PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A
MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

On a New Manometer, and on the Law of the Pressure of Gases between 1.5 and 0.01 Millimetres of Mercury

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IV. *On a New Manometer, and on the Law of the Pressure of Gases between 1·5 and 0·01 Millimetres of Mercury.*

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Introduction.

THE behaviour of air and other gases at low densities is a subject which presents peculiar difficulties to the experimenter, and highly discrepant results have been arrived at as to the relations between density and pressure. While MENDELEEF and SILJERSTRÖM have announced considerable deviations from BOYLE'S law, AMAGAT* finds that law verified in the case of air to the full degree of accuracy that the observations admit of. In principle AMAGAT'S method is very simple. The reservoir consists mainly of two nearly equal bulbs, situated one above the other and connected by a comparatively narrow passage. By the rise of mercury from a mark below the lower bulb to another on the connecting passage, the volume is altered in a known ratio which is nearly that of 2 : 1. The corresponding pressures are read with a specially constructed differential manometer. Of this the lower part which penetrates the mercury of the cistern is single. Near the top it divides into a U, widening at the level of the surface of the mercury into tubes of 2 centims. diameter. Higher up again these tubes re-unite and by means of a three-way tap can be connected either with an air-pump or with the upper bulb. Suitable taps are provided by which the two branches can be isolated from one another. During the observations one branch is vacuous and the other communicates with the enclosed gas, so that the difference of levels represents the pressure. This difference is measured by a cathetometer.

It is evident that when the pressure is very low the principal difficulty relates to the measurement of this quantity, and that the errors to be feared in respect to volume and temperature are of little importance. AMAGAT, fully alive to this aspect of the matter, took extraordinary pains with the manometer and with the cathetometer by which it was read. An insidious error may enter from the refraction of the walls of the tubes through which the mercury surfaces are seen. But after all his precautions AMAGAT found that he could not count upon anything less than

* 'Ann. de Chimie,' vol. 28, p. 480, 1883.

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$\frac{1}{100}$ millim., even in the means of several readings. It may be well to give his exact words (p. 494) :—" Dans les expériences dont je donnerai plus loin les résultats numériques, les déterminations sont faites en général en alternant cinq fois les lectures sur chaque menisque; les lectures étaient faites au demi-centième, et les divergences dans les séries régulières oscillent ordinairement entre un centième et un centième et demi; en prenant la moyenne, il ne faut pas compter sur plus d'un centième; et cela, bien entendu, sans tenir compte des causes d'erreur indépendantes de la lecture cathétométrique. . . . . . . Les résultats numériques consignés aux Tableaux que je vais donner maintenant sont eux-mêmes la moyenne de plusieurs expériences; car, outre que les lectures ont été faites en général cinq fois en alternant, on est toujours, après avoir réduit le volume à moitié, revenu au volume primitif, puis au volume moitié: chaque expérience a donc été faite aux moins deux fois, et souvent trois et quatre."

The following are the final results for air :—

Pression initiale en millims.	$\frac{pv}{p'v'}$.	Pression initiale en millims.	$\frac{pv}{p'v'}$.
millims.		millims.	
12·297	0·9986	1·898	1·0050
12·260	1·0020	1·852	0·9986
10·727	0·9992	1·751	[1]·0030
7·462	1·0013	1·457	1·0150
7·013	1·0015	1·414	1·0143
6·210	1·0021	1·377	1·0042
6·160	1·0025	1·316	1·0137
4·946	1·0010	1·182	1·0030
4·275	1·0048	1·140	1·0075
3·841	1·0027	1·100	0·9999
3·770	1·0019	0·978	1·0160
3·665	0·9999	0·958	1·0100
3·165	1·0015	0·860	1·0045
2·531	1·0013	0·295	0·9680
2·180	1·0015		

Since, as it would appear, the "initial" pressure is the smaller of a pair, the lowest pressure concerned is about ·3 millim. of mercury, and the error at this stage is about 3 per cent. It is not quite clear which is which of pv and $p'v'$. For while it is expressly stated that p is smaller than p', the nature of v'/v is given at 2·076. I think that this is really the value of v/v'. But any lingering doubt that may be felt upon this point is of no consequence here, inasmuch as AMAGAT's comment upon the tabular numbers is " On ne saurait donc se prononcer, ni sur les sens ni même sur l'existence de ces écarts."

After such elaborate treatment by the greatest authority in these matters, the question would probably have long remained where AMAGAT left it, had not C. BOHR found reason to suspect the behaviour of *oxygen* at low pressures. This led to a prolonged and apparently very careful investigation, of which the conclusion was that at a pressure of ·7 millim. of mercury the law connecting pressure and volume is subject to a *discontinuity*.

"1. Bei einer Temperatur zwischen 11° und 14° C. weicht der Sauerstoff innerhalb der beobachteten Druckgrenzen von der BOYLE-MARIOTTE'schen Gezetze ab. Die Abhängigkeit zwischen Volumen und Druck für einen Werth des letztgenannten, grösser als 0·70 mm., kann man annähernd durch die Formel

$$(p + 0{\cdot}109)\, v = k$$

ausdrücken, während die Formel für Werthe der Drucke, welche kleiner als 0·70 mm. sind:

$$(p + 0{\cdot}070)\, v = k$$

ist.

2. Sinkt der Druck unterhalb 0·70 mm., so erleidet der Sauerstoff eine Zustandsveränderung; er kann wieder durch ein Erhöhen des Druckes bis über 0·70 mm die ursprüngliche Zustandsform übergeführt werden."*

Fig. (1) is a reproduction of one of BOHR's curves, in which the ordinate represents pv and the abscissa represents p on such a scale that 1 millim. of mercury

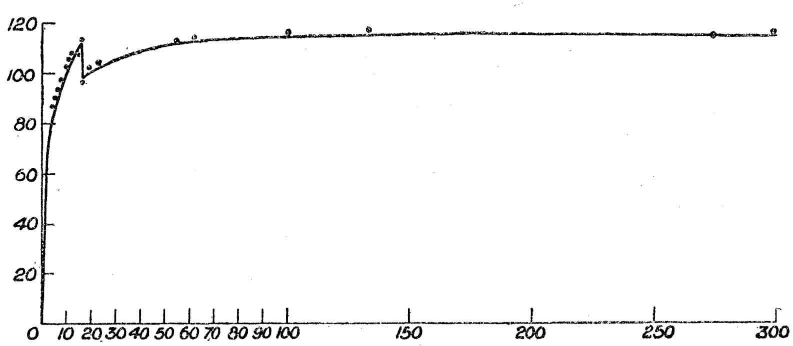

Fig. 1.

corresponds to the number 20. It will be seen that at the place of discontinuity a change of pv to no less than $\frac{1}{10}$ of its amount occurs with no perceptible concomitant change in the value of p. In the neighbourhood of the discontinuity the pressure is uncertain. Thus (p. 475) "Wenn man bei einer gewissen Sauerstoffmenge im Rohre α das Quecksilber erst in der Art einstellt, dass der Druck einen etwas geringeren Werth als 0·70 millim. hat, und dann durch Verringern des Volumens den Druck über 0·70 millim. steigert (z.B. bis 0·8 millim.), so zeigt sich, dass dieser Druck nicht constant bleibt, sondern im Verlaufe von 3—5 Stunden bis zu einem Werthe sinkt, der ungefähr 10 Proc. kleiner ist, als der ursprüngliche."

* 'Wied. Ann.,' vol. 27, p. 479, 1886.

So far as I am aware, no attempt to repeat BOHR's difficult and remarkable experiments has been recorded, but some confirmation of anomalous behaviour of oxygen in this region of pressure is afforded by the observations of RAMSAY and BALY.* SUTHERLAND† interprets the results as a "Spontaneous Change of Oxygen into Ozone and a Remarkable Type of Dissociation," and connects therewith some observations of CROOKES relating to radiometer effects in oxygen gas. On the other hand, chemical tests applied by Professor THRELFALL and Miss MARTIN‡ failed to indicate the presence of ozone in suitably expanded oxygen.

Improved Apparatus for Measuring very small Pressures.

In spite of the interest attaching to the anomaly encountered by BOHR, I should hardly have ventured to attack the question experimentally myself, had I not seen my way to what promised to be an improved method of dealing with very small pressures. In operations connected with the weighing of gases, extending over a series of years, I have had much experience of a specially constructed manometric gauge in which an iron rod provided above and below with suitable points is actually applied to the two mercury surfaces arranged so as to be situated in the same vertical line.§ Although *two* variable quantities had to be adjusted—the pressure of the gas *and* the supply of mercury—no serious difficulty was encountered; and the delicacy obtained in the observation of the approximation of a point and its image in the mercury surface with the assistance of an eye-lens of 25 millims. focus was very satisfactory. In order to get actual measures of the delicacy, a hollow glass apparatus in the form of a fork was mounted upon a levelling table. The stalk below was terminated with a short length of rubber tubing compressible by a screw. This allowed the supply of mercury to be adjusted. The mercury surfaces in the U were about 20 millims. in diameter, and were exposed to the air. They were to be adjusted to coincidence with needle points, rigidly connected to the glass-work, by suitable use of the compressor and of the screw of the levelling table. Readings of the latter in successive and independent settings showed that a degree of accuracy was attainable much superior to the limit fixed by AMAGAT for the best work with the cathetometer. It is unnecessary to record the numbers obtained at this stage of the work, inasmuch as the final results to be given below prove that the errors of setting are considerably less than $\frac{1}{1000}$ millim.

It will now be possible to form a preliminary idea of the proposed manometer. The readings of the levelling screw, obtained as above, may be regarded as corre-

* 'Phil. Mag.,' vol. 38, p. 301, 1894.

† 'Phil. Mag.,' vol. 43, p. 201, 1897.

‡ 'Proc. Roy. Soc. of New South Wales,' 1897.

§ "On the Densities of the Principal Gases," 'Proc. Roy. Soc.,' vol 53, p. 134, 1893.

sponding to the zero of pressure, or rather of pressure difference. If the pressures operative upon the mercury surfaces be slightly different, the setting is disturbed; and the change of reading at the screw required to re-establish the adjustment represents the difference of pressures. In order to interpret the result absolutely it is only necessary to know further the pitch of the levelling screw, the leverage with which it acts, and the distance between the points to which the mercury surfaces are set. If the space over one mercury surface be vacuous, the change of reading at the levelling screw represents the absolute pressure in the space over the other mercury surface.

The difficulty, which will at once present itself to the mind of the reader, in the use of a manometer on this plan, is the necessity for a flexible connection between the instrument and the rest of the apparatus, such as the air-pump and the vessel in which the pressure is required to be known. With the aid of short lengths of rubber tubing this requirement could be easily met, but the class of work for which such a manometer is wanted would usually preclude the use of rubber. In my apparatus the requisite flexibility is obtained by the insertion of considerable lengths (3 metres) of glass tubing between the manometer and the parts which cannot turn with it. Although the adjustment was made by the screw of a levelling table as described, the actual readings were taken by the mirror method, the supports of the mirror being connected as directly as possible with the points whose angular motion is to be registered. In this way we become independent of the rigidity of the glass-work, and are permitted to use wood freely in the levelling table and in its supports. It frequently happened that an adjustment left correct was found to be out after an interval. The screw had not been moved, but the mirror-reading was altered. On resetting by use of the screw, the original mirror-reading was recovered within the limits of error.

The essential parts of the manometer, as finally employed, are shown (fig. 2) in elevation and plan, and the general scheme of the mounting is indicated in fig. 3. At A is the stalk of the glass fork, of such length that the mercury in the hose below is always at a pressure above atmosphere; B, B are bulbs of about 25 millims. diameter, at

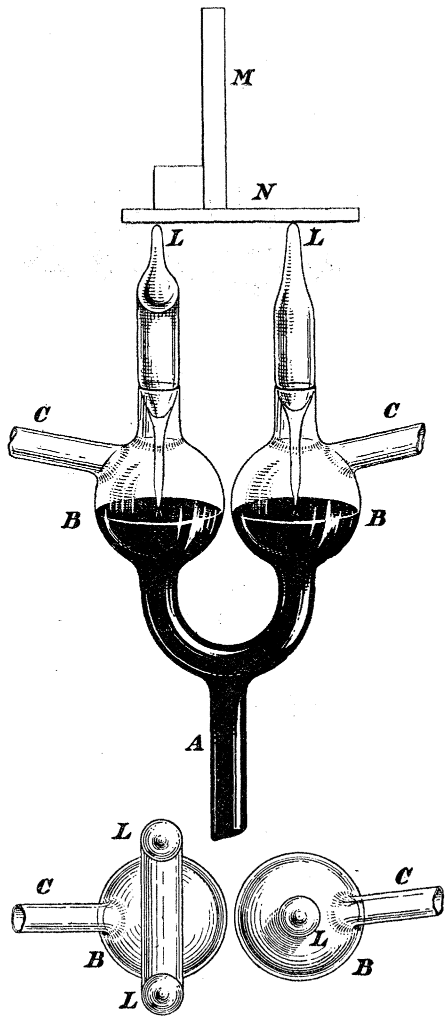

Fig. 2.

the centres of which are situated the *points*. These are of glass,* which need not be opaque; and they must be carefully finished upon a stone. A considerable degree of sharpness is desirable, but *similarity* is more important than the extreme of sharpness. In the actual apparatus complete similarity was not attained, and

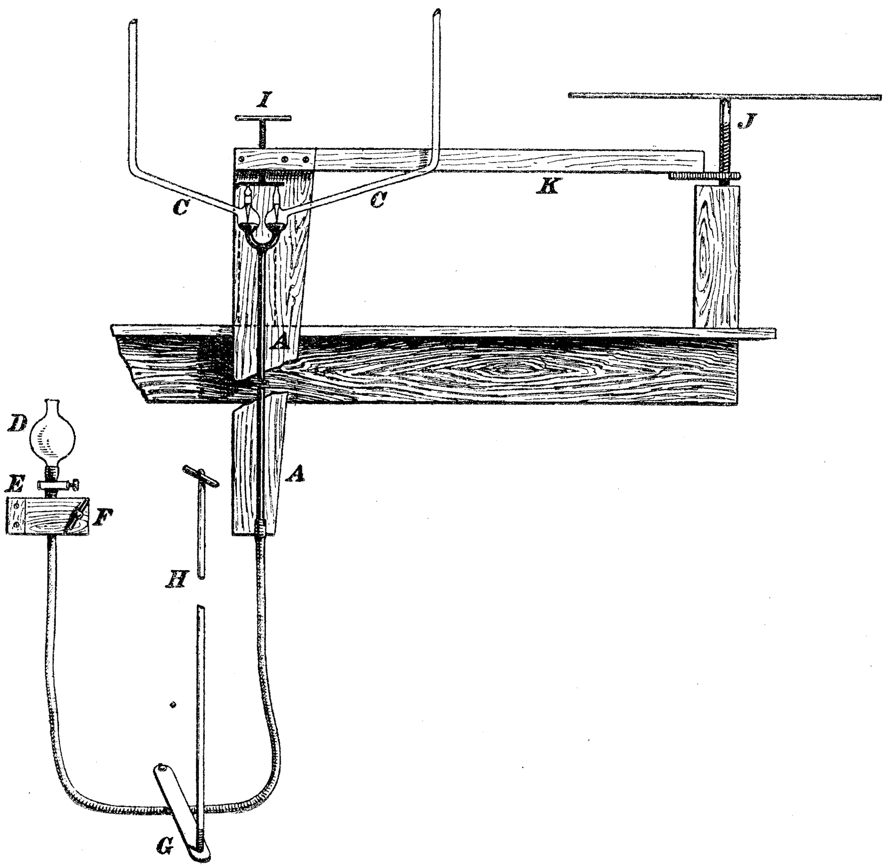

Fig. 3.

in the first trials the difference was rather embarrassing. However, after a little practice the eye becomes educated to set the mercury to each point in a constant manner, and this is all that is really required. The same consideration shows that minute outstanding capillary differences should not lead to error. It may be remarked that the mercury is always on the rise at the time of adjustment, and in fact it was found best to make it a rule not to allow the points to be drowned at any time when it could be avoided. After such a drowning it was usually (perhaps always) found that the mercury surface was disturbed by the *proximity* of the points without actual contact, an effect attributed to electrification.

The presentation of the point to the mercury, or rather of the point to its image as seen by reflection in the mercury, was examined with the aid of two similar eye-lenses (not shown) of 22 millims. focus. The illumination, from a small gas flame

* At first iron needle points were tried.

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suitably reflected by mirrors, was from behind, and it and the lenses were so arranged that both points could be seen without a motion of the head. Precautions were required to prevent the radiation from the gas flame and from the observer from producing disturbance, especially by unequal heating of the two limbs of the U. The U itself was well bandaged up, and between it and the observer were interposed sheets of copper and of insulating material so as to ensure that at all events there should be no want of symmetry in any heating that might take place.

The adjustment itself is a *double* one, requiring both the use of the levelling screw J and an accurate feed of mercury. The hose terminates as usual in a small mercury reservoir D. This facilitates the preliminary arrangements, but in use the reservoir is cut off by a screw clamp E just below it. The rough adjustment of the supply of mercury is effected by a large wooden compressor F. The fine adjustment required for the actual setting is a more delicate matter. The first attempts were by fine screw compressors acting upon the pendent part of the hose, but the tremors thence arising were found very disturbing. A remedy was eventually applied by operating upon the part of the hose which lies flat upon the floor or rather on the bottom of a mercury tray. The compressor is shown at G, fig. 3; the screw being provided with a long handle H to bring it within convenient reach. The advantage accruing from this small device would scarcely be credited.

The glass-work is attached by cement to a board, which hangs downwards in face of the observer and is itself fixed rigidly to the levelling stand K. This is supported at two points I, which define the axis of rotation, and by a finely adjustable screw J, within reach of the observer. The whole stands in a very steady position upon the floor of an underground cellar in my country house.

The arrangements for the connection of the mirror must now be described. The glass stems, whose lower extremities form the "points," are prolonged upwards by substantial tubing, and terminate above in three slightly rounded ends, L, L, suitable for the support of the mirror platform N. The two supports necessary on the left are obtained by a symmetrical branching of the tube on that side. The platform is of worked glass, so that a slight displacement of the contacts has no effect on the slope of the mirror. The latter is of worked glass silvered in front. Suitable stops are provided to guide the mirror platform into the right position and to prevent accidents, but these exercise no constraint.

The axis I I about which the apparatus rotates is horizontal and parallel to the face of the mirror, so that the sine of the angle θ of rotation from the zero position represents the difference of levels of the mercury surfaces. The axis I I lies approximately in the mirror surface and at about the middle of the height of the operative part. The rotation of the mirror is observed in the usual way by means of a telescope and vertical millimetre scale. The aperture of the object-glass is 30 millims., and the distance from the mirror 3150 millims. The readings can be taken to about ·1 millim.

In many kinds of observation the zero can only be verified at intervals, as it requires the pressures over the mercury to be equalised. On the whole the zero was tolerably constant to within two or three-tenths of a millimetre of the scale. A delicate level was attached to the telescope to give warning of any displacement of the stand (all of metal) or of the ground.

The differences of pressure to be evaluated are not quite in simple proportion to the scale reading from zero. The latter varies as tan 2θ, while the former varies as sin θ. The correcting factor is therefore

$$\frac{\sin\theta}{\frac{1}{2}\tan 2\theta} = 1 - \tfrac{3}{2}\theta^2 \quad \text{approximately.}$$

If the zero reading (in millimetres) be a, and the current reading x, D the distance between telescope and mirror,

$$\theta = \frac{x - a}{2\mathrm{D}} \quad \text{approximately;}$$

so that the correcting factor is

$$1 - \tfrac{3}{2}\frac{(x-a)^2}{4\mathrm{D}^2}.$$

The actual correction to be applied to $(x - a)$ is thus

$$-\tfrac{3}{2}\frac{(x-a)^3}{4\mathrm{D}^2}.$$

In practice $(x - a)$ rarely exceeded 350, for which the correction would be $-1 \cdot 6$. When $(x - a)$ falls below 120, the correction is insensible.

The next question is the reduction to absolute measure. What (corrected) scale-reading corresponds to 1 millim. actual difference of mercury levels? The distance between the points is 27·3 millims., so that 1 millim. mercury corresponds to 231 millims. of the telescope scale. The highest pressure that could be dealt with is about $1\frac{1}{2}$ millims. of mercury.

The above reckoning proceeds upon the supposition that the distance between the points can be regarded as invariable. Certain small discrepancies manifested at the higher slopes of the apparatus induced me to examine the question more particularly, for it seemed not impossible that owing to the bending of the glass-work some displacement might occur. But a rather troublesome measurement of the actual distance in various positions by means of microscopes negatived this idea. I would however recommend that this point be kept specially in view in the design of any subsequent apparatus of this kind.

Experiments to determine the Relation of Pressure and Volume at given Temperature.

In order to test BOYLE's law one of the lateral branches C is connected to the air-pump and the other to the chamber in which the gas is contained. The pump is of the Toepler form, and is provided with a bulb containing phosphoric anhydride. No tap or contracted passage intervenes between the pump-head and B. A lateral channel communicates with a three-way tap, by which this side of the apparatus can be connected with the gas-generating vessel. The third way leads to a blow-off under mercury more than a barometer-height below.

The two sides of the apparatus are connected by a cross-tube which can be closed or opened by means of a tap. The plug of this tap is provided with a wide bore. When it is intended to read the zero, the tap is open. If desired, the mercury may be raised in the Toepler so as to prevent the penetration of gas into the pump-head. When pressures are to be observed, the tap of the cross-tube is closed, and a good vacuum is made on the pump side. No particular difficulty was experienced with the vacuum. In the use of the Toepler the mercury was allowed to flow out below, and was transferred at intervals to the movable reservoir. The latter was protected from atmospheric moisture by a chloride of calcium tube. When, after standing five or ten minutes, the mercury was put over, and, on impact, gave a hard metallic sound with inclusion of no more than a small speck of gas, the vacuum was nearly sufficient, and no further change could be detected at the manometer. The capacity of the pump-head was two or three times that of the remaining space to be exhausted.

In the earlier experiments the gas-containing tube, placed vertically, was graduated to 50 cub. centims. at intervals of 10 cub. centims. Prolonged below by more than a barometer-height of smaller tubing, it terminated in a hose and mercury reservoir, the latter protected by chloride of calcium. In order to get rid of most of the adherent moisture and carbonic anhydride, the tubes on both sides of the apparatus were heated pretty strongly in a vacuous condition. The first trial was with oxygen in the hope of at once obtaining a confirmation of BOHR's anomaly; but not succeeding in this, I fell back upon nitrogen and hydrogen. With a vacuum on the pump side, readings of pressure were taken with the mercury in the chamber at 0 and at 50 cub. centims., and the ratio of pressures (about 2 : 1) was deduced. When this had been repeated, some of the gas was allowed to escape by opening the cross-tap, the zero was again observed, and the vacuum re-established on the pump side. Another ratio of pressures could now be obtained, corresponding to the same (unknown) volumes as before, but to a different total pressure.

In utilising the ratios of pressure thus obtained, it was of course necessary to consider how far the temperature could be assumed to be unchanged within each pair of pressures brought into comparison. The general temperature of the cellar was extremely uniform, and no difference could be read upon a thermometer worth taking into account. Passing over this question for the present, we may consider how far the results conformed to BOYLE'S law. The agreement of the ratios, except, perhaps, at the highest pressures of about $1\frac{1}{2}$ millims. of mercury, was sufficiently good, and of itself goes a long way to confirm BOYLE'S law. In strictness, all that the constancy of the ratio can prove is that the relation between pressure (p) and density (ρ) is of the form

$$p = \kappa\rho^{n} \qquad (1),$$

where n is some numerical quantity. To limit n to the value unity, the constancy of the ratios might be followed up into the region of pressure for which BOYLE'S law is known to hold, but this can scarcely be said to have been done here. Otherwise, we need to know what the ratio of densities in the two positions of the mercury really is, and not merely that it remains constant.

In the case of the original volume chamber the first was the method employed. The smaller volume, defined by the upper mark in the volume tube and by the "point" in the manometer, was fitted with dry air at a known atmospheric pressure. The included air was then isolated and expanded until it occupied the larger (approximately double) volume, and the new pressure determined by observation of the difference of levels in the tube and in a mercury reservoir similarly fashioned. The operation was rather a difficult one, and the result was only barely accurate enough. The ratio of volumes thus determined by use of BOYLE'S law, as applied to air at atmospheric and half atmospheric pressures, agreed sufficiently well with the ratio of pressures found by the manometer for rare hydrogen and nitrogen; and thus BOYLE'S law may be considered to be extended to these rare gases. The rarefaction was carried down to a total pressure of only ·02 millim. At this stage discrepancies of the order of 5 per cent. are to be expected.

Having obtained fairly satisfactory results with hydrogen and nitrogen, I returned to oxygen, fully expecting to verify the anomalous behaviour described by BOHR. In this I have totally failed. The gas was prepared by heating permanganate of potash, dried by phosphoric anhydride, and may be regarded as fairly pure. The region of pressure round ·7 millim. was carefully examined, use being made of the intermediate divisions of the 50 cub. centims. range of volume. No unsteadiness of the kind indicated by BOHR, or appreciable departure from BOYLE'S law, was detected. And when the pressures were diminished down to a few hundredths of a millimetre, there was no falling off in the product of pressure and volume. The observations were repeated a second time with a fresh supply of oxygen.

The experience gained up to this date (August, 1900) showed that the manometer worked well, and that there was no difficulty about the vacuum, but I was not altogether satisfied with the way in which the volumes had been determined. There was some want of elegance, to say the least, in using BOYLE'S law for this purpose, and barely adequate accuracy in the application itself. The latter objection might have been overcome by the use of a suitable cathetometer, but such was not to hand. The most direct method by actually gauging with mercury the spaces concerned being scarcely feasible, I devised another method which has the advantage of easy execution and is practically independent of the assumption of BOYLE's law. The opportunity was taken to increase the range over which the volume could be varied.

The new chamber, composed mainly of tubing of 18 millims. diameter, is graduated at intervals of 10 cub. centims. over a total range of 200 cub. centims. It is prolonged above and below by narrow tubing in order to connect it with the sloping manometer bulb and with the hose and mercury reservoir as before. The zero mark is situated on the upper tube a few centimetres above its junction with the wider one. It is scarcely necessary to say that no rubber was employed except for the hoses, and that these were always occupied by mercury under a pressure above atmosphere. The mercury reservoirs themselves were protected against damp by chloride of calcium.

If we call the ungauged volume (from the zero mark to the bulb of the sloping manometer with "point" set) V, and the gauged volume v, the total volume occupied by the gas is $V + v$; and the problem is how to determine V. If we may assume the correctness of BOYLE's law for rare gases and may rely upon the sloping manometer, the process is simple enough. We have only to find the pressures exerted by the included gas at volumes V and $V + v$, whence by BOYLE's law the ratio of these volumes is known and thus V determined in terms of v. In order to avoid the use of BOYLE's law, further observations are necessary.

The requisite data can be obtained by changing the quantity of gas. Suppose that with the original quantity of gas certain pressures, P, P′, correspond to total volumes, $V + v_1$, $V + v_2$, and that with a reduced amount of gas the *same* pressures are recorded with volumes $V + v_3$, $V + v_4$. Since the pressure is a function of the density, whether BOYLE's law be applicable or not, it must follow that

$$\frac{V + v_1}{V + v_2} = \frac{V + v_3}{V + v_4} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2),$$

whence V is determined in terms of the known volumes v_1, v_2, v_3, v_4. It may be remarked that this argument does not assume even the correctness of the scale of pressures.

In carrying out the method practically it was necessary to work to the fixed marks of the volume chamber, and thus the same pressures could not be recovered *exactly*. But the use of BOYLE's law in order to make what is equivalent to small corrections is unobjectionable.

With this explanation it may suffice to give the details of an actual determination executed with nitrogen. With the original quantity of gas, volumes $V + 70$, $V + 170$ gave pressures proportional to 345·4, 184·9. Sufficient gas was now removed to allow the remainder to give nearly the same higher pressure as before with $v = 0$. Thus, corresponding to volumes V + 0, V + 40 the pressures were 344·9, 183·3 We have now only to calculate V from the equation

$$\frac{V + 40}{V} = \frac{344 \cdot 9}{183 \cdot 3} \frac{184 \cdot 9}{345 \cdot 4} \frac{V + 170}{V + 70},$$

or

$$V^2 + 110\,V + 2800 = 1 \cdot 0072\,(V^2 + 170\,V);$$

whence

$$V = 45 \cdot 5 \text{ cub. centims.}$$

The adopted value, derived from observations upon nitrogen and hydrogen, is

$$V = 45 \cdot 6 \text{ cub. centims.}$$

In charging the apparatus, the first step is to make a good vacuum throughout, the cross-tap being open. The gas supply being started, the first portions are allowed to blow off from under mercury, and then, by use of the three-way tap, a sufficiency is introduced into the apparatus to an absolute pressure of, perhaps, 10 centims. of mercury. The gas-leading tube would then be sealed off. Ultimately the remainder of the supply tube and the blow-off tube were exhausted to diminish the risk of leakage.

The "nitrogen" was prepared from air by passage over red-hot copper and desiccation with phosphoric anhydride. Accordingly it contained argon to the amount of about 1 per cent.

In taking a set of observations the procedure would be as follows. Assurance having been obtained that the vacuum was good, the next step would be to set the mercury in the volume chamber so that $v = 190$ cub. centims., then after a few minutes to adjust the sloping manometer and to read the telescope scale. It was of course necessary to ensure that sufficient time was allowed for uniformity of pressure to establish itself, and observations were frequently renewed after a quarter of an hour or longer. In the case of oxygen, to be considered later, several hours were sometimes allowed. If operations were leisurely conducted, with first a rough setting of the volume and then a rough setting of the manometer followed by accurate settings in the same order, little or no change could afterwards be detected. Indeed I was rather surprised to find how rapidly equilibrium seemed to be established. The next smaller volume, *e.g.*, $v = 150$, would then be observed, and so on until $v = 40$. In observations to be used for the examination of BOYLE's law v was not further reduced, as too much stress might thereby be thrown upon the accuracy of V. The same observations were then repeated in reverse order and the mean taken. The numbers recorded are thus the mean of two settings only of the manometer.

The next step was to allow about half the gas to escape. The mercury at the pump was allowed to rise so as to cut off the pump-head and $V + v$ was so adjusted as to be equal to the volume remaining upon the other side, about 130 cub. centims. The cross-tap was then opened, and after a sufficient interval of time the zero, corresponding to no pressure, was read. In the course of the observations upon nitrogen, extending over ten days, the zero varied from 43·5 to 43·8. Whenever possible the zero used for a set was the mean of values found before and after.

The annexed tables give the results for nitrogen in detail. In Table I., dealing with the highest quantity of gas, the first column gives the volume (V = 45·6 cub. centims.); the second represents the pressure, being the mean of the two actually read numbers (expressing millimetres of telescope scale) less the zero reading 43·7 and corrected to infinitely small arcs as already explained. The third column is the logarithm of the product of the first two, and should be constant if BOYLE's law holds. The fourth column gives the approximate value of the pressure in millimetres of mercury; the fifth the deviation of pv from the mean taken as unity. In the sixth column is shown the amount by which the observed value of p exceeds that requisite in order to make pv constant, expressed in millimetres of mercury.

TABLE I.—Nitrogen.

November 9–11, Zero = 43·7.

Volume in cub. centims.	Pressure in scale divisions.	Log. product.	Pressure in millims. Hg.	Deviation of pv.	Error of p in millims.
V + 70	345·4	·6013	1·49	+ ·0002	+ ·0003
V + 80	318·3	·6018	1·38	+ ·0014	+ ·0019
V + 90	294·1	·6007	1·27	– ·0012	– ·0015
V + 110	256·8	·6016	1·11	+ ·0009	+ ·0010
V + 130	227·4	·6013	·98	+ ·0002	+ ·0002
V + 150	203·7	·6004	·88	– ·0018	– ·0016
V + 170	184·9	·6005	·80	– ·0014	– ·0011
V + 190	169·8	·6021	·73	+ ·0021	+ ·0015
		·6012			

TABLE II.—Nitrogen.

November 11–12, Zero = 43·7.

Volume in cub. centims.	Pressure in scale divisions.	Log. product.	Pressure in millims. Hg.	Deviation of pv.	Error of p in millims.
V + 0	344·9	·1966	1·49	+ ·0007	+ ·0010
V + 10	282·3	·1958	1·22	– ·0012	– ·0015
V + 20	239·5	·1962	1·04	– ·0002	– ·0002
V + 40	183·3	·1956	·79	– ·0016	– ·0013
V + 60	148·8	·1963	·64	·0000	·0000
V + 80	125·2	·1966	·54	+ ·0007	+ ·0004
V + 110	101·1	·1968	·44	+ ·0012	+ ·0005
V + 150	80·2	·1955	·35	– ·0018	– ·0006
V + 190	66·9	·1976	·29	+ ·0030	+ ·0009
		·1963			

TABLE III.—Nitrogen.

November 13, Zero = 43·6.

Volume in cub. centims.	Pressure in scale divisions.	Log. product.	Pressure in millims. Hg.	Deviation of pv.	Error of p in millims.
V + 40	91·1	·892	·394	·000	·0000
V + 60	73·9	·892	·320	·000	·0000
V + 80	62·3	·893	·269	+ ·002	+ ·0005
V + 110	50·2	·893	·217	+ ·002	+ ·0004
V + 150	39·6	·889	·171	− ·007	− ·0012
V + 190	33·1	·892	·143	·000	·0000
		·892			

TABLE IV.—Nitrogen.

November 14, Zero = 43·5.

Volume in cub. centims.	Pressure in scale divisions.	Log. product.	Pressure in millims. Hg.	Deviation of pv.	Error of p in millims.
V + 40	46·0	·595	·199	+ ·005	+ ·0010
V + 60	37·1	·593	·160	·000	·0000
V + 80	31·1	·592	·135	− ·002	− ·0003
V + 110	25·1	·592	·109	− ·002	− ·0002
V + 150	20·1	·595	·087	+ ·005	+ ·0004
V + 190	16·5	·590	·071	− ·007	− ·0005
		·593			

TABLE V.—Nitrogen.

November 16, Zero = 43·5.

Volume in cub. centims.	Pressure in scale divisions.	Log. product.	Pressure in millims. Hg.	Deviation of pv.	Error of p in millims.
V + 40	22·8	·290	·099	·000	·0000
V + 60	18·6	·293	·081	+ ·007	+ ·0006
V + 80	15·6	·292	·067	+ ·005	+ ·0003
V + 110	12·7	·296	·055	+ ·014	+ ·0008
V + 150	9·9	·287	·043	− ·007	− ·0003
V + 190	8·15	·283	·035	− ·016	− ·0006
		·290			

TABLE VI.—Nitrogen.

November 17–18, Zero = 43·7.

Volume in cub. centims.	Pressure in scale divisions.	Log. product.	Pressure in millims. Hg.	Deviation of pv.	Error of p in millims.
V + 40	11·40	·989	·049	+ ·005	+ ·0002
V + 60	9·10	·983	·039	– ·009	– ·0004
V + 80	7·65	·983	·033	– ·009	– ·0003
V + 110	6·25	·988	·027	+ ·002	+ ·0001
V + 150	5·10	·999	·022	+ ·028	+ ·0006
V + 190	4·05	·980	·017	– ·016	– ·0003
		·987			

TABLE VII.—Nitrogen.

November 18–19, Zero = 43·8.

Volume in cub. centims.	Pressure in scale divisions.	Log. product.	Pressure in millims. Hg.	Deviation of pv.	Error of p in millims.
V + 40	5·90	·703	·026	+ ·014	+ ·0004
V + 60	4·60	·686	·020	– ·026	– ·0005
V + 80	4·15	·717	·018	+ ·047	+ ·0008
V + 110	3·10	·683	·013	– ·033	– ·0004
V + 150	2·55	·698	·011	+ ·002	·0000
		·697			

In the second set the quantity of gas had been adjusted to give a suitable pressure with $v = 0$. It is from it and from Table I. that the data were obtained for the calculation of V already given.

These tables give a fairly complete account of the behaviour of nitrogen from a pressure of about 1·5 millims. down to ·01 millim. of mercury. In each set the range of pressure is nearly in the ratio of 3 : 1, and overlaps the range of the preceding and following sets. An examination of the fifth column shows no indication of departure from BOYLE'S law. The sixth column allows a judgment to be formed of the degree of accuracy to which the law is verified. It gives the amount by which p exceeds the value necessary in order that pv should be absolutely constant, expressed in millimetres of mercury. The errors thus exhibited include not only those arising in the setting of the manometer and the reading of the telescope, but also those entailed in the measurements of volume, and in consequence of fluctuations of temperature. The latter source of error is of course more important at the higher pressures. It will be seen that the accuracy attained is very remarkable. Even at the higher pressures the mean error is only about ·001 millim., while at the lower pressures of Tables III.—VII. the mean error is less than ·0004 millim. And it must be remembered that the numbers to which these errors relate are the means of *two* observations only.

As a means of dealing with very small pressures, the sloping manometer has proved itself in a high degree satisfactory, the performance being some twenty-five times better than AMAGAT's standard. It could hardly have been expected that the mean error would prove to be less than one wave-length of yellow light.* Considered as a pressure, the mean error corresponds to the change of barometric pressure accompanying an elevation of 4 millims.

On hydrogen more than one series of observations have been carried out. The specimen that will be given is not in some respects the most satisfactory, but it is chosen as having been pursued to the greatest rarefactions. The gas was dried carefully with phosphoric anhydride and was introduced into the apparatus as already described. It is thought sufficient to record only numbers corresponding to the three last columns of Tables I.—VII., the first column giving the pressure in millims. of mercury, the second the deviation of pv from the mean value of the set taken as unity, the third the error in p from what would be required to make pv absolutely constant.

* I had at one time contemplated an apparatus from which a further ten-fold increase in accuracy might be expected. Two beams of light, reflected nearly perpendicularly from the mercury surfaces, would be brought to interference by an arrangement similar to that used in investigating the refractivity of gases ('Proc. Roy. Soc.,' vol. 59, p. 200, 1896; vol. 64, p. 97, 1898). Preliminary trials proved that the method is feasible; but the delicacy is excessive in view of the fact that according to HERTZ the pressure of mercury vapour at common temperatures itself amounts to ·001 millim.

TABLE VIII.—Hydrogen. October–November, 1900.

Pressure in millims. Hg.	Deviation of pv.	Error of p in millims.	Pressure in millims Hg.	Deviation of pv.	Error of p in millims.
1·43	+ ·0025	+ ·0036	1·44	+ ·0018	+ ·0026
1·31	+ ·0030	+ ·0039	1·18	− ·0005	− ·0006
1·20	+ ·0002	+ ·0002	1·00	+ ·0009	+ ·0009
1·11	− ·0012	− ·0013	·87	+ ·0007	+ ·0006
·97	− ·0005	− ·0005	·77	+ ·0005	+ ·0004
·86	− ·0002	− ·0002	·62	·0000	·0000
·77	− ·0016	− ·0012	·57	− ·0028	− ·0016
·70	− ·0025	− ·0017	·52	− ·0009	− ·0005
·64	+ ·0007	+ ·0004	·48	− ·0018	− ·0009
—	—	—	·42	+ ·0018	+ ·0008
·769	+ ·0021	+ ·0016	·386	·0000	·0000
·624	+ ·0028	+ ·0017	·315	+ ·0044	+ ·0014
·524	·0000	·0000	·264	+ ·0023	+ ·0006
·423	+ ·0002	+ ·0001	·213	+ ·0014	+ ·0003
·335	− ·0037	− ·0012	·168	− ·0072	− ·0012
·279	− ·0018	− ·0005	·140	− ·0014	− ·0002
·196	+ ·0079	+ ·0015	·098	− ·009	− ·0009
·158	+ ·0046	+ ·0007	·080	·000	·0000
·133	+ ·0053	+ ·0007	·068	+ ·005	+ ·0003
·106	− ·0053	− ·0006	·055	+ ·007	+ ·0004
·085	− ·0037	− ·0003	·044	+ ·007	+ ·0003
·070	− ·0083	− ·0006	·036	− ·005	− ·0002
·051	+ ·007	+ ·0004	·027	− ·047	− ·0013
·041	+ ·002	+ ·0001	·023	+ ·016	+ ·0004
·034	− ·009	− ·0003	·018	− ·054	− ·0010
·027	− ·023	− ·0006	·016	+ ·021	+ ·0003
·023	+ ·036	+ ·0009	·013	+ ·040	+ ·0005
·018	− ·014	− ·0003	·010	+ ·019	+ ·0002

In several of the sets of observations recorded in Table VIII., there would seem to be a tendency for the positive errors to concentrate towards the beginning, *i.e.*, for pv to diminish slightly with p. It was at this stage that a suspicion arose that the distance between the glass points of the manometer might not be quite constant, but, as has been related, the suspicion was not verified. It is just possible that at the higher pressures and smaller volumes the temperature changes were not insensible. It is probable that they would operate in the direction mentioned, inasmuch as at the smaller volumes a larger proportion of the gas would be in the connecting tubes at a higher level in the room, and therefore warmer. Considerable precaution was taken, and I was not able to satisfy myself that disturbance due to temperature really existed. In another series of observations on hydrogen the tendency was scarcely apparent, and it remains doubtful whether there is any real indication of departure from BOYLE's law. It may be noted that interest was concentrated rather upon the lower pressures, and that perhaps less pains were taken over the readings of the higher pressures, where in any case the error would be a smaller proportion of the whole. Also some of the observations were not repeated. Another point that may be noted is that the means are chosen with respect to the values of pv, and that a different choice would in many cases materially reduce the mean error in the last column.

Having thoroughly tested the apparatus and the method of experimenting with hydrogen and nitrogen, I returned with curiosity to the case of oxygen. Special pains were taken to ensure that the gas should be pure and above all dry. To this end glass tubes were prepared containing permanganate of potash and phosphoric anhydride, and these were connected by sealing to one of the branches of the 3-way tap. A high vacuum having been made throughout, heat was gradually applied, and some of the oxygen allowed to blow off. The phosphoric tube (of considerable capacity) was then allowed to stand full of gas for some little time, after which the necessary gas to a pressure of about 10 centims. was allowed to enter the apparatus by means of the 3-way tap. With regard to the maintenance of the purity of the gas under rarefaction, it may be remarked that the method of experimenting was favourable, inasmuch as the last stages were not reached until the apparatus had been exposed to the gas under trial for a week or two. Any contamination that might be communicated from the glass during the first few days would for the most part be removed before the final stages were reached.

Before the regular series was commenced, special observations extending over several days were made in the region of pressure (from 1 millim. to ·5 millim.) where BOHR found anomalies. No unsteadiness could be detected. Whatever reading was obtained within a few minutes of a change of pressure was confirmed after an interval of an hour or more. For example, on November 29, at $12^h\ 25^m$ the pressure which had stood for some time at ·80 millim. was lowered to ·65 millim. At $8^h\ 0^m$ the pressure was unaltered. In no case was the behaviour in any way different to that which had been observed with the other gases. It is true that when the observations were reduced one preliminary set showed an excess of pressure at the smaller volumes similar to that recorded in the case of hydrogen, but the tendency is scarcely visible in the regular series now to be given, which extended from November 27 to December 9.

An examination of the numbers in the Table IX. shows that BOYLE's law was observed, practically up to the limits of the accuracy of the measurements, and in particular that there was no such falling off in the value of pv at low pressures as was encountered by BOHR. What can be the cause of the difference of our experiences I am at a loss to conjecture. I can only suppose that it must be connected somehow with the quality of the gas, complicated perhaps by interaction with the glass or with the mercury.

TABLE IX.—Oxygen.

Pressure in millims. Hg.	Deviation of *pv*.	Error of *p* in millims.	Pressure in millims. Hg.	Deviation of *pv*.	Error of *p* in millims.
1·53	+ ·0016	+ ·0024	·580	− ·0035	− ·0020
1·17	− ·0012	− ·0014	·472	+ ·0005	+ ·0002
·95	+ ·0005	+ ·0005	·396	− ·0007	− ·0003
·80	+ ·0007	+ ·0006	·321	+ ·0016	+ ·0005
·65	+ ·0012	+ ·0008	·255	+ ·0012	+ ·0003
·57	− ·0009	− ·0005	·212	+ ·0016	+ ·0003
·51	− ·0014	− ·0007	—	—	—
·47	− ·0014	− ·0007	—	—	—
·43	+ ·0009	+ ·0004	—	—	—
·288	+ ·002	+ ·0007	·142	+ ·005	+ ·0007
·233	·000	·0000	·115	+ ·009	+ ·0011
·196	·000	·0000	·094	− ·019	− ·0018
·159	+ ·005	+ ·0008	·077	·000	·0000
·125	− ·002	− ·0003	·062	+ ·012	+ ·0007
·103	− ·009	− ·0010	·051	− ·012	− ·0006
·068	− ·002	− ·0002	·034	·000	·0000
·056	+ ·005	+ ·0003	·029	+ ·059	+ ·0017
·048	+ ·019	+ ·0009	·022	− ·042	− ·0009
·038	+ ·009	+ ·0004	·019	+ ·023	+ ·0004
·029	− ·019	− ·0005	·014	− ·035	− ·0005
·025	− ·009	− ·0002	—	—	—

The final result of the observations on the three gases may be said to be the full confirmation of BOYLE's law between pressures of 1·5 millims. and ·01 millim. of mercury. If there is any doubt, it relates to the case of hydrogen, which appears to press somewhat in excess at the highest pressures. But when we consider the smallness of the amount and the various complications to which it may be due, as well as *à priori* probabilities, we may well hesitate to accept the departure from BOYLE's law as having a real existence.

So far as the present results can settle the question, they justify to the full the ordinary use of McLEOD's gauge within the limits of pressure mentioned and for nitrogen and hydrogen gases. The same might be said for oxygen; but until the discrepancy with the conclusions of BOHR can be explained, the necessity for some reserves must be admitted.

In any case the new manometer has done its work successfully, and is proved to be capable of measuring small pressures to about $\frac{1}{2000}$ of a millimetre of mercury. It was constructed under my direction by Mr. GORDON.