XVII. *On the Molecular Mobility of Gases.*

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Received May 7,—Read June 18, 1863.

The molecular mobility of gases will be considered at present chiefly in reference to the passage of gases, under pressure, through a thin porous plate or septum, and to the partial separation of mixed gases which can be effected, as will be shown, by such means. The investigation arose out of a renewed and somewhat protracted inquiry regarding the diffusion of gases (which depends upon the same molecular mobility), and has afforded certain new results which may prove to be of interest in a theoretical as well as in a practical point of view.

In the Diffusiometer, as first constructed, a plain cylindrical glass tube, about 10 inches in length and rather less than an inch in diameter, was simply closed at one end by a porous plate of plaster of Paris, about one-third of an inch in thickness, and was thus converted into a gas-receiver[*]. A superior material for the porous plate has since been found in the artificially compressed graphite of Mr. Brockedon, of the quality used for making writing-pencils. This material is sold in London in small cubic masses about 2 inches square. A cube may easily be cut into slices of a millimetre or two in thickness by means of a saw of steel spring. By rubbing the surface of the slice without wetting it upon a flat sand-stone, the thickness may be further reduced to about one-half of a millimetre. A circular disc of this graphite, which is like a wafer in thickness but possesses considerable tenacity, is attached by resinous cement to one end of the glass tube above described, so as to close it and form a diffusiometer (fig. 1). The tube is filled with hydrogen gas over a mercurial trough, the porosity of the graphite plate being counteracted for the time by covering it tightly with a thin sheet of gutta percha (fig. 2). On afterwards removing the latter, gaseous diffusion immediately takes place through the pores of the graphite. The whole hydrogen will leave the tube in forty minutes or an hour, and is replaced by a much smaller proportion of atmospheric air (about one-fourth), as is to be expected from the law of the diffusion of gases. During the process, the mercury will rise in the tube, if

Fig. 1.

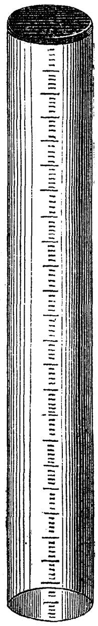
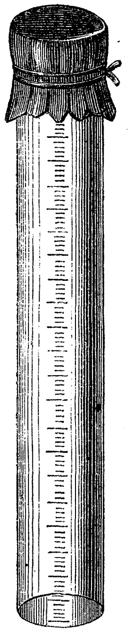


Fig. 2.



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[*] "On the Law of the Diffusion of Gases," Transactions of the Royal Society of Edinburgh, vol. xii. p. 222; or Philosophical Magazine, 1834, vol. ii. pp. 175, 269, 351.

allowed, forming a column of several inches in height—a fact which illustrates strikingly the intensity of the force with which the interpenetration of different gases is effected. Native graphite is of a lamellar structure, and appears to have little or no porosity. It cannot be substituted for the artificial graphite as a diffusion-septum. Unglazed earthenware comes next in value to graphite for that purpose.

The pores of artificial graphite appear to be really so minute, that a gas *in mass* cannot penetrate the plate at all. It seems that molecules only can pass; and they may be supposed to pass wholly unimpeded by friction, for the smallest pores than can be imagined to exist in the graphite must be tunnels in magnitude to the ultimate atoms of a gaseous body. The sole motive agency appears to be that intestine movement of molecules which is now generally recognized as an essential property of the gaseous condition of matter.

According to the physical hypothesis now generally received*, a gas is represented as consisting of solid and perfectly elastic spherical particles or atoms, which move in all directions, and are animated with different degrees of velocity in different gases. Confined in a vessel the moving particles are constantly impinging against its sides and occasionally against each other, and this contact takes place without any loss of motion, owing to the perfect elasticity of the particles. If the containing vessel be porous, like a diffusiometer, then gas is projected through the open channels, by the atomic motion described, and escapes. Simultaneously the external air is carried inwards in the same manner, and takes the place of the gas which leaves the vessel. To this atomic or molecular movement is due the elastic force, with the power to resist compression, possessed by gases. The molecular movement is accelerated by heat and retarded by cold, the tension of the gas being increased in the first instance and diminished in the second. Even when the same gas is present both within and without the vessel, or is in contact with both sides of our porous plate, the movement is sustained without abatement—molecules continuing to enter and to leave the vessel in equal number, although nothing of the kind is indicated by change of volume or otherwise. If the gases in communication be different but possess sensibly the same specific gravity and molecular velocity, as nitrogen and carbonic oxide do, an interchange of molecules also takes place without any change in volume. With gases opposed of unequal density and molecular velocity, the permeation ceases of course to be equal in both directions.

These observations are preliminary to the consideration of the passage through a graphite plate, in one direction only, of gas under pressure, or under the influence of its own elastic force. We are to suppose a vacuum to be maintained on one side of the porous septum, and air or any other gas, under a constant pressure, to be in contact with the other side. Now a gas may pass into a vacuum in three different modes, or in two other modes besides that immediately before us.

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* D. BERNOULLI, J. HERAPATH, JOULE, KRÖNIG, CLAUSIUS, CLERK MAXWELL, and CAZIN. The merit of reviving this hypothesis in recent times and first applying it to the facts of gaseous diffusion, is fairly due to Mr. HERAPATH. See 'Mathematical Physics,' in two volumes, by JOHN HERAPATH, Esq. (1847).

1. The gas may enter the vacuum by passing through a minute aperture in a thin plate, such as a puncture in platinum foil made by a fine steel point. The rate of passage of different gases is then regulated by their specific gravities, according to a pneumatic law which was deduced by Professor JOHN ROBISON from TORRICELLI'S well-known theorem of the velocity of efflux of fluids. A gas rushes into a vacuum with the velocity which a heavy body would acquire by falling from the height of an atmosphere composed of the gas in question, and supposed to be of uniform density throughout. The height of the uniform atmosphere would be inversely as the density of the gas, the atmosphere of hydrogen, for instance, sixteen times higher than that of oxygen. But as the velocity acquired by a heavy body in falling is not directly as the height, but as the square root of the height, the rate of flow of different gases into a vacuum will be inversely as the square root of their respective densities. The velocity of oxygen being 1, that of hydrogen will be 4, the square root of 16. This law has been experimentally verified[*]. The relative times of the effusion of gases, as I have spoken of it, are similar to those of molecular diffusion; but it is important to observe that the phenomena of effusion and diffusion are distinct and essentially different in their nature. The effusion movement affects masses of gas, the diffusion movement affects molecules; and a gas is usually carried by the former kind of impulse with a velocity many thousand times as great as is demonstrable by the latter.

2. If the aperture of efflux be in a plate of increased thickness, and so becomes a tube, the effusion-rates are disturbed. The rates of flow of different gases, however, assume again a constant ratio to each other when the capillary tube is considerably elongated, when the length exceeds the diameter by at least 4000 times. These new proportions of efflux are the rates of the "Capillary Transpiration" of gases[†]. The rates are found to be the same in a capillary tube composed of copper as they are in glass, and appear to be independent of the material of the capillary. A film of gas no doubt adheres to the surface of the tube, and the friction is really that of gas upon gas, and is consequently unaffected by the tube-substance. The rates of transpiration are not governed by specific gravity, and are indeed singularly unlike the rates of effusion.

The transpiration-velocity of oxygen being 1, that of chlorine is 1·5, that of hydrogen 2·26, of ether vapour the same or nearly the same as that of hydrogen, of nitrogen and carbonic oxide half that of hydrogen, of olefiant gas, ammonia, and cyanogen 2 (double or nearly double that of oxygen), of carbonic acid 1·376, and of the gas of marshes 1·815. In the same gas the velocity of transpiration increases with increased density, whether occasioned by cold or pressure.

The transpiration-ratios of gases appear to be in direct relation with no other known property of the same gases, and they form a class of phenomena remarkably isolated from all else at present known of gases.

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[*] "On the Motion of Gases," Philosophical Transactions, 1846, p. 573.

[†] Ibidem, p. 591; and Philosophical Transactions, 1849, p. 349.

There is one property of transpiration immediately bearing upon permeation of the graphite plate by gases. The capillary offers to the passage of gas a resistance analogous to that of friction, proportional to the surface, and consequently increasing as the tube or tubes are multiplied in number and diminished in diameter, with the area of discharge preserved constant. The resistance to the passage of liquid through a capillary was observed by POISEUILLE to be nearly as the fourth power of the diameter of the tube. In gases the resistance also rapidly increases; but in what ratio, has not been observed. The consequence, however, is certain, that as the diameter of the capillaries may be diminished beyond any assignable limit, so the flow may be retarded indefinitely, and caused at last to become too small to be sensible. We may then have a mass of capillaries of which the passages form a large aggregate, but are individually too small to allow a sensible flow of gas under pressure. A porous solid mass may possess the same reduced permeability as the congeries of capillary tubes. Indeed the state of porosity described appears to be more or less closely approached by all loosely aggregated mineral masses, such as lime-plaster, stucco, chalk, baked clay, non-crystalline earthy powders like hydrate of lime or magnesia compacted by pressure, and in the highest degree perhaps by artificial graphite.

3. A plate of artificial graphite, although it appears to be practically impermeable to gas by either of the two modes of passage previously described, is readily penetrated by the agency of the molecular or diffusive movement of gases. This appears on comparing the time required for the passage through the plate of equal volumes of different gases under a constant pressure. Of the three gases, oxygen, hydrogen, and carbonic acid, the time required for the passage of an equal volume of each through a capillary glass tube, in similar circumstances as to pressure and temperature, was formerly observed to be as follows:—

	Time of capillary transpiration of equal volumes.
Oxygen	1
Hydrogen	0·44
Carbonic acid	0·72

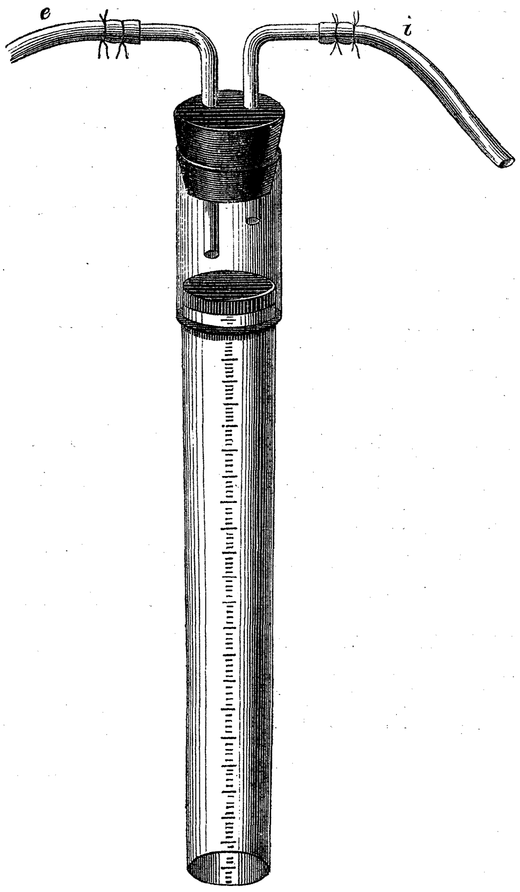
Now through a plate of graphite, half a millimetre in thickness, the same gases were observed to pass, under a constant pressure of a column of mercury of 100 millimetres in height, in times which are as follows:—

	Time of molecular passage.	Square root of density (oxygen 1).
Oxygen	1	1
Hydrogen . . .	0·2472	0·2502
Carbonic acid . .	1·1886	1·1760

It appears that the times of passage through the graphite plate have no relation to the capillary transpiration-times of the same gases as first quoted. The new times in question, however, show a close relation to the square roots of the densities of the respective gases, as is seen in the last Table; and they so far agree with theoretical *times of diffusion* usually ascribed to the same gases.

These results were obtained by means of the graphite diffusiometer already referred to, which was a plain glass tube about 22 millimetres in diameter, closed at one end by the graphite plate. In order to conduct gas to the upper surface of the graphite plate, a little chamber was formed above the plate, to which the gas was conveyed in a moderate stream by the entrance-tube *e* (fig. 3); while the gas brought in excess was constantly escaping into the air by the open issue-tube *i*. The chamber was formed of a short piece of glass tube, about 2 inches in length, cemented over the upper end of the diffusiometer. The upper opening of this short tube was closed by a cork perforated for the entrance- and exit-tubes. It will be observed that by this arrangement the upper surface of the graphite plate was constantly swept by a stream of gas, which was under no additional pressure beyond that of the atmosphere, a free escape being allowed by the exit-tube. The gas also was always dried before reaching the chamber. The diffusiometer stood over mercury, and was raised or lowered by the lever movement introduced by Professor BUNSEN in his very exact experiments upon gaseous diffusion*. To obtain the pressure of 100 millimetres of mercury, the diffusiometer was first entirely filled with mercury and then raised in the trough. Gas gradually entered till the column of mercury in the tube fell to 100 millimetres. The mercury was then maintained at this height, by gradually raising the tube in proportion as gas continued to enter and the mercury to fall, so as to maintain a constant difference of level of 100 millimetres, as observed by the graduation inscribed upon the tube itself, between the level of the mercury in the tube and trough. The experiment consisted in observing the time in seconds which the mercury took to fall 10 millimetre divisions with each gas. The constant volume of gas which entered was 2·2 cubic centimetres (0·1342 cubic inch). Two experiments were made with each gas.

Fig. 3.



Oxygen entered in 898 and 894 seconds; mean 896 seconds.

Hydrogen in 222 and 221 seconds; mean 221·5 seconds.

Carbonic acid in 1070 and 1060 seconds; mean 1065 seconds.

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* BUNSEN's 'Gasometry' by ROSCOE.

In such experiments the same gas exists on both sides, and also occupies the pores of the diaphragm. But the molecular movement within the pores in a downward direction is not fully balanced by the molecular movement in an upward direction, owing to the less tension, by 100 millimetres, of the gas below the diaphragm and within the tube than the gas above and without. The influx of gas indicates the difference of molecular movement in opposite directions. Taking the full tension of the gas above the diaphragm at 760 millimetres, that below would be 660 millimetres, and the movement downwards and that upwards are represented by these numbers respectively.

To increase the inequality of tension and favour the passage of gas through the graphite plate, a diffusion-tube was now used, 48 inches in length, or of the dimensions of a barometer-tube, by which a Torricellian vacuum could be commanded. The pneumatic trough in which this gas-tube was suspended consisted of a pipe of gutta percha of equal length, closed at the bottom by a cork, and widening into a funnel-form at the top. In one modification of the instrument it was found convenient to cement a capillary glass tube to the side of the glass diffusiometer, within about 15 millimetres of the upper end of the tube. An opening into the upper part of the glass tube was thus obtained, by means of which the gas contained in the diffusiometer could escape when the latter was depressed in the mercurial trough. A flexible tube with clip was attached to the capillary tube referred to, so that the latter could be closed. From the same opening a specimen of the gas contained in the diffusiometer could be drawn when required for examination.

In another and more serviceable modification of this barometrical diffusiometer a large space was obtained above the mercurial column, by surmounting the long glass tube, unprovided with a graphite plate, by a glass jar about half a litre in capacity. This jar was more correctly a small bell jar (fig. 4) open at top. It was fitted in an inverted position, as in fig. 5, to the open end of the long glass tube *d*, by means of a cork and cement. The large upper opening was closed by a circular plate of gutta percha (fig. 5), about 10 millimetres, or nearly half an inch, in thickness. This disc of gutta percha had two perforations at *f* and *g* (fig. 6), the former of which was fitted above with a wide glass

Fig. 4.

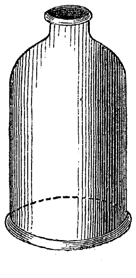


Fig. 5.

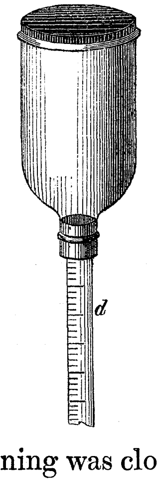
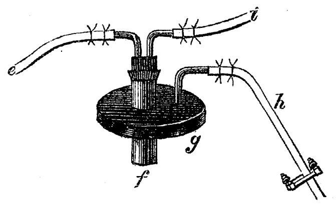
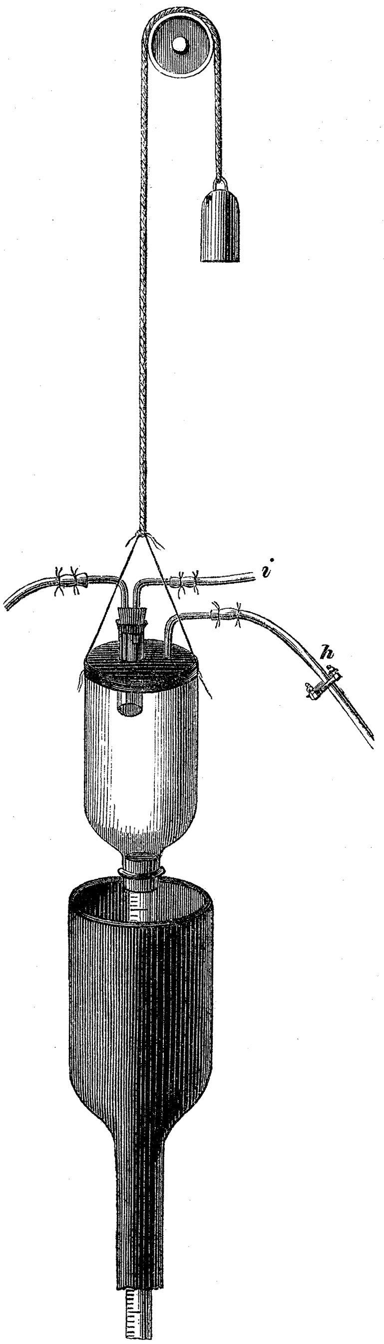


Fig. 6.



tube. The tube *f* was closed below by the plate of graphite, and above with a perforated cork carrying a quill tube, *e*. This quill tube was the entrance-tube for gas, and was accompanied by the usual issue-tube, *i*. The other aperture in the gutta-percha cover was fitted with a plain quill tube *h*, which did not descend below the level of the gutta percha, and formed a tube of exit. No difficulty was found in making all these junctions air-tight, by applying the heated blade of a knife to fuse the gutta percha in contact with the glass. Gutta percha is indeed of no ordinary value in the construction of pneumatic apparatus. The graphite plate itself required to be not less than 1 millimetre in thickness, in order to support the pressure of a whole atmosphere, to which it is exposed in the present apparatus. This barometrical diffusiometer is supported from above by a cord passing over a pulley, and is duly counterpoised by a hanging weight.

Fig. 7.



In operating, the first point is to expel the air from the barometer-tube and upper chamber. The instrument (fig. 7) is sunk completely in the mercurial trough previously described, till the whole is filled, and mercury enters the quill tube of exit, *h*. The caoutchouc extension of this tube is then closed by a pinch. The diffusiometer is now elevated 30 or 40 inches, when the mercury sinks in the glass tube till it comes to stand at the barometric height for the time, leaving the upper chamber entirely vacuous. The gas to be tried has in the mean time been made to stream over the upper surface of the graphite plate, exactly as in the experiment with the former diffusiometer. The graphite is permeated by the gas, and the mercury in the diffusiometer-tube begins to fall, but it now falls slowly, owing to the considerable vacuous space to be filled. It is allowed to fall about half an inch, and the exact time is then noted, by a watch, when the mercury passes a certain point in the graduation of the tube, and again when the mercury descends to another fixed point an inch or two below the former. The time of permeation of a certain volume of gas is thus ascertained in seconds. The experiment is immediately repeated with two or more gases in succession, in similar circumstances as to pressure, and with great care taken to ensure uniformity of temperature during the whole period.

In a series of four experiments made with hydrogen, the mercury fell from 758 to

685 millims. (29·9 inches to 27 inches) in 252, 256, 254, and 256 seconds; mean 254·5 seconds.

In three experiments with oxygen the mercury fell through the same space in 1019, 1025, and 1024 seconds; mean 1022·7 seconds:

$$\frac{1022{\cdot}7}{254{\cdot}5}=4{\cdot}018.$$

The times of these gases appear therefore to be as 1 to 4·018, while the times calculated as being inversely as the square root of the densities of the same gases are as 1 to 4.

On another day, with a different height of the barometer, four gases were passed through the graphite plate in succession through a somewhat shorter range, namely, from 754 to 685 millims. (29·7 to 27 inches).

The time of permeation of air was 884 and 885 seconds; mean 884·5 seconds.

The time of carbonic acid was 1100 and 1106 seconds; mean 1103 seconds.

The time of oxygen was 936, 924, and 930 seconds; mean 930 seconds.

The time of hydrogen was 229, 235, and 335 seconds; mean 233 seconds.

These times of permeation are in the following proportion:—

	Times of the permeation of equal volumes of gas through graphite.
Oxygen	1
Air	0·9501
Carbonic acid . . .	1·1860
Hydrogen	0·2505

These numbers approach so closely to the square roots of the density, or the theoretical diffusion-times of the same gases, namely, oxygen 1, air 0·9507, carbonic acid 1·176, and hydrogen 0·2502, that they may be held to indicate the prevalence of a common law. They exclude the idea of capillary transpiration, which gives to the same gases entirely different numbers.

The movement of gases through the graphite plate appears to be solely due to their own proper molecular motion, quite unaided by transpiration. It seems to be the simplest possible exhibition of the molecular or diffusive movement of gases. This pure result is to be ascribed to the wonderfully fine (minute) porosity of the graphite. The interstitial spaces appear to be sufficiently small to extinguish capillary transpiration entirely. The graphite plate is a pneumatic sieve which stops all gaseous matter in mass, and permits molecules only to pass.

It is worth observing what result a plate of more open structure, such as stucco, will give in comparison with graphite. For the graphite plate, a cylinder of stucco, 12 millims. in thickness, was accordingly substituted, and gas allowed to percolate at both low and high pressures, as in the former experiments with graphite.

1. Under a constant pressure of 100 millims. of mercury, gas was allowed to enter through 100 millim. divisions of the diffusiometer.

With air, the time in two experiments was 515, and again 515 seconds.

With hydrogen 178 seconds, and again 178 seconds:

$$\frac{515}{178}=2{\cdot}894.$$

2. Under a pressure beginning with 710 millims. (28 inches) and ending with 660 millims. (26 inches), the time with air was 374 and 375 seconds; mean 374·5 seconds. The time with hydrogen was 129 and 130 seconds; mean 129·5 seconds:

$$\frac{374{\cdot}5}{129{\cdot}5}=2{\cdot}891.$$

The stucco cylinder of the preceding experiments had been dried over sulphuric acid, without the application of heat. It was further desiccated at 60° C. for twenty-four hours, in order to find whether the porosity would be altered. The ratio of the time of hydrogen to that of air now became 1 to 2·788 at the lower degree of pressure, and 1 to 2·744 at the higher degree of pressure.

It will be observed that the theoretical diffusion-ratio of hydrogen to air, which is 1 to 3·80, is greatly departed from in these experiments with stucco. The ratio appears to be tending to the proportion of the transpiration-times of the same gases, namely, 1 to 2·04. In an experiment recorded by BUNSEN, the ratio observed between the times of hydrogen and oxygen in passing, under a small degree of pressure, through stucco dried by heat was so low as 1 to 2·73, the stucco being probably less dense than in the experiments before us.

With stucco the permeation of gases *under pressure* appears to be a mixed phenomenon—to some extent molecular diffusion into a vacuum, such as holds with the plate of graphite, but principally capillary transpiration of gas in mass.

The diffusiometer was now closed by a plate of white biscuitware, 2·2 millims. in thickness. The time of fall at the constant pressure of 100 millims., through a range of forty divisions of the diffusiometer, was, for air 1210 seconds, for hydrogen 321 seconds.

$$\begin{matrix}\text{Air . . . . .} \\ \text{Hydrogen . . .}\end{matrix}\ \frac{1210}{321}=3{\cdot}769.$$

The time, again, from 736 to 685 millims. (29 to 27 inches) was, for air 685 and 684 seconds; mean 684·5 seconds; and for hydrogen 183, 183, and 184 seconds; mean 183·3 seconds.

$$\begin{matrix}\text{Air . . . . .} \\ \text{Hydrogen . . .}\end{matrix}\ \frac{684{\cdot}5}{183{\cdot}5}=3{\cdot}754.$$

The stoneware was evidently of a much closer texture than stucco, and the ratio appears again less influenced by capillary transpiration. In fact the molecular ratio of 1 to 3·80 is approached within 1 per cent. Biscuitware therefore appears to be but little inferior to graphite for such experiments, a circumstance which is important, as the latter is not easily procured and cannot be converted into tubes and other convenient forms like plastic clay.

Further, the rate of passage of gas through the plate of graphite appears to be closely proportional to the pressure. The resistance was increased by augmenting the thickness of the plate to 2 millims.; and with air and hydrogen at a pressure maintained constant at 50 and 100 millims., the time was observed that the gas took to enter 10 linear millimetre divisions of the tube.

	Seconds.	Ratio.
Air under pressure of 100 millims. . . .	1925	1
Air under pressure of 50 millims. . . .	3880	2·015
Hydrogen under pressure of 100 millims.	497	1
Hydrogen under pressure of 50 millims.	1022	2·056

By halving the pressure the time of passage is doubled, or increased somewhat more. Greater pressures might probably give a rate of passage corresponding more exactly with the pressure.

The ratio between the comparative times of the two gases in the last experiments may also be noticed, the observations having been made in similar circumstances as to pressure and temperature.

Barom. 760 millims.; Therm. 12°·9 C. At pressure of 50 millims.

$$\begin{array}{l}\text{Air} \ldots\ldots\ldots \\ \text{Hydrogen} \ldots\ldots\end{array} \frac{3880}{1022}=3{\cdot}796.$$

Barom. 760 millims.; Therm. 12°·9 C. At pressure of 100 millims.

$$\begin{array}{l}\text{Air} \ldots\ldots\ldots \\ \text{Hydrogen} \ldots\ldots\end{array} \frac{1925}{497}=3{\cdot}873.$$

The observation was repeated at the pressure of 100 millims. with barometer at 754 millims. and thermometer at 10° C.

$$\begin{array}{l}\text{Air} \ldots\ldots\ldots \\ \text{Hydrogen} \ldots\ldots\end{array} \frac{1920}{498}=3{\cdot}855.$$

The velocity of hydrogen appears, as usual, to be nearly 3·8 times that of air; $\frac{1}{\sqrt{0{\cdot}6926}}=3{\cdot}7994$.

An experiment was made at the same time as the former series upon a mixture of 95 hydrogen and 5 air, which gave an unlooked for result that led to a great deal of inquiry. It is known that such a mixture is effused through an aperture in a fine plate in a time which is as the square root of the density of the mixture, and therefore nearly the arithmetical mean of the two gases effused separately. But in transpiration by a capillary, a mixture of 95 hydrogen and 5 air requires a considerably longer time than the gases transpired separately. In fact 5 per cent. of air retards the transpiration of hydrogen nearly as much as 20 per cent. of air would retard the effusion of hydrogen*. Now the mixture in question permeates the graphite plate in 527·5 seconds, while the calculated mean of the times of the two gases is 562·1 seconds.

The mixture has therefore passed neither in the effusion time, nor in a longer time

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* Philosophical Transactions, 1846, p. 628.

as it would do by capillary transpiration, but, singular to say, in a time considerably shorter than either. The gas that came through was found by analysis to be *altered in composition.* It contained more hydrogen and less air than the original mixture. Hence it passed through with increased rapidity. On consideration it appeared that such a separation of the mixed gases must follow as a consequence of the movement being molecular. Each gas is impelled by its own peculiar molecular force, which, as has been seen, is capable of causing hydrogen to permeate the graphite plate about 3·8 times as rapidly as air.

Each gas may permeate a graphite plate into a vacuum with the same relative velocity as it diffuses into another gaseous atmosphere, but it remains a question whether the velocities of permeation and diffusion are absolutely as well as relatively the same. To illustrate this point, hydrogen and air were first allowed to permeate into a vacuum, and then to diffuse into each other, through the same graphite plate, which was 1 millim. in thickness. The plate was a circular disc of 22 millims. in diameter.

The mercurial column in the barometrical diffusiometer fell from 762 to 685 millims. (30 inches to 27) with air in 878 seconds, and with hydrogen in 233 seconds.

$$\begin{array}{l} \text{Air} \; . \; . \; . \; . \; . \\ \text{Hydrogen} \; . \; . \end{array} \; \frac{878}{233}=3{\cdot}768.$$

The volume of gas which produced this effect was found by the calibration of the tube to be 8·85 cub. centims. Hence 1·22 cub. centim. of the hydrogen entered the diffusiometer in 60 seconds, or one minute. But the pressure under which the hydrogen gas entered was the mean of 762 to 685 millims., or 723·5 millims.; while a whole atmosphere (the height of the barometer at the time) was 765 millims. The volume of the gas has therefore to be increased as 723·5 to 765 to give the full action of a vacuum. The volume becomes 1·289 cub. centim. in one minute.

When the diffusiometer was filled with hydrogen and the gas allowed to diffuse into air, the rise of the mercury was pretty uniform for the first five minutes, being 15·5 millim. divisions in the first two minutes, 7 in the third minute, 7·5 in the fourth minute, and 7 in the fifth minute, making 37 divisions in five minutes. But as in diffusion 1 air may be supposed to enter the tube for 3·8 hydrogen which escape, the hydrogen which diffused was more than 37 divisions, by $\frac{1}{3{\cdot}8}$, that is, by about 10 divisions. Hence 47 divisions of hydrogen have diffused into air in five minutes. These divisions measured, by the calibration of the tube, 6·215 cub. centims. One-fifth of this amount, that is, 1·243 cub. centim., diffused in one minute. The result of the whole is that in one minute there passed of hydrogen through the graphite plate,

1·289 cub. centim. by permeation into a vacuum,
1·243 cub. centim. by diffusion into air.

The numbers indicate a close approach to equality in the velocities of permeation into a vacuum and of diffusion into another gas, through the same porous diaphragm. The diffusion appears the slower of the two by a small amount; but this is as it should be, our estimate of the diffusion-velocity being certainly underrated; for the initial diffusion, or even the diffusion in the first minute, must obviously be somewhat greater than the average of the first five minutes, which we have taken to represent it—the hydrogen necessarily diffusing out in a diminishing progression, or more slowly in proportion as air has entered the diffusiometer. It is strictly the initial velocity of diffusion (that of the first second if it could be obtained) that ought to be compared with the percolation into a vacuum.

In fine, there can be little doubt left on the mind that the permeation through the graphite plate into a vacuum and the diffusion into a gaseous atmosphere, through the same plate, are due to the same inherent mobility of the gaseous molecule. They are the exhibition of this movement in different circumstances. In interdiffusion we have two gases moved simultaneously through the passages in opposite directions, each gas under the influence of its own inherent force; while with gas on one side of the plate and a vacuum on the other side, we have a single gas moving in one direction only. The latter case may be assimilated to the former if the vacuum be supposed to represent an infinitely light gas. It will not involve any error, therefore, to speak of both movements as gaseous diffusion,—the diffusion of gas into gas (double diffusion) in one case, and the diffusion of gas into a vacuum (single diffusion) in the other. The inherent molecular mobility may also be justly spoken of as the diffusibility or diffusive force of gases.

The diffusive mobility of the gaseous molecule is a property of matter fundamental in its nature, and the source of many others. The rate of diffusibility of any gas has been said to be regulated by its specific gravity, the velocity of diffusion having been observed to vary inversely as the square root of the density of the gas. This is true, but not in the sense of the diffusibility being determined or *caused* by specific gravity. The physical basis is the molecular mobility. The degree of motion which the molecule possesses regulates the volume which the gas assumes, and is obviously one, if not the only, determining cause of the peculiar specific gravity which the gas enjoys. If it were possible to increase in a permanent manner the molecular motion of a gas, its specific gravity would be altered, and it would become a lighter gas. With the density is also associated the equivalent weight of a gaseous element, according to the doctrine of equal combining volumes.

Diffusion of mixed gases into a vacuum, with partial separation—Atmolysis.

Oxygen and hydrogen.—A diffusiometer of the same construction as that described (fig. 3, p. 389), with a graphite plate of 1 millim. in thickness, was now employed. The upper surface of the plate was swept by a current of the mixed gas proceeding from a gas-holder, the excess of gas being allowed to escape into the atmosphere, as usual, by an open exit-tube. The gas was drawn through the graphite by elevating the diffusiometer containing a column of mercury, from its well, so as to command a partial vacuum in the upper part of the tube. Care is taken that any gas, left in the upper part of the diffusiometer-tube before the experiment begins, should be of the same composition as the gas to be allowed afterwards to enter, so that, on starting, the gas may be uniform in composition on both sides of the graphite plate. The height of the mercurial column, which measures the aspirating force of the diffusiometer, is preserved uniform by gradually raising the tube in the mercurial trough in proportion as gas enters and the mercury falls. The diffusiometer is suspended from the roof of the apartment by a cord passing over a pulley and properly weighted, as in former experiments.

The mixture to be diffused consisted of nearly equal volumes of oxygen and hydrogen. The effect of different degrees of pressure on the amount of separation produced was first observed. It will be seen that as the pressure or aspirating force is increased the amount of separation becomes greater. Barom. 0·759 millim.; therm. 18°·3 C.

Diffusion into a partial vacuum.

	Oxygen.	Hydrogen.
Composition of original mixture in 100 parts	49·3	50·7
Diffused by pressure of 100 millims.	47·0	53
Diffused by pressure of 400 millims.	37·5	62·5
Diffused by pressure of 673 millims. (mean of 635–710)	26·4	73·6
Diffused by pressure of 747 millims. (mean of 736–759)	22·8	77·2

In the last observation, or that with the greatest pressure (747 millims.), the oxygen is reduced to 22·8 per cent. and the hydrogen increased to 77·2 per cent. of the diffused mixture, showing a considerable separation. The mixed gases appear to make their way through the graphite plate independently, each following its own peculiar rate of diffusion.

But it is only under the aspiration of a complete vacuum that the separation can attain its maximum, and reach the full difference that may exist between the special diffusibilities of the two gases. The reason is that while we have the original mixture on both sides of the plate, and of equal tension, the gases are not at rest, but diffusion is proceeding as actively through the plate in opposite directions, as if the gases were different or the tension unequal on the two sides. This is a condition of the molecular mobility of gases (p. 386). The tension therefore being supposed to differ by 100 millims. only, as when the gas above the plate was of 759 millims. tension, and below of 659 millims. (in the first experiment of the last series), then 100 volumes only out of 759 of the mixture are subject to separation. But while these 100 volumes press through they are accompanied by 659 volumes of unchanged mixture. The latter 659 volumes are replaced by an equal bulk of unchanged mixture diffused from below, so that the volumes are not disturbed by this portion of the molecular interchange.

The amount of separation, then, attainable by transmitting a mixed gas through a porous diaphragm by pressure will be in proportion to the pressure—that is, to the inequality of tension on different sides of the diaphragm.

Oxygen and nitrogen.—The separation of the gases of the atmosphere by transmission through the graphite plate has a peculiar interest.

In an experiment resembling those last described, atmospheric air was swept over the upper surface of a graphite plate having a thickness of 2 millims. The gas that penetrated into the vacuum contained, as was to be expected, the lighter and more diffusible constituent in excess. It gave by the pyrogallic acid and potash process of LIEBIG,

Oxygen	20
Nitrogen	80

This was an increase in the nitrogen of quite 1 per cent.; for air, analysed for comparison at the same time and in the same manner, gave oxygen 21·03 and nitrogen 78·97.

It may be legitimately inferred from the last experiment, that if pure hydrogen in a diffusiometer were allowed to diffuse into the atmosphere through a porous plate, the portion of air which then enters the diffusiometer should also have its composition disturbed. A diffusion of hydrogen through a graphite plate was interrupted before completion. The air which had entered was found to consist of

Oxygen	19·77
Nitrogen	80·23
	100·00

The increase of nitrogen is 1·23 per cent.

While the nitrogen is increased and the oxygen diminished in the air which makes its way under pressure through the graphite, the converse effect must be produced on the air left behind. But the latter result of atmolysis cannot be made apparent without a change in the mode of experimenting.

With the view of effecting an increase in the proportion of oxygen, a volume of air, confined in a jar suspended over mercury, was allowed to communicate through a graphite plate of 2 millims. in thickness, with a vacuum sustained by means of an air-pump, the gauge being about 1 inch only below the height of the barometer during the whole time of experimenting.

The jar containing the air to be atmolysed was formed of a plain glass cylinder, open at both ends, and about 400 millims. in height (15·75 inches). The upper end was closed by a thick plate of gutta percha cemented on. This plate was itself penetrated by a wide glass tube, descending about an inch into the jar. The last tube carried the graphite disc, which was 27 millims. (1·04 inch) in diameter, sufficient to close the lower end of the tube upon which it was cemented. The other or upper end of the same tube was fitted with a cork and quill tube, and was put into communication with a large bell jar upon the plate of the air-pump.

The permeation was slow, owing to the unusual thickness of the graphite plate, occupying three hours to drain away one-half of the original volume of air in the jar. The air remaining behind in the jar was examined in a series of experiments, in which the original volume was reduced to one-half, one-fourth, one-eighth, and one-sixteenth.

The residual air, reduced to one-half, gave in two experiments 21·4 and 21·57 per cent. of oxygen, the air of the atmosphere being by the same analytical process 21 per cent.

Reduced to one-fourth of its volume, the residual air gave, in two experiments, 21·95 and 22·01 per cent. of oxygen.

Reduced to one-eighth of its volume, the air gave 22·54 per cent. of oxygen.

Reduced to one-sixteenth of its volume, the air gave 23·02 per cent. of oxygen. The proportion of oxygen had therefore increased about one-tenth in the last experiment, where the effect is greatest.

When the numbers are compared, it appears that by a reduction to half its volume the air gains about one-half per cent. of oxygen; when this last air is reduced to one-half again, another half per cent. of oxygen is gained, and so on—the gain in the proportion of oxygen increasing in an arithmetical ratio, while the volume of air is diminished in a geometrical ratio, or as the powers of the number 2.

Reduction of 1 volume of air	Proportion of oxygen per cent.	Increase of oxygen.
To 1 volume	21	0
To 0·5 volume	21·48	0·48
To 0·25 volume	21·98	0·98
To 0·125 volume	22·54	1·54
To 0·0625 volume	23·02	2·02

The densities of oxygen and nitrogen approach too nearly to admit of any considerable separation being effected by this method. The density of oxygen being taken as 1, that of nitrogen is 0·8785. The square roots of these numbers are 1 and 0·9373, which are inversely as the diffusive velocity of the two gases.

	Diffusive velocity.
Oxygen	1
Nitrogen	1·0669

The velocity of nitrogen therefore exceeds that of oxygen by about 6·7 per cent. Hence by a simple diffusion of a whole volume of air the oxygen could only be increased 6·7 per cent., according to theory. In experiments such as the preceding only one-half of the volume of the air is diffused, and consequently only one-half of the stated amount of concentration of oxygen could possibly be produced at each step. About three-fourths of the theoretical separation is actually obtained, although the apparatus works at an obvious disadvantage from the air within the jar being at rest.

This diffusive method of separation recalls the original observation of DÖBEREINER on the escape of hydrogen gas from a fissured jar standing over water, which will always hold its place in scientific history as the starting-point of the experimental study of gaseous diffusion. That observation proved to be an instance of double diffusion, air entering the jar by the fissure at the same time that hydrogen escaped by it—although, as DÖBEREINER looked upon the phenomenon, it was more akin to single diffusion or the passage of gas in one direction only*.

The atmolytic power of other diffusing plates was tested, besides the artificial graphite.

The barometrical diffusiometer already described was closed by a plate of *red unglazed*

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* Annales de Chimie, 1825.

earthenware, 4 millims. in thickness, which was attached to the glass by resinous cement.

Dry air was swept over the upper surface, as in operating with the graphite plate. With a mercurial column of 340 millims. falling to 200 millims., the air which entered was found to contain 79·45 per cent. of nitrogen, instead of 79. With a column of mercury, maintained at 508 millims. in the tube, the air entering contained 79·72 nitrogen, and with a column beginning at 761 millims., the full barometrical height, and falling to 679 millims. in seven minutes, the air entering contained 80·21 nitrogen. This is a full degree of separation, exceeding 1 per cent., while the time was greatly shorter than with graphite. Thermometer 19°·5 C.

With a diffusing plate of gypsum (stucco) 10 millims. in thickness, the proportion of nitrogen was also increased, although less considerably than with biscuitware. The standard proportion of nitrogen observed in atmospheric air being 78·99 per cent., the air drawn into the diffusiometer was as follows:—

	Proportion of nitrogen per cent.
In air entering over column of 330—200 millims. mercury .	79·26
In air entering over column 508 millims.	79·32
In air entering over column 761—685 millims.	79·53
In air entering over column 761—685 millims.	79·69

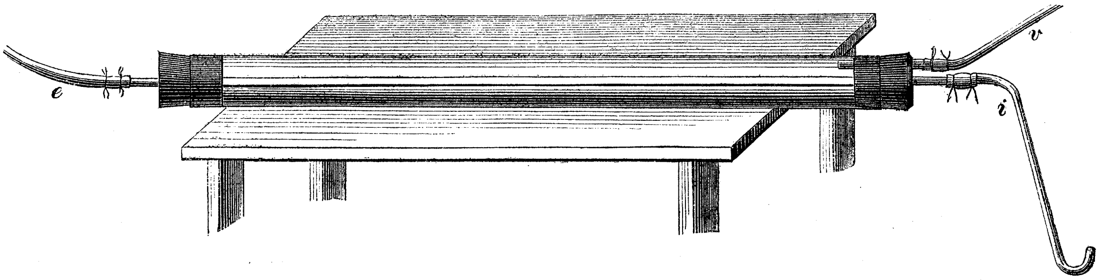
The separation is sufficiently decided, and is certainly remarkable considering the comparatively loose texture of the stucco plate. The gas entered in the two last experiments in about one minute, which appears too rapid a passage, and not to be attended with increased separation, compared with the immediately preceding experiment, in which the pressure was less and the passage of the gas proportionally slower. In all such highly porous plates, we have always to apprehend the passage of a large proportion of the gas in the manner of capillary transpiration, where no separation takes place.

It may be concluded that all porous masses, however loose their texture, will have some effect in separating mixed gases moving through them under pressure. The air entering a room by percolating through a wall of brick or a coat of plaster will thus become richer in nitrogen, in a certain small measure, than the external atmosphere.

The Tube Atmolyser.

In the application of diffusion through a porous septum to separate mixed gases, as a practical analytical method, it is desirable that the process should be more rapid than it can be made with the use of graphite and other diffusing-plates of small size, and also that the process should if possible be a continuous one. Both objects are attained in a considerable degree by adapting a tube of porous earthenware to the purpose. Nothing has been found to answer better than the long stalk of a Dutch tobacco-pipe used as the porous tube. A tube of this description, about 2 feet long and having an internal diameter of 2·5 millims., is fixed by means of perforated corks within a glass or metallic tube, a few inches less in length and about 1½ inch in diameter (*e*, *i* fig. 8), as in the construction of a Liebig condenser. A second quill tube (*v*) is inserted in one of the end corks, and affords the means of communication between the annular space and the vacuum of an air-pump. The external surface of the corks, and of those portions of the pipe-stalk which project beyond the enclosing tube, should be coated with a resinous varnish, to render them impermeable to air. Now, a good vacuum being obtained within the outer tube, and sustained by the action of an air-pump, the mixed gas is made to enter and traverse the clay tube. More or less of gas is drained off through the porous walls and pumped away, while a portion courses on and escapes by the other extremity of the clay tube, where it may be collected. The stream of gas diminishes as it proceeds, like a river flowing over a pervious bed. The lighter and more diffusive constituent of the mixed gases is drawn most largely into the vacuum, leaving the denser constituent, in a more concentrated condition, to escape by the exit end of the clay tube. The more slowly the mixed gas is moved through that tube, the larger the proportion of light gas that is drained off into the vacuum, and the more concentrated does the heavy gas become. The rate of flow of the mixed gas can be commanded by either discharging it from a gas-holder, or drawing it into a gas-receiver, in either case by a regulated pressure.

Fig. 8.



To observe the effect of a more or less rapid passage through the tube atmolyser, the impelling pressure was varied so as to allow a constant volume of half a litre of atmospheric air to pass through and be collected in different periods of time. The clay tube used in these particular experiments was not a tobacco-pipe, but a wide unglazed tube, about 431 millims. (17 inches) long and 19 millims. (0·75 inch) in internal diameter. It was required to place so wide a tube in a vertical position, and to admit the air by the upper and draw it off by the lower extremity of the tube. The proportion of oxygen in the half-litre of air collected was as follows:—

	Oxygen per cent.		
	Experiment 1.	Experiment 2.	Mean.
When collected in 1 minute	21·00	......	......
When collected in 13 minutes	22·33	22·25	22·29
When collected in 75 minutes	22·77	23·02	22·89
When collected in 120 minutes	23·25	23·22	23·23
When collected in 304 minutes	23·54	23·51	23·53

The proportion of oxygen in the air circulated appears thus to increase with the slowness of its passage through the tube atmolyser. The proportion of air drawn into the air-pump vacuum must be very large when the time is protracted; but the additional concentration of oxygen appears small.

The preceding observations being made by means of a porous tube which may be considered wide and of considerable capacity with reference to its internal surface, the experiment was varied by substituting a porous tube about eight times as long, very narrow, and therefore of small internal capacity. This second atmolyser was composed of twelve ordinary tobacco-pipe stems, each about 10 inches in length and of 1·9 millim. internal diameter, connected together by vulcanized caoutchouc adapters so as to form a single tube. Having flexible joints, the tube was folded up and placed within a glass cylinder that could be exhausted. Air was then circulated through this atmolyser by the pressure of several inches of water. The instrument appeared to work with most advantage when the air delivered at the exit-tube amounted to about one-fourth of a litre per hour. A volume of 268 cubic centimetres, which had circulated in one hour, was found to contain 24·37 per cent. of oxygen. The current was then made slower, so that only 108 cub. centims. of gas passed and were collected in one hour, but with little further concentration of the oxygen. The result, however, is interesting as being the highest concentration of oxygen yet obtained by an instrument of this kind. The air collected was composed of

Oxygen	24·52
Nitrogen	75·48
	100·00

The increase of oxygen is 3·5 per cent.; that is, an increase of 16·7 upon 100 oxygen originally present in the air.

With the single pipe-stalk, 24 inches long, first described, the oxygen of atmospheric air was concentrated about 2 per cent. when one litre was transmitted in one hour. Of 450 cub. centims. of air collected in that time, the composition proved to be

Oxygen	23·12
Nitrogen	76·88
	100·00

About 9 litres were drawn into the vacuum at the same time.

The separation of the gases of atmospheric air is a severe trial of the powers of the atmolyser, owing to the small difference in the specific gravities of these gases. But where a great disparity in density exists, the extent of the separation may become very considerable.

Several experiments were made upon a mixture of equal volumes of oxygen and hydrogen carried through the single tube atmolyser, 24 inches in length.

1. Of the mixture described, 7·5 litres entered the tube and 0·45 litre was collected in one experiment. The mixture was composed as follows:

	Oxygen.		Hydrogen.
Before traversing the atmolyser . .	50	+	50
After traversing the atmolyser . .	92·78	+	7·22

2. In another similar experiment, 14 litres of the mixed gas entered the tube and 0·45 litre was delivered in a period of two hours. The result was—

	Oxygen.		Hydrogen.
Before traversing the atmolyser .	50	+	50
After traversing the atmolyser .	95	+	5

Here the proportion of hydrogen is reduced from 50 to 5 per cent.

3. Of the explosive mixture, consisting of 1 volume oxygen and 2 volumes hydrogen, 9 litres were transmitted and 0·45 litre collected in one hour. The change effected was found to be as follows:—

	Oxygen.		Hydrogen.
Before traversing the atmolyser .	33·33	+	66·66
After traversing the atmolyser . .	90·7	+	9·3

The result in such experiments is striking, as the gas ceases to be explosive after traversing the porous tube, and a lighted taper burns in it as in pure oxygen. A mixture of oxygen and hydrogen is not explosive till the hydrogen rises to 11 per cent.

To illustrate the analogy of diffusion into a vacuum with diffusion into air, the outer glass tube of the diffuser was now withdrawn, and the porous tube of the instrument was exposed directly to the air of the atmosphere. A mixture of equal volumes of oxygen and hydrogen was again transmitted at the same rate of velocity as in experiment 1.

The gas atmolysed and collected was found to consist of

Oxygen	51·75
Hydrogen	5·47
Nitrogen	42·78
	100·00

And may be represented as containing

Oxygen	40·38
Hydrogen	5·47
Air	54·15
	100·00

A nearly similar concentration of the oxygen of the mixed gas is here observed as appeared in experiment 1; but the gas collected is now diluted with air which has entered by diffusion. The external air manifestly discharges the same function in the latter experiment which the air-pump vacuum discharged in the former experiment.

Interdiffusion of Gases—double diffusion.

The diffusiometer was much improved in construction by Professor Bunsen, from the application of a lever arrangement to raise and depress the tube in the mercurial trough; but the mass of stucco forming the porous plate in his instrument appears too voluminous, and, from being dried by heat, is liable to detach itself from the walls of the glass tube. The result obtained of 3·4 for hydrogen, which diverges so far from the theoretical number, is, however, no longer insisted upon by that illustrious physicist. It is indeed curious that my old experiments generally rather exceeded than fell short of the theoretical number for hydrogen; $\sqrt{0 \cdot 06926} = 3 \cdot 7994$. With stucco as the material, the cavities existing in the porous plate form about one-fourth of its whole bulk, and affect sensibly the ratio in question according as they are or are not included in the capacity of the instrument. Beginning the diffusion always with these cavities, as well as the tube, filled with hydrogen, the numbers now obtained with a stucco plate of 12 millims. in thickness and dried without heat, were 3·783, 3·8, and 3·739 when the volume of the cavities of the stucco is added to both the air and hydrogen volumes diffused; and 3·931, 3·949, and 3·883 when such addition is not made to these volumes. The graphite plate, on the other hand, being very thin, and the volume of its pores too minute to require to be taken into account, its action is not attended with the same uncertainty. With a graphite plate of 2 millims. in thickness, the number for hydrogen into air was 3·876, instead of 3·8; and for hydrogen into oxygen 4·124, instead of 4. With a graphite plate of 1 millim. in thickness, hydrogen gave 3·993 to air 1. With a plate of the same material 0·5 millim. in thickness, the proportional number for hydrogen to air rose to 3·984, 4·068, and 4·067. An equally considerable departure from the theoretical number was observed when hydrogen was diffused into oxygen or into carbonic acid, instead of air. All these experiments were made with dry gases and over mercury. It appears that the numbers are most in accordance with theory when the graphite plate is thick, and the diffusion slow in consequence. If the diffusion be very rapid, as it is with the thin plates, something like a current is possibly formed within the channels of the graphite, taking the direction of the hydrogen and carrying back in masses a little air, or the slower gas, whatever it may be. I cannot account otherwise for the slight predominance which the lighter and faster gas appears always to acquire in diffusing through the porous septum.

Interdiffusion of Gases without an intervening septum.

The relative velocity with which different gases diffuse is shown by the diffusiometer, but the absolute velocity of the molecular movement cannot be ascertained by the same instrument. For that purpose it appears requisite that a gas should be allowed to diffuse into air through a wide opening.

In certain recent experiments, a heavy gas, such as carbonic acid, was allowed to rise by diffusion into a cylindrical column of air, pretty much as the saline solution is allowed to rise into a column of water in my late experiments upon the diffusion of liquids. This method of gaseous diffusion appears to admit of considerable precision, and deserves to be pursued further. A glass cylinder of 0·57 metre (22·44 inches) in height had the lower tenth part of its volume occupied with carbonic acid, and the upper ninetenths with air, in a succession of experiments: thermometer 16° Cent. After the lapse of a certain number of minutes, the upper tenth part of the volume was drawn off from the top of the jar and examined for carbonic acid. Before the carbonic acid appeared above, it had ascended, that is, it had diffused a distance of 0·513 metre, or rather more than half a metre. After the lapse of 5 minutes, the carbonic acid so found in two experiments amounted to 0·4 and 0·32 per cent. respectively. In 7 minutes, the carbonic acid observed was 1·02 and 0·90 per cent.; mean 0·96 per cent. The effect of diffusion is now quite sensible, and it may be said that about 1 per cent. of carbonic acid has diffused to a distance of half a metre in seven minutes.

A portion of carbonic acid has therefore travelled by diffusion at an average rate of 73 millims. per minute. It may be added that hydrogen was found to diffuse downwards, in air contained in the same cylindrical jar, at the rate of 350 millims. per minute, or about five times as rapidly as the carbonic acid ascended. In these experiments the glass cylinder was loosely packed with cotton wool, to impede the action of currents in the column of air; but this precaution was found to be unnecessary, as similar results were afterwards obtained in the absence of the cotton. To illustrate the regularity of the results, I may complete this statement by exhibiting the proportion of carbonic acid found in the upper stratum already referred to, after the lapse of different periods of time.

	Carbonic acid per cent.		
	Experiment 1.	Experiment 2.	Mean.
After 5 minutes	0·4	0·32	0·36
After 7 minutes	1·02	0·90	0·96
After 10 minutes	1·47	1·56	1·51
After 15 minutes	1·70	1·68	1·69
After 20 minutes	2·41	2·69	2·55
After 40 minutes	5·60	5·15	5·37
After 80 minutes	8·68	8·82	8·75

In eighty minutes the proportion of carbonic acid had risen to 8·75 per cent., 10 per cent. being the proportion which would indicate the completion of the process of diffusion.

The same intestine movement must always prevail in the air of the atmosphere, and with even greater velocity, in the proportion of 1 to 1·176, the relative diffusion-ratios of carbonic acid and air. It is certainly remarkable that in perfectly still air its molecules should spontaneously alter their position, and move to a distance of half a metre, in any direction, in the course of five or six minutes. The molecules of hydrogen gas disperse themselves to the distance of a third of a metre in a single minute. Such a molecular movement may become an agency of considerable power in distributing heat through a volume of gas. It appears to account for the high convective power observed in hydrogen, the most diffusive of gases.