

VIII. *The Distribution of Molecular Energy.*

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INTRODUCTION.

§ 1. THIS paper is primarily an attempt to deal with certain points connected with the application to the Kinetic Theory of Gases of BOLTZMANN'S Theorem on the partition of energy in a dynamical system.

It is found by experiment that the ratio of the two specific heats of certain monatomic gases (*e.g.*, mercury, argon) is $1\frac{2}{3}$. If we admit that the energy of these gases is distributed in the manner indicated by BOLTZMANN'S Theorem, then this theorem leaves no escape from the conclusion that the molecules of these gases must be rigid and geometrically perfect spheres. A similar difficulty arises in connection with other gases: the number of degrees of freedom which a consideration of the ratio in question leads us to expect a molecule of a gas to possess, is always less than the number which the spectrum of the glowing gas shows to actually exist. Further, BOLTZMANN'S Theorem excludes the possibility of the ratio of the two specific heats having any values except one of a certain series of values, whereas experiment shows that the ratio is not always equal to one of this series, although it is generally very near to such a value. Finally BOLTZMANN'S Theorem leaves no room for a variation of this ratio with the temperature, although such a variation is known to exist.

In the present paper I have tried to suggest a way by which it is possible to escape from this dilemma. As there is not sufficient known about the constitution of a molecule to enable it to be completely specified as a dynamical system, the paper is limited to the consideration of two imaginary types of molecules.

The conclusions arrived at are the same in each case. In the first place the distribution of energy which is given by BOLTZMANN'S Theorem is the only distribution which is permanent *under the conditions postulated by this theorem*. And in the second place, this law of distribution may break down entirely as soon as we

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admit an interaction, no matter how small, between the molecules and the surrounding ether. That such an interaction must exist is shown by the fact that a gas is capable of radiating energy. In fact, BOLTZMANN'S Theorem rests on the assumption that the molecules of a gas form a conservative dynamical system, and it will appear that the introduction of a small dissipation function may entirely invalidate the conclusions of the theorem.* Thus we may regard the BOLTZMANN distribution as unstable, in the sense that a slight deviation from perfect conservation of energy may result in a complete redistribution of the total energy, and it will appear that this new distribution of energy will lead to values for the ratios of the two specific heats which are not open to the objections mentioned above.

§ 2. A second difficulty, of a mathematical rather than physical nature, may be mentioned here, as it will occur incidentally in the course of the analysis. It is well illustrated by the consideration of an imaginary type of molecule which has been suggested by BOLTZMANN.† A loaded sphere, that is to say, a sphere of which the centre of gravity is at a small distance r from the geometrical centre, will, for the present purpose, possess five degrees of freedom, and this is true, however, small r may be. The ratio of the specific heats of an ideal gas whose molecules are of this type ought accordingly to be $1\frac{2}{5}$. If, however, r actually vanishes, the molecules must be regarded as completely symmetrical, and possessing only three degrees of freedom, so that the ratio ought now to be $1\frac{3}{5}$. There is thus seen to be a discontinuity when r has a zero value, and this requires investigation.

It must be borne in mind that a degree of freedom, for purposes of BOLTZMANN'S Theorem, is not identical with the usual dynamical degree of freedom. In the strict dynamical sense every sphere possesses six degrees of freedom, the principal momenta being the momenta of the centre of gravity in three rectangular directions and the three rotatory momenta about the principal axes of inertia. But if the sphere is perfectly smooth, rigid, and symmetrical, it is impossible to change the three latter momenta by the application of any forces which are at our disposal in the kinetic theory of gases, and for this reason the corresponding degrees of freedom must be left out of account, when applying BOLTZMANN'S Theorem. Similar remarks apply, in the case of the loaded sphere, to the degree of freedom which arises from rotation about the axis of symmetry, so that the loaded sphere must be supposed to possess five degrees of freedom, and not six.

* The matter may be looked at from a slightly different point of view as follows: If an interaction between matter and ether exists, no matter how small this interaction may be, the complete dynamical system will consist of the molecules of the gas, together with the ether, and must therefore be regarded as a system possessing an infinite number of degrees of freedom. Applying BOLTZMANN'S Theorem to this system we are merely led to the conclusion that no steady state is possible until all the energy of the gas has been dissipated by radiation into the ether. This application of the theorem may or may not be legitimate, but it is, I think, certain that no other application is legitimate.

† 'Vorlesungen über Gastheorie,' Part II., p. 129.

It is obvious that the degrees of freedom which have been rejected do not in any way influence the motion of the sphere, whereas if they are counted as separate degrees of freedom, the series of states through which the sphere is made to pass by varying all the co-ordinates, is no longer such as to satisfy MAXWELL'S condition of "Continuity of Path." (See § 11 of the present paper.)

PART I.

THE DISTRIBUTION OF ENERGY IN A GAS OF WHICH THE MOLECULES ARE LOADED SPHERES.

The Transfer of Energy caused by Collisions.

§ 3. We may begin with the consideration of a gas of which the molecules are loaded spheres of the kind mentioned in the last section. These spheres are to be perfectly elastic, each of radius a , and the centre of gravity of each is to be at a small distance r from the geometrical centre.

We require to find equations giving the transfer of energy between the various degrees of freedom in such a gas. If we know the law of distribution of the various co-ordinates of the molecules, we shall be able, upon making the usual assumptions of the kinetic theory, to calculate the number of collisions which are such that the values of the variables, which are required to completely specify a collision, lie within certain specified small ranges of value. At each of these collisions the transfer of energy is the same, a function of the variables which specify the collision; so that by multiplying this quantity by the number of collisions of the kind under consideration which occur during the interval dt , and integrating over all possible values of the variables which specify the collision, we shall obtain an expression for the transfer of energy during the time dt .

Let us denote the mean energy of translation of all the molecules at any specified instant by K , the mean energy of rotation by H . If we regard the number of molecules in the gas as infinite, we may regard the quantities H and K as varying continuously with the time, and the expressions which have just been found for the transfer of energy will enable us to calculate dH/dt and dK/dt corresponding to any state of the gas. The values of dH/dt , dK/dt will in general depend on r , a , ρ (the density of the gas) and the coefficients which occur in the various laws of distribution of co-ordinates.

If we consider the case in which $r = 0$, we find that no transfer of energy is possible, so that dH/dt , dK/dt must vanish with r . We further notice that these differential coefficients must remain unaltered, if $-r$ be written for r , so that, assuming for the moment that they can be expanded in ascending powers of r , we see that the lowest power of r which can occur is r^2 . We shall suppose r to be so small that terms in r^4 may be neglected in comparison with terms containing r^2 .

Since the total energy remains unaltered at every collision, we must have

$$dK/dt = -dH/dt;$$

it is therefore only necessary to calculate one of these differential coefficients.

§ 4. The state of a molecule at any instant will be determined by the following 12 variables,

- (i.) The co-ordinates in space of its centre of gravity x, y, z , and their time-rate of change u, v, w .
- (ii.) Any three independent variables, e, f, g , specifying the orientation in space of the molecule.
- (iii.) $\varpi_1, \varpi_2, \varpi_3$, the rotations about three principal axes, the last of these being the rotation about the axis of symmetry of the molecule.

Let accented letters refer to a second molecule; then a collision between these two molecules, if possible, is completely specified by the whole 24 variables, but these are not all independent, and the collision will, as regards transfer of energy, be sufficiently specified by the independent variables

$$u - u', v - v', w - w', \\ \varpi_1, \varpi_2, \varpi_3, \varpi'_1, \varpi'_2, \varpi'_3,$$

and six other variables to determine the direction in space of the axes of the molecules, and the line of centres.

Let the variables after collision be distinguished from those before collision by placing a bar over them, then we can from the ordinary equation of impact calculate the value of

$$\bar{c}^2 + \bar{c}'^2 - (c^2 + c'^2)$$

where $c^2 = u^2 + v^2 + w^2$, in terms of the variables before collision.

This expression must be a quadratic function of the velocities, and ϖ_3, ϖ'_3 cannot enter. If we write

$$(u - u')^2 + (v - v')^2 + (w - w')^2 = V^2, \\ \varpi_1^2 + \varpi_2^2 = \varpi^2,$$

it is easily seen that the expression must be of the form

$$c^2 + \bar{c}'^2 - (c^2 + c'^2) = \alpha_1 V^2 + \beta_1 (\varpi^2 + \varpi'^2) \dots \dots \dots (i),$$

where α_1, β_1 are functions of the six variables determining orientations in space, and are algebraical functions of r , in which the lowest power is r^2 .

§ 5. In calculating the number of collisions of this kind which are to be expected in the interval of time dt , a consideration enters, which does not enter in the simpler case in which the spheres are symmetrically loaded.

From the co-ordinates of the two molecules just before collision, we can trace back, as far as the previous collisions, the paths by which the molecules arrived at this position. If these paths are such that the spaces occupied by the two molecules, at any two corresponding points of these paths, are found to overlap, then it is clear that a collision of the kind we are investigating can only occur, either when the same two molecules have previously collided, or when one of them has collided with a third molecule within a certain small interval previous to the collision in question. In either case it would be wrong to calculate the probability of such a collision upon the assumption that the molecules of the gas are, in BOLTZMANN'S sense, *ungeordnet*.

When, however, terms of degree higher than r^2 are neglected, it will be legitimate to ignore this consideration altogether. For the number of collisions to which it applies will vanish with r , so that if equation (i.) be summed over all collisions, the terms on the right-hand side which are influenced by this consideration will be of a higher order in r than r^2 , and may accordingly be inaccurately calculated, without invalidating the result as far as terms in r^2 .

§ 6. When we agree to ignore this consideration, we may at once average equation (i.) over all values of the six variables of orientation. The probability of these variables having specified values at a collision is not independent of the velocities of the collision, but will be the same for all collisions such as we are now considering, in which these velocities have specified values. In this way we find that the mean increase in $c^2 + c'^2$ at a collision at which the velocities are $u, v, w, \varpi, u', v', w', \varpi'$, is of the form

$$r^2\{\alpha_2 V^2 + \beta_2(\varpi^2 + \varpi'^2)\} + \text{terms of a higher order in } r^* \quad \dots \quad \text{(ii.)},$$

in which α_2, β_2 are constants.

Now if we suppose that the gas has reached its present state through a series of natural processes, the law of distribution of velocities will depend only on c^2 and ϖ^2 . In the case in which $r = 0$, this law is known to be

$$e^{-hmc^2} f(\varpi) du dv dw d\varpi \quad \dots \quad \text{(iii.)}.$$

Hence in the case in which r is small, it may be taken to be

$$F(c, \varpi) du dv dw d\varpi \quad \dots \quad \text{(iv.)},$$

where F is a function of which the coefficients involve r , but is such that (iv.) reduces to (iii.) when $r = 0$.

* Direct calculation shows that the values of α_2, β_2 are $\alpha_2 = -\frac{2}{3\kappa^2}, \beta_2 = \frac{4}{3}$, where κ is the radius of gyration of a molecule about a line perpendicular to the axis of symmetry.

Calculated upon the usual assumption, the number of collisions which occur in a volume Ω of the gas and within a time dt , between pairs of molecules of which the velocities lie within a range $du dv dw d\varpi du' dv' dw' d\varpi'$ surrounding the values $u, v, w, \varpi, u', v', w', \varpi'$, is

$$\frac{\pi a^2 V dt}{\Omega} F(c, \varpi) F(c', \varpi') du dv dw d\varpi du' dv' dw' d\varpi'.$$

Hence referring to expression (ii.) we see that the total increase in the translational velocity of the gas, in time dt , is

$$\frac{1}{2} \iiint \iiint \iiint \frac{\pi a^2 V dt}{\Omega} F(c, \varpi) F(c', \varpi') [r^2 \alpha_2 V^2 + r^2 \beta_2 (\varpi^2 + \varpi'^2) + \dots] du dv dw d\varpi du' dv' dw' d\varpi'.$$

If we reject all terms of a degree higher than r^2 in r , this expression becomes

$$\frac{\pi a^2 dt}{2\Omega} r^2 \iiint \iiint \iiint V e^{-hm(c^2 + c'^2)} f(\varpi) f(\varpi') [\alpha_2 V^2 + \beta_2 (\varpi^2 + \varpi'^2)] du dv dw d\varpi du' dv' dw' d\varpi' \quad \dots \quad \text{(v.).}$$

Now the functional form represented by f is unknown, but the part of the above integral which contains α_2 depends only upon $\int f(\varpi) d\varpi$ and this can be seen to be proportional to ρ and to involve h . Let us denote $\int f(\varpi) d\varpi$ by ρI , so that I is a function of h only; then the part of (v.) which contains α_2 , contains $\rho^2 I^2$ multiplied by $\frac{\pi a^2 dt}{2\Omega} r^2$ and a function of h .

The part of (v.) which contains β_2 depends on I and also on $\int f(\varpi) \varpi^2 d\varpi$. If we write $\int f(\varpi) \varpi^2 d\varpi = \rho I \Psi$ (so that Ψ is the mean value of ϖ^2 taken over all the molecules of the gas), then this part of (v.) will be $\rho^2 I^2 \Psi$ multiplied by $\frac{\pi a^2 dt}{2\Omega} r^2$ and by a function of h .

Hence determining the functions of h from a consideration of dimensions, we find

$$\rho \frac{dK}{dt} = \alpha_2 \rho^2 h^{-3/2} + \beta_2 \rho^2 \psi h^{-1/2} \dots \dots \dots \text{(vi.),}$$

in which α_2, β_2 are constants; or in terms of H and K ,

$$\frac{dK}{dt} = \alpha \rho K^{3/2} + \beta \rho K^{1/2} H^* \dots \dots \dots \text{(vii.),}$$

in which the constants α, β do not in any way depend upon the law of distribution of velocities.

* Using the values for α, β given in the footnote on p. 401, we can find for α, β the values

$$\alpha = -\frac{32}{9} \frac{a^2 r^2}{m K^2} \sqrt{\frac{2\pi}{3m}}, \quad \beta = \frac{16}{3} \frac{a^2 r^2}{m K^2} \sqrt{\frac{2\pi}{3m}}.$$

In this way we can prove the relation $H = \frac{2}{3} K$, instead of assuming it.

In BOLTZMANN'S steady state, $dK/dt = 0$, and $H = \frac{2}{3}K$, since the energy is equally divided between the five degrees of freedom. This leads to the relation

$$\alpha = -\frac{2}{3}\beta,$$

and equation (vii.) may be written

$$\frac{dK}{dt} = \beta\rho\sqrt{K}(H - \frac{2}{3}K) \quad \dots \dots \dots \text{(viii.)}$$

The rate of variation of H on account of collisions is therefore given by

$$\frac{dH}{dt} = -\beta\rho\sqrt{K}(H - \frac{2}{3}K) \quad \dots \dots \dots \text{(ix.)}$$

Introduction of Dissipation.

§ 7. If the changes in the values of H and K arise solely from collisions, the equations just found will enable us to trace these changes, starting from any initial values. Let us, however, suppose that there is a second cause of change in H and K ; suppose that the angular velocity ϖ is retarded by a frictional reaction between the molecules and the surrounding medium, the amount of this retardation being $\epsilon\varpi$. It is not suggested that a reaction of this type exists in nature, but this reaction may be taken as being the simplest reaction possible, just as a loaded sphere has been taken as the simplest dynamical system which will serve our purpose. Due to a frictional reaction of this kind, the mean rotational energy H will suffer a decrease of amount $2\epsilon H$ per unit time.

The equations expressing the rates of change of H and K will therefore be

$$\frac{dK}{dt} = \beta\rho\sqrt{K}(H - \frac{2}{3}K) \quad \dots \dots \dots \text{(x.)}$$

$$\frac{dH}{dt} = -2\epsilon H - \beta\rho\sqrt{K}(H - \frac{2}{3}K) \quad \dots \dots \dots \text{(xi.)}$$

§ 8. A steady state is now impossible, on account of the dissipation of energy which takes place. If, however, we suppose the translational energy to be in some way increased at such a rate as exactly to counterbalance the loss of energy, the gas will rapidly assume a steady state given by $dH/dt = 0$, or, by equation (xi.),

$$2\epsilon H + \beta\rho\sqrt{K}(H - \frac{2}{3}K) = 0 \quad \dots \dots \dots \text{(xii.)}$$

The value of H corresponding to a given value of K is therefore

$$H = \frac{2}{3}K \left(1 + \frac{2\epsilon}{\beta\rho\sqrt{K}} \right) \quad \dots \dots \dots \text{(xiii.)}$$

Hence if ϵ , β , K have values such that ϵ is very great in comparison with $\beta\sqrt{K}$, then H will be very small in comparison with K . The rate at which the external agency introduces energy is $2\epsilon H$, and this may be made very small by supposing ϵ to be very small, although great in comparison with $\beta\sqrt{K}$. If this agency is removed

the state of the gas will only change very slowly, so that the state specified by equation (xiii.) may be appropriately described as the "approximately steady" state. When H vanishes in comparison with K , the equation giving this state takes the simpler form

$$\epsilon H = \frac{1}{3} \beta \rho K^{3/2} \dots \dots \dots (xiv.)$$

The conditions which have been found to be necessary in order that this state may exist, are that ϵ , β should be small, and that K should be so small that $\frac{\epsilon}{\beta \sqrt{K}}$ is very great. Thus the steady state will be possible for all temperatures below a certain temperature, namely, the temperature at which $\beta \sqrt{K}$ begins to be comparable with ϵ . Below this temperature H vanishes in comparison with K , and the rate of dissipation of energy is a small quantity of the second order.

It follows that if experiments are conducted at temperatures so low as to be below this critical temperature, no value of γ can possibly be observed except

$$\gamma = 1\frac{2}{3} \dots \dots \dots (xv.)$$

At higher temperatures, there is no definite ratio between H and K which tends to establish itself. In fact, if experiments are conducted with a view to determining γ , the value observed will depend on the past history of the gas and the duration of the experiment, so that γ may have any value between $1\frac{2}{3}$ and $1\frac{3}{5}$.

Thus it appears that if, under the conditions we are now considering, a consistent value is obtained for γ from experiments on the gas in question, this value can be no other than $1\frac{2}{3}$, and the temperature at which the experiments are conducted must be what has been referred to as a low temperature. It must be particularly noticed, that this temperature is only low relatively to the other temperatures considered: no knowledge as to its absolute value is possible so long as ϵ and r/a remain unknown quantities. If, however, for the moment, we assume that the present molecules are a fair representation of the molecules of an actual gas, and that the dissipation of energy caused by our assumed frictional reactions supplies a true analogy to radiation of energy in nature, then we can form some estimate as to what a "low" temperature must mean. It is a temperature at which H , and therefore the radiation, is inappreciable; that is to say, it is a temperature at which the gas is non-incandescent.

The Distribution of Energy in the approximately Steady State.

§ 9. To sum up, it appears that if we are willing to admit that our present dynamical system supplies a sufficiently good analogue to a real gas, then the introduction of a dissipation function will supply an explanation of the difficulties mentioned in the introduction, at any rate for the case of a non-luminous gas. Part II. of this paper consists of an effort to show that our present system is a fair analogy, if not

of an actual molecule, yet at any rate, of a dynamical system which contains all the features we believe to be essential to a molecule.

Referring back to equations (x.), (xi.) and (xiv.), it is now clear that, for a non-luminous gas, the equations determining H and K will be

$$dK/dt = -\frac{2}{3}\beta\rho K^{3/2} \quad \dots \dots \dots \text{(xvi.)},$$

and

$$\epsilon H = \frac{1}{3}\beta\rho K^{3/2} \quad \dots \dots \dots \text{(xvii.)}.$$

Equation (xvii.) is the relation between H and K which must now replace the equation of MAXWELL and BOLTZMANN, viz. :

$$H = \frac{2}{3}K.$$

It therefore appears that, in the present case, the total radiation will be proportional to $K^{3/2}$, and in the more general case discussed in Part II., the radiation will be seen to increase still more rapidly with the temperature. Thus it is easy to see how it is possible for the total radiation to increase very rapidly near the temperature of incandescence, whereas if we supposed the energy divided in any invariable ratio between the different degrees of freedom, it is difficult to see how the radiation could be anything but directly proportional to the temperature.

Extension of the foregoing Theory.

§ 10. It is possible, under certain conditions, to apply the above methods to a more general type of molecule.

Let the energy of the molecule consist partly of translational energy, and partly of various kinds of internal energy, potential as well as kinetic. The only case considered will be that in which the internal energy is small: the potential energy will therefore arise from small oscillations about a position of equilibrium; and these oscillations will be of definite period, and such as may be supposed to result in the emission of light possessing a line-spectrum. Thus the total energy corresponding to any such principal mode of vibration, will, when averaged over a large number of molecules, be half potential and half kinetic.

It is necessary for the success of the present method that the probability of a collision between two molecules should depend solely on their relative velocity, and not on their internal co-ordinates. Now a rotation is to be regarded as internal energy, and a rapid rotation will be equivalent to an increase of volume, and will therefore increase the probability of a collision unless the molecules are spheres of invariable radius, and of which the centres move in straight lines. Thus the molecules must either be spheres of which the centre of gravity and the geometrical centre coincide, or else as in the former case, they must differ by so little from this, that the divergence has no effect on the final result (*cf.* § 5).

We shall further suppose for the present that the internal energies are only slightly altered by collision, as was the case in the former problem.

The law of distribution of internal energy will now be independent of the velocity of translation, so that the mean value of the internal energy of any specified mode, will be the same whether the average is taken over all collisions or over all molecules.

The same notation as before will be used in connection with the motion of translation. The energies of the various internal modes will be denoted by $e_1, e_2 \dots$ and their mean values taken over all molecules by $E_1, E_2 \dots$. If t_1, r_1 are the potential and kinetic energies of which the sum is e_1 then the mean value of t_1 will be $\frac{1}{2}E_1$.

We begin by calculating the increase at any single collision in $(c^2 + c'^2)$, $(e_1 + e'_1)$, &c. Each of these quantities will be a quadratic function of the velocities concerned, and is symmetrical as regards the two molecules. We next assume the law of distribution of translational velocities to be

$$\phi(u, v, w) = Ae^{-hmc^2},$$

and average the values we have found over all collisions, the procedure being exactly identical with that already followed in the former problem.

For given velocities we arrive at an equation similar to equation (i.), p. 400. It is to be particularly noticed that the translational velocities can only enter through the term V^2 . We now continue in the manner of § 6. The factor V again occurs multiplying every integrand, and giving rise to the term \sqrt{K} in the final result.

By this means we arrive at equations similar to equations (viii.) and (ix.), p. 403, giving the rate of change of K, E_1, E_2, \dots arising from collisions. By what has been already said, these must be of the form—

$$dE_1/dt = \rho\sqrt{K}\{a_{11}E_1 + a_{12}E_2 + \dots + b_1K\}$$

$$dE_2/dt = \rho\sqrt{K}\{a_{21}E_1 + a_{22}E_2 + \dots + b_2K\},$$

and similar equations, together with

$$dK/dt = \rho\sqrt{K}\{c_1E_1 + c_2E_2 + \dots + cK\} \dots \dots \dots \text{(xviii).}$$

It is here assumed that a specified value of any internal velocity is just as probable as the equal negative velocity, otherwise the mean value of products of different velocities could not be supposed to vanish. The equations determining the steady state are

$$a_{11}E_1 + a_{12}E_2 + \dots + b_1K = 0,$$

$$a_{21}E_1 + a_{22}E_2 + \dots + b_2K = 0,$$

$$\dots \dots \dots$$

$$c_1E_1 + c_2E_2 + \dots + cK = 0 \dots \dots \dots \text{(xix).}$$

These equations are not independent; when they are added together the resulting equation vanishes identically in virtue of the fact that the mean total energy is, under all circumstances, unchanged by collisions.

Hence the equations can all be satisfied when the variables $E_1, E_2 \dots K$ are in a definite ratio. The distribution of energy indicated by this ratio will therefore be permanent, and since the equations which determine it are linear, it will be unique. This is the distribution discovered by BOLTZMANN, in which the energy is equally divided between the various degrees of freedom.

Continuity of Path.

§ 11. Any of the coefficients in the above system of equations may vanish; so that it will be possible for the equations to fall into two groups, in such a way that no variable occurs in both groups. The motion will in this case be steady provided all the variables of the first group are in a given ratio, and all the variables of the second group are in a given ratio, but there need be no fixed ratio between the two groups.

Thus the total energy of the first group will be divided according to BOLTZMANN'S Law, and the same applies to the second group, but the distribution between the two groups will not follow this law.

This is the analytical expression of MAXWELL'S condition as to "Continuity of Path."*

The Two Kinds of Internal Co-ordinates.

§ 12. Let us suppose, as before, that certain velocities are subject to a retardation proportional to the velocities. The mean energies arising from these degrees of freedom will be denoted by F_1, F_2, \dots , the letters E_1, E_2, \dots being reserved for those energies which are not dissipated by friction.

The system of equations (xviii., p. 406) must now be replaced by

$$\begin{aligned} dE_1/dt &= \rho\sqrt{K} \{ \Sigma a_{1s} E_s + \Sigma p_{1s} F_s + b_1 K \}, \\ dF_1/dt &= \rho\sqrt{K} \{ \Sigma q_{1s} E_s + \Sigma r_{1s} F_s + b'_1 K \} - \epsilon_1 F_1, \\ dK/dt &= \rho\sqrt{K} \{ \Sigma c_s E_s + \Sigma c'_s F_s + eK \} \dots \dots \dots (xx.). \end{aligned}$$

If we suppose that at a collision only a small amount of energy can be exchanged between the F modes and the remaining modes, then all the coefficients p, q, b' , and ϵ' will be small.

It is immediately obvious that equations (xx.) may be treated exactly as equations

* MAXWELL, 'Camb. Phil. Soc. Trans.,' vol. 12, p. 548; or 'Collected Works,' vol. 2, p. 714.

whereas BOLTZMANN'S theorem would lead to

$$\gamma = 1 + \frac{2}{m + n + 3}.$$

The equation (xxiv.) will only hold in the limit when the temperature $\theta = 0$. At other temperatures γ will have a slightly different value, since the F energies cannot be entirely neglected. Our results as before only hold up to the temperature at which the gas begins to emit an appreciable amount of radiant energy, and this temperature may be supposed to be somewhat above the point of incandescence.

Up to this point, F_1, F_2, \dots will always be in the same proportion to one another, so that the brightness of the various lines in the spectrum will be in a constant ratio, each being proportional to $\theta^{3/2}$.

§ 14. We have been working on the assumption that there is a complete absence of frictional forces acting on K, and on E_1, E_2, \dots . These assumptions, however, are not necessary. In the steady state we have from equation (xxiii.),

$$F_1 = \frac{\beta_1}{\epsilon_1} \rho K^{3/2},$$

where β_1 is a quantity which depends only on the construction of the molecule.* The temperatures which have been considered have been those for which $\frac{\beta_1}{\epsilon_1} \sqrt{K}, \frac{\beta_2}{\epsilon_2} \sqrt{K}$, &c., are all very small. But if for any single degree of freedom, say that for which the energy co-ordinate is F_1 , either ϵ_1 is exceptionally small or β_1 exceptionally great, the range of temperature will be greatly restricted on this account. At temperatures at which $\frac{\beta_1}{\epsilon_1} \sqrt{K}$ is large while the remaining similar quantities are small, it is clear that F_1 must be treated as an E co-ordinate.

At zero temperature all the energy co-ordinates to which friction corresponds must be regarded as F co-ordinates. As the temperature increases we must suppose these co-ordinates one by one to change from being F co-ordinates, and after occupying a position intermediate between that of an F and that of an E co-ordinate to finally become E co-ordinates. If there is a co-ordinate for which ϵ is extremely small, or β very great, that is to say, a co-ordinate corresponding to a degree of freedom which is only very slightly retarded by friction, or to one from which energy passes freely, then such a co-ordinate will become an E co-ordinate at such a low temperature that it may be regarded as always being an E co-ordinate.

* It may be noticed that the value of β_1 supplies a measure of the facility with which energy is exchanged between the F_1 mode and the other modes. If $\beta_1 = 0$, it is impossible for such an exchange to take place, and the F_1 mode does not satisfy the condition of continuity of path. Thus if friction dissipates the energy of the F_1 mode, the value of F_1 will finally be zero. If, however, we have $\beta_1 = 0$, together with $\epsilon_1 = 0$, the value of F_1 is indeterminate. The rotation of the loaded sphere about the axis of symmetry supplied a good illustration of a mode of energy for which $\beta = 0$.

Variation of γ with Temperature.

§ 15. Thus our conclusion is that it is not permissible to count the degrees of freedom; they must be weighted as well. We can write

$$\gamma = 1 + \frac{2}{3 + \sum a_s},$$

where a_s is the "weight" of the s th degree of freedom. So long as $\frac{\beta_s}{\epsilon_s}\sqrt{K}$ is small, we may put $a_s = 0$. When this quantity is very great, either owing to the greatness of K or the absence of ϵ_s , we put $a_s = 1$. For intermediate values of $\frac{\beta_s}{\epsilon_s}\sqrt{K}$, a_s will be a proper fraction, the value of which depends not only on the temperature but also on the series of changes through which the gas has passed.

As a consequence of this, it is clear that γ may be expected to vary with the temperature, and that it is no longer restricted to having one of the values given by the formula $1 + 2/n$. It would be going too far to expect any agreement with experiment at present, since we are considering a purely arbitrary type of molecule such as certainly does not exist in nature.

Case of a Diatomic Molecule.

§ 16. As an illustration of the foregoing theory, we may examine the case of a molecule which is composed of two atoms held together by an attractive force. The atoms can execute internal vibrations giving rise to the emission of light; for these vibrations we can suppose $\frac{\beta}{\epsilon}\sqrt{K}$ to be very small, so that $a = 0$. The molecule can rotate about its axis of symmetry, but we can suppose β to be zero, so that again $a = 0$. For the rotation about the two remaining axes β will be large, so that we may take $a = 1$. We can suppose that the oscillations of the atoms as a whole about their position of equilibrium are dissipated by radiation so that $a = 0$.*

This leads us to the value $\gamma = 1\frac{2}{3}$, a value which it is impossible to arrive at by means of BOLTZMANN'S theorem when we are considering a molecule which is made up of two separable parts, but which is nevertheless known to be the true value for many diatomic gases, such as hydrogen, nitrogen, and oxygen. If the present theory in

* Radiation of this kind would give rise to definite lines in the spectrum of a frequency which might, and probably would, be very different from the frequencies of the light vibrations given out by the internal vibrations of the atoms. In this connection it is of interest to remember that experiments with Hertzian vibrators have demonstrated the existence, in certain substances, of free periods of which the frequency is only about 1/1,000,000th of the frequency of the sodium lines. (P. DRUDE, 'Wied. Ann,' vol. 58, p. 1; vol. 59, p. 17; vol. 64, p. 131.)

any way corresponds to the facts, the molecules of these gases must possess a symmetry similar to that possessed by figures of revolution.

PART II.

THE DISTRIBUTION OF ENERGY IN A GAS OF WHICH THE MOLECULES ARE OF A MORE GENERAL TYPE.

Statement of Problem to be Discussed.

§ 17. Having discovered, by means of the simple dynamical illustration discussed in Part I., what sort of results are to be expected, it now becomes possible to examine the case in which the molecules form a more complex dynamical system, and as this may be done by an entirely different method from that previously followed, it is now possible to remove the restrictions which it was previously found necessary to impose on the nature of the molecules.

The molecules are, as before, supposed to be all exactly similar, but intermolecular forces are no longer excluded, and the radiation is supposed to be of a more general type.

Let us suppose that each molecule is a dynamical system, possessing in itself $k + n$ degrees of freedom in addition to the freedom of the molecule to move in space. There will therefore be $2(k + n) + 3$ co-ordinates required to specify the condition of a molecule apart from its position in space, and $4(k + n) + 8$ quantities are required to specify a collision.

The co-ordinates of position of any molecule will be

- x, y, z , the co-ordinates of its centre of gravity referred to axes fixed in space,
- $p_1, p_2, \dots p_n$, the co-ordinates which do not occur in the expression for the potential energy; as, for example, the co-ordinates which determine the orientation of a rigid body.
- $r_1, r_2, \dots r_\kappa$, the co-ordinates which do occur in the expression for the potential energy.

The co-ordinates of velocity will be

$$\begin{array}{llll} u_1, u_2, u_3 & \text{the time-differentials of } x, y, z. \\ q_1, q_2, \dots q_n & \text{,, ,, ,, } p_1, p_2, \dots p_n \\ s_1, s_2, \dots s_\kappa & \text{,, ,, ,, } r_1, r_2, \dots r_\kappa \end{array}$$

We shall write c^2 for $u^2 + v^2 + w^2$, and it will frequently be necessary, for the sake of brevity, to denote all co-ordinates of the same type by a single representative letter without a suffix.

Thus

$$f(p) = f(p_1, p_2, \dots p_n)$$

$$du = du_1 du_2 du_3, \text{ \&c.}$$

We shall assume that these co-ordinates are principal co-ordinates of the system, so that both the kinetic and potential energies will be the sums of squares. We may, in fact, write

$$2V = c_1 r_1^2 + c_2 r_2^2 + \dots + c_\kappa r_\kappa^2$$

$$2T = mc^2 + 2Q + 2S$$

where

$$2Q = b_1 q_1^2 + b_2 q_2^2 + \dots + b_n q_n^2$$

$$2S = d_1 s_1^2 + d_2 s_2^2 + \dots + d_n s_n^2.$$

We shall suppose the oscillations of the r, s co-ordinates to be so small as to be isochronous, and in this case the c and d coefficients will be constants. Since the r co-ordinates are to be very small, the "configuration" of a molecule may be supposed to be determined by its p co-ordinates.

With a view to simplifying subsequent analysis, we shall assume that the b 's also are constants. It will be seen that the character of our results is not materially modified by this simplification, and the assumption is, of course, legitimate if we suppose the molecule, except as regards small oscillations, to behave like a rigid body, the atoms never moving far from certain equilibrium positions. We shall suppose that the vibrations of the molecule result in a radiation of energy, and we accordingly assume a dissipation function G . This will be supposed to be a quadratic function of the s co-ordinates with constant coefficients; it will not in general be reducible to the sum of squares. The existence of G implies an interaction between matter and ether. The assumption that G contains no terms in u or q is in strictness only legitimate if we suppose the u and q velocities to be uninfluenced by the ether, but it is easy to see, as in § 14, that even if these velocities are acted upon by the ether, the neglect of these actions is of no importance so long as they are sufficiently small.

We have spoken of T and V as kinetic and potential energy, but there is no reason why these energies should not be regarded as electro-magnetic and electro-static energy, or indeed as energy of any other kind, provided only that it is always possible to deduce the equations of motion from the energy function by LAGRANGE'S method. But it is probably best to regard the system just specified as simply a dynamical system in the strictest sense, this system being capable of *illustrating* all the properties which experiment shows to be possessed by a molecule.

§ 18. Corresponding to a collision in the case of two spheres, we shall suppose that it is possible for an action to take place between two molecules, and this action will be spoken of as an "encounter." For the present, it is not necessary to specify the exact nature of an encounter, but it will be supposed

- (i.) that the duration of an encounter is infinitesimal, so that an encounter causes no direct change in the co-ordinates of position of a molecule,

- (ii.) that an encounter is similar to an impact in the former problem, in that it may or may not entirely change the translational velocities of the two molecules concerned, but that the internal velocities are only changed by a small amount.

The sudden increase in any quantity ξ consequent on an encounter will be denoted by $\Delta\xi$.

In virtue of the above assumptions

$$\Delta p = 0, \quad \Delta r = 0,$$

Δq and Δs are small, and Δu will in general be comparable with u .

A "collision" will be a special case of an encounter, and may be described as follows. Suppose that every molecule is surrounded by a small sphere, of which the centre coincides with the centre of gravity of the molecule, and which moves as though it were rigidly attached to the molecule. The radius of the sphere is not yet fixed, but it must be such that the sphere entirely encloses the matter of which the molecule is composed. Then a collision will be defined as an encounter which is such that the spheres of the two molecules which are engaged, intersect; the "duration" of a collision will be taken to be sufficiently long to include the whole interval from the instant at which the spheres first intersect to the instant at which they separate. The assumptions as to the nature of the gas, which are usually expressed by saying that the gas is *molekular-ungeordnet*, and that the number of collisions in which three or more molecules are engaged, is infinitely small in comparison with the number of binary collisions, will be replaced by the following assumptions:

- (i.) The duration of a collision is so short, that the positional co-ordinates may be treated as constant throughout the collision, while the velocity co-ordinates are abruptly changed.
- (ii.) The chance of any molecular sphere intersecting two other spheres at once, vanishes in comparison with the chance of its intersecting one other sphere.
- (iii.) The chance that a molecule A is found with all its co-ordinates within certain small ranges of values, which are such that the sphere of the molecule does not intersect any other sphere, depends solely upon the co-ordinates of the molecule A, and upon the potential upon A of the field of intermolecular force; it does not depend upon the arrangement of the other molecules.

The Characteristic Equation.

§ 19. Starting from the state of the gas at the time $t = 0$, we can arrive at the state after an interval dt , by imagining the following succession of events. Suppose in the first place that each molecule is allowed to move under

no force except its own internal forces for a time dt , and let all the collisions which would occur in this time be supposed to occur. After this imagine the molecules divided into pairs in every possible way and suppose an encounter to occur between the two molecules of every such pair. The duration of the encounter is to be dt ; during it the co-ordinates of each molecule are to change only on account of the forces of the encounter; that is, on account of the intermolecular forces existing between the two molecules under consideration. These encounters are to take place consecutively, not simultaneously.

It is easily seen that each molecule has now been acted upon by exactly the same forces by which in the actual course of events it would have been acted upon in the interval dt . Hence, since there is no limit to the smallness of dt , the final state of the gas is independent of the order in which this series of events takes place, and is identical with the state in which the gas would have been found if the forces had acted simultaneously.

Two points deserve attention in connection with this argument. Firstly, it might be objected that the changes in the co-ordinates of molecules which experience an actual collision are not additive, inasmuch as one of these changes is not infinitesimal. It is, however, clear that there is no necessity to take the *infinitesimal* changes into account at all in the case of these molecules, for the number of these molecules vanishes in comparison with the total number when dt is made to vanish. Secondly, it is true that the number of molecules within any specified limits will not always consist of the same individual molecules. But it is a fundamental assumption of the kinetic theory that any N molecules which have nothing in common except that certain co-ordinates have specified values, will behave exactly like N other similarly conditioned molecules.

We can therefore reduce the continuous changes of the co-ordinates of molecules which arise from the action of intermolecular forces, to a series of encounters of the kind described in § 18.

§ 20. To completely specify an encounter, we require the values of all the co-ordinates enumerated in § 17, of both molecules. It will, however, be convenient to write

$$x'' = x' - x,$$

with a similar notation for y, z, u, v, w , and to specify a collision by the values of x'', \dots instead of the values of $x' \dots$.

As regards the law of distribution of the various co-ordinates, we notice that whatever the values of the q, r, s , and u co-ordinates may be, the probability that the p co-ordinates lie within the limits dp may, in the absence of external forces, be taken to be $f(p) dp$ where $\int f(p) dp = 1$. Since the internal energy is only slightly changed by encounters, we shall again suppose that the distribution of internal

energy is independent of the translational energy, and hence we may suppose that the number of molecules per unit volume which lie within a range $dp dq dr ds du$ is

$$\Phi(u) F(q, r, s) f(p) dp dq dr ds du,$$

or, as it will be frequently written,

$$\Phi F f dp dP du,$$

dP being written for $dq dr ds$.

We shall suppose that the gas has adjusted itself so that the distribution of the energy of translation is the permanent distribution. Thus at a point at which the potential energy of a molecule is ψ we shall have

$$\Phi(u) = e^{-h(mc^2 + 2\psi)}.$$

As we are going to admit the existence of intermolecular forces, the potential of a molecule at a point will depend on the co-ordinates of the molecules as well as the position of the point. Thus ψ will in general be a function of x, y, z, p and r .

Let molecules of which the co-ordinates lie within limits $dp dP du$ be called molecules of class α ; if the limits are $dp' dP' du'$, let the molecules be described as molecules of class β . Each of these classes will consist of a number of molecules which is indefinitely small in comparison with the total number of molecules present.

At any moment, let us imagine all the molecules placed in position, except those belonging to one or other of these two classes. Let them produce a field of force such that if a molecule of class α is placed with its centre at the point x, y, z , then the potential of this molecule will be Ω .

Then the probability that a molecule of class α will be found with its centre within an element $dx dy dz$ at $x y z$ is

$$e^{-h(mc^2 + 2\Omega)} F f dp dP du dx dy dz.$$

Hence the total number of such molecules to be found in the whole unit volume may be obtained by integrating this expression over the whole volume, and may be written as

$$N_\alpha = e^{-h(mc^2 + 2\Psi)} F f dp dP du \dots \dots \dots (i.),$$

where

$$e^{-2h\Psi} = \iiint e^{-2h\Omega} dx dy dz \dots \dots \dots (ii.).$$

The integral is taken over the whole unit volume, since the integrand is supposed to vanish if the point x, y, z is such that the centre of a molecule of class α cannot be found there.

The quantity Ψ will be called the mean intermolecular potential for a molecule of class α . It is clearly a function of all the coefficients which occur in the law of distribution as well as of the co-ordinates of molecules of class α . If we remember

that the r co-ordinates are supposed to be very small, it is clear that it will be sufficient to imagine that Ψ is a function of

- (i.) h , on account of the way in which this coefficient enters in equation (ii.),
- (ii.) the coefficients occurring in $f(p)$ (these have, however, already been assumed to be invariable),
- (iii.) the p co-ordinates of molecules of class α .

Thus, for our purpose, ψ is a function of h and p only.

Fixing our attention on any one of these molecules of class α , the probability that the centre of a molecule of class β may be found within the limits $dx'' dy'' dz''$ measured relatively to the first molecule will be

$$e^{-h(mc'^2 + 2\Omega')} F' f' dp' dP' du' dx'' dy'' dz'',$$

where Ω' is the potential of a molecule of class β at this point. Now Ω' can be made up of two parts, Ω_1 the part due to the presence of the single molecule of the first class, and Ω_2 the part due to all the other molecules combined.

It is clear that Ω_1 will only depend on the two molecules of the encounter, and is therefore a function of $p p' r r' x'' y''$ and z'' .

The total number of encounters of the type we are now considering, namely those within limits

$$dp dP du dp' dP' du' dx'' dy'' dz'' \quad . \quad . \quad . \quad . \quad . \quad . \quad (iii.),$$

will be

$$\Sigma e^{-h(mc'^2 + 2\Omega_1 + 2\Omega_2)} F' f' dp' dP' du' dx'' dy'' dz'',$$

where the summation extends to all the molecules of class α .

This number may be written as

$$e^{-h(mc'^2 + 2\Omega_1)} F' f' dp' dP' du' \Sigma e^{-2h\Omega_2} dx'' dy'' dz''.$$

Now it is obvious that the mean value of $e^{-2h\Omega_2}$ taken over all the elements of volume included in the summation, will be $e^{2h\Psi'}$, where Ψ' is the mean intermolecular potential of a molecule of class β , and is therefore a function of h and p' only.

Thus, since the summation extends to N_a elements of volume,

$$\Sigma e^{-2h\Omega_2} dx'' dy'' dz'' = N_a e^{-2h\Psi'} dx'' dy'' dz'.$$

This gives us for the total number of encounters of the type we are considering,

$$e^{-h(m(c^2 + c'^2) + 2\Psi + 2\Psi' + 2\Omega_1)} FF' ff' dp dP du dp' dP' du' dx'' dy'' dz'';$$

or, if we write

$$\eta \equiv h(m(c^2 + c'^2) + 2\Psi + 2\Psi' + 2\Omega_1) \quad . \quad . \quad . \quad . \quad . \quad . \quad (iv.),$$

the number is

$$e^{-\eta} FF' ff' dp dP du dp' dP' du' dx'' dy'' dz'' \quad . \quad . \quad . \quad . \quad . \quad . \quad (v.).$$

Let us call encounters of this type, encounters of class A, and denote their number (expression (v.)) by N_A .

There will be a second class of encounters which will be called class B, such that the co-ordinates *after* the encounter lie within the limits (iii.), (p. 416). The co-ordinates before the encounter will accordingly lie within certain other limits,

$$dp \, dP \, du \, dp' \, dP' \, du' \, dx'' \, dy'' \, dz'' \dots \dots \dots \text{(vi.)},$$

surrounding certain values \bar{p} , \bar{P} . . . &c. By LIOUVILLE'S Theorem, the complete differential (vi.) is equal to the complete differential (iii.), hence the number of encounters of class B will, by comparison with (v.), be seen to be

$$e^{-\eta} \bar{F} \bar{F}' ff' dp \, dP \, du \, dp' \, dP' \, du' \, dx'' \, dy'' \, dz'',$$

the positional co-ordinates and therefore also f , f' , remaining unaltered by the encounter.

Let N_0 be the total number of molecules lying within a range dP . Then a certain number of encounters of class A will result in a unit loss to N_0 , a certain number of encounters of class B in a unit gain. Thus, if for one at least of the co-ordinates which are changed by the encounter, say ξ , we have $\Delta\xi > d\xi$, where Δ denotes an increase due to an encounter, then it is certain that the co-ordinate ξ will be placed outside the limit $d\xi$, and N_0 will accordingly be diminished by unity.

It is, however, conceivable that for every co-ordinate we may have $\Delta\xi < d\xi$, and in this case there is a probability λ that no single co-ordinate passes outside its limits, and therefore that the molecule after encounter must still be counted in N_0 . It is easy to see that the probability that the ξ co-ordinate remains within the limits $d\xi$ is $\left(1 - \frac{\Delta\xi}{d\xi}\right)$, and therefore that

$$\lambda = \Pi \left(1 - \frac{\Delta\xi}{d\xi}\right),$$

where Π denotes continued multiplication extending to all the q, s co-ordinates. The loss experienced by N_0 on account of encounters of class A will therefore be $(1 - \lambda) N_A$ where $\lambda = 0$ for certain values of $x'' y'' z''$, and is a proper fraction over the remainder, and the boundary of these regions depends on the co-ordinates of encounter.

It follows that as the result of encounters of classes A and B combined, there is a net gain to N_0 of

$$[(1 - \lambda)e^{-\eta} \bar{F} \bar{F}' - (1 - \lambda)e^{-\eta} FF'] ff' dp \, dP \, du \, dp' \, dP' \, du' \, dx'' \, dy'' \, dz''.$$

The expression in square brackets may be written as $\Delta \{(1 - \lambda)e^{-\eta} FF'\}$. Hence the total gain to N_0 arising from all classes of encounters will be

$$dP \int \Delta \{(1 - \lambda)e^{-\eta} FF'\} ff' dp \, du \, dp' \, dP' \, du' \, dx'' \, dy'' \, dz''. \dots \text{(vii.)}$$

Here, as throughout the paper, a single tall integral sign denotes integration over all values of the variables, of which the differentials occur after the sign of integration.

For those values of x'' , y'' , z'' , for which λ is different from zero, we have seen that $\Delta\xi$ is, for every co-ordinate ξ of the same order of small quantities as $d\xi$, and hence it follows that

$$\int \Delta \{ \lambda e^{-\gamma} FF' \} ff' dp du dp' dP' du' dx'' dy'' dz''$$

is of the same order of small quantities.

In the limit, when the differentials such as $d\xi$ are supposed to vanish, this integral will vanish also, so that we may put $\lambda = 0$ in expression (vii.).

The total gain to N_0 from all encounters is therefore $I dP$, where

$$I = \int \Delta \{ e^{-\gamma} FF' \} ff' dp du dp' dP' du' dx'' dy'' dz'' \dots \dots \dots \text{(viii.)}$$

§ 21. Now we have seen (§ 19) that the change in N_0 in time dt will arise from three causes—

- (α) the change arising from collisions,
- (β) the change arising from encounters other than collisions,
- (γ) the change arising from the change in the co-ordinates of the various molecules during the time dt , which would occur if there was no interaction between different molecules.

Now any molecule, A, will collide with a second molecule, B, in the interval of time dt , provided that at the beginning of this time the centre of A lies within a certain region of space; provided, that is, that $x'' y'' z''$ lie within certain limits. It is easily seen that these limits are arrived at by writing $dx'' = u_1'' dt$, and allowing for $y'' z''$ a range of values corresponding to points inside a certain circle of diameter equal that of a molecular sphere. Hence the increase in N_0 arising from cause (α) will be $J dP dt$ where

$$J = \int \Delta \{ e^{-\gamma} FF' \} ff' dp du dp' dP' du' u_1'' dy'' dz'' \dots \dots \dots \text{(ix.)}$$

and Δ denotes the increase due to a collision.

The increase arising from encounters other than collisions has already been found to be $I dP$ (see viii.), where Δ must denote the increase due to an encounter of which the duration is dt . Since dt is to be very small, we may replace Δ by $dt D/Dt$, where D/Dt denotes the rate of increase under the influence of intermolecular forces only. The increase to N_0 arising from cause (β) will therefore be $K dP dt$, where

$$K = \int \frac{D}{Dt} \{ e^{-\gamma} FF' \} ff' dp du dp' dP' du' dx'' dy'' dz'' \dots \dots \dots \text{(x.)}$$

§ 22. In addition to the gain or loss which has just been calculated, N_0 will experience a further gain or loss on account of the gradual changes in the co-ordinates of the various molecules.

Let ξ be a typical co-ordinate, and ξ_0 and $\xi_0 + \delta\xi_0$ the limits of the values of ξ for molecules counted in N_0 . After a time dt , ξ will have increased to $\xi + \frac{d\xi}{dt} dt$, so that some molecules will enter within the above limits, and others will pass out, in course of the time dt .

The molecules which enter within the limits will be those for which, at the beginning of the interval, ξ had a value which was between $\xi_0 - \left(\frac{d\xi}{dt}\right)_{\xi_0} dt$ and ξ_0 . The number of such molecules is accordingly

$$\frac{1}{\delta\xi_0} \left(N_0 \frac{d\xi}{dt} \right)_{\xi_0} dt.$$

Similarly the number of molecules which escape from between these limits is

$$\frac{1}{\delta\xi_0} \left(N_0 \frac{d\xi}{dt} \right)_{\xi_0 + \delta\xi_0} dt,$$

so that the resultant gain to N_0 on account of changes in the ξ co-ordinates, the other co-ordinates being supposed to remain constant, will be

$$- \frac{\partial}{\partial\xi} \left(N_0 \frac{d\xi}{dt} \right) dt.$$

There is no limit to the smallness of dt , so that if all the co-ordinates vary simultaneously, the gain to N_0 will be

$$- dt \sum \frac{\partial}{\partial\xi} \left(N_0 \frac{d\xi}{dt} \right)$$

or

$$- dt \sum \frac{\partial N_0}{\partial\xi} \frac{d\xi}{dt} - N_0 dt \sum \frac{\partial}{\partial\xi} \left(\frac{d\xi}{dt} \right)$$

in which the summation extends to all the co-ordinates q , r , and s .

The value of $d\xi/dt$ must be found from the equations of motion of the molecule when under the action of no external forces. If η be any co-ordinate of position, and E be written for the total energy $T + V$, then these equations will be of the form

$$\frac{d}{dt} \left(\frac{\partial E}{\partial \dot{\eta}} \right) = \frac{\partial E}{\partial \eta} - \frac{\partial G}{\partial \dot{\eta}}.$$

This leads to the following scheme of values for the various time-differentials

$$\begin{aligned} \frac{dp_1}{dt} &= q_1, & \frac{dq_1}{dt} &= 0, & \frac{dr_1}{dt} &= s_1, \\ \frac{ds_1}{dt} &= -\frac{c_1}{d_1} r_1 - \frac{1}{d_1} \frac{dG}{ds_1}, & \frac{du_1}{dt} &= 0. \end{aligned}$$

Now it appears from the scheme of values just found that terms of the form $\frac{\partial}{\partial \xi} \left(\frac{d\xi}{dt} \right)$ can only arise in connection with the s co-ordinates, so that $\Sigma \frac{\partial}{\partial \xi} \left(\frac{d\xi}{dt} \right)$ may be replaced by $-\epsilon$ where

$$\epsilon = \frac{1}{d_1} \frac{\partial^2 G}{\partial s_1^2} + \frac{1}{d_2} \frac{\partial^2 G}{\partial s_2^2} + \dots$$

Thus the gain to N_0 arising from the cause (γ) will be

$$- dt \Sigma \frac{\partial N_0}{\partial \xi} \frac{d\xi}{dt} + \epsilon N_0 dt \dots \dots \dots \text{(xi).}$$

We have now counted up all sources of change in N_0 ; we therefore have, as the equation to be satisfied by N_0 ,

$$\frac{\partial N_0}{\partial t} dt = J dP dt + K dP dt + \epsilon N_0 dt - dt \Sigma \frac{\partial N_0}{\partial \xi} \frac{d\xi}{dt} \dots \dots \text{(xii).}$$

§ 23. We have found the equation ((i.), p. 415),

$$N_a = e^{-h(mc^2 + \Psi^2)} F f dp du$$

and

$$N_0 = \Sigma N_a$$

where the summation is such as to cover all ranges of p and u .

We may therefore write

$$N_0 = HF dP$$

where H is given by

$$H = \int e^{-h(mc^2 + \Psi^2)} f dp du \dots \dots \dots \text{(xiii),}$$

and is therefore a function of h only.

Substituting this value of N_0 in equation (xii.), we have the equation

$$\frac{\partial}{\partial t} (HF) = J + K + \epsilon HF - H \Sigma' \frac{\partial F}{\partial \xi} \frac{d\xi}{dt} \dots \dots \dots \text{(xiv)}$$

Let us write $F = e^{-x}$ and substitute this value for F in the integrals J and K . We have

$$\begin{aligned} \Delta \{e^{-\eta} F F'\} &= \Delta e^{-(\eta + x + x')} \\ &= e^{-(\eta + x + x')} \{e^{-\Delta \eta + x + x'} - 1\} \end{aligned}$$

Referring to equation (iv.) we find that

$$\eta + x + x' = h \{m(c^2 + c'^2) + 2\Psi + 2\Psi' + 2\Omega\} + x + x'.$$

From the equation of energy (see p. 412),

$$\Delta \{m(c^2 + c'^2) + 2(Q + S + Q' + S')\} = 0.$$

Hence

$$\Delta(\eta + \chi + \chi') = -\Delta\zeta,$$

where

$$\zeta = 2h(Q + S + Q' + S') - \chi - \chi'.$$

In virtue of the assumptions which have been made, ζ is a small quantity, so that we may put

$$e^{\Delta\zeta} - 1 = \Delta\zeta,$$

and therefore

$$\Delta\{e^{-\eta} FF'\} = Fe^{-(\eta + \chi)} \Delta\zeta.$$

The same transformation holds if Δ is replaced by D/Dt . Hence we have (see equations (ix.) and (x.), p. 418).

$$J = FL, \quad K = FM,$$

where

$$L = \int e^{-(\eta + \chi)} \Delta\zeta ff' dp du dp' dP' du' u_1'' dy'' dz'' \quad \dots \quad (xv.),$$

$$M = \int e^{-(\eta + \chi)} \frac{D\zeta}{Dt} ff' dp du dp' dP' du' dx'' dy'' dz'' \quad \dots \quad (xvi.).$$

Making these substitutions, equation (xiv.) becomes

$$\frac{\partial H}{\partial t} F - HF \frac{\partial \chi}{\partial t} = F(L + M) + \epsilon HF + HF \Sigma' \frac{\partial \chi}{\partial \xi} \frac{d\xi}{dt},$$

or dividing throughout by HF ,

$$\frac{\partial \chi}{\partial t} = \frac{1}{H} \frac{dH}{dt} - \epsilon - \frac{1}{H} (L + M) - \Sigma' \frac{\partial \chi}{\partial \xi} \frac{d\xi}{dt} \quad \dots \quad (xvii.).$$

This is the characteristic equation satisfied by χ .

Form of General Solution.

§ 24. We must first examine in what way the integrals L and M involve q , r , and s . In L these co-ordinates are only involved through the factor $\Delta\xi$ which occurs in the integrand.

Now $\Delta r = 0$, and Δq , Δs can, from the equations of impact, be expressed as linear functions of all the velocities concerned. The coefficients will be functions of p , p' , r , r' , but we may as usual put r , $r' = 0$.

It follows that $\Delta\xi$ is a function of q , r , and s of degree equal to that of ξ , and will involve p , p' , u , u' as well as these variables. If, then, ξ is of degree n in q , r , and s , we may regard $\Delta\xi$ as a function of q , r , and s of degree n , of which the coefficients are functions of the variables with respect to which integration is performed in evaluating L . Hence after integration we shall have L as a function of q , r , and s of degree n .

In the same way, the variables q , r , and s only enter the integral M , through the term $D\xi/Dt$, and we may write

$$\frac{D\xi}{Dt} = \sum \frac{\partial \xi}{\partial \xi} \frac{D\xi}{Dt}.$$

Now $D\xi/Dt$ denotes the rate of increase in ξ owing to the action of forces of which the potential energy is Ω_1 .

Write $E = T + T' + \Omega_1$, then

$$\frac{D}{Dt} \left(\frac{dE}{d\eta} \right) = \frac{dE}{d\eta},$$

in which η is any one of the p or r co-ordinates, and $\dot{\eta}$ is the corresponding velocity co-ordinate.

Hence
$$\frac{Dq}{Dt} = \frac{1}{b_1} \frac{d\Omega_1}{dp_1}; \quad \frac{Dr_1}{Dt} = 0; \quad \frac{Ds_1}{Dt} = \frac{1}{a_1} \frac{d\Omega_1}{dr_1}.$$

The right-hand members of these equations will be functions of the p , p' , r , r' co-ordinates, but it is clearly legitimate to put r , r' all equal to zero, and regard the expressions as functions of p and p' only.

It therefore appears that $D\chi/Dt$ will be a function of q , r , and s , of which the degree is $(n - 1)$, and upon integration, that M is a function of q , r , and s of the same degree.

The terms $\frac{\partial \chi}{\partial t}$ and $\sum \frac{\partial \chi}{\partial \xi} \frac{d\xi}{dt}$ which occur in equation (xvii.) will be functions of q , r , and s of degree n .

§ 25. It is therefore clear that the correct form to assume for χ is a rational integral algebraic function of the co-ordinates q , r , and s .

If we assume χ to be the most general function of degree n in these co-ordinates, the coefficients being functions of the time, and if we substitute this assumed value for χ in equation (xvii.), we shall get, on each side of the equation, a function of q , r , and s of degree n .

If therefore we equate the coefficients of every term on the two sides of the equation, we shall have found a solution of equation (xvii.), p. 421, inasmuch as this equation is now satisfied identically for every value of q , r , and s .

The process of equating these coefficients leads to a series of differential equations, in which the time-rate of increase of every coefficient is given explicitly in terms of the other coefficients and of h . If, therefore, we suppose the coefficients to vary with the time in the manner given by these equations, the value of χ so obtained will be a solution of equation (xvii.) for all time. Since the equations involve h , and h varies with the time, one further equation is required before we can express the co-ordinates at any time in terms of the initial values of the co-ordinates and the time. This additional equation is supplied by the fact that N , the total number of molecules, remains constant.

We have (see § 23, equation (xiii.)),

$$N = \int HF dP = \int e^{-h(mc^2 + 2\psi)} fF dp dP du. \quad \dots \quad (\text{xviii.}),$$

and the equation $dN/dt = 0$ is the equation required. With the help of the other equations, it can be written so as to give dh/dt explicitly as a function of h and the other co-ordinates.

Thus if we have the initial form of χ given, we have obtained sufficient equations to enable us theoretically to determine χ at any subsequent time. It is not proposed to attempt the solution of the system of equations in the most general case; the discussion is confined to the modified forms which these equations assume in the two states of which the physical interest is greatest, namely the steady state, and the state in which the gas is non-luminous.

Solution in Steady State.

§ 26. The mathematical condition that a steady state may be possible, is that it may be possible for the time rates of variations of the coefficients to vanish simultaneously. From the equations found by equating to zero the time rates of all the coefficients except h , it is possible to find these coefficients in terms of h so that the condition for a steady state to be possible is that the function of h obtained by substituting these values in the expression for dh/dt shall vanish identically for all values of h . It is, however, known that the condition that a steady state shall be possible is that G shall be identically zero, and we may therefore begin by putting $G = 0$ and neglecting the equation $dh/dt = 0$.

Thus all the equations necessary are contained in the characteristic equation satisfied by χ , and this is now (*cf.* equation xvii., p. 421)

$$\frac{1}{H} (L + M) + \sum_1^{\kappa} \frac{\partial \chi}{\partial \xi} \frac{\partial \xi}{\partial t} = 0,$$

or substituting for $d\xi/dt$ from the scheme of p. 419,

$$\frac{1}{H} (L + M) + \sum_1^{\kappa} \left(\frac{\partial \chi}{\partial r_1} s_1 - \frac{c_1}{d_1} \frac{\partial \chi}{\partial s_1} r_1 \right) = 0. \quad \dots \quad (\text{xix.}).$$

Let us assume as a possible value for χ the most general expression of degree n in q , r and s , the coefficients now being independent of the time.

Consider the system of equations which is obtained when we equate to zero the coefficients of terms of degree n in equation (xix.). The terms of degree n in the integral L arise entirely from the terms of degree n in χ (see § 24). These terms

Solution for Low Temperatures.

§ 27. In the approximately steady state which was found to be possible at low temperatures, for the previous system of molecules, it was found that the various mean energies varied very slowly with the time. But if such a state were possible for the present system, it would not follow that χ would only vary slowly with the time, so that an approximate solution of $d\chi/dt = 0$, even if it could be found, would be useless.

Let us, however, examine under what circumstances we could have $d\chi/dt$ equal to zero, without approximation. From the remarks at the beginning of the last section, it is clear that the coefficients in χ can be so chosen as to make $d\chi/dt$ equal to zero, but that it is only in the event of G being absent, that these values will also make $dh/dt = 0$.

Let us suppose that by some external agency h is caused to increase uniformly throughout the whole gas, at a rate exactly equal to the rate at which it decreases in consequence of the value of dh/dt , found in the manner described at the beginning of § 26, being different from zero. Then a completely steady state will have become possible, and this is because the imaginary agency introduces exactly sufficient energy to compensate that lost by radiation. In a state such as that which, in the first part, was described as approximately steady, the radiation was very small. If a similar state can be shown to be possible in the present case, the radiation will be very small, and therefore the energy introduced from outside will be very small. Hence it will be legitimate to describe the state which would be arrived at by checking the external flow of energy as approximately steady.

The equation which leads to such a state is $d\chi/dt = 0$, or

$$\epsilon + \frac{1}{H} (L + M) + \sum_1^{\kappa} \left(\frac{\partial \chi}{\partial r} s_1 - \frac{c_1}{d_1} \frac{\partial \chi}{\partial s_1} r_1 \right) - \sum_1^{\kappa} \frac{1}{d_1} \frac{\partial \chi}{\partial s_1} \frac{\partial G_1}{\partial s_1} = 0 \quad \dots \quad (\text{xxi}).$$

The last term in equation (xxi.) is of the same degree as χ , so that just as in the last section it may be shown that χ cannot contain terms of a degree higher than the second. And for the same reason as before, χ cannot contain terms linear in any of the coefficients, so that we may assume

$$\chi = \sum \beta_1 q_1^2 + \sum \gamma_1 r_1^2 + \sum \delta_1 s_1^2 + \kappa_1.$$

Now at low temperatures all the terms in equation (xxi.) are small, except terms of the form

$$\frac{\partial \chi}{\partial r_1} s_1 - \frac{c_1}{d_1} \frac{\partial \chi}{\partial s_1} r_1.$$

These terms must therefore vanish approximately for all values of the variable, and this requires the relation

$$\gamma_1/\delta_1 = c_1/d_1.$$

This merely shows that, neglecting small quantities of the order of the coefficients in G , the energy of any of the r, s modes of vibration must be equally divided between kinetic and potential energy.

It is now clear, that at high temperatures the last term in equation (xxi.) is small in comparison with the others, so that the law of distribution will be very little altered by the presence of a dissipation function, whereas at sufficiently low temperatures, the term arising from the dissipation function becomes as important as any other term in the equation, and, therefore, the presence of a dissipation function, however small, will be sufficient to entirely alter the law of distribution.

And without investigating the solution of the system of equations which determine the coefficients in χ , it is clear that since they are all linear, every coefficient must be a single-valued function of h only. Hence, as before, there is only one approximately steady state for a given temperature, but it is no longer true that the various lines of the spectrum increase in brightness in the same ratio when the temperature is increased. Since the u, q modes of energy suffer very little loss of energy, and since energy passes freely between these modes, it follows that the energies of these modes will very approximately be distributed according to BOLTZMANN'S Law. Hence all that was said about the ratio of the two specific heats with reference to the former type of molecule considered, will apply also to molecules of the type which we have just been discussing.

PART III.

PHYSICAL CONSEQUENCES OF THE FOREGOING THEORY.

§ 28. We have thus been led to the same results in both parts of this paper. It seems natural to suppose that results which are qualitatively the same will be found to be valid for any gas, and, assuming this to be the case, to examine some of the consequences of these results.

Radiation at a given Temperature.

§ 29. In the first dynamical illustration, the radiation from each degree of freedom at temperature T was found to be proportional to $T^{3/2}$. In the second illustration, the expression for the radiation would have been too complicated for the calculation of it to have been profitable.

A modification of the system discussed in Part II., leads to an interesting expression for the radiation. In this modified system the molecules are to be spheres with modes of internal vibration to and from which energy only passes with difficulty. Each sphere is surrounded by a field of force, such that when two molecules

are in contact in any position, their potential has a constant value Ω . When two molecules are not very near, let us suppose that the transfer of energy between different r, s modes may be neglected, so that the main transfer of energy takes place through collisions.*

At any collision, the r, s energy of the colliding molecules will be small, so that the amount by which the r, s energy is increased will depend only on the u and q energies of the colliding molecules; that is to say, on the average, on h .

Thus if n collisions take place per unit time, the total transfer from the u, q modes of energy to any specified r, s mode may be taken to be Cn/h , where C is a constant for any particular r, s mode.

The sum of such amounts must be equal to the amount radiated per unit time, and may therefore be supposed to be roughly proportional to the energies of the r, s modes. It follows that for a single molecule the r, s energy is proportional to n/Nh .

Now we may take for the number of collisions

$$n = \frac{AN^2e^{-h\Omega}}{\sqrt{h}},$$

where A is a constant.

Hence

$$\frac{n}{Nh} = \frac{ANe^{-h\Omega}}{h^{3/2}},$$

and if ρ be the density, the radiation will be proportional to $\rho h^{-3/2} e^{-h\Omega}$, or, in terms of the temperature, to $\rho T^{3/2} e^{-\frac{c\Omega}{T}}$.

This example is of such a special nature that not much importance can be attached to the actual result obtained. It is, however, of interest, as showing that it is at any rate possible for the radiation to increase very rapidly with the temperature. A comparison with the result of § 9, shows that the introduction of a field of force has introduced a factor $e^{-\frac{c\Omega}{T}}$ into the expression for the radiation, and a factor of this form figures in every formula for radiation.†

The presence of the factor ρ multiplying the expression for the radiation, is an essential feature of the present theory.‡ If the exponential factor changes very rapidly with the temperature, so that the point of incandescence is sharply defined, then this point will clearly be almost independent of ρ , and variations in radiation on

* This assumption, although not stated explicitly in the investigation of Part II., is implied in the assumptions made there.

† WIEN and PLANCK give for the radiation in the part of the spectrum between λ and $\lambda + \delta\lambda$, the formula $c_1\lambda^{-5} e^{-\frac{c_2}{\lambda T}} d\lambda$. LORD RAYLEIGH, on theoretical grounds, suggests as an emendation $c_1T\lambda^{-4} e^{-\frac{c_2}{\lambda T}} d\lambda$. ('Phil. Mag.,' June, 1900.)

‡ [Added March 19, 1901.—I was not aware, when writing this, that the presence of the factor ρ had been detected experimentally. See LIVEING and DEWAR, 'Roy. Soc. Proc.,' 49, p. 217, or KAYSER, 'Handbuch der Spectroscopie' (1900), I., p. 143.]

account of density will be unnoticeable in comparison with variations on account of temperature.

It is, however, clear that in considering radiations from gases of great density, such as for example occur in the sun, the factor ρ would be of considerable importance.

Generalised Theory of Temperature.

§ 30. The state of a gas may be regarded as depending upon a principal temperature T , and also on a number of subsidiary temperatures τ_1, τ_2, \dots , each of these temperatures corresponding to one (or possibly more) of the degrees of freedom of the molecule. The principal temperature is to correspond to the three degrees of freedom implied by the possibility of translation through the ether, and to any other degrees of freedom which are such that their mean energy is at all temperatures equal to a third of the mean energy of translation.

The principal temperature is to be proportional to the mean energy of translation of a molecule and each subsidiary temperature proportional to the mean energy of each of the modes to which it corresponds. Thus two modes can only have the same subsidiary temperature when their mean energies are, under all circumstances, equal, as, for example, when they are the kinetic and potential energies of the same vibration. When the energy is equally distributed between all the degrees of freedom all these temperatures are to become equal.

We have found that at temperatures below the temperature of incandescence there is an approximately steady state in which

$$\tau_1 = \rho f_1(T), \quad \tau_2 = \rho f_2(T), \quad \&c.,$$

where $f_1(T)$, $f_2(T)$, &c., are functions of T , which at these temperatures are very small in comparison with T .

At higher temperatures we have not investigated the forms of τ_1, τ_2, \dots , but at infinite temperatures,

$$\tau_1 = \tau_2 = \dots = T.$$

§ 31. The steady state specified above was arrived at on the assumption that external agencies could only influence the energy of translation, and that the other energies were only influenced indirectly through changes in the energy of translation.

Thus the above equations will not hold in the presence of agencies which exert a direct influence on the subsidiary temperatures. Such influences may be looked for in the forces of chemical action, disturbances in the ether, and possibly in the cathode rays, if we suppose these rays to be streams of charged ions which are so small as to penetrate inside a molecule rather than act on the molecule as a whole.

When such agencies are present, the above equations must give place to others. The subsidiary temperatures which are most directly concerned may attain to

abnormally high values, and this may result in the phenomena of phosphorescence, chemi-luminescence, &c. To take a definite instance, suppose that τ_1 corresponds to a vibration in the molecule of frequency p . If a ray of light passes through the substance, those components of this wave of which the frequency is nearly equal to p will supply energy to the mode τ_1 of the molecules, and this energy will be distributed from the τ_1 mode to the other modes, and so through the substance. Thus the result is a heating of the substance, and an absorption band in the spectrum of the light transmitted through it. The illustration might be varied by supposing that energy could not easily distribute itself from τ_1 to all the other temperatures, but that it passed freely to a second temperature τ_2 . In this case the temperature τ_2 might conceivably attain to such a high value as to emit its own spectrum, and so set up fluorescence or calorescence.

The spectrum of the gas in any condition whatever will be arrived at by the superposition of the various spectra of the subsidiary temperatures, and the state of the gas as regards the emission of radiation will be completely specified by the values of the various subsidiary temperatures.

Thermodynamics.

§ 32. At temperatures at which the gas is dark, we may take

$$\tau_1 = \tau_2 = \dots = 0.$$

Thus at these temperatures we are only concerned with the principal temperature, and the total energy of the gas is proportional to this temperature. If n degrees of freedom correspond to this temperature, the ratio of the specific heats will be

$$1 + 2/n,$$

both specific heats being constant as regards the temperature. The view which we have put forward does not clash with the ordinary thermodynamics as regards dark gases.

When the subsidiary temperatures begin to have appreciable values the case is different. The total internal energy is now given by

$$W = C \{nT + \Sigma \kappa_1 \tau_1\},$$

where C is a constant, and κ_1 is the number of modes of energy of which the subsidiary temperature is τ_1 . The specific heat at constant volume is given by

$$C_1 = dW/dT = C \{n + \Sigma \rho \kappa_1 f'_1(T)\},$$

and therefore depends on both the temperature and density.

If a quantity dQ of work be absorbed by a gas,

$$\begin{aligned} dQ &= NdW - pdv \\ &= CN \left\{ ndT + \Sigma \kappa_1 d(\rho f_1(T)) \right\} - T\rho R d\left(\frac{1}{\rho}\right). \end{aligned}$$

If the gas be made to pass through any succession of states so as to return to the same temperature and density,

$$\int \frac{dQ}{T} = CN \Sigma \kappa_1 \int \frac{d(\rho f_1(T))}{T dT} dT.$$

Thus the second law of thermodynamics will only hold in special cases for a gas which is emitting radiation of any kind. This part of the subject of luminosity has, however, been developed by WIEDEMANN,* so that it seems unnecessary to pursue it any further here.

* E. WIEDEMANN, "Mechanics of Luminosity," 'Phil. Mag.,' vol. 28, 1889, p. 152, or 'Wied. Annalen' vol. 37, p. 181.