

LIMITING DENSITIES

By R. WHYTLAW-GRAY, F.R.S.

(EMERITUS PROFESSOR, LEEDS UNIVERSITY)

THE limiting density principle, due to Lord Rayleigh¹ and to D. Berthelot,² postulates that, at sufficiently low pressure, all gases and vapours obey the gas laws. This ideal state, in which $PV = RT$ exactly, lies far below atmospheric pressure. If, instead of working with gases at pressures not far removed from atmospheric, we could investigate the change in PV over a range say from 0.25 to 1 mm. pressure, it would for the majority of gases be exceedingly difficult to detect any deviations, even supposing that measurements could be made with the same percentage accuracy as at higher pressures. In this state all gases would obey Boyle's law, all would have the same coefficient of expansion, and since Avogadro's law would be strictly true a comparison of their densities would give an exact measure of their relative molecular weights.

Although this ideal state is in a pressure region in which exact measurements of density or compressibility are not practicable, precise data are available for a large number of gases between the pressure limits of 800 and 200 mm. of mercury. Very few have been obtained below 100 mm.

Now for all the permanent gases, *i.e.*, those gases which at normal temperatures are well above their critical temperatures, and for other gases as well, it has been found that over this pressure range PV is a strictly linear function of P , so that if we suppose this linearity to persist downwards we can find the value of PV for highly rarefied gases right down to the limit when P approaches zero. That is to say that, although we cannot make direct measurements on rarefied gases with high percentage accuracy, we can measure the deviation at higher pressures and from this calculate the behaviour at very low pressures.

Consider for example the gas oxygen. Its normal density is 1.42896 g. per litre at 0° and 1 atmosphere at sea level and latitude 45°. Hence 32 g. occupy $32/1.42896 = 22.3939$ litres under these conditions. That is, PV for this gas at 1 atmosphere is 22.3939 l. atm. mole⁻¹; on expansion PV increases linearly and on extrapolation to the limit becomes 22.4145 l. atm. mole⁻¹. Since the gas is now in the ideal state it is clear that 1 g.-mol. of a perfect gas (molecular weight = 32) would at N.T.P. occupy 22.4145 litres instead of 22.3939 litres actually occupied by 1 g.-mol. of oxygen. One g.-mol. of any other gas would in the limit when $P = 0$ have the same PV product, but of course each would have its own characteristic value when $P = 1$ atmosphere. This is shown graphically in the figure.

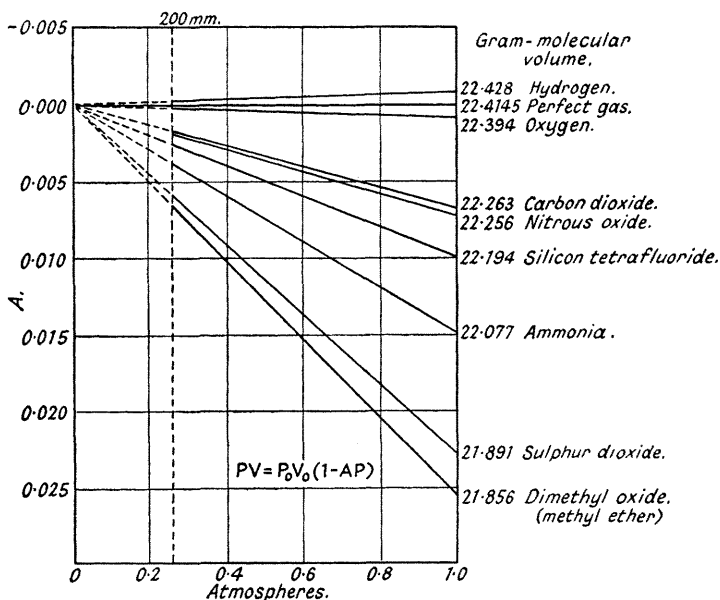
Now for oxygen the ratio of PV at 1 atmosphere to PV at zero pressure at 0°, *i.e.*, $(PV)_1/(PV)_0 = 22.3939/22.4145 = 0.99908 = (1 - 0.00092) = (1 - A)$,

¹ *Proc. Roy. Soc.*, 1892, 50, 448.

² *Compt. rend.*, 1898, 126, 954.

which is the deviation from Boyle's law when oxygen of unit PV at zero pressure is compressed to 1 atmosphere; A is called the compressibility coefficient and from the above relationship is clearly $[(PV)_0 - (PV)_1]/(PV)_0$, and since PV varies linearly with P the PV at any intermediate pressure can be calculated. Thus we get the general expression $pv = (pv)_0(1 - Ap)$, where pv and $(pv)_0$ are the values for any one mass of gas at any pressure in the vicinity of 1 atmosphere and at zero pressure, p being expressed in atmospheres.

The density of a perfect gas of molecular weight 32 is then the density of oxygen $\times 22.3939/22.4145 = 1.42896(1 - A) = 1.42765$, which is the limiting density of oxygen, or the density oxygen gas would have if it behaved as a perfect gas.



Hence if L_n^1 , L_n^2 , and L_n^3 are the normal densities of three gases of molecular weights M_1 , M_2 , and M_3 , and their respective compressibility coefficients are A_1 , A_2 , and A_3 , then their limiting densities L_{lim}^1 , L_{lim}^2 , and L_{lim}^3 are $L_n^1(1 - A_1)$, $L_n^2(1 - A_2)$, and $L_n^3(1 - A_3)$, so that

$$\frac{\text{Limiting density}}{\text{Normal density}} = 1 - A$$

Suppose L_n^1 , M_1 , and A_1 refer to oxygen, then the molecular weights of the other two are given by

$$M_2 = 32L_n^2(1 - A_2)/L_1(1 - A_1) \quad \text{and} \quad M_3 = 32L_n^3(1 - A_3)/L_1(1 - A_1)$$

or since $32/L_n^1(1 - A_1) = 22.4145$ l. atm.,

$$M_2 = 22.4145L_n^2(1 - A_2) \quad \text{and} \quad M_3 = 22.4145L_n^3(1 - A_3)$$

Frequently the compressibilities are expressed in another notation introduced by Ph. A. Guye,³ in which $P_0V_0/P_1V_1 = 1 + \lambda$ instead of $P_1V_1/P_0V_0 = 1 - A$ for the pressure range of 1 to 0 atmosphere. Hence, if the 0° isothermals are linear, $1 - A = 1/(1 + \lambda)$ and $A = \lambda/(1 + \lambda)$. For gases which exhibit small deviations from ideality, A is numerically nearly equal to λ , but for others the difference is significant. As W. Cawood and H. S. Patterson⁴ have pointed out, $1 + \lambda$ refers only to the ratio of PV at 1 atm. to PV at infinite dilution, and is inapplicable for intermediate pressures for which Berthelot's expression is more accurate. Guye's notation being used, the molecular weight M of a gas is given by

$$M = 22.4145L_n/(1 + \lambda)$$

and

$$\frac{\text{Normal density}}{\text{Limiting density}} = \frac{1}{1 - A} = 1 + \lambda$$

The question might be asked whether the correction factor $1 + \lambda$ or $1 - A$ could not be calculated with sufficient approximation from an equation of state such as that of van der Waals; for it can be shown that $1 + \lambda = (1 + a)(1 - b)$, where a and b are the well-known "constants", hence $M = 22.4145 \times L_n/(1 + a)(1 - b)$. Unfortunately, a and b are not constants and vary with temperature and pressure and when calculated from the critical constants and inserted in this expression give erroneous values for M . Guye in 1905 proposed a method of correction which he named "Reduction des Elements Critique" which gave for the permanent gases a satisfactory approximation but it has not proved of general applicability. More accurate values of $1 + \lambda$ or $1 - A$ can be obtained from the Beattie-Bridgeman equation, as J. B. M. Coppock⁵ has shown, but the various constants in this equation have to be found for each gas from high-pressure measurements.

It is clear then that with the help of the limiting density principle we can determine:

- (a) the relative molecular weights of gases directly in terms of the standard oxygen;
- (b) the volume of a gram-mole of a perfect gas at the ice point at a pressure of 1 atm., *i.e.*, the value of PV per mole in the equation $PV = RT_0$;
- (c) if the exact value for T_0 the temperature of melting ice is known, the fundamental constant R can be found.

The temperature of melting ice on the absolute or thermodynamic scale is defined in terms of the coefficient of expansion of a perfect gas, which can be deduced from the coefficients of expansion of real gases. Because of the deviations from the ideal, the coefficients of expansion at constant pressure (α) and constant volume (β) differ somewhat when, for any one gas, they are measured at the same initial pressure and over the same temperature range. When α and β are determined at lower and lower

³ *J. Chim. physique*, 1908, **6**, 769.

⁴ *J.*, 1933, 619.

⁵ *J. Physical Chem.*, 1933, **37**, 995.

initial pressures they approach each other and on extrapolation to the limit become identical, giving the one value γ , the expansion coefficient of a perfect gas. The exact evaluation of γ is of primary importance in thermometry. Starting with the work of Chappuis, much careful research of high accuracy has been carried out to determine this important coefficient in order to find the ice point on the absolute scale and to correct temperatures measured by gas thermometers. D. Berthelot in his classical memoir "Sur les Thermometres à Gaz" defined the general relationships between the compressibility coefficients of real gases and α and β , but accurate thermometry is a field in itself and cannot be discussed here. It must suffice to state that the most recent work, according to R. T. Birge,⁶ fixes the ice point on the absolute scale at $273.16^\circ \pm 0.01^\circ \text{K}$.

In what follows, the application of the limiting density principle to the determination of molecular and atomic weights will be considered.

The range of the method is, however, restricted, for although upwards of 100 stable gases are known these contain only 22 elements. If it could be extended to include vapours it would be possible to add another 10 or more elements to the total. Its great advantage over gravimetric analysis is that it provides a direct link with oxygen and thus avoids cumulative errors.

Of course its use as a check on chemically determined atomic weights depends upon the accuracy with which densities and compressibilities can be measured. Up to the present, in spite of much laborious research, data for only a limited number of gases are known with sufficient precision to give molecular weights accurate to 1 part in 10,000 or more. This is due in part to errors inherent in gasometric operations, and also to the difficulty of preparing many gases in a high state of purity. Then again, until recently the form of the PV - P isothermals for the easily condensable gases was doubtful, which made exact extrapolation to zero pressure uncertain.

The development, however, of more exact methods of measurement combined with improved ways of low-temperature fractionation and purification now make it possible to obtain more data of high precision.

Applications.—Gases the densities and compressibilities of which have up to the present been determined with accuracy are

- (1) The inactive gases with the exception of krypton and radon.
- (2) H_2 , N_2 , O_2 , CO , NO , N_2O , C_2H_4 , C_2H_2 , C_3H_8 , C_3H_6 , $(\text{CH}_3)_2\text{O}$, CH_3Cl , CH_3F , CF_4 , SiF_4 , HCl , HBr , NH_3 , PH_3 , SO_2 , H_2S , and SiH_4 .

Thus, apart from (1) for which no analytical data are possible, this list covers only the elements O (standard), H, N, C, S, Si, F, Cl, Br, and P. It could be extended to B, As, Sb, Ge, Se, Te, and I by utilising the hydrides or fluorides, which with the exception of H_2Se ⁷ have not been investigated with the object of finding molecular weights. Notwithstanding this limitation, physicochemical methods have played an important part in fixing accurate values for many atomic weight ratios.

⁶ *Rep. Progr. Physics*, 1941, **8**, 110.

⁷ P. Bruylants and A. Bytbeier, *Bull. Soc. chim. Belge*, 1912, 856.

When, after the discovery of argon, Rayleigh and afterwards Ledue found that the density of pure nitrogen indicated an atomic weight for this element very close to 14, an error in Stas's value 14.044 was suspected. Limiting-density determinations of nitric and nitrous oxides were made shortly afterwards by Ph. A. Guye⁸ and by R. W. Gray⁹ independently, which together with the analysis of the same oxides, definitely proved that this atomic weight could not exceed 14.01. It was then pointed out by Guye¹⁰ that this error in Stas's nitrogen indicated errors in many of the fundamental atomic weights including that of the sub-standard silver. These were only corrected after many years of careful research begun by Richards and his school at Harvard, and completed by G. P. Baxter, O. Höning Schmid, and others.

Later, the limiting-density method, applied to carbon monoxide¹¹ shortly after the discovery of ¹³C, indicated a proportion of about 1% of this isotope and an atomic weight of 12.01 for the mixed element, significantly higher than 12.00, the then-accepted value. Mass spectroscopy, as well as gravimetric analysis, has since confirmed the higher value. Again, accurate measurements carried out on highly purified specimens of the inactive gases have, with the exception of krypton, given atomic weights in close concordance with mass spectroscopy values.

Then there is the case of phosphorus, the atomic weight of which when first computed from Aston's earlier estimate in 1927 was found to be 30.978, a value so much lower than 31.02, well established by chemical methods, that the existence of higher isotopes was suggested. A careful determination of the limiting density of very pure phosphine by M. Ritchie¹² in 1930 led, however, to 30.977, which was confirmed in 1937 by O. Höning Schmid and W. Menn¹³ by the analysis of POCl₃ which gave 30.978, and in 1940 by Höning Schmid and F. Hirschbold-Wittner,¹⁴ who analysed POBr₃ and found 30.974. Subsequent and more accurate mass-spectrum determinations proved the element to be a simple one and gave the value 30.975. The accepted International value is now 30.98.

Usually, limiting-density methods give results in close agreement with mass-spectroscopy measurements; another instance is fluorine for which the limiting densities of CF₄ and CH₃F indicate a value slightly below 19 in agreement with Aston's latest measurements.

There is one striking instance, however, in which the data obtained by the mass spectrograph are in disaccord both with the results of chemical analysis and with limiting-density determinations. It is for the common element silicon, for which the value 28.063 has been accepted for many years and which is based on the analysis of SiCl₄ and SiBr₄ (by G. P. Baxter, P. F. Weatherill, and E. W. Scripture)¹⁵ by the standard method of silver titration. The limiting densities of SiH₄ and SiF₄ give respectively 28.112

⁸ *Compt. rend.*, 1905, **141**, 826; *Mem. Soc. Physique, Genève*, 1908, **35**, 615.

⁹ *J.*, 1905, **87**, 1601; Thesis, Bonn, 1907. ¹⁰ *J. Chim. physique*, 1906, **4**, 181.

¹¹ M. Woodhead and R. Whytlaw-Gray, *J.*, 1933, 846.

¹² *Proc. Roy. Soc.*, 1930, *A*, **128**, 551.

¹³ *Z. anorg. Chem.*, 1937, **235**, 129.

¹⁴ *Ibid.*, 1940, **243**, 355.

¹⁵ *Proc. Nat. Acad. Sci.*, 1923, **58**, 245.

and 28.105, whilst the most recent and reliable mass-spectrograph values are 28.087¹⁶ and 28.086.¹⁷ The latter are in close agreement with X-ray and density measurements made recently by T. Batuecas using crystalline quartz, who finds Si = 28.081. It might be argued that both limiting-density values are effected by errors which make them too large, were it not that Hönigschmid and M. Steinheil¹⁸ in 1924, using the same method as Baxter and his colleagues, obtained 28.105, and Weatherill and D. K. Brundage¹⁹ in 1932 from the ratio $\text{SiCl}_4/\text{SiO}_2$ deduced Si = 28.103. This interesting case clearly requires further investigation.

The Measurement of Densities and Compressibilities with High Accuracy

Densities.—More attention has been paid to the determination of the density of oxygen than to that of any other of the permanent gases. The relationship between its normal and limiting densities provides data from which the gas constant is calculated, as well as the gram-molecular volume of a perfect gas of molecular weight 32. The weight of a normal litre of this gas is hence an important standard.

Apart from the early work of Regnault in 1848, up to 1921 ten different workers in various countries have made 170 determinations of the weight of a normal litre. E. Moles²⁰ has recalculated all these data and reduced them to a common standard, and from all he obtains a mean value of 1.42892 ± 0.0003 for the weight of a litre of gas at N.T.P. at sea level and latitude 45° ($g = 980.616$). The mean values of different workers exhibit an extreme variation of 22×10^{-5} g., but the variations among the single results in any one series are much greater than this.

Rayleigh's²¹ investigation of the densities of the principal gases which appeared in 1893 set a standard of accurate measurement not always reached by subsequent workers. If we consider his 16 weighings of oxygen prepared by three different methods (chlorate, permanganate, and electrolysis) we find an extreme variation of 25×10^{-5} g., and the mean value for a normal litre was 1.42905, but Moles on recalculation reduces this to 1.42894 ± 0.00003 by making small corrections to the gravity factor, the vacuum contraction, and the coefficient used for the density of water for calculating the bulb volume. Work carried out since 1921 has furnished another 113 determinations of this important constant from two different laboratories. Thus from Harvard, G. P. Baxter and H. W. Starkweather²² find

$$L_n = 1.42898 \pm 0.00003 \text{ (mean of 65 determinations)}$$

$$L_n = 1.42897 \pm 0.00003 \text{ (mean of 6 determinations)}$$

whilst E. Moles²³ and his collaborators in Madrid in an extended series of researches from 1934 to 1937 find $L_n = 1.42894 \pm 0.00001$ (mean of 42).

¹⁶ D. Williams and P. Yuster, *Physical Rev.*, 1946, **69**, 556.

¹⁷ M. G. Inghram, *ibid.*, 1946, **70**, 653.

¹⁸ *Z. anorg. Chem.*, 1924, **141**, 101.

¹⁹ *J. Amer. Chem. Soc.*, 1932, **54**, 3932.

²⁰ *J. Chim. physique*, 1921, **19**, 100; *Z. anorg. Chem.*, 1927, **167**, 40.

²¹ *Proc. Roy. Soc.*, 1893, **53**, 144.

²² *Proc. Nat. Acad. Sci.*, 1924, **10**, 479; 1926, **12**, 699.

²³ "Poids Molec. et Atomique des Gaz", Collection Scientifique, Paris, 1938; *Instit. Internat. Co-oper. Intellect.*, pp. 30—35.

This last value has been corrected for adsorption and Moles contends that a similar correction should be applied to the Harvard results, bringing their final figure down to 1.42895, and he claims that the normal density of oxygen is now established with an accuracy of 1 part in 10^5 . This certainly represents the extreme limit of accuracy of which the method is capable when carried out with every modern refinement. However much one may be disposed to question this claim, it must be admitted that the individual values in his various series show a degree of concordance greater than any that has hitherto been obtained. Further, the admirable experimental methods he has developed and perfected over a number of years support his contention that systematic errors have been eliminated.

Compressibilities and Limiting Densities.—Two general methods are in use for determining the deviation from Boyle's law at constant temperature below one atmosphere. In (a) the isotherm or volumetric method, an unknown mass of gas is confined in a volumeter over mercury and connected with the lower chamber of a manometer carrying a point and forming the dead space. The volume is varied by withdrawing mercury from the volumeter, and the corresponding pressure read, after defining the volume of gas in the dead space by setting the point to the lower meniscus. The volumeter may be in the form of three or more bulbs connected by capillary tubing bearing marks which define predetermined volumes, or it may be a single bulb, and the volume increment is measured by weighing the mercury. Provided the temperature of the volumeter and the manometer is kept constant, the main error is in the pressure readings, for it is very difficult even with a good cathetometer and scale to reach an accuracy greater than ± 0.01 mm. Hence PV determinations are not usually attempted much below 200 mm.

In (b) the densities are determined in the usual way at a series of pressures, say at 1, 0.75, 0.5, 0.33 atm., and a set of values obtained of W/PV , where W is the mass of gas filling a density bulb of volume V at pressure P . In this way a series of values of density per unit pressure is obtained from which on extrapolation W/PV for $P = 0$, which is the limiting density, can be obtained directly. This method, due originally to Guye, has been largely used by recent workers. Thus, Baxter and Starkweather have employed it with success for neon, argon, oxygen, and nitrogen, and Moles for a whole series of gases. Its accuracy is limited not only by the precision reached in reading pressures but also by the difficulty of weighing gases at low pressures, especially those of low molecular weights such as methane and ammonia.

The various values for oxygen obtained by the two methods by different workers are shown in table on next page. There is close agreement in the mean values although method (a) shows a divergence of 1.2 parts in 10,000 between the extremes.

In addition to the two foregoing methods, the $1 + \lambda$ values can be deduced by extrapolation from measurements made at high pressures between, for example, 20 and 100 atmospheres. At first sight this procedure would appear of doubtful validity on account of the large extrapolation

Compressibility of oxygen at 0° at pressures below 1 atm.

Observer.	Isotherm method (a).	Observer.	Density method (b).
²⁴ Gray and Burt	1-00097	^{29a} Moles and Toral	1-000917
²⁵ Jaquerod and Scheuer	1-00097	^{29a} Moles and Roquero	1-000933
²⁶ Guye and Batuecas	1-00085	²² Baxter and Starkweather	1-000934
²⁷ Batuecas, Maverick, and Schlatter	1-00087	²⁹ Casado	1-000911
²⁸ Heuse and Otto	1-00097		
²⁹ Casado	1-00089		
Mean	1-00092	Mean	1-00093

necessary, but it must be remembered that the actual deviations from the ideal state are so much larger at high pressures that their magnitude can be determined with a higher percentage accuracy. Actually, as W. Wild³⁰ showed in 1931, the compressibility coefficients of the permanent gases from high-pressure data agree very closely with those measured directly at low pressure, and recently C. S. Cragoe³¹ in a critical analysis has recalculated the $1 + \lambda$ values from high-pressure data for He, A, N₂, O₂, and H₂ and assessed their probable errors in comparison with the data of Baxter and Starkweather, obtained directly by the density method. His results are striking and have a lower probable error than the low-pressure measurements. Thus for nitrogen from the data of A. Michels, H. Wouters, and J. de Boer,³² the values of $\lambda \times 10^5$ for nitrogen by different mathematical treatments are 45.42, 45.25, 45.32, ± 0.31 ; 45.32 ± 0.35 . For oxygen he finds $1 + \lambda = 1.000953$. One important point which is brought out by these high-pressure extrapolations is the very close approximation to linearity of the PV isotherms at low pressures. Thus if the high-pressure data are expressed by an expansion formula of the type $PV = A + Bp + cp^2$. . . the cp^2 term for the permanent gases is so small that its effect is negligible. For the more compressible gases high-pressure data of sufficient accuracy have not been available with the exception of those for CO₂ and C₂H₄, for which we have the measurements of Michels and his colleagues. An extended investigation of compressibilities over medium pressures, say 1—5 atmospheres, which, with one exception,⁴ has not been attempted since the time of Regnault, would be very valuable and for easily liquefiable gases would furnish data on the form of those isotherms at the lower pressures.

Taking then the mean values, for oxygen we have: normal density

²⁴ *J.*, 1909, 1635.

²⁵ *Mem. Soc. Physique, Genève*, 1908, **35**, 659.

²⁶ *J. Chim. physique*, 1923, **20**, 308.

²⁷ *Ibid.*, 1925, **22**, 131.

²⁸ *Ann. Physik*, 1929, Band 2, VIII Heft, 1012; 1930, Band 4, VI Heft, 778.

²⁹ Thesis, University of Santiago.

^{29a} Ref. 23, p. 47.

³⁰ *Phil. Mag.*, 1931, **12**, 42.

³¹ *J. Res. Nat. Bur. Stand.*, 1941, **26**, 495.

³² *Physica*, 1934, **1**, 587.

$L = 1.42896$; compressibility per atmosphere at 0° $1 + \lambda = 1.00092$ or
 $A = \lambda/(1 + \lambda) = 0.00092$

Limiting density, L_{lim} . $= 1.42896 (1 - 0.00092) = 1.42765$

Molecular volume at 0° of perfect

gas under normal conditions
 $(g = 980.616, \text{ lat. } 45^\circ), V_{45} = \frac{32}{1.42765} = 22.4145 \text{ l. atm. mole}^{-1} = RT_0$

It may be noted that the values for V_{45} obtained by different workers show small variations; thus Moles gives 22.4147 ± 0.0001 , Batuecas 22.4150 ± 0.0007 , and Casado 22.415 ± 0.002 , and the value considered most probable by Birge, 22.4151 ± 0.0006 , is based on $1 + \lambda$ for oxygen $= 1.000953$ from Cragoe's calculation from high-pressure data. Further, if the coefficient of expansion of a perfect gas is $1/273.16$, where 273.16° is the ice point on the absolute scale,

$$R = 22.4145/273.16 = 0.082056 \text{ l. atm. mole}^{-1}$$

Having fixed then the limiting density of oxygen within narrow limits, the molecular weights of other gases can be determined from the formula $M = 22.4145 L_n (1 - A)$, where L_n represents the weight of a normal litre of any gas, M its molecular weight, and A its compressibility coefficient between 0 and 1 atmosphere, or

$$M = \frac{L_{\text{lim}}^{\text{X}}}{L_{\text{lim}}^{\text{O}_2}} \times 32 = \frac{L_n^{\text{X}}(1 - A^{\text{X}})}{L_n^{\text{O}_2}(1 - A^{\text{O}_2})} \times 32$$

where $L_{\text{lim}}^{\text{X}}$ and L_n^{X} represent the limiting and normal densities of gas X, A^{X} its compressibility coefficient, and $L_n^{\text{O}_2}$ and $L_{\text{lim}}^{\text{O}_2}$ and A^{O_2} the corresponding values for oxygen.

Turning from oxygen to other gases, numerous determinations of densities and compressibilities have been made from about 1900 onwards. Not all of these can rank as high-precision data or can compare in accuracy with Rayleigh's densities of N_2 , CO , CO_2 , and N_2O which even to-day are very close to modern values.

D. Berthelot in his papers on limiting densities used Leduc's determinations, which agreed closely with Rayleigh's, but both these workers determined compressibilities at room temperatures and correction to 0° involves uncertainties (see Patterson and Cawood, *loc. cit.*). Guye in Geneva from 1903 onwards made a great contribution to accurate gas work, and with his collaborators Jaquerod, Scheuer, Baume, Moles, Batuecas, and others he studied H_2 , O_2 , N_2 , CO_2 , N_2O , NO , NH_3 , HCl , HBr , SO_2 , $(\text{CH}_3)_2\text{O}$, and CH_3Cl , and the work of this centre certainly laid the foundation on which much recent research has been built.

Elsewhere, notably in Ramsay's laboratory, new methods of gas manipulation, purification, and measurement were developed, and special studies were made of the physical constants of gases by Travers, Gray, Burt, and others (H_2 , O_2 , NO , HCl , He).

In more recent times the very accurate measurements carried out at the Reichsanstalt on the low-pressure compressibilities of H_2 , N_2 , O_2 , He , Ne , and A , by Heuse and Otto call for special mention, as do also the

Densities and compressibilities of gases at 0°

Observer.	Gas.	(a) 1 + λ .	(b) $L/nL_{lim.}$	Normal Density.	Mol. wt.	At. wt.
³³ Moles and Clavera 1927	N ₂	1.00046		1.25049	28.0164	14.0082
³⁴ Moles and Salazar . Moles and Garrido .	N ₂		1.00043			
²⁸ Heuse and Otto . . .	N ₂	1.00048				
³² Michels, Wouters, and de Boer, calc. by Cragoe from high press.	N ₂	1.000453			28.0149	14.0075
³⁵ Baxter and Stark- weather	N ₂		1.00041	1.25036	28.0152	14.0076
Baxter and Stark- weather 1925—28	A		1.00090	1.78364	39.944	
Baxter and Stark- weather	Ne		0.99941	0.89990	20.183	
Baxter and Stark- weather	He			0.17846	4.0002	
²⁸ Heuse and Otto 1930	He	0.99948				
³⁴ Moles and Salazar 1934	CO		1.00040	1.25001	28.0065	C = 12.0065
³⁶ Batuecas, Maverick, and Schlatter 1929	CO	1.00058				
³⁷ Schlatter 1930 . . .	CO	1.00048				
³⁸ Moles and Toral 1936	CO ₂		1.00694	1.97693(8)	44.007	C = 12.007
³⁹ Guye and Batuecas	CO ₂	1.0070(9)		1.97686	43.999(5)	„ = 12.000
⁴⁰ Moles, Toral, and Escribano	C ₂ H ₄	1	1.00730	1.26035(8)	28.046	„ = 12.007
⁴¹ Batuecas 1935 . . .	C ₂ H ₄	1.0078(0)		1.26041	28.032	„ = 12.000
⁴¹ Batuecas 1934 . . .	C ₂ H ₄		1.0203(0)	1.9148(5)	42.067	„ = 12.006
⁴² Casado 1943	(CH ₃) ₂ O	1.02574	1.02520	2.1079	46.068	„ = 12.010
					46.087	„ = 12.019
³⁸ Moles and Toral 1936	N ₂ O		1.00737	1.97821(5)	44.016(7)	N = 14.0083
⁴² Casado 1943	N ₂ O	1.00711	1.0070	1.9775	44.018	„ = 14.009
⁸ Guye 1905	NO			1.3402		
⁹ Gray 1906	NO			1.34027		
⁴³ Jaquerod and Scheuer	NO	1.00117			30.006	„ = 14.006
⁴⁴ Batuecas	NO	1.00111				
Moles, Sancho, and Roquero	NH ₃		1.01521	0.77140(2)	17.0328	„ = 14.009
Batuecas and Moles 1930			1.0155(7)	0.77170	17.0318	„ = 14.0078
⁴⁰ Moles, Toral, and Escribano	H ₂ S		1.01186	1.53842(6)	34.079	S = 32.063
Moles, Toral, and Escribano	SO ₂		1.0240	2.92654(7)	64.062	„ = 32.062
⁴⁵ Moles and Toral . .	SiF ₄	1.01004		4.69049	104.084	Si = 28.104
⁴⁶ Whytlaw-Gray and Burt 1909	HCl	1.00748		1.63915	36.469	
⁴⁷ Scheuer	HCl	1.00737		1.63909	36.465	
⁴⁸ Recalc. by Moles . .	HCl			1.63911		Cl = 35.457
⁴⁹ Batuecas and Moles 1926	CH ₃ Cl		1.0242	2.3070	50.4916	„ = 35.458
⁵⁰ Guye, Moles, ⁵¹ Rieman ⁵²	HBr	1.00932		3.64421	80.962	Br = 79.918
¹² Ritchie 1930	PH ₃	1.0091(2)		1.53072	34.000	P = 30.977

³³ *Z. anorg. Chem.*, 1927, **167**, 49. ³⁴ *Anal. Soc. Esp. Fis. Quím.*, 1934, **32**, 954.³⁵ *Proc. Nat. Akad. Sci.*, 1926, **12**, 20, 703; 1928, **14**, 50, 57; 1925, **11**, 231.³⁶ *J. Chim. physique*, 1929, **26**, 548.³⁷ *Ibid.*, 1930, **27**, 44.³⁸ *Sitzungsber. Akad. Wiss., Wien*, 1936, **145**, 948.

density and limiting-density data on O₂, N₂, He, Ne, and A furnished by the work of Baxter and Starkweather at Harvard.

From 1930 onwards Moles has been the most active worker in this field, and a constant advocate of gasometric as opposed to gravimetric methods for the determination of atomic weights (see reports on atomic weights of the International Committee). In conjunction with Batuecas and others he has revised much of the earlier work. For a number of years in Madrid he devoted all the resources of his laboratory to the development of a refined and improved technique, and he claims to have obtained a greater precision than any that has been reached hitherto. Quite recently important work of the same type has come from the laboratory of Batuecas at the University of Santiago.

All this laborious and careful work, developing slowly over many years, has been carried out by methods outlined in discussing oxygen. Alternative methods depending on the buoyancy principle have also been used which offer many advantages. These will be described later. In the table on preceding page are collected well-established data obtained by the orthodox methods.

Although the results obtained by different workers do not show as close an agreement as might be expected, the mean values of the atomic weights, *viz.*, C = 12.007, N = 14.008, S = 32.063, Cl = 35.457, Br = 79.918, P = 30.977, agree closely with International values. In the case of both Cl and Br this close agreement may be fortuitous, for the experimentally determined isothermals of HCl, HBr, and CH₃Cl exhibit a slight curvature and in consequence extrapolation to zero pressure is to some extent uncertain.⁵³

Small discrepancies of the order of a few parts in 10⁴ are apparent, especially in the $1 + \lambda$ values obtained by method (a). Many of these were determined by following the Geneva technique which is open to criticism because in each experiment three points only were obtained in the $PV-P$ graph and reliance was placed on a large number of experiments to give an accurate final mean, though individual experiments exhibited wide deviations. The exact determination of pressure, too, is a matter of extreme delicacy and difficulty when the highest possible accuracy is required; for, apart from errors inherent in scale and cathetometer, capillarity has to be taken into account unless manometer tubes of wide bore are employed as in Baxter and Starkweather's work in which the diameter was 3—4 cm. If this is done, dead-space errors in method

³⁹ *J. Chim. physique*, 1923, **20**, 308.

⁴⁰ *Trans. Faraday Soc.*, 1939, **35**, 1439.

⁴¹ *Bol. Univ. de Santiago*, 1935, Oct.—Dec.; *J. Chim. physique*, 1934, **31**, 165.

⁴² University of Santiago, Thesis, 1943.

⁴³ *Compt. rend.*, 1905, **140**, 1384.

⁴⁴ *J. Chim. physique*, 1925, **22**, 109.

⁴⁵ *Z. anorg. Chem.*, 1938, **236**, 225.

⁴⁶ *J.*, 1909, **95**, 1633.

⁴⁷ *Sitzungsber. Akad. Wiss., Wien*, 1911, **123**, IIA, 169, 52.

⁴⁸ *Z. physikal. Chem.*, 1925, **115**, Heft 1/2, 61.

⁴⁹ *Arch. Soc. Phys. Hist. Nat., Genève*, 1925, **42**, 120.

⁵⁰ *J. Chim. physique*, 1919, **17**, 141.

⁵¹ *Z. physikal. Chem.*, 1925, **115**, 61.

⁵² *J. Chim. physique*, 1917, **15**, 293.

⁵³ See Batuecas, *loc. cit.*; Baxter, *J. Amer. Chem. Soc.*, 1922, **44**, 595.

(a) due to meniscus volume fluctuations may be considerable. There is little doubt that in the past insufficient attention has been given either to the height or to the shape of the mercury meniscus in accurate manometry. This has recently been emphasised by Whytlaw-Gray and Teich.⁵⁴ It is surprising, too, that little use has been made of Rayleigh's point manometer in which a steel measuring rod, carrying points at predetermined distances apart, is applied directly to the two mercury surfaces. As Rayleigh showed, the accuracy with which a point can be set to a mercury surface is many times greater than the accuracy of measurement by the orthodox method of scale and cathetometer. Moreover, refraction errors are eliminated. J. T. Howarth and F. P. Burt,⁵⁵ in their work on acetylene, used a multiple-point manometer and also kept the manometer, volumeter, and connecting tubes strictly at the same temperature by immersion in melting ice and obtained a very accurate series of PV values strictly linear with respect to P . This admirable technique was used later by the Reichsanstalt workers Heuse and Otto.

In the work of Moles and his associates, as well as in that of Baxter and Starkweather, the density method was used for the determination of both the normal and the limiting densities. For many interesting details of refined experimentation the original papers must be consulted. In addition to the orthodox method of weighing gases in bulbs of different volumes, Moles used the volumeter method in which the purified gases were confined and measured in large vessels or volumeters surrounded in melting ice and weighed in much smaller vessels after adsorption on charcoal cooled in liquid air, a procedure employed previously by many workers but in his case used successfully as a proof of the avoidance of systematic errors. In one respect Moles's results⁵⁶ differ from those of the majority of previous experimenters in that he in conjunction with Crespi has measured the adsorption of his gases on glass surfaces and applied a correction to his final values. For liquefiable gases this correction is of significance. Thus for CO_2 and SO_2 in a 500-c.c. soda-glass bulb the correction at 1 atm. to the normal litre weights amount to 1 and 4.5 parts in 10^4 respectively. Although the agreement in the densities determined in bulbs and volumeters of various capacities after correction is very satisfactory, it may be questioned whether the data obtained in another apparatus, though made from the same glassware, are directly applicable to his various bulbs and volumeters. There is also an error due to the solution of gas in the stopcock grease and its subsequent evolution in a vacuum which nobody up to the present has investigated systematically and which in some cases may be as great as or greater than the adsorption error.

One very interesting feature of Moles's work is the closely linear relationship found between the "litre weights", *i.e.*, the densities determined at a series of pressures from 1 to 0.25 atm. and reduced to unit pressure, and pressure for the gases SO_2 , SiF_4 , H_2S , NH_3 —strong evidence that a linear extrapolation is valid for the liquefiable gases as it is for the

⁵⁴ *Trans. Faraday Soc.*, 1948, **44**, 770.

⁵⁵ *Ibid.*, 1925, **20**, 544.

⁵⁶ *Bull. Soc. chim. Belg.*, 1938, **47**, 405.

permanent gases. In the past, much discussion has ranged around this question of extrapolation and of the validity of different modes of mathematical treatment of experimental data.⁵⁷ Earlier results obtained with methyl ether and methyl chloride and also with hydrogen chloride by the isotherm method (a) give $PV-P$ curves concave towards the pressure axis; method (b) apparently usually gives straight lines, though the experimental evidence is not sufficiently accurate to exclude a slight curvature. Theoretically, a curvature in the direction observed (*i.e.*, concave towards the pressure axis) is to be expected. W. H. Keesom,⁵⁸ on the basis of van der Waals's equation, has calculated the curvature for the gases SiF_4 , NH_3 , and CO_2 , for which Moles finds a linear relation, and contends that it is great enough to raise by significant amounts the values of the molecular weights. The evidence for the linearity of the low-pressure isotherms of liquefiable gases was discussed by Moles⁵⁹ in 1938, and further work since then has gone far to confirm his conclusions.

Working with a differential compressibility apparatus similar to that described by C. G. Addingley and Whytlaw-Gray⁶⁰ but designed to eliminate capillarity and meniscus volume errors, G. A. Bottomley, D. Massie, and R. Whytlaw-Gray⁶¹ have obtained data for O_2 , CO , N_2O , CO_2 , C_2H_4 , and C_3H_8 over the pressure range of 800—100 mm., and in every case the deviation from a straight line was too small to be detected, although the error of measurement of individual points did not exceed a few parts in 10^5 .

Just recently SO_2 has been studied from atmospheric pressure down to 15 mm. and no definite evidence of curvature obtained. It seems clear then that even with such gases as sulphur dioxide and propane, the critical temperatures of which are respectively 157° and 96° , the use of an equation of the second degree (such as $pv = A + Bp + Cp^2$) is unnecessary, and that a significant departure from the linear does not occur at ordinary temperatures.

One comment may be made in considering the data in the table, and that is to draw attention to the fact that they are expressed in absolute measure and hence depend on an exact knowledge of the gravity factor in the laboratory where the measurements were made, the true height of the manometric column, the density of mercury, the density of water, etc. Possibly the slight differences obtained by various workers for the normal density of the same gas may in part be due to the use of factors which are not identical. Since molecular weights are purely relative, it is certainly better to compare gases with oxygen in the same apparatus and under precisely the same conditions as has been done in the latest work in this field.

Up to this point no mention has been made of hydrogen, though before

⁵⁷ R. T. Birge and F. A. Jenkins, *J. Chem. Physics*, 1934, **2**, 179; see also Batuecas (ref. 41).

⁵⁸ "Determination Physico-chimique des Poids Molec. et Atomique des Gaz", Collection Scientifique, Institut Internat. Co-operation Intellectuelle, Paris, 1938, p. 165.

⁵⁹ *Ibid.*, p. 187.

⁶⁰ *Trans. Faraday Soc.*, 1928, **24**, 378.

⁶¹ *Proc. Roy. Soc.*, 1949, in the press.

the discovery of deuterium many determinations were made of its density (Morley, Rayleigh, Leduc) and compressibility (Chappuis, Jaquerod, Guye, and others). It is a melancholy fact that all the determinations of the O/H atomic weight ratio made by either gravimetric analysis or physico-chemical methods are in error because the hydrogen used was deficient to a greater or lesser extent in the heavier isotope. No modern worker has had the courage to attempt to measure the density of chemical hydrogen or to redetermine its atomic weight. The present highly accurate value rests on mass-spectrograph measurements. The combining volumes of oxygen and hydrogen, however, are probably unaffected by a variation in deuterium content and the very accurate and beautiful work of F. P. Burt and E. C. Edgar,⁶² published in 1916, is one of the very few investigations which can be used to check the limiting-density principle. They found the ratio of the volumes containing equal numbers of molecules to be $H/O = 1.00144/1$ whilst if we calculate it from

$$\frac{(1 + \lambda)_{O_2}}{(1 + \lambda)_{H_2}} = \frac{1.00092}{0.99942}$$

we get 1.00150/1 and a direct differential method gave 1.00148/1, differences sufficiently small to be attributed to experimental error. Other instances in which a direct measurement of combining volumes has been made with any claims to accuracy are N_2/N_2O ,⁶³ $3H/N$,⁶⁴ and $H_2/HCl = 1.00790$,⁴⁸ whilst

$$(1 + \lambda)_{HCl}/(1 + \lambda)_{H_2} = \frac{1.00748}{0.99942} = 1.00806$$

but on account of various experimental difficulties none of these can be regarded as free from errors.

Limiting Pressures.—If purely comparative measurements are to be made with high accuracy there is much to be said for the use of a silica-fibre buoyancy microbalance, which consists of a small balance beam of fused silica swinging about a horizontally placed fibre at right angles to the beam and from one end of which a sealed buoyancy bulb is suspended. The microbalance, suitably mounted in a glass case, is observed with a low-power microscope, and its zero position defined in relation to a fixed pointer. The balance is in connection with a sensitive manometer, and in comparing gases the pressures at which the balance floats exactly about its zero point are determined. Thus the pressures at which two or more gases have the same density are compared instead of densities at the same pressure as in the older method. These microbalances can be made capable of detecting a change of density corresponding with a change of 0.001 mm. of air pressure or less, so that the error in the final result is determined mainly by the error in the pressure readings. Thus the many sources of error inherent in the weighing of gases in glass bulbs can be eliminated to a large extent. Further, the comparison of densities becomes a much quicker and simpler operation and requires relatively small amounts of

⁶² *Phil. Trans.*, 1916, A, 216, 413.

⁶³ *J. Chim. physique*, 1905, 3, 562.

⁶⁴ *Mem. Soc. Phys. Hist. Nat., Genève*, 1908, 35, 594.

gas. To get the ratio of the limiting densities, it is necessary to measure pressure ratios at two or more densities, which is done by altering the weight on the beam by means of small silica riders suspended above the buoyancy bulb.

The theory of the balance used in this way follows from Berthelot's definition of compressibility coefficient A , *i.e.*, $PV = (PV)_0(1 - AP)$, which in gram-mols. = $nRT(1 - AP)$. If w g. is the weight of gas of molecular weight M_1 displaced by the bulb, then since $n = w/M_1$,

$$P_1V_1 = \frac{w_1}{M_1}(1 - A_1P_1)RT \quad . \quad . \quad . \quad (1)$$

and with another gas of molecular weight M_2 , compressibility A_2 , and balancing pressure P_2 ,

$$P_2V_2 = \frac{w_2}{M_2}(1 - A_2P_2)RT \quad . \quad . \quad . \quad (2)$$

but since the volume of the bulb is fixed, $V_1 = V_2$, and since at the two balancing pressures both gases have the same density, $w_1 = w_2$. Hence, dividing (1) by (2), we have

$$\frac{P_1}{P_2} = \frac{M_2(1 - A_1P_1)}{M_1(1 - A_2P_2)} = r_1$$

At other densities we get other values of r , r_1 , r_2 , r_3 , etc., which when graphed against P_1 give the limiting value of r for $P_1 = 0$, which as can be seen from the equation is the inverse ratio of the molecular weights. If, as Berthelot assumed, and subsequent experience has confirmed, PV is a strictly linear function of P for the permanent gases, then it is true that the ratios also vary linearly with P_1 (in practice usually oxygen). Another advantage of the method is that it allows gases to be compared at relatively low pressures where an error in the compressibilities is not so important, but conversely, the calculation of compressibilities from ratios obtained at low pressures would not be so reliable as those deduced over a wider pressure range. The main disadvantage of the method is that adsorption errors might be more serious, for the buoyancy bulbs used are necessarily small, their volume varying from 2 to 10 c.c., and the ratio of surface to volume correspondingly large. To compensate for adsorption, an open bulb or other suitable surface is used as a counterpoise at the end of the beam remote from the buoyancy bulb in such a position that their surface moments are as nearly equal as possible. T. S. Taylor⁶⁵ was the first to construct and use a fibre suspension quartz microbalance in 1917 with which he compared the densities of H_2 , He, and O_2 ; later it was developed and modified in the Leeds Chemistry Department and has been used for accurate atomic weight determinations extending over a number of years.

In order to attain greater accuracy in temperature control, and also because the compressibilities decrease as temperatures rise, the workers in Leeds use thermostated water-baths for microbalance and manometer. Hence their results for relative densities at 1 atm. pressure are not directly

⁶⁵ *Physical Rev.*, 1917, **10**, 653.

comparable with measurements made at 0° c.—although, of course, the limiting-pressure ratios should be identical with limiting-density ratios, for in the limit all gases have the same expansion coefficient.

The values obtained by this method for the molecular weights of Xe, CO, CO₂, C₂H₄, C₃H₈, CH₃F, CF₄, H₂S, and SiH₄ are shown in the following table.

Limiting-pressure ratios

Observer.	Gas compared with O ₂	Limiting ratio, P_{O_2}/P .	Mol. wt.	Atomic weight.	Temp.
⁶⁶ Whytlaw-Gray, Patterson, and Cawood	Xe	4·1020	131·26	131·26	18°
¹¹ Woodhead and Whytlaw-Gray 1933	CO	0·87535	28·011	C = 12·011	19·8
⁶⁷ Patterson and Cawood 1936	CO ₂	1·3753(6)	44·0101	„ = 12·010	21
„ „ „ „	C ₂ H ₄	0·87673(5)	28·0556	„ = 12·012	21
⁶⁸ Casado } Massie, and Whytlaw-Gray }	C ₃ H ₈	1·37807	44·098	„ = 12·011	20·76
⁶⁷ Patterson and Cawood 1936	CF ₄	2·74966	87·989	F = 18·995	21
„ „ „ „	CH ₃ F	1·06349	34·0318	„ = 18·997	21
„ „ „ „	N ₂ O	1·37542	44·0135	N = 14·007	21
„ „ „ „	H ₂ S ⁷⁰	1·06504	34·081	S = 32·065	21
⁶⁹ Roberts } ⁷⁰ Cawood and Whytlaw-Gray }	SiH ₄	1·00451	32·144	Si = 28·112	21

It will be seen that the atomic weights determined by this method differ by small amounts from the corresponding figures in the table on p. 162. The mean value for carbon is here 12·011 as against 12·007, a difference of 3·3 in 10⁴. Moles attributes this to an adsorption error in the microbalance, but this criticism is certainly not valid for the CO/O₂ ratio. An examination of the work of Cawood and Patterson does show that adsorption may lead to erroneous results, especially if the surfaces of the balance are not entirely free from silica bloom. Since the publication of their paper, careful measurements of the adsorption on clean, freshly blown surfaces of vitreous silica have been made by T. H. Henry, G. A. R. Hartley, and R. Whytlaw-Gray ⁷¹ by a mercury-displacement method which shows that with these surfaces for the gases examined adsorption is remarkably small, about 20 times less than on soda glass, and provided the surfaces of the bulb and its counterpoise on the microbalance are similar to the surfaces of the larger bulbs on which adsorption measurements were made no significant error is likely. In the case of sulphur dioxide adsorption was measured by direct weighing on small bulbs similar to those used on the buoyancy balance and again the correction was found to be beyond the limits of experimental error. With some gases, however, silica behaves in an abnormal way. Thus hydrogen diffuses into

⁶⁶ *Proc. Roy. Soc.*, 1931, A, **134**, 7.

⁶⁷ *Phil. Trans.*, 1936, A, **236**, 77.

⁶⁸ *J.*, 1949, 1746.

⁶⁹ A. L. Roberts, Thesis, Leeds, 1930.

⁷⁰ "Poids Molec. et Atomique des Gaz", Paris, 1938, see ref. (58).

⁷¹ *Trans. Faraday Soc.*, 1939, **35**, 1452.

vitreous silica and it has not been found possible to get accurate comparisons between this gas and oxygen with the microbalance. With helium the effect is even greater. Ammonia was found in recent unpublished measurements to be nearly as strongly adsorbed on silica as on glass, and silicon tetrafluoride has an adverse effect on silica surfaces even after prolonged desiccation. With many gases, however, vitreous silica is undoubtedly preferable to glass, and as the appended table shows, it could be used with advantage for high precision determinations of densities, compressibilities, and coefficients of expansion of many gases.

Gas.	Silica,	Soda glass,	Jena glass,
	c.c. ($\times 10^{-6}$) adsorbed at 1 atm. press. per cm. ³ .		
	$T = 21^{\circ} \text{ c.}$	$T = 15^{\circ} \text{ c.}$	
SO ₂ , direct weighing, small bulbs ⁷²	14.5	290	130
SO ₂ , large bulbs, mercury displacement	11.0		
N ₂ O, displacement	1.61	63	20
CO ₂ , "	1.44	89	
C ₂ H ₄ , "	1.51	63	
N ₂ , "	0.74	—	
CO, "	0.44	23	
A, "	0.42		
O ₂ , "	0.20	41	
SiF ₄ , direct weighing ⁷²	45	96	
NH ₃ , ⁷² " "	310	490	150

(The above figures for glass are taken from a paper by E. Moles, *Bull. Soc. chim. Belg.*, 1938, **47**, 423. Those for silica are from *Trans. Faraday Soc.*, 1939, **35**, 1457.)

Returning to the atomic weight of carbon, it is remarkable that the Spanish workers have obtained results by the orthodox methods so consistently lower than those found by the microbalance. In view of the known variation in isotopic composition in carbon from different sources it might be supposed that the difference could be attributed to this cause. The maximum variation, however, found by Nier in carbon from a wide variety of sources was from 82.7 to 92.5 for the ratio of ¹²C to ¹³C, corresponding to $C = 12.0120$ and $C = 12.0105$, respectively, on the chemical scale, a variation only about half as great as the difference in question. It is difficult to believe that the gases used by Moles and his collaborators could have had such an abnormally high proportion of ¹²C. In view of the known variation in isotopic composition of other elements such as sulphur, it would seem desirable to use only material of definite isotopic composition for atomic-weight determinations.

The question might well be asked whether limiting-density measurements could be made with sufficient precision to detect definitely isotopic changes. It is certainly difficult when using the orthodox methods to be sure of small differences of the order of a few parts in 10⁵. Measurements with the

⁷² Driver, Thesis, Leeds, 1946.

microbalance would appear to offer a greater chance of success, provided of course that a sufficiently high degree of chemical purity in the gases examined could be ensured, for by this method errors inherent in weighing gases in bulbs are to a large extent eliminated.

Recently, a very accurate investigation on the limiting densities of very pure nitrogen and methane has been made by B. Lambert and his co-workers,⁷³ in the course of which they have studied in great detail the errors in the silica-fibre microbalance and also in the exact measurement of pressure. Using a very beautiful form of microbalance, they have been able to reach a remarkably high degree of precision. Although the object of the work was rather to demonstrate the degree of accuracy possible with the technique developed, yet the concordance of the measurements was such that isotopic variations could well have been detected. They find for the atomic weights of carbon and nitrogen 12.0112 and 14.0078, respectively.

A method of directly measuring small differences in gaseous densities was worked out by E. R. Roberts, H. J. Emeléus, and H. V. A. Briscoe⁷⁴ in 1939 in their work on ethyl- and dimethyl-deuteramines. In this, the two gases to be compared were contained in two vessels and adjusted to exactly the same density by means of a buoyancy microbalance. By an ingenious arrangement the pressure difference between the two was measured at constant volume on an oil gauge, a pair of constant-volume indicators or capastats being used for this purpose. By this device the pressure difference between the two gases at precisely the same density could be measured accurately without contact with oil.

A modification of this method has been used lately by B. Leadbeater and Whytlaw-Gray⁷⁵ to compare the densities of nitrogen and carbon monoxide. Instead of the capastats, the microbalance itself was used to measure the small difference in pressure which for this pair of gases at a filling pressure of about 350 mm. was of the order of 0.025 mm. After the densities of the nitrogen and carbon monoxide in the two vessels had been adjusted to equality, the connecting stopcock was opened and a small amount of carbon monoxide flowed through and mixed with the nitrogen until pressure equality was established. The pressure difference was measured by the deflection of the balance, which had been calibrated previously in terms of pressure.

This method of working, which is only applicable to gases of very nearly the same molecular weight, proved capable of measuring density differences up to 2 parts in 10^6 . Since air oxygen is heavier than water oxygen by nearly 7 parts in 10^6 , a direct measurement of this small difference is within the limits of experiment and there is little doubt that the method could be improved to detect still smaller changes.

In the case of carbon monoxide and nitrogen, measurements were made at two different densities so that the limiting ratio could be calculated. This was found to be, $\text{press. CO}/\text{press. N}_2 = 1.0001360$, so that if we assume

⁷³ Private communication.

⁷⁴ *J.*, 1939, 41.

⁷⁵ Leadbeater, Thesis, Leeds, 1946; *Proc. Int. Cong. Pure and Appl. Chem.*, 1947.

for carbon the value 12·0112, that of nitrogen is 14·0075. Birge calculates the most probable mass-spectrograph values for these two elements to be $C = 12\cdot0114$ and $N = 14\cdot0074$, so that in this case at least the limiting-density measurements have reached an accuracy as great as that of stoichiometric determinations.

To summarise the general conclusions of this Review, it is evident that the principle of limiting densities when applied to the determination of molecular atomic weights is capable of giving results of the highest accuracy especially when applied to the permanent gases. For the liquefiable gases it would seem that modern work has resolved the difficulties with which the measurement of these much larger deviations from the ideal state is fraught, and that uncertainties in the extrapolation to zero pressure have been much reduced, so that now, even if more precise data should bring to light a slight curvature in the isothermals, it will be possible to fix the limiting values within narrow limits. Very few attempts have been made to apply the principle to vapours. W. Ramsay and B. D. Steele⁷⁶ in 1903, using a modified and improved apparatus of the Hofmann type, determined the densities and the $PV-T$ variations down to pressures of about 40 mm. for a number of organic vapours, but the limiting values differed considerably and to varying extents from the expected values.

Batuecas⁷⁷ has recalculated all the results obtained by Ramsay and Steele and concluded that the accuracy of the experimental results was not as great as was supposed, and that the contention that the limiting-density method was inapplicable to vapours was by no means proved. Since 1903 very few vapour densities have been measured with the necessary accuracy to decide this question; the data only of A. Magnus and E. Schmid⁷⁸ need be considered. These workers obtained with chloroform and benzene values for the compressibilities and densities which, as Batuecas⁷⁹ has shown, give molecular weights in close agreement with standard numbers. It seems likely then that when the considerable experimental difficulties are overcome the principle can be extended to a wider range of elements.

⁷⁶ *Z. physikal. Chem.*, 1903, **44**, 348; *Phil. Mag.*, 1903, **6**, 492.

⁷⁷ *Z. physikal. Chem.*, 1939, *A*, **183**, 438.

⁷⁸ *Z. anorg. Chem.*, 1922, **120**, 232.

⁷⁹ *Ibid.*, 1941, **246**, 158.