

his giving no means of saturating the gases with aqueous vapour. He further measures his pressures to  $1/200$ th of a millimetre. His ratio for the volumes is given as

$$2\cdot00023,$$

or only  $1/10$ th of the difference from  $2\cdot0$  exactly of that found by the above-described experiments.

II. "On the Densities of the Principal Gases." By LORD RAYLEIGH, Sec. R.S. Received March 4, 1893.

In former communications\* I have described the arrangements by which I determined the ratio of densities of oxygen and hydrogen (15·882). For the purpose of that work it was not necessary to know with precision the actual volume of gas weighed, nor even the pressure at which the containing vessel was filled. But I was desirous before leaving the subject of ascertaining not merely the relative, but also the absolute, densities of the more important gases, that is, of comparing their weights with that of an equal volume of water. To effect this it was necessary to weigh the globe used to contain the gases when charged with water, an operation not quite so simple as at first sight it appears. And, further, in the corresponding work upon the gases, a precise absolute specification is required of the temperature and pressure at which a filling takes place. To render the former weighings available for this purpose, it would be necessary to determine the errors of the barometers then employed. There would, perhaps, be no great difficulty in doing this, but I was of opinion that it would be an improvement to use a manometer in direct connexion with the globe, without the intervention of the atmosphere. In the latter manner of working, there is a doubt as to the time required for full establishment of equilibrium of pressure, especially when the passages through the taps are partially obstructed by grease. When the directly connected manometer is employed, there is no temptation to hurry from fear of the entrance of air by diffusion, and, moreover (Note A), the time actually required for the establishment of equilibrium is greatly diminished. With respect to temperature, also, it was thought better to avoid all further questions by surrounding the globe with ice, as in Regnault's original determinations. It is true that this procedure involves a subsequent cleaning and wiping of the globe, by which the errors of weighing are considerably augmented; but, as it was not proposed to experiment further with hydrogen, the objection was of less force. In the case of the heavier

\* 'Roy. Soc. Proc.,' February, 1888; February, 1892.

gases, unsystematic errors of weighing are less to be feared than doubts as to the actual temperature.

In order to secure the unsystematic character of these errors, it is necessary to wash and wipe the working globe after an exhaustion in the same manner as after a filling. The dummy globe (of equal external volume, as required in Regnault's method of weighing gases) need not be wiped merely to secure symmetry, but it was thought desirable to do so before each weighing. In this way there would be no tendency to a progressive change. In wiping the globes the utmost care is required to avoid removing any loosely attached grease in the neighbourhood of the tap. The results to be given later will show that, whether the working globe be full or empty, the relative weights of the two globes can usually be recovered to an accuracy of about 0.3 milligramme. As in the former papers, the results were usually calculated by comparison of each "full" weight with the mean of the immediately preceding and following empty weights. The balance and the arrangements for weighing remained as already described.

#### *The Manometer.*

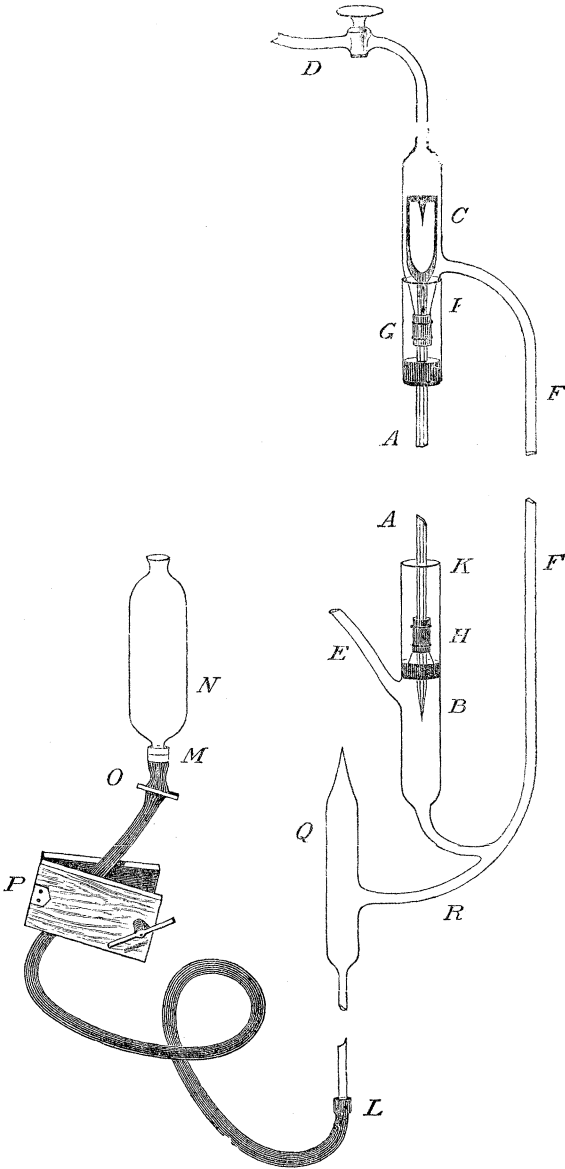
The arrangements adopted for the measurement of pressure must be described in some detail, as they offer several points of novelty. The apparatus actually used would, indeed, be more accurately spoken of as a manometric gauge, but it would be easy so to modify it as to fit it for measurements extending over a small range.

The object in view was to avoid certain defects to which ordinary barometers are liable, when applied to absolute measurements. Of these three especially may be formulated:—

- a. It is difficult to be sure that the vacuum at the top of the mercury is suitable for the purpose.
- b. No measurements of a length can be regarded as satisfactory in which different methods of reading are used for the two extremities.
- c. There is necessarily some uncertainty due to irregular refraction by the walls of the tube. The apparent level of the mercury may deviate from the real position.
- d. To the above may be added that the accurate observation of the barometer, as used by Regnault and most of his successors, requires the use of a cathetometer, an expensive and not always satisfactory instrument.

The guiding idea of the present apparatus is the actual application of a measuring rod to the upper and lower mercury surfaces, arranged so as to be vertically superposed. The rod AA, fig. 1, is of iron (7 mm. in diameter), pointed below B. At the upper end, C, it

FIG. 1.



divides at the level of the mercury into a sort of fork, and terminates in a point similar to that at B, and, like it, directed downwards. The coincidence of these points with their images reflected in the mercury

surfaces, is observed with the aid of lenses of about 30 mm. focus, held in position upon the wooden framework of the apparatus. It is, of course, independent of any irregular refraction which the tube may exercise. The verticality of the line joining the points is tested without difficulty by a plumb-line.

The upper and lower chambers C, B are formed from tubing of the same diameter (about 21 mm. internal). The upper communicates through a tap, D, with the Töppler, by means of which a suitable vacuum can at any time be established and tested. In ordinary use, D stands permanently open, but its introduction was found useful in the preliminary arrangements and in testing for leaks. The connexion between the lower chamber B and the vessel in which the pressure is to be verified takes place through a side tube, E.

The greater part of the column of mercury to which the pressure is due is contained in the connecting tube FF, of about 3 mm. internal diameter. The temperature is taken by a thermometer whose bulb is situated near the middle of FF. Towards the close of operations the more sensitive parts are protected by a packing of tow or cotton-wool, held in position between two wooden boards. The anterior board is provided with a suitable glass window, through which the thermometer may be read.

It is an essential requirement of a manometer on the present plan that the measuring rod pass air-tight from the upper and lower chambers into the atmosphere. To effect this the glass tubing is drawn out until its internal diameter is not much greater than that of the rod. The joints are then made by short lengths of thick-walled india-rubber H, G, wired on and drowned externally in mercury. The vessels for holding the mercury are shown at I, K. There is usually no difficulty at all in making perfectly tight joints between glass tubes in this manner; but in the present case some trouble was experienced in consequence apparently of imperfect approximation between the *iron* and the mercury. At one time it was found necessary to supplement the mercury with vaseline. When tightness is once obtained, there seems to be no tendency to deterioration, and the condition of things is under constant observation by means of the Töppler.

The distance between the points of the rod is determined under microscopes by comparison with a standard scale, before the apparatus is put together. As the rod is held only by the rubber connexions, there is no fear of its length being altered by stress.

The adjustment of the mercury (distilled in a vacuum) to the right level is effected by means of the tube of black rubber LM, terminating in the reservoir N. When the supply of mercury to the manometer is a little short of what is needed, the connexion with the reservoir is cut off by a pinch-cock at O, and the fine adjustment

is continued by squeezing the tube at P between a pair of hinged boards, gradually approximated by a screw. This plan, though apparently rough, worked perfectly, leaving nothing to be desired.

It remains to explain the object of the vessel shown at Q. In the early trials, when the rubber tube was connected directly to R, the gradual fouling of the mercury surface, which it seems impossible to avoid, threatened to interfere with the setting at B. By means of Q, the mercury can be discharged from the measuring chambers, and a fresh surface constituted at B as well as at C.

The manometer above described was constructed by my assistant, Mr. Gordon, at a nominal cost for materials; and it is thought that the same principle may be applied with advantage in other investigations. In cases where a certain latitude in respect of pressure is necessary, the measuring rod might be constructed in two portions, sliding upon one another. Probably a range of a few millimetres could be obtained without interfering with the india-rubber connexions.

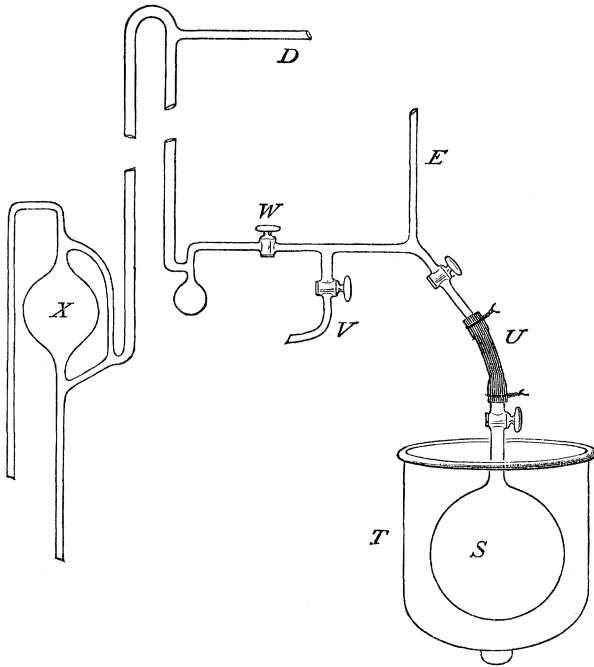
The length of the iron rod was obtained by comparison under microscopes with a standard bar R divided into millimetres. In terms of R the length at 15° C. is 762·248 mm. It remains to reduce to standard millimetres. Mr. Chaney has been good enough to make a comparison between R and the iridio-platinum standard metre, 1890, of the Board of Trade. From this it appears that the metre bar R is at 15° C. 0·3454 mm. too long; so that the true distance between the measuring points of the iron rod is at 15° C.

$$762\cdot248 \times 1\cdot0003454 = 762\cdot511 \text{ mm.}$$

#### *Connexions with Pump and Manometer.*

Some of the details of the process of filling the globe with gas under standard conditions will be best described later under the head of the particular gas; but the general arrangement and the connexions with the pump and the manometer are common to all. They are sketched in fig. 2, in which S represents the globe, T the inverted bell-glass employed to contain the enveloping ice. The connexion with the rest of the apparatus is by a short tube U of thick rubber, carefully wired on. The tightness of these joints was always tested with the aid of the Töppler X, the tap V leading to the gas-generating apparatus being closed. The side tube at D leads to the vacuum chamber of the manometer, while that at E leads to the pressure chamber B. The wash-out of the tubes, and in some cases of the generator, was aided by the Töppler. When this operation was judged to be complete, V was again closed, and a good vacuum made in the parts still connected to the pump. W would then be closed, and the actual filling commenced by opening V, and finally

FIG. 2.



the tap of the globe. The lower chamber of the manometer was now in connexion with the globe, and through a regulating tap (not shown) with the gas-generating apparatus. By means of the Töppler the vacuum in the manometer could be carried to any desired point. But with respect to this a remark must be made. It is a feature of the method employed\* that the exhaustions of the globe are carried to such a point that the weight of the residual gas may be neglected, thus eliminating errors due to a second manometer reading. There is no difficulty in attaining this result, but the delicacy of the Töppler employed as a gauge is so great that the residual gas still admits of tolerably accurate measurement. Now in exhausting the head of the manometer it would be easy to carry the process to a point much in excess of what is necessary in the case of the globe, but there is evidently no advantage in so doing. The best results will be obtained by carrying both exhaustions to the *same* degree of perfection.

At the close of the filling the pressure has to be adjusted to an exact value, and it might appear that the double adjustment required (of pressure and of mercury) would be troublesome. Such was not

\* Due to von Jolly.

found to be the case. After a little practice the manometer could be set satisfactorily without too great a delay. When the pressure was nearly sufficient, the regulating tap was closed, and equilibrium allowed to establish itself. If more gas was then required, the tap could be opened momentarily. The later adjustments were effected by the application of heat or cold to parts of the connecting tubes. At the close, advantage was taken of the gradual rise in the temperature which was usually met with. The pressure being just short of what was required, and V being closed, it was only necessary to wait until the point was reached. In no case was a reading considered satisfactory when the pressure was changing at other than a very slow rate. It is believed that the comparison between the state of things at the top and at the bottom of the manometer could be effected with very great accuracy, and this is all that the method requires. At the moment when the pressure was judged to be right, the tap of the globe was turned, and the temperature of the manometer was read. The vacuum was then verified by the Töppler.

#### *The Weights.*

The object of the investigation being to ascertain the *ratio* of densities of water and of certain gases under given conditions, the absolute values of the weights employed is evidently a matter of indifference. This is a point which I think it desirable to emphasise, because v. Jolly, in his, in many respects, excellent work upon this subject,\* attributes a discrepancy between his final result for oxygen and that of Regnault to a possible variation in the standard of weight. On the same ground we may omit to allow for the buoyancy of the weights as used in air, since only the *variations* of buoyancy, due, for example, to changing barometer, could enter; and these affect the result so little that they may safely be neglected.†

But, while the absolute values of the weights are of no consequence, their relative values must be known with great precision. The investigation of these over the large range required (from a kilogramme to a centigramme) is a laborious matter, but it presents nothing special for remark. The weights quoted in this paper are, in all cases, corrected, so as to give the results as they would have been obtained from a perfectly adjusted system.

\* 'Munich Acad. Trans.,' vol. 13, Part II, p. 49, 1880.

† In v. Jolly's calculations the buoyancy of the weights seems to be allowed for in dealing with the water, and neglected in dealing with the gases. If this be so, the result would be affected with a slight error, which, however, far exceeds any that could arise from neglecting buoyancy altogether.

*The Water Contents of the Globe.*

The globe being packed in finely-divided ice, was filled with boiled distilled water up to the level of the top of the channel through the plug of the tap, that is, being itself at 0°, was filled with water also at 0°. Thus charged the globe had now to be weighed; but this was a matter of some difficulty, owing to the very small capacity available above the tap. At about 9° there would be a risk of overflow. Of course the water could be retained by the addition of extra tubing, but this was a complication that it was desired to avoid. In February, 1882, during a frost, an opportunity was found to effect the weighing in a cold cellar at a temperature ranging from 4° to 7°. The weights required (on the same side of the balance as the globe and its supports) amounted to 0·1822 gram. On the other side were other weights whose values did not require to be known so long as they remained unmoved during the whole series of operations. Barometer (corrected) 758·9 mm.; temperature 6·3°.

A few days later the globe was discharged, dried, and replaced in the balance with tap open. 1834·1701 grams had now to be associated with it in order to obtain equilibrium. The difference,

$$1834\cdot170 - 0\cdot182 = 1833\cdot988,$$

represents the weight of the water less that of the air displaced by it. The difference of atmospheric conditions was sufficiently small to allow the neglect of the *variation* in the buoyancy of the glass globe and of the brass counterpoises.

It remains to estimate the actual weight of the air displaced by the water under the above mentioned atmospheric conditions. It appears that, on this account, we are to add 2·314, thus obtaining

$$1836\cdot30$$

as the weight of the water at 0° which fills the globe at 0°.

A further small correction is required to take account of the fact that the usual standard density is that of water at 4° and not at 0°. According to Broch (Everett's 'C.G.S. System of Units'), the factor required is 0·99988, so that we have

$$\frac{1836\cdot30}{0\cdot99988} = 1836\cdot52$$

as the weight of water at 4° which would fill the globe at 0°.

*Air.*

Air drawn from outside (in the country) was passed through a solution of potash. On leaving the regulating tap it traversed tubes



filled with fragments of potash, and a long length of phosphoric anhydride, followed by a filter of glass wool. The arrangements beyond the regulating tap were the same for all the gases experimented upon. At the close of the filling it was necessary to use a condensing syringe in order to force the pressure up to the required point, but the air thus introduced would not reach the globe. It may be well to give the results for air in some detail, so as to enable the reader to form a judgment as to the degree of accuracy attained in the manipulations.

Date.	Globe empty.	Globe full.	Temp. of manometer.	Correction to 15°.	Corrected to 15°.
1892.					
Sept. 24 ....	2·90941				
„ 27 ....	..	0·53327	17·8	-0·00112	0·53219
„ 28 ....	2·90867	..			
„ 29 ....	..	0·53271	15·7	-0·00028	0·53243
Oct. 1 ....	2·90923	..			
„ 3 ....	..	0·53151	12·7	+0·00093	0·53244
„ 4 ....	2·90872				
Tap regreased.					
„ 7 ....	2·91036				
„ 8 ....	..	0·53296	12·4	+0·00105	0·53401
„ 10 ....	2·91056	..			
„ 11 ....	..	0·53251	11·8	+0·00129	0·53380
„ 12 ....	2·91039	..			
„ 13 ....	..	0·53201	11·0	+0·00161	0·53362
„ 14 ....	2·91043	..			
„ 15 ....	..	0·53219	10·6	+0·00177	0·53396

The column headed “globe empty” gives the (corrected) weights, on the side of the working globe, required for balance. The third column gives the corresponding weights when the globe was full of air, having been charged at 0° and up to the pressure required to bring the mercury in the manometer into contact with the two points of the measuring rod.

This pressure was not quite the same on different occasions, being subject to a temperature correction for the density of mercury and for the expansion of the iron rod. The correction is given in the fifth column, and the weights that would have been required, had the temperature been 15°, in the sixth. The numbers in the second and sixth columns should agree, but they are liable to a discontinuity when the tap is regreased.

In deducing the weight of the gas we compare each weighing “full” with the mean of the preceding and following weights

“empty,” except in the case of October 15, when there was no subsequent weighing empty. The results are

September 27	.....	2·37686
„ 29	.....	2·37651
October 3	.....	2·37653
„ 8	.....	2·37646
„ 11	.....	2·37668
„ 13	.....	2·37679
„ 15	.....	2·37647
Mean	.....	<u>2·37661</u>

There is here no evidence of the variation in the density of air suspected by Regnault and v. Jolly. Even if we include the result for September 27th, obviously affected by irregularity in the weights of the globe empty, the extreme difference is only 0·4 milligram, or about 1/6000th part.

To allow for the contraction of the globe (No. 14) when weighed empty, discussed in my former papers, we are to add 0·00056 to the apparent weight, so that the result for air becomes

2·37717.

This is the weight of the contents at 0° and under the pressure defined by the manometer gauge at 15° of the thermometer. The reduction to standard conditions is, for the present, postponed.

#### *Oxygen.*

This gas has been prepared by three distinct methods: (a) from chlorates, (b) from permanganate of potash, (c) by electrolysis.

In the first method mixed chlorates of potash and soda were employed, as recommended by Shenstone, the advantage lying in the readier fusibility. The fused mass was contained in a Florence flask, and during the wash-out was allowed slowly to liberate gas into a vacuum. After all air had been expelled, the regulating tap was closed, and the pressure allowed gradually to rise to that of the atmosphere. The temperature could then be pushed without fear of distorting the glass, and the gas was drawn off through the regulating tap. A very close watch over the temperature was necessary to prevent the evolution of gas from becoming too rapid. In case of excess, the superfluous gas was caused to blow off into the atmosphere, rather than risk imperfect action of the potash and phosphoric anhydride. Two sets of five fillings were effected with this oxygen. In the first set (May, 1892) the highest result was 2·6272, and the

lowest 2·6266, mean 2·62691. In the second set (June, July, 1892) the highest result was 2·6273 and the lowest 2·6267, mean 2·62693.

The second method (*b*) proved very convenient, the evolution of gas being under much better control than in the case of chlorates. The recrystallised salt was heated in a Florence flask, the wash-out, in this case also, being facilitated by a vacuum. Three fillings gave satisfactory results, the highest being 2·6273, the lowest 2·6270, and the mean 2·62714. The gas was quite free from smell.

By the third method I have not as many results as I could have wished, operations having been interrupted by the breakage of the electrolytic generator. This was, however, of less importance, as I had evidence from former work that there is no material difference between the oxygen from chlorates and that obtained by electrolysis. The gas was passed over hot copper, as detailed in previous papers. The result of one filling, with the apparatus as here described, was 2·6271. To this may be added the result of two fillings obtained at an earlier stage of the work, when the head of the manometer was exhausted by an independent Sprengel pump, instead of by the Töppler. The value then obtained was 2·6272. The results stand thus :—

Electrolysis (2), May, 1892 .....	2·6272
"    (1)    "    .....	2·6271
Chlorates (5), May, 1892 .....	2·6269
"    (5), June, 1892 .....	2·6269
Permanganate (3), January, 1893 ..	2·6271
	<hr/>
Mean .....	2·62704
Correction for contraction ..	0·00056
	<hr/>
	2·62760

It will be seen that the agreement between the different methods is very good, the differences, such as they are, having all the appearance of being accidental. Oxygen prepared by electrolysis is perhaps most in danger of being light (from contamination with hydrogen), and that from chlorates of being abnormally heavy.

#### *Nitrogen.*

This gas was prepared, in the usual manner, from air by removal of oxygen with heated copper. Precautions are required, in the first place, to secure a sufficient action of the reduced copper, and, secondly, as was shown by v. Jolly, and later by Leduc, to avoid contamination with hydrogen which may be liberated from the copper. I have followed the plan, recommended by v. Jolly, of causing the gas to pass finally over a length of unreduced copper. The arrangements were as follows :—

Air drawn through solution of potash was deprived of its oxygen by reduced copper, contained in a tube of hard glass heated by a large flame. It then traversed a U-tube, in which was deposited most of the water of combustion. The gas, practically free, as the event proved, from oxygen, was passed, as a further precaution, over a length of copper heated in a combustion furnace, then through strong sulphuric acid,\* and afterwards back through the furnace over a length of oxide of copper. It then passed on to the regulating tap, and thence through the remainder of the apparatus, as already described. In no case did the copper in the furnace, even at the end where the gas entered, show any sign of losing its metallic appearance.

Three results, obtained in August, 1892, were—

August 8 .....	2.31035
„ 10 .....	2.31026
„ 15 .....	2.31024
Mean .....	<u>2.31028</u>

To these may be added the results of two special experiments made to test the removal of hydrogen by the copper oxide. For this purpose a small hydrogen generator, which could be set in action by closing an external contact, was included between the two tubes of reduced copper, the gas being caused to bubble through the electrolytic liquid. The quantity of hydrogen liberated was calculated from the deflection of a galvanometer included in the circuit, and was sufficient, if retained, to alter the density very materially. Care was taken that the small stream of hydrogen should be uniform during the whole time (about  $2\frac{1}{2}$  hours) occupied by the filling, but, as will be seen, the impurity was effectually removed by the copper oxide.† Two experiments gave—

September 17 .....	2.31012
„ 20 .....	2.31027
Mean .....	<u>2.31020</u>

We may take as the number for nitrogen—

	2.31026
Correction for contraction..	56
	<u>2.31082</u>

\* There was no need for this, but the acid was in position for another purpose.

† Much larger quantities of hydrogen, sufficient to reduce the oxide over several centimetres, have been introduced without appreciably altering the weight of the gas.

Although the subject is not yet ripe for discussion, I cannot omit to notice here that nitrogen prepared from ammonia, and expected to be pure, turned out to be decidedly lighter than the above. When the oxygen of air is burned by excess of ammonia, the deficiency is about 1/1000th part.\* When oxygen is substituted for air, so that all (instead of about one-seventh part) of the nitrogen is derived from ammonia, the deficiency of weight may amount to  $\frac{1}{2}$  per cent. It seems certain that the abnormal lightness cannot be explained by contamination with hydrogen, or with ammonia, or with water, and everything suggests that the explanation is to be sought in a dissociated state of the nitrogen itself. Until the questions arising out of these observations are thoroughly cleared up, the above number for nitrogen must be received with a certain reserve. But it has not been thought necessary, on this account, to delay the presentation of the present paper, more especially as the method employed in preparing the nitrogen for which the results are recorded is that used by previous experimenters.

*Reduction to Standard Pressure.*

The pressure to which the numbers so far given relate is that due to 762·511 mm. of mercury at a temperature of 14·85°,† and under the gravity operative in my laboratory in latitude 51° 47'. In order to compare the results with those of other experimenters, it will be convenient to reduce them not only to 760 mm. of mercury pressure at 0°, but also to the value of gravity at Paris. The corrective factor for length is 760/762·511. In order to correct for temperature, we will employ the formula‡  $1 + 0\cdot0001818 t + 0\cdot0000000017 t^2$  for the volume of mercury at  $t^\circ$ . The factor of correction for temperature is thus 1·002700. For gravity we may employ the formula—

$$g = 980\cdot6056 - 2\cdot5028 \cos 2\lambda,$$

$\lambda$  being the latitude. Thus, for my laboratory—

$$g = 981\cdot193,$$

and for Paris—

$$g = 980\cdot939,$$

the difference of elevation being negligible. The factor of correction is thus 0·99974.

The product of the three factors, corrective for length, for temperature, and for gravity, is accordingly 0·99914. Thus multiplied, the numbers are as follows:—

\* 'Nature,' vol. 46, p. 512.

† The thermometer employed with the manometer read 0·15° too high.

‡ Everett, p. 142.

Air.	Oxygen.	Nitrogen.
2·37512	2·62534	2·30883

and these may now be compared with the water contents of the globe, viz., 1836·52.

The densities of the various gases under standard conditions, referred to that of distilled water at 4°, are thus :—

Air.	Oxygen.	Nitrogen.
0·00129327	0·00142952	0·00125718

With regard to hydrogen, we may calculate its density by means of the ratio of densities of oxygen and hydrogen formerly given by me, viz., 15·882. Hence

Hydrogen.  
0·000090009.

The following table shows the results arrived at by various experimenters. Von Jolly did not examine hydrogen. The numbers are multiplied by 1000 so as to exhibit the weights in grams per litre :—

	Air.	Oxygen.	Nitrogen.	Hydrogen.
Regnault, 1847 . . . . .	1·29319	1·42980	1·25617	0·08958
Corrected by Crafts . . . . .	1·29349	1·43011	1·25647	0·08988
Von Jolly, 1880 . . . . .	1·29351	1·42939	1·25787	..
Ditto corrected . . . . .	1·29383	1·42971	1·25819	..
Leduc, 1891* . . . . .	1·29330	1·42910	1·25709	0·08985
Rayleigh, 1893 . . . . .	1·29327	1·42952	1·25718	0·09001

The correction of Regnault by Crafts† represents allowance for the contraction of Regnault's globe when exhausted, but the data were not obtained from the identical globe used by Regnault. In the fourth row I have introduced a similar correction to the results of von Jolly. This is merely an estimate founded upon the probability that the proportional contraction would be about the same as in my own case and in that of M. Leduc.

In taking a mean we may omit the uncorrected numbers, and also that obtained by Regnault for nitrogen, as there is reason to suppose that his gas was contaminated with hydrogen. Thus

Mean Numbers.			
Air.	Oxygen.	Nitrogen.	Hydrogen.
1·29347	1·42961	1·25749	0·08991

\* 'Bulletin des Séances de la Société de Physique.

† 'Comptes Rendus,' vol. 106, p. 1664.

The evaluation of the densities as compared with water is exposed to many sources of error which do not affect the comparison of one gas with another. It may therefore be instructive to exhibit the results of various workers referred to air as unity.

	Oxygen.	Nitrogen.	Hydrogen.
Regnault (corrected) . . . . .	1·10562	0·97138	0·06949
v. Jolly (corrected) . . . . .	1·10502	0·97245	
Leduc . . . . .	1·1050	0·9720	0·06947
Rayleigh . . . . .	1·10535	0·97209	0·06960
Mean . . . . .	1·10525	0·97218	0·06952

As usually happens in such cases, the concordance of the numbers obtained by various experimenters is not so good as might be expected from the work of each taken separately. The most serious discrepancy is in the difficult case of hydrogen. M. Leduc suggests\* that my number is too high on account of penetration of air through the blow-off tube (used to establish equilibrium of pressure with the atmosphere), which he reckons at 1 m. long and 1 cm. in diameter. In reality the length was about double, and the diameter one-half of these estimates; and the explanation is difficult to maintain, in view of the fact, recorded in my paper, that a prolongation of the time of contact from 4<sup>m</sup> to 30<sup>m</sup> had no appreciable ill effect. It must be admitted, however, that there is a certain presumption in favour of a lower number, unless it can be explained as due to an insufficient estimate for the correction for contraction. On account of the doubt as to the appropriate value of this correction, no great weight can be assigned to Regnault's number for hydrogen. If the atomic weight of oxygen be indeed 15·88, and the ratio of densities of oxygen and hydrogen be 15·90, as M. Leduc makes them, we should have to accept a much higher number for the ratio of volumes than that (2·0002) resulting from the very elaborate measurements of Morley. But while I write the information reaches me that Mr. A. Scott's recent work upon the volume ratio leads him to just such a higher ratio, viz., 2·00245, a number *a priori* more probable than 2·0002. Under the circumstances both the volume ratio and the density of hydrogen must be regarded as still uncertain to the 1/1000th part.

\* 'Comptes Rendus,' July, 1892.

## NOTE A.

*On the Establishment of Equilibrium of Pressure in Two Vessels connected by a Constricted Channel.*

It may be worth while to give explicitly the theory of this process, supposing that the difference of pressures is small throughout, and that the capacity of the channel may be neglected. If  $v_1, p_1$  denote the volume and pressure of the gas in the first vessel at time  $t$ ;  $v_2, p_2$  the corresponding quantities for the second vessel, we have

$$\begin{aligned} v_1 \frac{dp_1}{dt} + c(p_1 - p_2) &= 0, \\ v_2 \frac{dp_2}{dt} + c(p_2 - p_1) &= 0, \end{aligned}$$

where  $c$  is a constant which we may regard as the *conductivity* of the channel. In these equations inertia is neglected, only resistances of a viscous nature being regarded, as amply suffices for the practical problem. From the above we may at once deduce

$$\frac{d(p_1 - p_2)}{dt} + \left( \frac{c}{v_1} + \frac{c}{v_2} \right) (p_1 - p_2) = 0;$$

showing that  $(p_1 - p_2)$  varies as  $e^{-qt}$ , where

$$q = \frac{c}{v_1} + \frac{c}{v_2} = \frac{1}{\tau},$$

if  $\tau$  be the time in which the difference of pressures is reduced in the ratio of  $e : 1$ .

Let us now apply this result (*a*) to the case where the globe of volume  $v_1$  communicates with the atmosphere, (*b*) to the case where the globe is connected with a manometer of relatively small volume  $v_2$ . For (*a*) we have—

$$1/\tau = c/v_1,$$

and for (*b*)

$$1/\tau = c/v_2;$$

so that

$$\tau/\tau' = v_1/v_2.$$

For such a manometer as is described in the text, the ratio  $v_1/v_2$  is at least as high as 30; and in this proportion is diminished the time required for the establishment of equilibrium up to any standard of perfection that may be fixed upon.



FIG. 1.

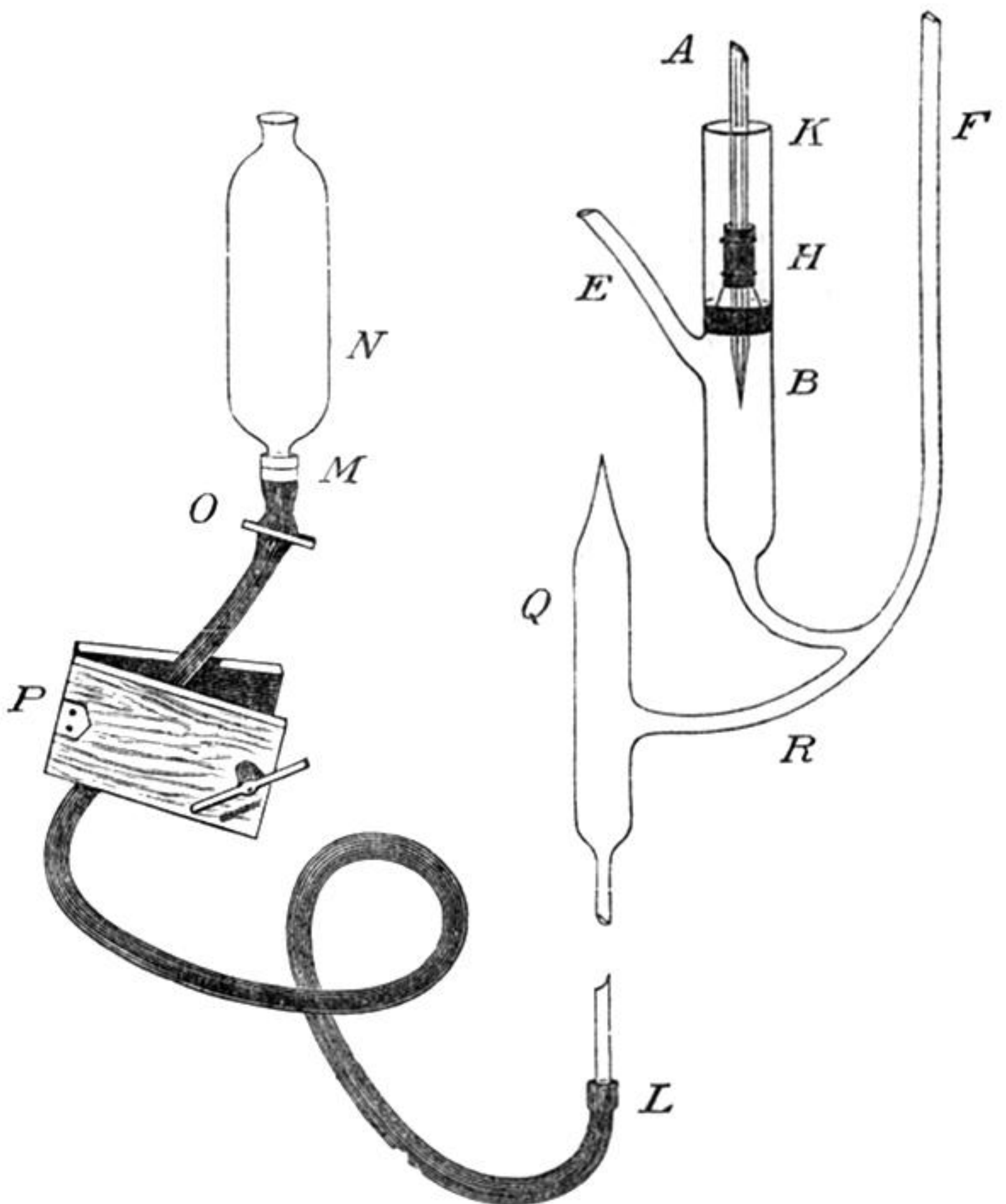
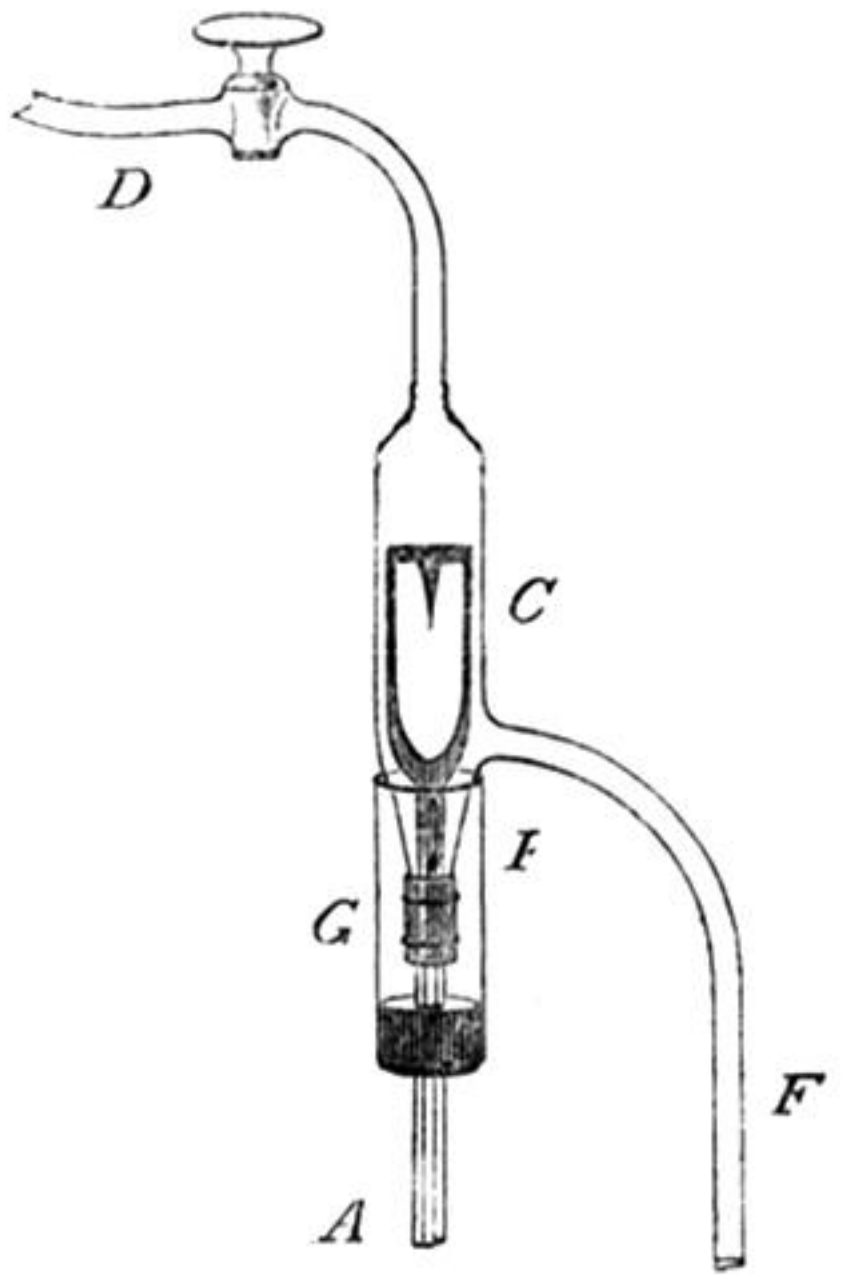


FIG. 2.

