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In all these sets of results the differences between the values in the third and fourth columns respectively are also within the limits of experimental error.

Example III. The decomposition of ammonium nitrite in aqueous solution into nitrogen and water, as being in accordance with monomolecular law, is also analogous to the case cited above, but at present difficulties have been experienced in fixing the conditions for obtaining a sufficient number of observations to apply the above equation. It has only been found possible to obtain at most two or three observations unless the volume of gas collected in each single observation is so small that the experimental error is thereby greatly increased.

Other examples of the above phenomena that have been observed are the decomposition of oxalic acid and of potassium ferrocyanide by concentrated sulphuric acid, but as regards both of these the formation of more than one gas within the solution renders the problem more complicated. The rate of evolution of oxygen from solutions of peroxides would probably present a similar and simple case, and others might also be cited, but in this communication it is only desired to point out a possible line of investigation upon the earlier stages of chemical reaction, which appear to be too often dismissed as inconsequent.

XXXV. *On the Vibrations set up in Molecules by Collisions.*

By J. H. JEANS, M.A., Isaac Newton Student and Fellow of Trinity College, Cambridge.*

§ 1. A STEEL ball dropped on to a rigid steel plate will rebound perhaps half a dozen times before its energy is appreciably lessened; this is because of the great elasticity of steel. If the kinetic theory of gases is true, a system of molecules must rebound from one another and from rigid walls many billions of times before the total energy is appreciably lessened. The aim of the present paper is to show that, in so far as the data available enable us to judge, molecules will possess sufficient elasticity for this to occur.

§ 2. Let us suppose that a molecule possesses, in addition to its motions of translation and rotation, small vibratory motions of which the oscillations are, in the cases we have to consider, so small as to be isochronous. Then the kinetic and potential

* Communicated by the Author.

energies of these vibrations will be expressible in the forms

$$2T = \alpha_1 \dot{\phi}_1^2 + \alpha_2 \dot{\phi}_2^2 + \dots \quad (1)$$

$$2V = \alpha_1 p_1^2 \phi_1^2 + \alpha_2 p_2^2 \phi_2^2 + \dots \quad (2)$$

where p_1, p_2, \dots are the frequencies of vibration.

We call one molecule A, and suppose that a second molecule B approaches A, has its velocity altered in direction by the forces exerted upon it by A, and finally recedes from A. Let the instant at which the force between these molecules begins to be appreciable be taken to be $t=0$, and the instant at which they are finally clear of each other's sphere of action be $t=\tau$. At any instant during the encounter let the forces exerted by B upon A be derivable from a force-function

$$V_1 \delta \phi_1 + V_2 \delta \phi_2 + \dots \quad (3)$$

Then the equations of motion are of the form (dropping suffixes)

$$\alpha \ddot{\phi} + \alpha p^2 \phi = V. \quad (4)$$

§ 3. Before $t=0$ the molecule would be describing a free vibration, say

$$\phi = C \cos pt + D \sin pt. \quad (5)$$

The impulse Vdt acting from $t=0$ to $t=dt$ sets up an additional free vibration of initial displacement zero and velocity Vdt/α ; the displacement of this additional vibration at any subsequent time is therefore $Vdt \sin pt/\alpha p$. By compounding all these vibrations with the original vibration (5), we obtain for the displacement at any instant subsequent to $t=\tau$, the well-known solution

$$\phi = C \cos pt + D \sin pt + \frac{1}{\alpha p} \int_{t'=0}^{t'=t} V_{t=t'} \sin p(t-t') dt'. \quad (6)$$

This may be written

$$\phi = (C - Y) \cos pt + (D + X) \sin pt, \quad (7)$$

where X and Y are obtained by equating real and imaginary parts in

$$X + iY = \frac{1}{\alpha p} \int_0^\tau V e^{ipt} dt. \quad (8)$$

§ 4. The square of the amplitude of vibration (5) is $C^2 + D^2$; that of (7) is $(C - X)^2 + (D + Y)^2$, so that the increase caused by collision is

$$X^2 + Y^2 - 2(CX - DY). \quad (9)$$

Now our final problem will be to find this quantity averaged over all the molecules and collisions in the gas. It is at once obvious that the last term vanishes on the average. Hence a correct result is obtained by ignoring the free vibration (5), and supposing that the collision simply sets up a vibration of amplitude $\sqrt{X^2 + Y^2}$, and therefore of energy $\frac{1}{2}\alpha p^2(X^2 + Y^2)$.

§ 5. In evaluating X and Y from equation (8), we shall suppose V divided into two parts, and shall consider at present only the part which is contributed by the motion of the centre of gravity of molecule B. A second part in V contributed by the rotation and small vibrations of the molecule B will be discussed later (§ 10).

If we integrate equation (8) by parts we get, since V vanishes at both limits,

$$X + iY = -\frac{1}{\alpha p^2} \int_0^\tau \frac{dV}{dt} e^{ipt} dt. \quad . \quad . \quad (10)$$

Not only V but all its differential coefficients must vanish at both limits, so that we may repeat the integration by parts indefinitely; after n integrations we obtain

$$X + iY = \frac{(-1)^n}{\alpha p (ip)^n} \int_0^\tau \frac{d^n V}{dt^n} e^{ipt} dt. \quad . \quad . \quad (11)$$

The value of $d^n V/dt^n$ will be comparable with unity provided that the unit of time selected is comparable with the scale of time-variation of V , and that n is not very great. Hence, if p is great when measured in these units, we see, from the presence of the factor $p^{-(n+1)}$ in (11), that X and Y will be very small.

Now for normal air the probable relative velocity of two molecules is of the order of 10^5 cm. per sec. From experiments on the viscosity &c. of gases, it is found that the distance apart of the centres of two molecules during an encounter—the distance which is usually described as the “diameter” of a molecule—is about 10^{-8} cm. The appropriate unit of time for that part of V which we are now discussing is therefore 10^{-13} sec. For p the value varies, so far as we know, from about 2×10^{15} per second in the case of ultra-red light to 8×10^{15} per second in the case of ultra-violet light. This gives for the value of p in the present units a range from 200 to 800. Since there is practically no limit to the value of n in (11), the factor $p^{-(n+1)}$ may be made very small. From this we conclude that practically no vibrations are set up in molecule A by the translational motion of

B, so long as the relative velocity is comparable with the average in normal air.

§ 6. A more convincing proof of the smallness of the integral in (8) is supplied by Cauchy's theorem. Imagine the function V evaluated for all values of t real and complex, then we have

$$\int V e^{ipt} dt = 2i\pi \Sigma R, \quad (12)$$

where the integral on the left-hand is taken from $t = -\infty$ to $t = +\infty$ along the real axis of t , and then back from $t = +\infty$ to $t = -\infty$ along a semicircle of infinite radius, having $t=0$ for centre. On the right-hand ΣR is the sum of the residues of the function $V e^{ipt}$ inside this semicircle.

The first part of the integral is $X + iY$. The second may be written

$$L \int_{R=\infty}^t V e^{ipR(\cos \theta + i \sin \theta)} R e^{i\theta} i d\theta,$$

and the integrand, in general, vanishes through the occurrence of the factor $e^{-pR \sin \theta}$, except near $\theta=0$, $\theta=\pi$, and here the contributions to the integral vanish on account of the factor $V d\theta$. Lastly, if the function V has an infinity occurring at $t=a+i\beta$, with residue u , ΣR may be written $\Sigma e^{ip(\alpha+i\beta)u}$, the summation extending over all infinities for which β is positive. Equation (12) accordingly becomes

$$X + iY = 2i\pi \Sigma e^{-p\beta} (\cos p\alpha + i \sin p\alpha) u. . . (13)$$

By hypothesis $p\beta$ is large, and it is also positive. Thus the smallness of $X + iY$ is guaranteed by the occurrence of the factor $e^{-p\beta}$.

§ 7. To take a definite example, suppose

$$V = \frac{1}{a^2 + t^2}$$

$$X + iY = \frac{1}{\alpha p} \int_{-\infty}^{+\infty} \frac{e^{ipt}}{a^2 + t^2} dt = \frac{\pi}{\alpha p} e^{-ap},$$

and the energy of vibration $\frac{1}{2} \alpha p^2 (X^2 + Y^2)$, is

$$\frac{\pi^2}{2\alpha} e^{-2ap}. \quad (14)$$

The appropriate unit of time in this case is of course a . If p in these units has a value 200 we see from (14) that the "elasticity" of the molecules has introduced a factor e^{-400} .

To take a second example, which is of interest as being a case of failure of the general proof of § 6, suppose that

$$V = e^{-\kappa t^2}$$

$$X + iY = \frac{1}{\alpha p} \int_{-\infty}^{+\infty} e^{ipt - \kappa t^2} dt = \frac{1}{\alpha p} \sqrt{\frac{\pi}{\kappa}} e^{-\frac{p^2}{4\kappa}}.$$

In this case the "elasticity" is represented in the energy of vibration by a factor $e^{-p^2/2\kappa}$. The appropriate unit of time is $\kappa^{-1/2}$, and if p is, in these units, represented by 200, $p^2/2\kappa = 20,000$, and the energy gained by the vibrations at collision is reduced by the "elasticity" to $e^{-20,000}$ of what it would otherwise have been.

§ 8. These two instances have been selected at random, but it is obvious enough, from the general theorems of §§ 5 and 6, that any other form for V would give a very similar result. The smaller of the two factors introduced by the "elasticity" of the molecule has been e^{-400} . This means that if the molecules were all moving with average velocity the number of collisions required to dissipate a given fraction of the energy would be increased by the "elasticity" in a ratio of about $e^{400} : 1$. In other words, the "elasticity" could easily make the difference between dissipation of energy in a fraction of a second and dissipation in billions of years.

§ 9. It has, however, been seen (§ 5) that appreciable vibrations will be set up by a collision in which the relative velocity is comparable with 2×10^7 cms. per second. We must therefore examine the frequency of such collisions in gases at normal temperatures.

The number of collisions in which the molecules have velocities between c and $c + dc$, c' and $c' + dc'$ inclined at an angle between ϕ and $\phi + d\phi$ is proportional to *

$$e^{-\frac{1}{2}hm(c^2 + c'^2)} c^2 c'^2 g \sin \phi d\phi dc dc', \quad \dots \quad (15)$$

where g is the relative velocity, given by

$$g^2 = c^2 + c'^2 - 2cc' \cos \phi. \quad \dots \quad (16)$$

Let us suppose that of the velocities c, c' the latter is the greater, and write

$$u = c' - c, \quad v = c' + c.$$

From equation (16) it follows that g must lie between u and v . By differentiation, keeping u, v and therefore also c, c' constant, we have $gdg = cc' \sin \phi d\phi$. Expression (15) is now proportional to

$$e^{-\frac{1}{2}hm(u^2 + v^2)} (v^2 - u^2) g^2 dg du dv.$$

* Boltzmann, *Gasttheorie*, i. p. 64, equation 61.

To obtain the number of collisions having values of g greater than G , this has to be integrated through all possible positive values of g, u, v , subject to

$$u < g < v, \quad g > G.$$

Integration with respect to g gives

$$\frac{1}{3} e^{-\frac{1}{2}hm(u^2+v^2)} (v^3-u^3) [g^3] du dv, \quad . \quad . \quad . \quad (17)$$

in which

$$\begin{aligned} [g^3] &= 0 \text{ when } v < G, \\ [g^3] &= v^3 - G^3 \text{ when } v > G, u < G, \\ [g^3] &= v^3 - u^3 \text{ when } u > G. \end{aligned}$$

On integrating (17) with respect to u, v we shall obtain the number required. When G is very great the only integrands which are of importance are those for which $u^2 + v^2$ is in the neighbourhood of its least possible value G^2 , i. e. those in the neighbourhood of $u=0, v=G$. In (17) we may therefore replace (v^3-u^3) by G^3 , and $[g^3]$ by v^3-G^3 , and therefore by $3G^2(v-G)$. We may also suppose the integration to extend from $v=G$ to $v=\infty$, and from $u=0$ to $u=\infty$. The integral is therefore

$$G^4 \int_0^\infty e^{-\frac{1}{2}hmu^2} du \int_G^\infty e^{-\frac{1}{2}hmv^2} (v-G) dv,$$

of which the value when G is large is found to be

$$\sqrt{\frac{\pi}{2h^5m^5}} G^3 e^{-\frac{1}{2}hmG^2},$$

in which the last factor is obviously of preponderating importance.

For air under normal conditions we have

$$hm = 3/2\bar{c}^2 = 6 \times 10^{-10}$$

approximately. The value of G must, as we have seen, be comparable with 2×10^7 . If we actually take this as the lowest value for which the vibrations are appreciable, we get $hmG^2 = 240,000$ and

$$e^{-\frac{1}{2}hmG^2} = e^{-120,000}.$$

If we take half the foregoing value for G ,

$$e^{-\frac{1}{2}hmG^2} = e^{-30,000},$$

so that the dissipation of energy takes place $e^{90,000}$ times more slowly in the former case than in the latter. If G were comparable with the mean velocity in the gas, the energy of the gas would probably be reduced to half its value in a

fraction of a second, but the figures we have obtained show that under the actual conditions it is quite possible for the energy to remain appreciably constant throughout unthinkable ages.

§ 10. We now discuss the vibrations set up in A by the rotation and small vibrations of molecule B. If the molecule is rotating with angular velocity ω , and vibrating with frequency q , there will be terms in the force exerted by this molecule of frequencies *

$$\omega, q, q \pm \omega, q \pm 2\omega. \dots \dots \dots (18)$$

Any one of these frequencies, say p' , will give rise to a term in V (equation 8) of the form

$$V_0 \cos p't + W_0 \sin p't,$$

where V_0, W_0 vary with the time as slowly as did the former V . The corresponding part of $X+iY$ may, from equation (8), be written in the form

$$\frac{1}{2\alpha p} \int_0^\tau \{V_0(e^{i(p+p')t} + e^{i(p-p')t}) - iW_0(e^{i(p+p')t} - e^{i(p-p')t})\} dt.$$

Each term can be treated in the same manner as before, and can be shown to be small, except when p is very nearly equal to p' ; *i. e.* when p is very nearly equal to one of the values given in (18).

Now ω varies from molecule to molecule, the most probable value being of the order of 10^{14} †. It therefore appears that $p-\omega, p+q-\omega$, &c. will be very small only for a very small fraction of the molecules, and obviously even when this is so, the vibration set up will be very small. Thus perceptible vibrations in A will in general only be excited by vibrations of the same period in B, *i. e.* when $p=q$. Physically speaking the mechanism of the transfer of energy is found in the "absorption" of light-waves. It seems unnecessary to bring forward calculations to show that this is small.

§ 11. If E is the mean-energy of translation of the molecules of a gas, F that of a single vibration, the equation expressing the rate of change in F is

$$\frac{dF}{dt} = -\epsilon F + \phi(E)F + f(E), \dots \dots (19)$$

where $-\epsilon F$ represents dissipation into the æther, $\phi(E)F$ represents the amount regained by "absorption," and $f(E)$ is the gain to F through collisions, which we have been

* "The Mechanism of Radiation," Phil. Mag. [6] ii. p. 242.

† *L. c.* p. 424.

estimating numerically. The gas assumes an approximately steady state*, given by $dF/dt=0$, or

$$F = \frac{f(E)}{\epsilon - \phi(E)} \cdot \cdot \cdot \cdot \cdot \quad (20)$$

Here $\epsilon - \phi(E)$ must be positive for physical reasons, and $f(E)$ has been seen to be very small. The whole question at this point fits on to the theory which I have attempted to develop in earlier papers, especially in that just referred to.

Collision of a Molecule with a Free Ion.

§ 12. If the body B is not a molecule but a free ion, two changes must be made.

Firstly, since the ion is of less mass than a molecule, its probable velocity will be greater. There are about 700 ions in the hydrogen atom, and therefore about 1400 in the molecule, so that the most probable value for the velocity of an ion at normal temperatures will be about $\sqrt{1400}$ times that for the hydrogen molecule, and therefore about 7×10^6 cms. per sec. This kinetic theory velocity is of course quite distinct from the "velocity of diffusion" under an electric force which is capable of direct measurement: it is probably more analogous to the velocity of the Becquerel rays.

Secondly, as the ion moves with greater velocity than the molecule, it will approach to within a shorter distance of the molecule A. Instead of 10^{-8} cm., the value found from kinetic theory experiments for the closest approach of two molecules, we must use 10^{-9} cm., the value found by Townsend, Rutherford and others from ionization experiments for the closest approach of ions and molecules.

The ratio of these two quantities— 7×10^6 cms. per sec. and 10^{-9} cm.—gives $(7 \times 10^{15})^{-1}$ second as the appropriate unit of time when discussing collisions between ions and molecules. In these units the frequency of vibration of the molecules is comparable with unity, so that appreciable vibrations will be set up by collisions with ions, and these vibrations may occur in all parts of the spectrum. The actual number 7×10^{15} might suggest that violet light would predominate, but the calculation is too rough for any stress to be laid on this result.

§ 13. To sum up briefly, we may say that the "elasticity" of molecules has been found to be amply sufficient to resist the slow attacks of other molecules, but not sufficient to resist the faster attacks of free ions.

* "The Distribution of Molecular Energy," Phil. Trans. cxcvi. p. 397.