L. *Theoretical Considerations respecting the Separation of Gases by Diffusion and similar Processes. By* LORD RAYLEIGH, *Sec. R.S.*[*]

THE larger part of the calculations which follow were made in connexion with experiments upon the concentration of argon from the atmosphere by the method of atmolysis [†]. When the supply of gas is limited, or when it is desired to concentrate the lighter ingredient, the conditions of the question are materially altered; but it will be convenient to take first the problem which then presented itself of the simple diffusion of a gaseous mixture into a vacuum, with special regard to the composition of the residue. The diffusion tends to alter this composition in the first instance only in the neighbourhood of the porous walls; but it will be assumed that the forces promoting .mixture are powerful enough to allow of our considering the composition to be uniform throughout the whole volume of the residue, and variable only with time, on account of the unequal escape of the constituent gases.

Let x, y denote the quantities of the two constituents of the residue at any time, so that $-dx$, $-dy$ are the quantities diffused out in time dt. The values of dx/dt, dy/dt will depend upon the character of the porous partition and upon the actual pressure; but for our present purpose it will suffice to express dy/dx, and this clearly involves only the ratios of the constituents and of their diffusion rates. Calling the diffusion rates μ, ν, we have

$$\frac{dy}{dx} = \frac{\nu y}{\mu x}. \qquad \qquad (1)$$

In this equation x, y may be measured on any consistent system that may be convenient. The simplest case would be that in which the residue is maintained at a constant volume, when x, y might be taken to represent the partial pressures of the two gases. But the equation applies equally well when the volume changes, for example in such a way as to maintain the total pressure constant.

The integral of (1) is

$$y^{1/\nu} = C x^{1/\mu}, \qquad \qquad (2)$$

where C is an arbitrary constant, or

$$y/x = C x^{-1+\nu/\mu}. \qquad \qquad (3)$$

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[*] Communicated by the Author.
[†] Rayleigh and Ramsay, Phil. Trans. clxxxvi. p. 206 (1895).

If X, Y be simultaneous values of x, y, regarded as initial,

$$\frac{y/x}{Y/X} = \left(\frac{x}{X}\right)^{-1+\nu/\mu}, \quad \ldots \ldots (4)$$

so that

$$x = X \left(\frac{y/x}{Y/X}\right)^{\mu/(\nu-\mu)} \quad \ldots \ldots (5)$$

In like manner

$$y = Y \left(\frac{x/y}{X/Y}\right)^{\nu/(\mu-\nu)} \quad \ldots \ldots (6)$$

If we write

$$\frac{y/x}{Y/X} = r, \quad \ldots \ldots (7)$$

r represents the enrichment of the residue as regards the second constituent, and we have from (5), (6),

$$\frac{x+y}{X+Y} = \frac{X}{X+Y} r^{\mu/(\nu-\mu)} + \frac{Y}{X+Y} r^{\nu/(\nu-\mu)}, \quad \ldots \quad (8)$$

an equation which exhibits the relation between the enrichment and the ratio of the initial and final total quantities of the mixture.

From (8), or more simply from (4), we see that as x diminishes with time the enrichment tends to zero or infinity, indicating that the residue becomes purer *without limit*, and this whatever may be the original proportions. Thus if the first gas (x) be the more diffusive ($\mu > \nu$), the exponent on the right of (4) is negative ; and this indicates that r becomes infinite, or that the first gas is ultimately eliminated from the residue. When the degree of enrichment required is specified, an easy calculation from (8) gives the degree to which the diffusion must be carried.

In Graham's atmolyser the gaseous mixture is caused to travel along a tobacco-pipe on the outside of which a vacuum is maintained. If the passage be sufficiently rapid to preclude sensible diffusion along the length of the pipe, the circumstances correspond to the above calculation ; but the agreement with Graham's numbers is not good. Thus in one case given by him * of the atmolysis of a mixture containing equal volumes of oxygen and hydrogen, we have

$$Y/X = 1, \quad y/x = 92 \cdot 78 / 7 \cdot 22,$$

so that $r = 13$ nearly. Thus, if in accordance with the view

* Phil. Trans. vol. cliii. p. 403 (1863).

usually held $\mu/\nu=4$, we should have from (8)

$$\frac{x+y}{X+Y}=\tfrac{1}{2}\times 13^{-\frac{4}{3}}+\tfrac{1}{2}\times 13^{-\frac{1}{3}}=\cdot 229\ ;$$

so that a reduction of the residue to ·229 of the initial quantity should have effected the observed enrichment. The initial and final volumes given by Graham are, however, 7·5 litres and ·45 litre, whose ratio is ·06. The inferior efficiency of the apparatus may have been due to imperfections in the walls or joints of the pipes. Such an explanation appears to be more probable than a failure of the law of independent diffusion of the component gases upon which the theoretical investigation is founded.

In the concentration of argon from a mixture of argon and nitrogen we have conditions much less favourable. In this case

$$\mu/\nu=\sqrt{20}/\sqrt{14}=\cdot 077.$$

If an enrichment of $2:1$ is required and if the original mixture is derived from the atmosphere by removal of oxygen, the equation is

$$\frac{x+y}{X+Y}=\cdot 99\times 2^{-6\cdot13}+\cdot 01\times\cdot 2^{-5\cdot13}$$
$$=\cdot 0142+\cdot 0029=\cdot 0171,$$

expressing the reduction needed. The results obtained experimentally (*loc. cit.*) were inferior in this case also.

When the object is the most effective separation of the components of a mixture, it is best, as supposed in the above theory, to maintain a vacuum on the further side of the porous wall. But we have sometimes to consider cases where the vacuum is replaced by an atmosphere of fixed composition, as in the well-known experiment of the diffusion of hydrogen into air through a porous plug. We will suppose that there are only two gases concerned and that the volume inside is given. The symbols x, y will then denote the partial pressures within the given volume, the constant partial pressures outside being α, β. Our equations may be written

$$\left.\begin{array}{l}dx=\mu(\alpha-x)dt\\dy=\nu(\beta-y)dt\end{array}\right\},\quad\cdot\quad\cdot\quad\cdot\quad\cdot\quad(9)$$

or on integration

$$x=\alpha+Ce^{-\mu t},\quad y=\beta+De^{-\nu t},\quad\cdot\quad\cdot\quad\cdot\quad(10)$$

C, D being arbitrary constants.

After a sufficient time x, y reduce themselves respectively to α, β, as was to be expected.

The constants μ, ν are not known beforehand, depending as they do upon the specialities of the apparatus as well as upon the quality of the gases. If we eliminate t, we get

$$y - \beta = E(x-a)^{\nu/\mu}, \quad \ldots \quad (11)$$

in which only the *ratio* ν/μ is involved.

As a particular case suppose that initially the inside volume is occupied by one pure gas and the outside by another, the initial pressures being unity. Then in (10)

$$a = 0, \quad \beta = 1, \quad C = 1, \quad D = -1;$$

we have

$$x = e^{-\mu t}, \quad y = 1 - e^{-\nu t}, \quad \ldots \quad (12)$$

and

$$x + y = 1 + e^{-\mu t} - e^{-\nu t} \quad \ldots \quad (13)$$

gives the total internal pressure. When this is a maximum or minimum, $e^{(\mu-\nu)t} = \mu/\nu$, and the corresponding value is

$$x + y = 1 + \left(\frac{\mu}{\nu}\right)^{-\frac{\mu}{\mu-\nu}}\left\{1 - \frac{\mu}{\nu}\right\}. \quad \ldots \quad (14)$$

Thus in the case of hydrogen escaping into oxygen, $\mu/\nu = 4$, and

$$x + y = 1 - 3 \times 4^{-\frac{4}{3}} = \cdot528,$$

the minimum being about half the initial pressure *.

Returning now to the separation of gases by diffusion into a vacuum, let us suppose that the difference between the gases is small, so that $(\nu - \mu)/\mu = \kappa$, a small quantity, and that at each operation one-half the total volume of the mixture is allowed to pass. In this case (8) becomes

$$\frac{1}{2} = \frac{X}{X+Y}r^{\frac{1}{\kappa}} + \frac{Y}{X+Y}r^{\frac{1+\kappa}{\kappa}} = r^{\frac{1}{\kappa}} \text{ nearly ;}$$

so that

$$r = \frac{y/Y}{x/X} = (\tfrac{1}{2})^{\kappa} \cdot \ldots \quad (15)$$

This gives the effect of the operation in question upon the composition of the residual gas. If s denote the corresponding symbol for the transmitted gas, we have

$$s = \frac{(Y-y)/Y}{(X-x)/X} = \frac{1 - y/Y}{1 - x/X} = \frac{1 - rx/X}{1 - x/X}$$

$$= 1 + \frac{(1-r)x/X}{1 - x/X} = 2 - r \text{ approximately,}$$

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* The most striking effects of this kind are when nitrous oxide, or dry ammonia gas, diffuse into the air through indiarubber. I have observed suctions amounting respectively to 53 and 64 centimetres of mercury.

since r is nearly equal to unity.   Accordingly

$$\frac{1}{s} = \frac{1}{2-r} = r \text{ nearly},$$

so that approximately s and r are reciprocal operations.   For example, if starting with any proportions we collect the transmitted half, and submit it to another operation of the same sort, retaining the half not transmitted, the final composition corresponding to the operations sr is the same (approximately) as the composition with which we started, and the same also as would be obtained by operations taken in the reverse order, represented by rs.   A complete scheme * on these lines is indicated in the diagram.   Representing the
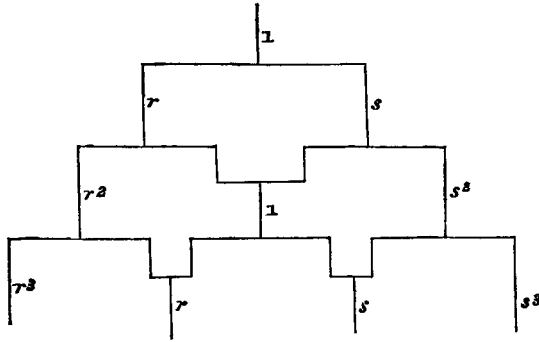
initial condition by unity, we may represent the result of the first operation by

$$\tfrac{1}{2}r + \tfrac{1}{2}s, \quad \text{or} \quad \tfrac{1}{2}(r+s),$$

in which the numerical coefficient gives the quantity of gas whose character is specified by the literal symbols.   The second set of operations gives in the first instance

$$\tfrac{1}{4}r^2 + \tfrac{1}{4}sr + \tfrac{1}{4}rs + \tfrac{1}{4}s^2,$$

or, after admixture of the second and third terms (which are of the same quality),

$$\tfrac{1}{4}(r^2 + 2rs + s^2) = \left(\frac{r+s}{2}\right)^2.$$

In like manner the result of the third set of operations may be represented by $\left(\dfrac{r+s}{2}\right)^3$, and (as may be formally proved by

* It differs, however, from that followed by Prof. Ramsay in his recent researches (Proc. Roy. Soc. vol. lx. p. 216, 1896).

" induction ") of n sets of operations by

$$\left(\frac{r+s}{2}\right)^n. \quad \ldots \ldots \ldots \quad (16)$$

When we take account of the reciprocal character of r and s, this may be written

$$\frac{1}{2^n}\left\{ r^n + n\,r^{n-2} + \frac{n(n-1)}{1\,.\,2} r^{n-4} + \ldots + n\,r^{-n+2} + r^{-n} \right\}, \quad (17)$$

the number of parts into which the original quantity of gas is divided being $n+1$. If n is even, the largest part, corresponding to the middle term, has the original composition[*].

It is to be observed, however, that so far as the extreme concentration of the less diffusive constituent is concerned these complex operations are entirely unnecessary. The same result, represented by $(\frac{1}{2})^n{}_{|}r^n$ will be reached *at a single operation* by continuing the diffusion until the residue is reduced to $(\frac{1}{2})^n$ of the original quantity, when its composition will be that denoted by r^n. And even as regards the extreme member at the other end in which the more diffusive constituent preponderates, it will be evident that the operations really required are comparatively simple, the extreme member in each row being derived solely from the extreme member of the row preceding[†].

If we abandon the supposition, adopted for simplicity, that the gas is divided into *equal* parts at each operation, we may still express the results in a similar manner. If ρ, σ be the fractions retained and transmitted, then $\rho + \sigma = 1$, and in place of (15) we get $\qquad r = \rho^k. \quad \ldots \ldots \ldots \quad (18)$

The relation between r and s is

$$\rho r + \sigma s = 1 \;; \quad \ldots \ldots \ldots \quad (19)$$

and the various portions into which the gas is divided after n sets of operations are represented by the various terms of the expansion of $\qquad (\rho r + \sigma s)^n, \quad \ldots \ldots \ldots \quad (20)$

the Greek letters and the numerical coefficients giving the quantity of each portion, and the Roman letters giving the quality. But it must not be forgotten that this theory all along supposes the difference of diffusivities to be relatively small.

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[*] There is here a formal analogy with the problem of determining the probability of a given combination of heads and tails in a set of n tosses of a coin; and the result of supposing n infinite may be traced as in the theory of errors.

[†] Possibly a better plan for the concentration of the lighter constituent would be diffusion along a column of easily absorbable gas, *e. g.* CO_2. The gas which arrives first at the remote end is infinitely rich in this constituent.