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L. Applications of Diffusion to Conducting Gases. By JOHN S. TOWNSEND, M.A., Cavendish Laboratory, Cambridge.*

THERE are many phenomena connected with charged and conducting gases which can be explained by diffusion. Before proceeding to its application to these gases it is necessary to solve some problems which apply not only to conducting gases, but also to gases in general. The question with which it is proposed to deal may be stated thus:—If there are two gases, A and B, contained inside a vessel the walls of which absorb A, what quantity of A will remain unabsorbed and be left distributed throughout B inside the vessel after a given time has elapsed?

The first section deals with the solution of this problem for the three particular cases where the boundary consists of a pair of parallel planes, a cylinder, and a sphere respectively. It will be supposed that the absorption of the gas A by the sides of the vessel is so complete as to reduce the pressure of A to zero at the surface. In order to obtain solutions that will apply to cases where the pressure at the surface is a small fixed value it will suffice to substitute $p + p'$ for p in the solutions obtained on the assumption that $p = 0$ at the surface.

In order that the effect of gravity may not disturb the distribution of the gases it will be supposed that the quantity of A is small compared with that of B.

The second section deals with the application of these results to the cases of charged and conducting gases.

* Communicated by Prof. J. J. Thomson, F.R.S.

Section I.

1. The conditions to be satisfied by p , the pressure of the gas A, are :—

$$\kappa \left(\frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2} \right) p = \frac{dp}{dt};$$

$p=0$ at the boundary $\phi(x, y, z)=0$, for all values of t ;

$p=p_0$ initially throughout the space bounded by $\phi=0$.

Let the gases be contained between two parallel plates. The boundary will then be the two planes $x=0$ and $x=a$.

In this case the differential equation reduces to

$$\kappa \frac{d^2 p}{dx^2} = \frac{dp}{dt},$$

the general solution of which is

$$p = \sum A \epsilon^{-\alpha^2 \kappa t} \sin(\alpha x + \beta), \quad . \quad . \quad . \quad (1)$$

where A , α , and β are to be determined by the conditions

$p=0$ when $x=0$ and $x=a$, for all values of t ;

$p=p_0$ when $t=0$ for all values of x between $x=0$ and $x=a$.

The first condition is satisfied by making $\beta=0$ and $\alpha = \frac{n\pi}{a}$.

The coefficients A are determined from the second condition by multiplying both sides of the equation (1) by $\sin \frac{n\pi x}{a} dx$ and integrating from $x=0$ to $x=a$.

Since

$$\int_0^a \sin \frac{n\pi x}{a} \sin \frac{n'\pi x}{a} dx = 0,$$

we obtain the following value of A_n , the coefficient of the term

$$\epsilon^{-\left(\frac{n\pi}{a}\right)^2 \kappa t} \sin \frac{n\pi x}{a}$$

in the Fourier's series (1),

$$A_n = -\frac{2p_0}{n\pi} \left[\cos \frac{n\pi x}{a} \right]_{x=0}^{x=a}.$$

Hence, when n is even $A_n=0$, and when n is odd $A_n = \frac{4p_0}{n\pi}$.

The equation (1) thus becomes

$$p = \frac{4p_0}{\pi} \sum_{n=1}^{n=\infty} \epsilon^{\frac{-(2n-1)^2\pi^2\kappa t}{a^2}} \frac{\sin \frac{(2n-1)\pi x}{a}}{2n-1}.$$

This value of p is unaltered by changing x into $a-x$, showing, as it should, that at any time the distribution is symmetrical with respect to a plane midway between the two plates.

Let q_t denote the mass of the gas A which remains mixed with B after the gases have been allowed to remain between the two plates for a time t , and q_0 the initial mass of A between the two plates. We have

$$\frac{q_t}{q_0} = \frac{\int_0^a p dx}{p_0 a} = \frac{8}{\pi^2} \sum_{n=0}^{n=\infty} \epsilon^{\frac{-(2n-1)^2\pi^2\kappa t}{a^2}} \frac{1}{(2n-1)^2}.$$

Hence

$$q_t = q_0 \frac{8}{\pi^2} \sum_{n=1}^{n=\infty} \epsilon^{\frac{-(2n-1)^2\pi^2\kappa t}{a^2}} \frac{1}{(2n-1)^2}.$$

2. Let the gases be contained inside a cylinder of radius a . The differential equation then becomes

$$\frac{\kappa}{r} \frac{d}{dr} r \frac{dp}{dr} = \frac{dp}{dt},$$

where r is the cylindrical coordinate which denotes the distance of any point from the axis.

Let $p = f(r)\epsilon^{-a^2\kappa t}$, and we obtain the equation

$$\frac{1}{r} \frac{d}{dr} r \frac{df}{dr} = -a^2 f$$

to determine f .

The solution of this equation is

$$f = AJ_0(ar) + BV_0(ar),$$

and since the gas has a finite pressure at the centre we must reject the second term, so that we get

$$p = \Sigma AJ_0(ar)\epsilon^{-a^2\kappa t}.$$

The condition that $p=0$ at the surface is satisfied if a be so determined as to satisfy the equation $J_0(ar)=0$.

Hence

$$p = A_1 J_0(a_1 r) \epsilon^{-a_1^2 \kappa t} + A_2 J_0(a_2 r) \epsilon^{-a_2^2 \kappa t} + \&c.,$$

where $a_1, a_2, \&c.$ are the roots of $J_0(x)=0$.

The coefficients A are determined by using the second condition which p must satisfy: $p=p_0$ when $t=0$.

Hence

$$p_0 = A_1 J_0(\alpha_1 r) + A_2 J_0(\alpha_2 r) + \&c.$$

for all values of r .

Multiplying each side of this equation by $r J_0(\alpha_n r) dr$, and integrating from $r=0$ to $r=a$, we obtain

$$A_n = \frac{-2p_0}{a\alpha_n J_0'(\alpha_n a)} = \frac{2p_0}{a\alpha_n J_1(\alpha_n a)},$$

since

$$\int_0^a r J_0(\alpha_n r) J_0(\alpha_n r) dr = 0, \quad \int_0^a r J_0^2(\alpha_n r) dr = \frac{a^2}{2} J_0'^2(\alpha_n a),$$

and

$$\int_0^a r J_0(\alpha_n r) dr = \frac{-a}{\alpha_n} J_0'(\alpha_n a)^*.$$

Hence the value of p expressed as a function of r and t is

$$p = \frac{2p_0}{a} \left[\frac{J_0(\alpha_1 r)}{\alpha_1 J_1(\alpha_1 a)} e^{-\alpha_1^2 \kappa t} + \frac{J_0(\alpha_2 r)}{\alpha_2 J_1(\alpha_2 a)} e^{-\alpha_2^2 \kappa t} + \&c. \right].$$

The ratio of q_t , the mass of the gas A which remains unabsorbed at the time t , to the original mass in the cylinder is

$$\frac{2 \int_0^a p r dr}{p_0 a^2} = 4 \left[\frac{e^{-\alpha_1^2 \kappa t}}{a^2 \alpha_1^2} + \frac{e^{-\alpha_2^2 \kappa t}}{a^2 \alpha_2^2} + \&c. \right].$$

3. When the gases are contained inside a spherical boundary the differential equation becomes

$$\frac{\kappa}{r^2} \frac{d}{dr} \left(r^2 \frac{dp}{dr} \right) = \frac{dp}{dt},$$

which can also be written

$$\kappa \frac{d^2}{dr^2} (rp) = \frac{d(rp)}{dt}.$$

The solution of which is

$$rp = \Sigma A \sin(\alpha r + \beta) e^{-\alpha^2 \kappa t}.$$

The condition $p=0$ at the boundary $r=a$ is satisfied if $\beta=0$

and $\alpha = \frac{n\pi}{a}$.

* Lord Rayleigh: 'Theory of Sound,' sections 203, 204.

So that equation (1) becomes

$$rp = \sum_{n=1}^{n=\infty} A_n \sin \frac{n\pi r}{a} e^{-\frac{n^2\pi^2}{a^2}\kappa t}.$$

The coefficients A_n are determined, as before, by making $p=p_0$ and $t=0$ simultaneously, and we have

$$\begin{aligned} \frac{aA_n}{2} &= p_0 \int_0^a r \sin \frac{n\pi r}{a} dr \\ &= p_0 \frac{a^2(-1)^{n-1}}{n\pi}. \end{aligned}$$

Hence

$$rp = \frac{2ap_0}{\pi} \sum_{n=1}^{n=\infty} (-1)^{n-1} \frac{e^{-\frac{n^2\pi^2}{a^2}\kappa t}}{n} \sin \frac{n\pi r}{a};$$

and the ratio $\frac{qt}{q_0}$ becomes in this case

$$\frac{6}{\pi^2} \sum_{n=1}^{n=\infty} e^{-\frac{\pi^2 n^2}{a^2}\kappa t} \frac{1}{n^2}.$$

By means of this equation a rough estimate could be made of the amount of impurity (A) that would be removed from a gas (B) by bubbling through a liquid which absorbed the gas A.

The solution shows that $\frac{qt}{q_0}$ is constant when $\frac{t}{a^2}$ is constant; or that in order to reduce the quantity of the gas A by a given fraction the time the bubble takes to rise in the liquid must be proportional to the square of its radius. When $\frac{qt}{q_0}$ is small, account need only be taken of the first term, and the value of $\frac{qt}{q_0}$ is easily calculated when κ is known.

Section II.

4. The number of charged carriers or ions which are present in a gas and give rise to conductivity is very small compared with the total number of molecules of the gas. These charged carriers we will suppose constitute the gas A, and the rest of the molecules will be denoted as the gas B.

Let m be the mass of a carrier; e its charge; u, v, w the velocities of A parallel to the axes; p the pressure of A; n the number of carriers per cubic centimetre; X, Y, Z the electric forces.

We have

$$nm \frac{du}{dt} = nXe - \frac{dp}{dx} - \alpha nu,$$

and two similar equations from which the motion of the gas A can be determined. The value of α as given by Maxwell (J. C. Maxwell, "Dynamical Theory of Gases," Phil. Mag. 1868, vol. xxxv.) is $hA_1 \frac{\rho \rho_2}{n} = hA_1 m \rho_2$. In this case ρ_2 is the density of B, which remains constant, so that α is also constant.

Since m is so small compared with the other quantities we may omit the first term, and we obtain

$$Xe = \frac{1}{n} \frac{dp}{dx} + \alpha u. \quad . \quad . \quad . \quad . \quad . \quad (1)$$

If X is large, so that $\frac{1}{n} \frac{dp}{dx}$ is small in comparison with Xe , we have the velocity u proportional to X ; and if V is the velocity of the carrier when acted on by a force of 1 volt per centimetre, we have

$$\alpha = \frac{e}{300V}.$$

Hence when X , Y , and Z are zero, equation (1) reduces to

$$\frac{1}{n} \frac{dp}{dx} + \frac{e}{300V} u = 0. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

Let N = number of molecules in a cubic centimetre of gas at pressure p_0 and temperature 15°C . (being the temperature at which we suppose the conductivity is determined), then

$$\frac{p}{n} = \frac{p_0}{N}.$$

Hence from equation (2)

$$-pu = \frac{300V}{e} \frac{p_0}{N} \frac{dp}{dx}; \quad . \quad . \quad . \quad . \quad . \quad (3)$$

similarly

$$-pv = \frac{300V}{e} \frac{p_0}{N} \frac{dp}{dy}, \quad \text{and} \quad -pw = \frac{300V}{e} \frac{p_0}{N} \frac{dp}{dz}.$$

The equation of continuity is

$$\frac{dp}{dt} + \frac{d}{dx}(pu) + \frac{d}{dy}(pv) + \frac{d}{dz}(pw) = 0.$$

Substituting for $\frac{d}{dx}(pu)$, $\frac{d}{dy}(pv)$, and $\frac{d}{dz}(pw)$ their values derived by differentiating equations (3), we arrive at the equation

$$\frac{dp}{dt} = \frac{300Vp_0}{Ne} \nabla^2(p),$$

which is the general equation we assumed in Section I.

Thus the value of the constant κ is $\frac{300Vp_0}{Ne}$.

5. The loss of conductivity of a gas is due partly to the recombination of some of the positively charged carriers with the negatively charged ones, and partly to the carriers coming into contact with the conductors. It is with this latter phenomenon that we are here chiefly concerned. By substituting the above value of κ in the three solutions obtained in Section I. we obtain expressions which give the loss of conductivity of a gas due to the diffusion of the carriers towards the sides of the vessel which contains it. This loss of conductivity takes place in a closed vessel without any electromotive force acting on the gas.

When a carrier comes into contact with a conductor it either gives up its charge, or remains in contact with the surface. From the way in which the equations in Section I. were solved, it is clear that the solutions apply to the case where the carrier, instead of giving up its charge to the side, induces an opposite charge on the conductor, and is held attracted to the surface by the electric force arising from its image. The solutions apply equally well on the hypothesis that the carrier discharges and comes back into the gas. In this case we have a slight increase in the number of molecules of B, less than one part in 10^{10} ; so that the correction to be applied would amount to calculating the difference of the rate of diffusion of A through a gas having a density greater than B in the proportion of $10^{10} + 1$ to 10^{10} , which of course can in no way affect the original solution.

If we leave out of consideration the recombination of the ions or charged carriers, we see that the conductivity of a gas will fall from p_0 to p in a time t , where the ratio of p_0 to p is

$$\frac{8}{\pi^2} \sum_{n=1}^{n=a} \epsilon^{\frac{-(2n-1)^2 \pi^2 \kappa t}{a^2}} \frac{1}{(2n-1)^2}$$

when the gas is contained between two parallel plates at a distance a apart;

$$4 \left[\frac{\epsilon^{-\alpha_1^2 \kappa t}}{a^2 \alpha_1^2} + \frac{\epsilon^{-\alpha_2^2 \kappa t}}{a^2 \alpha_2^2} + \&c. \right]$$

when the gas is contained inside a cylinder of radius a ; and

$$\frac{6}{\pi^2} \sum_{n=1}^{\infty} \epsilon^{-\frac{\pi^2 n^2}{a^2} \kappa t} \frac{1}{n^2}$$

when the gas is contained inside a sphere of radius a , where $\kappa = \frac{300 p_0 V}{Ne}$.

These equations show how much more rapidly the conductivity is destroyed in smaller vessels than in larger ones.

Let us take the case of oxygen which has been made a conductor by Röntgen rays; let the charge on each carrier be x times the charge that an atom of oxygen carries in electrolysis, which we will denote by E .

One electromagnetic unit of quantity evolves 1.2 cub. cent. of hydrogen and .6 cub. cent. of oxygen from an electrolytic cell, at ordinary temperature and pressure $p_0 = 10^6$.

The number of atoms in .6 cub. cent. is $2N_x$ (6), and the quantity of electricity that they carry is $\frac{1}{2}$ an electromagnetic unit, or $\frac{3}{2} 10^{10}$ electrostatic units.

Hence

$$1.2NE = \frac{3}{2} 10^{10} \quad \text{or} \quad NE = \frac{10^{10}}{.8},$$

so that
$$Ne = \frac{x 10^{10}}{.8}.$$

The velocity of the carrier under an electromotive force of a volt per centimetre is (E. Rutherford, Phil. Mag. 1897, vol. xlv.) 1.6 centim. per second; so that

$$\kappa = \frac{300 \times 10^6 \times 1.6 \times .8}{x 10^{10}} = \frac{3.84}{x} 10^{-2}.$$

6. Let us consider more particularly the second case, which would apply to a conducting gas passing along tubing, and find what the loss of conductivity of Röntgenized oxygen will be in passing along a tube, 10 centim. long and 1 millim. radius, at the rate of 100 centim. a second.

For simplicity we will suppose that the velocity is uniform,

so that the time that any portion of the gas will be in the tube will be $\frac{1}{10}$ of a second.

The ratio of the conductivity of the gas entering the tubing to the conductivity of the gas as it escapes will, therefore, be

$$4 \left[\frac{\epsilon^{-\alpha_1^2 \kappa t}}{a^2 \alpha_1^2} + \frac{\epsilon^{-\alpha_2^2 \kappa t}}{a^2 \alpha_2^2} + \&c. \right] = R.$$

The values of $a\alpha_1$, $a\alpha_2$, &c. which are the positive roots of $J_0(x) = 0$ are 2.404, 5.520, 8.654, &c. (Lord Rayleigh, 'Theory of Sound,' section 206).

Substituting for a , α_1 , α_2 , &c. their values we obtain

$$R = 4 \left[\frac{\epsilon^{\frac{-(2.4)^2 \kappa t}{a^2}}}{(2.4)^2} + \frac{\epsilon^{\frac{-(5.5)^2 \kappa t}{a^2}}}{(5.5)^2} + \&c. \right],$$

where $a = \frac{1}{10}$, $t = \frac{1}{10}$, $\kappa = \frac{3.84 \times 10^{-2}}{x}$.

So that

$$R = 4 \left[\frac{\epsilon^{\frac{-2.21}{x}}}{5.76} + \frac{\epsilon^{\frac{-11.6}{x}}}{30.2} + \&c. \right] = \frac{1}{13} \text{ q. p.}$$

If x were unity, in other words if the ion in the oxygen which is conducting under Röntgen rays were to carry the same charge as it does in electrolysis, then the conductivity of the gas would be reduced to $\frac{1}{13}$ of its value by passing it along a tube 10 centimetres long and 1 millimetre radius at the rate of 100 centimetres per second.

It is interesting to find what would be the effect of the attraction, towards the sides of a tube made of conducting material, of each individual carrier by its own image in the conductor. It is quite evident that this effect only comes in when the carrier is near the surface, so that we can regard the radius of curvature of the tube as large in comparison with the distance of the carrier from the surface. When this distance is x , the force on the carrier will be $\frac{e^2}{4x^2}$, and under

this force it would travel at the rate of $\frac{e}{4x^2} \times \frac{1.6}{300}$, since under a volt a centimetre it travels at the rate of 1.6 centimetres per second.

Hence we have

$$u = \frac{10^{-10} \times 120}{x^2} = -\frac{dx}{dt},$$

assuming that the atomic charge on oxygen is 10^{-10} ; therefore

$$dt = -\frac{10^9}{12} x^2 dx.$$

Let us find the distance of a particle x_0 which in a time t would reach the side: we have

$$t = - \int_{x_0}^{10^9} \frac{10^9}{12} x^2 dx = \frac{10^9 x_0^3}{36};$$

when $t = \frac{1}{10}$ we have $x_0 = \frac{\sqrt[3]{3 \cdot 6}}{10^3}$.

So that in the case we are considering a layer of $1 \cdot 5 \times 10^{-3}$ thickness of the gas would have its conductivity destroyed in $\frac{1}{10}$ of a second owing to the mutual attraction between each ion and its image. The ratio of this volume to the total volume of the tube is $\frac{2\pi \times 1 \cdot 5 \times 10^{-3}}{\pi r}$, which becomes 3×10^{-2}

when $r = \cdot 1$. Hence in this case the loss of conductivity due to the carriers attracting themselves up to the sides is small compared with the loss of conductivity due to diffusion.

7. When there is an excess of carriers charged with electricity of one kind the gas not only conducts but exhibits the properties of a charged body. The motion of the carriers in such a gas is somewhat complicated, as both the diffusion and the effect of mutual repulsion have to be taken into account. When the charge per c. c. is small we can leave the latter effect out of account and consider only the diffusion. The equations (5) Section II. can then be applied to charged gases, and we can look upon them as particular cases of conducting gases. The properties of these gases vary in many ways in regard to their power of retaining their conductivity; thus some of them can be passed along tubing, bubbled through liquids, or sent through gauze or wool without losing more than from 20 to 50 per cent. of their conductivity, whereas others are made perfect non-conductors when similarly treated. The equations (5) Section II. show that rate of loss of conductivity by coming into contact with conductors increases very rapidly with V the velocity of the carrier under an electromotive force of 1 volt per centimetre. We should, therefore, expect that for those gases which retain their conductivity after bubbling through liquids &c. the value of V is small compared with its value for gases which retain none of their conductivity after similar treatment. In support of this explanation we have the following results:—The conductivity of a gas which has been made a conductor by means of Röntgen rays is destroyed by passing the gas through wool or bubbling through sulphuric acid, and the velocity of the carrier under an electromotive force of a volt per centimetre is (for air)

1.4 centimetres per second (J. J. Thomson and E. Rutherford, *Phil. Mag.* Nov. 1896 ; E. Rutherford, *Phil. Mag.* Nov. 1897). The gases evolved from a sulphuric acid electrolyte retain a large fraction of their charge after passing through wool or bubbling through a liquid, and for the oxygen the velocity of the carrier is only 2.2×10^{-4} centimetres per second when acted on by the same force (John S. Townsend, *Phil. Mag.* Feb. 1898).

We have here supposed that e , the charge on the carrier, is the same in each case. This assumption is reasonable from theoretical considerations, but it has not yet been established upon experimental evidence that when an elementary gas conducts the carriers have the same charge as the atoms carry in electrolysis. Information on this point might be gained by testing experimentally the result obtained in § 6.

Many examples of this latter kind are to be found in newly prepared gases. In most of these cases it is easy to account for the growth of the carrier to a large size owing to the presence of gases or vapours which would condense round the charge and thus increase the size of the carrier. The velocity V would thus be greatly diminished.

When newly prepared gases are evolved from a solution it is probable that the electrification is acquired immediately as the gas is generated, so that each little bubble of the gas as it rises in the liquid contains carriers which are charged. Since these bubbles are small it would only require a very short time for carriers which diffused rapidly to be completely discharged by striking the liquid round the bubble, so that in order that an appreciable number of charged carriers should escape with the gas from the liquid it is necessary to assume that they diffuse slowly, or what amounts to the same thing, that they should be large compared with molecules.

8. When the number of carriers charged with positive and negative electricity respectively is unequal, the electrostatic field which is created tends to drive those carriers which are in excess towards the walls of the containing vessel. This effect is easily calculated for the case where the carriers are all charged with electricity of the same sign. Let ρ be the density of electrification, u, v, w the velocities parallel to the axes, and ϕ the electric potential.

In order to determine the motion we have three equations of the form

$$\alpha^u = -\frac{1}{n} \frac{dp}{dx} - e \frac{d\phi}{dx}.$$

The term $\frac{1}{n} \frac{dp}{dx}$ does not increase with ρ since both p and n are proportional to ρ , so that if we suppose ρ to be above a certain value this term may be omitted in comparison with $-e \frac{d\phi}{dx}$.

Writing the equation of continuity in the form

$$\frac{1}{\rho} \frac{\delta \rho}{\delta t} + \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz} = 0,$$

where $\frac{\delta}{\delta t}$ denotes the total differentiation of ρ with respect to t , we obtain on substituting for $u v w$ the above values

$$\frac{\alpha}{\rho} \frac{\delta \rho}{\delta t} + 4\pi e \rho = 0.$$

So that

$$\rho = \frac{\rho_0}{1 + \frac{4\pi e \rho_0}{\kappa} t},$$

which shows that after a time t the density is a function of t alone, and does not vary from point to point in the gas, if ρ_0 is constant initially throughout the gas. The reduction of the charge due to this effect is usually large compared with the reduction due to diffusion when ρ is greater than 10^{-4} . The two effects can easily be distinguished from one another, since $\frac{q_t}{q_0}$ in this case is a function of ρ_0 , the initial density of electrification, and is independent of the form of the vessel. (J. S. Townsend, *loc. cit.*)

It does not appear that the effect of mutual repulsion would be instrumental in increasing the discharging power of a charged gas as it passed through fine gauzes, since the gauzes may be considered part of the boundary, the form or extent of which in no way affects the above value of ρ .

LI. *Microscopic Images and Vision*. By LEWIS WRIGHT*.

1. **T**HE discussion by Lord Rayleigh and Dr. Stoney† has thrown considerable further light upon a subject which has been discussed for many years; but there seems still something to be added from the point of view of the microscopist, for whom there is at issue in it a very important

* Communicated by the Author.

† Phil. Mag. Aug., Oct., Nov., Dec. 1896.