large in comparison with  $b'$ ,  $b'$  is the volume of the sphere whose radius is the mean minimum distance between the centres of two molecules during a collision. Bearing this in mind and comparing equations (3) and (1), it will be seen that  $P\left(v-\frac{b'}{2}\right)$  is two-thirds of the mean kinetic energy of a molecule, and therefore

$$kt \frac{\frac{Pb'}{kt}}{\frac{Pb'}{kt} - 1} + \frac{Pb'}{2} = \frac{2}{3} \frac{m\bar{V}^2}{2} \dots \dots (4)$$

The left-hand side of (4) with  $h\nu$  substituted for  $Pb'$  is Planck's modified expression for the mean energy of a resonator of period  $\nu$ .

The distinction which is drawn above between thermodynamic temperature and the kinetic energy of a degree of freedom we regard as a provisional hypothesis which needs to be more carefully examined.

NOTE.—The above communication is a portion of a paper written in January 1919. It has been kept with a view to testing its practical applicability. However, in the correspondence of the April number of this Journal, M. N. Shaha and S. N. Basu refer to a paper on the Equation of State published by them in 1918 which had escaped our notice. In this communication the authors deduce from the well-known Boltzmann's entropy theory the equation

$$p = -\frac{Rt}{2b} \log \frac{v-2b}{v},$$

which (since  $2b=b'$ ) is identical with the characteristic equation deduced by us from apparently entirely different considerations. This agreement in the final results of two different modes of attacking the problem makes it desirable that the publication of our method of obtaining the above equation should not be further delayed.

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