

than when it was saturated with moisture. The following are the limits between which the coefficients of diffusion of ions, produced by point discharges, were found to vary :—

Positive ions in dry air .....	0·0247—0·0216
Negative ions in dry air.....	0·037 —0·032
Positive ions in moist air .....	0·028 —0·027
Negative ions in moist air .....	0·039 —0·037

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“Static Diffusion of Gases and Liquids in Relation to the Assimilation of Carbon and Translocation in Plants.”\* By HORACE T. BROWN, F.R.S., LL.D., and F. ESCOMBE, B.Sc., F.L.S. Received May 31,—Read June 14, 1900.

(Abstract.)

This paper is intended to be the first of a series descriptive of the work carried out by the authors in the Jodrell laboratory on the fixation of carbon by green plants, and deals mainly with the purely physical processes by which atmospheric carbon dioxide gains access to the active centres of assimilation.

The new evidence which F. F. Blackman brought forward in 1895 in favour of the gaseous exchanges of leaves taking place exclusively through the stomatic openings, presents at first sight certain difficulties of a physical nature, which have led to an examination of the whole question of the free diffusion of carbon dioxide at very low tension, and under a set of conditions very different from those under which the previous determinations of the coefficient of diffusion of carbon dioxide and air have been made by Loschmidt and others, where the gases were initially of equal tension, and the ratios of mixture departed widely from those of ordinary atmospheric air. The inquiry has led to the discovery of some new facts connected with the static diffusion of gases and liquids, which are of considerable interest, not only from the physical point of view, but from the explanations they suggest of certain natural processes which are primarily dependent on diffusivity.

The method employed in the first instance for the determination of the diffusivity of atmospheric carbon dioxide was one of *static diffusion* down a column of air of a definite length, towards an absorptive surface at the bottom of the column. When a static condition has been established, there is a steady flux of the carbon dioxide down the

\* The title of the paper as communicated to the Society was “Some New Observations on the Static Diffusion of Gases and Liquids, and their Significance in certain Natural Processes occurring in Plants.”

air column which may be quantitatively investigated by the same simple mathematical treatment as the "flow" of heat in a bar when the permanent state has been reached, or the "flow" of electricity between any two regions of a conductor maintained at a constant difference of potential.

By a long series of experiments of this nature it was found that the diffusivity constant,  $k$ , for very dilute  $\text{CO}_2$  does not materially depart from the value assigned to it by Loschmidt and others, when experimenting with much higher ratios of mixture, and that the difference is certainly not of sufficient magnitude to be taken into serious account in the study of the natural processes of gaseous exchange in the assimilating organs of plants.

In the static diffusion of a gas, vapour, or solute, as the case may be, the amount of substance diffusing in a given time, all other conditions being the same, is directly proportional to the sectional area of the column. It is found, however, that if the flow is partially obstructed by interposing at any point in the line of flow a thin septum pierced with a circular aperture, the rate of flow across unit area of the aperture is greater than it would be across an equal area of the unobstructed cross-section of the column at this point. If the margin around the aperture has a width of at least three or four times its diameter, the rate of flow is now found to be directly proportional to the *linear dimensions* of the aperture and not to its area, so that the velocity of flow through unit area varies inversely as the diameter.

A large number of experiments on the diffusion of carbon dioxide, water-vapour, and sodium chloride in solution, are given in support of this proposition. All these show that the rate of diffusion across such a septum, all other conditions being the same, is directly proportional to the diameter of the aperture, and not, as might have been expected, to its area.

Exactly the same result is obtained when small circular discs of an absorbent, such as a solution of caustic alkali, are surrounded by a wide rim and exposed to *perfectly still* air, the amount of carbon dioxide absorbed under these conditions being proportional to the *diameters* of the discs.

If, however, there are any sensible air currents the absorption becomes proportional to the areas.

These two sets of phenomena may be explained as follows:—

In the case of the absorbing disc in perfectly still air, the convergent streams of carbon dioxide creep through the air towards the absorbing disc, establishing a steady gradient of density, and this creep will be a flux perpendicular to the lines of equal density, which form curved surfaces or "shells" surrounding the disc and terminating in the rim. The state of things is exactly analogous to the electric field in the neighbourhood of a conductor of the same shape and

dimensions as the absorbent disc.\* In the case of the gas, the curves or "shells" of equal density are the analogues of the similarly curved surfaces of equipotential above the electrified disc, whilst the converging lines of creep or flux of the gas are the analogues of the lines or tubes of force which bend round into the disc as they approach it.

If we consider two such absorbent discs of different diameters, the curved surfaces in each system corresponding to a given density will be found at actual distances from the discs which are in the same proportion to each other as are the diameters of the discs. In other words, the gradient of density on which the rate of flow depends will be proportional to the diameters of the discs, which is exactly what is found experimentally.

This case of an absorbent disc is the exact converse of one which has been theoretically investigated by Stefan, viz., the conditions of evaporation of a liquid from a circular surface. He found that the lines of flux of the vapour proceeding from the surface of the liquid must be hyperbolas, whilst the curved surfaces of equal pressure of the vapour must form an orthogonal system of ellipsoids, having their foci, like the hyperbolas, in the bounding edges of the disc. This was a purely mathematical deduction which has never been verified experimentally, but it will be seen that the exactly converse phenomena of diffusion are in complete agreement with it.

In the other case of a diffusive flow through a circular aperture in a diaphragm, the lines of flow, which are *convergent* as they approach the aperture, bend round their foci situated in the edges of the disc and form a *divergent* system on the other side. If the chamber into which they pass is a perfectly absorbent one, and is sufficiently large, there will be formed on the inner side of the diaphragm a system of density shells similar to those outside, but with the gradient of density centrifugally instead of centripetally arranged. This system of shells is termed negative, and is as effective as the outer positive system in regulating the flow according to the "diameter law," so that this law will still hold good even if the outer air currents are sufficient to sweep away the external positive shells altogether.

All the known facts of diffusion through circular apertures in a diaphragm are in complete accord with the above explanation, which is fully elaborated in the original paper.

By diffusing colouring matter through apertures in a septum, under such conditions as to prevent convection currents, the "density shells" have been rendered visible, and it has been shown that their ellipsoidal form is exactly that which is demanded by the above hypothesis. Moreover, this method gives an experimental demonstration of the more rapid projection of the diffusing particles from the edges of the

\* The authors are indebted to Dr. Larmor for this suggestion of the electrostatic analogy.

aperture than from a point nearer its centre, a fact completely in harmony with the deduction of Stefan regarding the evaporation of liquids under analogous conditions.

The various cases which present themselves in practice with regard to the rate of diffusion through single apertures in a diaphragm are then discussed from the above point of view, and simple formulæ for the determination of this rate for single and double systems of density shells are established: (1) for cases where the thickness of the diaphragm is negligible, and (2) for other cases where the apertures become more or less tubular. In a subsequent section of the paper it is shown how closely the observed facts conform to these deductions, and that in static diffusion through apertures in a septum we have a new and accurate method for the determination of the diffusivity constants of atmospheric  $\text{CO}_2$ , of the vapours of liquids, and of substances in a state of solution.

Since the velocity of the diffusive flow through unit area of an aperture in a diaphragm varies inversely with the diameter, it might reasonably be expected that a diaphragm could be so perforated with a series of very small holes arranged at suitable distances from each other, as to exercise little or no sensible obstruction when it was interposed in a line of diffusive flow, although the aggregate area of the small holes might represent only a small fraction of the total area of the septum. Multiperforate diaphragms of this kind were found to possess all the remarkable properties which had been anticipated.

The material used for the septa was very thin celluloid, which was perforated at regular intervals with holes of about 0.38 mm. in diameter. Details of a number of experiments with such diaphragms are given, in which it is shown that they may be so arranged as to produce but little obstructive influence on the diffusive flow of a gas when the total area of the apertures amounts only to about 10 per cent. of the area of the septum, and that nearly 40 per cent. of the full diffusive flow may be maintained when the number of the apertures is so far reduced as to represent an area of only 1.25 per cent. of the full area of the septum.

The explanation is to be found in the local intensification of the gradient of density in the immediate neighbourhood of the diaphragm, and which does not extend to the column away from the apertures. This disturbance of gradient is brought about by the rapid convergence of the lines of flux, and their divergence on the other side, with the consequent formation of a system of "density shells" over each aperture. A system of perforations of this kind may be compared with a system of conductors electrified to a common potential, the density of the diffusing substance above the apertures corresponding to electric potential, and the non-absorbing portions of the diaphragm to a surface formed by lines of electric force. Just as the electric capacity of a

plate is not much reduced by cutting most of it away, so also is it possible to block out a large portion of the cross-section of the diffusing column without materially altering the general static conditions on which the flow depends.

The importance of these results in relation to diffusion through porous septa is next considered, diffusion through a thin porous septum being only an extreme case of free diffusion through a multiperforate diaphragm, whose apertures are so far reduced in size as to materially interfere with the mass movement of the diffusing substance.

A section of the paper is devoted to the application of these new observations to the processes of gaseous and liquid diffusion in living plants, and it is pointed out that the structure of a typical herbaceous leaf illustrates in a striking manner all the physical properties of a multiperforate septum. Regarded from this point of view it is shown that the stomatal openings and their adjuncts constitute even a more perfect piece of mechanism than is required for the supply of carbon dioxide for the physiological needs of the plant, and instead of expressing surprise at the comparatively large amount of the gas which an assimilating leaf can take in from the air, we must in future rather wonder that the intake is not greater than it actually is.

From data afforded by actual measurements of the various parts of the stomatal apparatus of the sunflower it is shown that an extremely small difference of tension of the carbon dioxide within the leaf, as compared with that in the outer air, will produce a gradient sufficient to account for the observed intake during the most active assimilation.

It is also shown that the large amounts of water-vapour which pass out of the leaf by transpiration are well within the limits of diffusion, and that it is unnecessary to assume anything like mass movement in the outcoming vapour.

The translocation of solid material from cell to cell in the living plant is next considered, especially with reference to this transference, being, at any rate in part, brought about by means of the minute openings in the cell-walls through which the connecting threads of protoplasm pass. Notwithstanding the very small relative sectional area of these perforations, they probably exercise an important function in cell-to-cell diffusion, in virtue of their properties as multiperforate septa.

There are two appendices to the paper, one in which a full description is given of a series of experiments on the absorption of carbon dioxide by solutions of caustic alkali from air in movement; the second being devoted to a detailed description of the methods used for accurately determining the carbon dioxide absorbed.

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