

# Static Diffusion of Gases and Liquids in Relation to the Assimilation of Carbon and Translocation in Plants

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VIII. *Static Diffusion of Gases and Liquids in relation to the Assimilation of Carbon and Translocation in Plants.*

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DURING the course of an investigation which we have been carrying out in the Jodrell Laboratory during the past two or three years, with the ultimate object of extending our knowledge of the process of the fixation of carbon by green plants, we have been led to examine somewhat minutely the purely physical processes by which the carbon dioxide of the atmosphere is in the first place able to gain access to the active centres of assimilation. In following up this line of work we have been led to some unexpected results, and to the discovery of certain facts connected with gaseous and liquid diffusion which have been hitherto unnoticed, and which appear to be of considerable interest, not only in their physical aspects, but also from the explanations they suggest of certain natural processes in plants (and perhaps also in animals) in which the transference of gaseous or dissolved substances depends more or less on *diffusivity*.

In the present communication, which is intended to be one of a series descriptive of our researches, we shall, as far as possible, confine ourselves to the physical phenomena, touching only on the physiological questions in so far as they are necessary.

That the entry of atmospheric carbon dioxide into an assimilating leaf takes place by some process of *diffusion* has, as far as we know, never been seriously questioned; in fact, from what is known of the structure and function of the leaf, any other supposition, which would necessarily imply some form of mass movement of the inter-changing gases, is quite inconceivable. The discussion may therefore be limited to a consideration of whether the gaseous exchanges of assimilation and respiration are to be accounted for by some form of osmosis through the cuticle and epidermis of the leaf, or whether they are due in the first place to free diffusion through the open stomata with which the vast majority of the green organs of plants are so richly furnished.

With the exception of the work of GARREAU, who had already indicated as early as 1850\* that there was some sort of relation between the distribution of stomata and the evolution of carbon dioxide in the respiratory process, the experimental

\* 'Ann. Sci. Nat. (Bot.)' (3), 13, 321.

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evidence, up to 1895, appeared to be in favour of the exchange being independent of the stomatic openings.\* In that year F. F. BLACKMAN brought before this Society the results of an important investigation which once more directed attention to a subject which had been considered by most physiologists as definitely settled ('Phil. Trans.,' B, vol. 186 (1895), pp. 485 and 503).

It was shown, in the first place, that certain experiments on which BOUSSINGAULT had relied for proof of the efficacy of cuticular exchange were entirely inconclusive, owing to his having employed atmospheres charged with too large an amount of carbon dioxide. It is true that under these very artificial conditions an amount of carbon dioxide sufficient for the ordinary requirements of assimilation can pass across the cuticle and epidermis by osmosis, but it was left to BLACKMAN to show that for much lower tensions of  $\text{CO}_2$ , which are still considerably in excess of those of ordinary air, no appreciable diffusion of the gas into the leaf takes place if the stomates have been previously blocked.

Results of a much more positive kind were, however, obtained by the use of a delicate and ingenious apparatus which enabled BLACKMAN to determine the rate of the gaseous exchanges of the respiratory and assimilatory processes taking place on the two sides of a leaf on which the relative distribution of stomata is known. As regards the respiratory process, his results indicated a very remarkable degree of correspondence between the amount of carbon dioxide liberated by the two surfaces and the number of stomatic openings per unit of area of these same surfaces. By a modification of the experiments in which air artificially charged with small quantities of carbon dioxide was drawn simultaneously over the two sides of a leaf submitted to conditions favourable to assimilation, it was further shown that the abstraction of the carbon dioxide from the air stream and its ingress into the leaf was evidently related to the distribution of stomata, although in this respect the correspondence, owing to the very minute quantity of gas dealt with, was not so well marked as in the process of respiration.†

The general conclusions drawn by BLACKMAN are that, under normal conditions, osmosis through the cuticle and epidermis does not play any appreciable part in the gaseous exchanges of a respiring or assimilating leaf, and that "practically the sole pathway of carbon dioxide into or out of the leaf is by the stomata," that is to say, by a process of free diffusion through open apertures.

Convincing as these experiments appeared to be in themselves, certain physical considerations, to which we shall presently refer, rendered it difficult to accept without reserve the conclusions which were drawn from them, and it was therefore

\* A good critical *résumé* of the state of our knowledge of these questions up to 1895 will be found in BLACKMAN's paper, 'Phil. Trans.,' B, vol. 186, p. 503.

† We are informed by Mr. BLACKMAN that since the publication of his paper of 1895 he has succeeded in obtaining with his apparatus much more satisfactory evidence of the correspondence of the ingress of the carbon dioxide with the distribution of stomata on the two sides of the leaf.

deemed expedient, in the first place, to repeat BLACKMAN's experiments in a somewhat different form. For this purpose we used an apparatus which had been constructed for an extended series of observations on the assimilatory and respiratory processes of plants.

A full description of this apparatus, and of the detailed results obtained with it, will be given in a subsequent communication.

For this particular purpose it was so arranged that comparatively large volumes of air of known carbon dioxide content were passed simultaneously and separately over the two sides of an assimilating or respiring leaf, the amount of the gas being again determined in the outgoing air stream by passing it through a solution of caustic soda in a Reiset apparatus. A very accurate method for determining the carbon dioxide absorbed by the alkali was adopted, which will be found described in the second Appendix to this paper.

It will be noticed that in principle, though not in details, the process resembled that carried out by BLACKMAN, but larger areas of leaf surface could be employed, and the actual amounts of carbon dioxide dealt with were much greater.

The general results arrived at were as follows :—

- (1) If the leaf is *hypostomatous* the respiratory and assimilatory exchanges of gases take place only through the *lower* side of the leaf, that is to say, through the side to which the stomatic openings are confined.
- (2) If the leaf is *hyperstomatous* the exchanges take place only through the *upper* side, *i.e.*, the side which is alone furnished with stomata.
- (3) In *amphistomatous* leaves, that is, in leaves furnished with stomata on *both* sides, respiratory and assimilatory exchanges are carried on by both surfaces of the leaf.
- (4) In the last-mentioned case the respiratory egress and assimilatory ingress of the dilute atmospheric carbon dioxide bear a rough quantitative relation to the distribution of stomata on the two leaf surfaces; but during assimilation in bright sunlight there is a greater intake of carbon dioxide into the upper leaf surface than would be expected from a mere consideration of the ratio of distribution of stomata on the two sides. In light of a less degree of intensity there is a nearer approach to a correspondence of the assimilatory and stomatic ratios, but it is seldom a very close one.

It will be observed that our general conclusions confirm in all essential points those of BLACKMAN, so that if we further take into consideration the impermeability of the cuticle and epidermis of leaves to carbon dioxide of low tension, the evidence is most strongly in favour of his generalisation that the "sole pathway of carbon dioxide into or out of the leaf is by the stomata." This view of course implies that the gaseous exchanges are brought about solely by *free diffusion*, an explanation which can only be accepted unreservedly if it can be shown that interdiffusion of



carbon dioxide and air can take place through apertures like those of the stomata with sufficient rapidity to account for the result.

The difficulties in accepting free diffusion as the true explanation of the intake of carbon dioxide appear at first sight very formidable, if we take into consideration (1) the comparatively large amount of carbon dioxide absorbed by a given area of a leaf in active assimilation; (2) the extremely low partial pressure of carbon dioxide in the atmosphere, amounting in the ordinary way only to 2·8 parts per 10,000; and (3) the very small relation which the area of the stomatic openings bears to the area of the leaf surface on which they are distributed.

As a concrete example we will take the case of a leaf with which we have done a considerable amount of work, that of *Catalpa bignonioides*, in which we have carefully determined both the number of the stomata (which here occur only on the lower surface) and the area of the stomatal slits when fully opened. This leaf, when placed under favourable conditions for assimilation, can abstract from ordinary air containing three parts of CO<sub>2</sub> per 10,000, about ·07 cub. centim. of carbon dioxide (measured at 0° and 760 millims. bar.) per square centim. of leaf surface per hour. The stomatal slits when fully open have an area of ·0000618 square millim.,\* and since there are 145 of them on each square millim. of leaf, the area of the stomatal openings only represents ·9 per cent. of the total surface of the leaf on which they occur. It follows from this that if we regard the whole of the carbon dioxide as entering the leaf through these openings, diffusion must take place through them at the rate of  $\frac{100 \times \cdot 07}{\cdot 9} = 7\cdot77$  cub. centims. per square centim. per hour. Now it will be seen

later on that the surface of a strong solution of caustic soda, when freely exposed to moderately still air containing the normal amount of carbon dioxide (three parts per 10,000 by volume), absorbs that gas at ordinary temperatures at the rate of only about ·120 cub. centim. per square centim. per hour, and when the rate of the air current passing over the surface is increased the maximum absorption is found to be ·177 cub. centim. per square centim. per hour. It follows, therefore, that the absorption of atmospheric carbon dioxide by the whole of the under surface of an assimilating leaf like that of the *Catalpa*, must proceed at about one-half the rate which the same absorptive surface of leaf would possess if it were covered with a constantly renewed film of a solution of caustic alkali: we may say, in fact, that the coefficient of absorption of the leaf surface under these conditions is about half that of the surface of the alkaline solution. If, however, we assume that the absorption of carbon dioxide in the leaf takes place only through the stomatal openings—which occupy at the outside not more than ·9 per cent. of this leaf area—we arrive at the

\* The average measurements of a large number of stomatal slits, which are elliptical in shape, gave a length (L) of ·01861 millim. and a breadth (B) of ·00423. The area of the slit is given with sufficient approximation by the expression  $LB\frac{\pi}{4}$ , which in this case is ·0000618 sq. millim. This is equal in area to a circle of ·0088 millim. diameter.

somewhat remarkable conclusion that during assimilation the absorption per unit area of these openings must be from 43 to 64 times as fast as the absorption of a unit area of a freely exposed solution of caustic alkali. In other words, under the natural conditions of assimilation the stomatal openings, supposing them alone to be operative, must take in carbon dioxide from the air about 50 times as fast as they would do supposing it were possible to fill them with a constantly renewed solution of caustic alkali.

A consideration of such facts as these leads us to demand more evidence before we can unreservedly accept the proposition that the gaseous exchanges of assimilation take place exclusively through the fine openings of the leaf stomata. It is, in fact, imperative to demonstrate beyond all doubt that such a view is in no way inconsistent with the known or ascertainable properties of carbon dioxide and air, as regards their powers of *interdiffusion* under conditions comparable with those existing in the living leaf.

In its simplest form the problem resolves itself into a study of the free diffusion of very dilute carbon dioxide through small apertures of known dimensions, opening out into an internal space whose limiting walls are more or less absorbent of the gas, and expose a surface which is very large compared with the area of the apertures.

The investigation of this question has carried us much farther than we originally anticipated, and has necessitated a careful study of diffusive phenomena generally, and especially of *static diffusion*; whilst it has led us to certain important conclusions as to the remarkable influence exerted by perforated septa on the diffusive flow of gases and liquids generally.

GRAHAM, as is well known, first determined the *relative velocities* with which gases diffuse into each other through an intervening *porous septum*, and demonstrated the simple law which expresses the relation of these velocities to the respective densities of the mixing gases. He clearly saw, however, that the *absolute* velocity of diffusion could only be ascertained by allowing the gases to mix through a wide opening, by what is now known as *free diffusion*.

The experiments which he made in this direction were apparently few in number, and were confined to the interdiffusion of carbon dioxide and air, and hydrogen and air. They are described very briefly in the concluding section of his paper on the "Molecular Mobility of Gases" ('Phil. Trans.,' 1863, 385), entitled "Interdiffusion of Gases without an Intervening Septum." The experiments were made by filling the lower tenth of a cylindrical jar with carbon dioxide, and determining after the lapse of a definite time the amount of that gas contained in the upper tenth drawn from the top of the jar. When hydrogen was employed the jar was of course inverted. Beyond showing that a portion of the carbon dioxide can diffuse through air at the rate of 7·3 centims. per minute, whilst a sensible portion of hydrogen travels at the rate of 35 centims. in the same time, or about five times as fast, these experiments did not lead very far, and the numerical results do not lend themselves

to a determination with any degree of accuracy of the absolute values of inter-diffusion: they formed, however, a starting-point for LOSCHMIDT, who, in 1870, gave an account of an elaborate research on the interdiffusivity of gases when no porous septum intervenes. 'Wien. Akad. Ber.,' 61 (Abtheil. 2), (1870), 367; *ibid.*, 62 (Abtheil. 2), 468.

LOSCHMIDT employed a tube of 97.5 centims. in length and 2.6 centims. in diameter, closed at the ends and capable of being separated into two halves, which could, at will be connected through a carefully made screw-valve opening to the full diameter of the tube. The two halves of the tube, after being filled with the purified and dried gases at an equal pressure, were brought together in a vertical position, with the denser gas below. Communication was then established between the two halves of the tube by opening the screw-valve, and after a certain time this was again closed, and the mixtures of gases in the two halves were analysed.

If the vertical tubes are of no great height and the gases are at equal pressures and temperatures, and can only move in a vertical direction  $x$ , the partial pressure  $p_1$  of the one gas in height  $x$  and time  $t$ , satisfies the partial differential equation

$$\frac{dp_1}{dt} = k \frac{d^2 p_1}{dx^2},$$

where  $k$ , which under certain defined conditions is constant for any pair of gases, represents the *coefficient of diffusion* or *diffusivity*, and measures the speed with which the one gas penetrates the other.

If we take the centimetre, gramme, and second as units, then  $k$  may be defined as the mass of gas which passes in one second of time across a section of 1 square centim. in area when the variation of density of the gas across such a section is unity per centim. of length.

It is sometimes more convenient to regard  $k$  as representing the number of cub. centims. of the gas, measured at the temperature of the experiment, which will pass across a section of 1 square centim. in area when the fall of pressure is 1 atmosphere in 1 centim. The two expressions are identical if  $g$ , the acceleration due to gravity, is constant.

LOSCHMIDT determined the value of  $k$  in *absolute units*\* for a considerable number of pairs of gases. He found that the diffusivity coefficient was in all cases approximately inversely proportional to the geometrical means of the molecular weights, when the gases were under one atmosphere of pressure, so that if we denote the molecular weights of the constituent gases of any pair by  $m_1, m_2$ , then  $k \propto (\sqrt{m_1 \cdot m_2})$

\* LOSCHMIDT expressed  $k$  in  $\frac{\text{square metre}}{\text{hour}}$  units, so that his values represent the number of cubic metres of the gas at 0° C. and 760 millims. pressure which would pass per hour across a section of 1 square metre of area when the gradient of density varies by 1 atmosphere in a length of 1 metre. To convert LOSCHMIDT'S values into ordinary C.G.S. units they must be multiplied by 2.77.

is nearly constant if the gases have no chemical action on each other. This law is in harmony with the kinetic theory, from which in fact it is deducible.

$k$  was also found by LOSCHMIDT to vary inversely as the pressure  $p$  of the inter-diffusing gases, and directly as the square of the *absolute* temperature, so that

$$k^{\circ} = k \left( \frac{T^{\circ}}{T} \right)^2 \cdot \frac{760}{p},$$

where  $k^{\circ}$  represents the diffusivity at  $0^{\circ}$  C. and 760 millims. bar. ; and  $T^{\circ}$  and  $T$  the temperatures on the absolute scale.\*

For the combination carbon dioxide + air, which is the important one for our purpose, LOSCHMIDT found  $k^{\circ} = \cdot 1423$ .

Whether  $k$  as ordinarily defined is a true physical constant, or is subject to variation with the ratio of the mixture of the interdiffusing gases, has occupied the attention of several physicists, and is a subject of considerable importance in the present inquiry, where we are dealing with the diffusive flow of atmospheric carbon dioxide whose dilution is excessively great.

O. E. MAYER, in his 'Kinetic Theory of Gases,' in deducing the theoretical formula of diffusion from the kinetic considerations of MAXWELL and STEFAN, showed that whilst theory is in accordance with observation in so far as the influence of temperature and pressure of the mixture are concerned, the formula also leads to the conclusion that the value of  $k$  should vary with the number of the molecules of one or the other kind of gas in unit volume of the mixture, and that  $k$  "therefore assumes a different value at every different place in the mixture that is being formed by the diffusion," and that the observed coefficients will not perfectly agree if they are deduced from observations made with unequal ratios of mixture.

This important problem has been attacked experimentally by WAITZ, VON OBERMAYER, and WINKELMANN.

WAITZ ('Ann. Phys. Chem.,' 17 (1882), 201), in working with carbon dioxide and air determined the extent of the mixing of the two gases in various parts of the column by means of a JAMIN's interference refractometer, and found that the values of  $k$  sensibly increased with the ratio of the mixture. He obtained the following results at different heights of the column.

$$k_0 \cdot 12887, \quad k_1 \cdot 13107, \quad k_2 \cdot 13326, \quad k_3 \cdot 13660$$

VON OBERMAYER ('Wien. Akad. Ber.,' vol. 85 (Abtheil. 2), pp. 147 and 748 ; *ibid.*, vol. 87, p. 188) having found values for the coefficients of diffusion which differed from LOSCHMIDT's more than could be accounted for by errors of observation, repeated the experiments with a new form of apparatus suggested by STEFAN's work on the diffusivity of the vapours of liquids. He found that  $k$  increased somewhat

\* The temperature variant  $(T^{\circ}/T)^2$  is almost strictly correct for the carbon dioxide and air, but v. OBERMAYER has found that the exponent for most other gases differs widely from 2. 'Wien. Akad. Ber.,' 1880, vol. 81 (Abtheil. 2), p. 1102.



with the duration of the experiment, so that here again an increased ratio of mixture of the gases resulted in a slight but sensible variation of the coefficient in the same direction as indicated by WAITZ's experiments.

VON OBERMAYER's values for carbon dioxide and air, given in the second paper cited above, and reduced to C.G.S. units, are as follows :—\*

Duration of diffusion.	$k^\circ$ .
10 minutes . . . . .	·1299
15 „ . . . . .	·1320
40—45 „ . . . . .	·1337
1 hour . . . . .	·1348

In all attempts hitherto made to determine the interdiffusivity of gases, these were initially at *equal pressure*, and therefore contained an equal number of molecules in equal volumes, so that the one gas had to diffuse against an equal and opposite flow of the other. This is a totally distinct set of conditions from those of the problem before us, where we require to investigate the rate of the diffusive flow of carbon dioxide of very low initial pressure down a stationary column of air on its way to an absorbent surface. The new conditions are in fact practically the same as those referred to by HAUSMANINGER and by O. E. MAYER (see MAYER's 'Kinetic Theory of Gases,' Engl. ed., 1899, p. 267), who state that in order to more fully elucidate the theory of diffusion we require to determine the value of  $k$  in gaseous mixtures containing only small masses of one of the constituents.

Let us, in the first instance, imagine a vertical cylinder filled with ordinary air at a perfectly uniform temperature and of exactly the same composition as that of the outside atmosphere, the length of the cylinder being such as to cause no appreciable difference in the density of the air column. If we regard any plane surface within the enclosed air it follows from the kinetic theory that in a given time the same average number of carbon dioxide molecules will cross this plane in opposite directions, and there will, consequently, be no change in the average distribution of the gases throughout the cylinder.

Now let us imagine that the bottom of the cylinder is suddenly made capable of absorbing carbon dioxide. The molecules of the gas which now strike the bottom of the cylinder during the first very small interval of time, will be wholly or partially trapped, according to the more or less perfect absorptive power of the surface, and a very thin stratum of air, parallel to and immediately above the absorbing surface, will become partly depleted of its carbon dioxide.

\* These small differences in the value of  $k^\circ$  found in the same series of experiments no doubt denote slight variation with the ratio of mixture. But from a comparison of the actual values of  $k$  obtained by different observers it is evident that they have no real significance beyond the second decimal place.

If we now consider the interchange of carbon dioxide which takes place between this partially depleted layer and the one of equal thickness immediately above it, it is manifest that in a given interval of time a larger number of  $\text{CO}_2$  molecules must pass from the higher to the lower stratum than from the lower to the higher, the "balance of exchange" being consequently in favour of the lower layer. This condition will be rapidly and continuously propagated from below upwards, and, providing the air immediately outside the cylinder is maintained of uniform composition, and the air within the cylinder is perfectly free from convection and thermal currents, a *static condition* will soon be established in the column. When this has been attained we may regard the uncompensated balances of exchange between any contiguous layers in the cylinder as constituting a steady *flux* or *drift* of carbon dioxide in the direction of the axis of the cylinder from the outer air to the absorbent surface.

By adopting a simple mental device of this kind we can avoid the necessity of constantly referring all the observed facts to the kinetic exchange of particles between the contiguous layers of the gases, and so enormously simplify a study of the phenomena of static diffusion, which now become capable of simple mathematical treatment similar to that employed for investigating the "flow" of heat in a bar after 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.

When static diffusion is established under the conditions mentioned above, the following statements will hold good:—

- (1) The same quantity (mass) of carbon dioxide will pass through every cross-section of the column in a given time.
- (2) The quantity (mass) of the gas flowing down columns of equal length and equal cross-section, in equal times, will be directly proportional to the difference of the partial pressures of the carbon dioxide at the mouth of the cylinder and immediately above the absorbing surface. This can be verified by experiment.
- (3) For equal differences of partial pressure of carbon dioxide at the two ends of the column the flow will be inversely proportional to the *length* of the column,\* when all other conditions are the same. This deduction can also be experimentally verified, as will be shown later on.
- (4) When the area of the absorbing surface is the same as that of the cross-section of the column, the amount of gas absorbed will be proportional to that area, and also to the *time*, provided the absorbent is a perfect one, or that its absorbing power varies directly with the pressure of the carbon dioxide at the limiting surface of the gas and the absorbent.

\* It is assumed that the composition of the air is maintained constant by a slow stream flowing across the mouth of the cylinder. If the outer air is *perfectly still* a small correction has to be applied to the length of the column, the nature of which will be explained later on.

The following is the general expression for such a condition of static diffusion as we are considering, where  $Q$  represents the amount of carbon dioxide flowing down the cylinder towards the absorptive surface,  $A$  the area of the cross-section,  $L$  the length of the column,  $t$  the time, and  $\rho$  and  $\rho_1$  the density or partial pressure of carbon dioxide in the outer air and at the surface of the absorbent respectively.

$$Q = k \frac{\rho - \rho_1}{L} A \cdot t,$$

$k$  being the diffusivity constant of carbon dioxide and air.

$\frac{\rho - \rho_1}{L}$  is the "gradient of density" or "concentration gradient" of the carbon dioxide, and this must be constant for unit thickness of any two contiguous layers taken at right angles to the axis of the cylinder.

When we are dealing with a *perfect absorbent*, the density  $\rho_1$  at the immediate surface of the absorbing layer is *zero*, and the gradient of density then becomes  $\frac{\rho}{L}$ . If we take  $r$  to represent this value for a layer of unit thickness, then for unit area and unit time,

$$Q = kr.$$

That is to say, the mass of carbon dioxide absorbed by unit area of the absorbing surface in unit of time is represented by a constant  $\times$  gradient of density.\*

We are not aware that any attempt has hitherto been made to investigate the diffusivity of a *gas* by the static method, but this is not surprising, since the conditions rendering such an investigation possible are of comparatively rare occurrence, as it is necessary for one of the gases to be present in the mixture in a small proportion only, and to find an absorbent which will both rapidly remove the rarer constituent and admit of its subsequent determination.

But although this particular kind of gaseous diffusion, which is one in constant operation in nature, has not been dealt with experimentally, the exactly converse problem of the behaviour of the vapour escaping from an evaporative surface of liquid has received a certain amount of attention from mathematical physicists.

STEFAN in 1873 ('Wien. Akad. Ber.', vol. 68 (1873), 385) was the first to investigate experimentally and theoretically the rate of evaporation of a liquid in a tube whose open end is in free communication with the outer air, and he demonstrated that the theory of the diffusion of gases is strictly applicable to a case of this kind.

STEFAN'S experiments were made with *ether* evaporating into free air from tubes

\* Since equal masses of carbon dioxide must pass every cross-section of such a cylinder in equal times, and the density of the gas diminishes uniformly from layer to layer as we go downwards in arithmetical progression, it follows that the *velocity of the molecular drift* of the carbon dioxide must vary inversely with its density. The velocity here referred to is of course that of the uncompensated resultant movement of the molecules along the line of diffusive flow, against the resistance exerted by the air molecules.

having a diameter of .64 millim. and 6.16 millims. He summarises his results as follows :—

- (1) When the steady condition has been established, the rate of evaporation is inversely proportional to the distance of the surface of the liquid from the open end of the tube, providing, in such tubes as he used, this distance is not less than 10 millims.
- (2) The rate of evaporation is independent of the diameter of the tube ; that is to say, evaporation is directly proportional to the *area* of the liquid surface exposed.
- (3) The rate of evaporation increases with the temperature, and is proportional to the logarithm of a fraction whose numerator is the atmospheric pressure at the time of the experiment, and whose denominator is this same air pressure diminished by the maximum pressure of the vapour. This value is represented by  $\log \frac{P}{P - p}$ , where  $P$  is the atmospheric pressure, and  $p$  the maximum vapour pressure corresponding to the temperature of observation.

In a later paper ('Wien. Akad. Ber.,' vol. 83 (1881), Abtheil. 2, p. 613), to which we shall again have occasion to refer, STEFAN shows that the theory of gaseous diffusion of gases is strictly applicable in such a case as above, if the liquid has a plane surface, and the partial pressure of the vapour is identical at all points of the cross-section of the open end of the tube. When the static condition is attained, the same amount of vapour passes through each cross-section of the tube in unit time, and this amount is proportional to the area of cross-section. He expresses the rate of evaporation by the general formula

$$V = \frac{k}{h} \log \frac{P - p''}{P - p'},$$

where  $V$  is the amount of liquid evaporated in unit time from a unit area of the liquid surface ;  $P$  the combined pressure of the gas and vapour, which is the same inside and outside the tube ;  $p'$  and  $p''$  the partial pressure of the vapour at the surface of the liquid and at the free end of the tube respectively ; and  $h$  the distance of the surface of the liquid from the open end of the tube.

The principles laid down by STEFAN were applied by WINKELMANN for determining the diffusive coefficients of vapours in different gases, and he described his results in detail in a series of papers from 1884 to 1886. ('Wied. Ann.,' vol. 22 (1884), p. 1 ; *ibid.*, vol. 23, p. 203 ; *ibid.*, vol. 26 (1885), p. 105 ; *ibid.*, vol. 27 (1886), p. 479.)

The static diffusion of soluble substances through their liquid solvents was investigated by FICK in 1855 ('Pogg. Ann.,' vol. 94, p. 59, and 'Phil. Mag.' (4), vol. 10,



p. 30), who showed for the first time that the formulæ of FOURIER for the steady conduction of heat in solid conductors are applicable to diffusion phenomena.

These results, and also those of GRAHAM, have been minutely discussed by STEFAN from the mathematical standpoint ('Wien. Akad. Ber.,' vol. 78 [2], 957; *ibid.*, vol. 79 [2], 161).

The initial stages of the assimilation of carbon by green plants must depend in the first instance on the purely physical process of *static diffusion*, no matter whether we regard this process as being carried on exclusively by the leaf stomata, or in part by the stomata and in part by osmosis through the cuticle and epiderm. We have already seen that there are reasons, both experimental and theoretical, for regarding the interdiffusivity of carbon dioxide and air as varying with the ratio of mixture of the two gases; and since the natural processes must necessarily be carried on with a ratio of mixture of carbon dioxide and air far removed from any ratios of mixture hitherto investigated, it becomes a matter of considerable importance to ascertain if the diffusivity of carbon dioxide, in the high state of dilution in which it occurs in the atmosphere, departs materially from the value ordinarily assigned to it. We have attempted to answer this question experimentally by employing a process of free static diffusion down tubes of definite dimensions which were so arranged as to be absorptive at one end.

Before we could hope to attain to any reasonable degree of success in this direction, it was necessary to satisfy the following conditions of experiment:—

- (1) We must have at the bottom of the diffusion tube either a perfect absorber of carbon dioxide, that is to say, one which will maintain a *zero* pressure immediately above it, so that the velocity of flow along the tube is at a maximum, and is only limited by the "resistance" of the air column; or, if the absorbent is not a perfect one, we must know sufficiently about its powers in this direction to be able to determine the partial pressure of the carbon dioxide in the immediate neighbourhood of its surface.
- (2) We must have some extremely accurate method for determining the absorbed carbon dioxide.
- (3) The diffusion tube must be kept perfectly free from convection currents.
- (4) We must know very accurately the mean pressure of the carbon dioxide in the outer air during the experiment.

With regard to (1) we have found that a normal solution of sodium hydroxide may be employed as an absorbing medium under certain special conditions.

Our experiments on the absorbing power which such solutions exercise on a stream of air rapidly moving over its surface are described in Appendix I. to this paper, and the results are such as to suggest that even in diffusion tubes of considerable length, the absorption may probably not keep pace with the diffusive flow if the

area of surface exposed by the liquid is only equal to that of the cross-section of the tube.

We can, however, remove this objection by considerably enlarging the diffusion tube at the bottom, so that the surface of the exposed solution is considerably greater than its area of cross-section, and so increase the power of absorption until the maximum rate of diffusive flow of the carbon dioxide down the tube is attained. The most convenient method for carrying this out is to attach to the bottom of the diffusion tube a specially constructed flask, having a neck of about 7·0 centims. in length, and of exactly the same diameter as that of the diffusion tube, *i.e.*, about 2 centims. The solution of caustic soda is placed in the flask, and exposes a surface of from 20 to 25 times the area of the neck of the tube. The result of this arrangement is to reduce the partial pressure of the carbon dioxide in the air of the flask to so low a point as to ensure a steady flow of the gas down the tube at a rate which is only limited by its diffusivity. Thus the effect is the same as would be induced by the presence of a perfectly absorbent surface at the bottom of a straight-sided tube having a length equal to that of the diffusion tube, *plus* a certain correction due to the flask.

If the value of  $k$  is already known, this correction for the flask, which we may term its "straight-tube equivalent," may be determined by noting the amount of carbon dioxide absorbed under known conditions by the flask without any tube attached. If we denote the straight-tube equivalent by  $x$ , the amount of the gas passing 1 square centim. of the cross-section of the neck in unit time by  $Q$ , and the density of the  $\text{CO}_2$  in the outer air by  $\rho$ , then

$$x = \frac{k\rho}{Q}.$$

But in the case before us,  $k$  and  $x$  are both unknown, so that we must proceed in a different manner.

Two exactly similar flasks are taken, containing equal volumes of the absorptive solution, and to the neck of one of these is attached a tube of known length and of the same diameter as the neck, the other flask remaining as it was.\* The amount of carbon dioxide absorbed from the air in a given time is noted in each case, the conditions of exposure being similar. If  $Q$  denotes the quantity absorbed by the flask alone,  $Q_1$  the amount absorbed in the case where the tube is attached, and  $L$  the length of the tube, then the straight-tube equivalent of the flask,  $x$ , is determinable from the equation

$$x = \frac{Q_1(L + x)}{Q}.$$

\* In order to reduce the difficulties due to convection currents, we have generally determined the straight-tube equivalent from two simultaneous experiments made with a long and a short tube attached to the flask and bent at right angles, thus avoiding the use of the open flask.

When the straight-tube equivalent of a flask is once determined, this value can always be applied as a correction for the length of the attached diffusion tube. With the particular form of flask we have used the correction, determined from the average of a large number of experiments, closely approximates to the length of the neck. The reason for this will be more apparent later on.

(2) Since the actual amounts of carbon dioxide which have to be estimated in the absorbent liquid are necessarily small, the success of any method of diffusion of this kind must largely depend on the degree of accuracy with which such determinations can be made. This has been a subject for long and laborious investigation, and in Appendix II. to this paper we have described in detail a method which admits of any required refinement of accuracy in this direction. It is one which has the great advantage of being independent of any determination of the total acid equivalent of the alkali, either at the beginning or end of the process, so that there are no cumulative and other sources of error such as there are when we have to determine a small difference between two large values.

(3) As might be expected when experiments on diffusion have to be carried on under the prescribed conditions for a considerable time (often amounting to several days or even weeks), one of the principal difficulties encountered is that due to *convection currents* in the diffusion tube. It will be readily seen that this difficulty increases with the length of the tube, for since the diffusion flow towards the absorbent surface, and consequently the amount of  $\text{CO}_2$  absorbed in a given time, varies inversely as the length of the tube, a given amount of convection will introduce a much larger percentage error in the determination of  $k$  made with long than with short tubes. The possible influence of convection in a tube of 100 centims. in length and 2 centims. in diameter will be seen from the following considerations. In such a tube, assuming LOSCHMIDT's value for  $k$  to be correct, the amount of carbon dioxide which could reach the absorptive surface at the bottom of the tube by static diffusion from an atmosphere containing the normal amount of that gas would be '0048 cub. centim. per hour, measured at  $0^\circ \text{C.}$ , and 760 millim. bar. Now this amount could also be supplied to the absorbent by a current of air circulating from top to bottom of the tube at a rate of only a little more than 2.0 millims. per minute; so that a convection current of this low velocity of flow would result in doubling the apparent value of the coefficient of the diffusion.

In order to avoid sources of error of this kind, the experiments were carried on in a room which was maintained at a very constant temperature, every precaution being taken to keep the air as still as possible; and it was also found necessary to reduce the diameter of the tubes to about 2 centims. When straight upright diffusion tubes are used, there is always some risk of slow currents being produced by slight differences of temperature in the column induced by the evaporation of liquid at the bottom of the tube, and besides this, such an arrangement seemed open to another objection to which reference must be made. During the static diffusion of

the carbon dioxide, the amount of this gas decreases progressively from the mouth of the tube to the absorbing surface, and it did not seem improbable that, notwithstanding the very low initial pressure of the gas, this diminution in density from the top to the bottom might, under the action of gravity, result in a sufficient amount of instability in the column of the diffusing gas to produce a greater flow towards the absorbent than is due to diffusion only. Comparative experiments made with upright tubes and with a tube bent vertically downwards, and containing the absorbent liquid in the shorter limb, indicated that any error introduced by instability of the column must be very small. In all our later experiments we have made use of *horizontal* diffusion tubes connected with the absorbing flasks by short right-angled bends. With this arrangement there is much less risk of disturbance, either from ordinary convection currents or from any possible instability of the diffusing column of gas such as might arise in a vertical tube.

(4) For a determination of the partial pressure of the carbon dioxide in the outer atmosphere during the experiments, large and accurately measured volumes of air were aspirated through a Reiset apparatus containing a solution of caustic soda, in which the absorbed gas was afterwards estimated. A full description of this process, which we have employed very extensively in our work on plant assimilation, will find its place in a subsequent communication.

*Determination of the Diffusivity of Atmospheric Carbon Dioxide by Static Diffusion down Tubes towards an Absorptive Surface.*

When straight cylindrical tubes of different lengths are made absorbent of carbon dioxide at the bottom by solutions of caustic soda, it may be shown that, for equal pressures of the gas in the outer air, the rate of flow of the carbon dioxide across unit area of cross-section is inversely proportional to the length of the tubes.

In order to verify this two diffusion tubes, having the dimensions given below, and constructed in a very similar manner to burettes, were filled through side tubes up to a certain mark, whose distance from the mouth of the tube was accurately known, with a normal solution of sodium hydroxide, in which the amount of pre-existing carbonate had been determined by the double titration process of Appendix II.

At the close of the experiment the tubes were emptied with all due precautions, and the carbonate again determined by the same process.\* The experiments were carried on in a room maintained at a uniform temperature and with all possible precautions to avoid convection. The results are given below :—

\* It must be understood that in all these and subsequent experiments extreme precautions were taken to prevent any access of atmospheric  $\text{CO}_2$  to the alkaline solution except such as reached it during the diffusion process. It is unnecessary to specify what the precautions were in order to avoid absorption during the transference of the liquid, since they are such as would suggest themselves to anyone working on such a subject.



TABLE I.

Tube.	Length.	Diam-eter.	Area of cross-section.	Duration of ex-periment in hours.	CO <sub>2</sub> in air, parts per 10,000.	CO <sub>2</sub> diffused.		Ratios of CO <sub>2</sub> dif-fused per unit area of cross-section.	Inverse ratios of lengths of tubes.
						Total in cub. centims. at 0 and 760 millims.	Per sq. centim. per hour $Q_v^\circ$ .		
(1)	centims. 109·75	centims. 2·35	sq. centims. 4·337	404·8	3·27	3·970	cub. centims. ·00226	1·00	1·00
(2)	39·9	2·37	4·411	404·4	3·27	9·616	·00538	2·38	2·74

Another experiment on similar lines gave the following results. No. (3) was made with a tube bent vertically downwards, whilst (4) and (5) were upright tubes :—

(3)	59·3	2·35	4·337	477·1	3·39	6·448	·003116	1·00	1·00
(4)	120·3	2·35	4·337	479·9	3·39	3·006	·001444	0·46	0·49
(5)	40·0	2·37	4·411	477·5	3·39	10·625	·005044	1·62	1·48

These experiments, indicating as they do a variation in the diffusive flow which is inversely proportional to the length of the column, demonstrate the accuracy of the general expression already given for the static diffusion of a gas down a tube (see p. 232).

$$Q = \frac{k(\rho - \rho_1) A \cdot t}{L}.$$

They also show that the value of  $\rho_1$ , the density of the carbon dioxide at the immediate surface of the absorbent, must either be *zero*, corresponding to perfect absorption, or if  $\rho_1$  has a sensible value, this, too, must vary inversely with the length of the column.

The experiments described in Appendix I. on the absorption of alkaline surfaces exposed to a moving current of air, show that under those particular conditions absorption and density of CO<sub>2</sub> are proportional, so that there is some probability that in these tube experiments a similar relation may exist which would account for the diffusive flow being in the inverse proportion of the length of column, even if the absorption were not perfect.

If the absorption of the alkaline solution is imperfect  $\rho_1$  will have a sensible value, and under these circumstances the value of  $k$  will be lower than it should be, when all other errors incident to the method are avoided.

Experiments (3), (4), and (5) in the last table may be used for obtaining a first approximation to  $k$  for atmospheric CO<sub>2</sub>.

The mean temperature of the air of the room during the 20 days the experiments lasted was  $6^{\circ}\cdot6$  C., and the mean height of the barometer 758·8 millims., whilst the mean content of  $\text{CO}_2$  was 3·39 parts per 10,000.

The diffusivity,  $k^{\circ}$ , of the atmospheric carbon dioxide at  $0^{\circ}$  C., in C.G.S. units, is obtained from the equation :—

$$k^{\circ} = \frac{Qv \cdot L \cdot 760}{3600 \rho \cdot p} \cdot \left(\frac{T^{\circ}}{T}\right)^2,$$

in which

$Qv$  = the number of cub. centims. of  $\text{CO}_2$ , *measured at the mean temperature and pressure of the experiment*, which passes across a *square centim.* of the cross-section of the tube in *one hour*.

$\rho$  = the volume of  $\text{CO}_2$  contained in unit volume of air.

$L$  = the length of the tube in centims.

$T^{\circ}$  = the zero of absolute temperature.

$T$  = the mean temperature during the experiment, expressed on the absolute scale.

$p$  = the mean barometric pressure in millims. of mercury.

The following are the actual values of  $k^{\circ}$  given by Experiments (3), (4), and (5)—

	$Qv$ .	$k^{\circ}$ .
(3)	·003196	·155
(4)	·001478	·145
(5)	·005174	·169
		<hr/>
Mean . . . .		·156
		<hr/>

In another experiment with a vertical tube of 39·9 centims. in length and 2·37 centims. diameter diffusion was carried on for 404·4 hours, in an atmosphere with a mean  $\text{CO}_2$  content of 3·27 parts per 10,000, the mean temperature being  $12^{\circ}\cdot8$  C.

This gave the following values :—

$$(6) \quad \begin{aligned} Qv &= \cdot00563 \\ k^{\circ} &= \cdot174 \end{aligned}$$

The conditions of unstable equilibrium already referred to may to some slight extent affect Experiments (4), (5), and (6), since they were made with vertical tubes, but the same objection does not apply to (3), in which the tube for the greater part of its length was bent downwards. All the results would, however, be affected if the absorption were not perfect, for then the value of  $p_1$  at the surface of the liquid would be appreciable, and the flow of carbon dioxide down the tube would not attain its maximum value, which is conditioned by its diffusivity.

In the next series of experiments we attempted to meet these objections by using *horizontal* diffusion tubes which were connected with flasks exposing a surface of the

alkaline solution from 20 to 25 times greater than the area of cross-section of the tube, as described on p. 235. In this manner we have good reason to believe that practically perfect absorption is ensured, and the amount of flow of the  $\text{CO}_2$  is limited merely by its diffusivity.

The absorption flasks each contained 200 centims. of a 4·24 per cent. solution of caustic soda, in which the amount of carbonate at the commencement of each experiment was most accurately known, and the horizontal diffusion tubes were connected with their necks through short bends. Each experiment lasted from two to three weeks, and was carried on in a room with a northern aspect, specially set aside for the purpose, and where there was but little variation of temperature, and an almost perfect freedom from air currents.

All the extreme precautions were taken which had been suggested by several months of preliminary work, the laborious part of the process consisting in the frequent determinations of the carbon dioxide in the air of the room, which were necessary in order to obtain an accurate estimate of the mean tension of that gas throughout the experiment. This was effected by drawing a slow current of air from the immediate neighbourhood of the apparatus through a Reiset tower placed in an adjoining apartment. A much more ready way of ascertaining the mean content of the  $\text{CO}_2$  of the air in experiments of this kind, which last a considerable time, is to determine the actual amount of  $\text{CO}_2$  absorbed from the still air of the room during the whole period by an open flask exposing a considerable surface of caustic soda solution, and placed alongside the diffusion apparatus. If the rate of the diffusive flow into the flask for a definite partial pressure of  $\text{CO}_2$  has once been accurately ascertained, such a simple piece of apparatus enables us to determine with considerable accuracy the mean pressure of the gas during a long period of exposure. It was only towards the close of the experiments we are now describing that we felt sufficient confidence in this method to recommend its application, and hitherto we have only used it as a check on direct determinations made with the Reiset apparatus.

In the following table we give the results of all our determinations of the diffusivity of atmospheric carbon dioxide with the horizontal tubes. The straight-tube equivalent of the flasks was in all cases 7 centims., which has been added to the lengths of the diffusion tubes.

TABLE II.

No.	Duration of experiment in hours.	Length of tube in centims. corrected.	Diameter. centims.	Total CO <sub>2</sub> diffused, cub. centims. at 0° C. and 760 millims.	CO <sub>2</sub> diffused per sq. centim. per hour measured at temperature and pressure of experiment <i>Q<sub>vt</sub></i> .	Mean temperature, C.	Mean barometer.	Mean CO <sub>2</sub> content of air, parts per 10,000.	<i>k</i> °.
(6)	500·9	18·0	2·32	23·89	·01175	7°·7	751·2	3·70	·151
(7)	501·0	75·0	2·32	6·33	·00311	7°·7	751·2	3·70	·167
(8)	501·0	18·0	2·32	20·88	·01036	9°·1	763·4	3·61	·133
(9)	384·0	20·1	2·28	14·91	·00989	13°·3	766·3	3·39	·146
(10)	383·7	19·9	2·30	15·49	·01260	13°·3	766·3	3·39	·185
(11)	384·8	36·6	2·23	8·81	·00609	13°·3	766·3	3·39	·164
(12)	386·4	37·3	2·20	7·91	·00559	13°·3	766·3	3·39	·154
Mean <i>k</i> ° . . .									·157

The eleven different experiments which we have made on the static diffusion of the highly dilute carbon dioxide of the atmosphere in what is practically a stationary column of air give a mean value for *k*° of ·158, expressed in C.G.S. units. The values obtained by previous observers for the interdiffusivity of CO<sub>2</sub> and air for much higher ratios of mixture, and with the gases at equal tension, are as follows :—

	<i>k</i> °.
LOSCHMIDT . . . . .	·142
VON OBERMAYER . . . . .	·135
WAITZ . . . . .	·151—·158
WAITZ, recalculated by VON OBERMAYER . . . . .	·131—·137

In the last-mentioned experiments the gases were perfectly *dry*, which was not the case in our own experiments, and it now remains to be seen how far this fact is likely to affect our results.

The interdiffusivity of CO<sub>2</sub> and water vapour may be calculated from the general formula  $k^\circ (\sqrt{m_1 \cdot m_2}) = \text{a constant}$ ; where  $m_1$  and  $m_2$  denote the molecular weights of the diffusing gases. When *k* is expressed in C.G.S. units the constant has a value of 2·527, so that the interdiffusivity of CO<sub>2</sub> and water vapour will be expressed by

$$\frac{2\cdot527}{\sqrt{22 \times 9}} = \cdot179.$$

This corresponds exactly with the value deduced by WINKELMANN from STEFAN'S kinetic formula, but the experimental value found by WINKELMANN for the static evaporation of water in tubes opening out into a constantly renewed atmosphere of CO<sub>2</sub> was *k*° = ·130 to ·133.



In order to obtain some idea of the possible effect on our results of the presence of aqueous vapour in the column of air, we have assumed the lower experimental value to be correct, and have further assumed that in one of our diffusion tubes of 50 centims. in length the air immediately over the absorbing liquid is saturated with water vapour, the temperature being  $15^{\circ}\text{C.}$ , and that the outer air is perfectly dry. This is of course an extreme case to take.

Under these conditions the average pressure of the aqueous vapour in the tube will be  $\cdot0083$  of an atmosphere, and the pressure of the air itself  $\cdot9917$ . If we take our mean value of  $\cdot158$  for the diffusivity of the  $\text{CO}_2$ , the corrected value  $x$  for *dry* air will be given by the equation

$$\cdot9917x + (\cdot0083 \times \cdot130) = \cdot158,$$

hence  $x = \cdot1583$ .

It is clear, therefore, that we can entirely neglect the presence of aqueous vapour in our experiments.

It must be borne in mind that the foregoing experiments on the static diffusion of carbon dioxide were not undertaken for the purpose of establishing exact physical constants, but in order to ascertain if the high degree of dilution of that gas as it occurs in the atmosphere is followed by any alteration in its coefficient of diffusion of sufficient magnitude to be taken into account in the study of the natural processes of gaseous exchange in the assimilating organs of plants. Without special enquiries, we did not feel justified in applying to such cases the constants of diffusivity which had been determined on ratios of mixture and by experimental methods of diffusion so widely different from those which occur in nature.

Our general results indicate that no appreciable error is likely to be introduced into the study of such natural processes by employing the commonly received values of  $k$  for carbon dioxide and air; at the same time the values we have obtained for the diffusivity of atmospheric carbon dioxide by this particular static method show some departure from those obtained for very different ratios of mixture by LOSCHMIDT, WAITZ, and VON OBERMAYER.

It is true that the difference between our value and LOSCHMIDT's is not much greater than that existing between the determinations of LOSCHMIDT and those of WAITZ as recalculated by VON OBERMAYER, but it is in a direction contrary to that indicated by the latest development of the kinetic theory of diffusion by O. E. MEYER, which leads us to expect for very dilute  $\text{CO}_2$  a somewhat lower value for  $k$  than we actually find. This discrepancy may be due to residual errors inherent to the method of tube diffusion, and we have consequently devised another statical method which is particularly applicable to atmospheric  $\text{CO}_2$ . This will be found described in a subsequent section of the paper, since it cannot be properly discussed until we have considered the observations which gradually led up to it.

*Static Diffusion through Apertures in a Septum.*

When a condition of static equilibrium has been established in a diffusing column of gas, vapour, or solute, as the case may be, the amount of diffusion, under like conditions, is proportional to the sectional area of the column, the case being exactly analogous to the steady flow of heat in a conductor.

We have found, however, that if we partially obstruct the mouth of the diffusion tube with a septum having a circular aperture, or if we interpose such a septum anywhere in the line of flow, diffusion is modified in a remarkable and unexpected manner.

In our early experiments on this subject we attempted to investigate this problem by covering dishes, containing absorbent solutions of caustic soda, with thin glass or metal discs having central apertures of various sizes, and ascertaining from the amount of carbon dioxide absorbed the relative velocity with which diffusion takes place per unit area of the aperture.\*

These first attempts were necessarily very crude, and the results were much interfered with by convection currents, but they were sufficient to indicate that after the aperture in the cover had been reduced to a certain point, the carbon dioxide passing through unit area of aperture in a given time showed a marked *increase*, which could not be satisfactorily accounted for by the mere difference in the gradient of the partial pressures of the gas inside and outside the covered dish.

This led us to investigate the influence of a perforated diaphragm on the diffusion of atmospheric CO<sub>2</sub> down a column of air in which the flow was at a maximum, that is to say, only limited by the coefficient of diffusion of the gas.

The interesting fact was then brought to light that as the end of the tube was restricted the diffusive flow *per unit area of aperture* rapidly increased, and that when the central hole had been diminished beyond a certain size relative to the cross-section of the column, the amount of gas which passed became proportional to the *linear dimensions of the apertures*.

This is well shown in the following experiments :—

A series of similar flat-bottomed flasks was taken, having necks about 7 centims. long and about 23 millims. diameter at the mouth. When 200 cub. centims. of a normal caustic soda solution was introduced, the surface of the absorbing liquid, which was about 10 centims. in diameter, maintained the pressure of the carbon dioxide in the air of the flask at so low a point as to induce what was practically a maximum diffusive flow down the tube forming the neck. When such a flask was exposed to comparatively still air, containing the normal amount of CO<sub>2</sub>, a very steady and uniform absorption took place at the rate of about .25 cub. centim. of the gas per hour.

\* A brief description of these earlier experiments will be found in the Presidential Address to Section B of the British Association, Dover Meeting, 1899.

The perforated septa which were used for partially closing the openings of some of the flasks had to be disposed in such a manner as to avoid all possibility of any  $\text{CO}_2$  gaining access to the absorbent except through the aperture of known dimensions, and it was the more necessary to take extreme precautions in this respect since the duration of some of the experiments with small apertures had to be extended over several weeks in order to obtain a sufficiently large amount of absorption for accurate titration. In this particular instance the following plan was adopted, although in subsequent experiments a much simpler one was found to be sufficient :—

The neck of the flask passed through the bottom of a small glass cup to which it was cemented, the shallow annular space thus formed being filled with mercury. A flat-bottomed thin nickel crucible was then inverted over the mouth of the flask, the edges of this metal thimble dipping into the mercury in the cup, which thus formed a perfect seal. The bottom of the thimble was perforated with a well cut circular hole of any desired size.

When the metal thimble was *imperfurate* it was found that the alkaline liquid in the flask could remain for several weeks without undergoing any change in the original amount of carbonate it contained.\*

The flasks were all charged at the same time with a given amount of the caustic soda solution, after displacing the air in them with air artificially freed from carbon dioxide, and they were afterwards submitted to identical conditions during the diffusion process, the open flask with which the comparisons were made being replaced three or four times in the course of the experiment, so as to avoid any undue carbonating of the alkali.

A summary of the results is here given :—

TABLE III.

No.	Diameter of aperture.†	Time of diffusion in hours.	Total $\text{CO}_2$ diffused.	$\text{CO}_2$ diffused per hour.	$\text{CO}_2$ diffused per sq. centim. of aperture per hour.	Ratio of areas of apertures.	Ratio of diameters of apertures.	Ratio of $\text{CO}_2$ diffused in unit time.
(1)	millims. 22·7	—	cub. centims. —	cub. centims. ·2380	·0588	1·00	1·00	1·00
(2)	12·06	476·5	44·22	·09280	·0812	·28	·53	·39
(3)	12·06	477·1	48·57	·10180	·0891	·28	·53	·42
(4)	5·86	478·8	26·61	·05558	·2074	·066	·25	·23
(5)	6·03	643·1	40·21	·06252	·2186	·07	·26	·26
(6)	3·233	863·0	34·41	·03988	·4855	·023	·14	·16
(7)	3·216	863·8	34·30	·03971	·4852	·020	·14	·16
(8)	2·00	1007·8	24·16	·02397	·7629	·007	·088	·10
(9)	2·117	1007·3	26·28	·02608	·8253	·008	·093	·10

\* A very careful series of test experiments was made, which showed that the long-continued contact of the alkaline solution with the glass had no influence on the final determination of the  $\text{CO}_2$  by the double titration method described later on.

† The measurement of the apertures was kindly undertaken by Sir WILLIAM ABNEY, who applied his special optical method for this purpose.

It will be noticed, on comparing the three last columns of the table, that, with the exception of Nos. (2) and (3), where the diameter of the aperture was more than one-half of that of the unrestricted opening of the flask, the rates of diffusion follow very closely *the ratios of the diameters of the openings*, and are very far removed indeed from the ratios of the areas. In the exceptional cases (2) and (3) the rate of diffusion lies almost exactly half-way between the diameter and area ratios. We shall see later on the explanation of this.

This same apparatus can also be used to demonstrate the relative rates of diffusion of *aqueous vapour* through similar apertures. It is only necessary to replace the caustic soda solution with strong sulphuric acid, and to weigh the flasks from time to time, after exposing them to the influence of the atmosphere. Since it is only comparative results which are aimed at, any variation in the moisture of the air during the experiment does not matter since it affects all the flasks equally. The following results were so obtained with apertures of 2·117, 3·233, and 5·84 millims. diameter :—

TABLE IV

No.	Diameter of aperture.	Aqueous vapour diffused in 5 days.	Aqueous vapour diffused in 10 days.	Aqueous vapour diffused in 16 days.
	millims.	grammes.	grammes.	grammes.
(1)	2·117	·135	·305	·535
(2)	3·233	·209	·475	·806
(3)	5·840	·322	·715	1·220

In the next table are given the ratios of the amounts of aqueous vapour diffused in equal times, and, for comparison, the ratios of both the areas and the diameters of the aperture. It will be noticed that the amount of diffusion is again controlled by the *linear dimensions* of the apertures and not by their areas.

TABLE V.

No.	Ratios of first weighings.	Ratios of second weighings.	Ratios of third weighings.	Ratios of <i>areas</i> of apertures.	Ratios of <i>diameters</i> of apertures.
(1)	1·00	1·00	1·00	1·00	1·00
(2)	1·55	1·55	1·50	2·3	1·52
(3)	2·38	2·54	2·28	7·6	2·75

Hitherto we have been considering instances of inward static diffusion towards an absorptive surface, but exactly the same effect can be produced by the outward diffusion of a vapour through an aperture in a septum when there is a constant difference maintained between the partial pressure of the vapour inside and



outside the vessel containing the liquid. This is indicated by the following experiments :—

Small glass cylinders filled with water to about 1 centim. of the top were closed with zinc discs of about .5 millim. in thickness with central apertures of known size, and were placed in a large exsiccator over sulphuric acid, which was put in a room where the temperature was constant. The amount of liquid which evaporated through the apertures was estimated from time to time by weighing the cylinders. The results are tabulated below :—

TABLE VI.

No.	Diameter of aperture.	Evaporation in first period of 5 days.	Evaporation in second period of 7 days.	Evaporation in third period of 6 days.
(1)	millims. 2·4	grammes. ·1370	grammes. ·2100	grammes. ·1735
(2)	4·9	·3230	·4845	·4490

TABLE VII.—Giving Ratios of Evaporation in the above Experiments.

No.	Ratios of evaporation in first period.	Ratios of evaporation in second period.	Ratios of evaporation in third period.	Ratios of <i>areas</i> of apertures.	Ratios of <i>diameters</i> of apertures.
(1)	1·00	1·00	1·00	1·00	1·00
(2)	2·35	2·30	2·58	4·16	2·04

It is seen that the amounts of liquid evaporated under these conditions in equal times, are in no way proportional to the respective *areas* of the apertures, but approximate to the ratios of their *linear dimensions*. The approximation in this case would have been much closer had a thinner disc of metal been used as the septum.

From the well-known fact that the laws of diffusion of substances in solution are the same as those for the diffusion of gases and vapours, it might be reasonably expected that the “diameter law” would also hold good for *solutes*.

In order to demonstrate this, it is necessary in the first instance to adopt some plan by which the mobility of the solvent may be so far reduced as to allow the static condition, or an approximation towards it, to be established, without interfering with the natural gradient of density of the solute by currents in the liquid. This can be accomplished by using a solution of the substance to which about 5 per cent. of gelatine has been added.\*

\* Several observers have previously used gelatine or agar-agar in diffusion experiments, and have found that the rapidity of diffusion is practically the same as with water only.

A solution containing 5 per cent. of gelatine and 4 per cent. of sodium chloride was run whilst warm into flat-bottomed, cylindrical, tinned vessels, each with a small circular aperture bored in the bottom, the flat margin around the hole having a breadth at least five or six times the diameter of the aperture. When the mixture had set the lower part of the vessel was freed from gelatine, which was then carefully cut flush with the hole. The cylinders were suspended in water, which was kept constantly stirred, and was sufficiently large in volume to maintain the density of the diffusing salt at the limiting surface of the gelatine and water practically at zero, and the diffused sodium chloride was from time to time determined in the usual manner with a standard solution of silver nitrate.

The following is an example of such an experiment :—

TABLE VIII.—After about 23 Hours' Diffusion.

No.	Diameter of aperture for diffusion.	Hours.	Total NaCl diffused.	NaCl diffused per hour.	Ratios of <i>areas</i> of apertures.	Ratios of <i>diameters</i> of apertures.	Ratios of NaCl diffused.
(1)	millims. 3·0	23·0	grammes. ·0438	grammes. ·00190	1·0	<b>1·00</b>	<b>1·00</b>
(2)	6·3	22·7	·1047	·00461	4·1	<b>2·10</b>	<b>2·39</b>
(3)	12·8	22·4	·2503	·01116	18·1	<b>4·26</b>	<b>5·71<sup>a</sup></b>

TABLE IX.—After a further Diffusion of about 24 Hours in a fresh Amount of Water.

No.	Diameter of aperture for diffusion.	Hours.	Total NaCl diffused.	NaCl diffused per hour.	Ratios of <i>areas</i> of apertures.	Ratios of <i>diameters</i> of apertures.	Ratios of NaCl diffused.
(1)	millims. 3·0	22·8	grammes. ·0420	grammes. ·00184	1·0	<b>1·00</b>	<b>1·00</b>
(2)	6·3	22·1	·0930	·00420	4·1	<b>2·10</b>	<b>2·33</b>
(3)	12·8	23·0	·2040	·00886	18·1	<b>4·26</b>	<b>4·88</b>

These results show that when a fairly static condition is attained, the rates of diffusion of the salts correspond closely to the *diameters* of the apertures, and are very far removed from the ratios of the areas.

If instead of carrying on the diffusion through apertures in a diaphragm we employ straight-sided cylinders or tubes, allowing the water to come into contact with the entire cross-section of the column of salted gelatine, the result is altogether different. In such a case, as is shown by the experiment next quoted, the rate of diffusion is proportional to the *area* of the cross-section exposed, not to its diameter,

just as it is in gaseous diffusion under analogous conditions, or in the evaporation of liquids in tubes, as shown by STEFAN and by WINKELMANN.

Diffusion from the open end of tubes of different diameters containing salted gelatine :—

TABLE X.—After 21 Hours' Diffusion.

No.	Diameter of tube.	NaCl diffused.	Ratios of diameters of tubes.	Ratios of areas of tubes.	Ratios of NaCl diffused.
(1)	millims. 30·25	grammes. ·5785	1·9	3·9	3·6
(2)	15·25	·1579	1·0	1·0	1·0

TABLE XI.—After a Second Period of 20·8 Hours.

No.	Diameter of tube.	NaCl diffused.	Ratios of diameters of tubes.	Ratios of areas of tubes.	Ratios of NaCl diffused.
(1)	millims. 30·25	grammes. ·2626	1·9	3·9	3·56
(2)	15·25	·0737	1·0	1·0	1·00

It would be an easy matter to give many more examples of the remarkable and unexpected effect produced on a static flow of diffusing gas, vapour, or solute, when we interpose a diaphragm pierced with a single circular aperture of known dimensions, but sufficient proof has already been given that the magnitude of the effect is dependent on the linear dimensions of the aperture. It follows of course from this, that the velocity of the flow through unit area of such an aperture must vary inversely as the diameter, and it consequently became a matter of extreme interest to investigate the influence of a diaphragm perforated with many small holes, since one would be led to anticipate that, under ideal conditions, a selection of the right number, size, and distribution of the apertures ought to result in causing but little obstruction in the diffusive flow, although the combined area of the apertures might only represent a comparatively small percentage of that of the obstructing septum.

Before proceeding to describe our experiments in this direction, it will, however, be convenient to ascertain how we can reasonably explain the phenomena so far observed.

In our earlier experiments\* on the diffusion of atmospheric carbon dioxide through varying apertures in the cover of a dish which was partially filled with an absorb-

\* See Presidential Address to Section B, British Association, Dover Meeting, 1899.

ing alkaline solution, the fact that the velocity of diffusion per unit area increased as the aperture was diminished did not excite any surprise, since it was clear that the gradient of density of the  $\text{CO}_2$  of the outer atmosphere, and of the air above the absorbent, was necessarily an increasing one, a state of things which would naturally result in a somewhat increased flow. When, however, the area of the aperture was made very small compared with that of the absorbing surface, and the partial pressure of the  $\text{CO}_2$  in the air of the dish had consequently been reduced almost to a vanishing quantity, it was found that a further diminution in the size of the hole was still attended with a very marked increase in the rate of flow per unit area, and that this increase was far larger than could be reasonably accounted for by any ordinary differences of density gradient in the  $\text{CO}_2$ .

It became still more impossible to regard this as a sufficient explanation, when further investigation with improved methods and apparatus had brought out the "diameter law," and it was discovered that the effect could also be produced in a static flow which had attained a maximum velocity consistent with the diffusivity of the substance.

It is to Dr. J. LARMOR that we owe a most fruitful suggestion which has resulted in a complete and satisfactory explanation of the phenomena, and we must here take the opportunity of expressing our thanks, not only for this suggestion, but for much help and guidance which Dr. LARMOR has from time to time given us during this research, and without which it would probably not have advanced beyond an empirical stage.

Let us in the first place consider the simple case of a circular disc, capable of absorbing carbon dioxide, and freely exposed to the air, the disc being surrounded with a rim in the same plane, and of a width three or four times its diameter.

If the air above the disc is *perfectly still*, the convergent streams of carbon dioxide will creep through the air towards the disc, establishing a steady gradient of density, and this creep will be a flux perpendicular to the lines of equal density, which will thus form curved surfaces, or "shells," surrounding the disc and terminating in the rim.

The problem is mathematically the same as that presented by the electric field in the neighbourhood of a conductor embedded in a surrounding non-conducting surface, and having the same shape and dimensions as the absorbent disc. The curved surfaces or "shells" of the gas of equal density are, in fact, the exact 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.

By the aid of this electrostatic analogy we can explain why the flow of the diffusing gas is found to vary with the linear dimensions of the absorbing disc.

This will be rendered evident on referring to fig. 1 (p. 256), which represents a system of "shells" or zones of equal density arranged at such distances as to



approximately represent equal differences of pressure of the atmospheric  $\text{CO}_2$ , and also the lines of flow perpendicular to them.\*

These shells must vary in density outwards from zero at the absorbent surface, if this is perfectly absorbent, to a density corresponding to the maximum pressure of the carbon dioxide in the atmosphere, a point which theoretically is at infinite distance from the disc, but which is practically reached at a distance of five or six times its diameter. If we had two such figures of different sizes, drawn to relative scale, one in fact the magnified image of the other, any curved surface corresponding to a given density would be found at actual distances from the discs which would be proportional to their diameters. This, of course, means that the gradient of density, on the magnitude of which the flow into unit area depends, must vary inversely as the diameters of the discs, a result sufficient to account for all the observed facts.

The case of such an absorbent disc as we have been considering is the exact converse of one which has been theoretically explored by STEFAN ('Wien. Akad. Ber.,' 1881, vol. 83, Abtheil. 2, p. 613), the conditions of evaporation from a circular surface of liquid. He also makes use of the electrostatic analogy, and the results of his mathematical analysis show that the amount of evaporation in such cases is proportional to the linear dimensions of the liquid surface, and not, as is commonly supposed, to its area. The lines of flux of the vapour proceeding from the liquid he finds to be *hyperbolas*, whose foci lie in the bounding edge of the circular surface. The curved surfaces of equal pressure of the vapour overlying the disc form an orthogonal system of ellipsoids, also having their foci in the edge of the disc, and since these ellipsoids come closer together at the margin than they do nearer the middle of the liquid disc (see fig. 1), STEFAN concludes that evaporation proceeds more rapidly from the edge than from the centre of the disc.

It must be remembered that this was a purely mathematical deduction, which, as far as we know, has never been experimentally verified in the form which STEFAN gave it. It is, however, in complete agreement with the reverse phenomena of absorption by a circular surface, and with many other facts recorded in this paper.

SRESNEWSKY ('Beibl.,' 7, p. 888, 1883), in some observations on the evaporation of liquid drops, showed that the amount of evaporation of such drops is probably proportional to the circumference and not to the superficies.

WINKELMANN ('Wied. Ann.,' vol. 3 (1888), 401) attacked experimentally that portion of the problem relating to the differential evaporation from different portions of a circular free surface of liquid. His results, although indicating a larger amount of evaporation from the edge, do not give a numerical correspondence with STEFAN's predictions, but this WINKELMANN attributes rather to the incompleteness of his method than to anything faulty in STEFAN's deductions. On this question we shall have something to say later.

\* See CLERK MAXWELL'S 'Electricity and Magnetism,' vol. 1, fig. 10, on which the curves of equal density given in our figures are based.

The formula which STEFAN deduced to express the amount of evaporation from a circular liquid surface was

$$M = 4k\alpha \times \frac{P - p''}{P - p'},$$

where  $M$  is the mass of liquid vaporised in a given time;  $k$ , the coefficient of diffusion of the vapour;  $\alpha$  the radius of the liquid disc;  $P$  the atmospheric pressure;  $p'$  and  $p''$  the pressure of the vapour at the surface and very far away from it, respectively.

This formula is practically identical with one which was given to us by Dr. LARMOR as applicable to the reverse process of absorption of atmospheric  $\text{CO}_2$  by a perfectly absorbing circular disc—

$$Q = 2k\rho D,$$

where  $Q$  is the amount absorbed in a given time;  $k$  the coefficient of diffusion of  $\text{CO}_2$  in air;  $\rho$  the density of the atmospheric  $\text{CO}_2$  at a point very far removed from the disc; and  $D$  the diameter of the disc. The formula was deduced from the known laws of the diffusion of gases, and the electrostatic analogy above referred to, without any knowledge of STEFAN'S previous work, and the following proof of it was given, which has the advantage over STEFAN'S that it is intelligible to the non-mathematician:—

*Absorbing Disc.*

Gradient of density  $\rho$  corresponds to  
Absorption =  $k \times$  gradient.

$$\therefore \text{Total absorption} = \frac{k}{\frac{1}{4\pi}} \cdot \frac{D}{\pi} \cdot \rho = 4k\rho D.$$

*Electrified Disc.*

Gradient of potential (V).  
Density of charge =  $\left(\frac{1}{4\pi}\right) \times$  gradient.

$$\text{Electric capacity} = \frac{D}{\pi}.$$

$$\text{Total charge} = \frac{D}{\pi} \cdot V.$$

For one side only of the disc it is therefore  $2k\rho D$ .

In attempting to verify this formula experimentally by determining the amount of atmospheric carbon dioxide which can be absorbed by circular surfaces of solutions of caustic alkali we are at once met by two difficulties. In the first place the "shells" of equal density, which according to the above view are formed over the surface, must necessarily be very unstable and subject to dispersal by the slightest current of air, and the larger the absorbing disc the less stable the shells must become. In the second place such solutions, although good absorbers of  $\text{CO}_2$ , are by no means perfect ones, as will be more fully shown in the Appendix to this paper dealing with the behaviour of solutions of caustic alkali towards very dilute carbon dioxide. The quantitative relations between  $Q$  and  $k$  in the above formula depend on the tension of the absorbed gas being zero at the limiting surface of the liquid and

the air, or at any rate having a definite and known relation to the maximum tension of the gas in the outer air.

But although a full verification could not reasonably be expected by this mode of experimenting, it certainly did seem probable, if the above theoretical views were correct, that we should find absorption following the linear dimensions of the discs rather than their areas.\*

When circular dishes containing normal soda solution are exposed to air which is kept as still as possible, the absorption is proportional to the *areas* exposed if their diameters exceed 5 to 6 centims., but the case is different if smaller discs are used, and the proper facilities are given for the production of stable density "shells."

Small burette-like tubes of known capacity, and varying from 5 to 40 millims. in diameter, and furnished with small glass stopcocks, were accurately fitted into brass discs about 10 centims. in diameter, in such a manner that the ground edges of the tube were exactly in the plane of the upper surface of the disc, which thus formed a broad rim round the mouth of the tube.

The apparatus having been fixed within a curtained recess of a room set apart for the experiments, the air of which could be kept very still, the tubes were completely filled with a 4 per cent. caustic soda solution in which the pre-existing carbonate was accurately known. The solution thus formed an absorbent disc practically in the same plane as the brass rim around it.† Evaporation was made good from time to time by the further addition of a few (measured) drops of the same solution.

At the close of the experiment, the caustic soda was drawn off with all necessary precautions, and the carbon dioxide it had absorbed was determined.

The following is a typical example of the results so obtained :—

TABLE XII.  
(Duration of experiment about 24 hours.)

Diameter of liquid disc.	CO <sub>2</sub> absorbed per hour.		Ratios of areas.	Ratios of diameters.	Mean ratios of areas and diameters.	Ratios of CO <sub>2</sub> absorbed.
	Found.	Calculated from formula.				
millims.	cub. centims.	cub. centims.				
10·25	·176	·390	1·0	1·0	1·0	1·0
20·25	·537	·770	3·9	1·9	2·9	3·0
29·25	·941	1·115	8·1	2·8	5·4	5·3
40·00	1·621	1·525	15·2	3·9	9·5	9·2

\* The case in fact would be analogous to STEFAN'S evaporation problem reversed, when the partial pressure  $p'$  of the vapour at the surface of the liquid is not at its maximum for the temperature and pressure of the experiment, and its true value is unknown. All other conditions being the same, we should still expect the value of  $M$  to vary with the diameters of the discs, but the value of  $k$  would not be determinable.

† It is desirable to smear the edge of the tube with a trace of vaseline to prevent creeping of the solution and efflorescence of the soda.

It is seen from the last two columns that the amounts of  $\text{CO}_2$  absorbed in equal times are almost exactly proportional to the mean ratios of the diameters and areas.

The same result is also shown by the following two experiments :—

TABLE XIII.  
(Duration of exposure, 2 days.)

Diameter of liquid disc.	$\text{CO}_2$ absorbed per hour.	Ratios of areas.	Ratios of diameters.	Mean ratios of areas and diameters.	Ratios of $\text{CO}_2$ absorbed.
millims. 5·0 20·25	cub. centims. ·043 ·431	1·0 16·4	1·0 4·0	1·0 10·2	1·0 10·0
5·0 20·25	·051 ·542	1·0 16·4	1·0 4·0	1·0 10·2	1·0 10·6

If the air above the discs were in *very slight movement*, it would tend to produce exactly the effects observed ; that is to say, we should expect under these conditions to find the ratios of absorption of the carbon dioxide falling somewhere intermediate between the ratios of the areas and those of the diameters.

By taking further extreme precautions against this disturbance, and by comparing two discs of *small diameter*, so as to further increase the stability of the “shells,” we finally obtained the following result, which approximates very much closer to the “diameter law.”

TABLE XIV.  
(Duration of experiment, 43—44 hours.)

Diameter of liquid disc.	$\text{CO}_2$ absorbed.		Ratios of areas.	Ratios of diameters.	Ratios of $\text{CO}_2$ absorbed.
	Total.	Per hour.			
millims. 5·0 10·25	1·974 4·890	·044 ·111	1·0 4·2	1·0 2·05	1·0 2·47

We thus see that the observed differences in the velocity of the diffusive flow of a substance through apertures of various sizes in an obstructing diaphragm are exactly paralleled by similar differences in suitable absorptive surfaces, the amount diffused or absorbed depending on the *linear dimensions* of the aperture or surface, as the case may be. That there should be a common explanation of two such similar sets of phenomena appears to be almost certain, and in the case of the absorptive surface no explanation appears possible other than that already given, and postulating



the existence of a system of overlying equi-density shells brought into existence by the converging streams of the gas on their way to the absorbing surface.

There is, however, one important difference between the behaviour of absorbing discs, and of perforations in a septum dividing two regions of different density. In the former case, as we have just seen, the absorption, according to linear dimensions, is extremely sensitive to any disturbance which may be supposed to affect the stability of the overlying "shells," whereas in the case of a perforated diaphragm, through which, for instance, atmospheric carbon dioxide is diffusing, no special precautions to keep the outer air quite still are requisite; in fact, we may obtain good indications of the "diameter law" under these conditions from air which is in distinct movement, a movement far more than sufficient to sweep away and destroy the efficacy of any shells over an absorbing alkaline solution of the same shape and size.

In the case of the absorbent disc, the convergent hyperbolic lines of flux of the carbon dioxide all terminate in the surface of the disc, and normal to it, where they are trapped by the absorbent. (See fig. 1, p. 256.) With the perforated diaphragm, on the other hand, the lines of flow, which are convergent as they approach the disc, 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, we shall have formed on the inner side of the diaphragm a system of "shells" of equal density exactly similar to those of the outside; but with the gradient of density in the opposite direction, the density decreasing from the diaphragm inwards (fig. 2). This system of internal "shells," which we may designate as *negative*, will of course be shielded from the direct action of currents in the outer air, if the aperture is not large, and they will manifestly be as effective in regulating the inflow according to the linear dimensions of the aperture as the outer or positive shells, whilst they are quite independent of the latter, which may be completely swept away, without interfering with the "diameter law."\*

This view is perfectly in accord with the facts, and it also explains why in Experiments 2 and 3, Table III., p. 244, the amount of diffusion was found to be intermediate between the diameter and area ratios of the apertures, the rim or margin of the aperture in these cases not being sufficiently wide to allow a complete system of internal shells to be formed.

\* It must be understood that we are only speaking here of the *relative* rates of diffusion through apertures of different sizes and under similar conditions. The actual rate of diffusion through an aperture is, as will be shown later, much influenced according to whether we have a single or double system of shells.

*Experimental Demonstration of the Formation of Ellipsoidal "Shells" of Equal Density during Diffusion through an Aperture in a Diaphragm.*

All the phenomena of diffusion through apertures in a diaphragm, or into an absorbent surface surrounded by a broad rim, admit of a complete and satisfactory explanation if we assume that the converging or diverging lines of flow to or from the aperture or absorbing surface result in the production of a system of "shells" of equal density, which locally alter the gradient in the immediate neighbourhood of the septum.

The proof of the formation of such "shells" is, however, not confined to a line of reasoning which is partly deductive and based on the electrostatic analogy, for we have been able to obtain an experimental verification of their existence. Liquid diffusion in gelatine is admirably suited for this purpose, the diffusing solute being either a coloured substance or one whose progress of diffusion may be observed by its reaction with another substance diffusing in the opposite direction.

In our experiments with coloured substances we have generally employed a .05 per cent. solution of methylene blue in 5 per cent. aqueous gelatine, the dye being allowed to diffuse into a clear gelatine solution of similar strength.

When studying diffusion through apertures in a diaphragm, a large rectangular cell with plate-glass sides was used, and this was so constructed as to be capable of being divided horizontally into two partitions by a thin plate of celluloid, tin-foil, or some other convenient septum. This septum was perforated with a hole of known dimensions, one compartment being filled with clear gelatine and the other with gelatine and dye, the two solutions only being in contact across the perforation.

It is extremely interesting to watch the changing form of the limiting surface of dye and colourless gelatine under these circumstances as diffusion progresses. Its ellipsoidal shape is well shown, especially in the very early stages, the major axes of the ellipsoids being in the plane of the septum, and their common foci in the edges of the circular hole. It is also seen that the surfaces of equal density approach nearer to each other at the diaphragm than farther away from it, thus accounting for the more rapid lateral creep of the dye at the margin of the hole. This last-mentioned fact illustrates experimentally the deduction of STEFAN, to which we have already called attention, that, in the strictly analogous phenomenon of evaporation from a circular disc, evaporation is greater at the edges of the disc than nearer the centre.

As the diffusion progresses the spheroid of coloured gelatine approaches nearer to the dimensions of a hemisphere, which, however, it never actually reaches.

Such experiments, conducted side by side with apertures of different sizes, can be made to illustrate the "diameter law" if the volumes of the spheroids proceeding from apertures of different diameter are compared for equal times of diffusion. This is shown in the following table for two sets of measurements :—

TABLE XV.

Diameter of aperture.	Volume of spheroid.	Ratios of areas of apertures.	Ratios of diameters of apertures.	Ratios of volumes of spheroids.
millims.	cub. centims.			
(1) 5·5	7·068	1·0	1·0	1·0
(2) 12·0	14·365	4·76	2·18	2·03
(3) 5·5	13·805	1·0	1·0	1·0
(4) 12·0	33·716	4·76	2·18	2·44

*Theoretical Considerations of the Effect of the Combined Systems of "Shells" of Equal Density on Diffusion through Apertures and Tubes.*

In considering somewhat in detail the various cases which may present themselves in practice, we will, in the first place, deal with the two single systems of shells represented in figs. 1 and 2, which are in every respect complementary to one another. In fig. 1 we have a representation of the "positive" shells overlying a perfectly absorbent circular surface; and in fig. 2 the corresponding system of "negative"

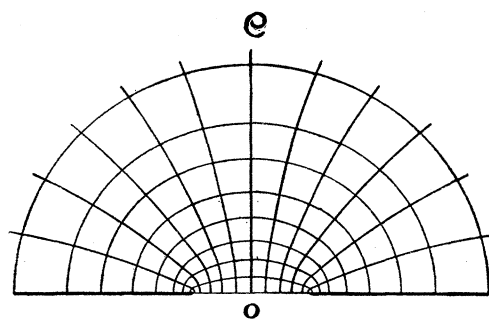


Fig. 1

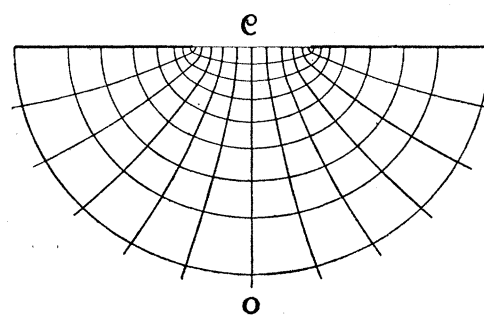


Fig. 2

shells, such as would be produced on the inner side of a perforated diaphragm opening into a large chamber in which the density of the diffusing gas or substance is kept practically at zero, the density immediately outside the diaphragm being supposed to be kept at a maximum by a current of the gas or liquid moving with sufficient velocity in a horizontal plane to prevent external shell formation. In the first case, fig. 1, the density of the diffusing substance will vary from  $\rho$ , at a remote point above the disc, to zero at the surface of the absorbent; whilst in the case represented in fig. 2, the density is  $\rho$  in the plane of the aperture, becoming zero remote from the aperture, inside the vessel covered by the diaphragm. If  $\rho$  has the same value in each case, and the disc and aperture have the same dimensions, the same mass of substance will diffuse across any two shells of the two systems in a given time.

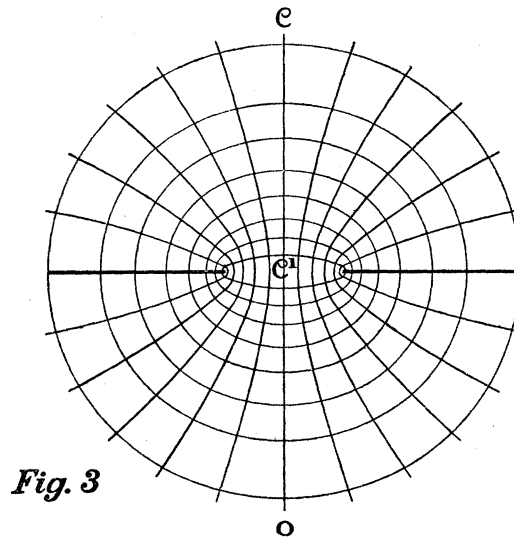
If the shells were hemispherical, the density of any two shells of the same system would be inversely proportional to their radii, the velocity of drift varying inversely as the square of the radii. But the projection of the shells is elliptical, not circular, the ellipses having their foci in the edges of the circle forming the absorbent disc or perforation. These ellipses are not of the same shape and become practically semicircular at three or four times the diameter of the aperture; so that at this distance the difference in density, plus or minus, according to whether we are regarding the positive or negative shells, will follow the law of the radii of the shells, but this will not be so at nearer distances.

The formula representing the amount of diffusion in a given time is the same in each case, viz. :—

$$Q = 2k\rho D,$$

where  $Q$ ,  $k$ ,  $\rho$  and  $D$  have the same significance as on p. 251.

In fig. 3 we have the combination of shells of equal density, both positive and negative, such as are produced on either side of a perforated diaphragm of no sensible thickness, when there are no disturbing currents outside.



**Fig. 3**

The variation in density of the outer positive shells in this combination will be from  $\rho$  at a remote distance, to  $\rho_1$  at the aperture itself, whilst the variation in the inner negative shells will be from  $\rho_1$  at the aperture to zero at some distance from it.

The mass of substance diffusing through the positive shells will be  $2k(\rho - \rho_1)D$ , whilst that passing through the inner negative shells will be represented by  $2k\rho_1D$ .

But the amount diffusing through each system in a given time is the same, so that we have

$$2k(\rho - \rho_1)D = 2k\rho_1D,$$

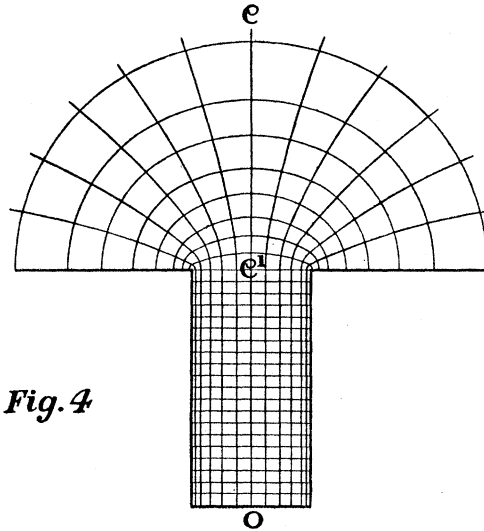
hence  $\rho_1 = \frac{1}{2}\rho$ .

That is to say, the absorptive power of the combined system of positive and negative shells is equal to that of a single system of positive shells of half the density.



tive shells is only half that of the negative shells alone, when the density immediately outside the aperture is kept constant at  $\rho$  by a moving current of the gas or liquid. This is a deduction of some moment which has certain important applications.

We will now consider the case in which positive shells are formed over a *tube* or *cylinder*, surrounded by a rim at the mouth, static diffusion being supposed to take place down the tube, the bottom of which is perfectly absorbent. (See fig. 4.)



**Fig. 4**

The density at the immediate mouth of the tube being taken at  $\rho_1$ ,  $\rho$  being again the density at a remote point, the diffusion through the shell part of the system external to the tube will be  $2k(\rho - \rho_1)D$ , whilst that in the tube itself, as we have seen in the earlier part of the paper, must be represented by  $\frac{k\rho_1 \cdot A}{L}$ , where  $A$  is the area of the cross-section of the tube and  $L$  its length. We thus have the equation

$$2k(\rho - \rho_1)D = \frac{k\rho_1 \cdot A}{L},$$

in which  $\rho_1$  is the only unknown.

The general effect of external shells of this kind on tube diffusion is to somewhat increase the *resistance* of the column to the diffusive flow; in other words, to practically increase the length of the column, so that in its simplest form the problem resolves itself into a determination of a certain correction  $x$ , which, in the double system of fig. 4, has to be added to the length of the tube  $L$ , so as to obtain the same diffusive flow when the density of the diffusing gas varies from  $\rho$  at the mouth to zero at the bottom of the tube.

From the equations

$$2k(\rho - \rho_1)D = \frac{k\rho_1 \cdot A}{L} = \frac{k\rho \cdot A}{L + x},$$

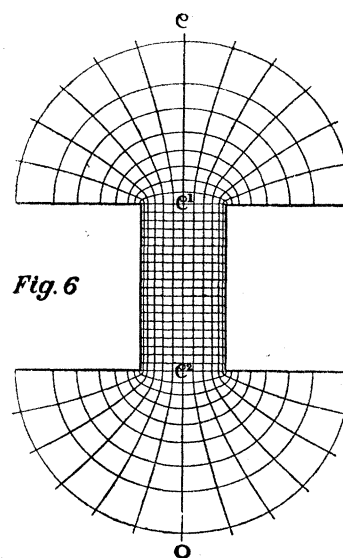
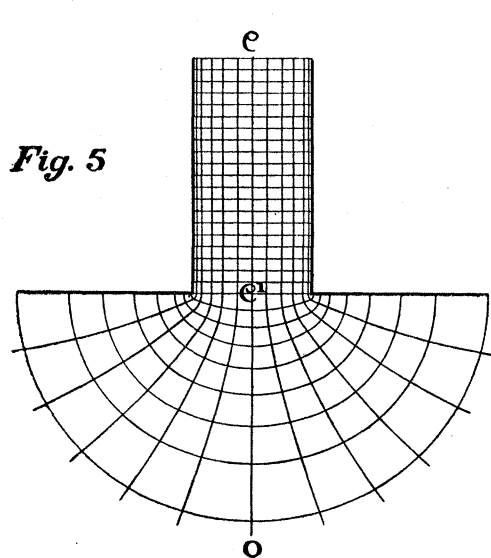
it follows that for a circular opening  $x = \frac{1}{8} \pi D$ , or  $\cdot 393 \times$  diameter.

It is interesting to note that this correction exactly corresponds with the lower limit which Lord RAYLEIGH has assigned to the resistance for necks of resonators in the form of circular cylinders ('Phil. Trans.,' vol. 161 (1870), 77), and it appears also that HELMHOLTZ found the same quantity as an approximate correction to be added to the length of an organ pipe. Since the electrostatic analogy was also employed by Lord RAYLEIGH in his investigations, it is perhaps the less to be wondered at that methods so apparently different should lead to the same general result.

In fig. 5 we have a case of diffusion down a tube which opens out at the bottom into an absorptive chamber, the density at the open mouth of the tube being supposed to be kept constant at  $\rho$ , the density at the bottom of the tube being  $\rho_1$ . Thus we get the equation

$$2k\rho_1 D = \frac{k(\rho - \rho_1)A}{L}.$$

In this case the value of  $\rho_1$  corresponds with that for  $\rho - \rho_1$  for equal lengths and diameters where we have the arrangement of fig. 4. The correction  $\alpha$  for the length of the tube will again be  $\cdot 393 \times$  diameter.



We finally come to the case given in fig. 6, in which we have a set of shells at either end of the tube, the fall of density through the whole system being from  $\rho$  to 0. In this arrangement the density at one end of the tube may be represented by  $\rho_1$ , and at the other end, where the density is less, by  $\rho_2$ . This gives us the following equations:—

$$(1) \quad 2k(\rho - \rho_1)D = \frac{k(\rho_1 - \rho_2)A}{L} \quad (2)$$

$$(3) \quad = 2k\rho_2 D.$$

2 L 2

From (1) and (3)  $\rho_2 = (\rho - \rho_1)$ , and by substitution

$$2k(\rho - \rho_1)D = \frac{kA(2\rho_1 - \rho)}{L},$$

from which it can be shown that the correction to be applied to the length of a tube of circular cross-section is '786 times its diameter, that is to say,  $2x$ , or double the correction of that which is required for the system of fig. 4. Such a case may therefore be dealt with very simply by considering the combined action of the triple system as the equivalent of a tube of the same diameter, but of a length of  $L + 2x$ , and at the two ends of which the density of the diffusing substance is maintained at  $\rho$  and 0 respectively;  $x$  being equal to '393 times the diameter of the tube. The rate of diffusion will thus be represented by the equation

$$Q = \frac{k\rho A}{L + 2x}.$$

#### *Diffusion through Multi-perforate Septa.*

We have seen how, by varying the size of a circular aperture in a diaphragm which divides two regions of unequal density, the velocity of the diffusive flow between these two regions is made to vary directly as the linear dimensions of the aperture, the quantity of diffusing substance passing per unit area of the aperture consequently increasing in the inverse ratio of the diameters. Reasoning from this fact we were led to anticipate that a thin septum might be so pierced with a number of small perforations, arranged at suitable distances, that it would exercise but a small amount of obstruction on a diffusive flow under favourable conditions, although the aggregate area of the perforations might represent only a small percentage of the total area of the septum.

Our early attempts to verify this deduction experimentally were made by perforating with a fine needle thin pieces of cardboard, previously rendered impervious by saturation with paraffin, and fixing these on small glass dishes partly filled with caustic soda solution. By comparing the amount of atmospheric carbon dioxide absorbed in this manner with that absorbed by open dishes placed under like conditions, it was at once seen that perforated septa of this kind do possess all the remarkable properties which we had been led to expect. But the material of which these septa was made was only suitable for rough preliminary work, and the method of perforation left much to be desired. We finally selected thin photographic celluloid as the best material for the diaphragms, using the ordinary roller Kodak film, which usually varies in thickness from '08 to '1 millim.\* By a series of preliminary experiments we found that this film in its imperforate state is quite impervious to atmospheric carbon dioxide.

\* Mica is not suitable for this special purpose, since, owing to its laminated structure, it is difficult to punch regularly-shaped holes in it in the manner described above.

In order to perforate the film with small holes of a uniform size and distributed in a definite manner, the following plan was adopted :—

A fine No. 11 sewing needle was broken evenly across the middle, where its diameter had been measured under the microscope, and was fixed in such a manner as to admit of its being used as a small punch. A piece of paper accurately ruled into squares of a millimetre was then placed on a smooth surface of soft lead, and over this again was laid the transparent celluloid film, through which the holes were punched with the broken needle at any desired distance from each other. In this manner a series of well-cut round holes was obtained, perfectly free from burr, and of a uniform diameter of  $\cdot 380$  millim., this being verified by micrometer measurement.

Before describing our experiments on gaseous diffusion, we will briefly draw attention to some preliminary experiments on the diffusion of *coloured liquids* through such perforated septa, which illustrate in a general manner their remarkable properties.

Several small glass cylinders about 33 millims. in diameter and 6 centims. high were cut in half, and the edges were ground flat. The lower half of each cylinder was filled with a clear solution of 5 per cent. gelatine, and whilst this was still mobile the mouth of the cylinder was closed with one of the perforated diaphragms. After the setting of the gelatine and the removal of any excess which had exuded through the perforations, the other half of the cylinder was placed in position, and the space so formed over the septum was filled with a similar solution of gelatine to which had been added  $\cdot 05$  per cent. of methylene blue. The extent of the diffusion of the dye into the clear gelatine below was observed from time to time, and was compared with the diffusion in a cylinder prepared in a similar manner, but without the intervention of any diaphragm between the coloured and uncoloured gelatine.

The number, size, and distribution of holes in the three diaphragms will be seen on reference to Table XVII.

TABLE XVI.—Distance Traversed by Diffusing Dye in Cylinders in Equal Times.

Time in hours.	Without septum.	Septum (1).	Septum (2).	Septum (3).
	millims.	millims.	millims.	millims.
18	13·75	13·7	12·0	10·4
23	15·0	15·0	13·5	—
42	20·7	20·7	18·5	18·3

The relative lengths of the columns of diffused dye are not in themselves a measure of the amount of diffusion, since the average density of the column may vary. In comparing the experiments made with Septum (1) with those without any intervening septum it was clear, however, from the exact correspondence of the gradation of



colour, and of the lengths, that the intervention of a diaphragm which only presented a clear area of about 11 per cent. of that of the cross-section of the column had not resulted in any sensible obstruction of the diffusive flow. In the other instances, where the clear areas of the diaphragms amounted only to 2·82 and 1·25 per cent. of the cross-section, the flow had, it is true, suffered some obstruction, but the amount of diffusion still represented a large proportion of that taking place in the open cylinder.\*

When using these multi-perforate celluloid diaphragms for experiments on the diffusion of atmospheric carbon dioxide they were fixed, by means of paraffin luting, over the open ends of short glass tubes about 3·4 centims. in diameter. The lower ends of the tubes were furnished with a side tube and stop-cock for running in the caustic soda solution to any desired height, and also with a somewhat long delivery tube, as in a burette, for drawing off the solution into the titration vessel.

The following table gives the full particulars of the six diaphragms which were employed :—

TABLE XVII.  
(Thickness of septum, 0·1 millim.)

No. of septum.	Diameter of each hole in millims.	Distance apart in millims.	Distance apart in terms of diameters.	Number of holes per sq. centim. of septum.	Percentage area of holes on unit area of septum.
(1)	·380	1·0	2·63	100·00	11·34
(2)	·380	2·0	5·26	25·00	2·82
(3)	·380	3·0	7·8	11·11	1·25
(4)	·380	4·0	10·52	6·25	·70
(5)	·380	5·0	13·1	4·0	·45
(6)	·380	6·0	15·7	2·77	·31

The experiments were carried on in still air for periods of from one to two days, the carbon dioxide which had diffused through the diaphragm being then determined by titrating the absorbing liquid, whose surface was at a definite distance from the under side of the obstructing septum.

The amounts of CO<sub>2</sub> which had diffused in each case were compared with the amounts which would have diffused down the open tube under like conditions, supposing no obstructing septum had been present. This was calculated from (1) the known diffusivity of CO<sub>2</sub> in air; (2) the dimensions of the tubes, and (3) the mean density of the CO<sub>2</sub> in the air of the room during the experiment. The formula used has the general expression

$$Q = \frac{k\rho A}{L + x},$$

\* It would be comparatively easy to make those experiments with diffusing dyes more strictly quantitative by redissolving the diffusate in a given volume of water and determining the colour intensities by means of the tintometer.

as given on p. 258, corresponding to the condition of single "shell" formation over a tube having a broad rim at its mouth, as in fig. 4.\*

The following table gives the summary of a series of experiments made with the diaphragms described in Table XVII., when the surface of the absorbing liquid was at a uniform distance of 4 centims. from the diaphragm :—

TABLE XVIII.

(Length of Tube, L = 4 centims.)

No. of septum.	Diameter of tube.	Area of tube.	CO <sub>2</sub> diffused through septum per hour.	Open tube diffusion per hour.	Percentage of septum diffusion on open tube diffusion.	Percentage area of holes in septum.
	centims.	sq. centims.	cub. centims. (at 0° and 760 millims.).	cub. centims. (at 0° and 760 millims.).		
(1)	3·450	9·348	·361	·346	104·3	11·34
(2)	3·425	9·186	·148	·342	43·2	2·82
(3)	3·471	9·456	·131	·352	37·2	1·25
(4)	3·480	9·511	·110	·353	31·1	·70
(6)	3·471	9·456	·0683	·334	20·4	·31

The numbers in the last column but one show the relation of the flow with the septum in position to that which would have taken place down the open tube; whilst the last column gives the aggregate area of the perforations expressed as a percentage on the total cross-section. A comparison of these two sets of numbers gives a striking illustration of the comparatively small amount of influence exerted on the diffusive flow by a multi-perforate septum under suitable conditions, an influence out of all proportion to the actual obstruction of *area* by the solid portions of the septum.

For instance, in No. 1, although more than 88 per cent. of the cross-section of the tube has been stopped out, the increased velocity through the remaining 11·34 per cent. has been sufficient to maintain a flow practically equal to that of the

\* The details of the calculation are as follows, where  $Qv^\circ$  is the volume of CO<sub>2</sub> diffusing down the open tube in one hour, expressed in cub. centims. at 0° and 760 millims. bar. :—

$$Qv^\circ = \frac{k\rho A \cdot 3600 \cdot T^\circ \cdot p}{(L + x) T \cdot 760}.$$

Here  $k$  is the coefficient of diffusivity of CO<sub>2</sub> in air in C.G.S. units *at the temperature of the experiment*;  $\rho$  the density of the CO<sub>2</sub> in the atmosphere;  $A$  the area of the tube in sq. centims.;  $T^\circ$  and  $T$  the temperature of 0° C. and the mean temperature of the experiment on the absolute scale; and  $L$  the length of the tube in centims.;  $x$  the correction for the length =  $\cdot 392 \times$  diameter;  $k$  is obtained from  $k^\circ$  by the formula

$$k = k^\circ \left( \frac{T}{T^\circ} \right)^2.$$

unobstructed tube.\* Again, we find in (4) that 30 per cent. of the open-tube diffusion has taken place, although the aggregate area of the holes amounts only to .7 per cent. of the cross-section. In (6) the results in the same direction are still more striking.

When the distance between the absorbing surface and the diaphragm is decreased to 1 centim., the actual flow of  $\text{CO}_2$  is increased, but the septum diffusion is a smaller fraction of the open-tube diffusion under similar conditions. This is shown in the following series of experiments:—

TABLE XIX.  
(Length of Tube,  $L = 1$  centim.)

No. of septum.	Diameter of tube.	Area of tube.	$\text{CO}_2$ diffused through septum per hour.	Open tube diffusion per hour.	Percentage of septum diffusion on open tube diffusion.	Percentage area of holes in septum.
	centims.	sq. centims.	cub. centims. (at $0^\circ$ and 760 millims.).	cub. centims. (at $0^\circ$ and 760 millims.).		
(1)	3.450	9.347	.433	.771	56.1	11.34
(2)	3.425	9.186	.401	.775	51.7	2.82
(3)	3.471	9.456	.312	.768	40.6	1.25
(4)	3.480	9.511	.241	.767	31.4	.70
(5)	3.425	9.186	.156	.744	20.9	.45
(6)	3.450	9.347	.106	.740	14.0	.31

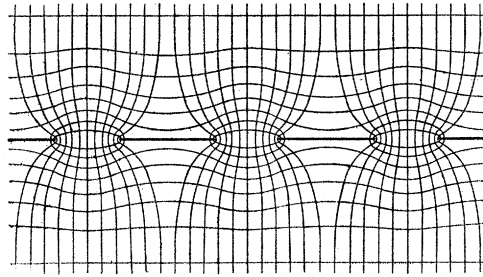
The results obtained with multi-perforate septa are precisely those which might be expected from our previous observations on the intensification of the diffusive flow produced by the gradual decrease in the size of single apertures. When such a septum is placed over a tube down which static diffusion is going on, there is a local disturbance and intensification of the gradient in the immediate neighbourhood of the septum, which does not extend to those parts of the column at some distance from it. This disturbance is brought about by the convergence of the axial lines of flux on the one side of the diaphragm and their divergence on the other, with the consequent formation of a system of density shells on either side of each aperture.

Perforations of this kind may be compared with a system of conductors electrified to a common potential, the density of the diffusing substance near the apertures

\* In Experiment No. 1, with 100 perforations to the sq. centim., the interposition of the diaphragm has given rise to an apparent slight *increase* in the flow. This cannot be really the case, since the septum must always act as an obstruction, although it may be a small one. The explanation in this instance is to be found in the imperfect shell-formation over the holes and the want of absolute stillness in the air. Under these circumstances rather more  $\text{CO}_2$  will pass through the diaphragm, and the ratio of septum diffusion to open-tube diffusion will be somewhat increased.

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 considerably altered by cutting parts of it away, and leaving an open framework, consisting of portions at the same potential, so also is it possible to block out a considerable portion of the cross-section of the diffusing column without materially altering the general static conditions on which the flow depends.

In fig. 7 we have attempted to illustrate in a diagrammatic form what takes place when a multi-perforate diaphragm is introduced into a line of static flow of a diffusing gas or solute. At a distance away from the openings the lines of flux (analogous to lines or tubes of force) are sensibly parallel, and become convergent as they approach the diaphragm, the velocity at the same time increasing owing to the local alteration



*Fig. 7*

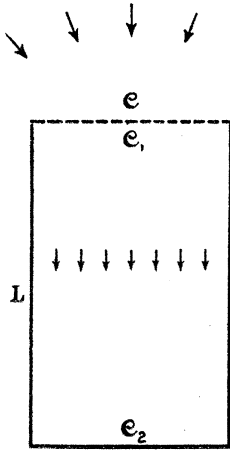
of gradient produced by the ellipsoidal “density shells” (lines of potential) around the openings. As the hyperbolic lines of flux pass through the apertures they begin to diverge, but since these divergent streams, proceeding from adjacent holes, cannot cross each other, they bend round and once more become parallel, the velocity at the same time diminishing. It is this bending round of the lines of flow to and from the diaphragm which explains the striking fact that the apertures under favourable conditions of distribution may be almost as efficient as if the diaphragm were non-existent.\*

The resistance which a multi-perforate diaphragm can introduce into a statically diffusing column of any length, can be approximately calculated if we suppose the apertures to be arranged at a sufficient distance apart *to allow each aperture to exercise its power without interference by its neighbours*, and this resistance can be compared with that of the open tube under like conditions. We have already shown that the resistance of an open tube of length  $L$ , will be  $L + x$ , where  $x = \frac{1}{8} \pi \times$  diameter.

\* After we had constructed this schematic diagram, our attention was called to a paper on the “Reflection and Transmission of Electric Waves by a Metallic Grating,” by Professor HORACE LAMB (‘Proc. Lond. Mathemat. Soc.,’ vol. 29, p. 523, 1898), where an exact diagram is given of the cognate problem of the lines of electric flow as disturbed by a plane grating composed of parallel metallic strips placed perpendicular to its direction.



If the multi-perforate septum or screen is at the mouth of the tube, as in the accompanying diagram, fig. *a*, where  $\rho$  = the density of the diffusing substance a little way above the screen,  $\rho_1$  a little way below it, and  $\rho_2$  the density at the absorbing surface at the bottom of the tube, which has a length  $L$ ;  $A$  the area of cross-section of the tube of diameter  $D$ ;  $n$  the number of apertures in the septum having a length  $l$ , corresponding to the thickness of the septum; and  $a$  the sectional area of a single aperture, then, for the combination of tube and screen, the quantity  $Q$  of the substance diffusing in unit of time is,\*

Fig. *a*.

(1) For the septum :—

$$Q = k \frac{na(\rho - \rho_1)}{l + .785d},$$

and (2) for the tube :—

$$Q = k \frac{A(\rho_1 - \rho_2)}{L + .392D}.$$

These amounts are equal, consequently by elimination of  $\rho_1$

$$Q \left\{ \frac{l + .785d}{nak} + \frac{L + .392D}{Ak} \right\} = \rho - \rho_2,$$

so that

$$Q = k \frac{A(\rho - \rho_2)}{L + .392D + \frac{A}{na}(l + .785d)}.$$

Hence the effect of the resistance introduced by the screen or septum is to increase the effective length  $(L + .392D)$  of the open tube by

$$\frac{A}{na}(l + .785d).$$

We thus have a means of approximately determining, in terms of the tube length, the resistance of any multi-perforate septum, providing its apertures are small and are sufficiently far apart not to sensibly interfere with each other. The flow will of course be inversely proportional to the resistance.

The actual resistance of the screen under these conditions will be a constant, and the obstruction which it produces will consequently bear a less proportion to the total resistance of tube + screen the longer the tube becomes.

This deduction is verified by a comparison of the experimental results obtained with similar screens on tubes of different lengths, as given in Tables XVIII. and XIX.

In order to see how far the above theoretical considerations enable us to predict the behaviour of screens of known dimensions, we have calculated the flow of

\* We have again to express our thanks to Dr. LARMOR for much assistance in the development of these formulæ.

atmospheric  $\text{CO}_2$  which ought to pass through each of the screens (1) to (6) of Table XVII., when these are used with a tube of 1 centim. in length, on the assumption that each hole works independently of its neighbours. The values so calculated are, in the following table, compared with the experimental values, both sets of numbers being expressed as percentages on the full flow of the unobstructed tube of length  $L + x$ .

TABLE XX.

No. of screen (see Table XVII.).	Distance of apertures apart in diameters.	Resistance of open tube, $L + x$ .	Resistance of tube and screen, $L + x + \frac{A}{na}(l + .785d)$ .	Theoretical flow through screen, expressed as a percentage on open tube diffusion.	Observed flow, expressed as a percentage on open tube diffusion.
(1)	2.63	2.352	2.684	87.6	56.1
(2)	5.26	2.342	3.674	63.7	51.7
(3)	7.8	2.360	5.360	44.0	40.6
(4)	10.52	2.364	7.693	30.7	31.4
(5)	13.1	2.342	10.677	21.9	20.9
(6)	15.7	2.352	15.142	15.5	14.0

It will be observed that, provided the apertures in the septum are set at a minimum distance of about 10 diameters apart, the flow through the screens approximates closely to that deducible from theory. When, however, the holes are much more closely packed, the experimental flow is less than that calculated by the formula, which postulates the non-interference of the holes with each other's action. We may conclude therefore that the interference of the density shells of small holes, set at 10 diameters and more apart, is small, each hole beyond this limit acting almost independently according to the diameter law.

*The Bearing of these Results on Diffusion through Porous Septa.*

If we imagine the perforations of a diaphragm, such as we have been considering, to be gradually diminished in size, we shall at last reach a point at which any *mass movement* of the diffusing gas or solute becomes more and more difficult, and movement of this kind may finally only become possible where there is a considerable difference of pressure on the two sides of the septum. Under these conditions we shall have all the phenomena of *porous diffusion* or *diffusion through a semi-permeable membrane*. But we have no reason to believe that the "diameter law" will cease to be followed in such cases, provided the pores are not sufficiently near to interfere with each other, and are not of molecular dimensions. We must consequently regard porous diffusion as an extreme case of free diffusion through a

multi-perforate diaphragm, where the molecular fluxes are much intensified by the minuteness of the pores in the manner we have indicated.\*

A comparison has never yet been made experimentally between the diffusive flow through thin porous septa and through clear openings of equal area, but it is quite evident that under favourable circumstances such septa, even if made of fairly dense material, will produce less obstruction than is ordinarily believed.

The conditions of diffusion through a single pore of this description are similar to those of fig. 6, providing the pores are not too close together, the amount of diffusion per unit of time being represented by

$$Q = \frac{k\rho A}{L + 2a}.$$

The formula developed in the last section is, however, more convenient for estimating the efficiency of a septum of known thickness, and with pores of known dimensions.

As an example we have calculated the efficiency of an open cylindrical tube of 1 sq. centim. in section, and 1 centim. long, as compared with that of the same tube under like conditions when the mouth is closed with (1) a septum of .1 millim., and (2) a septum of .05 millim. in thickness; each septum being supposed to have pores of .011 millim. in diameter, arranged at distances of 10 diameters apart, at which distance, as we have previously seen, the fine openings will practically cease to have any influence on each other.

It will be remembered that the resistance of the diaphragm expressed in terms of the length of the tube is  $\cdot 392 D + \frac{A}{na} (l + \cdot 785 d)$ , the efficiency being inversely proportional to the resistance.

The values in this case in centims. are as follows :—

*For Open Tube*,  $L = 1\cdot 0$ ;  $D = 1\cdot 1284$ ; and  $A = 1\cdot 0$ .

*For Septum (1)*,  $l = \cdot 01$ ;  $d = \cdot 0011284$ ; and  $a = 10^{-6}$  sq. centim.

*For Septum (2)*,  $l = \cdot 005$ ;  $d = \cdot 0011284$ ; and  $a = 10^{-6}$  sq. centim.  $n$ , the number of pores on the septum at 10 diameters apart = 8264.

TABLE XXI.

No.	Resistance of open tube, $L + \cdot 392D$ .	Resistance of tube + septum, $L + \cdot 392D + \frac{A}{na} (l + \cdot 785d)$ .	Efficiency of tube + septum compared with tube alone, per cent.	Percentage area of septum occupied by the pores.
(1)	centims. 1·440	centims. 2·757	52·2	·82
(2)	1·440	2·152	66·9	·82

\* The argument here used is equally applicable to anastomosing non-cylindrical pores.

*The Determination of Coefficients of Diffusion by means of Perforated Septa.*

It is evident from the foregoing considerations that, under favourable conditions, the rate of flow of diffusible substances through an aperture or apertures in a septum ought to afford a simple and convenient method for determining *coefficients of diffusion* in certain cases. Our experiments indicate that the process is one which admits of a considerable degree of exactness, and that it will be of great use, not only in establishing the values of  $k$ , but also in throwing more light upon a question of great theoretical interest, the variation of diffusivity of certain gases with varying ratios of mixture.

So far we have only applied the new method (1) to atmospheric carbon dioxide, (2) to aqueous vapour at low tensions diffusing into air; and (3) to solutions of sodium chloride.

*(1) Experiments on Atmospheric CO<sub>2</sub>.*

These were made by allowing the CO<sub>2</sub> of ordinary air to diffuse through a single aperture, or a series of very small apertures, into a space which was kept practically free from CO<sub>2</sub> by complete absorption with solutions of caustic alkali.

In the first series described, we employed a thin celluloid septum of about .1 millim. thickness fixed at the mouth of a short burette-like tube of about 4 centims. in diameter, containing the absorbent.

By a series of preliminary experiments with apertures of .375 millim. in diameter, gradually decreasing in number, it was found that when the number of the holes had been decreased past a certain point, the velocity of the ingoing CO<sub>2</sub>, estimated by the amount absorbed in a given time, became constant, this point of maximum velocity, all other conditions being the same, being conditioned solely by the diffusivity. When the level of the liquid in the tube was from 2 to 3 centims. from the top, we found that ten or twelve of these small holes, evenly distributed over the disc, were not too many to employ.

As the experiments were carried on in perfectly still air (the CO<sub>2</sub> content of which was, of course, accurately determined) and the velocity of ingress, owing to the small size of the holes, was considerable, we had all the conditions for the perfect formation of the double system of shells of equal density as shown in fig. 3; hence the general formula for the diffusion should be

$$Q = k\rho D.$$

Since, however, the thickness of the celluloid septum, although small, is not altogether negligible, where the greatest possible accuracy is required, the formula representing the rate of diffusion for a single aperture should be

$$Q = \frac{k\rho A}{l + 2x},$$

whence

$$k = \frac{Q(l + 2x)}{\rho A}$$



The following are the details of two such experiments :—

TABLE XXII.

Number of apertures . . . . .	12
Diameter of each aperture . . . .	·375 millim.
Thickness of septum . . . . .	·10 „
$l + 2x = \cdot 0394$ centim.	
Mean temperature . . . . .	15°·0 C.
Mean pressure . . . . .	757·9 millims.
Mean content of air in CO <sub>2</sub> . . .	3·29 per 10,000.

(In (1) the absorbent liquid was at a distance of 2 centims. from top of tube, in (2) it was at 3 centims.)

No.	Time in hours.	CO <sub>2</sub> diffused in cub. centims. at 0° and 760 millims.			$k^\circ$ .
		Total.	Total per hour.	Per hole per hour $Qv^\circ$ .	
(1)	215·3	13·839	·06427	·00535	·153
(2)	216·2	13·632	·06305	·00525	·151

In the next experiment diffusion was carried on in a similar manner through a *single aperture* of 4 millims. diameter, made in a *mica* plate of (3) ·11 millim. and (4) ·10 millim. in thickness.

$l + 2x$ (3) ·325 centim., (4) ·324 centim.	
Mean temperature . . . . .	15° C.
Mean pressure . . . . .	757·9 millims.
Mean content of air in CO <sub>2</sub> . . .	3·29 parts per 10,000.

TABLE XXIII.

No.	Time in hours.	CO <sub>2</sub> diffused. cub. centims. at 0° and 760 millims.		$k^\circ$ .
		Total.	Total per hour.	
(3)	212·3	15·308	·07210	·149
(4)	211·5	15·882	·07509	·155

It will be noted that the values of  $k^0$  given by this method for atmospheric CO<sub>2</sub>

approximate fairly closely to those obtained by static diffusion along tubes (see p. 241), but we have reason to believe that this new method is more accurate than tube diffusion, and it has the advantage in occupying much less time for an experiment.

The values obtained are almost identical with those of WAITZ, but depart somewhat from the value  $\cdot 133$  deduced by STEFAN and O. E. MEYER from theoretical considerations based on the coefficient of viscosity of the two gases, carbon dioxide and air (see O. E. MEYER'S 'Kinetic Theory,' p. 275, Engl. ed., 1899), and also from the commonly received value of  $\cdot 142$  obtained by LOSCHMIDT for much higher ratios of mixture.

According to the kinetic theory of diffusion of STEFAN and MAXWELL, diffusivity should be as constant a property as conductivity of heat in a solid, but O. E. MEYER'S expansion of this theory leads to a somewhat different conclusion, which may be expressed as follows:—If the total number of molecules in unit volume of a mixture of two diffusing gases is represented by  $N$ , and the changing number of molecules of the constituents by  $N_1$ ,  $N_2$  respectively, then the diffusivity will be found to vary slightly with the ratio of mixture  $N_1/N_2$ , whereas according to STEFAN and MAXWELL'S views the coefficient of diffusion is independent of this ratio.

In the case of  $\text{CO}_2$  and air MEYER'S theory leads to a *lower* coefficient of diffusion than  $\cdot 142$  for the extremely dilute  $\text{CO}_2$  with which we have to deal in ordinary air, whereas we find a distinctly *higher* value than this, one in fact which is quite as high as some of those obtained by the ordinary methods of mixture originally employed by LOSCHMIDT.

## (2) *Diffusion of Aqueous Vapour in Air.*

An attempt was made to determine the value of  $k$  for aqueous vapour at low tensions when diffusing into air, in the following manner:—

Small dishes or cylinders, from 4 to 6 centims. in diameter, were covered with thin mica discs which were fixed on to them with Canada balsam. The discs were perforated with a single central hole of 4 millims. in diameter, water being poured into the vessels to about 1.5 centims. from the top. These vessels, after being weighed, were placed in a spacious exsiccator which exposed a large surface of concentrated sulphuric acid, so that evaporation through the small aperture took place into an atmosphere practically free from vapour. The exsiccator was covered outside with a thick non-conducting layer of cotton-wool, and was placed in a room kept as nearly as possible at constant temperature.

The surface of the water in the dish being very large, compared with the size of the aperture in the mica cover, the air of the dish above the liquid was saturated with water vapour, which was consequently at the maximum pressure corresponding to the temperature of the experiment. The amount of vapour which diffused into the dry air of the exsiccator was determined at intervals of two or three days by weighing the dish.

The value of  $\rho$ , the density of the water vapour in the air of the covered dish, is determinable from its maximum pressure for the mean temperature, and, since the pressure of the vapour in the air of the exsiccator is kept practically at zero, we can determine the value of  $k$ , representing the diffusivity of water vapour in air, by applying the same formula for double density-shell formation as we did in the case of the  $\text{CO}_2$ .

The following results were obtained in this manner, the value of  $k'$  representing the diffusivity for the mean temperature of experiment :—

TABLE XXIV.

No.	Time in hours.	Diameter of aperture.	H <sub>2</sub> O vapour diffused.		$\rho$ .	Temperature.	Barometer.	$k'$ .
			Total.	Total per hour.				
(1)	97·9	millims. 4·0	gramme. ·3836	gramme. ·003918	·00001129	12·9	756·6	·253
(2)	93·2	4·0	·4074	·004371	·00001244	14·5	756·9	·257
(3)	96·3	4·0	·4591	·004767	·00001353	15·9	759·9	·251
(4)	121·4	4·0	·6234	·005135	·00001427	16·8	755·9	·256

In order to render the values of  $k'$  strictly comparable they must be reduced to  $k^\circ$ , representing the diffusivity of aqueous vapour in air at  $0^\circ\text{C}$ ., by the formula

$$k' = k^\circ \left( \frac{T}{T^\circ} \right)^n.$$

The value of the exponent  $n$  has not been determined for aqueous vapour and air, but it cannot be far removed from 2, which is the value used by WINKELMANN in reducing his observations;  $k^\circ$  then assumes the following values in our experiments :—

	$k^\circ$ .
(1). . . . .	·231
(2). . . . .	·234
(3). . . . .	·224
(4). . . . .	·227
Mean. . . . .	·229

This corresponds almost exactly with the value ·230, calculated according to STEFAN's kinetic formula of diffusion.

WINKELMANN, by observing the rate of evaporation of water in narrow tubes ('Ann. Phys. Chem.,' vol. 22 (1884), p. 22), found the following values at  $92^{\circ}4$  and  $49^{\circ}5$ , the ratios of mixture being represented respectively by  $N_1/N_2 = 288/442$  and  $N_1/N_2 = 44.8/685.2$  :—

$$k^{92^{\circ}4} \cdot 2992 = k^{\circ} \cdot 167,$$

$$k^{49^{\circ}5} \cdot 2848 = k^{\circ} \cdot 204.$$

The pressures of the vapour in our experiments, which were made between  $12^{\circ}9$  and  $16^{\circ}8$ , correspond to ratios of mixture lying between  $11.1/745.5$  and  $14.2/741.7$ , which ought to give values of  $k^{\circ}$  higher than the highest value  $\cdot 204$  found by WINKELMANN, but the difference actually observed appears to be somewhat greater than can be accounted for by the mere diminution of the ratio of mixture.

The success of WINKELMANN'S method depends entirely on the maintenance of the maximum tension of aqueous vapour immediately above the surface of the evaporating liquid in the tube. If, as seems highly probable from his description of the experiments, this tension is not at a maximum, WINKELMANN'S results must certainly yield lower numbers for  $k$  than the actual values.

Although our method gives numbers agreeing so remarkably closely with the diffusivity calculated from STEFAN'S formula, there is not the same agreement with the theoretical values deduced from MEYER'S formula, which according to WINKELMANN are  $k^{\circ} \cdot 159$  and  $k^{\circ} \cdot 184$ , for tensions of vapour at  $92^{\circ}4$  and  $49^{\circ}5$  respectively.

### (3) *Experiments with Solutions of Sodium Chloride.*

These were made in a manner similar to those described on p. 247.

The solution of salt with 5 per cent. of added gelatine was contained in cylindrical vessels, to whose lower ends were cemented thin mica plates perforated with a circular hole of known diameter. Sufficient space was given in the gelatine for the formation of "density shells" of a radius of at least five or six times the diameter of the aperture, and the cylinders were suspended in a relatively large volume of water in which the diffused salt was determined at suitable intervals. When downward diffusion is employed it is unnecessary to keep the water stirred in order to get the full effect. By this arrangement the density of the sodium chloride was kept practically at zero at the limiting surface of the gelatine and the water of the outer vessel, and the disposition of the "density shells" in the gelatine ought to correspond to that of fig. 1 (see p. 256), diffusion taking place according to the general formula

$$Q = 2k\rho D.$$

When corrected for the thickness of the diaphragm this becomes

$$Q = \frac{k\rho A}{l + x},$$



and after the static condition has been established, which in this case requires from 15 to 20 hours,  $k$  is given by the following formula,  $Q$  representing the actual weight of the salt diffused in one hour :—

$$k = \frac{Q(l + x)}{\rho \cdot A \cdot 3600}.$$

The following are some of the experimental results obtained in this manner, the diffusivity  $k'$  being that corresponding to the mean temperature of each experiment :—

TABLE XXV.

No.	Duration of experiment in hours.	Diameter of aperture.	Thickness of septum.	Concentration of solution. Weight in volume per cent.	$\rho$ .	NaCl diffused, grammes.		Temperature.	$k'$ .
						Total.	Per hour.		
(1)	47·7	millims. 4·0	millims. ·1	5·5	·055	·1223	·00250	10°·0	·0000174
(2)	22·4	4·0	·1	5·5	·055	·0585	·00261	10°·5	·0000178
(3)	23·7	4·0	·1	5·5	·055	·0644	·00271	12°·2	·0000185
(4)	23·8	4·0	·1	5·5	·055	·0661	·00277	12°·6	·0000189

These values are higher than those deduced by STEFAN from GRAHAM'S experiments on the diffusion of 10 per cent. NaCl solutions in water, which when reduced to C.G.S. units are as follows :—

Temp. C.	$k'$ .
9°—10° . . . . .	·0000114
11°·75 . . . . .	·0000118
9°·0 . . . . .	·0000106
10°·0 . . . . .	·0000108
10°·0 . . . . .	·0000103

Other determinations of the diffusivity of NaCl have been made by SCHEFFER, DE HEEN, and SCHUMEISTER, who found at 20° C. :—

	$k'$ .
SCHEFFER . . . . .	·0000134
DE HEEN . . . . .	·0000140
SCHUMEISTER . . . . .	·0000127

*An Application of the foregoing Observations to certain Natural Processes of Diffusion in Plants.*

The problems suggested in the first place by a study of the gaseous interchanges going on in a leaf have led us to regard the general phenomena of diffusion from a new point of view, and it now remains to be seen how far the results of these inves-

tigations enable us to gain a deeper insight into the mechanism of the natural processes which formed the starting-point of this research.

The structure of a typical herbaceous leaf is one eminently suited for producing all the remarkable diffusive phenomena which we have found associated with multi-perforate septa.

If we take a special case, such as that of the under-side of the leaf of *Helianthus annuus*, we find the impervious cuticle and epidermis pierced at regular intervals with minute elliptical openings whose apertures are capable of being regulated by the state of turgescence of the guard-cells.

These openings, the stomates, are in immediate communication, through a large intercellular space, the respiratory cavity, with the numerous and roomy interspaces of the loosely packed cells of the spongy parenchyma. We have in fact an arrangement which virtually amounts to a multi-perforate diaphragm extended over a chamber whose interior presents a very large absorptive surface to the atmospheric carbon dioxide which enters through the fine apertures.

Where the stomates open into the respiratory cavity there is ample space for the formation of the negative "shells" of equal density which must necessarily be produced by the divergent molecular drift of the carbon dioxide entering the leaf. The spacing of the stomates on the leaf, if we regard them as circular openings, is about 8 diameters apart, a distribution which, as we have seen, would allow each single opening to exercise nearly its full efficiency without interference with its neighbour.

The extent of the absorption of the carbon dioxide of the air in the cellular interspaces must determine the gradient of density of that gas between the exterior and interior of the leaf, and the amount which enters through an individual stomate must be conditioned by this gradient, and also by the *linear dimensions* of the opening of the stomate.

In order that we might be in a position to form some idea of the maximum amount of atmospheric carbon dioxide which can pass through a single stomate under favourable conditions, that is to say, the maximum efficiency of the apparatus regarded from a physical point of view, we have determined with some degree of accuracy the actual dimensions of its various parts in the case of the *Helianthus*.

When a partially open stomate is observed in a median transverse section the approaching lips of the guard-cells are seen to divide the stomatal tube into an outer vestibular opening (*Vorhof*), and an inner portion (*Hinterhof*) which opens into the respiratory cavity; but when the stomate is fully open the recession of the lips of the guard-cells results in the formation of a continuous, short, straight-sided tube, of a length of about .014 millim., that is to say, about equal to the thickness of the cuticle and epidermis, and elliptical in section.

The average area of the elliptical cross-section of a perfectly open stomatal tube was found to be .0000908 square millim., which is equal to the area of a circle of .0107 millim. in diameter.

From STEFAN'S theoretical investigations of the relative amount of evaporation

from circular and elliptical surfaces of equal area, and from the correspondence which is found to hold good between such phenomena and those of diffusion, we may with perfect safety assume that an elliptical tube, such as we are considering, will function almost exactly the same as a cylindrical tube having the same area of cross-section. The "diffusion tube" of the stomatal apparatus of *Helianthus* will therefore be equivalent to a cylindrical tube of the following dimensions:—

Length . . . . .	·014 millim. (·0014 centim.)
Diameter . . . . .	·0107 „ (·00107 „ )
Area of cross-section .	·0000908 sq. millim. ( $10^{-7} \times 9\cdot08$ sq. centim.)

We are now in a position to determine the maximum amount of carbon dioxide which can pass through tubes of this nature by applying the principles which have been developed at an earlier stage of this paper.

In the first instance let us imagine the most favourable conditions possible, the stomates being wide open, the partial pressure of the atmospheric carbon dioxide at the mouth of the stomates being kept constant by a moving air current, and that of the respiratory cavity and the connected intercellular interspaces being maintained practically at *zero* by the absorbent and assimilatory action of the surrounding parenchyma cells. In this condition of things the inner part of the leaf will be a perfect "sink" of carbon dioxide, and the amount of gas in cub. centims. (measured at 0° C. and 760 millims.) which will be absorbed by 1 square centim. of leaf per hour will be represented by

$$Q = \frac{k\rho \cdot A \cdot y \cdot 3600}{l + x}$$

where	$k$ = diffusivity of $\text{CO}_2$ in C.G.S. units = ·145.
	$\rho$ = density of $\text{CO}_2$ in outer air in atmospheres = ·0003.
	$A$ = area of stomate = $10^{-7} \times 9\cdot08$ centims.
	$y$ = number of stomates per sq. centim. = 33,000.
	$l$ = length of stomatic tube = ·0014 centim.
	$x = \frac{1}{8}\pi \times \text{diameter} = \cdot00042$ centim.

Hence  $Q = 2\cdot578$  cub. centims. per hour per sq. centim.

If we suppose the air outside the leaf to be perfectly still,\* so that density "shells" are formed outside as well as inside the leaf, the denominator of the fraction in the last equation becomes  $l + 2x$ , and the maximum amount of carbon dioxide entering the leaf per square centim. per hour will be 2·095 cub. centims.

Both these values are very much in excess of the actual amounts of  $\text{CO}_2$  taken in by a leaf when actively assimilating.

\* The epidermal hairs which frequently occur on the underside of many leaves may be sufficient to prevent air currents from sweeping away the external density "shells" in many cases, and the manner in which some stomates (*e.g.*, *Aloë nigricans*) are sunk in the thick epidermis must also contribute to the same end.

When a leaf is assimilating at the rate of 1·8 grammes of carbohydrate per square metre of leaf surface per hour, the greatest amount which has hitherto been recorded for *Helianthus annuus* by the weighing method of SACHS, it does not require a greater intake of carbon dioxide than ·134 cub. centim. per square centim. per hour; that is to say, only from 5·2 to 6·3 per cent. of the maximum amount which the diffusion apparatus of the leaf would be capable of effecting if the interior of the leaf were a perfect "sink" of atmospheric carbon dioxide.

The great difference between the observed intake of  $\text{CO}_2$  and the maximum possible intake deduced from a consideration of the physical mechanism of the leaf is of course due to the fact that the pressure of the gas in the respiratory cavity and interspaces is still considerable, even during active assimilation, so that there is only a very small gradient between the external and internal gas, due to the imperfection of the absorption.\*

From the data already given it is possible to deduce the average pressure of the carbon dioxide in the interior of the assimilating leaf when that of the outer air is known. Under like conditions the rate of intake will depend on the magnitude  $\rho - \rho_1$ , where  $\rho$  and  $\rho_1$  represent the pressures of the carbon dioxide in the outer air and in the intercellular spaces respectively.

When  $\rho_1 = 0$  we have seen that the intake may amount to 2·578 cub. centims. per square centim. per hour when the outer air is in motion, and 2·095 cub. centim. when the air is still. Under these two sets of conditions during normal assimilation the partial pressure of the  $\text{CO}_2$  inside the leaf will therefore be as follows,  $\rho$  being taken as unity :—

$$(1) \quad 1 - \frac{\cdot 134}{2\cdot 578} = \cdot 9481$$

$$(2) \quad 1 - \frac{\cdot 134}{2\cdot 095} = \cdot 9361$$

In other words, it is only necessary to have a difference of pressure in the carbon

\* It is a matter of some interest in connection with the above remarks to determine the relation which exists between the area of an open stomate and the superficial area of the cells of the spongy parenchyma immediately corresponding to it, and forming the absorptive surface for the entering  $\text{CO}_2$ . We have endeavoured to ascertain this in the two cases of *Helianthus annuus* and *Catalpa bignonioides*. Owing to the irregular contour of the cells the difficulties of measurement are considerable, and the results must only be regarded as approximations.

Underlying 1 sq. millim. of the under surface of the leaf of *Helianthus* there were found to be 2096 cells of spongy parenchyma, each one having a superficies of ·002017 sq. millim., so that the total surface area of the cells corresponding to 1 sq. millim. of leaf is  $2096 \times \cdot 002017 = 4\cdot 228$  sq. millims. The aggregate area of the 219 open stomates of the 1 sq. millim. of under surface was  $219 \times \cdot 0000908 = \cdot 01988$  sq. millim.; hence the fraction

$$\frac{\cdot 01988}{4\cdot 228} = \frac{1}{212}$$

represents the ratio of the area of one stomatal opening to the area of the cells of the spongy parenchyma corresponding to it.

The ratio in the case of *Catalpa* is much greater than this, amounting to about  $\frac{1}{1159}$ .



dioxide of the outer and inner air of from 5 to 6·5 per cent. in order to get a sufficient gradient to account for the full observed intake of the gas into the leaf of *Helianthus*.

In these calculations we have assumed the stomates to be open to their widest possible extent, but a correction can readily be applied for any degree of opening short of this by bearing in mind that, under like conditions, the intake will vary directly as the diameter of the apertures when these are regarded as circular openings.\*

The structure of a typical herbaceous leaf is an admirable example of adaptation to natural laws, which in this particular instance have only recently become known to us. It illustrates in a striking manner all the physical properties of the multi-perforate diaphragm, which, with its minute apertures set at from 6 to 8 diameters apart, and representing only 1 to 3 per cent. of free area, yet allows a perfectly free interchange of gases on its two sides, whilst at the same time affording every protection to the delicate structures underlying it.

Regarding the arrangement merely as that of a piece of physical apparatus for producing rapid diffusion, it certainly appears at first sight to be 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 our surprise at the comparatively large amount of that gas which a leaf can absorb from the air, we must in future rather wonder that the intake is not greater than it actually is.

But if the limitations to the absorption of carbon dioxide are not to be found in any imperfections of the stomatal apparatus of the leaf, we must seek them elsewhere.

The first explanation which naturally suggests itself is that, in the particular case we are considering, the chlorophyll bodies are performing the maximum amount of work of which they are capable, and that the 134 cub. centim. of gas absorbed by the sq. centim. of leaf per hour is a measure of the maximum elaborative power of the assimilatory centres. Such, however, cannot be the true explanation, since with good illumination the power of assimilation, within certain limits, is always found to increase with every slight increase in the amount of carbon dioxide in the outer air. We shall in fact show in a subsequent paper that there is within these limits a remarkable quantitative correspondence between increased pressure of  $\text{CO}_2$  and increased assimilation.

The restriction in the absorption of the gas by the leaf must rather be sought in the difficulty which the gaseous carbon dioxide experiences in passing from the

\* It will be seen that the diameters of the stomates under consideration might be reduced to from  $\frac{1}{15}$  to  $\frac{1}{20}$  of their maximum and yet still allow a sufficient amount of  $\text{CO}_2$  to pass for the maximum observed assimilation, providing the absorption were perfect. This is an important fact, when we bear in mind the rôle which the stomates play in transpiration.

intercellular spaces through the cell-walls of the assimilating parenchyma. The penetration of these cell-membranes must necessarily be preceded by the *solution* of the gas, and any phenomena of diffusion which take place between this point and the assimilating centres must be referred to liquid and not to gaseous diffusion.

GRAHAM, in his Bakerian Lecture of 1850 ('Chemical and Physical Researches,' p. 446), showed that the "liquid diffusion of carbonic acid is a slow process compared with its gaseous diffusion, quite as much as days are to minutes." We have in this fact something more than a suggestion of where we may expect to find the point of greatest resistance in the path of the carbon dioxide on its way from the outer air to the chlorophyll corpuscles, and where at any rate one important "throttle-valve" of the assimilatory process is situated.

The accelerating action of a multi-perforate diaphragm on a diffusive flow is independent of the direction of the flow, so that the arrangement which we find in the leaf is as efficient in promoting the egress of the excess of oxygen liberated during assimilation, and the carbon dioxide evolved during the respiratory process, as it is in promoting the ingress of the atmospheric carbon dioxide itself.

It remains now to be seen how far the *transpiration of water* through the leaf stomates may be regarded as a phenomenon of diffusion. Any outward molecular flow of this kind may take place without interfering with the simultaneous interchange of other gases, whereas, if transpiration is in any way dependent on an actual *mass movement* of the aqueous vapour, conditioned by increased pressure within the interspaces of the leaf, the escape of water in this form through the narrow openings of the stomates might seriously interfere with the gaseous interchanges.

For the purposes of calculation we have assumed that the temperature of the insulated leaf is  $20^{\circ}$  C., and that the aqueous vapour in the respiratory cavity is maintained at the maximum pressure corresponding to this temperature, *i.e.*, the equivalent of 17.4 millims. of mercury. The pressure of the vapour in the outer air has been taken at one quarter of this amount, *i.e.*, 4.3 millims. of mercury, so that the fall of pressure between the inner and outer air amounts to  $17.4 - 4.3 = 13.1$  millims.

The maximum amount of water vapour,  $Q$ , in grammes, which can diffuse out through the 33,000 open stomates of 1 sq. centim. of *Helianthus* leaf in one hour may be deduced from the equation on p. 269,  $k$ , the diffusivity of water vapour in air at  $20^{\circ}$  C., being taken at .228, and  $\rho$ , the weight of 1 cub. centim. of the vapour, at  $20^{\circ}$  and 13.1/760 millims. pressure, at .00001295 gramme.

The value of  $Q$  is found to be .1730, so that the possible transpiration which can take place *by diffusion* under these conditions from 1 sq. metre of the leaf with fully opened stomates in one hour is 1730 cub. centims.

The maximum amount of transpiration which we have ever obtained experi-

mentally from a cut leaf placed in bright sunshine and with its petiole immersed in water, is 276 cub. centims. per sq. metre per hour, or less than one-sixth of the above amount, so we may conclude that the relatively large amounts of water which pass out of the leaf may be fully accounted for by *diffusion only*.

The translocation of material from cell to cell in the living tissues of plants has generally been regarded by physiologists as being dependent on a process of diosmosis through the intervening cell-membrane.

The difficulties in the way of accepting this explanation do not lie so much in the possible resistance of the thin cell-wall itself to the osmotic passage of diffusible substances, as in the known properties of the outer limiting surfaces of the protoplasm. These, as is well shown by the phenomena of plasmolysis, possess to a remarkable extent the properties of semi-permeable membranes, that is to say, the ectoplasm, whilst allowing the ready passage of water in either direction, exhibits in the living cell a very marked resistance to the entrance or exit of solutes, even when these have a high degree of diffusivity. There are reasons for believing that this property is confined to the external portion of the ectoplasmic layer, and that it is conditioned not by any essential difference of composition in this layer, but merely by the position it occupies as a limiting surface, its physical properties being thereby modified much in the same manner as are those of water by surface tension. Be that as it may, however, the resistance of this surface layer to free diffusion must certainly act as a formidable barrier to the interchange of material from cell to cell in the plant, if we regard this interchange as being carried on in the manner usually supposed.

But the whole aspect of this question has been profoundly modified of late years by the recognition that the contiguous cells of a plant are in direct communication with each other by means of fine protoplasmic threads, which traverse minute perforations in the cell-wall. The researches of WALTER GARDINER and others have shown that the isolated instances of this kind which were known in the sieve-tubes and certain endosperm cells, are typical of plant tissue generally, and he regards these channels of communication as playing an important part not only in the conduction of impulses, but also in the conduction of nutritive substances from cell to cell.

The description and illustrations which GARDINER gives ('Roy. Soc. Proc.' vol. 62, p. 100) of the minute perforations which exist in the closing membranes of the pits and walls of vegetable cells, certainly suggest that such structures are eminently fitted for producing all the diffusive phenomena which we have found to belong to multi-perforate septa, and it is impossible to read the descriptions without being struck with the fact that such an arrangement is admirably adapted to bring about a local concentration of gradient and an enhanced flow through the separating cell-membrane, when there is the slightest difference of osmotic pressure between two contiguous cells.

PFEFFER, in his 'Physiology of Plants' (Engl. edition, 1900, p. 114), when discussing the probable rôle of these fine plasmatic connections, while not actually denying that they may play an accessory part in translocation, states "there are, however, no observations in favour of the view that such transference is of importance in the translocation of nutritive or excretory substances from one cell to another. Were the latter the case, the fineness of the threads would render necessary extremely active streaming currents directed both towards the interior and the exterior of the cell; and to such, as well as to any passive diffusion through their substance, the relatively trifling total sectional areas of the threads would interpose a marked hindrance." In another place he also remarks that the minute diameter of the connections must necessitate the expenditure of a large amount of energy to secure transference.

These objections to the possible efficacy of the minute openings in the cell-wall as paths of conduction may hold good as regards mass movement from cell to cell by actual streaming of the protoplasm through them, but they are scarcely applicable to the case of "pits," where the communication is by minute pores in a very thin closing membrane dividing recessed portions of contiguous cells, which must be to a great extent out of the direct line of the general protoplasmic streaming.

If we suppose the ends of two such pits to open out into neighbouring cells between which there is a slight gradient of density for any particular solute, then, if the dividing membrane is relatively very thin and the perforations are numerous, the flow of the diffusing substance, with densities of  $\rho$  and  $\rho_1$  at the two open ends, may go on almost as rapidly through the "multi-perforate septum" as if no closing membrane were present.

It is much to be regretted that at the present time we have no measurements which will enable us to determine how far the principles of diffusion through perforated septa, as laid down in this paper, are applicable to such special cases. We may, however, obtain some rough idea of the possible effects by assuming a case where we have two pits of contiguous cells of a diameter of 1/100 millim., and of a united length of 1/100 millim.; the dividing membrane being supposed to have a thickness of 1/10,000 millim., and to be studded with pores of 1/100,000 millim. diameter arranged at 8 diameters apart.

Although the aggregate area of these pores will only represent '84 per cent. of the total area of the dividing membrane, it can be shown that they will allow of a diffusive flow equal to 61 per cent. of that which would pass under like conditions through the open pits, supposing no dividing membrane to be present.

If such pits were packed fairly closely together on the cell-walls, their general effect would be to materially reduce the resistance to the passage of diffusible substances, whilst all the structural advantages conferred by the cell-wall would be retained.



## APPENDIX I.

*The Absorption of Carbon Dioxide from Air in Motion by the Free Surface of Solutions of Caustic Alkali.*

When a solution of caustic alkali is freely exposed to the air, it might reasonably be expected that the rate at which it absorbs carbon dioxide would be found to vary very much with the degree of movement in the air and liquid respectively, and with the concentration of the solution. We have found, however, that the rate of absorption is not affected by varying these conditions to anything like the extent that might be anticipated. In the following table we have given a number of experiments of this kind, which were made by exposing solutions of caustic soda to the air for a period of from six to eight hours in shallow dishes of about 10 centims. in diameter, the carbon dioxide absorbed being determined by the titration method described in Appendix II.

In the first series the experiments were made in the open air of the garden adjoining the Jodrell Laboratory.

TABLE XXVI.

Date.	Concentration of NaHO solution.	CO <sub>2</sub> absorbed per hour per sq. centim. of liquid surface.	State of atmosphere.
1898.	per cent.	cub. centims. at 0° C. and 760 millims.	
January 1 . .	4·0	·148	Good breeze.
„ 11 . .	3·1	·154	Still. „
„ 14 . .	3·4	·107	„
„ 14 . .	3·4	·118	„
„ 26 . .	3·0	·124	Almost still.
„ 26 . .	3·0	·126	„
February 2 . .	3·6	·147	Gale. „
„ 2 . .	3·6	·141	„
„ 8 . .	3·0	·116	Fair breeze.
„ 8 . .	3·0	·121	„
„ 15 . .	3·0	·124	„
„ 15 . .	3·0	·110	„
March 1 . .	10·0	·139	Stiff breeze.
„ 1 . .	10·0	·125	„
„ 2 . .	7·89	·136	Strong breeze.
	Mean . .	·128	

In the next series the experiments were again conducted out of doors, but a small mechanical stirrer, driven by a water motor, was inserted into the liquid. A rapid

renewal of the liquid at the surface was in this way ensured, but without sensibly altering the area of the surface.

TABLE XXVII.—(With Stirrer.)

Date.	Concentration of NaHO solution.	CO <sub>2</sub> absorbed per hour per sq. centim. of liquid surface.	State of atmosphere.
1898.	per cent.	cub. centim. per 0° C. and 760 millims.	
May 16 . . .	4·2	·143	Fair breeze.
„ 17 . . .	4·2	·122	Slight breeze.
„ 18 . . .	4·0	·092	No breeze.
June 6 . . .	4·0	·101	Slight breeze.
	Mean . .	·114	

In the next series of Table XXVIII., the exposures of the alkaline solution were made in an empty greenhouse, adjoining the laboratory. The windows were slightly open, but the dishes were protected from sensible draughts. The results may be taken as representing the absorptions from fairly still air by *normal* NaHO solution.

TABLE XXVIII.—(Still Air.)

Date.	NaHO solution.	CO <sub>2</sub> absorbed per hour per sq. centim. of liquid surface.
1898.		cub. centim. at 0° C. and 760 millims.
November 30 .	Normal	·120
December 6 .	„	·101
1899.		
January 2 . .	„	·118
„ 4 . . .	„	·116
„ 9 . . .	„	·109
„ 12 . . .	„	·093
„ 16 . . .	„	·103
February 6 . .	„	·125
„ 8 . . .	„	·098
„ 14 . . .	„	·111
„ 28 . . .	„	·124
March 6 . . .	„	·131
	Mean . . .	·112

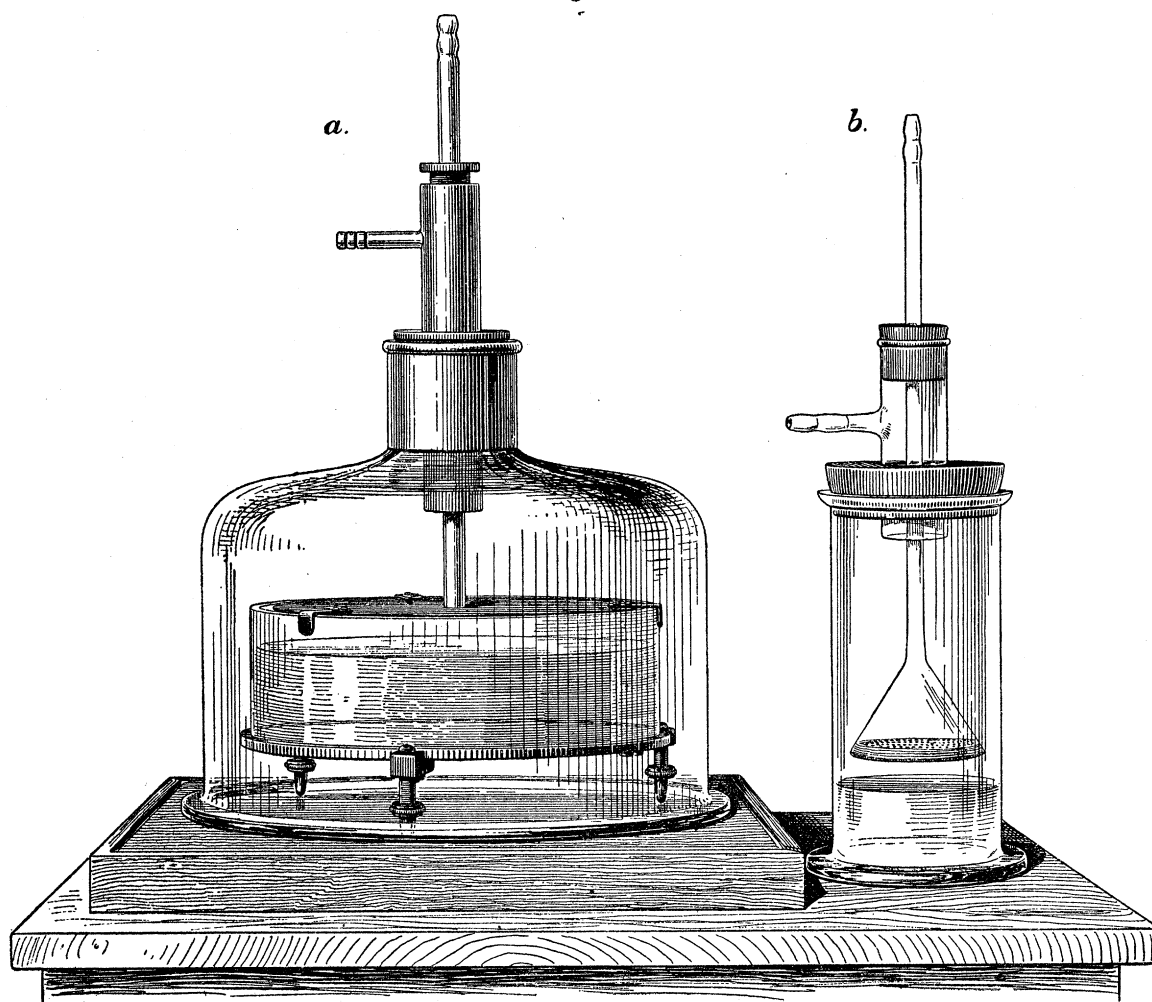
It will be noted that the absorption from rapidly moving air is only about 15 per cent. greater than it is from fairly still air.

The object of these experiments in the first instance was to compare the absorptive power of the free surface of an alkaline solution with that of a green leaf assimilating under favourable conditions of insolation. This comparison can be made by calculating the amounts of a  $C_6H_{12}O_6$  carbohydrate corresponding to the mean absorption in the two sets of experiments of Tables XXVI. and XXVIII., and they are found to be equivalent to an assimilation of 1.720 and 1.505 grammes per square metre per hour, amounts well within the maximum assimilation which has been observed in the case of the Sunflower leaf.

In order to investigate more completely the absorption of dilute carbon dioxide by alkaline solutions, and to study the influence of varying tension on absorption, a special apparatus was constructed which admitted of a stream of air being drawn over the surface of the liquid at a definite rate, the average content of the air in carbon dioxide being also known.

The arrangement of this apparatus is shown in fig. 8*a*. A circular glass dish filled

Fig. 8.



with the alkaline solution to within 1 centim. of the top was placed on a small levelling stand, and was covered with a flat bell-jar which rested air-tight on a ground-glass sole. Through a stuffing-box at the top of the bell-jar passed a metal tube terminating below in a brass disc, which was of slightly less diameter than the dish, and which could be brought down to within a certain distance of the level of the liquid. Another side tubulure at the top of the bell was connected with a water aspirator through a meter for measuring the air which passed. When the pump was in action, the air from the outside passed down the central tube to the surface of the solution in the dish, and then passed radially over its surface in a stream of definite thickness, escaping between the edges of the disc and the sides of the dish. If ordinary air from the outside was employed, a simultaneous determination was made of the amount of  $\text{CO}_2$  it contained, and if air containing a less or a greater amount of  $\text{CO}_2$  than ordinary air was used a split current was employed, one part going to the Reiset apparatus and a separate meter for determination, the other part of the current passing through the bell-jar.\*

The amount of  $\text{CO}_2$  absorbed by the alkaline surface in a given time was estimated by the double-titration method (see Appendix II.).

The total volume of air passed and the original amount of  $\text{CO}_2$  it contained being known, as well as the thickness and diameter of the circular sheet of air passing over the liquid surface, we have all the data necessary for determining the mean content of the air in  $\text{CO}_2$  and its mean velocity. In the following table are given the results of six such experiments, in which the mean content of  $\text{CO}_2$  varied from about one-quarter to twice the normal amount of that of ordinary atmospheric air. The metal disc was placed at a uniform distance of 1 centim. from the surface of the absorbing liquid.

TABLE XXIX.

No.	Air passed per hour.	Mean velocity of air current in metres per hour.	Mean $\text{CO}_2$ content of air in parts per 10,000.	$\text{CO}_2$ absorbed per sq. centim. of liquid surface per hour.	Ratios of mean tensions of $\text{CO}_2$ in air.	Ratios of $\text{CO}_2$ absorbed.
	litres.			cub. centim. at $0^\circ \text{C}$ . and 760 millims.		
(1)	264.2	182	.662	.0406	.26	.28
(2)	265.2	183	.839	.0490	.33	.34
(3)	284.9	196	2.412	.1349	.95	.94
(4)	252.5	174	2.535	.1430	1.00	1.00
(5)	265.5	183	4.103	.2106	1.61	1.47
(6)	257.8	178	6.084	.2998	2.40	2.09

The two last columns of this table bring out very clearly that the rate of absorp-

\* The exact methods employed for determining the  $\text{CO}_2$  in the air will be described in a subsequent communication.



tion is *directly proportional to the partial pressure of the carbon dioxide in the moving air*. The correspondence of the ratios of tension and of absorption when the carbon dioxide is lower than the normal amount of about 2·6 parts per 10,000, is very close indeed. The same degree of correspondence is not maintained with the higher concentrations, a fact due to the air current in these cases not having been sufficiently rapid to give the maximum absorption possible.

With the experience gained with the above apparatus a much smaller and more convenient one was constructed which admitted of much higher velocities of air current, and had the extra advantage that it was not necessary to transfer the soda solutions to another vessel for titration.

This simple apparatus is shown in fig. 8*b*. It consists of a glass cylinder of about 15·5 centims. long, and 6·5 centims. wide, closed at the mouth with an india-rubber plug with a central perforation, through which passes a short wide tube of 2·5 centims. diameter, opening out into the cylinder below and having a side tube for connection with the meter and aspirator. The upper end of the wide tube is closed with a cork, through which passes a narrower tube terminating below in a funnel whose width is slightly less than that of the cylinder. The mouth of the funnel is closed with a perforated porcelain disc which is luted in with paraffin. When air is aspirated through the side tube it enters the apparatus down the narrow tube, and passing through the perforated plate impinges on the surface of the solution of caustic soda and escapes laterally. The funnel can be brought to any desired distance from the liquid surface by sliding its attached tube through the cork at the top.

The solution is run into the cylinder up to a certain mark through an india-rubber cap temporarily placed over its mouth, and a similar arrangement at the close of the experiment allows an exact titration of the liquid without removal to another vessel.

The surface exposed by the absorbent solution was 34·4 sq. centims., and in all the following experiments the perforated plate which distributed the air was adjusted at a distance of 1 centim. above the liquid.

In the first series of experiments with this apparatus (see Table XXX.) are shown the effects due to considerable variations in the velocity of the air current. In the last column the results are all reduced to a uniform tension corresponding to three parts by volume of  $\text{CO}_2$  in 10,000 of air, and the differences in them are due to variations in velocity only, the temperature and concentration of the solutions being practically the same. It will be noticed that when the air current has attained a mean velocity of something like 300 metres per hour a further increase has no practical influence on the absorption.

TABLE XXX.

No.	Mean temp.	Litres of air passed per hour at N.T.P.	Mean velocity of air in metres per hour.	Mean content of air in CO <sub>2</sub> .	CO <sub>2</sub> absorbed per sq. centim. of surface per hour in cub. centim. at N.T.P.	
					Observed.	Corrected for 3 parts in 10,000.
(1)	° C. 14·4	91·9	156	parts per 10,000. 2·57	·127	·148
(2)	15·0	182·6	311	2·86	·165	·172
(3)	14·5	295·2	503	3·07	·182	·177

Another series of experiments was made to determine the influence of concentration of the caustic soda solution on the rate of absorption, ordinary air of known CO<sub>2</sub> content being drawn over the surface at a sufficient speed to give the maximum absorption in each case.

The accompanying table gives a condensed account of these results, subject, however, to further slight corrections for differences produced by variations of temperature.

TABLE XXXI.

No.	Approximate concentration of NaHO.	Temperature.	CO <sub>2</sub> in cub. centims. at N.T.P. absorbed per sq. centim. of surface per hour, corrected for 3 parts CO <sub>2</sub> per 10,000.
(1)	2 normal	° C. 15·6	·170
(2)	2 "	12·4	·171
(3)	3 "	14·3	·137
(4)	$\frac{1}{2}$ "	14·8	·145
(5)	$\frac{1}{4}$ "	13·7	·117

The absorption by the 2 normal solution is nearly the same as that of normal, but any further increase in concentration results in a diminution in the absorption. There is also a marked falling off in the absorbing capacities of solution of  $\frac{1}{2}$  and  $\frac{1}{4}$  normal.

The apparatus we have just described is well adapted to show how the coefficient of absorption of a caustic soda solution varies directly with the tension of the carbon dioxide in the moving air current. It may in fact be used for actually determining the amount of CO<sub>2</sub> in the air without any necessity for measuring the volume passing through the apparatus. All that it is necessary to do is, with fixed conditions of concentration of the solution and temperature, to ensure a very rapid stream of air

over the liquid—more than sufficient to give the maximum absorption—and to note the duration of the experiment. The increase in the amount of  $\text{CO}_2$  in the liquid, reduced to cub. centims. per sq. centim. of surface per hour, is a measure of the mean pressure of the gas in the air during the experiment.

The following example of such a controlled determination may be quoted :—

A stream of air was partially depleted of its carbon dioxide by passing a portion of it through a tower containing granulated soda-lime. The currents after being reunited were again split, one part being passed over the surface of a normal  $\text{NaHO}$  solution in the absorption apparatus just referred to, and the other through a Reiset apparatus and meter for an accurate determination of its carbon dioxide.

In the surface-absorption apparatus, the temperature being  $12^{\circ}\cdot 0$  to  $12^{\circ}\cdot 5$  C., maximum absorption took place at the rate of  $\cdot 0961$  cub. centim. of  $\text{CO}_2$  per sq. centim. per hour. It had been previously found that in the same apparatus, under similar conditions, and with air containing three parts per 10,000 of  $\text{CO}_2$ , the maximum rate of absorption was  $\cdot 177$  cub. centim. per sq. centim. per hour. Since the absorptions are proportional to the pressures, we should expect in this case that the air stream would contain  $3 \times \cdot 0961 / \cdot 177 = 1\cdot 63$  parts per 10,000. The actual amount found by direct determination in the Reiset apparatus was  $1\cdot 67$  parts per 10,000.

It is by no means easy to find a complete explanation of all the phenomena presented by the absorption of atmospheric carbon dioxide from a moving current of air by the free surface of an absorbent, such as a solution of sodium hydroxide.

Supposing such a surface to be *perfectly absorbent*, that is to say, one which can trap all the molecules of carbon dioxide which reach it in their excursions, allowing none to be reflected, then any process of mechanical mixing of the air which would produce a more rapid renewal of the impoverished layer above the liquid would tend to diminish the thickness of this layer, to increase the gradient, and to produce a more rapid absorption, which would only be limited by the mean square speed for the carbon dioxide molecules. The fact that the limit of absorption is reached by a very low velocity of air current, shows that we have to deal with a surface of very imperfect absorption, from which a very large proportion of the molecules must rebound, just as they do from the non-absorbing surfaces of the retaining walls of the vessel. That there should be a constant relation between the entrapped molecules and the total number of molecules in unit volume of the superincumbent air, as shown by the strict proportionality between absorption and the partial pressure of the carbon dioxide, was perhaps to be expected, but the reason for the limited absorption is not quite so evident.

The maximum amount of  $\cdot 177$  cub. centim. of  $\text{CO}_2$  per sq. centim. per hour absorbed from ordinary air is almost exactly the quantity which a perfect absorbent should take in for the same time and area when the density varies from the normal amount of  $\cdot 0003$  of an atmosphere to zero in a layer of 1 centim. thick. It is quite impossible, however, that the partially depleted layer in our experiments should have a thickness in

any way approaching to this, and we must consequently look to the properties of the solution itself for the conditions of limitation. If they were due to the alkaline carbonate formed at the surface of the solution not being removed with sufficient rapidity, we ought to find increased agitation of the liquid and increased concentration to have a distinct effect in promoting absorption, which is certainly not the case after a very moderate concentration is reached.

It seems possible that the true explanation may be found in the "dead space" in chemical action which LIEBREICH has found to exist within a sensible distance of the surface of liquids, and which appears to have some connection with the physical condition of the molecules at the bounding surface. (See 'Berlin. Akad. Ber.,' 1886, 959; 'Zeit. f. physikal. Chem.,' vol. 5, 529; *ibid.*, vol. 8, 83.) If ordinary chemical reactions are weakened, or altogether in abeyance, within a certain range of the surface tension, as LIEBREICH's experiments suggest, the first stages of the absorption of carbon dioxide by the alkaline liquid may be practically the same as those of a surface of *water* only, and the limitation of the process and its independence of the concentration of the alkali within certain limits become easier of comprehension.

## APPENDIX II.

### *Method used for determining the Carbon Dioxide absorbed by solutions of Sodium Hydroxide.*

This method is substantially the same as one proposed by P. HART for the estimation of the relative amounts of caustic soda and sodium carbonate in soda-ash ('Journ. Soc. Chem. Ind.,' 1887, p. 347). It has hitherto been regarded more from the point of view of its ready application than its exactness, but when certain precautions are taken, and pure caustic soda is employed, the method is capable of a high degree of precision, and affords one of the most accurate means we have of determining small amounts of carbon dioxide.

It is based on double titration with two indicators, the one, phenolphthalein, being sensitive to  $\text{CO}_2$ , whilst the other, methyl-orange, only reacts with an excess of the mineral acid (hydrochloric) used in the titration.

The first stage in the process is the addition of the phenolphthalein indicator, followed by the mineral acid to complete disappearance of the pink colour. This marks the point of the total conversion of the neutral into acid carbonate, or, speaking more precisely, the point at which the liberation of the first trace of  $\text{CO}_2$  takes place.

Up to this stage no account need be taken of the actual amount of acid used, although it is of course an advantage to know something like the volumetric relations of the alkaline and acid solutions.

In order to avoid increasing the volumes unduly, which would tend towards



diminishing the sensitiveness of the reaction, we have generally used in the first titration a more or less strong acid, varying between normal and 6 normal, until the pink colour of the phenolphthalein becomes somewhat faint, the addition of 1/10 normal acid being then made to complete disappearance of the colour. Whilst the stronger acid is being run in it is advisable to keep the solution in constant rotation, and this is an absolutely necessary precaution to take when unusually strong acid is used, or when there is much carbonate present, otherwise acid carbonate is locally decomposed and  $\text{CO}_2$  is evolved.

After the addition of the methyl-orange the titration must be carried on with carefully standardised acid, the strength of which is regulated by the desired degree of accuracy, and also by the final volume of the liquid. We have generally employed 1/10 normal hydrochloric acid for this purpose.

It will be noticed that by this method the determination of the amount of  $\text{CO}_2$  absorbed by the caustic soda depends merely on the amount of dilute acid required between the first reaction with phenolphthalein and the second with methyl-orange, the stage corresponding to the complete decomposition of the acid carbonate; and that it is entirely independent of the relations of the total acid equivalents of the alkali before and after absorption. By this means we avoid the errors incident to all methods which depend on the determination of small differences between two large values.

It is essential that the caustic soda should be absolutely free from alumina and iron, which interfere with the sharpness of the second titration, consequently caustic soda made from metallic sodium should be employed. If a trace of alkaline silicate is present it interferes somewhat with the delicacy of the phenolphthalein reaction, a fact which has also been noticed by LETTS and BLAKE in the titration of baryta solutions ('Proc. Royal Dublin Soc.' ix. (1900), p. 152). This is, however, not a matter of such great importance in this method as it is in one dependent upon the exact titration of the whole of the alkali. The difficulty may be avoided by using freshly prepared solutions, and by the selection of a glass which is not readily attacked by caustic soda.\*

The titrations were carried out in cylindrical bottles or flasks, provided with a caoutchouc cap bearing two tubulures, through which the delivery tubes of the burettes could be inserted. The use of this cap prevents the absorption of  $\text{CO}_2$  from the air, but it is obviously not needed during the second titration.

The burettes used for the soda solution were filled from the stock-bottles through side tubes, and were furnished at the top with guard-tubes containing soda-lime, the air in the burettes and titration vessels being first replaced with air freed from  $\text{CO}_2$  by its passage through a WINKLER's absorption apparatus.

In determining the final point in the first titration it is best to take the meniscus

\* The suggestion of LETTS and BLAKE to coat the inside of the glass vessels with paraffin would no doubt prove of service in removing this source of inconvenience.

of the liquid as a criterion, since colour can be seen there when scarcely appreciable in the body of the liquid. As a control on the disappearance of the colour, we used, in the earlier part of our work, a vessel of the same shape and size as the titration vessel and containing water, but owing to the slight green coloration, due to the glass, we subsequently used a control in which the meniscus was made perfectly colourless by adding to the water a few drops of soda and very dilute phenolphthalein. For the second titration an acid control was always used, containing the same amount of methyl-orange as the liquid titrated, and brought to a constant and arbitrary tint of acidity.

The following table gives the results of a series of experiments carried out for the purpose of testing the degree of accuracy attainable by the process.

Measured quantities of a 1/10 normal solution of  $\text{Na}_2\text{CO}_3$  solution were added to 100 cub. centims. of a 4 per cent. solution of pure caustic soda in which the amount of pre-existing carbonate had been accurately determined. A re-determination of the carbonate was then made, the difference in the two determinations expressed in cub. centims. of  $\text{CO}_2$  being then compared with the amount added.

TABLE XXXII.

No.	$\text{CO}_2$ added to 100 cub. centims. of $\text{NaHO}$ solution.	$\text{CO}_2$ found.	Difference.
	cub. centims. at $0^\circ \text{C}$ . and 760 millims.	cub. centims. at $0^\circ \text{C}$ . and 760 millims.	cub. centims.
(1)	1·18	1·05	·13
(2)	11·83	11·77	·06
(3)	29·59	29·40	·19
(4)	59·18	59·03	·15
(5)	112·37	112·41	·04

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