XXXV. On some problems in the kinetic theory of gases

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supposing the pressure to follow the law (31) applicable when $2r > a$, is

$$\int_0^{\frac{1}{2}a} \frac{2}{r} \cdot \frac{\pi a^5}{40} \cdot 4\pi r^2 \, dr = \frac{\pi^2 a^7}{40}.$$

The work required to generate a cavity for which $2r > a$ is therefore less than if the ultimate law prevailed throughout by the amount

$$\frac{\pi^2 a^7}{4}\left(\frac{1}{10} - \frac{1}{18} - \frac{1}{35}\right) = \frac{\pi^2 a^7}{4 \cdot 9 \cdot 7}. \quad \cdot \quad \cdot \quad \cdot \quad (33)$$

<div align="center">[To be continued.]</div>

XXXV. *On some Problems in the Kinetic Theory of Gases.* By S. H. BURBURY, *F.R.S.**

Maxwell's *Law of Distribution.*

1. WHEN a gas or mixture of gases is at rest in the normal state, the distribution of velocities among the molecules may be defined thus:—Take an origin O, and let the vector velocity of each molecule be represented by a line drawn from O. Then the number per unit of volume of molecules of mass M, whose velocities are represented by lines from the origin to points within the element of volume $d\mathrm{Q}$ at P, is

$$\mathrm{N}\left(\frac{h\mathrm{M}}{\pi}\right)^{\frac{3}{2}} \epsilon^{-h\mathrm{M} \cdot \mathrm{OP}^2} \, d\mathrm{Q} \, ;$$

where N is the number of molecules of mass M in unit of volume, and $\dfrac{3}{2h}$ is the mean kinetic energy of a molecule.

2. I shall employ two other variables :—

Let V denote the vector velocity of the common centre of gravity of two molecules whose masses are M and m. Call this their *common velocity.*

Let R denote the velocity of M, r that of m, relative to this common centre of gravity. Then the velocity of M is the resultant of V and R, that of m is the resultant of V and r.

The relative velocity of M and m is $R + r$, and shall be denoted by ρ, so that

$$\frac{R}{r} = \frac{m}{M}, \quad \rho = \frac{M + m}{m} R = \frac{M + m}{M} r.$$

3. The molecules whose velocities are represented by lines

<div align="center">* Communicated by the Author.</div>

from the origin to points within the element of volume dQ at P shall be said to have velocities OP (dQ). Or if we give to dQ any particular form, as $\omega^2 d\omega\, dS$, ω being OP and dS being a small solid angle, we may speak of the velocities OP $(\omega^2 d\omega\, dS)$. If λ, μ, ν be direction-cosines of the axis of a cone containing the elementary solid angle dS, we may speak of the direction $\lambda\,\mu\,\nu\,dS$ as comprising all lines drawn from the vertex of that cone and falling within it; and $\lambda\mu\nu\omega^2 d\omega\, dS$ as comprising all velocities between ω and $d\omega$ in directions within that cone.

4. *In* Maxwell's *distribution, if we consider all pairs of molecules,* M *and* m, *having common velocity* V, *and relative velocity* R$+$r, *for given* V *all directions of* R *or* r *are equally probable.*

Let $\quad$ OC$=$V, $\quad$ PO$p=$R$+r$,

$$\frac{PO}{pO} = \frac{m}{M} = \frac{R}{r}.$$

If OC be given, the number of the pairs in question for which the angle POC lies between θ and $\theta + d\theta$ is proportional to

$$\epsilon^{-h(M\,.\,PC^2 + m\,.\,pC^2)} \sin\theta\, d\theta.$$

Now

$$M\,.\,PC^2 + m\,.\,pC^2 = MR^2 + mr^2 + \overline{M+m}\ V^2$$
$$-2(M\,.\,R - m\,.\,r)V\cos\theta,$$

which is independent of θ because $MR - mr = 0$. The number is therefore proportional to $\sin\theta\, d\theta$, and this proves the proposition.
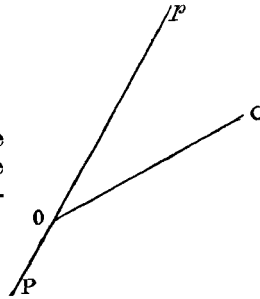
5. *If the molecules behave in their mutual encounters as elastic spheres, then for given direction of the relative velocity before encounter, all directions after encounter are equally probable.*

I think it unnecessary to give a proof of this proposition.

6. (a) *Every distribution of velocities among the molecules which satisfies the condition that for given* V *all directions of* R *are equally probable, is undisturbed by encounters, or by the mutual action of the molecules, and is therefore, in the absence of external forces, stationary.*

(b) *No distribution whatever of velocities among the molecules is undisturbed by encounters, or by the mutual action of the molecules, unless it satisfies the condition that for given* V *all directions of* R *are equally probable.*

Of these theorems (*a*) corresponds to the well-known pro-

position that Maxwell's distribution is stationary. The con-
verse (*b*) is founded on Boltzmann's proof (*Sitzungsberichte,*
Vienna, 1872), but is much simplified by using V and R for
variables.

We will prove these theorems, (*a*) and (*b*), first on the
hypothesis that the molecules are to be treated as elastic
spheres. We will suppose two classes of molecules having
mass M and *m* respectively. It will be sufficient if we prove
our propositions for the encounters of M with *m*.

Let $F(x\,y\,z)\,dx\,dy\,dz$, or $F.dx\,dy\,dz$, be the number per
unit of volume of molecules of mass M whose velocities are
represented by lines from the origin to points within the ele-
ment of volume $dx\,dy\,dz$ at $x\,y\,z$. Similarly $f(x'\,y'\,z')\,dx'\,dy'\,dz'$,
or $f.dx'\,dy'\,dz'$, is the corresponding number for the *m*'s. If
$x\,y\,z$ be denoted by P, and $x'\,y'\,z'$ by p, we will write F_P and
f_p for F and f.

Let C be the point $\xi\,\eta\,\zeta$. Consider all the pairs, M and *m*,
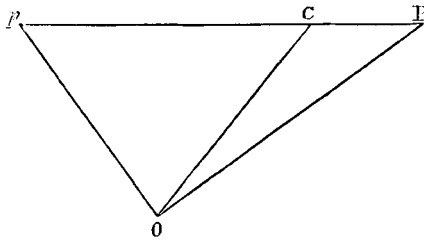
which have O C for common velocity. About C as centre
describe two spherical shells, one with radii $R\ldots R+dR$, the
other with radii $r\ldots r+\dfrac{M}{m}\,dR$. Let P be a point in the first

shell. The common velocity being OC, and the velocity of M
being OP, the velocity of *m* is O*p*, where *p* is a determinate
point in the second shell, namely in PC produced so that
$\dfrac{Cp}{CP}=\dfrac{M}{m}$. And so f_p can be expressed as a function of $\xi\,\eta\,\zeta$,
and of $x\,y\,z$, the coordinates of P.

The effect of an encounter between M and *m* under these
circumstances is, without altering V, to substitute for PC*p*
some other common diameter of the spherical shells as the
relative velocity. Let it be P'C*p'*. Then all directions of
P'C*p'*, given PC*p*, are equally probable.

The number of pairs M and *m* per unit of volume and time,
having OC for common velocity, for which the relative velocity
is PC*p*(*d*S) before, and P'C*p'*(*d*S') after, encounter, *d*S and

dS' being small solid angles, is

$$\frac{dS'}{4\pi} F_P f_p \, dS \, \pi s^2 \rho, \text{ that is } F_P f_p \frac{dS \, dS'}{4\pi} \pi s^2 \rho,$$

where s is the sum of the radii of M and m.

The number of pairs for which it is $P'Cp'(dS')$ before, and $PCp(dS)$ after, encounter is

$$\frac{dS}{4\pi} F_{P'} f_{p'} \, dS' \, \pi s^2 \rho, \text{ that is } F_{P'} f_{p'} \frac{dS \, dS'}{4\pi} \pi s^2 \rho.$$

If, then, $F_P f_p = F_{P'} f_{p'}$, the number per unit of volume and time of pairs for which the relative velocity turns, as the result of encounter, from PCp to $P'Cp'$ is equal to the number for which it turns from $P'Cp'$ to PCp. And if this is true, given C, for every two directions of PCp, and for all positions of C, it follows that the distribution of velocities is not affected by encounters between M and m.

Now $F_P f_p$ represents the chance that, given $V = OC$, the relative velocity shall have direction PCp. And we see that if, given OC, this chance be the same for all directions through C, the distribution of velocities is not affected by encounters. So (*a*) is proved.

If for some two directions of the diameter $F_{P'} f_{p'} \neq F_P f_p$ we proceed as follows, adapting Boltzmann's proof.

Let

$$H = \iiint dx \, dy \, dz \, F(x\,y\,z)(\log F(x\,y\,z) - 1)$$
$$+ \iiint dx \, dy \, dz f(x\,y\,z)(\log f(x\,y\,z) - 1),$$

the limits being in each case $\pm \infty$, or, as we will write it,

$$H = \iiint dx \, dy \, dz \{ F(\log F - 1) + f(\log f - 1) \} ;$$

then

$$\frac{dH}{dt} = \iiint dx \, dy \, dz \left\{ \frac{dF}{dt} \log F + \frac{df}{dt} \log f \right\}.$$

Now F is supposed to vary only by encounters between the M's and the m's. Therefore

$$\frac{dF_P}{dt} = T'_P - T_P ;$$

where T_P is the number per unit of time of encounters with the m molecules which the M molecules with velocity OP undergo, and T'_P is the number per unit of volume and time of encounters between M and m from which M issues with velocity OP. Now P being given, and the velocity of M being OP, C or $\xi \eta \zeta$ may have any position whatever, and

the position of p is determined by that of C.   Hence

$$T_P = F_P \iiint d\xi \, d\eta \, d\zeta \, \pi s^2 \rho f_p,$$
$$= \iiint d\xi \, d\eta \, d\zeta \, \pi s^2 \rho F_P f_p \, ;$$

and since all the directions of the relative velocity before encounter are equally probable,

$$T'_P = \iiint d\xi \, d\eta \, d\zeta \, \pi s^2 \rho \, \frac{1}{4\pi} \iint F_{P'} f_{p'} \, dS,$$

in which $\iint dS$ denotes integration for all directions of the diameter, $P'Cp'$, of the spheres described about C, or $\xi \, \eta \, \zeta$, through P.   Let $\dfrac{1}{4\pi} \iint F_{P'} f_{p'} \, dS$ be denoted by $\overline{F_{P'} f_{p'}}$, then, given P,

$$\frac{dF_P}{dt} = \iiint d\xi \, d\eta \, d\zeta \, \pi s^2 \rho \, (\overline{F_{P'} f_{p'}} - F_P f_p),$$

and by symmetry $\dfrac{df_p}{dt}$ has the same value.   In this equation $f_{p'}$ and f_p are supposed to be expressed as functions of $\xi \, \eta \, \zeta$ and the coordinates of P or P'.

In order to find $\dfrac{dH}{dt}$, we multiply $\dfrac{dF_P}{dt}$ by $\log F_P$ and $\dfrac{df_p}{dt}$ by $\log f_p$, and then integrate over all positions of P in space.   If PCp and $P'Cp'$ be any two diameters of the spherical shells described with radii R and r about C, $\dfrac{dH}{dt}$ will contain the term

$$\pi s^2 \rho \, (\log F_P + \log f_p) \, (F_{P'} f_{p'} - F_P f_p) \, ;$$

that is

$$\pi s^2 \rho \log (F_P f_p) \, (F_{P'} f_{p'} - F_P f_p).$$

By symmetry, as P' is a position which P will assume in the integration, $\dfrac{dH}{dt}$ will also contain the term

$$\pi s^2 \rho \log (F_{P'} f_{p'}) \, (F_P f_p - F_{P'} f_{p'}).$$

And adding the two terms together, $\dfrac{dH}{dt}$ contains the term

$$\pi s^2 \rho \log \frac{F_P f_p}{F_{P'} f_{p'}} \, (F_{P'} f_{p'} - F_P f_p),$$

and will consist wholly of a series of terms of that form.

Now this expression is necessarily negative unless $F_{P'} f_{p'} = F_P f_p$, and is then zero.   Therefore $\dfrac{dH}{dt}$ is necessarily

negative unless $F_{P'}f_{p'} = F_P f_p$ for every two directions of the diameter through C; that is unless, for given V, all directions of the relative velocity are equally probable. Now in stationary motion H must be invariable with the time. Therefore the motion is not stationary, or the distribution of velocities is not unaltered by encounters, unless the condition be satisfied. So (*b*) is proved.

7. We will next assume that the two molecules M and *m* act on each other with finite forces. Then in the infinitely short time *dt* the relative velocity is by their mutual action during encounter turned through some small angle; and generally also altered in magnitude, in such manner as that

$$\tfrac{1}{2}\frac{Mm}{M+m}\rho^2 + \chi = \text{constant,}$$

χ being the potential of the mutual action.

It is not necessary to restrict the number of *m* molecules which may simultaneously be in encounter with, and affect the motion of, a given M. But by the superposition of small motions, we may regard the total time-variation of the velocity of M as the sum, or resultant, of the time-variation due to the action of all the *m* molecules separately, each acting for the time *dt*. We can then prove that for any given class of M's with any class of *m*'s, as the result of their mutual action, $\dfrac{d\mathrm{H}}{dt}$ is negative unless the condition is satisfied, in which case it is zero.

The mutual action is assumed to depend on the relative positions, not on the velocities, of M and *m*.

We assume also the distribution to be uniform in space, so that the number per unit of volume of any given class of molecules is independent of the position.

Let, then, at any instant the distance between M and *m* be between q and $q+dq$.

Let the common velocity be OC$=$V, and let the velocity of M be OP($R^2\, d\mathrm{R}\, d\mathrm{S}$).

The velocity of *m* or O*p* is then determined by these conditions. In order completely to define the motion we require one other coordinate of position. Let it be θ. Consequently the number of pairs M and *m* satisfying these conditions at any instant is $F_P f_p R^2\, d\mathrm{R}\, d\mathrm{S}\, dq\, d\theta$. Call this the first state.

By mutual action V is not affected. The motion under the influence of the mutual action is determinate, and after time *at* the same variables shall be denoted by accented letters. Then q', R', S', θ' are functions of q, R, S, θ, known if the

Y 2

law of mutual action is known. Call this the second state. The number of pairs, M and m, in the second state, at any instant is $F_{P}' f_{p}' R'^2 dR' dS' dq' d\theta'$.

Now by a known theorem (Boltzmann, *Sitzungsberichte*, Vienna, 1871; Watson, ' Kinetic Theory of Gases,' Prop. III.),

$$R^2 dR \, dS \, dq \, d\theta = R'^2 dR' \, dS' \, dq' \, d\theta',$$

or, since

$$dq = -\rho dt, \text{ and } dq' = -\rho' dt,$$

$$R^2 dR \, dS \, d\theta \, \rho dt = R'^2 dR' \, dS' \, d\theta' \, \rho' dt.$$

The number of pairs which in unit of volume and time dt pass by their mutual action from the first to the second state is

$$F_{P} f_{p} R^2 dR \, dS \, d\theta \, \rho dt \; ;$$

and the number which so pass from the second state to the first is

$$F_{P}' f_{p}' R'^2 dR' \, dS' \, d\theta' \, \rho' dt.$$

If therefore

$$F_{P}' f_{p}' = F_{P} f_{p},$$

the number of pairs which pass from the first to the second state is equal to the number which pass from the second to the first in the same time, and this being true for all positions of C and of P, the distribution of velocities is unaffected by the mutual action of M and m.

If $F_{P}' f_{p}' \neq F_{P} f_{p}$, then we form $\dfrac{dH}{dt}$ as before, and it will as before consist of a series of terms, each of the form

$$\log \frac{F_{P} f_{p}}{F_{P}' f_{p}'} (F_{P}' f_{p}' - F_{P} f_{p}),$$

and is therefore necessarily negative until for given C, $F_{P'} f_{p'}$ becomes equal to $F_{P} f_{p}$ for all directions through C.

8. The complete expression for $\dfrac{dH}{dt}$ in case of elastic spheres is

$$\iiint d\xi \, d\eta \, d\zeta \int_{0}^{\infty} dR \pi s^2 \rho \cdot R^2 \iint dS \log (Ff)\{\overline{F'f'} - Ff\},$$

where $\iint dS$ denotes integration over a spherical shell described with radii $R \ldots R + dR$ about the point $\xi \eta \zeta$ as centre, and $\overline{F'f'}$ denotes the mean value of Ff for all positions of the diameter of that shell.

This may be put in the form

$$\int_0^\infty dV V^2 \int_0^\pi d\alpha 2\pi \sin\alpha \int_0^\infty dR \pi s^2 \rho R^2 \iint dS \log (Ff)(\overline{F'f'}-Ff),$$

where α is the angle made by OC with a given line—or, changing the order of integration, $\dfrac{dH}{dt} =$

$$\int_0^\infty dV V^2 \int_0^\infty dR \pi s^2 \rho R^2 \int_0^\pi d\alpha 2\pi \sin\alpha \iint dS \log (Ff)(\overline{F'f'}-Ff).$$

9. In case of finite forces acting between the molecules, we have no such simple expression as $\pi s^2 \rho$ to denote the number per unit of time of encounters between two molecules with relative velocity ρ. We might define an encounter to be a case in which the relative velocity of two molecules is turned by their mutual action through an angle exceeding a certain limit, reckoning from the time when mutual action begins, to a time when it has ceased, to be appreciable. If with that definition we denote by $\pi s^2 \rho$ the number of encounters per unit of time, s is generally a function of ρ or of R. We might use $\pi s^2 \rho$ in this sense for any medium in which the coincidence of two or more encounters for the same molecule simultaneously is so rare as to be negligible.

10. The equation

$$F_P f_p = F_{P'} f_p$$

is satisfied by

$$F_P = C\epsilon^{-hM \cdot OP^2},$$
$$f_p = C'\epsilon^{-hm \cdot Op^2},$$

where C, C' are constants, because if PCp, QCq be two diameters of the spherical shells,

$$M \cdot OP^2 + mOp^2 = M \cdot OQ^2 + mOq^2.$$

It is also satisfied by

$$F_P = C\epsilon^{-hM(OP^2+u^2-2uOP\cos\beta)},$$
$$f_p = C'\epsilon^{-hm(Op^2+u^2-2uOp\cos\beta')},$$

where u is a constant line measured in any direction, and β, β' are the angles made by OP and Op with that direction, because $M.OP \cos\beta + m.Op \cos\beta'$ has the same value for all directions of PCp. These are the values of F_P and f_p when both sets of molecules, M and m, have the same velocity, u, combined with the velocities required by the kinetic theory for a gas at rest.

A motion of this description is called by Professor Tait

" mass motion." I prefer to call it a *motion of simple trans-lation*. Since the equation $F_P f_p = F_{P'} f_{p'}$ is satisfied by such a motion, the distribution of velocities is unaffected by en-counters. As is otherwise also evident, because the motion of translation does not affect the relative velocities, it is not necessary that u should be small. It may, for instance, be the earth's motion in space. If, however, u be very small in a motion of this kind, the number per unit of volume of mole-cules of mass M whose velocities are between ω and $\omega + d\omega$ in direction $\lambda \mu \nu dS$ is

$$M\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\epsilon^{-hM\omega^2}\omega^2\, d\omega\, dS(1 + 2\lambda hM\omega u),$$

the direction of u being taken for axis of x.

On Disturbed States of a Gas.

11. Thus far we have treated only of a gas at rest or in simple translation, in both of which cases $\dfrac{dH}{dt} = 0$. Both may be regarded as normal states. We come now to consider cer-tain disturbances in which, by the action of external causes, the gas is maintained in a state differing from the normal state. We might suppose generally the number per unit of volume of molecules of mass M having velocities $\lambda \mu \nu \omega^2 d\omega\, dS$ to be

$$F(\omega)\omega^2 d\omega\, dS,$$

and

$$F(\omega) = N\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\epsilon^{-hM\omega^2}\{1 + \Sigma C_i Y_i\},$$

where the Y's are any spherical harmonic functions referred to the origin, the C's functions of ω, and $\Sigma C_i Y_i$ is supposed very small compared with unity. In the problems with which we shall deal the harmonics will be of the first and second orders only.

12. In such a system H differs from the minimum value which it would have were there no external disturbing causes. Encounters between the molecules tend to diminish H, and so to reduce the system to the normal condition, and the rate of diminution of H increases with the increase of the distur-bance. If there be an external cause always producing the disturbance at a constant rate, a state of steady motion will be reached in which the disturbance is diminished by encoun-ters as fast as it is increased by the operation of external conditions. We shall denote by $\dfrac{dH}{dt}$ the time-variation of H

due to encounters, and by $\dfrac{\partial H}{\partial t}$ its time-variation due to external causes. In steady motion

$$\frac{d H}{dt} + \frac{\partial H}{\partial t} = 0.$$

In like manner for any other function, as F, $\dfrac{dF}{dt}$ shall be the time-variation due to encounters, $\dfrac{\partial F}{\partial t}$ that due to external causes, and the condition for steady motion is

$$\frac{dF}{dt} + \frac{\partial F}{\partial t} = 0.$$

13. Let us consider the case of two sets of molecules, each subject to a small disturbance.

For the M set let

$$F(\omega) = N\left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hM\omega^2}(1 + X).$$

For the m set let

$$f(\psi) = n\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hm\psi^2}(1 + x).$$

Here N and n are the numbers of molecules per unit volume of the M and m sets respectively, and X and x represent the disturbances.

Let us form the spherical shells described about C, with radii R, r as in (6). Let PCp be any common diameter, and

$$\omega = OP, \quad \psi = Op.$$

Let X_P, x_p be the values of X and x at P and p respectively. In that case

$$M\omega^2 + m\psi^2 = (M + m)V^2 + MR^2 + mr^2$$

$$= (M + m)V^2 + \frac{Mm}{M + m}\rho^2$$

$$= (M + m)\left(V^2 + \frac{M}{m}R^2\right).$$

and

$$\overline{F'f'} - Ff = Nn\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \epsilon^{-h\left(\overline{M+m}V^2 + \frac{Mm}{M+m}\rho^2\right)}\{\overline{X+x} - (X_P + x_p)\},$$

where

$$\overline{X + x} = \frac{1}{4\pi}\iint (X_P + x_p)\, dS,$$

the integral being over the whole spherical surfaces, that is for all directions of $P'Cp'$.

Also

$$\log (Ff) = \log \{ F(OP) \cdot f(Op) \}$$

$$= -h\left(\overline{M+m}V^2 + \frac{Mm}{M+m}\rho^2\right) + X_P + x_p + \log\left(Nn\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\left(\frac{hm}{\pi}\right)^{\frac{3}{2}}\right).$$

And therefore

$$\iint dS \log (Ff)(\overline{F'f'} - Ff)$$

$$= Nn\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \epsilon^{-h\left(\overline{M+m}V^2 + \frac{Mm}{M+m}\rho^2\right)} \left\{ \overline{X+x} \iint (X+x)dS - \iint(X+x)^2 dS \right\}$$

$$= Nn\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \epsilon^{-h\left(\overline{M+m}V^2 + \frac{Mm}{M+m}\rho^2\right)} 4\pi\left\{ |\overline{X+x}|^2 - (\overline{X+x})^2| \right\},$$

the last factor being the square of the mean *minus* the mean of the square of $X_P + x_p$, for all directions of PCp.

Hence we can find $\dfrac{dH}{dt}$ in the form

$$\frac{dH}{dt} = 4\pi \frac{M+m}{m} Nn\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \int_0^\infty dV \cdot V^2 \int_0^\infty dR\pi s^2 R^3 \times$$

$$\times \epsilon^{-h\left(\overline{M+m}V^2 + \frac{Mm}{M+m}\rho^2\right)} \int_0^\pi d\alpha 2\pi \sin \alpha \left\{ |\overline{X+x}|^2 - (\overline{X+x})^2| \right\},$$

in which $\dfrac{M+m}{m}R$ is written for ρ.

EXAMPLES.

14. *Diffusion.*—Two reservoirs, A and B, are connected by a uniform horizontal tube. In A is a mixture of two gases, gas M and gas m, in certain proportions. In B is a mixture of the same two gases in different proportions. The temperature and pressure of the mixture are the same in either reservoir and at all points in the tube between them. Gas M is of greater density in A than in B.

Then a stream flows through the tube, of M from A to B, of m from B to A. If the proportions in which the gases are mixed in the reservoirs be maintained constant, as if for instance the reservoirs were of infinite extent, the stream becomes steady.

Let N be the number per unit of volume of molecules of gas M, n the number for gas m, at any point in the tube. By Avogadro's law $N + n$ is constant throughout, or taking the axis of the tube for that of x,

$$\frac{dN}{dx} = -\frac{dn}{dx}.$$

The stream velocity is assumed to be very small compared with the molecular velocity of mean square. The problem of diffusion is to find the stream velocity.

Take as an element of volume in the tube a cylinder of length δx, and whose base is unit area parallel to yz.

Let N be the number per unit of volume of molecules M at the left-hand face (towards A) of that cylinder. Then the number at its right-hand face is

$$N + \delta x \frac{dN}{dx}, \quad \text{that is } N - \delta x \frac{dn}{dx}.$$

The number of M molecules of the class $\lambda \mu \nu \omega^2 \, d\omega \, dS$ which enter the cylinder through its left-hand face in unit of time is

$$\lambda N \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hM\omega^2} \omega^3 d\omega \, dS.$$

The number of the same class which pass out of the cylinder through its right-hand-face in unit of time is

$$\lambda \left(N - \delta x \frac{dn}{dx}\right)\left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hM\omega^2} \omega^3 d\omega \, dS;$$

and therefore, but for encounters, the number of molecules M of the class $\lambda \mu \nu \omega^2 \, d\omega \, dS$ within our cylinder would be increased in unit of time by the quantity

$$\lambda \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \frac{dn}{dx} \delta x \, \epsilon^{-hM\omega^2} \omega^3 d\omega \, dS,$$

or the number per unit of volume would be increased by

$$\lambda \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \frac{dn}{dx} \epsilon^{-hM\omega^2} \omega^3 d\omega \, dS.$$

Therefore

$$\frac{\partial F}{\partial t} = \lambda \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \frac{dn}{dx} \epsilon^{-hM\omega^2} \omega.$$

This is a zonal harmonic function of the first order about the axis of x. In this case we shall assume

$$F = N \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \epsilon^{-hM\omega^2} \left\{ 1 + \lambda \phi(\omega^2) \right\},$$

where $\phi(\omega^2)$ is an undetermined function of ω. The disturbance is of the first order.

15. *Conduction of heat in a single gas.*—Let there be a horizontal tube, AB, filled with a single gas. Let the temperature be higher at A than at B, and be maintained constant at each of those points, and let the pressure be uniform throughout the tube, so that $\dfrac{N}{h} = P$, a constant, proportional to the pressure. With the same notation as in the last example, let us consider the molecules of the class $\lambda \mu \nu \omega^2 d\omega\, d\mathrm{S}$ which enter the elementary cylinder from the left in unit of time. Their number is, putting k for hm,

$$\lambda \mathrm{N}\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2}\omega^3 d\omega\, d\mathrm{S}.$$

The number of the same class which pass out of the elementary cylinder by its right-hand face per unit of time is

$$\lambda \mathrm{N}\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2}\omega^3 d\omega\, d\mathrm{S}.$$

$$+ \lambda \delta x \frac{d}{dx}\left\{ \mathrm{N}\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2}\right\} \omega^3 d\omega\, d\mathrm{S},$$

N and k being variable.

Therefore, but for encounters, the number of the class within our elementary cylinder would be increased in unit of time by

$$-\lambda \delta x \frac{d}{dx}\left(\mathrm{N}\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2}\right) \omega^3 d\omega\, d\mathrm{S},$$

or the number of the class per unit of volume would be increased in unit of time by

$$-\lambda \frac{d}{dx}\left(\mathrm{N}\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2}\right) \omega^3 d\omega\, d\mathrm{S}\ ;$$

that is by

$$\lambda \mathrm{P}\epsilon^{-k\omega^2}\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \omega^3 d\omega\, d\mathrm{S}\left(k\omega^2 - \frac{5}{2}\right)\frac{dk}{dx}.$$

This is positive or negative according as $k\omega^2 >$ or $< \dfrac{5}{2}$.

For high values of ω there is an increase, for low values a diminution. This increase or diminution is in steady motion compensated by encounters, because molecules with high velocities are on average moving more to the right than to the

left, and lose velocity in direction x by encounters. Here

$$\frac{\partial F}{\partial t} = \lambda P \left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega \left(k\omega^2 - \frac{5}{2}\right) \frac{dk}{dx}.$$

And we assume

$$F = N \left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \left(1 + \lambda \phi(\omega^2)\right),$$

where $\phi(\omega^2)$ is an undetermined function. The disturbance is of the first order.

16. *Viscosity of a single gas.*—A gas on either side of the plane of xz is uniform throughout as regards temperature and density. On the negative side of the plane $y = -a$ the gas has, and is constrained to maintain, a constant velocity, v, of simple translation in direction x. And on the positive side of the plane $y = +a$, a constant velocity $-v$ of simple translation in that direction. The problem is to find the quantity of x momentum which under those circumstances is carried across unit area of the plane of xz per unit of time in the positive direction by molecules crossing that plane. Take any two planes parallel to xz and distant δy from each other. Suppose for a moment that on the negative side of the negative plane the gas has a velocity, v, of simple translation in direction x. Then the number of the class

$$\lambda \, \mu \, v \, \omega^2 \, d\omega \, dS$$

per unit of volume is

$$N \left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^2 d\omega \, dS \{1 + 2\lambda k\omega v\}.$$

The number of this class which cross the negative plane in the positive direction per unit of area and time is

$$N \left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^3 d\omega \, dS \{\mu + 2\lambda \mu k\omega v\}.$$

The number of the same class that cross the positive plane in the positive direction per unit of area and of time is

$$N \left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^3 d\omega dS \left\{\mu + 2\lambda \mu k\omega \left(v + \delta y \frac{dv}{dy}\right)\right\}.$$

And, but for encounters, the class within the layer between the planes would gain in number per unit of volume and time by the quantity

$$-N \left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2} \omega^3 d\omega \, dS . \lambda \mu . 2k\omega \frac{dv}{dy}.$$

In steady motion the number of the class in question is diminished by encounters by the same quantity.

The motion of the gas is a motion of simple translation with velocity $v = -qy$ in direction x, where q is constant, combined with a disturbance of the second order symmetrical about the plane $x = y$. In this case we should assume

$$F = N\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-k\omega^2}\left(1 + \lambda\mu\phi(\omega^2)\right),$$

where $\phi(\omega^2)$ is an undetermined function, and

$$\frac{\partial F}{\partial t} = -N\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \epsilon^{-2k\omega^2}\lambda\mu \cdot 2k\omega^2\frac{dv}{dy}.$$

17. The complete solution of any problem of the kind would have to be found from the equation

$$\frac{dF}{dt} + \frac{\partial F}{\partial t} = 0,$$

expressing the steadiness of the motion for each class of molecules. It does not appear that in case of diffusion we can obtain a solution by assuming the two gases to have a motion of simple translation, one in one direction and the other in the opposite.

Relation of Diffusion &c. to Temperature.

Without obtaining a complete solution of any of these problems, we can by means of the equation

$$\frac{dH}{dt} + \frac{\partial H}{\partial t} = 0$$

determine the relation in which the solution, whatever it may be, stands to the absolute temperature of the system.

18. When the disturbance is of the first order the solution proposed is, using X to denote the disturbance as in (13),

$$X = \lambda\chi(h)\phi(hM\omega^2),$$

in which $\chi(h)$ is a function of h to be determined, and $\phi(hM\omega^2)$ is a function of $hM\omega^2$, containing only odd positive powers of $\omega\sqrt{hM}$, as for instance

$$\phi(hM\omega^2) = C_0\omega\sqrt{hM} + C_1(hM)^{\frac{3}{2}}\omega^3 + \&c.,$$

where the C's are numerical.

Similarly in dealing with two gases, we shall assume

$$x = \lambda'\chi(h)\phi'(hm\psi^2),$$

and ϕ' has similar form. With these values of X and x,

$$\iint X dS = \chi(h)\iint \lambda\phi(hM\omega^2)dS,$$

the integration being over the spherical surface, described about C, as in (6).

Now, if λ_c μ_c ν_c be direction-cosines of OC, and OP$=\omega$,

$$\lambda\omega = \lambda_c(V - R\cos E) + \sqrt{1-\lambda_c^2}\, R\sin E\cos\gamma,$$

where E is the angle OCP, and γ is the angle between the plane OCP and a fixed plane, and therefore the second term disappears when we form the integral

$$\iint dS\lambda\omega\frac{\phi(h M\omega^2)}{\omega}.$$

Also, since $\omega^2 = V^2 + R^2 - 2VR\cos E$, we may write, expressing Taylor's theorem,

$$\frac{\phi(h M\omega^2)}{\omega} = \epsilon^{-2VR\cos E\, p}\frac{\phi(h M\overline{V^2 + R^2})}{\sqrt{V^2 + R^2}},$$

where

$$p = \frac{d}{dV^2}.$$

Thus we obtain

$$\iint X dS = \lambda_c\chi(h)\int_0^\pi dE\, 2\pi\sin E(V - R\cos E)\epsilon^{-2VR\cos E\, p}\frac{\phi(h M\overline{V^2 + R^2})}{\sqrt{V^2 + R^2}}.$$

The integration according to E can now be effected in a series, and with the assumed form of $\phi(h M\omega^2)$ no negative powers of V or R will appear. $\iint x\, dS$ can be treated in the same way.

By an extension of this method we might form $\dfrac{dF_P}{dt}$ in a series of positive powers of ω, and we should then have theoretically sufficient data for determining the coefficients C_0, C_1, &c. in the expression for $\phi(h M\omega^2)$ by equating to zero the coefficients of powers of ω in the expression

$$\frac{dF_P}{dt} + \frac{\partial F_P}{\partial t} = 0.$$

In order to find $\chi(h)$ we resume the discussion of the equation

$$\frac{dH}{dt} + \frac{\partial H}{\partial t} = 0.$$

19. If in the expression

$$\left(\frac{h M}{\pi}\right)^{\frac{3}{2}}\left(\frac{h m}{\pi}\right)^{\frac{3}{2}}\int_0^\infty dV\, \epsilon^{-h\overline{M+m}V^2}V^2\int_0^\infty dR\, \epsilon^{-h\frac{M}{m}\overline{M+m}R^2}R^2\phi(h M\overline{V^2 + R^2})$$

all the integrations were effected, the result would be independent of h, whatever the form of ϕ might be. As we

may express it, the above function is, as a function of h, of zero dimensions. Therefore, since $X = \lambda\chi(h)\phi(hM\omega^2)$ &c., the expression

$$\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\left(\frac{hm}{\pi}\right)^{\frac{3}{2}}\int_0^\infty dV\epsilon^{-h\overline{M+m}V^2}V^2\int_0^\infty dR\epsilon^{-h\frac{M}{m}\overline{M+m}R^2}\pi s^2\rho$$

$$\times \int_0^\pi d\alpha 2\pi \sin \alpha \overline{X+x|^2}$$

must have, as a function of h, dimensions $\dfrac{(\chi(h))^2}{\sqrt{h}}$, the factor $\sqrt{h}$ appearing in the denominator on account of the introduction of $\pi s^2\rho$, or $\pi s^2 \dfrac{M+m}{m}R$, πs^2 being in the cases now considered independent of ρ.

In like manner the expression

$$\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\left(\frac{hm}{\pi}\right)^{\frac{3}{2}}\int_0^\infty dV\epsilon^{-h\overline{M+m}V^2}V^2\int_0^\infty dR\epsilon^{-h\frac{M}{m}\overline{M+m}R^2}R^2\pi s^2\frac{M+m}{m}R$$

$$\times\int_0^\pi d\alpha\, 2\pi \sin \alpha \iint \overline{(X+x)^2}dS$$

will, as a function of h, have dimensions $\dfrac{(\chi(h))^2}{\sqrt{h}}$.

And therefore $\dfrac{dH}{dt}$ (see (13)) will, as a function of h, have dimensions $\dfrac{(\chi(h))^2}{\sqrt{h}}$.

20.   We have next to treat $\dfrac{\partial H}{\partial t}$ in the same way. The result will be different for diffusion and for conduction of heat. In diffusion

$$\frac{\partial F}{\partial t} = \lambda\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\epsilon^{-hM\omega^2}\omega\frac{dn}{dx},$$

$$\frac{\partial f}{\partial t} = \lambda'\left(\frac{hm}{\pi}\right)^{\frac{3}{2}}\epsilon^{-hm\psi^2}\psi\frac{dn}{dx}.$$

Also

$$\log F = \log\left\{N\left(\frac{hM}{\pi}\right)^{\frac{3}{2}}\right\} - hM\omega^2 + \lambda\chi(h)\phi(hM\omega^2),$$

$$\log f = \log\left\{n\left(\frac{hm}{\pi}\right)^{\frac{3}{2}}\right\} - hm\psi^2 + \lambda'\chi(h)\phi'(hm\psi^2).$$

Now if we form

$$\frac{\partial H}{\partial t} = \iiint dx\, dy\, dz \left\{ \frac{\partial F}{\partial t} \log F + \frac{\partial f}{\partial t} \log f \right\},$$

the terms containing λ or λ' in the first degree disappear, and so

$$\frac{\partial H}{\partial t} = \chi(h) \frac{dn}{dx} \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \iiint dx\, dy\, dz\, \lambda^2 \epsilon^{-hM\omega^2} \omega \phi(hM\omega^2)$$

$$+ \chi(h) \frac{dn}{dx} \left(\frac{hm}{\pi}\right)^{\frac{3}{2}} \iiint dx'dy'dz'\lambda'^2 \epsilon^{-hm\psi^2} \psi \phi'(hm\psi^2),$$

where

$$\omega^2 = x^2 + y^2 + z^2,$$

$$\psi^2 = x'^2 + y'^2 + z'^2.$$

As a function of h, this expression has dimensions $\dfrac{\chi(h)}{\sqrt{h}}$, $\sqrt{h}$ appearing in the denominator in consequence of the factors ω and ψ.

21. Now by virtue of the equation

$$\frac{dH}{dt} + \frac{\partial H}{\partial t} = 0,$$

$\dfrac{dH}{dt}$ and $\dfrac{\partial H}{\partial t}$ will, as functions of h, have the same dimensions. And therefore in diffusion $\dfrac{(\chi(h))^2}{\sqrt{h}}$ has the same dimensions as $\dfrac{\chi(h)}{\sqrt{h}}$, or $\chi(h)$ is a constant, independent of h.

But the stream of gas M through the tube, that is the *rate of diffusion* for given space variation of density, is

$$N \left(\frac{hM}{\pi}\right)^{\frac{3}{2}} \int_0^\infty d\omega \epsilon^{-hM\omega^2} \omega^2 \omega \chi(h) \phi(hM\omega^2),$$

and therefore varies as $\dfrac{1}{\sqrt{h}}$, or as the square root of the absolute temperature. This is a consequence of the assumption that πs^2 is independent of R, and therefore holds only for elastic spheres.

22. We will now treat conduction of heat in the same way. Since the disturbance is of the first order, we shall as before assume for the solution $\lambda\chi(k)\phi(k\omega^2)$, k being written for hm. Then $\dfrac{dH}{dt}$ will, as a function of k, have the same dimensions as before, viz.

$$\frac{(\chi(k))^2}{\sqrt{k}}.$$

In forming $\dfrac{\partial H}{\partial t}$ we have now the factor $P\omega\dfrac{dk}{dx}$, instead of $\omega\dfrac{du}{dx}$ as in diffusion. Also $k=\dfrac{3}{2\tau}$, if τ be the absolute temperature and

$$\frac{dk}{dx} = -\frac{3}{2\tau^2}\frac{d\tau}{dx} = -\frac{2}{3}k^2\frac{d\tau}{dx}.$$

We have now to compare two systems in each of which P is constant throughout the tube, but has not necessarily the same constant value in both systems, and k has different values in the two systems.

We may make

(1) P the same, that is $\dfrac{N}{k}$ the same, in both systems.

(2) N the same in both systems.

In case (1) $\dfrac{\partial H}{\partial t}$, as a function of k, has dimensions $k^2\,\dfrac{\chi(k)}{\sqrt{k}}$.

In case (2) it has dimensions $k\dfrac{\chi(k)}{\sqrt{k}}$.

Now the flow of heat per unit of time through a section of the tube, that is the *rate of conduction*, is

$$N\left(\frac{k}{\pi}\right)^{\frac{3}{2}}\int_0^\infty d\omega\epsilon^{-k\omega^2}\omega^4\chi(k)\,\omega\phi(k\omega^2),$$

and therefore varies

in case (1) as $\sqrt{k}$, or as $\dfrac{1}{\sqrt{\tau}}$,

in case (2) as $\dfrac{1}{\sqrt{k}}$, or as $\sqrt{\tau}$.

We have then the following result. Assuming that the molecules may be treated, as regards their mutual encounters, as elastic spheres, the *rate of conduction of heat* between points of equal pressure but unequal temperature varies, as between two systems with the same pressure, inversely, and as between two systems with the same density directly, as the square root of the absolute temperature.

23. When the disturbance is of the second order, as in the problem of viscosity, the mean value of $\lambda\mu$, given E, is (see figure, § 6)

$$\frac{3}{2}\cos^2 \text{COP} - \frac{1}{2}, \quad \text{or} \quad \frac{3}{2}\left(\frac{V-R\cos E}{\omega}\right)^2 - \frac{1}{2}.$$

In order in this case to prevent the appearance of negative

powers of V and R in the differentiation, we should assume $\phi(k\omega^2)$ to consist of even powers of $\omega\sqrt{k}$.

As the result when all the integrations are effected, $\dfrac{d\mathrm{H}}{dt}$ will be a function of k of dimension $\dfrac{(\chi(k))^2}{\sqrt{k}}$. And $\dfrac{\partial \mathrm{H}}{\partial t}$ of dimensions $\chi(k)$.

So we should obtain

$$\frac{(\chi(k))^2}{\sqrt{k}} = \chi(k) \text{ or } \chi(k) = \sqrt{k}.$$

But the excess of momentum carried in the positive direction through unit area of the plane of xz, on which the viscosity depends, varies as

$$\left(\frac{k}{\pi}\right)^{\frac{3}{2}} \int_0^\infty d\omega \epsilon^{-k\omega^2} \omega^4 \chi(k)\phi(k\omega^2) \; ;$$

that is varies as $\dfrac{1}{\sqrt{k}}$, or as the square root of the absolute temperature.

24. The above results are obtained on the hypothesis that πs^2 is independent of ρ or R, and therefore only on the hypothesis that the molecules may be treated as elastic spheres. On any other hypothesis πs^2 is a function of R, and as such will affect the integration according to R, and the degree in h or k which $\dfrac{d\mathrm{H}}{dt}$ assumes as the result of that integration. For instance, if the molecules be centres of force repelling one another with a force varying as $\dfrac{1}{\rho^5}$, $\pi s^2 \propto \dfrac{1}{\rho}$. In this case, in dealing with diffusion $\dfrac{d\mathrm{H}}{dt}$ will be proportional to $(\chi(h))^2$, instead of $\dfrac{(\chi(h))^2}{\sqrt{h}}$ as in the case of elastic spheres, and the rate of diffusion would vary as $\dfrac{1}{h}$, that is as the absolute temperature, instead of as the square root of the absolute temperature.

If the experiments from which it appeared that the rate of diffusion varies as the square root of the temperature can be relied on as giving exact, and not merely approximate, results, they afford ground for the inference that molecules of gases may, as regards their mutual encounters, be treated as elastic spheres.