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On the Compressibility of Gases between One Atmosphere and Half an Atmosphere of Pressure

Lord Rayleigh

Phil. Trans. R. Soc. Lond. A 1905 **204**, 351-372
doi: 10.1098/rsta.1905.0009

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IX. *On the Compressibility of Gases between One Atmosphere and Half an Atmosphere of Pressure.*

By Lord Rayleigh, *O.M., F.R.S.*

Received January 17,—Read February 2, 1905.

The present* is the third of a series of memoirs in which are detailed observations upon the compressibility of the principal gases at pressures from one atmosphere downwards. In the first† of these the pressures dealt with were exceedingly low, ranging from 1·5 millims. to 0·01 millim. of mercury, and the use of a special and extraordinarily delicate manometer allowed the verification of Boyle's law to be pushed to about $\frac{1}{2000}$ of a millimetre of mercury.

In the second‡ memoir the products of pressure and volume at constant temperature (that of the room) were compared when the pressure was changed from 75 millims. to 150 millims. of mercury—in the ratio of 2 : 1. The ratio of the products (denoted by B) would be unity according to Boyle's law; for the more condensable gases, *e.g.*, nitrous oxide, it exceeds unity. The following were the final mean values :—

Nature of gas.	B.
Air	·99997
Hydrogen	·99997
Oxygen.	1·00024
Nitrous oxide.	1·00066
Argon	1·00021
Carbonic oxide§.	1·00005

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* A Preliminary Notice containing many of the results now recorded in greater detail was published in 'Roy. Soc. Proc.,' February, 1904.

† 'Phil. Trans.,' A 196, pp. 205–223, 1901; "Scientific Papers,' vol. 4, p. 511.

‡ 'Phil. Trans.,' A 198, pp. 417–430, 1902. On p. 428, line 8 from bottom, read $1 + m\tau$ instead of $1 - m\tau$.

§ The number for carbonic oxide was obtained subsequently to the publication of the memoir. It is the mean of two sets of observations, giving severally 1·00003 and 1·00008. The gas was prepared from ferrocyanide of potassium (see 'Roy. Soc. Proc.,' vol. 62, p. 204, 1897; 'Scientific Papers,' vol. 4, p. 347).

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The deviations from unity in the cases of oxygen and argon were thought to exceed the errors of observation. The results presently to be given for oxygen render it probable that the larger half of the deviation was, in fact, error. At any rate, BOYLE'S law was sensibly observed by air, hydrogen and carbonic oxide.

The method employed in this research appeared to be satisfactory, and I was desirous of extending it to higher pressures, still, however, below the atmospheric, as to which there seemed to be a great dearth of information. I could find only some incidental observations by AMAGAT* on air and carbonic acid, and these it may be well to quote:—

Air.		Acide carbonique.	
Pression initiale en centimètres.	$\frac{pv}{p'v'}$.	Pression initiale en centimètres.	$\frac{pv}{p'v'}$.
37·314	1·0003	37·760	1·0026
37·318	1·0002	37·724	1·0022
31·523	1·0000	37·561	1·0025
30·613	1·0027	24·970	1·0015
25·393	1·0010	24·974	1·0020
25·376	1·0005	24·948	1 0015
24·830	·9997	24·947	1·0021
24·841	1·0002		

The pressures were as 2 : 1, and the "initial pressure" p was the smaller. The temperature was from 17° C. to 19° C. The ratio $pv/p'v'$ is what I have denoted by B. It will be seen that the numbers for air exhibit considerable discrepancies.

The earlier entries in AMAGAT'S table correspond pretty closely with the observations that I proposed to undertake. Besides the general elucidation of the behaviour of gases at reduced pressures, the object in view was to obtain material for comparing the densities of various gases at great rarefactions. In the actual weighings of gases the pressure in the containing vessel is usually atmospheric, but the ratios of densities so obtained are not immediately available for inferring molecular weights according to AVOGADRO'S rule. This rule can only be supposed to apply with rigour when the gases are so far rarefied as to come within the range of BOYLE'S law.† For this purpose it is advisable that the range of pressure employed should be sufficient to give accuracy, but not so high that the application to AVOGADRO'S rule involves too

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* 'Ann. de Chimie,' tome xxviii., 1883.

† The application of this idea to oxygen and hydrogen was made in my paper "On the Relative Densities of Oxygen and Hydrogen," 'Roy. Soc. Proc.,' vol. 50, p. 448, 1892; 'Scientific Papers,' vol. 3, p. 525. My hesitation then and later to push the investigation further, so as to obtain corrections to the relative densities observed at atmospheric pressure, arose from the uncertainties in which the anomalous observations of MENDELEEF and SILJERSTRÖM had enveloped the behaviour of gases at low pressures.

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much extrapolation. The comparison of volumes at pressures atmospheric and half atmospheric seems to meet these requirements, though we must not forget that (apart from theory) the result is still of the nature of an extrapolation. On this subject reference may be made to a paper by Sir W. RAMSAY and Dr. B. STEELE.*

The guiding idea in the present apparatus, as in that of 1902, is the use of two 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 connected 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 connection can readily be 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.† An iron measuring rod, AB, is actually applied to the two mercury surfaces, arranged so as to be vertically superposed. This rod is of about 7 millims. diameter and is pointed below, A. At the upper end, B, it divides at the level of the mercury into a sort of fork, and terminates in a point similar to that at A, and, like it, directed downwards. The coincidence of these points with their images reflected at the mercury surfaces is observed with the aid of lenses of 20 millims. focus suitably held in position. It is, of course, independent of any irregular refractions which the walls of the tube may exercise. In each manometer the distance between the points is 15 inches or 381 millims.

The internal diameter of the tubes, constituting the upper and lower chambers of the manometers, is 22 millims. This is the diameter at the level of the "points" to which the mercury surfaces are set. At the places where the iron rod emerges above and below into the open, the glass is contracted until it becomes an approximate fit, and air-tightness is secured with the aid of cement.

General Arrangement of Apparatus.

With one important difference to be explained presently the general scheme is the same as in 1902 and is sketched in fig. 1. The left-hand manometer can be

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* "On the Vapour-Densities of some Carbon Compounds; an attempt to determine their Molecular Weights," 'Phil. Mag.,' Oct., 1893.

† 'Roy. Soc. Proc.,' vol. 53, pp. 134–149, 1893; 'Scientific Papers,' vol. 4, p. 41.

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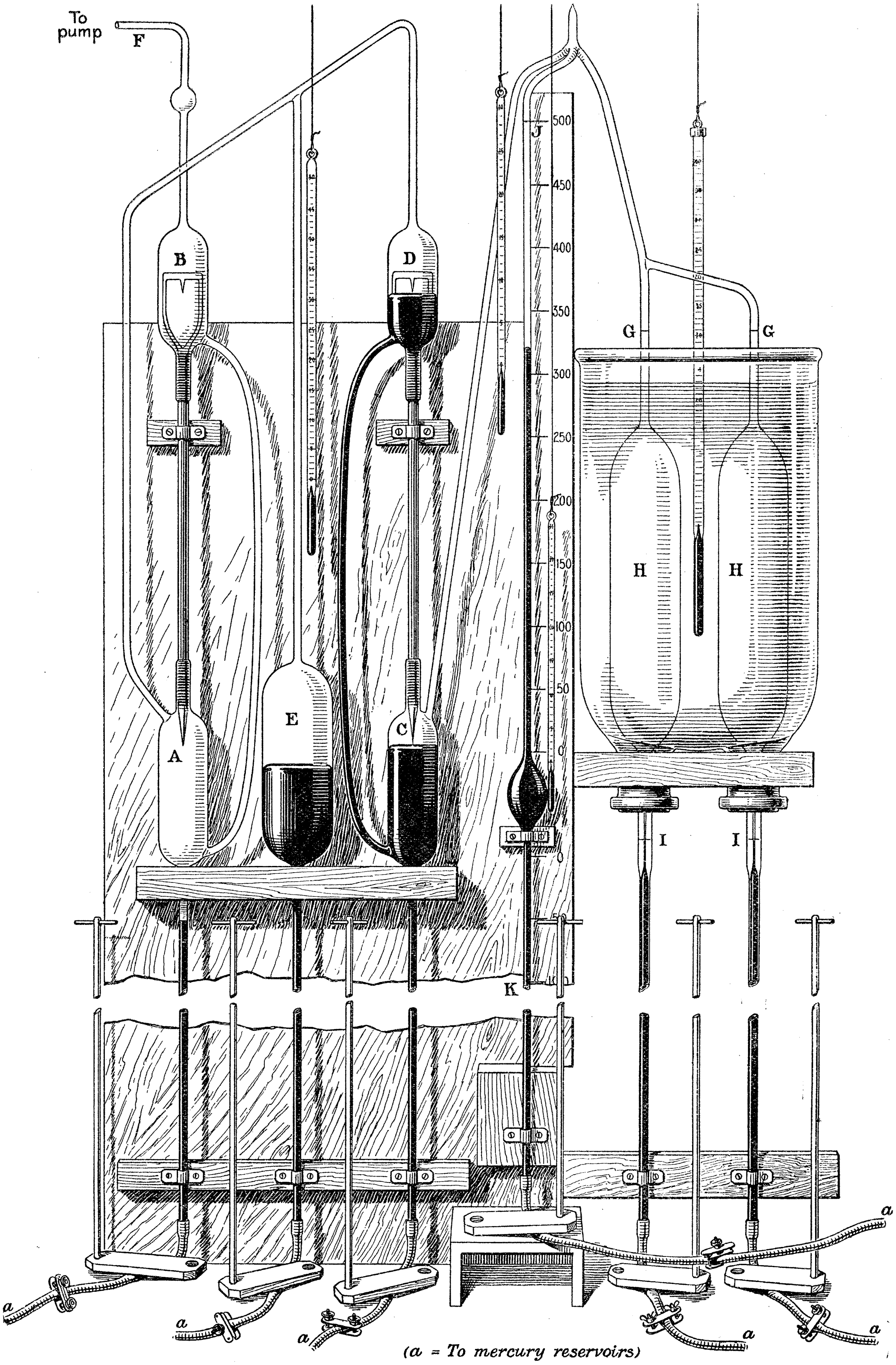

Fig. 1.

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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 reservoirs H, H. It is here that the novelty enters. In the 1902 apparatus the two equal bulbs were superposed, being connected by a narrow neck. For the doubled volume, both bulbs were occupied by gas; but for the single volume, only the upper one was available. For the comparison of the single and double volume, a principal factor of the final result, preliminary gauging had to be relied upon. In the new apparatus it was desired largely to increase the volumes, and it was both more advantageous and more convenient to place the two bulbs H side by side. The temperature conditions are thereby improved; but what I wish to emphasize at present is the elimination, thereby rendered possible, of dependence upon preliminary gauging, for either bulb is now available for the single volume; and if both are symmetrically employed in each set of observations, the mean necessarily corresponds to half the total volume, *whether or not the two single volumes are precisely equal.* The volumes are defined, as usual, by marks GG, II, upon the associated tubes above and below. The use of the side-tube JK will be explained presently.

When, as shown, the mercury stands at the lower marks I, the double volume is in use, 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 ABF to the pump. When the mercury is raised through one of the bulbs to the upper mark G, the volume is halved and the pressure to be dealt with is doubled. Gas sufficient to exert the single pressure (381 millims.) must be supplied to the intermediate chamber E, which is now isolated from the pump by the mercury standing up in the curved tube AB. Both manometers can now be set and the doubling of the pressure verified.

The communication through to the pump is unobstructed, 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 delivering under mercury, by means of which a wash-out of the generating vessels can be effected when it is not convenient to evacuate them. The six tubes of glass leading downwards from the gas reservoirs, manometers, &c., are all well over a barometer-height in length, and are terminated by suitable indiarubber hoses and reservoirs for the supply of mercury.* By this precaution the internal pressure on the hoses is guaranteed to exceed the external atmospheric pressure, and under this condition the use of indiarubber seems to be free from serious objection. If, however, the external pressure be allowed to be in excess, there are soon signs of the percolation of air and probably of moisture.

When settings are actually in progress, the mercury in the hoses is isolated from

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* These reservoirs were protected from external moisture by tubes of chloride of calcium.

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that in the reservoirs by pinch-cocks, and the adjustment of the supply is effected by squeezing the hoses. As explained in my first paper, the final adjustment must be made by squeezers which operate upon parts of the hoses which lie flat upon the large wooden tray underlying the whole.

The Side Apparatus.

The use of this was fully explained in my former paper. By the employment of manometric gauges we are enabled to dispense with scales and cathetometers; but since (save as to a small temperature correction) the pressures are defined beforehand, the adjustment is thrown upon the volume. The variable volume is introduced at the side tube JK, which, with its associated bulb, allows of the elimination from the results of the volume which cannot be directly gauged, including that over the mercury in the lower chamber of the right-hand manometer when set. The tubes above and below the bulb were calibrated in the usual manner.* It should be remarked that the diagram shows the mercury in the side apparatus in a position suitable for a measurement at the *doubled* pressure, while in the rest of the apparatus the position of the mercury corresponds to the *single* pressure.

General Sketch of Theory.

It will be convenient to repeat this, nearly as given in the former paper. To save complication, it will be supposed that the temperature is constant, not only throughout the whole apparatus at one time, but also at the four different times concerned.

V_1 = volume of two large bulbs H, H together between GG, II (about 633 cub. centims.).
V_3 = volume between CJGG (the ungauged space).
V_4 = measured volume on upper part of JK from highest mark J downwards.
V_5 = measured volume, including bulb of side apparatus, from highest mark J downwards.
P_1 = smaller pressure (height of mercury in right-hand manometer).
P_2 = larger 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 $(\frac{1}{2}V_1+V_3+V_4)$, *the quantity of gas being the same.* Hence the equation

$$P_1(V_1+V_3+V_5) = BP_2(\tfrac{1}{2}V_1+V_3+V_4),$$

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* The whole of the apparatus was made under my instructions by the late Mr. Gordon, who also took a large part in the observations. I take this opportunity of recording my indebtedness to his faithful assistance over a long series of years.

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

$$P_1(V_3+V'_5) = BP_2(V_3+V'_4);$$

whence by subtraction

$$P_1(V_1+V_5-V'_5) = BP_2(\tfrac{1}{2}V_1+V_4-V'_4).$$

From this equation V_3 has been eliminated, and B is expressed by means of P_1/P_2 and the actually gauged volumes $V_5-V'_5$, $V_4-V'_4$. 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 BOYLE's law be closely followed, there is nothing to prevent both $V_5-V'_5$ and $V_4-V'_4$ from being very small. Except the preliminary comparison of the manometers, the whole of the data required for the verification are then contained in the observations of each set.

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.

Of these four were employed. The first gave the temperature (τ) of the manometric columns; the second gave the temperature (T) of V_3; the third that of the bulb of the side apparatus (t). The temperature of the water-bath, in which are contained the principal bulbs, is of course the most important. The water was stirred continuously by a stream of air, and the temperature was taken by a thermometer that could be read to $\frac{1}{100}$ of a degree C. No observations were begun until it had been ascertained that the temperature of the water was slowly rising. It is important to understand what really are the demands made upon this thermometer. It was arranged that the mean temperature θ_1 when the double volume was in use should be almost the same as for the single volumes θ_2. The difference was usually less than $\frac{1}{100}$ of a degree and rarely exceeded $\frac{2}{100}$ or $\frac{3}{100}$. Under these circumstances the use of the thermometer was practically only to identify the same temperature on different days, and the actual error of its readings and even of its scale of temperature were of but secondary importance. Comparisons with other thermometers showed that there were no errors which could possibly become sensible. The precautions necessary, in order that the other thermometers should do their work satisfactorily, were indicated in the former paper. In the present work the number of intervening screens was increased.

It is desirable to emphasise that most of the errors that could arise from imperfect

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action of the thermometers is eliminated in the actual results, which depend only upon a comparison between operations with and without the large bulbs. For example, suppose that there is an error in the rather ill-defined temperature of the space V_3. The conditions are the same whether the large bulbs are in use or not; and thus whatever error occurs in the one case may be expected to repeat itself in the other. So far as this repetition is complete, the error disappears in the comparison. Again, it might happen that one of the large bulbs tended to be warmer than the other or than the thermometer. But this, so far as it is constant, could lead to no error, the effect when the bulb is used alone being compensated by the effect when it forms one of the pair. Purely accidental errors are, in any case, eliminated when the mean is taken of a number of observations.

The Large Reservoirs.

The tubes forming the principal parts are of glass, 25 centims. in length, 41 millims. in internal diameter, and about $2\frac{1}{4}$ millims. thickness in the walls. There are prolongations above and below of narrow bore, upon which are placed the marks defining the volumes.

As has been explained, the accurate comparison of these volumes is unnecessary. As it happens, the actual volumes between the marks are so nearly equal that it is difficult to say which is the larger. The total volume V_1, required only to be roughly known for the sake of the subsidiary terms, is 632·6 cub. centims.

But there is another question to be considered. The single bulbs are used under an internal pressure of an atmosphere. Under the same pressure the combined volume of both bulbs would of course be exactly double the mean of those of the bulbs used separately. But when the bulbs are in combination, the internal pressure is reduced to half an atmosphere, and the bulbs contract. A correction is thus necessary which runs similarly through all the results calculated on the supposition that the ratio of volumes is exactly 2 : 1.

The amount of the correction has been determined in two ways. Direct observation of the change of level of water filling the bulb and standing in the small upper prolongation, when the internal pressure was changed from one atmosphere to half atmosphere, gave a total relative alteration of $4{\cdot}4 \times 10^{-5}$ per half atmosphere, of which $2{\cdot}3 \times 10^{-5}$ would be due to the contraction of the water. The difference, viz., $2{\cdot}1 \times 10^{-5}$, represents the relative contraction or expansion of the volume per half atmosphere of pressure.

A calculation founded upon the measured dimensions of the tubes, including the thickness of the walls, combined with estimates of the elasticity of the glass, gave $2{\cdot}0 \times 10^{-5}$ per half atmosphere, in better agreement than could have been expected.

The real ratio of volumes with which we are concerned in these experiments is thus not 2 exactly, but

$$2\,(1 - {\cdot}000021).$$

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The value of B calculated without allowance for this correction would be too large, so that a gas which really obeyed BOYLE'S law exactly would appear to be too condensable, like CO_2. From a value of B so calculated we are to subtract ·000021.

Comparison of Manometers.

This comparison is effected by combining the manometers in parallel so that the mercury at the lower levels is subject to the pressure of one continuous quantity of gas, while the mercury at the upper levels is *in vacuo*, or at any rate under the pressure of the same very rare gas. Any difference that may manifest itself may be estimated by finding what change of gas-volume is required in order to pass from the pressure appropriate to one manometer to that appropriate to the other.

The first matter requiring attention is the verticality of the measuring rods, or rather of the lines joining the *points* actually applied to the mercury. The points were visually projected upon a plumb-line, hung a few centimetres away, and were observed through a hole of 2 millims. or 3 millims. diameter perforated in a black card. If the adjustment is perfect the same position of the card allows accurate projection upon the thread of the upper and lower points; if not, the necessary motion of the card, perpendicular to the line of sight, gives data for estimating the amount of the error. If x and y be the linear horizontal deviations from true adjustment thus determined in *any* two perpendicular planes, l the length of the rod, the angular error is $\surd(x^2+y^2)\div l$, and the proportional error of height for the present purpose is $\frac{x^2+y^2}{2l^2}$. When the manometers were compared, no value of x or y exceeded $\frac{1}{2}$ millim., so that with $l = 380$ millims. the error of verticality could be neglected.

In effecting the comparison of the manometers, both mercury levels must be set *below* (in order to make the gas volume definite), while the settings above are made alternately. It was at once apparent, when the right-hand manometer was set, that the rod on the left was a little too long, a perceptible interval being manifest between the upper point and the mercury. In these experiments the total gas volume was about 2845 cub. centims., the principal part being the volume of a large bottle protected from rapid changes of temperature by a packing of sawdust. The necessary changes were produced by causing mercury to rise and fall in a vertical tube of small bore, the position of the meniscus being noted at the moment when a setting was judged to be good. The settings of the two manometers must be made alternately in order to eliminate temperature changes; and the result of each set of observations was derived from the means of four settings of one manometer, and of five of the other. The lowering of the mercury in the auxiliary tube required to pass from a setting of the left-hand manometer to a setting of the right-hand manometer, was found on three separate days to be 50·3 millims., 51·3 millims., 49·9 millims., or,

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as a mean, 50·5 millims. As regards the section of the auxiliary tube, it was found that a mercury thread occupying 85 millims. of it weighed 5·335 grammes. The proportional difference of volume is thus

$$\frac{50{\cdot}5 \times 5{\cdot}335}{85 \times 13{\cdot}54 \times 2845} = {\cdot}000082\,;$$

and the same fraction represents the proportion by which the left-hand measuring rod exceeds in length its fellow on the right. It would seem that by this procedure the lengths of the rods are compared to about a millionth part.

In the notation employed in the calculations

$$H_1 = 1{\cdot}000082\,H_2,$$

whence

$$\frac{H_1+H_2}{2H_2} = 1{\cdot}000041.$$

It may be observed that an error in the comparison of H_1 and H_2 enters to only half its amount into the final result.

The Observations.

The manipulation necessary to imprison the right quantity of gas was described in the former paper. When this has once been secured the observations are straightforward. On each occasion 6 readings were taken, extending over about an hour, during which time the temperature always rose, and the means were combined into what was treated as one observation.

A complete set usually included eight observations at the high pressure, in four of which one large bulb was in use, and in the second four the other bulb. Interpolated in the middle of these were the observations (usually six in number) of the low pressure where both large bulbs were occupied by gas. Further, each set included eight observations relating to the side apparatus, in which the large bulbs stood charged with mercury. In this way each set contained within itself complete material for the elimination of V_3, which might possibly vary from time to time with the character of the contact between mercury and glass in the lower chamber of the right-hand manometer. Finally the means were taken of all the corresponding observations, no further distinction being maintained between the two large bulbs.

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

I.	V_1	θ_1	V_3	T_1	V_5	t_1
II.	$\frac{1}{2}V_1$	θ_2	V_3	T_2	V_4	T_2
III.	—	—	V_3	T_3	V'_5	t_3
IV.	—	—	V_3	T_4	V'_4	T_4

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In the first observation V_1 is the volume of the two large bulbs together and θ_1 the temperature of the water-bath, reckoned from some convenient neighbouring temperature as standard. V_3 is the ungauged volume already discussed whose temperature T_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 associated thermometer. In the second observation $\frac{1}{2}V_1$ is the (mean) volume of a single 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 T_2. III. and IV. represent the corresponding observations when the large bulbs are not used. The temperatures of the mercury in the manometric columns are represented by τ_1, τ_2, τ_3, τ_4.

As an example of the actual quantities, the observations on hydrogen, April 9–24, 1903, may be taken. The values of V_1 and V_3 are approximate.

$$V_1 = 632{\cdot}6, \quad V_3 = 11{\cdot}02, \quad V_5 = 13{\cdot}978, \quad V_4 = 1{\cdot}504,$$

$$V_5 - V'_5 = -{\cdot}650, \quad V_4 - V'_4 = -{\cdot}245.$$

$$\theta_1 = -{\cdot}007, \quad \theta_2 = +{\cdot}001; \quad t_1 = +{\cdot}31, \quad t_3 = -{\cdot}01.$$

$$T_1 = +{\cdot}69, \quad T_2 = +{\cdot}78, \quad T_3 = +{\cdot}23, \quad T_4 = +{\cdot}25.$$

$$\tau_1 = +{\cdot}43, \quad \tau_2 = +{\cdot}54, \quad \tau_3 = +{\cdot}05, \quad \tau_4 = +{\cdot}11.$$

The volumes are in cubic centimetres and the temperatures are in Centigrade degrees, reckoned from 11°.

The Reductions.

The simple theory has already been given, 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 the mercury and of the iron in the manometers. If the actual heights of the mercury (at the same temperature) be H_1, H_2, we have for the relative *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 occupyimg a known volume is to be found by dividing the volume by the absolute temperature. Hence each volume is to be divided by $1+\beta\theta$, $1+\beta T$, $1+\beta t$, as the case may be, where β is the reciprocal of the absolute temperature chosen as a standard for the set. Thus in the above example for hydrogen, $\beta = \frac{1}{273+11} = \frac{1}{284}$.

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Our equations expressing that the quantities of gas are the same at the single and at the doubled pressures accordingly take the form

$$\frac{H_2}{1+m\tau_1}\left\{\frac{V_1}{1+\beta\theta_1}+\frac{V_3}{1+\beta T_1}+\frac{V_5}{1+\beta t_1}\right\}=\frac{B(H_1+H_2)}{1+m\tau_2}\left\{\frac{\frac{1}{2}V_1}{1+\beta\theta_2}+\frac{V_3+V_4}{1+\beta T_2}\right\},$$

$$\frac{H_2}{1+m\tau_3}\left\{\frac{V_3}{1+\beta T_3}+\frac{V'_5}{1+\beta t_3}\right\}=\frac{B(H_1+H_2)}{1+m\tau_4}\,\frac{V_3+V'_4}{1+\beta T_4},$$

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

By subtraction and neglect in the small terms of the squares of the small temperature differences, we obtain

$$\begin{aligned}\frac{1}{(1+m\tau_1)(1+\beta\theta_1)}-\frac{B(H_1+H_2)}{2H_2(1+m\tau_2)(1+\beta\theta_2)}\\ =\frac{V_3}{V_1}\{m(\tau_1-\tau_3-2\tau_2+2\tau_4)+\beta(T_1-T_3-2T_2+2T_4)\}\\ -\frac{2V_4}{V_1}\{m(\tau_2-\tau_4)+\beta(T_2-T_4)\}\\ +\frac{V_5}{V_1}\{m(\tau_1-\tau_3)+\beta(t_1-t_3)\}\\ +\frac{2(V_4-V'_4)}{V_1}\{1-m\tau_4-\beta T_4\}\\ -\frac{V_5-V'_5}{V_1}\{1-m\tau_3-\beta t_3\}.\end{aligned}$$

The first three terms on the right, viz., those in V_3, V_4, V_5, vanish if $\tau_1=\tau_3$, $\tau_2=\tau_4$, $T_1=T_3$, $T_2=T_4$, $t_1=t_3$. If in general R denote the sum of the five terms, we may write with sufficient approximation for the actual experiments

$$B=\frac{2H_2}{H_1+H_2}+m(\tau_2-\tau_1)+\beta(\theta_2-\theta_1)-R.$$

It may be well to exhibit further the steps of the reduction in the case of hydrogen above detailed. The five terms composing R are

$$\begin{aligned}\text{Term in } V_3 &= -\cdot000038\\ \text{,, } V_4 &= -\cdot000009\\ \text{,, } V_5 &= +\cdot000026\\ \text{Term in } V_4-V'_4 &= -\cdot000775\\ \text{,, } V_5-V'_5 &= +\cdot001027\\ \hline R &= +\cdot000231\end{aligned}$$

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Thus

$$\begin{aligned} 2H_2/(H_1+H_2) &= 1-{\cdot}000041 \\ m(\tau_2-\tau_1) &= +{\cdot}000019 \\ \beta(\theta_2-\theta_1) &= +{\cdot}000028 \\ -R &= -{\cdot}000231 \\ \hline B &= {\cdot}999775 \end{aligned}$$

In the above calculation the volumes of the principal capacities at the two pressures have been assumed to be as 2 : 1 exactly. As has already been explained, the value of B so obtained is subject to correction of ·000021 to be subtracted.

Hence

$$B = {\cdot}99975,$$

a result in strictness applicable to the temperature 11·0 C. The hydrogen is somewhat less compressible than according to Boyle's law, as was to be expected from its known behaviour at pressures above atmosphere.

The Results.

After the above explanation it will suffice to record the final results of the various sets of observations.

HYDROGEN.

Date.	Source.	Temperature.	B.
January 17 to 27, 1903	Palladium	10·6	·99974
„ 30 to February 10, 1903 . . .	„	10·6	·99974
April 9 to 24, 1903	„	11·0	·99975
Mean		10·7	·99974

In the case of hydrogen the agreement of single results is remarkably good. This gas, as well as all the others, was carefully dried with phosphoric anhydride.

CARBONIC OXIDE.

Date.	Source.	Temperature.	B.
May 2 to 14, 1903.	Ferrocyanide.	11·7	1·00033
„ 19 to 29, 1903.	„	12·5	1·00024
June 17 to 29, 1903	„	14·5	1·00024
July 1 to 15, 1903	„	16·6	1·00023
Mean		13·8	1·00026

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The gas was prepared from ferrocyanide of potassium and sulphuric acid,* and purified from CO_2 by a long tube of alkali. It is barely possible that the abnormally high number which stands first in the table may be due to imperfect purification on that occasion; on principle, however, it is retained, as no suspicion suggested itself at the time.

NITROGEN.

Date.	Source.	Temperature.	B.
July 23 to August 5, 1903	Chemical	16·5	1·00012
August 7 to 19, 1903	,,	16·4	1·00022
October 5 to 20, 1903	,,	15·4	1·00011
,, 28 to November 9, 1903	From air.	13·2	1·00015
November 10 to 23, 1903	,,	12·9	1·00016
Mean		14·9	1·00015

The "chemical" nitrogen was from potassium nitrite and ammonium chloride. That "from air" was prepared by bubbling air through ammonia and passing over red-hot copper and sulphuric acid, with the usual precautions. It contained about 1 per cent. of argon; but this could hardly influence the observed numbers.

OXYGEN.

Date.	Source.	Temperature.	B.
November 25 to December 5, 1903 . . .	Permanganate	12·4	1·00034
December 8 to 19, 1903	,,	10·9	1·00042
December 21, 1903, to January 5, 1904. .	,,	10·2	1·00038
Mean		11·2	1·00038

It remains to record certain results with air (free from H_2O and CO_2). It is curious that the greatest discrepancies show themselves here.

The earlier observations, at the end of 1902, were made before the apparatus was perfected, and gave as a mean B = 1·00022. Subsequently, return was made to air.

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* See 'Roy. Soc. Proc.,' vol. 62, p. 204, 1897; 'Scientific Papers,' vol. 4, p. 347.

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AIR.

Date.	Temperature.	B.
April 1 to 11, 1904	9·5	1·00035
April 12 to 26, 1904	11·3	1·00016
May 14 to 26, 1904	13·5	1·00018
Mean	11·4	1·00023

In partial explanation of the high number which stands first, it should perhaps be mentioned that the set of observations in question was incomplete. Owing to an accident, it was impossible to return from the lower pressure to the higher pressure, as had been intended.

It may be well to repeat here that

$$\mathrm{B} = \frac{pv \text{ at } \frac{1}{2} \text{ atmosphere}}{pv \text{ at } 1 \text{ atmosphere}},$$

the temperature being constant and having the values recorded in each case.

Although the accordance of results seems to surpass considerably anything attained in observations below atmosphere at the time this work was undertaken, I must confess that, except in the case of hydrogen, it is not so good as I had expected in view of the design of the apparatus and of the care with which the observations were made. I had supposed that an error of 3 parts in 100,000 (at the outside), corresponding to $\frac{1}{100}$° C., was as much as was to be feared. As it is, I do not believe that the discrepancies can be explained as due to errors of temperature, or of pressure, or of volume so far as the readings are concerned. But it is possible that a variable contact between mercury and glass in the lower chamber of the first manometer may have affected the volume in an uncertain manner, though care was taken to obviate this as far as could be. It is to be remembered, however, that, except as to the comparison of the two manometers, all sources of error enter independently in each set of observations; and that a mere repetition of the readings without a change in the gas or in the pressure (from half atmosphere to one atmosphere, or *vice versâ*) gave very much closer agreements.

The values of B here discussed are the same as those given in the Preliminary Notice,* except that no account was there taken of the small deviation in the ratio of volumes from 2 : 1 in consequence of the yielding to pressure. If we measure p in atmospheres and assume, as has been usually done, *e.g.*, by REGNAULT and VAN DER WAALS, that at small pressures the equation of an isothermal is

$$pv = \mathrm{PV}\,(1+\alpha p),$$

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* 'Roy. Soc. Proc.,' 73, p. 153, February, 1904.

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where PV is the value of the product in a state of infinite rarefaction, then

$$B = \frac{1+\frac{1}{2}\alpha}{1+\alpha} = 1-\tfrac{1}{2}\alpha,$$

or

$$\alpha = \frac{1}{pv}\frac{d\,(pv)}{dp} = 2\,(1-B).$$

In applying α to correct the observed densities of gases at atmospheric pressure, we are met with the consideration that α is itself a function of temperature, and that the value of α really required for our purpose is that corresponding to 0° C., at which temperature the weighing vessels are charged with gas.* In the case of the principal gases α is so small that its correction for temperature was not likely to be important for the purpose in hand, but when we come to CO_2 and N_2O the situation might well be altered. If we know the pressure-equation of the gas, there is no difficulty in calculating a correction to α in terms of the critical constants. I had, in fact, calculated such a correction for carbonic acid after VAN DER WAALS, when I became acquainted with the memoir of D. BERTHELOT,† in which this and related questions are admirably discussed. The "reduced" form of VAN DER WAALS' equation is

$$\left(\pi+\frac{3}{v^2}\right)(v-\tfrac{1}{3}) = \tfrac{8}{3}\theta\,;$$

pressure, volume and temperature being expressed in terms of the critical values. From this we find

$$\frac{1}{\pi v}\frac{d\,(\pi v)}{d\pi} = \frac{1}{8\theta}\left(1-\frac{27}{8}\frac{1}{\theta}\right);$$

and the effect of a change of temperature upon the value of α is readily deduced. Indeed, if the pressure-equation and the critical values could be thoroughly trusted, there would be no need for experiments upon the value of α at all. The object of such experiments is to test a proposed pressure-equation, or to find materials for a new one; but consistently with this we may use a form, known to represent the facts approximately, to supply a subordinate correction.

A careful discussion of the available data relating to various gases has led D. BERTHELOT to the conclusion that the facts at low pressure are not to be reconciled with VAN DER WAALS' equation, either in its original form or as modified by CLAUSIUS (*i.e.*, with the insertion of the absolute temperature in the denominator of the cohesive term).

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* Except in the comparison of hydrogen and oxygen.

† "Sur les thermomètres à gaz," 'Travaux et Mémoires du Bureau International,' tome XIII. I am indebted to the Director for an early copy of this memoir, and of that of CHAPPUIS presently to be referred to.

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MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES
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The equation which best represents the relation of $d(\pi v)/d\pi$ to temperature is

$$\frac{d(\pi v)}{d\pi} = \tfrac{1}{4}\left(1 - \frac{6}{\theta^2}\right),$$

corresponding to the pressure-equation for *low densities*

$$\left(\pi + \tfrac{16}{3}\frac{1}{\theta v^2}\right)\left(v - \tfrac{1}{4}\right) = \tfrac{32}{9}\theta.$$

Also

$$\frac{1}{\pi v}\frac{d(\pi v)}{d\pi} = \frac{9}{128\,\theta}\left(1 - \frac{6}{\theta^2}\right).$$

As an example, let us apply this formula to find for oxygen what change must be made in α in order to pass from the temperature of the observations (11·2° C.) to 0° C. If θ_0 be the value of θ for 0° C., we have

$$\theta_0 = \frac{273}{273-118} = \frac{273}{155}, \qquad \theta = \frac{273+11\cdot 2}{155} = \frac{284\cdot 2}{155}.$$

The factor by which the observed value of α must be multiplied is thus

$$\frac{\theta_0^{-1} - 6\,\theta_0^{-3}}{\theta^{-1} - 6\,\theta^{-3}}$$

being the same whether the pressures be reckoned in terms of the critical pressure or in atmospheres. In the case of oxygen the factor is

$$\frac{\cdot 568 - 1\cdot 097}{\cdot 545 - \cdot 973} = \frac{\cdot 529}{\cdot 428} = 1\cdot 236.$$

The observed value of α is $-\cdot 00076$, corresponding to 11·2° C. Hence at 0° C. we should have

$$\alpha = -\cdot 00076 \times 1\cdot 236 = -\cdot 00094.$$

It will be seen that the correction has a considerable relative effect; but α is so small that the calculated atomic weights are not much influenced. It must be admitted, however, that observations for the present purpose would be best made at 0° C.; to this, however, my apparatus does not lend itself.

The following table embodies the results thus obtained.

Gas.	B.	α.	Temperature.	α corrected to 0° C.
			° C.	
Oxygen	1·00038	−·00076	11·2	−·00094
Hydrogen	·99974	+·00052	10·7	+·00053
Nitrogen	1·00015	−·00030	14·9	−·00056
Carbonic oxide	1·00026	−·00052	13·8	−·00081
Air	1·00023	−·00046	11·4	—
Carbon dioxide	1·00279	−·00558	15·0	−·00668
Nitrous oxide	1·00327	−·00654	11·0	−·00747

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The experiments on carbonic anhydride and on nitrous oxide were of later date, having been postponed until the apparatus had been well tested on other gases.

In both these cases it was found that the readings were less constant than usual, signs being apparent of condensation upon the walls of the containing vessels, or possibly upon the cement in the manometer. Under these circumstances it seemed desirable to avoid protracted observations and to concentrate effort upon reproducing the conditions (especially as regards time) as closely as possible with and without the use of the large bulbs. In this way, for example, the question of the cement is eliminated. Condensation upon the walls of the large bulbs themselves, if it occurs, cannot be eliminated from the results; all that we can do is not unnecessarily to increase the opportunity for it by allowing too long a time. It is certain that, unless by chance, these results are less accurate than for the other gases, *i.e.*, less accurate absolutely, but the value of α is so much larger that in a sense the loss of accuracy is less important. Two entirely independent results for nitrous oxide agreed well. They were:—

November 22, 26, 1904	B = 1·003295
„ 23, 29, 1904	B = 1·003252
Mean	B = 1·00327

The gas was from the same supply as had been used for density determinations.

In applying these results to correct the ratios of densities as observed at atmospheric pressure to what would correspond to infinite rarefaction, we have, taking oxygen as a standard, to introduce the factor $(1+\alpha)/(1+\alpha_0)$, α_0 being the value for oxygen. Taking α from the third column, which may be considered without much error to correspond to a temperature of 13° C. throughout, and also from the fifth column, we have:—

Gas.	Correcting factor for about 13° C.	Correcting factor for 0° C.
Hydrogen	1·00128	1·00147
Nitrogen	1·00046	1·00038
Carbonic oxide	1·00024	1·00013
Carbon dioxide	·99518	·99426
Nitrous oxide	·99422	·99347

The double of the first number in the second column, viz., 2·00256, represents, according to AVOGADRO'S law, the volume of hydrogen which combines with one volume of oxygen to form water, the pressure being atmospheric and the temperature 13° C. SCOTT gave 2·00245 for 16° C. In his later work MORLEY found 2·0027, but

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this appears to correspond to 0° C. The third column in the above table gives for this temperature 2·0029. The agreement here may be regarded as very good.

In correcting the densities directly observed at 0° C., in order to deduce molecular weights, we must use the third column of the above table.* Oxygen being taken as 32, the densities of the various gases at 0° C., and at atmospheric and very small pressures, as deduced from my own observations,† are :—

Gas.	Atmospheric pressure.	Very small pressure.
H_2	2·0149 (16° C.)	2·0173 = 2 × 1·0086
N_2	28·005	28·016 = 2 × 14·008
CO	28·000	28·003
CO_2	44·268	44·014
N_2O	44·285	43·996

From the researches of M. LEDUC and Professor MORLEY it is probable that the above numbers for hydrogen are a little, perhaps nearly one thousandth part, too high. The correction to very small pressures has to be made in a different manner for hydrogen and for the other gases, in consequence of the fact that the observed ratio of densities corresponded not to 0° C., but to 16° C.‡ Now the observed values of B for hydrogen and oxygen relate to about 11° C., so that if we correct α to 0° C., we are, in fact, altering it in the wrong direction. I have employed as the correcting factor to 16° C. the value 1·00118.

It may be noticed that the discrepancy between my ratio of hydrogen to oxygen and that of M. LEDUC is partially explained by the fact that my comparisons were at 16° C., and his at 0° C.

The uncorrected number for nitrogen (14·003 corresponding to O = 16) has already been given,§ and contrasted with the 14·05 obtained by STAS. This question deserves the attention of chemists. If AVAGADRO's law be strictly true, it seems impossible that the atomic weight of nitrogen can be 14·05.

The atomic weight of carbon can be derived in three ways from these results. First from CO and O :—

$$\begin{array}{r} \text{CO} = 28{\cdot}003 \\ \text{O} = 16{\cdot}000 \\ \hline \text{C} = 12{\cdot}003 \end{array}$$

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[*] The correction for temperature was neglected in the Preliminary Notice.

[†] 'Roy. Soc. Proc.,' vol. 53, p. 134, 1893; vol. 62, p. 204, 1897. 'Scientific Papers,' vol. 4, pp. 39, 352. Also for Nitrous Oxide, 'Roy. Soc. Proc.,' vol. 74, p. 181, 1904.

[‡] See 'Roy. Soc. Proc.,' vol. 50, p. 448, 1892; 'Scientific Papers,' vol. 3, p. 533.

[§] RAYLEIGH and RAMSAY, 'Phil. Trans.,' A, vol. 186, p. 187, 1895; 'Scientific Papers,' vol. 4, p. 133.

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Secondly from CO_2 and O :—

$$\begin{array}{r} CO_2 = 44{\cdot}014 \\ O_2 = 32{\cdot}000 \\ \hline C = 12{\cdot}014 \end{array}$$

Thirdly from CO_2 and CO. This method is independent of the density and compressibility of oxygen :—

$$\begin{array}{r} 2CO = 56{\cdot}006 \\ CO_2 = 44{\cdot}014 \\ \hline C = 11{\cdot}992 \end{array}$$

It will be seen that the number for CO_2 is too high to give the best agreement. Were we to suppose that the true number for CO_2 was 44·004, instead of 44·014, we should get by the second method 12·004 and by the third 12·002, in agreement with one another and with the result of the first method. The alteration required is less than one part in 4000, and is probably within the limits of error for the compressibility (as reduced to 0° C.), and perhaps even for the density. The truth is that the second and third methods are not very advantageous for the calculation of the atomic weight of carbon, and would perhaps be best used conversely.

Finally the molecular weight of N_2O allows of another estimate of that of nitrogen. Thus

$$\begin{array}{r} N_2O = 43{\cdot}996 \\ O = 16{\cdot}000 \\ \hline N_2 = 27{\cdot}996, \end{array}$$

whence $N = 13{\cdot}998$.

It should be remarked that these results relative to CO_2 and N_2O depend very sensibly upon the correction of α from about 13° C. to 0° C., and that this depends upon the discussion of M. D. BERTHELOT. M. BERTHELOT has himself deduced molecular weights in a similar manner, founded upon LEDUC's measures of densities.

It remains to refer to some memoirs which have appeared since the greater part of the present work was finished. Foremost among these is that of M. CHAPPUIS,* who has investigated in a very thorough manner the compressibilities of hydrogen, nitrogen, and carbonic anhydride at various temperatures and at pressures in the neighbourhood of the atmospheric. For hydrogen M. CHAPPUIS finds at 0° C. $\alpha = +{\cdot}00057$ per atmosphere, and for nitrogen $\alpha = -{\cdot}00043$. In the case of carbonic anhydride pv departs sensibly from a linear function of p. M. BERTHELOT gives as a more accurate expression

$$pv = 1 - \frac{{\cdot}00670}{v},$$

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* "Nouvelles Études sur les Thermomètres à gaz," 'Extrait du tome XIII. des Travaux et Mémoires du Bureau International des Poids et Mesures.'

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founded on Chappuis' measures and applicable at 0° C. The unit of pressure is here the atmosphere. According to this, for $p = 1$ we get $pv = 1 - {\cdot}00665$, as compared with $pv = 1$ for $v = \infty$, in close agreement with my value recorded above.

A comparison of Chappuis' method and apparatus with mine may not be without interest. On his side lay a very considerable advantage in respect of the "nocuous space" V_3, inasmuch as this was reduced to as little as 1·1 cub. centims., whereas mine was ten times as great. The advantage would be important when working at temperatures other than that of the room. Otherwise, the influence of V_3 did not appear to prejudice my results, except in so far as V_3 might be *uncertain* from capillarity in the manometer; and this cause of error would operate equally in Chappuis' apparatus.

So far as a 2 : 1 ratio suffices, my method of varying the volume seems the better, and, indeed, not to admit of improvement.

In the manometric arrangements it would seem that both methods are abundantly accurate, so far as the readings are concerned. I am disposed, however, to favour a continual verification of the vacuum by the Töpler pump, and, what is more important, a method of reading which is independent of possible errors arising from irregular refraction at the walls of the manometric tubes.

It may be remarked that, with a partial exception in the case of CO_2, M. Chappuis' work relates to pressures *above* atmosphere.

Other papers which have appeared since my Preliminary Notice are those of M. Guye, working both alone and with the assistance of collaborators.[*] Several of these relate to the atomic weight of nitrogen and insist on the discrepancy between the number resulting from density and that of Stas. Among the methods employed is that of decomposing nitrous oxide by an incandescent iron wire and comparing the original volume with the residual nitrogen. In my hands[†] this method failed to give good results, in consequence, apparently, of the formation of higher oxides of nitrogen.

P.S., March 6.—Some observations upon Ammonia may here be appended. The gas was evolved (almost without warmth) from the solution in water, and was dried by very slow passage over fragments of caustic potash. The precautions mentioned under nitrous oxide were here followed with more minute care. The glass surfaces were in contact with the gas for weeks, either at half atmospheric or whole atmospheric pressure, and the observations at full pressure were not commenced until that pressure had prevailed for a day or more. On the reduction of pressure to the half atmospheric, ammonia was sensibly liberated from the walls, and perhaps from the cement in the manometer. In the observations to be compared, the *same*

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[*] 'C. R.,' April 25, May 16, June 13, July 4, October 31, 1904.

[†] 'Roy. Soc. Proc.,' vol. 62, p. 204, 1897; 'Scientific Papers,' vol. 4, p. 350.

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interval was allowed to elapse between the reduction of pressure and the corresponding readings, whether the big bulbs were in use or not. Any anomalies not dependent upon the walls of the big bulbs themselves are thus eliminated. In addition to commercial ammonia, a special sample prepared by Dr. SCOTT in accordance with STAS' directions was employed. It will be seen that there is no certain difference between the results from the two kinds.

The departure from BOYLE's law, in this case, is almost more than can be provided for in the side apparatus. It became therefore necessary to allow a small difference of temperature between the high- and low-pressure observations such as would somewhat prejudice the accuracy of the results, were it possible to expect the attainment of the same high degree of accuracy as for the less condensable gases. Under the actual circumstances the variation of temperature was of no importance.

AMMONIA.

Date.	Source.	Temperature.	B.
		° C.	
December 31, 1904, January 4, 1905 .	Commercial	10·3	1·00647
„ 28, 1904, „ 5, 1905 .	„	9·2	1·00631
Mean	Commercial	9·7	1·00639
January 23, 25, 1905	SCOTT'S	9·6	1·00630
„ 24, 27, 1905	„	9·8	1·00617
Mean	SCOTT'S	9·7	1·00624
Mean of all		9·7	1·00632

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