# XIX. On the Motion of Gases.—Part II.

By Thomas Graham, Esq., F.R.S., F.C.S., Professor of Chemistry in University College, London; Hon. Fellow of the Royal Society of Edinburgh; Corresponding Member of the Institute of France, of the Royal Academies of Sciences of Berlin and Munich, of the National Institute of Washington, &c.

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ALL experiments on the velocity with which different gases rush into a vacuum, or pass under pressure through an aperture in a thin plate, are in strict accordance with the physical law that the times of passage for equal volumes are proportional to the square roots of the densities of the various gases. Besides being the law of "Effusion," this is also the law of the Diffusion of one gas into an atmosphere of another gas. The result in both cases is simply and exclusively a consequence of specific gravity.

The velocity with which gases of different nature pass through a tube is necessarily much influenced by the law of their effusion, when the tube is short and approaches in character to an aperture in a thin plate. But if the length of the tube is progressively increased, its diameter or the aperture remaining constant, then while the resistance increases and the passage for all gases becomes greatly slower, the velocities of the different gases are found rapidly to diverge from those of their effusion. The velocities of different gases appear at last however to attain a particular ratio with a certain length of tube and resistance; and preserve the same relation to each other for greater lengths and resistances. After attaining this constant ratio, the passage of all the gases becomes slower, exactly in proportion to the increased length of the tube, that is, in proportion to the resistance. The different gases are now equally affected by the resistance, and their relative velocities are therefore undisturbed and remain constant. The effect of the law of effusion upon the velocities is no longer sensible, and appears to be eliminated.

As the rates of passage of different gases through a tube appear to depend upon a new and peculiar property of gases, I have spoken of it as the Transpiration or Transpirability of gases. The rates of transpiration appear not to be affected by the material of the tube, as they are found the same for capillary tubes of glass and of copper and for a porous mass of stucco. I may add that such experiments exhibit a constancy and possess a neatness and precision which is very extraordinary. The experiments of M. Poiseuille indicate an equally remarkable constancy and premoceculis.

cision of result in the passage of Liquids through capillary tubes, which has been fully confirmed by M. Regnault\*.

The experiments of my former paper afford good grounds for assuming the existence of a relation in the transpirability of different gases, of an equally simple nature as that which is recognised among the specific gravities of gases, or even as the still more simple ratios of their combining volumes. Compared with solids and liquids, matter in the form of gas is susceptible of small variation in physical properties, and exhibits only a few grand features. These differences of property which are preserved amidst the prevailing uniformity of gases, may well be supposed to be among the most deep-seated and fundamental in their nature with which matter is endowed. It was under such impressions that I have devoted an amount of time and attention to the determination of this class of numerical constants, which might otherwise appear disproportionate to their value and the importance of the subject. As the results, too, were entirely novel, and wholly unprovided for in the received view of the gaseous constitution, of which indeed they prove the incompleteness, it was the more necessary to verify every fact with the greatest care.

Perhaps the most general and simple result which I can offer is, that the transpiration velocity of hydrogen is exactly double that of nitrogen. These gases it will be remembered have a less simple relation in density, namely 1 to 14. This was the conclusion respecting the transpiration of these gases in my former paper, and I have obtained since much new evidence in its favour. The transpirability of carbonic oxide, like the specific gravity of that gas, appears also to be identical with that of nitrogen.

The result which I would place next in point of accuracy and importance is, that the transpiration velocity of oxygen is related to that of nitrogen in the inverse ratio of the densities of these gases, that is as 14 to 16. In equal times it is not equal volumes but equal weights of these two gases that are transpired; the more heavy gas being more slowly transpired in proportion to its greater density. Mixtures of oxygen and nitrogen have the mean velocity of these two gases, and hence the time of air is also found to be proportional to its density when compared with the time of oxygen.

The relation between nitrogen and oxygen is, I believe, equally precise as that between nitrogen and hydrogen. The densities calculated from the atomic weights of oxygen and nitrogen, namely, 16 and 14, being 1 for oxygen, 0.9010 for air and 0.8750 for nitrogen; the observed times of transpiration of equal volumes of the same gases are for oxygen 1, air 0.8970 to 0.9010, and for nitrogen from 0.8680 to 0.8708.

These slight deviations I look upon as of the same character as those which accurate determinations of the densities of the same gases indicate from their calculated or theoretical density; the observed densities of air and nitrogen being 0.9038 and

<sup>\*</sup> Rapport sur un Mémoire de M. le Docteur Poiseuille, ayant pour titre, "Recherches expérimentales sur le mouvement des liquides dans les tubes des très-petits diamètres." Annales de Chimie et de Physique, 3<sup>me</sup> série, t. vii. p. 50.

0.8785 referred to oxygen as unity (Regnault), instead of 0.9010 and 0.8750; or the observed difference in density is sensibly less than it should be by theory. The departure from the law in the transpiration of the same gases is certainly somewhat wider, and it is in the opposite direction; the difference in the observed times of transpiration being greater instead of less than the calculated times.

The points respecting transpiration which still most demand consideration are the following:—

- 1. Determination of the resistance and of the dimensions of the capillary at which the transpiration of gases becomes normal; and the properties of serviceable capillary tubes.
  - 2. New determinations of the transpiration of various gases and vapours.
- 3. Influence of change of density and elasticity, produced by change of pressure, upon transpiration.
  - 4. Influence of temperature upon transpiration.

#### I. CAPILLARY TUBES FOR TRANSPIRATION.

The transpiration of some gases appears to become sooner normal than others, that is, in capillary tubes which are less elongated or less contracted than is necessary for other gases. This was first observed on breaking down and using portions of the glass capillary tube, H of my former paper, which was comparatively wide, being about 0.0222 inch, or  $\frac{1}{4.5}$ th of an inch in diameter, with the great original length of 22 feet; when it allowed 1 cubic inch of air to pass under the pressure of one atmosphere into a vacuum in 15.64 seconds, or it discharged 3.84 cubic inches of air per minute.

The following table exhibits the times of transpiration of equal volumes of several gases by this capillary reduced in length to a little under 20 feet. The table contains two series of experiments. The first is the transpiration time of a constant volume of the gases drawn from a globular vessel standing over water, into a sustained vacuum. This vessel was terminated above and below by glass tubes, forming hollow axes to the globe. The measure transpired was the capacity of the vessel between a mark on the lower and a mark on the upper tube, and amounted to 56.5 cubic inches. The second series, which consists of carbonic acid gas, with air for comparison, is the transpiration of these gases into a nine-pint jar or receiver upon the plate of an air-pump, beginning the experiment with an exhaustion of 28.5 inches by the attached barometer, and terminating at 23.5 inches. It was necessary to measure the volume of carbonic acid in this manner after transpiration and not before it, to avoid the error which the solution of a portion of this gas in water might introduce. The gases all passed through a drying tube containing asbestos moistened with oil of vitriol, before reaching the capillary.

Gas transpired.	Experi- ment I.	Experi- ment II.	Mean.	Air=1.	Oxygen=1.	Observations.
Oxygen Air Hydrogen Protocarb. hydrogen (CH <sub>2</sub> ). Carbonic oxide	1146 1032 509 631 994	1147 1032 510 630	1146·5 1032· 509·5 630·5 994·5	1.0000	1.0000 0.9001 0.4443 0.5499 0.8674	Ваг. 29·696. Тетр. 67° Ганк

798.5

0.8366

0.7529

668

798

668

Carbonic acid.....

799

668

Table I.—Transpiration by Capillary H 237.875 inches in length, and  $\frac{1}{45}$  inch in diameter.

I produce these results principally to show how small the variation is in carefully made experiments, not amounting to more than 1 second in times which exceed 1000 seconds for two of the gases, as well as to afford standard numbers to compare with those obtained for reduced lengths of the same tube.

Bar. 29.602. Temp. 69° FAHR.

Table II.—Transpiration times of equal volumes by Capillary H of different lengths.

Length of capillary.	Oxygen.	Air.	Carbonic oxide.	Carbonic acid.	Protocarburetted hydrogen.	Hydrogen.
237.875 inches=1.0000	1	0.9001	0.8674	0.7529	0.5499	0.4443
0.8539 0.6521	1	0·8983 0·9009	0.8681	0.7585	0.5506	0·4422 0·4434
0.4513	1	0.9013	0.8743	0.7900	0.5636	0.4424
0.3195	1	0.9131	0.8793	0.8501	0.5826	0.4041
0.2149	1	0.9149	0.8799	0.8849	0.6049	0.3842
0.1234	1	0.9131	0.8790	0.8802	0.5860	0.3924
18.125  inches = 0.0762	1	0.9138	0.8879	1.0395	0.5948	0.3879

The absolute times of transpiration varied with air from 1032 seconds for the greatest to 116 seconds for the shortest length of the capillary.

It will be remarked that the transpiration times of air and hydrogen are preserved with the greatest uniformity, while the length of the capillary is reduced from 1 to 0.4513, air varying only from 0.9001 to 0.9013, and hydrogen from 0.4443 to 0.4424. The variation of the rate of carbonic oxide is more sensible although still small, namely, from 0.8674 to 0.8743. Protocarburetted hydrogen, however, rises for the same change in the tube from 0.5499 to 0.5636, and carbonic acid still more considerably, namely, from 0.7529 to 0.7900. The resistance of the tube is insufficient for shorter lengths, the influence of effusion becoming manifest, and most conspicuously so in carbonic acid. The times of effusion of equal volumes, to which the gases are now converging, although with unequal degrees of rapidity, are, for oxygen 1, air 0.9507, carbonic oxide 0.9356, carbonic acid 1.1760, protocarburetted hydrogen 0.7071, and hydrogen 0.2502.

An important conclusion to be drawn from these results is, that the transpiration of all gases does not become normal for the same length of tube or amount of resistance, but that a greater length of the tube and consequent resistance is more necessary for some than for others. Carbonic acid in particular, of which the effusion rate differs so widely from its transpiration rate, appears to require a considerably greater resistance than the other gases transpired to bring it to a uniform rate. Indeed the results respecting that gas suggest the inquiry whether the resistance is sufficient with the present capillary in its greatest length, and whether the true transpiration time for this gas may not be less than 0.75, the number provisionally adopted. Let us therefore observe the effect of greatly increased resistances upon the transpiration of this and other gases.

A thermometer tube of the finest flat bore was selected, K, of which  $52\frac{1}{2}$  inches contained only 13.5 grains of mercury. The bore was not quite uniform, 0.6 grain of mercury occupying 2 inches of the cavity at each end of the tube and 2.3 inches near the middle. Under the pressure of 1 atmosphere, 1 cubic inch of air passed into a vacuum by this capillary in 151.3 seconds, or the discharge of air was not more than 0.4 cubic inch per minute. The resistance was therefore ten times greater than in the capillary H when of its greatest length of 22 feet.

Air and other gases were transpired through K into a two-pint jar placed upon the plate of an air-pump, or into a space amounting to 71.08 cubic inches, till the attached barometer of the air-pump fell from 28.5 to 25.5 inches.

- (1.) The time required by air in three experiments was 1075, 1073 and 1074 seconds; and for oxygen in two experiments 1192 and 1192 seconds; the temperature being 56° Fahr. and the height of the barometer 30·162 inches. This gives 0·9010 as the transpiration time of air, referred as usual to the time of oxygen as 1, the result accidentally coinciding with the theoretical number for air.
- (2.) The time required by hydrogen in two experiments was 552 and 550 seconds. the time of air being 1081, 1079, 1082 and 1080 seconds; thermometer 57° and barometer 29.918 inches. Dividing the mean number for hydrogen 551 by the mean number for air 1080.5, we obtain 0.5099 as the time of hydrogen, that of air being 1. To reduce the time of hydrogen to that of oxygen as 1, we have to multiply 0.5099 by 0.9010, which gives 0.4593 as the transpiration time of hydrogen. This is a considerable departure from the theoretical number 0.4375; but it was found to be due to a small addition of air to the gas, which it obtained from the water over which it stood in the pneumatic trough, and necessarily much longer than usual, from the slow manner in which it was removed by transpiration through the present capillary. In a series of experiments made with hydrogen containing 1, 2, 4, 25, 50 and 75 parts of oxygen in 100 of the mixture, this capillary was found to give the transpiration times 0.4901, 0.5055, 0.5335, 0.7750, 0.9061 and 0.9718. Half a per cent. of air would therefore more than account for the increased time observed with the first In experiments, also, made with other equally fine capillaries, when the hvdrogen.

hydrogen was preserved in a state of great purity by transmitting it by a bent tube from the generating retort to the upper part of the pneumatic receiver, and in large volumes, so that the gas never passed through water, and was retained only a very short time in contact with the surface of that liquid, the transpiration time then fell, as will afterwards appear, quite as low as the theoretical number.

(3.) The transpiration of carbonic oxide took place in 1051 and 1051 seconds, against 1090 and 1089 seconds for air; thermometer 58° Fahr., barometer 29.866. This gives for carbonic oxide the transpiration times 0.9646, air =1; and 0.8690, oxygen =1. The transpiration time of the same gas by the former capillary H was 0.8674; while the number corresponding with the theoretical density of the gas is 0.8750.

The capillary K was now shortened to 39.375 inches, and the following experiments were made with it.

(1.) Carbonic acid was transpired in 661 and 659 seconds, thermometer 58°, and barometer 30°024. The time of oxygen was 900 and 903 seconds. The means give 0.7321 as the transpiration time of carbonic acid, a number considerably less than 0.75, and confirming my suspicion that the latter number was too high, and that the resistance of H was not sufficiently great to eliminate the whole influence of effusion in this gas. It may be remarked, in passing, that the new number for carbonic acid approaches 0.7272, which is equal to  $\frac{16}{22}$ , or is the reciprocal of the density of carbonic acid gas. Such a relation suggests the idea that carbonic acid possesses the time of oxygen, (of which gas, carbonic acid contains its own volume,) diminished by the carbon present, which gives an additional momentum corresponding to its weight to the compound gas, and acts thus entirely in increasing its velocity.

In another series of experiments the numbers were 659 and 659 for carbonic acid, against 900 and 902 for oxygen; thermometer 58°, and barometer 30.052. This gives 0.7303 as the transpiration time of carbonic acid.

(2.) Without entering into a detail of the experiments, I may add, that the capillary K of its present length gave 0.9034 as the transpiration time of air and 0.4500 as the transpiration time of hydrogen; the time of the latter gas being undoubtedly elevated by a minute impurity, as in the former case.

The length of capillary K was now reduced to 26.25 inches, and in order to increase the transpiration time, which fell to about 567 seconds for air, the range of the attached barometer observed was increased from 3 to 5 inches, the observations being made at 28.5 and 23.5 inches of the barometer attached to the air-pump.

- (1.) The times for air were 946 and 945 seconds; the time for oxygen 1053 seconds, giving 0.8979 as the transpiration time of air; thermometer 57° and barometer 30.096.
- (2.) The times for carbonic acid were 773 and 773 seconds, the times for air observed immediately before being 942 and 943 seconds; thermometer 57° and barometer 29.982. This gives 0.8202 as the transpiration time for carbonic acid referred to air, and 0.7361 referred to oxygen.

The length of the capillary K being now reduced to 13·125 inches, air was found to enter so as to depress the attached barometer from 28·5 to 25·5 inches in 284 seconds, and from 28·5 to 23·5 inches in 472 seconds; thermometer 56° and barometer 29·758 inches. To obtain longer times, the two-pint jar, used as the aspiratorjar, was replaced by the six-pint jar, which last gives an available vacuous space estimated at 201·78 cubic inches. The fall of the attached barometer continued to be observed from 28·5 to 23·5 inches.

(1.) The times of air were 1348 and 1353 seconds; the times of oxygen 1498 and 1499 seconds; thermometer 58° and barometer 29.628. The means give 0.9013 as the transpiration time of air.

Observing only through the smaller range of the attached barometer, namely, from 28.5 to 25.5 inches, the following results were obtained:—

- (1.) The time of air was 809, 809 seconds.
- (2.) The time of carbonic oxide was 780 and 779 seconds.
- (3.) The time of hydrogen was 399, 400 and 398 seconds.
- (4.) The time of carbonic acid was 658 and 657 seconds.

The experiments were made successively in the order in which they are stated, with the thermometer at 59° and the barometer from 29.450 to 29.422. The results may be given as follows:—

	Air=1.	Oxygen=1.
Carbonic oxide	0·9635	0.8671
Hydrogen	0·4932	0.4438
Carbonic acid	0·8127	0.7314

Table III.—Transpiration times.

The transpiration times of the second column are obtained by multiplying the times of the first column by 0.9, a number which represents the time of air with sufficient accuracy, the time of oxygen being 1. It will be observed that the number for carbonic oxide remains wonderfully constant for all lengths of K; that the number for hydrogen 0.4438 now approaches more nearly to 0.4375, probably as nearly as a slight impurity of the gas, resulting from its short contact with water, would admit; and that the number for carbonic acid 0.7314, is still low, and does not differ much from 0.7272.

In a second series of experiments, which need not be detailed, numbers corresponding closely with the preceding were obtained; namely, 0.9003 for air, 0.8656 for carbonic oxide, and 0.7336 for carbonic acid.

The capillary K was reduced to 8.75 inches, or to one-sixth of its original length, the six-pint jar being retained as the aspirator-jar, and the fall of the attached barometer observed from 28.5 to 23.5 inches.

(1.) The times of air were 933 and 933 seconds; of oxygen 1036, 1036 and 1037

seconds; of carbonic oxide 897, 897 seconds; thermometer from 59° to 60°, and barometer from 29·1 to 29·134 inches. These experiments give the following transpiration times:—

Oxygen	•			•	•	•	•	1
Air								
Carbonic	oxi	de						0.8656

(2.) The times of air were 920 and 920 seconds; of hydrogen 450 and 451 seconds; of carbonic acid 763, 762 seconds; thermometer 58°, barometer 29°346. The resulting transpiration times for hydrogen and carbonic acid are 0°4886 and 0°8288, the time of air being 1; or multiplying by 0°9 so as to have oxygen 1—

Hydrogen				•	•	•	0.4398
Carbonic acid	•	•	•		•	٠	0.7459

(3.) Experiments on the same gases were repeated at a temperature lower by 10° Fahr. The times of air were 902 and 902 seconds; of hydrogen 442 and 444 seconds, and of carbonic acid 742 and 742 seconds; thermometer 48° Fahr., barometer 29.334. These numbers give the transpiration times 1, 0.4911, and 0.8226 for air, hydrogen and carbonic acid respectively; or, with oxygen as 1,—

Hydrogen			•	•	0.4419
Carbonic acid					0.7403

Another series of experiments gave for carbonic acid the transpiration time 0.7432 at 43°, and with barometer 29.620. It will be observed that the time for carbonic acid now begins to rise, as if the capillary were too short and the resistance insufficient to neutralize entirely the effect of effusion in that gas. The times however of air, hydrogen and carbonic oxide continue normal.

Experiments were made with the same capillary reduced to 6.4375 inches, or to one-eighth of its original length, which are still pretty normal. The times for air were 670 and 670 seconds; for oxygen 746 and 745 seconds; for hydrogen 322 and 322 seconds; for carbonic acid 563 and 562 seconds, with thermometer from 61° to 62°, and barometer from 29.832 to 29.826. These give the transpiration ratios,—

Oxygen	•		•	•	•	•	•			1
Air		• .							•	0.8987
Hydrogen		•		•		•		•		0.4319
Carbonic a	cic	$\mathbf{d}$								0.7545

For shorter lengths of the capillary K, the deviation from the transpiration rates becomes very notable. I shall supply the results of such experiments, as they illustrate the progress of the deviation from the transpiration rates in a short and narrow capillary, while the results of Table II. page 352, show the progress of this deviation in a long and comparatively wide capillary.

	teng	gtns.		
Length of capillary.	Oxygen.	Air.	Hydrogen.	Carbonic acid.
4·3125 inches. 3·25	1	0·8985 0·9035	0·4250 0·4176	0·7770 0·8059

1

2.1875

1.125

Table IV.—Transpiration times of equal volumes, by Capillary K of reduced lengths.

The absolute times for air, with the tubes of these four different lengths, were 473, 370, 270 and 178 seconds; the temperature varying from 61° to 63°, and the barometer from 29.562 to 29.782 inches. These times, it will be observed, do not become shorter, exactly as the length of the tube is diminished, but less rapidly in a very sensible degree. This is owing to the interference of effusion.

0.9121

0.9199

0.3969

0.3876

0.8446

0.9379

When K was 4·3125 inches in length it allowed 1 cubic inch of air to pass into a vacuum, under the pressure of 1 atmosphere, in 14 seconds; or it discharged 4·3 cubic inches of air per minute. The discharge by the capillary H of its greatest length, 237·875 inches, was 3·84 cubic inches per minute. These two tubes therefore offer a nearly equal resistance to the passage of air under pressure. On comparing the first lines of Tables II. and IV., however, it will be perceived that the transpiration rates of hydrogen and carbonic acid are sensibly more normal for the long than for the short tube, although the difference is not great. Still it appears that contracting the diameter of a tube does not produce an equally available resistance as increasing its length. In other respects the progress of the deviation from the normal transpiration rates of the same gas, and of different gases compared together, in proportion as the resistance diminishes, appears to follow the same law in the short as in the long tube.

While discussing the properties of capillaries of different dimensions, I may allude to results obtained by another capillary M, of the same extreme length, 52.5 inches, and of nearly the same resistance as K, but of which the bore was cylindrical and not flat like that of K. The bore of M was not highly uniform, 0.75 grain of mercury occupying a length of the cavity which varied from 3.3 inches at one end to 2.3 inches at the other end of the tube. It was employed with the two-pint aspirator-jar, and the fall of the attached barometer was observed through the usual range from 28.5 to 23.5 inches.

- (1.) This capillary gave the transpiration time of air 0.8997, a highly normal result.
- (2.) The times for air in two experiments being 1133 and 1132 seconds, the times of carbonic acid were 913 and 911 seconds; thermometer 68° and barometer 29.672.

Transpiration time of carbonic acid . . . . . . . . 0.7247

In a second series of experiments made upon the same gases, the times of air being 1104 and 1103 seconds, the times of carbonic acid were 892 and 892 seconds; and MDCCCXLIX.

3 A

of hydrogen 534 and 534 seconds; thermometer 58° 5, barometer 30.068. These observations give the transpiration time 0.7275 for carbonic acid and 0.4355 for hydrogen.

(3.) The times of air being 1109 and 1109 seconds, the times of carbonic oxide were 1070 and 1070 seconds; thermometer 67°.5, barometer 29.808.

Transpiration time of carbonic oxide . . . . . . . . 0.8683

(4.) The times of air being 1098 and 1099 seconds, the times of nitrogen were 1064 and 1062 seconds; thermometer 64° to 65°, barometer 29.904.

(5.) The times of air being 1084 and 1084 seconds, the times of hydrogen were 529 and 529 seconds; thermometer 69°, barometer 30.242 inches.

Transpiration time of hydrogen . . . . . . . . . . . . . . . 0.4392

In the present experiments with hydrogen, the precautions formerly referred to for excluding as much as possible the access of a sensible trace of air from the water of the pneumatic trough were put in practice. The times obtained for this and all the other gases, with the present capillary, will be observed to be in the highest degree normal.

(6.) The times of air being 1095 and 1096 seconds, those of olefant gas were 641, 641 and 641 seconds; thermometer 69°, barometer 30·102.

Transpiration time of olefiant gas . . . . . . . . . 0.5265

The time formerly obtained for the same gas by the capillary H of small resistance was 0.5186. This new capillary M was afterwards very fully employed in determining the times of various other gases and vapours, and in examining the influence of pressure and temperature. It is therefore desirable to have the preceding results which this capillary gives with the more familiar gases.

(7.) The times of air being 1120 and 1120 seconds, those of protocarburetted hydrogen (the gas of the acetates) were 684, 686 and 685 seconds; thermometer 61°.5, barometer 29.844.

Transpiration time of protocarburetted hydrogen . . . 0.5504

The time 0.5515 was formerly obtained for this gas by capillary E, which was a long tube of small resistance, very like capillary H.

(8.) The times of air being 1110 and 1111 seconds, those of binoxide of nitrogen ( $NO_2$ ) were 1070, 1070 and 1070 seconds; thermometer  $60^{\circ}$ .5, barometer 29.948 to 29.782 inches.

Transpiration time of binoxide of nitrogen . . . . . 0.8672

This result is in accordance with the conclusion drawn from my former experiments upon the same gas, made with capillary E, namely, that the time of nitric oxide gas coincides with that of nitrogen and carbonic oxide.

(9.) Observations were made with the same capillary M a little reduced in length, namely, to 50.5 inches, and with a smaller aspirator-jar; the range observed of the attached barometer being still from 28.5 to 23.5 inches.

It now gave for the transpiration time of air 0.8984.

The times for air being 460 and 459 seconds, those of carbonic acid were 381 and 381 seconds, and those of protoxide of nitrogen (NO) 380 and 380 seconds; thermometer 56°, barometer 29.674.

Transpiration time of carbonic acid . . . . . . 0.7448

Transpiration time of nitrous oxide . . . . . 0.7429

results which illustrate the identity in transpiration rate of these two gases, which have also the same specific gravity, and appear to correspond remarkably in several other physical properties.

The difference of resistance to the passage of a gas offered by the various capillary tubes already used is certainly considerable; the resistance for equal lengths of tube being in round numbers fifty times greater in the new capillaries K and M, than in the old capillaries E and H. But large as is this range, in which a remarkable uniformity of transpiration rate of the gases has been observed, it may still be much extended. The capillaries of extreme resistance to which I shall now refer, have great advantages over the others already described, and form the instruments which I would recommend for the further study of the laws of transpiration.

A thermometer tube of the finest cylindrical bore being selected, a portion of about 8 inches is taken, and being progressively heated and softened at the lamp, is crushed up into a length of 1 inch or less, which can be done without obliterating the cavity. The cylindrical mass is then, while still soft, drawn out into a tube of ten or twelve times its original length. A thin and extremely fine capillary tube is thus obtained, which is much more regular in bore than might be expected from the description of its preparation. It is convenient to divide the rod, which is less in diameter than a fine straw, into lengths of  $4\frac{1}{2}$  inches, and to seal immediately the open extremities of each piece. A transpiration capillary was formed of a bundle of thirty of these little rods, which were placed together within a short glass tube, as a case, of about  $3\frac{1}{2}$  inches in length and half an inch in diameter; so that the ends of the rods projected at both ends of the tube. The rods were fixed within the tube by stucco, which was dried and afterwards, while warm, soaked in melted bees'-wax. These arrangements being entirely completed, and the bundle proved to be impervious to air, the ends of the rods were now broken off, and the tubes thus opened. The transpiration instrument P consisted of a bundle of thirty such capillary tubes, each about 4 inches in length. Each end of the solid cylinder was connected with a block-tin tube of the same diameter by means of a thick vulcanized caoutchouc adopter. One of these tin tubes was connected with the aspirator-jar, or left open to the air, and the other connected with the receiver containing the gas to be transpired.

The mode of conducting the experiment was further changed. Instead of drawing the gas through the capillaries into an exhausted receiver or vacuum, the gas was compressed in a stout metallic receiver or condenser, provided with a mercurial pressure gauge, by which the elasticity of the gas within could be observed\*. This

<sup>\*</sup> Phil. Trans. 1846, Plate XXXIII. fig. 3.

gauge tube was a barometer about 70 inches in length, with a vacuum above the mercury. The gas was allowed to escape from the condenser through the capillaries into the open atmosphere, or into a space containing air, of which the tension was preserved uniform, and which formed an artificial constant atmosphere, the time being noted which the mercury in the gauge tube of the condenser took to fall through a fixed range of 2, 4 or 10 inches, according to the degree of compression. The available capacity of the condenser was about 72 cubic inches.

The resistance of the fine capillary tube of the present bundle was not less than 400 times greater than the resistance of the finest tubes hitherto used, namely K and M, the comparison being made between equal lengths of the different tubes.

# Experiments with compound Capillary P.

(1.) Dry oxygen was thrown by a syringe into the condenser till the pressure indicated by the pressure gauge exceeded, by more than 20 inches, the pressure of the external atmosphere. The gas was then allowed to escape from the condenser through the capillaries into the atmosphere, and the times noted which the mercury of the pressure gauge took to fall from 20 to 15, 10, 8, 6, 4 and 2 inches.

Pressure by gauge barometer.	Experiment I.	Experiment II.	Experiment III.		
inches.		<b>"</b>	ő		
15	241	240	241		
10	$\begin{array}{c} 352 \\ 202 \end{array}$	353	352 200		
8	262 266	202 266	265		
4	379	382	378		
2	653	650	647		
From 20 to 2 inches	2093	2093	2083		

Table V.—Transpiration of Oxygen.

(2.) A similar series of experiments was made on the transpiration of compressed air, of which the results are as follows:—

Pressure by gauge barometer.	Experiment I.	Experiment II.				
inches. 20 15 10 8 6	ő 217 316 181 239	ő 217 316 181 238				
4 2	400 524	400 524				
From 20 to 2 inches	1877	1876				

Table VI.—Transpiration of Air.

Both these last series and the series which follows on carbonic acid were made

with the thermometer at 66°, and barometer from 30·144 to 30·112 inches. Means were taken to preserve the temperature constant during this and similar experiments, by immersing the condenser, and also the capillary, in vessels of water of which the temperature was watched by an assistant and preserved uniform.

The average times of falling from a pressure of 20 to 10 inches are for oxygen and air, 593 and 533 seconds respectively; numbers which are in the proportion of 1 to 0.8988. The average times from 10 to 6 inches are 467 and 419.5 seconds; that is, as 1 to 0.8983: from 6 to 2 inches, 1030 inches and 924 seconds; that is, as 1 to 0.8971. The average whole time of escape, or during the fall from 20 to 2 inches, is 2088 seconds for oxygen and 1876.5 seconds for air, numbers which are in the proportion of 1 to 0.8987.

The transpiration time of air is therefore highly uniform under different pressures, and approaches closely to its theoretical density or time 0.9010.

(3.) The parallel experiments on compressed carbonic acid gas escaping into air are contained in the following Table:—

Pressure by gauge barometer.	Experiment I.	Experiment II.
inches. 20 15 10 8	0 178 260 148	0 178 260 148
6 4 2 From 20 to 2 inches	195 278 475 ———————————————————————————————————	195 279 474 1534

TABLE VII.—Transpiration of Carbonic Acid.

Comparing these times with the times of oxygen, we obtain the following results:-

# Transpiration times of Carbonic Acid.

From 20 to	10 inches pressure						0.7384
From 10 to	6 inches pressure					•	0.7345
From 6 to	2 inches pressure	•	•	• ,	•		0.7311
From 20 to	2 inches (average)						0.7346

The times for carbonic acid have not the nearly perfect uniformity of those of air, for different pressures, but still their relation is close, particularly in the lower part of the scale where times are long and can be best observed. The time from 4 to 2 inches is 474.5 seconds with carbonic acid and 650 seconds with oxygen, which give as the transpiration time of carbonic acid 0.7300.

It will be observed how nearly the times for this gas approach 0.7272, the reciprocal of its density.

In a second series of experiments made upon carbonic acid, at the same time as

those which follow upon hydrogen, the transpiration times which were obtained for the three portions of the scale already described were 0.7344, 0.7388 and 0.7294, which approach the speculative number for carbonic acid quite as closely as the experiments previously detailed.

(4.) The hydrogen was prepared (as was always the case) from zinc which contained no arsenic, and was passed through a wash bottle containing oxide of lead dissolved in caustic soda, and dried by passing over asbestos moistened with oil of vitriol. The thermometer was 67° and the barometer 29.506 inches.

Dressayes by gayes havemeter	A	ir.	Hydrogen.		
Pressure by gauge barometer.	Experiment I.	Experiment II.	Experiment I.	Experiment II.	
inches. 20 15 10 8 6 4	00 221 328 188 251 422 579	00 221 328 185 251 423 580	0 107 158 92 121 176 310	0 107 159 91 121 178 308	
From 20 to 2 inches	1989	1988	964	964	

Table VIII.—Transpiration of Air and Hydrogen.

The results calculated from the means of these experiments are as follows, the transpiration time of air being taken as 0.9:—

	Air =1.	Oxygen =1.
From 20 to 10 inches From 10 to 6 inches From 6 to 2 inches From 20 to 2 inches	0·4845 0·4866 0·4859 0·4867	0·4352 0·4371 0·4364 0·4371

Transpiration times of Hydrogen.

The experimental times for hydrogen vary only in the smallest degree at different pressures, and almost coincide with the theoretical time for this gas, 0.4375, which is one-half of the time of nitrogen and 7-16ths of that of oxygen. This result is so important that I shall make no apology for presenting another series of experiments in which hydrogen was compared directly with oxygen.

The temperature during the following experiments was 67°, and the barometer 29.420 to 29.458 inches.

Duaggiana har may an haramatar	Hydi	ogen.	Oxygen.		
Pressure by gauge barometer.	Experiment I.	Experiment II.	Experiment I.	Experiment II.	
inches. 20	ő	ő	ő	ő	
15	107	107	242	246	
10	158	158	263	260	
8 6	91 120	90 120	208 274	208 274	
4	174	175	396	398	
2	298	299	687	687	
From 20 to 2 inches	948	949	2170	2173	

TABLE IX.—Transpiration of Hydrogen and Oxygen.

By dividing the means of the hydrogen numbers by the means of the oxygen numbers, as usual, we obtain the following results:—

# Transpiration times of Hydrogen.

From 20 to	10 inches		•			•	•	0.4380
From 10 to	6 inches					•		0.4367
From 6 to	2 inches	•		•	•	•	•	0.4363
From 20 to	2 inches							0.4370

These results are therefore in entire concordance with the preceding series, and with 0.4375 as the transpiration time of hydrogen gas.

(5.) A series of experiments were made on the transpiration of carbonic oxide in conjunction with those last related.

Table X.—Transpiration of Carbonic Oxide.

Pressure by gauge barometer above 1 atmosphere.	Experiment I.	Experiment II.
inches. 20 15 10 8 6 4	0 213 315 181 241 346	0 213 315 181 241 346
From 20 to 4 inches	1296	1296

The experiments on this gas are only given from 20 to 4 inches, some error of observation having occurred in taking the times at 2 inches. Comparing them with the last experiments on oxygen, we obtain the following results:—

Transpiration time of Carbonic Oxide.

From 20 to	10 inches				•			0.8727
From 10 to	6 inches	•						0.8755
From 6 to	4 inches		•	ě	•	•	•	0.8715
From 20 to	4 inches			•				0.8737

The transpiration time of carbonic oxide thus appears to be uniform at different pressures, and to correspond very closely with its theoretical density, 0.8750. The transpiration times of this gas and of nitrogen no doubt correspond with each other as closely as their densities, and are both double the time of hydrogen.

It thus appears that the results obtained by means of the sheaf of capillaries of extreme resistance are the most uniform of all, and that they afford a confirmation of the conclusions drawn from the results of former capillaries of greatly less resistance, which it is difficult to withstand. These conclusions are, that the times of passage through capillary tubes, of equal volumes of different gases under the same pressure, approximate to, and have their limit in, the following numbers:—

# Transpiration times.

Oxygen.	•	• .	•		•		•	٠.		•	1.
Air	•		•							•	0.9010
Nitrogen	and	l ca	ırb	oni	c o	xid	le			•	0.8750
Hydrogen	ì .					•			•		0.4375
Carbonic	aci	d						•			0.7272

The times of oxygen, nitrogen, carbonic oxide and air, are directly as their densities, or equal weights of these gases pass in equal times. Hydrogen passes in half the time of nitrogen, or twice as rapidly for equal volumes. The result for carbonic acid appears at first anomalous. It is, that the transpiration time of this gas is inversely proportional to its density, when compared with oxygen. It is to be remembered, however, that carbonic acid is a compound gas, containing an equal volume of oxygen. The second constituent carbon which increases the weight of the gas, appears to give additional velocity to the oxygen in the same manner and to the same extent as increased density from pressure, or from cold (as I believe I shall be able to show), increases the transpiration velocity of pure oxygen itself. A result of this kind shows at once the important chemical bearing of gaseous transpirability, and that it emulates a place in science with the doctrines of gaseous densities and combining volumes.

The circumstance that the transpiration time of hydrogen is one-half of that of nitrogen, indicates that the relations of transpirability are even more simple in their expression than the relations of density among gases. In support of the same assertion may be adduced the additional fact, that binoxide of nitrogen, although differing in density, appears to have the same transpiration time as nitrogen. Protoxide of nitrogen and carbonic acid have one transpiration time, so have nitrogen and carbonic oxide, as each pair has a common density.

#### II. TRANSPIRATION OF VARIOUS GASES AND VAPOURS.

# 1. Protocarburetted Hydrogen, CH<sub>2</sub>.

It is necessary to mention how this gas was prepared, as it is one, like olefant gas, of which we are never quite certain of the absolute purity. Six hundred grains of dried acetate of soda, the same weight of fused hydrate of potash, and nine hundred grains of unslaked quick-lime, all in fine powder, were well-mixed in a coated Florence flask used as a retort, and the gas brought off by heat. The last portions of gas were rejected. The hydrate of baryta never, in my hands, gave so pure a gas, when substituted for the hydrate of potash. Free hydrogen, the usual impurity in this gas, I have formerly shown to have scarcely any effect upon the rate of carburetted hydrogen, when present only to the extent of a few per cent.

The old experiments with the long 20 feet capillaries E and H, of small resistance, agreed remarkably in the transpiration time 0.5515 for this gas. With capillary M, 52.5 inches in length, and transpiring into a vacuum, I obtained 684, 686, 685 seconds as the time for this gas, against 1120 and 1120 seconds for air; thermometer 62°, and barometer 29.844 inches. This gives 0.5504 for carburetted hydrogen for a capillary of great resistance. This gas, in a state of compression, was transpired by the same capillary into air as in the experiments to follow on oleflant gas. The results, without details, were as follows: thermometer 64°, barometer 30.050 to 30.074.

Transpiration of Protocarburetted Hydrogen (into air) by Capillary M, 52.5 inches in length.

	Air $=1$ .	Oxygen =1.
From 20 to 10 inches From 10 to 6 inches From 6 to 4 inches From 4 to 2 inches From 2 to 1 inch  From 10 to 1 inch	0.6304 0.6254 0.6269 0.6335 0.6349	0·5495 0·5490 0·5515 0·5525 0·5607

The transpiration of this gas appears highly uniform at different pressures. Excluding the two observations at the extremes of the scale, the mean result is—

Transpiration time of protocarburetted hydrogen . . . 0.5510.

A repetition of the last experiments gave a slightly different series of numbers, namely, 0.5583, 0.5497, 0.5541, 0.5523, 0.5549; showing that the slight departure from uniformity among the results at different pressures before observed is of an accidental nature, and does not follow any fixed law. The mean of the three preferable new observations gives 0.5510, or precisely the same result as the former series.

This number for protocarburetted hydrogen closely approaches 0.5536, which is seven elevenths, or  $\frac{14}{22}$  of 0.870, the time of nitrogen. The numerical relation may be MDCCCXLIX.

accidental, but the circumstances that 14, which expresses the density and time of nitrogen, is double the time of hydrogen 7, and that 22 expresses the density of carbonic acid, to which carburetted hydrogen presents a certain chemical analogy in composition, appear to afford some physical basis for it.

The time of protocarburetted hydrogen may also be stated to be one-fourth more than 0.44, the usually observed time of hydrogen itself.

# 2. Olefiant Gas.

The circumstance that olefiant gas has the same theoretical density as nitrogen and carbonic oxide, and yet differs greatly from these gases in transpirability, gives a peculiar interest to the transpiration time of that gas. The olefiant gas used was always prepared in the following manner:—Fifty-four volumes (water ounce measures) of oil of vitriol were mixed with twenty-eight volumes of water and cooled, which gave an acid of specific gravity 1.600. To this twenty-four volumes of alcohol, generally of specific gravity 0.84, were added, and the mixture allowed to stand over night. The gas was evolved by a heat of about 320° Fahr., and transmitted, for the purpose of purifying it through five wash-bottles, the first containing potash, the second water, the third oil of vitriol, the fourth potash, and the fifth oil of vitriol. The process yielded a good deal of ether, with a large product of gas.

My old experiments, with capillary H of great length but small resistance, gave 0.5186 as the transpiration time of this gas. I subsequently obtained the number 0.5241 with capillary K of 8.75 inches in length, and also of small resistance. With capillary M of 52.5 inches in length, and of considerable resistance, I also obtained the number 0.5265; the gas in all these cases passing into the nearly vacuous jar under the pressure of the atmosphere. But the most complete series of experiments was made upon this gas in a compressed state, in the globular digester of 72 cubic inches in capacity, the gas escaping into air. The capillary M was employed of 50.5 inches in length.

Height of gauge barometer		Air.	Olefiant gas.			
above 1 atmosphere.	Experiment I. Experiment II.		Experiment I.	Experiment II.		
inches. 20 15 10 8 6 4 2	0 198 285 161 213 307 530 529	0 196 285 161 213 307 530	0 116 165 93 120 174 301 299	0 116 165 93 121 174 301 300		

TABLE XI.—Transpiration of Olefiant Gas and Air (into air).

The fall from 20 to 10 inches requires 482 seconds in air and 281 in olefiant gas,

numbers which are as 1 to 0.5830. The ratios or transpiration times appear in the following Table:—

Transpiration	times	of	Olefiant	Gas.
---------------	-------	----	----------	------

	Air = 1.	Oxygen =1.
From 20 to 10 inches From 10 to 6 inches From 6 to 4 inches From 4 to 2 inches From 2 to 1 inch	0·5830 0·5709 0·5667 0·5679 0·5656	0·5212 0·5103 0·5066 0·5085 0·5081

In reducing these results from the scale of air to that of oxygen, the following coefficients were used as the transpiration times of air. They were obtained by experiment. From 20 to 10 inches air =0.8941; from 10 to 6 inches 0.8939; from 6 to 4 inches 0.8941; from 4 to 2 inches 0.8967; from 2 to 1 inch 0.8967; the air coefficients being all sensibly lower than 0.9.

The transpiration time of this gas appears to vary at different parts of the scale of pressure fully more than carbonic acid does. This may arise, as with carbonic acid, from the extreme difference which exists between the effusion and transpiration rate of the gas.

Hence an unusually great resistance, which is only met in the lower part of the scale, is required to eliminate completely the influence of effusion upon the transpiration rate. The smallest transpiration time observed above for olefiant gas is 0.5066, which certainly does not differ much from 0.5, or half the time of oxygen. But it would be premature to adopt that relation definitively, as a number nearer to 0.51 would be the more legitimate expression of the whole results.

In a second series of experiments conducted precisely in the same manner, with the thermometer at 67° and the barometer 30.020 to 30.034, the results were as follows:—

Transpiration time of Olefant Gas (into air).

	Air $= 1$ .	Oxygen =1.
From 20 to 10 inches From 8 to 6 inches From 6 to 4 inches From 4 to 2 inches From 2 to 1 inch  From 20 to 1 inch	0·5855 0·5745 0·5663 0·5642 0·5647	0·5234 0·5136 0·5062 0·5043 0·5048

The same remarks apply to the last as to the immediately preceding series of experiments; the two series agreeing together most closely. The mean of the three times observed in the range of pressure from 6 inches to 1 inch is 0.5051; and the least transpiration time observed for olefiant gas (from 4 to 2 inches pressure) is 0.5043.

To contrast the two different methods of transpiration, that of condensed gas escaping into air, and of gas under the usual pressure of the atmosphere only, or under a less pressure, passing into a vacuum, a third series of experiments was made upon olefiant gas. The same globular condenser being full of olefiant gas, of the tension of the atmosphere at the time, which was 30.034 inches, the gas was allowed to escape through the capillary M into the receiver of an air-pump kept vacuous by constant exhaustion. It was thus transpired into a vacuum but with constantly diminishing force, for the force with which the gas was sent out would diminish of course in proportion as the globular receiver was emptied. The barometric gauge tube of this receiver, being closed at top and vacuous, gave the necessary means of observing the progress of the escape of the gas as it was transpired into the vacuum. In the following table of observations, the first column of the height of the gauge barometer is its absolute height, and expresses the whole tension or elasticity of the gas. Thermometer 67°.

TI '-1.4 of source become story	Olefiant gas.		Air.			
Height of gauge barometer.	Experiment I.	Experiment II.	Experiment I.	Experiment II.		
inches. 30 25 20 18	0 191 276 152	0 191 276 152	0 327 480 267	0 327 480 267		
16 14 12 10	187 242 318 446	187 242 319 446	316 432 558 773	315 430 558 771		
From 20 to 10	1347	1345	2346	2341		

TABLE XII.—Transpiration of Olefiant Gas.

The results are sensibly different in one part of the scale from those obtained by the other method of transpiration, as will be seen by comparing the following statement with the former results.

Transpiration	of Olefiant	Gas	(into a	vacuum	).

	Air = 1.	Oxygen =1.
From 30 to 20 inches From 20 to 16 inches From 16 to 14 inches From 14 to 12 inches From 12 to 10 inches	0·5791 0·5476 0·5615 0·5717 0·5777	0·5212 0·4928 0·5054 0·5145 0·5199
From 30 to 10 inches	0.5743	0.5169

The time seems to increase as we descend in the scale, or with the resistance, with the exception of the first observation, which probably is made to deviate from the general progression by some accidental cause. It would probably be more cor-

rect to take the first and second times together, or the whole fall from 30 to 16 inches, which gives—

	Air $=1$ .	Oxygen =1.
Transpiration time of olefiant gas	0.5659	0.5093

The times from 30 to 14 inches, 0.5093 and 0.5054, will thus closely approach to the average time obtained by the other method. But under 14 inches of pressure, where the transpiration becomes extremely slow as the resistance is greatly increased, the times rise to 0.5145 and 0.5199. In the present state of our knowledge respecting transpiration, it is difficult to decide upon the comparative value of these results, and to say which represents best the true transpiration time of olefiant gas. An unexplained variation of  $1\frac{1}{2}$  per cent. in the transpiration time of this gas must at present be admitted, which is a much greater latitude in the results than was observed with nitrogen, hydrogen, protocarburetted hydrogen, or even with carbonic acid.

### 3. Ammonia.

This gas is supposed to have certain chemical relations to olefant gas, although differing very widely from the latter in its physical properties. The theoretical density of ammonia is 8.5, that of oxygen being 16; or 539.6 to oxygen 1000. It is therefore considerably lighter than olefant gas; it is also liquefied by pressure, and highly soluble in water, which the latter is not.

This gas was always dried by passing over fragments of fused hydrate of potash. The mode of operating with gases like ammonia, which cannot be retained over water, found most convenient was to maintain a continued and copious evolution of the gas during the whole period of the transpiration experiments, conveying the gas into an empty bottle in the first instance, of which the cork was perforated by three tubes. By one of these tubes the gas entered this bottle, by another the portion of gas required for transpiration was conducted to the capillary, and the third, which was bent downwards and its extremity allowed to dip a line or two into a little cup of water, formed a waste-pipe or relief tube, by which the excess of gas evolved escaped into the atmosphere. The same method was equally applicable to hydrogen, carbonic acid, chlorine, &c., and does away with the necessity of collecting these gases over water, and so exposing them to contamination.

(1.) This gas was transpired by capillary K, 8.5 inches in length, into the six-pint aspirator-jar upon the plate of the air-pump, through the usual range of 28.5 to 23.5 inches on the gauge barometer; thermometer 54°, barometer 29.772 inches. In two experiments with air the times were 982 and 981 seconds; in three experiments with ammonia 546, 546, and 546 seconds. This gives 0.5563 for the time of ammonia referred to air, or multiplying this number by 0.9 to reduce it to the scale of oxygen =1, we have,—

 The conclusion suggested by this result, that the transpiration time of ammonia is one-half that of oxygen, is not supported so strongly by capillary tubes of great resistance.

(2.) Experiments were made with capillary M, 52·5 inches in length; thermometer 61°, barometer 29·900 to 29·908 inches. The time of air being 1110, 1111, and 1111 seconds, that of ammonia was 632, 632, and 632 seconds; as 1 to 0·5688. Referred to oxygen, the result becomes—

Transpiration time of ammonia . . . . . . . . . 0.5119

A second series of experiments with the same capillary, thermometer 61°.5 and barometer 29.800 to 29.810, gave a very similar result, namely, 1121 and 1123 seconds for air, and 640 and 640 seconds for ammonia; numbers which are as 1 to 0.5704, and give,—

Transpiration time of ammonia . . . . . . . . . . . . . . . . 0.5134

(3.) A third series of experiments was made upon this gas under pressure in the globular digester, and escaping into air by the sheaf of thirty capillary tubes P. The thermometer was at 60°, and the barometer from 29.888 to 29.918 inches during the experiments.

Height of gauge barometer	Α	Air.		nonia.	
above I atmosphere.	Experiment I.	Experiment I. Experiment II.		Experiment II.	
inches.	ő	ő	ő	ő	
15	218	217	124	124	
10	319	321	182	182	
8	186	186	107	106	
6 .	243	243	138	139	
4	354	355	201	201	
2	621	621	350	357	
1	635	645	352	350	
From 20 inches to 1	2576	2588	1454	1459	

Table XIII.—Transpiration of Ammonia (into air).

The observation at 1 inch, or even at 2 inches, does not admit of the same precision as in the higher parts of the scale, owing to the slowness with which the mercury descends, leaving a doubtful period of 3 or 4 seconds which the mercury is in passing the mark. The experiments at different parts of the scale, it will be seen, concur in giving nearly the same result, except for the last inch, where this uncertainty appears to have occasioned a sensible error.

Transpiration times of Ammonia at different pressures.

	Air =1.	Oxygen =1.
From 20 to 10 inches From 10 to 6 inches From 6 to 2 inches From 2 to 1 inch	0·5693 0·5711 0·5684 0·5484	0·5112 0·5128 0·5104 0·4936

The common multiplier by which the numbers of the oxygen scale have been derived from the air scale is 0.898. Excluding the last result, we have, on the oxygen scale,—

The mean transpiration time of ammonia . . . . . . 0.5115

This time for ammonia corresponds very closely with the results previously obtained by the long single capillary M, namely, 0.5119 and 0.5134. The coincidence in the rates of M with those of the compound capillary, for a liquefiable gas like ammonia, is a circumstance of considerable importance, as a large proportion of the experiments which I have to detail on gases of this class were made with the first-named only of these capillaries. The number for ammonia certainly approaches to 0.5076 and 0.5093, the mean transpiration-times of olefant gas, but cannot be said to coincide with them, and is of course somewhat more distant from 0.5.

# 4. Cyanogen.

This gas was prepared from well-crystallized and perfectly dry cyanide of mercury. To secure its purity the gas was besides passed over red oxide of mercury and chloride of calcium. The gas was conveyed to the capillary in the same manner as ammonia. The capillary employed was the long tube M, of 52.5 inches, the gas under the pressure of the atmosphere being drawn into the two-pint aspirator-jar, exhausted as usual upon the plate of an air-pump. Thermometer 60°, barometer from 29.910 to 29.864 inches.

The experiments were made in the following order:—air, 1113, 1114 seconds; cyanogen, 626, 628, 627 and 627 seconds; air, 1117, 1117 seconds. The slight increase of the air-time in the last-made experiments is undoubtedly owing to the fall of the barometer. The ratio of the cyanogen to the first air-time is 0.5631, and to the second air-time 0.5613; or 0.5068 and 0.5052, with oxygen =1. The mean of the two results gives,—

Transpiration time of cyanogen . . . . . . . . . . . 0.5060

The transpiration time of cyanogen may therefore be confounded with that of olefiant gas, 0.5076, transpired in the same manner, although the densities of these two gases differ so widely as 14 to 26 (oxygen =16).

# 5. Hydrocyanic Acid.

A considerable quantity of the absolute acid was prepared by distilling 15 ounces of crystallized ferrocyanide of potassium with 9 ounces of oil of vitriol diluted by an equal weight of water. The liquid acid was afterwards dried by digesting it over pounded chloride of calcium.

As hydrocyanic acid is liquid at the usual temperature, air or hydrogen saturated with the vapour of the acid was transpired instead of the pure substance itself. The air or hydrogen was made to stream through the liquid acid contained in a wash-bottle to a depth of 2 inches, and surrounded with water to which a slight heat was applied, so as to maintain the water and wash-bottle at the fixed temperature of the

experiment, and to compensate for the cold of evaporation. The tension of the hydrocyanic acid vapour at 59°, the temperature of the experiments, was found to be 18.8 inches. The composition of the mixed vapour operated upon was—

				Volu	mes.
Air or hydrogen .				10.8 or	36.48
Hydrocyanic acid	•	•	•	18 <sup>.</sup> 8 or	63:52
				29.6	100.00

The vapour was transpired under the pressure of the atmosphere by the capillary M, 52.5 inches in length, into the two-pint aspirator-jar, through the usual range (28.5 to 23.5 inches) of the attached barometer. Thermometer 59°, barometer 29.518 to 29.644 inches.

The transpiration time of air was 1138 and 1138 seconds in two experiments. The time of air impregnated with hydrocyanic acid was 807, 809, 808, 808 seconds, in four experiments; which gives to the latter the ratio of 0.7100. Multiplying by 0.9, we obtain—

Transpiration time of air saturated with hydrocyanic acid vapour at 59° 0.6390.

It is obvious therefore that hydrocyanic acid vapour is greatly more transpirable than air. The theoretical density of hydrocyanic acid vapour is 13.5, the density of oxygen being 16.

Hydrogen gas equally impregnated with hydrocyanic acid vapour was transpired in the times 579 and 579 seconds, which gives the ratio to air of 0.5088. Multiplying by 0.9, we obtain—

Transpiration time of hydrogen saturated with hydrocyanic acid vapour at 59°, 0.4579.

Judging from our former results on mixtures of hydrogen with denser gases, in which it appeared that the rate of the mixture never deviated far from that of the dense gas in a state of purity, unless the proportion of hydrogen exceeded 50 per cent, it may be inferred that the transpiration time of pure hydrocyanic acid vapour is between 0.4375, the time of hydrogen, and 0.4579, the observed time, but much nearer to the latter than to the former. For the transpiration of gaseous mixtures of more nearly equal density, it is known, on the contrary, that the transpiration time does not deviate far from the mean time of the constituents when transpired separately. Taking the transpiration time of air as 0.9, and that of hydrocyanic acid vapour as 0.46, then 36.48 volumes of the first and 63.52 volumes of the second would give a mean time of 0.6205.

The time observed of a mixture in these proportions was 0.6390.

Hydrocyanic acid is composed of equal volumes of cyanogen and hydrogen united without condensation. The transpiration time of the compound gas is intermediate between the times of its constituents.

### 6. Hydrosulphuric Acid.

This gas was evolved by the action of hydrochloric acid upon the sulphide of antimony; it was washed with water, and afterwards dried by passing over chloride of calcium.

(1.) Hydrosulphuric acid was first transpired by a short length of capillary M, of 8.75 inches, into the six-pint aspirator-jar, through the usual range of 28.5 to 23.5 inches of the attached barometer: thermometer 62°, barometer 29.674 to 29.652 inches. The following observations were made in the order in which they are related:—times of air, 999 and 1001 seconds; of hydrosulphuric acid, 692, 692 seconds; of hydrosulphuric acid gas saturated with the vapour of bisulphide of carbon, 682, 680 seconds; and lastly, of hydrosulphuric acid again, 685, 685 seconds.

The ratio of the first hydrosulphuric acid to air is 0.691, and of the second 0.685; the ratio of the hydrosulphuric acid saturated with the vapour of bisulphide of carbon is 0.681, or differs little from that of hydrosulphuric acid itself; showing that these two sulphur compounds nearly coincide in transpirability. Multiplying these results by 0.9, we have—

Transpiration time of hydrosulphuric acid (1)	•				0.6219
Transpiration time of hydrosulphuric acid (2)		•	•	•	0.6165
Mean transpiration time			•		0.6192

This gas proved less uniform in its rate in different experiments than I have generally observed for other gases, at least with the present capillary.

In a repetition of the preceding experiments, thermometer 60°, barometer 29.860 to 29.858, the times observed were for air, 982, 983 and 981 seconds; for hydrosulphuric acid saturated with bisulphide of carbon, 659, 659, 659 seconds; and for hydrosulphuric acid alone, 663, 664 seconds; which give the ratios to air of 0.6711 and 0.6746. And multiplying by 0.9, we have—

Transpiration time of hydrosulphuric acid . . . . . 0.6071

(2.) Hydrosulphuric acid gas was also transpired by means of the long capillary M, 52.5 inches in length, into the two-pint aspirator-jar. It was then supplied from a wash-bottle with a relief tube as in the experiments upon cyanogen and ammonia, without being retained over water. Thermometer 59°.5 Fahr., barometer 29.550 to 29.292.

The times of air were 1134, 1134 seconds; of hydrosulphuric acid, 782, 780 seconds; of hydrosulphuric acid carried through a column of bisulphide of carbon  $2\frac{1}{2}$  inches in depth and kept at the fixed temperature of  $59^{\circ}.5$ , 773, 771, 772 seconds. These give the ratios to air, of 0.6887 for hydrosulphuric acid, and 0.6808 for hydrosulphuric acid saturated with the vapour of bisulphide of carbon at  $59^{\circ}.5$ . Also, multiplying by 0.9,—

Transpiration time of hydrosulphuric acid . . . . . 0.6198

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This last result almost coincides with the first determinations with the short capillary M, namely 0.6192. The mean of the two results is,—

Transpiration time of hydrosulphuric acid . . . . . 0.6195

The mercury in the gauge tube of the air-pump was soiled by these experiments, and the tube required to be cleaned after them.

# 7. Bisulphide of Carbon.

At the temperature of 63°, the tension of the vapour of bisulphide of carbon was observed to be 10·462 inches. Experiments were made with air, oxygen, hydrogen and carbonic acid gases, all saturated with the vapour of bisulphide of carbon at 63° and with barometer from 29·874 to 29·850 inches. The short capillary K, 8·75 inches in length, was made use of, and the gas was transpired into the six-pint aspirator jar. The gases were impregnated by the vapour in passing through a large U-shaped tube filled with cotton-wick which was moistened by the liquid bisulphide of carbon.

Air alone was transpired in 982 and 981 seconds; air saturated with bisulphide of carbon vapour in 837 and 838 seconds; oxygen saturated with bisulphide of carbon vapour in 895 and 896 seconds; hydrogen saturated with bisulphide of carbon vapour in 662 and 661 seconds; carbonic acid saturated with bisulphide of carbon vapour in 763 and 762 seconds. The ratios appear in the following Table:—

Transpiration	times of	different	gases	saturated	with	CS.	at.	63°	
a i anspiration	umes or	um creati	Subco	Sucurucu	AA TOTI	COO	$\alpha $	vu	

	Air =1.	Oxygen =1.
Oxygen Air Carbonic acid Hydrogen	0·8533 0·7769	0.8212 0.7679 0.6992 0.6065

It may be safely concluded that the transpiration time of bisulphide of carbon is not less than 0.6065, but probably sensibly greater. It must, according to former observations, approach very closely to, if it does not actually coincide with, 0.6195, the transpiration time of hydrosulphuric acid gas.

## 8. Sulphurous Acid.

This gas was evolved by the action of copper upon sulphuric acid, was washed with water, and conveyed in a continuous manner to a bottle with a relief tube from which the capillary was supplied, as in the experiments with ammonia and cyanogen. The gas was dried by passing over pumice soaked in oil of vitriol before reaching the capillary.

(1.) With short capillary K, 8.75 inches in length, the six-pint aspirator-jar, and usual range from 2.85 to 23.5 inches: thermometer 53°, barometer 29.964 to 29.942 inches.

The time of air was 970, 970 seconds; of sulphurous acid, 714 and 711 seconds; ratio of latter to air, 0.7345. Multiplying by 0.9, we obtain—

Transpiration time of sulphurous acid . . . . . . . 0.6610

(2.) With the long capillary M, 52.5 inches in length, this gas was transpired into the two-pint jar: thermometer 60°.5, barometer 29.880 to 29.878 inches.

The time of air was 1120, 1120 and 1120 seconds; the time of sulphurous acid 814, 811 and 812 seconds. Using the two last observations only for sulphurous acid, we obtain the transpiration time 0.7245 for that gas, air being 1; or multiplying by 0.9,—

Transpiration time of sulphurous acid . . . . . . . 0.6520

In a second series of experiments with the same capillary, thermometer 58° and barometer from 29.880 to 29.886, the following observations were made. Time of air, 1105, 1111, 1105 and 1111 seconds; time of sulphurous acid, 798, 797 and 798 seconds, and ratio to air 0.7199. This gives—

Transpiration time of sulphurous acid . . . . . . . 0.6479

The mean of the two results by this capillary gives—

Transpiration time of sulphurous acid . . . . . . . 0.6500

# 9. Sulphuric Acid.

Both air and oxygen gas saturated with the vapour of anhydrous sulphuric acid were transpired under the pressure of the atmosphere into an air-pump vacuum, by the short capillary K, 8.75 inches in length. Certain new arrangements of the apparatus, however, were required in operating upon so highly corrosive a vapour as that of sulphuric acid. Two ounces of the solid sulphuric acid were melted by heat in a U-tube stuffed with asbestos, and having while liquid impregnated the asbestos, were allowed to cool and become solid again before the air or other gas to be saturated with sulphuric acid vapour was conducted through the U-tube. For the tin conducting tubes of the former arrangements, glass tubes were substituted, and the air-pump was employed to exhaust a stout globular glass globe of six pints in capacity and provided with three openings, which was employed as the aspirator cavity. Two of the openings of the globular receiver were in the sides and one at the bottom of the receiver; by one of the former openings the globular receiver was connected with the transpiring capillary and by the other with the air-pump; a tube containing carbonate of potash being interposed between the receiver and the air-pump, to arrest the acid vapours and prevent them from reaching the air-pump, when the latter was used for exhausting the globular receiver. The third and lower opening communicated with a gauge barometer, by which the tension of the gas or vapour within the globular receiver was observed. The mercury in this barometer was found to adhere slightly to the glass and not to descend with an entirely level surface in the transpiration experiments, owing to a slight chemical action of the acid vapour upon the

mercury. This circumstance prevents the times being observed with the same precision as in other gases.

With the thermometer from 72° to 74°, and barometer from 30.076 to 30.028 inches, the times of descent of the gauge barometer from 28.5 to 23.5 inches were, with air, 865 and 863 seconds; with air saturated with sulphuric acid vapour at 73° Fahr., 960, 961, and 958 seconds. The ratio of the last times to air is 1.1106; and multiplying by 0.9, we obtain,—

Transpiration time of air saturated with vapour of  $SO_3$  at  $73^\circ$ ... 0.9993 The tension of the vapour of anhydrous sulphuric acid at  $73^\circ$  was observed to be 11.50 inches.

The experiments on sulphuric acid vapour were repeated: thermometer 67°.5, barometer 29.914 to 29.908 inches; the range of the gauge barometer now observed, however, being only from 28.5 to 24.5 inches.

The time for air was 695 and 694 seconds; for oxygen saturated with the vapour of sulphuric acid at 67°.5, 786 and 782 seconds; for oxygen alone at 68°, 774 seconds; and for air alone again 692 seconds. The result to be deduced is,—

Transpiration time of oxygen saturated with vapour of SO<sub>3</sub> at 67°.5 . . 1.0130

The sensible equality of the times of air observed at the beginning and end of the experiments proves that the working of the apparatus was not deranged by the sulphuric acid vapour. It is evident that the time of pure sulphuric acid vapour itself cannot deviate far from that of oxygen gas. Sulphuric acid appears to be one of the very few gases, the transpirability of which, if not really coincident with, is slightly inferior to, or slower than, that of oxygen.

### 10. Chlorine.

The transpiration time of chlorine has a peculiar interest as that of an elementary substance. The same arrangements were had recourse to with this corrosive gas as with sulphuric acid. It was found necessary, in addition, to preserve a small column of water above the mercury in the gauge barometer, to defend the metal from the action of the chlorine, or at least to prevent the surface of the metal from becoming foul and adhesive. This gas immediately reached the capillary, like ammonia, from a bottle with a relief tube, to permit the escape of the redundant supply. It was dried by means of chloride of calcium.

(1.) The transpiration was made by capillary K, 8.75 inches in length, into the six-pint globular receiver as aspirator, from 28.5 to 23.5 inches by the gauge barometer attached to the latter: thermometer 70° to 71°, barometer 30.222 to 30.208 inches.

The times of air in two experiments were 865 and 866 seconds; the times of chlorine 670 and 672 seconds; giving the ratio to air of 0.7753. Multiplying the latter number by 0.9, we have—

Transpiration time of chlorine . . . . . . . . . . 0.6978

(2.) In a second series of experiments with the same capillary, the following

observations were made; the thermometer being 72° to 74°, and barometer 30.248 to 30.218 inches.

The times of air were 858, 860 and 859 seconds; the times of carbonic acid 711 and 712 seconds; the times of chlorine 670, 670, 670 and 670 seconds; the time of air again 866 and 867 seconds. A slight increase in the air-time is observed, after the chlorine experiments, but I would refer this increase more to the rise of two degrees in temperature between the first and last observations, than to any derangement in the apparatus. Taking the last observed air as the standard of comparison for the chlorine, and the first observed air for the carbonic acid, we find—

	Air=1.	Oxygen=1.
Transpiration time of chlorine Transpiration time of carbonic acid	0·7732 0·8282	0·6959 0·7454

But the true transpiration time of chlorine gas is probably less than 0.6959, for the true time of carbonic acid is certainly less than 0.7454, the time obtained above for the latter gas. The present capillary, it has been already remarked, is one of too small resistance to bring out the true transpiration time of a gas whose effusion rate differs very widely from its transpiration rate. The present experiment indeed is not inconsistent with the true transpiration time of chlorine, being 2 or 3 per cent. lower than that observed, or falling as low as 0.66, that is, two-thirds of the time of oxygen.

(3.) The transpiration of chlorine was also observed by means of the long capillary M, 52.5 inches in length, with the same six-pint glass globular receiver as aspiratorjar. The fall observed by the gauge barometer was only 3 inches, or from 28.5 to 25.5 inches. Thermometer 58°, barometer 29.742 inches.

The time of air was 1907 and 1911 seconds; of chlorine 1432 and 1395 seconds. The difference of 37 seconds in the two observed times of chlorine, which is so considerable, arose from the action of chlorine upon the mercury; for notwithstanding that the latter was covered with water, its surface became so uneven that the observations could not be made with any great nicety. The first observation of chlorine gives the time of that gas 0.7501 referred to air, and 0.6751 referred to oxygen; the second observation gives the time of chlorine 0.7307 referred to air, and 0.6576 referred to oxygen. Calculating from 1413.5 seconds, the mean of the two observed times for chlorine, we obtain—

	Air = 1.	Oxygen=1.
Transpiration time of chlorine	0.7404	0.6664

The transpiration time of chlorine appears therefore to be about two-thirds of the time of oxygen; or, chlorine passes through a tube with  $1\frac{1}{2}$  time the velocity of oxygen.

# 11. Bromine and Hydrochloric Acid.

The only observations which I possess upon the transpiration of these two substances were made by means of the short capillary K, of 8.75 inches in length, the six-pint globular receiver being the aspirator, and the fall being as usual from 28.5 to 23.5 inches of the gauge barometer. For both the bromine and hydrochloric acid the bottle and relief tube were employed also as before, to regulate the supply of gas to the capillary. Chloride of calcium was employed to dry the gases.

The time of air was 846, 848 seconds; of hydrochloric acid, 693, 693 seconds; of air saturated with the vapour of bromine at 75°, 889, 889 and 889 seconds; of hydrogen saturated with the vapour of bromine, 760, 760 seconds: thermometer from 73° to 75°, barometer 30·230 to 30·178 inches. In an observation which was made at the same time upon the tension of bromine vapour, it was found that liquid bromine placed in an air-pump vacuum depressed the mercurial gauge 9·19 inches at 75°, which may therefore be taken as the tension of the vapour of bromine in the present experiments. The results are as follows:—

	Air=1.	Oxygen=1.
Transpiration time of hydrochloric acid gas	1.0496	0·7363 0·9446 0·8076

It appears that the transpiration time of hydrochloric acid observed, 0.7363, is greater than that of chlorine, 0.66, while that of hydrocyanic acid was found less, on the contrary, than that of cyanogen.

Bromine vapour increases the transpiration time of air, and is therefore less transpirable. This vapour, however, does not appear to be greatly more transpirable than sulphuric acid vapour or oxygen gas.

The ether employed was carefully washed with water, to deprive it of alcohol, and afterwards dried by agitation with pounded chloride of calcium. Dry hydrogen and other gases were impregnated with the vapour of this substance in the same manner as with bromine.

(1.) The first experiments were made with the short capillary K, 8.75 inches in length; the gas being transpired as usual under the pressure of the atmosphere into the exhausted six-pint aspirator jar, through the range from 28.5 to 23.5 inches of the gauge barometer of the air-pump: thermometer 56°, barometer 29.670 to 29.708 inches. The tension of the ether vapour at 56° being found 12.85 inches, the mixture transpired may be represented as composed of 12.85 volumes ether vapour and 16.85 volumes gas; or of 43.26 ether vapour and 56.74 gas in 100 volumes.

The time of air was 988, 988 seconds; of hydrogen 474, 473 seconds; of hydrogen gas saturated with ether vapour at 56°, 498, 500 seconds; of oxygen gas saturated with ether vapour at the same temperature, 696 and 695 seconds. The transpiration times deducible from these observations are,—

	Air=1.	Oxygen=1.
Transpiration time of hydrogen	0.5051	0·4312 0·4546 0·6336

It thus appears that the transpiration time of hydrogen, 0.4312, is only increased to 0.4546 by 43.26 per cent. of ether vapour. As the influence of hydrogen upon the rate of transpiration of the dense gases and vapours is scarcely sensible, this may be held as proving that the time of ether vapour does not sensibly exceed the time of the hydrogen mixture, 0.4546. But as the experiment has been made with a capillary of small resistance, it is not impossible that the normal time of ether vapour may be still sensibly less.

(2.) The capillary M, 52.5 inches in length, with the two-pint aspirator, was now used, the other arrangements remaining as before: thermometer 68°.5 to 69°, barometer 30.242 to 30.264 inches.

The time of air was 1084, 1084 seconds; of air saturated with ether at 68°.5 (59.5 ether vapour to 40.5 air), 675, 676 and 673 seconds; of hydrogen saturated with ether vapour at 68°.5 (59.5 ether vapour to 40.5 hydrogen), 533, 529 and 531 seconds; of oxygen saturated with ether vapour at 68°.5 (59.5 ether vapour to 40.5 oxygen), 728, 725 and 727 seconds; of hydrogen alone, 529, 529 seconds. The tension of ether vapour was observed at the time to be 17.95 inches at 69°. The results deduced from these experiments are as follows:—

	Air=1.	Oxygen=1.
Transpiration time of ether vapour and air	0.4898	0·5601 0·4408 0·6039 0·4392

In this capillary of great resistance, the time of hydrogen is therefore not sensibly affected by nearly one and a half times its volume of ether vapour, from which it may be inferred that the transpiration time of ether vapour itself does not diverge sensibly from that of hydrogen. The near if not perfect coincidence in transpirability in these two substances is very remarkable, considering their great dissimilarity in physical characters, particularly in weight, the densities of hydrogen and ether vapour being as 1 to 37.

Although hydrogen and ether may have the same transpirability, still the influence which each of these gases exerts upon the transpiration of other gases with which it is mixed, is widely different. It will be seen by the experiments above on ether and air, or ether and oxygen, that the transpiration time inclines most to the ether rate, while in hydrogen mixtures the time also deviates from the mean of the mixed gases, but greatly in the direction of the rate of the other gas, and not towards the hydrogen rate. The density of a gas is no doubt an important element in this influence.

In an experiment with the short capillary K, the time of olefant gas was reduced from 0.5246 to 0.4816, by saturation with ether vapour at 60°.5.

The rates of hydrogen and ether appear to diverge from each other in experiments made at a high temperature. The water in the copper trough in which the long capillary M was always placed, with the view of commanding a constant temperature, was heated to 203° (95° centig.), and preserved at that temperature during the continuance of the following experiments. Thermometer in air 60° 5, barometer 29.956 to 29.982 inches.

Time of air 1634 and 1637 seconds; of hydrogen, 798 and 797 seconds; of hydrogen saturated with ether vapour at 60°.5, 863, 863 seconds. As the gas transpired was measured at 60°.5 instead of 203°, the temperature at which it passed through the capillary, these times fall to be diminished in the proportion of the volume of air at 203° and at 60°.5 respectively. We thus obtain as the three mean times in which equal volumes were transpired at 203°,—air 1282.4 seconds, hydrogen 625.9 seconds, and hydrogen saturated with ether vapour at 60°.5, 677.3 seconds.

	Air=1.	Oxygen=1.
Transpiration time at 203° FAHR. of hydrogen	0·4880 0·5281	0·4392 0·4753

While air and hydrogen preserve, at 203°, their usual ratio of transpirability, ether vapour appears therefore to become sensibly less transpirable at the high temperature.

# 13. Methylic Ether (Oxide of Methyl, C<sub>2</sub>H<sub>3</sub>O).

This vapour was evolved in a continuous manner in proportion as required for transpiration, with the arrangements necessary for gases soluble in water. The vapour was passed over both hydrate of potash and chloride of calcium. The experiments were made with the short capillary K, 8.75 inches in length, like the first experiments with common ether. Thermometer 56°, barometer 29.650.

Time of air 993 and 991 seconds; of methylic ether, 532 and 532 seconds; of methylic ether saturated with the vapour of common ether at 56°, 508, 506 and 507 seconds.

Transpiration	times.
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	Air=1.	Oxygen = 1.
Methylic ether	0·5363 0·5111	0·4826 0·4600

The time of methylic ether, 0.4826, is decidedly longer than that of common ether, 0.4546, as the latter was formerly observed by the same capillary; and consequently an addition of ether vapour shortens the methylic ether time, as appears in the second experiment, where the transpiration time of such a mixture falls to 0.4600.

# 14. Hydrochloric Ether (Chloride of Ethyl, C<sub>4</sub> H<sub>5</sub> Cl).

The experiments were made with the same short capillary K, 8.75 inches in length, and with the other arrangements as for the two preceding ethers. Thermometer 56°, barometer from 29.794 to 29.758 inches.

The time of air was 980 and 981 seconds; of hydrochloric ether, 548, 544 and 543 seconds.

	Air=1.	Oxygen $= 1$ .
Transpiration time of hydrochloric ether	0.5543	0.4988

It would be unsafe to draw any conclusion from a single experiment upon this ether and that experiment made with a capillary of inferior resistance, but it may be remarked that the time of this ether approaches to half the time of oxygen, while the density of the vapour is little more than double that of this gas; the theoretical density of hydrochloric ether vapour being 32.25 to hydrogen 1 and oxygen 16.

# 15. Hydrochloric Methylic Ether (Chloride of Methyl, C<sub>2</sub> H<sub>3</sub> Cl).

This ether, which like the two last is entirely vaporous at the temperature of the experiments, was prepared by distilling together half a pound of wood-spirit, one and a half pounds of oil of vitriol and one pound of common salt. The gas was exposed to a large quantity of dilute caustic soda in two wash-bottles, and dried afterwards by chloride of calcium. The same capillary and arrangements were employed as in the immediately preceding experiments. Thermometer 54°, barometer 29.862 to 29.856 inches.

The time of air was 973, 973 seconds; of chloride of methyl, 592, 587 and 582 seconds; of chloride of methyl again, after changing the solution of caustic soda in the wash-bottles, 592 and 592 seconds. Calculating from the last observed time of chloride of methyl, we have—

	Air=1.	Oxygen = 1.
Transpiration time of chloride of methyl	0.6084	0.5475

It thus appears that the chloride of methyl has a longer time, or is more slowly transpired than the corresponding chloride of ethyl; as the oxide of methyl was also found to be less transpirable than the oxide of ethyl. Indeed the difference between the two oxides and between the two chlorides appears to be the same, or about 0.045

in both cases. This is in accordance with the general observation, that transpiration is promoted by increase of density. The theoretical density of chloride of methyl is 25.25 to hydrogen 1 and oxygen 16.

### 16. Water.

Although great care was always taken to dry air when transpired, as well as other gases, in all experiments, still it does not appear that the rate of air is much affected by the presence of aqueous vapour unless the latter is present in considerable proportion.

The times observed by capillary K, 8.75 inches in length, into a vacuum, were for air dried by chloride of calcium 1008 seconds, and for air drawn afterwards directly from the atmosphere, of which the temperature was 60° and the dew-point 32°, 1006 and 1006 seconds. So small a difference may be due to accidental causes.

With dry air at 60°, the times with the same capillary were, upon another occasion, 1021 and 1021 seconds; and with air of 60° temperature, but containing aqueous vapour with the dew-point at 38°, 1018 and 1017 seconds.

In other experiments, the presence of aqueous vapour appeared to occasion a sensible retardation in the time of air. The transpiration was made into a vacuum by the capillary M, 52.5 inches in length; the temperature of the capillary being maintained at 58°.5, and the barometer varying from 29.798 to 29.832 inches. The air was charged with vapour by passing through a tube filled with cotton wick, which had been previously moistened with dilute sulphuric acid of different strengths. The time of dry air was 1115, 1115 seconds; of air carried over the fourth hydrate of sulphuric acid (HO.SO<sub>3</sub>+3HO), 1117, 1117 seconds; of air passed over the eighth hydrate (HO . SO $_3+7$ HO), 1120 and 1121 seconds; of air passed over the eighteenth hydrate (HO.SO<sub>3</sub>+17HO), 1122, 1122 and 1121 seconds. Here we observe in the dampest air a slight but sensible increase of the air time, not exceeding 7 seconds. But on repeating the experiment immediately afterwards with dry air, the time was 1120 and 1119 seconds, or within two seconds of the immediately preceding observations with moist air. Indeed the transpiration of moist air appears to produce a slight but sensible retardation of a persistent character, probably from the condensation of a film of moisture on the inner surface of the capillary, which is not immediately removed by the subsequent passage of dry air.

With the same capillary, thermometer 57° and barometer 30·136 to 30·078 inches, dry air was transpired in 1089, 1089 seconds; dry hydrogen in 532 and 532 seconds; air saturated with aqueous vapour at 57°·5 in 1098, 1098 seconds; hydrogen saturated with aqueous vapour at the same temperature, in 548 and 548 seconds; and lastly, dry air, first in 1106 seconds, and afterwards in 1084 and 1085 seconds. Here the damp air is less transpirable, volume for volume, than dry air by 9 seconds. Also, dry air immediately following the damp air does not recover its usual transpirability in the first experiment.

These experiments upon damp and dry air seem to indicate that the transpiration

time of aqueous vapour does not differ greatly from that of air itself. The influence of aqueous vapour upon the time of hydrogen, however, is considerably less than that of air upon the same gas, and therefore suggests a more rapid transpiration.

### 17. Alcohol.

Air was impregnated with the vapour of alcohol of specific gravity 0.835 at 60°, barometer 29.358. The tension of the vapour of alcohol of specific gravity 0.813 at 60° is estimated at 1.23 inch. The capillary K, 8.75 inches in length, was made use of, with an air-pump vacuum, as in all these experiments.

The time of dry air was 1013 and 1014 seconds; of air containing alcohol vapour, 1011 and 1012 seconds. The rate of air is scarcely affected, and consequently the time of alcohol vapour must approximate to that of air.

## 18. Naphtha and Coal-gas.

In experiments made with air saturated with the vapour of coal-tar naphtha at 62°, the capillary K being employed, the times obtained for air alone were 978 and 979 seconds; for air saturated with naphtha vapour, 949 and 949 seconds. The transpiration time of air is diminished 30 seconds, showing that the volatile hydrocarbons of naphtha are highly transpirable, like ether vapour. The time of coal-gas, taken from the service-pipes of a London company, and observed in the same circumstances, was 621 and 622 seconds; of the same coal-gas impregnated with naphtha vapour, 621 and 621 seconds, or the naphtha vapour produced no sensible change in the transpirability of the gas; showing a near coincidence in their transpirabilities. The transpiration time of the coal-gas, reduced to the oxygen scale, is 0.5716, or a little more than protocarburetted hydrogen, 0.5510.

That a considerable quantity of naphtha vapour was taken up by the coal-gas, notwithstanding that its transpiration was unaffected, appears in certain experiments which were made with a particular object upon the effusion of the same gases. capillary was removed and replaced by a plate of platinum foil, G of former paper, having an extremely minute aperture, the other arrangements remaining the same. The gases were all moistened with water. For the passage of equal volumes into an air-pump vacuum (the six-pint aspirator-jar, through the usual range from 28.5 to 23.5 inches of the attached barometer), the times were, at 61°, for air, 434 and 434 seconds; for hydrogen, 139 and 139 seconds; for coal-gas, 314 and 314 seconds; for coal-gas saturated with naphtha vapour at 61°, 331 and 331 seconds; for hydrogen and naphtha vapour, 194 and 193 seconds; and for air with naphtha vapour, 503 and 503 seconds. It is to be remembered that the densities of the gases effused are in the proportion of the squares of these times, and may be deduced from the latter. The time of coalgas is increased by the addition of naphtha vapour, but to a much less extent, than hydrogen and air are, no doubt from the former being from the first partially saturated with naphtha vapour.

A good deal of light could be obtained, I believe, upon the composition and value of coal-gas by a combination of effusion and transpiration experiments. Great density, which would be indicated by slow effusion, is always valuable, unless when occasioned by air, carbonic oxide or carbonic acid, which gases exclusively make the transpiration slow; so that slow effusion with rapid transpiration would mark the coal-gas of superior quality.

### III. TRANSPIRATION OF AIR OF DIFFERENT DENSITIES OR ELASTICITIES.

A series of observations on air varying in density from 0.5 to 2 atmospheres, made with the long 20-feet capillary E in my former paper, appeared to establish the conclusion that "for equal volumes of air of different densities, the times of transpiration are inversely as the densities." The law of Effusion, or flow of air into a vacuum by an aperture in a plate, is entirely different; equal volumes of air of all densities passing in equal times.

With the short capillary K, 8.75 inches in length, the result was now found to be materially different. Air in three different states of rarefaction was drawn into a sustained vacuum from a globular receiver of which the capacity was 56.5 cubic inches, standing over water. To command the desired density of the air in the globular receiver, the little system of the latter and the basin of water in which it stood was retained within a large air-pump receiver, the atmosphere of which was adjusted to the requisite pressure. Thermometer 62°, external barometer from 29.984 to 29.936 inches.

Transpiration of equal volumes of Air.

Density or elasticity.	Time in seconds.		
Density of elasticity.	Experiment I.	Experiment II.	
1 atmosphere	2948	2173 2946 5288	

It will be observed that the time 5292 seconds for air of 0.5 density is considerably more than double 2172 seconds, the time for air of 1 density.

With compressed air, varying in density from 1 to 2.5 atmospheres, the deviation from the law was equally conspicuous; the times of transpiration of equal volumes at 1, 1.25, 1.5, 1.75, 2 and 2.5 atmospheres, being in the ratio of 1, 0.8625, 0.7553, 0.6834 and 0.5519, instead of 1, 0.8, 0.6666, 0.5714, 0.5 and 0.4.

On operating, however, with the long capillary M, 52.5 inches in length, and of great resistance, results were again obtained in strict accordance with the law. The air was drawn from a metallic digester provided with a gauge barometer, in which it was preserved of a constant elasticity; this digester itself being supplied from a second similar digester, in which the air was in a state of still higher compression.

The air was transpired into the two-pint aspirator-jar (capacity about 72 cubic inches) upon the plate of the air-pump, for the usual range of the gauge barometer from 28.5 to 23.5 inches. Thermometer 66°, external barometer 30.122 to 30.086 inches.

Density or elasticity.	Time in	seconds.	Reduced time	Calculated or
Density of elasticity.	Experiment I.	Experiment II.	of means.	theoretical times
1 atmosphere	1095 707 493 359 277 218 176	1096 707 493 359 276 217 176	1095·5 883·1 739·5 628·25 553 489·4 440	1095·5 884·8 737·3 632 553 491·5

Transpiration of equal volumes of Air.

The column of "Time in seconds" contains the times of the fall of the air-pump barometer from 28.5 to 23.5 inches actually observed, and which are produced by the admission to the aspirator-jar of an equal volume of air of constant density. These times must therefore be multiplied by the density in atmospheres of the air transpired, to obtain the reduced times of the following column. It will be observed that these reduced times are in perfect harmony with the "Calculated times" of the last column. Indeed nothing could illustrate more strongly the great precision of which transpiration experiments are susceptible, than these results.

The conclusion to be drawn from the present observations with the capillary M, and the old observations with E, as compared with the observations made with the short capillary K, is that to bring out the normal effect of densities on transpiration, a greater resistance and length of tube are necessary than are required for the observations of the normal relations in the transpiration times of such gases as oxygen, nitrogen and hydrogen; for the short capillary K, which fails so much in the law of densities, exhibits the other relations nearly with as much accuracy as the long capillary M. The marked superiority also of the 20-feet tube E over the 8-inch tube K, although the power of resistance of these two capillaries is nearly equal, suggests again the idea that resistance produced by elongation of the capillary acts differently from an equal resistance produced by contracting the diameter of the capillary, and more advantageously in transpiration experiments.

# IV. TRANSPIRATION OF AIR AND OTHER GASES AT DIFFERENT TEMPERATURES.

The experiments which I have made upon the transpiration of air and also of other gases at different temperatures are very numerous, but not altogether satisfactory. Looking upon the experiments as only preliminary, I shall confine myself at present to a statement of results without detail, and endeavour to return to the subject at some future opportunity.

The transpiration of equal volumes becomes slower as the temperature rises. The experiments which follow upon air, carbonic acid and hydrogen, were made upon different days with slightly different barometric pressures, so that the absolute times of one gas cannot be compared with another; but this is unnecessary for our present purpose. The capillary employed was M, 52.5 inches in length, and of great resistance.

m	Time in seconds.		
Temperature.	Air.	Carbonic acid.	Hydrogen.
32 FAHR.	1054-1	857:9	545.4
59	1092.8	897.4	<b>557·8</b>
86	1133.4	931.5	577.7
113	1175.7	969.4	598.8
140	1211	993.9	615.9

Table XIV.—Transpiration of equal volumes at different temperatures.

The difference of time of transpiration at the two extreme temperatures, 32° and 140°, is 157.9 seconds for air, 136 seconds for carbonic acid, and 70.5 seconds for hydrogen. The differences, calculated in the proportion of the transpiration times of the same gases at the temperatures usually observed (56° to 74°), namely air 0.9, carbonic acid 0.73, and hydrogen 0.44, are for carbonic acid 128.1 seconds instead of 136, and for hydrogen 73.2 seconds instead of 70.5. It would be unsafe to conclude from these small deviations that the transpiration of the three gases in question is unequally affected by heat in the range of temperature from 32° to 140°; for at temperatures distant from the temperature of the atmosphere, the unavoidable errors of observation increase in magnitude. The increment upon the time of air was 156.2 seconds, and upon hydrogen 62.8 seconds, at 140°, in a repetition of the same experiments.

My most unexceptionable experiments all concur in showing that no sensible change takes place in the transpiration ratios of hydrogen, nitrogen and carbonic oxide, at temperatures so high as 347° Fahr. Thus the observed transpiration times of a mixture of equal volumes of hydrogen and carbonic oxide at 60° and 347°, were 0.8870 and 0.8853; the transpiration times of air observed at the same temperatures being taken as unity. The transpiration times of a mixture of equal volumes of hydrogen and nitrogen, referred to the times of air in the same manner, were at 65°, 0.8939; at 347°, 0.8924; again, at 64°.5, 0.8930; and at 347°, 0.8872. The transpiration ratios are thus as nearly as possible constant at these widely distant temperatures.

The transpiration times of air and hydrogen alone, at 203°, were found on two different occasions as 1 to 0.4841, and 1 to 0.4880. Multiplying these hydrogen times by 0.9 to bring them to the scale of oxygen, we have for the transpiration times of

hydrogen at 203°, 0.4357 and 0.4392, numbers which might have been obtained at atmospheric temperatures.

Carbonic acid, however, appears to present a sensible deviation from this uniformity of rate. In a series of observations made upon this gas at 60°, 203°, 299° and 347°, its transpiration time referred to air at the same temperatures was 0.8291, 0.8551, 0.8777 and 0.8907; and referred to oxygen, 0.7448, 0.7541, 0.7741 and 0.7855. The transpiration time of carbonic acid at 347° varied in other experiments from 0.7729 to 0.7905, the time of oxygen being 1. The protoxide of nitrogen gave the number 0.7969 at the same high temperature.

The time of oxygen appears also to become relatively slower at high temperatures, although much less considerably than carbonic acid. It gave the numbers 0.8877 and 0.8860 for air at 347°, instead of 0.8984, the number at low temperatures. As we may assume from its uniform relation to hydrogen that the nitrogen remains constant, it follows that the oxygen has become relatively slower in transpiration at the high temperature.

If oxygen deviates from a supposed normal rate at high temperatures, it cannot necessarily coincide with that rate at any lower temperature, which is accidental, such as that of the atmosphere. But this influence of heat upon the transpiration time of oxygen is, I believe, still sensible at the low temperature in question.

By increasing the time of oxygen, this influence of heat may be the cause of that slight deviation, so uniform in its amount, of the observed times of air and nitrogen from their theoretical times, which was always remarked. I am disposed then to look upon the slight inconstancy of transpiration rate observed in some gases at different temperatures, as a fact of the same class as the deviations from their theoretical specific gravities observed in a greater or less degree in the same substances, and to those other points in which all the gaseous bodies we have to operate upon depart in some measure from the mechanical idea of a perfect gas.

The normal effect of temperature upon transpiration, as observed in air, varies I find with the resistance of the capillary in a much higher degree than any other property of transpiration; the retardation from the same change of temperature being much greater in a capillary of great than small resistance. The resistance of a capillary such as M, which exhibits so exactly the law of densities, is insufficient to bring out the full effect of temperature. With the fine tubes of the compound capillary, on the other hand, the limit to the retarding influence of heat seems to be reached. The retardation then appears to be simply in proportion to the expansion; and rarefaction by heat, therefore, to have the same effect upon transpiration as expansion from diminished pressure.

In illustration of this inequality of action upon heated air, I may refer to results obtained by two capillary tubes of small and of intermediate resistance, before stating the normal results of capillaries of extreme resistance.

With the copper capillary tube described in my former paper, and which admitted

1 cubic inch of air into a vacuum in 22 seconds, the time of passage of a constant volume of air into a vacuum was 853 seconds at 60°, 899 seconds at 116°, and 924.5 seconds at 152°. The theoretical times, or those corresponding to the rarefaction by heat at these temperatures, are 853, 945 and 1004 seconds. Here the observed times at 116° and 152°, are 46 and 79.5 seconds shorter respectively than the times obtained by calculation; and the difference in transpirability observed at the high and low temperatures only amounts to about one-half of what it should be.

With capillary M, of which the resistance is seven times greater than the last capillary, the observed times of air at 59° (15° centig.), and at 203° (95° centig.), were 1106.5 and 1286.4 seconds. The time at the higher temperature is 1400 seconds by calculation, and the observed time is therefore 113.6 seconds deficient. The difference at the high and low temperatures amounts to nearly two-thirds of the difference which theory requires. The deviation is therefore less than with the preceding capillary.

Air compressed in the globular digester with pressure gauge, of which the capacity was reduced to about 10 cubic inches by the introduction of mercury, was transpired by a small capillary V, 3 inches in length, into the atmosphere, from a pressure beginning at 17 inches above that of the barometer. Thermometer 50°, barometer 29:546 to 29:590.

The resistance of this capillary is excessive. Under a pressure of 17 inches of mercury, 1 cubic inch of air is transpired in 2329 seconds, or the volume transpired is 0.0258 cubic inch per minute.

D	Time in	seconds.	Ratio at 203°,
Pressure by gauge barometer.	Thermometer 50° Fahr. Thermometer 203° Fahr.		Time at $50^{\circ} = 1$ .

1445

1541

4356

17 inches.

From 17 to 14 inches......

16

15

Table XV.—Transpiration of air under pressure (into air) at different temperatures.

1.7000

1.6900

1.6880

1.6924

2329

2442

2601

7372

Now the volume of air at  $32^{\circ}$  being =1, at  $50^{\circ}$  it is 1.0366, and at  $203^{\circ}$ , 1.3480. But it must be remembered that the volume actually transpired in the experiment was greater at  $203^{\circ}$  than that at  $50^{\circ}$ , in proportion as the volume of air is expanded at the higher of these two temperatures, that is as 1.3480 to 1.0366 (volume at  $32^{\circ}=1$ ). It is therefore necessary to reduce the observed times of the table at  $203^{\circ}$  in that proportion. The time from 17 inches to 16 is thus reduced from 2329 to 1792.5 seconds, which last is the true time of the passage of the same volume at  $203^{\circ}$  as passed at  $50^{\circ}$ . The law requires that the times of equal volumes should be inversely as the densities of air at these temperatures, or as 1.0366 to 1.3480. Thus calculated from

1370 seconds, the time at 50°, the time at 203° is 1780.9 seconds; the time actually observed was 1792.5 or 11.6 seconds more, a close approximation considering the difficulties of the experiment.

But the resistance does not require to be so excessive as in capillary V to bring out the law of temperature. It appeared equally distinct in a capillary tube, having only one-ninth of the resistance of V for equal lengths. This tube however was used in lengths of  $4\frac{1}{2}$  inches (instead of 3 inches), so that its resistance is properly stated at one-sixth of V. A sheaf was put together of thirty lengths of the new tube, forming the compound capillary Q. The digester was employed of its full capacity, of 72 cubic inches, to contain the compressed air, which was allowed to escape by the channels of Q into the atmosphere. The range of pressure was from 20 inches to 8. The observed times at  $49^{\circ}$  and  $203^{\circ}$  without reduction were 802, 799 and 798 seconds at the low temperature, and 1350 and 1347 seconds at the high temperature. Taking the means 800 and 1349 seconds and reducing as in the experiments with V, we have  $1036\cdot1$  seconds for the high temperature. Now the calculated time for that temperature is  $1041\cdot6$  seconds, or only  $5\cdot5$  seconds above the observed time. The barometer during these experiments marked from  $30\cdot044$  to  $30\cdot058$  inches.

In another series of experiments, the time observed at 49° being 797 seconds, the times observed after reduction, at certain intermediate temperatures, were as follows:—

Temperature.	Observed time.	Calculated time.	Error of observation.
49 Fahr. 96	797 879•3	797 87 <b>0</b> •4	+ 8.9
141	950-1	935.8	+14.3
203	1020.8	1032-1	-11.3

Table XVI.—Times of transpiration of Air (into air) in seconds.

The deviations of the observed from the calculated times, from 8.9 to 14.3 seconds, are small considering the difficulty of maintaining the temperature constant in the experiments. Nor are they always in the same direction. This appears in a third series of experiments, conducted in the same manner as the last, of which I subjoin the results.

Table XVII.—Times of transpiration of Air (into air) in seconds.

Temperature.	Observed time.	Calculated time.	Error of observation.
49 Fahr. 96 141	797 897·3 932·3	797 870·4 940·8	+8•9 -8•5

These observations leave little doubt that the transpiration of air at different temperatures takes place according to the law by which the times above have been cal-

culated. In one experiment which was made upon oxygen at 49° and 203°, the increase upon the time at the higher temperature corresponded within 0.7 per cent. of the increase upon the time of air, and evidently followed the same ratio. I may add that the transpiration times of air and oxygen, as determined by a single observation in each case, were 0.9058 to 1 for the compound capillary Q, and 0.9020 to 1 for the single capillary V of extreme resistance.

In conclusion I may sum up the general results hitherto obtained in this inquiry.

1. The velocities with which different gases pass through capillary tubes bear a constant relation to each other, and appear to constitute a peculiar and fundamental property of the gaseous form of matter, which I have termed transpirability. The constancy of these relations, or of the transpiration times, has been observed for several of the gases for tube resistances varying in amount from 1 to 1000. These relations, there is reason to believe, are more simple in their expression than the densities of the gases. The following relations are particularly remarkable.

The velocity of hydrogen is exactly double that of nitrogen and carbonic oxide.

The velocities of nitrogen and oxygen are inversely as the specific gravities of these gases.

The velocity of binoxide of nitrogen is the same as that of nitrogen and carbonic oxide.

The velocities of carbonic acid and protoxide of nitrogen are equal, and directly proportional to their specific gravities, when compared with oxygen.

The velocity of protocarburetted hydrogen is 0.8, that of hydrogen being 1.

The velocity of chlorine appears to be  $l\frac{1}{2}$  that of oxygen; of bromine vapour and sulphuric acid vapour the same as that of oxygen.

Ether vapour appears to have the same velocity as hydrogen gas.

Olefiant gas, ammonia and cyanogen to have equal or nearly equal velocities, which approach closely to double the velocity of oxygen.

Hydrosulphuric acid gas and bisulphide of carbon vapour appear to have equal or nearly equal velocities.

The compounds of methyl appear to have a less velocity than the corresponding compounds of ethyl, but to be connected by a certain constant relation.

- 2. The resistance of a capillary tube of uniform bore to the passage of any gas is directly proportional to the length of the tube.
- 3. The velocity of passage of equal volumes of air of the same temperature but of different densities or elasticities, is directly proportional to the density.
- 4. Rarefaction by heat has a similar and precisely equal effect in diminishing the velocity of the transpiration of equal volumes of air, as the loss of density and elasticity by diminished pressure has.
- 5. A greater resistance in the capillary is required to bring out the third result, or the law of densities, than appears necessary for the first and second results; and a

resistance still further increased, and the highest of all, to bring out the fourth result or the law of temperatures.

6. Finally, it will be remarked throughout, that transpiration is promoted by density, and equally whether the increased density is due to compression, to cold, or to the addition of an element in combination, as the velocity of oxygen is increased, by combining it with carbon without change of volume, in carbonic acid gas.

It was no part of my plan to investigate the passage of gases through tubes of great diameter, and to solve pneumatic problems of actual occurrence, such as those offered in the distribution of coal-gas by pipes. But I may state that the results must be similar, with truly elastic gases such as air and carburetted hydrogen, whether the tubes are capillary or many inches in diameter, provided the length of the tube is not less than 4000 times its diameter, as in the long glass capillaries of my early experiments. The small propulsive pressure applied to coal-gas is also favourable to transpiration, as well as the great length of the mains; and I should therefore expect the distribution of coal-gas in cities to exemplify approximately the laws of gaseous transpiration. The velocity of coal-gas should be 1.575, that of air being 1, under the same pressure (p. 383). And with a constant propulsive pressure in the gasometer, the flow of gas should increase in volume with a rise of the barometer or with a fall in temperature, directly in proportion to the increase of its density from either of these causes.