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Bakerian Lecture: On the Law of the Pressure of Gases between 75 and 150 Millimetres of Mercury

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IX. Bakerian Lecture.—*On the Law of the Pressure of Gases between 75 and 150 Millimetres of Mercury.*

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In a recently published paper* I have examined, with the aid of a new manometer, the behaviour of gases at very low pressures, rising to 1·5 millims. of mercury, with the result that Boyle's law was verified to a high degree of precision. There is, however, a great gap between the highest pressure there dealt with and that of the atmosphere—a gap which it appeared desirable in some way to bridge over. The sloping manometer, described in the paper referred to, does not lend itself well to the use of much greater pressures, at least if we desire to secure the higher proportional accuracy that should accompany the rise of pressure. The present communication gives the results of observations, by another method, of the law of pressure in gases between 75 millims. and 150 millims. of mercury. It will be seen that for air and hydrogen Boyle's law is verified to the utmost. In the case of oxygen, the agreement is rather less satisfactory, and the accordance of separate observations is less close. But even here the departure from Boyle's law amounts only to one part in 4000, and may perhaps be referred to some reaction between the gas and the mercury. In the case of argon too the deviation, though very small, seems to lie beyond the limits of experimental errors. Whether it is due to a real minute departure from Boyle's law, or to some complication arising out of the conditions of experiment, must remain an open question.

In the case of pressures not greatly below atmosphere, the determination with the usual column of mercury read by a cathetometer (after Regnault) is sufficiently accurate. But when the pressure falls to say one-tenth of an atmosphere, the difficulties of this method begin to increase. The guiding idea in the present investigation has been the avoidance of such difficulties by the use of manometric gauges combined in a special manner. The object is to test whether when the volume of a gas is halved its pressure is doubled, and its attainment requires two gauges indicating pressures which are in the ratio of 2 : 1. To this end we may employ a pair of independent gauges as nearly as possible similar to one another, the similarity being tested by combination in parallel, to borrow an electrical term. When con-

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nected below with one reservoir of air and above with another reservoir, or with a vacuum, the two gauges should reach their settings simultaneously, or at least so nearly that a suitable correction may be readily applied. For brevity we may for the present assume precise similarity. If now the two gauges be combined *in series*, so that the low-pressure chamber of the first communicates with the high-pressure chamber of the second, the combination constitutes a gauge suitable for measuring a doubled pressure.

The Manometers.

The construction of the gauges is modelled upon that used extensively in my researches upon the density of gases, so far as the principle is concerned, although of course the details are very different. In fig. 1 A and B represent 3/4 size the lower and upper chambers. As regards the glass-work, these communicate by a short neck at D as well as by the curved tube ACB. Through the neck is carried the glass measuring-rod FDE, terminating downwards at both ends in carefully prepared points E, F. The rod is held, at D only, with cement, which also completely blocks up the passage, so that when mercury stands in the curved tube the upper and lower chambers are isolated from one another. The use of the gauge is fairly obvious. Suppose for example that it is desired to adjust the pressure of gas in a vessel communicating with G to the standard of the gauge. Mercury standing in C, H is connected to the pump until a vacuum is established in the upper chamber. From a hose and reservoir attached below, mercury is supplied through I until the point F and its image in the mercury surface nearly coincide. If E coincides with its image, the pressure is that defined; otherwise adjustment must be made until the points E, F both coincide with their images, or as we shall say until both mercury surfaces are *set*. The pressure then corresponds to the column of mercury whose height is the length of the measuring-rod between the points E, F. The verticality of E F is tested with a plumb-line.

The measuring-rods appear somewhat slender; but it is to be remembered that the instruments are used under conditions that are almost constant. So far as the comparison of one gas with another is concerned, the qualification "almost" may indeed be omitted. The coincidence of the points and their images is observed with the aid of four magnifiers of 20 millims. focus, fixed in the necessary positions.

General Arrangement of Apparatus.

In fig. 2 is represented the connection of the manometers with one another and with the gas reservoirs. The left-hand manometer can be connected above through F with the pump or with the gas supply. The lower chamber A communicates with the upper chamber D of the right-hand manometer and with an intermediate reservoir E, to which, as to the manometers, mercury can be supplied from below. The lower chamber C of the right-hand manometer is connected with the principal gas reservoir. This consists of two bulbs, each of about 129 cub. centims. capacity, connected together by a neck of very narrow bore. Three marks are provided, one G above the upper bulb, a second H on the neck, and a third I below the lower

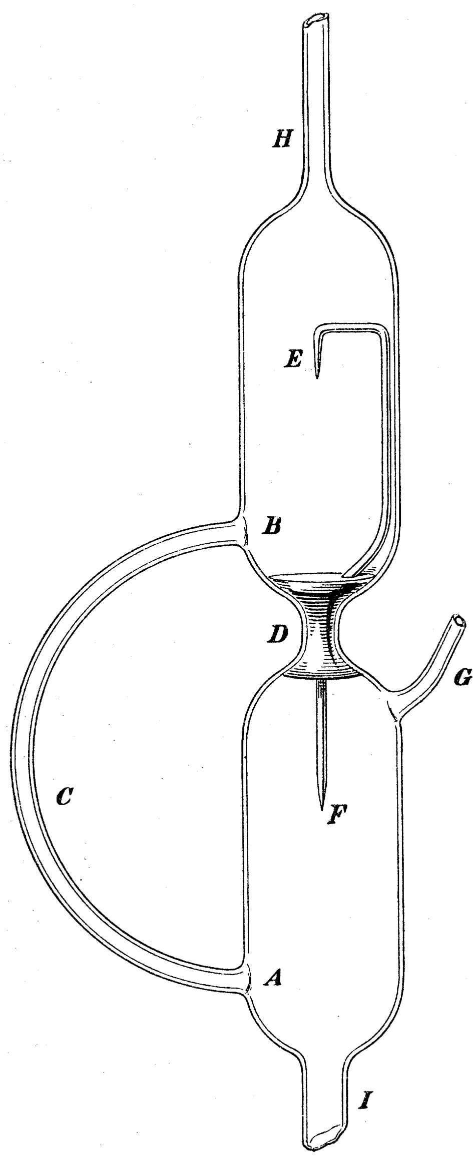

Fig. 1.

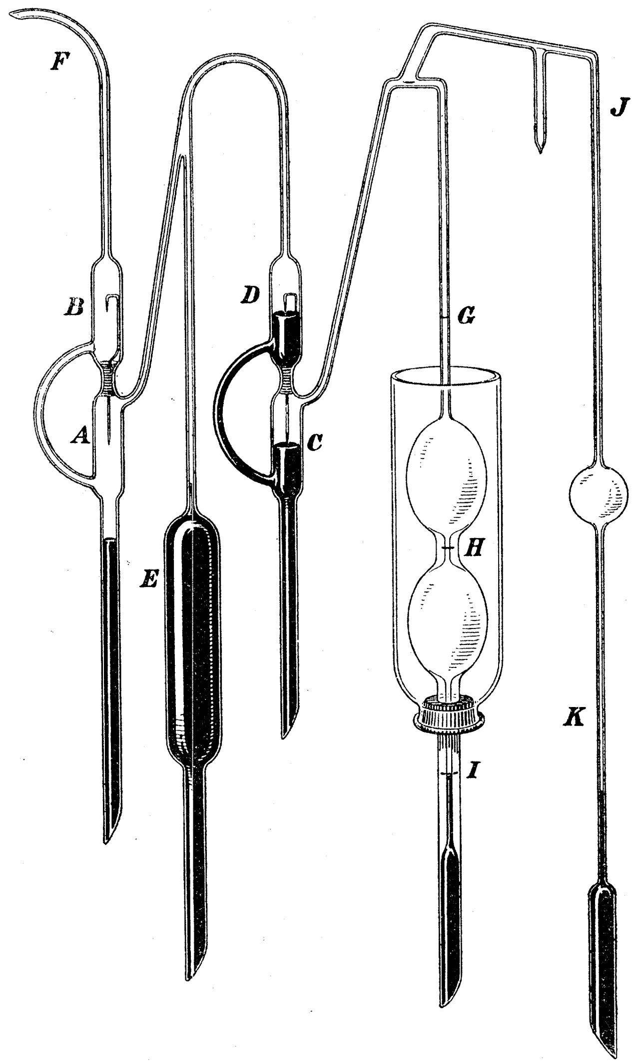

Fig. 2.

bulb, so adjusted that the included volumes are nearly equal. The use of the side-tube JK will be explained presently.

When, as shown, the mercury stands at the lower mark, the double volume is in action and the pressure is such as will balance the mercury in one (the right-hand) manometer. A vacuum is established in the upper chamber D from which a way is open through AB to the pump. When the mercury is raised to the middle mark H, the volume is halved, and the pressure to be dealt with is doubled. Gas sufficient to exert the single pressure (75 millims.) must be supplied to the intermediate chamber, which is now isolated from the pump by the mercury standing up in AB. Both manometers can now be set, and the doubling of the pressure verified.

The communication through F with the pump is free from obstruction, but on a side tube a three-way tap is provided communicating on the one hand with the gas supply and on the other with a vertical tube, more than a barometer-height long and terminating below under mercury, by means of which a wash-out of the generating vessels can be effected when it is not desired to evacuate them. The five tubes leading downwards from A, E, C, I, K are all over a barometer-height in length and are terminated by suitable hoses and reservoirs for the supply of mercury. When settings are actually in progress, the mercury in the hoses is isolated from the reservoirs by pinch-cocks and the adjustment of the supply is effected by squeezing the hoses. As explained in my former paper, the final adjustment must be made by squeezers which operate upon parts of the hoses which lie flat upon the large wooden mercury tray underlying the whole. The adjustment being somewhat complicated, a convenient arrangement is almost a necessity.

The Side Apparatus.

By the aid of these manometers the determination of pressure is far more accurate than with the ordinary mercury column and cathetometer, but since the pressures are defined beforehand, the adjustment is thrown upon the volume. The variable volume is introduced in the side-tube JK. This was graduated to $\frac{1}{2}$ cub. centim., in the first instance by mercury from a burette. Subsequently the narrow parts above and below the bulb (which as will presently be seen are alone of importance) were calibrated with a weighed column of mercury of volume equal to $\frac{1}{2}$ cub. centim. and occupying about 80 millims. of the length of the tube. The whole capacity of the tube between the lowest and highest marks was $20\frac{1}{2}$ cub. centims. The object of this addition is to meet a difficulty which inevitably presents itself in apparatus of this sort. The volume occupied by the gas cannot be limited to the capacities susceptible of being accurately gauged. Between the upper mark G and the mercury surface in C when set, a volume is necessarily included which cannot be gauged with the same accuracy as the volumes between G and H and between H and I. The simplest view of the side apparatus is that it is designed to measure this volume. In the notation subsequently used V_3 is the volume included when the mercury stands at C, at G, and at the top mark J. Let us suppose that with a certain quantity of gas imprisoned it is necessary in order to set the manometer CD, the upper chamber being vacuous, to add to V_3 a further volume V_5, amounting to the greater part of the capacity of the side-tube, so that the whole volume is $V_3 + V_5$.

When the second manometer is brought into use, the volume must be halved, for which purpose the mercury is raised through the bulb until it stands somewhere in the upper tube. The whole volume is now $V_3 + V_4$. And since

$$V_3 + V_5 = 2(V_3 + V_4),$$

we see that

$$V_3 = V_5 - 2V_4,$$

which may be regarded as determining V_3, V_4 and V_5 being known. A somewhat close accommodation is required between V_3, about 19 cub. centims. in my apparatus, and the whole contents of the side-tube.

General Sketch of Theory.

As the complete calculation is rather complicated on account of the numerous temperature corrections, it may be convenient to give a sketch of the theory upon the assumption that the temperature is constant, not only throughout the whole apparatus at one time, but also at the four different times concerned. We shall see that it is not necessary to assume BOYLE'S law, even for the subsidiary operations in the side-tube.

V_1 = volume of two large bulbs together between I and G (about 258 cub. centims.),
V_2 = volume of upper bulb between G and H,
V_3 = volume between C, G and highest mark J on side-tube,
V_4 = measured volume on upper part of J from highest mark downwards,
V_5 = measured volume, including bulb, of side apparatus from highest mark downwards,
P_1 = small pressure (height of mercury in right-hand manometer),
P_2 = large pressure (sum of heights of mercury in two manometers).

In the first pair of operations when the large bulbs are in use, the pressure P_1 corresponds to the volume $(V_1 + V_3 + V_5)$, and the pressure P_2 corresponds to $(V_2 + V_3 + V_4)$, *the quantity of gas being the same.* Hence the equation

$$P_1(V_1 + V_3 + V_5) = B\,P_2(V_2 + V_3 + V_4) \quad . \quad . \quad . \quad . \quad . \quad . \quad (1),$$

B being a numerical quantity which would be unity according to BOYLE'S law. In the second pair of operations with a *different quantity of gas* but with the *same pressures*, the mercury stands at G throughout, and we have

$$P_1(V_3 + V_5') = B\,P_2(V_3 + V_4') \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2);$$

whence by subtraction

$$P_1(V_1 + V_5 - V_5') = B\,P_2(V_2 + V_4 - V_4') \quad . \quad . \quad . \quad . \quad . \quad . \quad (3).$$

From this equation V_3 has been eliminated and B is expressed by means of P_1/P_2, and the actually gauged volumes V_1, V_2, $V_5 - V_5'$, $V_4 - V_4'$. It is important to remark that only the *differences* $(V_5 - V_5')$, $(V_4 - V_4')$ are involved. The first is measured on the lower part of the side-apparatus and the second on the upper part, while the capacity of the intervening bulb does *not* appear.

If the principal volumes V_1 and V_2 are nearly in the right proportion, there is nothing to prevent both $V_5 - V_5'$ and $V_4 - V_4'$ from being very small. When the temperature changes are taken into account, V_3, V_4, V_5 are not fully eliminated, but they appear with coefficients which are very small if the temperature conditions are good.

Thermometers.

As so often happens, much of the practical difficulty of the experiment turned upon temperature. The principal bulbs were drowned in a water-bath which could be effectively stirred, and so far there was no particular impediment to accuracy. But the other volumes could not so well be drowned, and it needed considerable precaution to ensure that the associated thermometers would give the temperatures concerned with sufficient accuracy. As regards the side-tube, a thermometer associated with its bulb and wrapped well round with cotton-wool was adequate. A third thermometer was devoted to the space occupied by the manometers and the tube leading from C to J. It was here that the difficulty was greatest on account of the proximity of the observer. Three large panes of glass with enclosed air spaces were introduced as screens, and although the temperature necessarily rose during the observations, it is believed that the rise was adequately represented in the thermometer readings. A single small gas flame, not allowed to shine directly upon the apparatus, supplied the necessary illumination, being suitably reflected from four small pieces of looking-glass fixed to a wall behind the glass points of the manometers.

As regards the success of the arrangement for its purpose, it is to be remembered that by far the larger part of any error that might arise is *eliminated in the final result*, since it is only a question of a *comparison* of observations with and without the large bulbs. Any systematic error made in the first case as regards the temperature of the undrowned capacities will be repeated in the second, and so lose its importance. A similar remark applies to any deficiency in the comparison of the three thermometers with one another.

Comparison of Large Bulbs.

This comparison needs to be carried out with something like the full precision aimed at in the final result, although it is to be noted that an error enters to only the half of its proportional amount, since we have to do not with the ratio of the capacities of the two bulbs, but with the ratio of the capacity of the upper bulb to the capacity of the two bulbs together. Thus if the volume of the upper bulb be unity and that of the lower $(1 + \alpha)$, the ratio with which we are concerned is $2 + \alpha : 1$, differing from $2 : 1$ by the proportional error $\frac{1}{2}\alpha$.

To adjust the capacities to approximate equality and to determine the outstanding difference, the double bulb was mounted vertically, in connection above with a Töpler pump and below with a stop-cock, such as is used with a mercury burette. The "marks" were provided by small collars of metal embracing tubing of 3 millims. bore and securely cemented, to the lower edge of which the mercury could be set as in reading barometers. A measuring flask, with a prolonged neck consisting of uniform tubing of 6 millims. diameter, was prepared having nearly the same capacity as the bulbs. The mercury required at a known temperature to fill the upper bulb between the marks was run from the tap into this flask. Air specks being removed, the flask was placed in a water-bath and the temperature varied until the mercury stood at a fixed mark upon the neck of the flask. Subsequently the mercury required at the same temperature to fill the lower bulb between the middle and the lower marks was measured in the same way. On a mean of two trials it was found that the flask needed to be 2°·4 C. warmer in the second case than in the first, showing that the capacity of the lower bulb was a little the smaller. Taking the relative expansions of mercury and glass for one degree to be ·00016, we get as the proportional difference ·00038. Thus in the notation already employed,

$$V_1 : V_2 = 2 - \cdot 00038 = 1 \cdot 99962 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4).$$

It appeared that so far as the measurements were concerned this ratio should be correct to at least $\frac{1}{200000}$; but disturbances due to pressure introduce uncertainty of about the same order.

Comparison of Gauges.

A simple method of comparing the gauges is to combine them in parallel so that the pressures in the lower chambers are the same, and also the pressures in the upper chambers, and then to find what slope must be given to the longer measuring-rod in order that its effective length may be equal to that of the shorter rod maintained vertical. The mercury can then be set to coincidence with all four points, and the equality of the gauges so arranged actually tested. It is afterwards an easy matter to calculate back so as to find the proportional difference of heights when both measuring-rods are vertical. Preliminary experiments of this kind upon the gauges, mounted on separate levelling stands and connected by india-rubber tubing, had shown that the difference was about $\frac{1}{800}$ part.

It would be possible, having found by the combination in parallel an adjustment to equality, to maintain the same sloped position during the subsequent use when the gauges must be combined in series. But in this case it would hardly be advisable to trust to wood-work in the mounting. At any rate in my experiments the gauges were erected with measuring-rods vertical, an arrangement which has at least the advantage that a displacement is of less importance as well as more easily detected. At the close of the observations upon the various gases it became necessary to compare the gauges with full precision.

For this purpose, they were connected (without india-rubber) in parallel, the upper chambers of both being in communication with the pump, and the lower chambers of both in communication with the gas reservoirs G I. Had the lengths of the measuring-rods been absolutely equal, this equality would be very simply proved by the possibility of so adjusting the pressure of the gas and the supply of mercury to the two manometers that all four mercury surfaces could be *set* simultaneonsly. It was very evident that no such simultaneous setting was possible, and the problem remained to evaluate the small outstanding difference. To pass from one manometer to the other, either the volume or the temperature had to be varied.

In principle it would perhaps be simplest to keep the volume constant and determine what difference of temperature (about half a degree) would be required to make the transition. But the temperature of the undrowned parts (now increased in volume) could not be ascertained with great precision, so that I preferred to vary the volume and to trust to alternations backwards and forwards for securing that the mean temperature in the two cases to be compared should not be different. Thus in one set, including seven observations following continuously, four alternate observations were settings with one manometer and three were settings with the other. According to the thermometers, the mean temperature in the first case was for the drowned volume 11°·38 and for the (much smaller) undrowned volume 12°·76. In the second case the corresponding temperatures were 11°·39 and 12°·80, so that the differences could be neglected. The volume changes were effected in the side-tube J K, and the mean difference in the two cases was ·411 cub. centim. It will be understood that in order to define the volume *both* manometers were always set *below*. The whole volume was reckoned at 294 cub. centims., of which about 258 cub. centims. represents the capacity of the bulbs G I drowned in the water-bath. According to these data the proportional difference in the lengths of the measuring-rods, equal to the proportional difference of the above determined volumes, is ·00140. Two other similar sets of observations gave ·00136, ·00137; so that the mean adopted value is ·00138. The measuring-rod of the manometer on the *right*, fig. 2, is the longer.

As in the case of the volumes, any error in the above comparison is halved in the actual application. If H_2 be the length of the rod in the right-hand manometer, H_1 the length on the left, we are concerned only with the ratio $H_1 + H_2 : H_2$. And from the value above determined we get

$$\frac{H_1 + H_2}{H_2} = 1 \cdot 99862 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5).$$

The Observations.

In commencing a set of observations the first step is to clear away any residue of gas by making a high vacuum throughout the apparatus, the mercury being lowered below the manometers and bulbs. The mercury having been allowed to rise into the pump head of the Töpler, the gas to be experimented on is next admitted to a pressure of about 75 millims. This occupies the manometers, the bulbs, and part of the capacity of the intermediate chamber E. The passage through the right-hand manometer is then closed by bringing up the mercury to the neighbourhood of C, and by rise of mercury from I to H the pressure is doubled in the upper bulb. The next step is to cut off the communication between A and B, and to renew the vacuum in B. If the right amount of gas has been imprisoned, it is now possible to make a setting, the mercury standing at A, C, H, and in the side apparatus somewhere in the upper tube below J. If, as is almost certain to be the case in view of the narrowness of the margin, a suitable setting cannot be made, it becomes necessary to alter the amount of gas. This can usually be effected, without disturbing the vacuum, by lowering the mercury at C and allowing gas to pass in pistons in the curved tube CD either from the intermediate chamber to the bulbs, or preferably in the reverse direction.

When the right amount of gas has been obtained, the observations are straightforward. On such occasion six readings were usually taken, extending over about an hour, during which time the temperature always rose, and the means were combined into what was considered to be one observation.

A complete set included four observations with the large bulbs at 150 millims. pressure and four at 75 millims. To pass to the latter the mercury must be lowered from H to I and in the left-hand manometer, and the pump worked until a vacuum is established in D. It was considered advisable to break up one of the sets of four; for example, after two observations at 150 millims. to take four at 75 millims., and afterwards the remaining pair at 150 millims. In this way a check could be obtained upon the quantity of gas, of which some might accidentally escape, and there were also advantages in respect of temperature changes. These eight observations with the large bulbs were combined with four in which the side apparatus was alone in use, the mercury standing all the while at G. Of these, two related to the 75 millims. pressure and two to the 150 millims. Finally, the means were taken of all the corresponding observations.

The following table shows in the notation employed the correspondence of volumes and temperatures :—

I.	V_1	θ_1	V_3	τ_1	V_5	t_1
II.	V_2	θ_2	V_3	τ_2	V_4	τ_2
III.	—	—	V_3	τ_3	V_5'	t_3
IV.	—	—	V_3	τ_4	V_4'	τ_4

In the first observation V_1 is the volume of the two large bulbs and θ_1 the temperature of the water-bath, reckoned from some convenient neighbouring temperature as a standard. V_3 is the ungauged volume already discussed whose temperature τ_1 is given by the upper thermometer. V_5 is the (larger) volume in the side apparatus whose temperature t_1 is that of the lower thermometer. In the second observation V_2 is the volume of the upper bulb and θ_2 its temperature. V_4 is the volume in the side apparatus whose temperature, as well as that of V_3, is taken to be τ_2, the mean reading of the upper thermometer. III. and IV. represent the corresponding observations in which the large bulbs are not filled. The reading of the water-bath thermometer is in every case denoted by θ, that of the upper thermometer by τ, and that of the lower thermometer by t. The temperature of the columns of mercury in the manometers is also represented by τ.

As an example of the actual quantities, the observations on air between October 28 and November 5 may be cited. The values of V_1 and V_3 are approximate. As appears from the formulæ, V_3 occurs with a small coefficient, as does also V_1, except in the ratio $V_1 : V_2$ otherwise provided for. We have

$$V_1 = 258{\cdot}4, \qquad V_3 = 19{\cdot}05\,;$$

$$V_4 = {\cdot}810, \qquad V_5 = 20{\cdot}493\,;$$

$$V_4 - V_4' = {\cdot}0841, \qquad V_5 - V_5' = {\cdot}0266\,;$$

$$\theta_1 = -{\cdot}077, \qquad \theta_2 = -{\cdot}059\,; \qquad t_1 = {\cdot}257, \qquad t_3 = {\cdot}141\,;$$

$$\tau_1 = {\cdot}092, \qquad \tau_2 = {\cdot}186, \qquad \tau_3 = -{\cdot}033, \qquad \tau_4 = {\cdot}100.$$

The volumes are in cubic centimetres and the temperatures are in Centigrade degrees reckoned from 14°.

An effort was made, and usually with success, to keep all the temperature differences small, and especially the difference between θ_1 and θ_2. It is desirable also so to adjust the quantities of gas in the two cases that $V_4 - V_4'$, $V_5 - V_5'$ shall be small.

The Reductions.

The simple theory has already been stated, but the actual reductions are rather troublesome on account of the numerous temperature corrections. These, however, are but small.

We have first to deal with the expansion of mercury in the manometers. If, as in

(5), the actual heights of the mercury (at the same temperature) be H_1, H_2, we have for the corresponding *pressures* $H/(1 + m\tau)$, where $m = \cdot 00017$. Thus in the notation already employed

$$P_1 = \frac{H_2}{1 + m\tau_1}, \quad \text{or} \quad \frac{H_2}{1 + m\tau_3},$$

and

$$P_2 = \frac{H_1 + H_2}{1 + m\tau_2}, \quad \text{or} \quad \frac{H_1 + H_2}{1 + m\tau_4}.$$

The quantity of gas at a given pressure occupying a known volume is to be found by dividing the volume by the absolute temperature. Hence each volume is to be divided by $1 + \beta\theta$, $1 + \beta\tau$, $1 + \beta t$, as the case may be, where β is the reciprocal of the absolute temperature taken as a standard. Thus in the above example for air (p. 426), $\beta = \frac{1}{273 + 14} = \frac{1}{287}$. Our equations, expressing that the quantities of gas are the same at the single and at the double pressure, accordingly take the form

$$\frac{H_2}{1 + m\tau_1}\left\{\frac{V_1}{1 + \beta\theta_1} + \frac{V_3}{1 + \beta\tau_1} + \frac{V_5}{1 + \beta t_1}\right\} = \frac{B(H_1 + H_2)}{1 + m\tau_2}\left\{\frac{V_2}{1 + \beta\theta_2} + \frac{V_3 + V_4}{1 + \beta\tau_2}\right\},$$

$$\frac{H_2}{1 + m\tau_3}\left\{\frac{V_3}{1 + \beta\tau_3} + \frac{V_5'}{1 + \beta t_3}\right\} = \frac{B(H_1 + H_2)}{1 + m\tau_4}\,\frac{V_3 + V_4'}{1 + \beta\tau_4},$$

where B is the numerical quantity to be determined—according to BOYLE's law identical with unity.

By subtraction we deduce

$$\frac{1}{(1 + m\tau_1)(1 + \beta\theta_1)} - \frac{BV_2(H_1 + H_2)}{V_1H_2(1 + m\tau_2)(1 + \beta\theta_2)}$$

$$= \frac{V_3}{V_1}\left\{\frac{B(H_1 + H_2)}{H_2(1 + m\tau_2)(1 + \beta\tau_2)} - \frac{B(H_1 + H_2)}{H_2(1 + m\tau_4)(1 + \beta\tau_4)} - \frac{1}{(1 + m\tau_1)(1 + \beta\tau_1)} + \frac{1}{(1 + m\tau_3)(1 + \beta\tau_3)}\right\}$$

$$+ \frac{B(H_1 + H_2)V_4}{H_2V_1}\left\{\frac{1}{(1 + m\tau_2)(1 + \beta\tau_2)} - \frac{1}{(1 + m\tau_4)(1 + \beta\tau_4)}\right\}$$

$$- \frac{V_5}{V_1}\left\{\frac{1}{(1 + m\tau_1)(1 + \beta t_1)} - \frac{1}{(1 + m\tau_3)(1 + \beta t_3)}\right\}$$

$$+ \frac{B(H_1 + H_2)(V_4 - V_4')}{H_2V_1}\,\frac{1}{(1 + m\tau_4)(1 + \beta\tau_4)}$$

$$- \frac{V_5 - V_5'}{V_1}\,\frac{1}{(1 + m\tau_3)(1 + \beta t_3)} \quad \ldots \quad (6).$$

The first three terms on the right, viz., those in V_3, V_4, V_5, vanish if $\tau_1 = \tau_3$,

$\tau_2 = \tau_4$, $t_1 = t_3$. In the small terms we expand in powers of the small temperatures (τ, t), and further identify $B(H_1 + H_2)/H_2$ with 2. The five terms on the right then assume the form

$$\frac{V_3}{V_1}\{(m+\beta)(\tau_1 - \tau_3 - 2\tau_2 + 2\tau_4) + \beta^2(2\tau_2^2 - 2\tau_4^2 - \tau_1^2 + \tau_3^2)\}$$
$$-\frac{2V_4}{V_1}\{(m+\beta)(\tau_2 - \tau_4) - \beta^2(\tau_2^2 - \tau_4^2)\}$$
$$-\frac{V_5}{V_1}\{m(\tau_3 - \tau_1) + \beta(t_3 - t_1) + \beta^2(t_1^2 - t_3^2)\}$$
$$+\frac{2(V_4 - V_4')}{V_1}\{1 - (m+\beta)\tau_4 + \beta^2\tau_4^2\}$$
$$-\frac{V_5 - V_5'}{V_1}\{1 - m\tau_3 - \beta t_3 + \beta^2 t_3^2\},$$

in which $m\beta$ and m^2 are neglected, while β^2 is detained. In point of fact, the terms of the second degree were seldom sensible.

Taking the data above given for the observations on air October 28—November 5, we find

Term in V_3	. . . .	$= -\cdot000012$
,, V_4	. . . .	$= -\cdot000002$
,, V_5	. . . .	$= +\cdot000034$
,, $(V_4 - V_4')$	. . . .	$= +\cdot000652$
,, $(V_5 - V_5')$	. . . .	$= -\cdot000103$
		$+\cdot000569$

For the first term on the left of (6), we find

$$\frac{1}{(1 - m\tau_1)(1 + \beta\theta_1)} = 1\cdot000256\ ;$$

so that

$$B = \frac{V_1 H_2 (1 + m\tau_2)(1 + \beta\theta_2)}{V_2 (H_1 + H_2)} \times \cdot999687,$$

or when the numerical values are introduced from (4), (5),

$$B = 1\cdot00002.$$

The deviation from BOYLE's law is quite imperceptible.

It may be noted that a value of B exceeding unity indicates an excessive compressibility, such as is manifested by carbonic acid under a pressure of a few atmospheres.

The Results.

Little now remains but to record the actual results. All the gases were, it is needless to say, thoroughly dried.

Air.

Date.	B.
April 15–29, 1901	·99986
May 22–28, 1901	1·00003
October 28–November 5, 1901	1·00002
Mean	·99997

Hydrogen.

Date.	B.
July 6–13, 1901	·99999
July 16–23, 1901	·99996
Mean	·99997

The hydrogen was first absorbed in palladium, from which it was driven off by heat as required.

Oxygen.

Date.	B.
June 7–17, 1901	1·00022
July 21–July 1, 1901	1·00044
September 18–30, 1901	1·00005
October 10–18, 1901	1·00027
Mean	1·00024

The two first fillings of oxygen were with gas prepared by heating permanganate of potash contained in a glass tube and sealed to the remainder of the apparatus. The desiccation was, as usual, by phosphoric anhydride. In the third and fourth fillings the gas was from chlorate of potash and had been stored over water.

Nitrous Oxide.

Date.	B.
July 31–August 5, 1901	1·00059
August 8–24, 1901	1·00074
Mean . .	1·00066

Argon.

Date.	B.
December 28–January 1, 1902 . . .	1·00024
January 2–9, 1902	1·00019
Mean . .	1·00021

The argon was from a stock which had been carefully purified some years ago and has since stood over mercury. In this case the two sets of observations recorded related to the same sample of gas imprisoned in the apparatus. In all other cases the gas was renewed for a new set of observations.

With regard to the accuracy of the results it was considered that systematic errors should not exceed $\frac{1}{10000}$. In the comparison of one gas with another most of the systematic errors are eliminated, and the mean of two or three sets should be accurate according to the standard above stated. That nitrous oxide should show itself more compressible than according to BOYLE's law is not surprising, but there appear to be deviations also in the cases of oxygen and argon. Whether these deviations are to be regarded as real departures from BOYLE's law, or are to be attributed to some complication relating to the glass or the mercury cannot be decided. At any rate they are very minute. It will be noted that the oxygen numbers are not so concordant as they ought to be. I am not in a position to suggest an explanation, and the discrepancies were hardly large enough to afford a handle for further investigation.

If we are content with a standard of $\frac{1}{5000}$, we may say that air, hydrogen, oxygen, and argon obey BOYLE's law at the pressures concerned and at the ordinary temperatures (10° to 15°).

Throughout the investigation I have been efficiently assisted by Mr. GORDON, to whom I desire to record my obligations.