Dissociation under a Temperature Gradient. By P. A. M. DIRAC, St John's College. (Communicated by Mr R. H. FOWLER, Trinity College.)

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If a gas, each of whose molecules is capable of dissociating into two similar molecules, be kept at a constant temperature, it would attain an equilibrium state in which the rate at which double molecules dissociate is equal to the rate at which they are formed by recombination of single molecules, there being a different equilibrium state for each different temperature. If, now, the gas be subjected to a temperature gradient, the concentrations necessary for equilibrium would be different at different points, so there would be diffusion between the two kinds of molecules, a steady state being attained when the rate of diffusion of double molecules into any region is equal to their excess rate of decomposition over their rate of formation within that region.

We shall consider the case of a tube of the gas of unit section, closed at each end, the ends being maintained at different temperatures. There will be a continuous flow of double molecules from the cold end to the hot end, where they dissociate and flow back to the cold end. Since two single molecules possess more energy than a double one, these flows will cause a transfer of energy across the central sections of the tube in addition to that transferred by ordinary thermal conduction. So if the sides of the tube are non-conducting, there must be a greater temperature gradient at the ends of the tube than in the middle, in order that the same amount of energy may cross each section of the tube. Also, at the hot end double molecules dissociate more rapidly than they are formed, so that there must be an excess in the concentration of the double molecules here over their concentration when in equilibrium at the same temperature with no temperature gradient. Similarly there is a deficiency of double molecules at the cold end.

Hence if observations could be made of the concentrations or temperature gradient at either end, the 'velocity' of dissociation and recombination could be calculated, in terms of the other physical constants of the gas.

§ 1. *Equations for the Steady State.*

Let z be the co-ordinate of a point along the tube, T the temperature, and ν_1 and ν_2 the numbers per unit volume of single and double molecules at that point.

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The pressure must be constant all along the tube. This gives, assuming the ideal gas laws to hold,

$$(\nu_1 + \nu_2)\, T = \text{constant}.$$

Let μ_1 and μ_2 be the numbers per unit volume of single and double molecules when in equilibrium at the same temperature and pressure with no temperature gradient. Then

$$(\mu_1 + \mu_2)\, T = \text{same constant},$$

so that

$$\nu_1 = \mu_1 + \sigma, \quad \nu_2 = \mu_2 - \sigma \qquad \ldots\ldots\text{(i)},$$

where σ is a measure of the difference in the state of the gas caused by the temperature gradient.

The total mass crossing any section of the tube is zero. This gives

$$\nu_1 U_1 + 2\nu_2 U_2 = 0 \qquad \ldots\ldots\text{(ii)},$$

where U_1 and U_2 are the mean z components of the velocities of single and double molecules.

The total energy crossing a section of the tube is the same all the way along the tube. Thermal conduction will cause a transfer of energy across any section at the rate $-\kappa \dfrac{dT}{dz}$, where κ is the thermal conductivity at that section. In addition, there is an excess of $U_1\nu_1$ single molecules crossing the section and returning as double molecules. This results in a transfer of energy across the section at the rate $\frac{1}{2}kU_1\nu_1$, where k is the heat of dissociation per double molecule (kinetic energy as well as potential). We therefore get the equation

$$-\kappa \frac{dT}{dz} + \tfrac{1}{2}kU_1\nu_1 = A \qquad \ldots\ldots\text{(iii)},$$

where A is the total rate of flow of energy along the tube.

For ordinary diffusion with D as diffusion coefficient, we have the equations

$$U_1\nu_1 = -D\frac{d\nu_1}{dz}, \quad U_2\nu_2 = -D\frac{d\nu_2}{dz} = D\frac{d\nu_1}{dz},$$

$$U_1 - U_2 = -D\left(\frac{1}{\nu_1}\frac{d\nu_1}{dz} - \frac{1}{\nu_2}\frac{d\nu_2}{dz}\right) = -D\frac{d}{dz}\log\frac{\nu_1}{\nu_2}.$$

The first two of these equations are true only when the total number of molecules crossing any section is zero. When this condition is not satisfied, as in the present case, the only equation given by the laws of diffusion is the third one, which involves only relative velocities. If there is a temperature gradient, this equation becomes

$$U_1 - U_2 = -D\frac{d}{dz}\log\frac{\nu_1}{\nu_2} + D'\frac{d}{dz}\log T \qquad \ldots\ldots\text{(iv)},$$

where D' is related to the thermal diffusion coefficient.

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The excess rate of recombination of single molecules over their rate of formation per unit volume at a given temperature, will be proportional to σ if σ is small. This means that if a small part of the gas were isolated, it would tend to its equilibrium state according to the law $\frac{d\sigma}{dt} = -H\sigma$, or $\sigma \propto \exp(-Ht)$, where H is a constant for any given temperature, and is a measure of the velocity of dissociation and recombination. This excess must be balanced by the excess number of single molecules flowing into unit volume by diffusion, so that

$$H\sigma = -\frac{d}{dz}(U_1\nu_1) \qquad \text{.....(v).}$$

We thus have five equations for the five unknown variables ν_1, ν_2, U_1, U_2, T. The coefficients κ, D and D' are functions of the temperature and of σ, but as we are assuming σ is small, we may take for these coefficients their values when σ is zero, so that they are functions of T only. H and k are also functions of T only.

From (i) $$\log\frac{\nu_1}{\nu_2} = \log\frac{\mu_1}{\mu_2} + \log\left(1+\frac{\sigma}{\mu_1}\right) - \log\left(1-\frac{\sigma}{\mu_2}\right)$$

$$= \log\frac{\mu_1}{\mu_2} + \sigma',$$

where $$\sigma' = \left(\frac{1}{\mu_1} + \frac{1}{\mu_2}\right)\sigma,$$

neglecting σ^2.

Van 't Hoff's isochore gives

$$\frac{2}{\mu_1}\frac{d\mu_1}{dT} - \frac{1}{\mu_2}\frac{d\mu_2}{dT} = \frac{d}{dT}\log\frac{\mu_1^2}{\mu_2} = \frac{k}{RT^2} \qquad \text{.....(vi),}$$

R being Boltzmann's gas constant.

From the equation $(\mu_1 + \mu_2)T = \text{constant}$, we have

$$\frac{1}{\mu_1+\mu_2}\left(\frac{d\mu_1}{dT} + \frac{d\mu_2}{dT}\right) = -\frac{1}{T}.$$

Subtracting this equation from (vi) we find that

$$\frac{\mu_1+2\mu_2}{\mu_1+\mu_2}\left(\frac{1}{\mu_1}\frac{d\mu_1}{dT} - \frac{1}{\mu_2}\frac{d\mu_2}{dT}\right) = \frac{k}{RT^2} + \frac{1}{T},$$

or $$\frac{d}{dT}\log\frac{\mu_1}{\mu_2} = \frac{\mu_1+\mu_2}{\mu_1+2\mu_2}\left(\frac{k}{RT^2} + \frac{1}{T}\right).$$

Equation (iv) now becomes

$$U_1 - U_2 = -D\frac{d}{dz}\log\frac{\mu_1}{\mu_2} + D'\frac{d}{dz}\log T - D\frac{d\sigma'}{dz}$$

$$= -D\frac{\mu_1+\mu_2}{\mu_1+2\mu_2}\left(\frac{k}{RT^2} + \frac{1}{T}\right)\frac{dT}{dz} + \frac{D'}{T}\frac{dT}{dz} - D\frac{d\sigma'}{dz}.$$

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Eliminating U_2 by means of (ii),

$$U_1\left(1+\frac{\nu_1}{2\nu_2}\right)=-\left[D\frac{\mu_1+\mu_2}{\mu_1+2\mu_2}\left(\frac{k}{RT^2}+\frac{1}{T}\right)-\frac{D'}{T}\right]\frac{dT}{dz}-D\frac{d\sigma'}{dz}\quad\text{...(vii).}$$

Substituting this value for U_1 in (iii),

$$A=-\kappa\frac{dT}{dz}-\frac{\nu_1\nu_2 k}{\nu_1+2\nu_2}\left\{\left[D\frac{\mu_1+\mu_2}{\mu_1+2\mu_2}\left(\frac{k}{RT^2}+\frac{1}{T}\right)-\frac{D'}{T}\right]\frac{dT}{dz}+D\frac{d\sigma'}{dz}\right\}.$$

The ν's may be replaced by the corresponding μ's in this equation without affecting its order of accuracy. This gives

$$A=-\kappa'\frac{dT}{dz}-\frac{\mu_1\mu_2}{\mu_1+2\mu_2}kD\frac{d\sigma'}{dz}\qquad\text{.....(viii),}$$

where $$\kappa'=\kappa+\frac{\mu_1\mu_2 k}{\mu_1+2\mu_2}\left[D\frac{\mu_1+\mu_2}{\mu_1+2\mu_2}\left(\frac{k}{RT^2}+\frac{1}{T}\right)-\frac{D'}{T}\right].$$

κ' may be called the apparent thermal conductivity of the gas, since $\frac{d\sigma'}{dz}$ is negligible throughout most of the length of the tube, so that κ' determines the amount of heat flowing along the tube per unit temperature gradient.

From (iii) and (v)

$$-\frac{d}{dz}\left(\frac{2A}{k}+\frac{2\kappa}{k}\frac{dT}{dz}\right)=H\sigma=\frac{\mu_1\mu_2}{\mu_1+\mu_2}H\sigma'\qquad\text{.....(ix).}$$

We now have two equations for the two unknowns T and σ'. To obtain an approximate solution for an end of the tube, we may give to the coefficients κ, κ', μ_1, μ_2, k, D and H their constant values at the temperature of the end.

Equations (viii) and (ix) now reduce to

$$\sigma'=-\frac{\mu_1+\mu_2}{\mu_1\mu_2}\frac{2\kappa}{kH}\frac{d^2T}{dz^2}$$

$$=\frac{\mu_1+\mu_2}{\mu_1+2\mu_2}\frac{2\kappa D}{\kappa' H}\frac{d^2\sigma'}{dz^2},$$

or $$\frac{d^2\sigma'}{dz^2}=\beta^2\sigma',$$

where $$\beta=\sqrt{\frac{\mu_1+2\mu_2}{\mu_1+\mu_2}\frac{\kappa' H}{2\kappa D}}.$$

This gives $$\sigma'=Be^{\pm\beta(z-z_0)},$$

where z_0 is the co-ordinate of the end of the tube considered, and the + or − sign must be chosen so as to make σ very small in the middle of the tube.

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From (viii) $$\frac{dT}{dz} = -\frac{A}{\kappa'} - \frac{\mu_1\mu_2}{\mu_1+2\mu_2}\frac{kD}{\kappa'}\frac{d\sigma'}{dz},$$

whence $$T = -\frac{A}{\kappa'}z - \frac{\mu_1\mu_2}{\mu_1+2\mu_2}\frac{kD}{\kappa'}Be^{\pm\beta(z-z_0)} + \text{constant}.$$

The constant of integration B can be determined from the terminal condition that $U_1 = U_2 = 0$ when $z = z_0$. Using (iii) and (vii) we get for the end of the tube

$$-\frac{dT}{dz} = \frac{A}{\kappa},$$

and $$\frac{A}{\kappa}\left[D\frac{\mu_1+\mu_2}{\mu_1+2\mu_2}\left(\frac{k}{RT^2}+\frac{1}{T}\right) - \frac{D'}{T}\right] = D\frac{d\sigma'}{dz} = \pm DB\beta.$$

The value of σ at the end is therefore

$$\sigma_0 = \frac{\mu_1\mu_2}{\mu_1+\mu_2}B = \pm\frac{\mu_1\mu_2}{\mu_1+2\mu_2}\frac{A}{\kappa\beta}\left[\frac{k}{RT^2}+\frac{1}{T}-\frac{D'}{DT}\frac{\mu_1+2\mu_2}{\mu_1+\mu_2}\right]$$

$$= \pm\frac{\mu_1+2\mu_2}{\mu_1+\mu_2}\frac{\kappa'-\kappa}{\kappa}\frac{A}{Dk\beta},$$

while the exponential term in the expression for the temperature has the end value

$$-\frac{\mu_1\mu_2}{\mu_1+2\mu_2}\frac{kD}{\kappa'}\sigma_0' = \mp\frac{\kappa'-\kappa}{\kappa\kappa'}\frac{A}{\beta}$$

§ 2. *Approximate Numerical Values.*

To obtain an estimate of the order of magnitude of the various quantities, we may assume the following numerical values for the coefficients in C.G.S. units and ° C. and calories:—

$$D = 0{\cdot}1;\ \kappa = 5\times10^{-5};\ T = 300;\ (\mu_1+\mu_2)k = 0{\cdot}2$$

(corresponding to a heat of dissociation of 5000 cals. per grm. molecule); $\frac{A}{\kappa'}$ = mean temperature gradient = 10.

From experiments on thermal diffusion by Chapman and Dootson* it appears that D' (which is related to Chapman's thermal diffusion coefficient D_t by the formula $D' = \frac{(\nu_1+\nu_2)^2}{\nu_1\nu_2}D_t$) can be neglected without causing an error of more than about 2 °/₀.

We now find roughly $$\beta = 4{\cdot}2\sqrt{H},$$

$$\sigma_0 = 0{\cdot}03H^{-\frac{1}{2}}(\mu_1+\mu_2),$$

terminal value of exponential part of $T = 3H^{-\frac{1}{2}}$.

* *Phil. Mag.* xxxiii. p. 248 (1917).

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§ 3. *Conclusion.*

The temperature gradient will cause a measurable change in the concentrations at the ends of the tube if H is of the order of magnitude 1 sec.$^{-1}$, while an even larger value for H would give a measurable deviation from uniformity in the temperature curve. Observations of either the concentrations (which could be made optically in the case of a gas whose colour changes when it dissociates) or the temperature at an end would enable the velocity H to be calculated, provided the other physical constants of the gas were known. The only coefficients which cannot be found easily (other than D' which can be neglected) are κ and D, but it would be possible to obtain approximate values for them from the Kinetic Theory from observations on viscosity and diffusion with other gases, and κ', which can be measured directly, would provide a check for these values.

The difficulty in making the required measurements at the end of the tube is that the quantities to be measured fall off rather rapidly according to an exponential law with space constant β^{-1}, which is about 2 mm. with the numerical values previously taken when H is 1 sec.$^{-1}$.

The analysis holds unchanged for a gas whose molecules dissociate into two different kinds of molecules, provided each of these kinds of molecules has the same diffusion coefficient with the undissociated gas, it being only necessary to let ν_1 mean the total number of single molecules of both kinds per unit volume. When this diffusion condition is not satisfied, the concentrations of the two kinds of single molecules will no longer be everywhere equal, but even in this more general case the same end effects will occur.

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