# 209. A Comparison of the Densities of Carbon Monoxide and Oxygen, and the Atomic Weight of Carbon.

By Maurice Woodhead and Robert Whytlaw-Gray.

Since the discovery that carbon is a mixed element and contains a proportion of the isotope $C^{13}$ along with $C^{12}$, it has become clear that the value 12·00 accepted for its atomic weight by the International Commission is too low.

Aston has shown that the weight of the atom $C^{12}$ on the $O^{16}$ basis is 12·0036, which, when reduced to the standard of chemical oxygen, becomes 12·0010 or 12·0023, depending on whether the abundance ratio $O^{16} : O^{18}$ determined by Mecke and Child (*Physical Rev.*, 1930, **36**, 330) or by Naudé (*Z. Physik*, 1931, **68**, 362) is considered the more probable. The chemical atomic weight of carbon is therefore greater than 12·001, but in view of the difficulty of determining by the methods of band spectroscopy the proportions of the two isotopes, an upper limit cannot be fixed.

The evidence on which the chemical atomic weight is founded rests (*a*) on the values obtained by Richards and Hoover (*J. Amer. Chem. Soc.*, 1915, **37**, 95) eighteen years ago, for the stoicheiometric ratio $Na_2CO_3 : NaBr : Ag$, and (*b*) on the densities and compressibilities of various gases containing carbon.

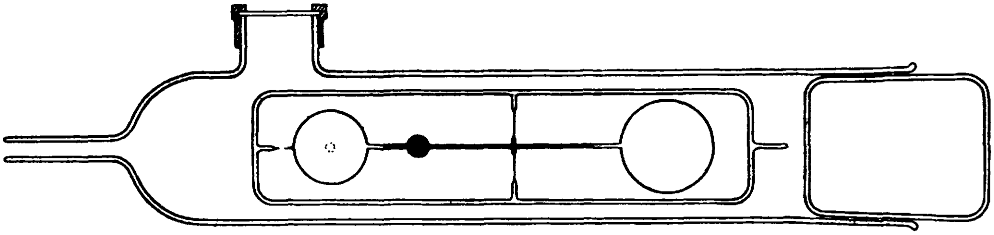
With regard to (*a*), it may be remarked that the individual experiments lead to values for carbon ranging from 11·997 to 12·008, and according to Moles the mean is uncertain to the extent of ± 0·011% of a unit (*J. Chim. physique*, 1917, **15**, 51), whilst the physico-chemical data taken into account indicate that carbon lies between 11·996 and 12·008. It is obvious that the uncertainty in the atomic weight of this important element is considerable.

Now, of the gases employed in determining this constant, carbon monoxide presents many advantages, for not only does it deviate least from Boyle's law, but it can easily be prepared in a state of high purity. Its density was determined by Rayleigh (*Proc. Roy. Soc.*, 1897, **62**, 204), who obtained with gas from three different sources a series of very concordant weighings, in satisfactory agreement with the earlier value of Leduc; recently, Pire and Moles (*Ann. Soc. Fís. Quím.*, 1929, **27**, 267) from the results of an elaborate investigation have obtained a value in close accord with Rayleigh's. On account, however, of an uncertainty in the compressibility of the gas, little attention has been directed to the atomic weight of carbon deduced from these data. Even now, when the compressibility of carbon monoxide has been fixed within narrow limits by the careful researches of Batuecas, Maverick, and Schlatter (*J. Chim. physique*, 1930, **27**, 45), it seems to have escaped notice that the data favour a figure for the atomic weight of carbon very much higher than the accepted value or any proposed by the workers in band spectroscopy. Thus, if we take the actual ratio of the densities of carbon monoxide and oxygen found by Rayleigh and by Leduc and the values 1·00048 and 1·00094 (Wild, *Phil. Mag.*, **1931**, **12**, 41) for the compressibilities at 0° (1 + λ) of the two gases respectively, we obtain for the atomic weight of carbon the three values: Rayleigh, 12·011(8); Leduc, 12·015(5); Pire and Moles, 12·008(5). In calculating the last value we have used 1·42892 for the weight of a normal litre of oxygen, a figure based on the work of Moles and Gonzales (*J. Chim. physique*, 1921, **19**, 310).

It is evident, then, that even if we leave out of account the measurements of Leduc, which are founded on fewer and less concordant experiments than the other two, the data indicate that the atomic weight of carbon is nearer 12·01 than 12·00.

The object of the present work was to compare directly, under the same conditions and with as high an accuracy as possible, the densities of oxygen and carbon monoxide at a series of pressures, so as to be able to calculate, without assuming any values for the compressibilities, the molecular weight of carbon monoxide.

This has been done by using a fibre suspension silica buoyancy balance and the method used is in all respects closely similar to that employed in the determination of the atomic weight of xenon (*Proc. Roy. Soc.*, 1931, *A*, **134**, 7). Briefly, it consists in determining the ratio of the pressures at which the two gases have the same density, and then by altering the load on the beam to make a second and possibly a third measurement of the pressure ratio at another or two other densities. From these ratios the limiting value of the pressure ratio can be easily found by linear extrapolation, and the ratio of the molecular weights of the gases calculated.



Experimentally the investigation differed from that of xenon in several important details which will now be briefly described.

*Pressure Measurement.*—Since larger volumes of gas were available, there was no necessity to restrict the manometer tubing to a narrow bore, and so, to avoid capillarity corrections, it was constructed of tubing of 30 mm. diameter. The whole of the manometer was contained in a thermostat tank with plate-glass sides, and the temperature was kept constant to 0·01°. The glass scale was placed alongside the manometer in the tank and was carefully calibrated section by section by comparison with a 200-mm. scale made by the Société Génevoise and guaranteed to be accurate to within 2μ. Pressure was read by means of a swinging cathetometer, the micrometer of which read directly to 0·01 mm. The illumination of the mercury surfaces was carefully controlled by two sliding shutters of blackened metal placed in the tank immediately behind the manometer tubes.

The balance used was of the form shown in the fig., and with its stand and supports was made entirely of fused silica. The whole fitted into a cylindrical glass case which was closed by a ground-glass stopper and furnished with a side window through which the pointer could be viewed. The buoyancy bulb had a capacity of about 8 c.c. and was counterpoised by a smaller bulb with a hole in it and a small sphere of silica. The diameter of the buoyancy bulb was $\sqrt{2}$ times that of the counterweight bulb, and both were of nearly the same weight, so that it was possible in constructing the beam to arrange that the surface moments on either side of the fibre suspension were nearly equal and in this way to eliminate largely any effect due to unequal adsorption. The balance was larger than that used for xenon, the total length of the beam and bulbs being about 10 cm. Glass case and balance were mounted rigidly inside a metal cylinder immersed in a tank through which a constant stream of water was pumped from a large thermostat. By this means the temperature could be kept constant within ± 0·02° for long periods.

When making observations, any smaller variations were recorded by means of sensitive mercury thermometers. The sensitivity of the balance was usually adjusted so that a difference in pressure of 0·005 mm. in oxygen could be detected easily. When working at the lowest pressure this was increased to 0·002 mm., and when so adjusted the balance had a period of 20 secs. Had it been necessary, the sensitivity could have been considerably increased.

The apparatus was set up on a stone table in a basement room where vibration was a minimum. The balance case was connected to the manometer through a gold tube, to keep out most of the vapour of mercury, and a short length of capillary tubing. The volume of the connecting tubes leading to the gas trains was kept as small as possible so that, when measurements were being made, only a small fraction of the total gas was outside the thermostats.

The accuracy of the measurements depends largely on the zero point of the balance remaining constant over the period of time necessary to replace one gas by another and measure the pressures. At first, we found that a slow shift of the zero point took place, especially when the balance case was left evacuated over-night or for long periods. This effect was finally traced to a vapour given off by the rubber grease used on the stopper of the balance case and on the stopcocks. In a vacuum this diffused rapidly, and since it entered the case at one end and was adsorbed preferentially by the counterweight bulb, the balancing pressure with gas from the same sample gradually diminished. It was found that this slow zero drift could be very greatly reduced by using " Apiezon " grease in place of the usual tap lubricants (see Burch, *Proc. Roy. Soc.*, 1929, *A*, **123**, 271). When this was done after the taps had been cleaned and the balance washed and baked at 200° in dust-free air, a perfectly constant zero could be maintained as a rule for several weeks.

*Purity of Gases.*—The greatest care was taken to obtain oxygen and carbon monoxide in the highest state of purity.

The oxygen was made by heating, in a high vacuum, pure specimens of (*a*) potassium permanganate, (*b*) potassium chlorate (fused previously in a vacuum) in presence of manganese dioxide as a catalyst. Both samples of gas were passed over two long horizontal tubes containing 50% potassium hydroxide solution, then over solid potash, soda-lime, and phosphoric anhydride, and finally liquefied and fractionated.

Special care was taken to ensure the complete absence of air, and also that the gas was thoroughly dried (see Stock and Ritter, *Z. physikal. Chem.*, 1926, **124**, 204). The absence of air was proved conclusively by igniting a little pure phosphorus in a silica tube containing some of the oxygen; no residual gas from 50 c.c. could be detected, and since 1 cub. mm. was easily seen, the nitrogen content was well below 1 part in 50,000 parts.

Moisture was excluded by a liberal use of the purest phosphoric anhydride, followed by liquefaction and fractionation, and in some cases the gas was kept over phosphoric anhydride for long periods. The best test of the purity of the gas was the constant value obtained for the balancing pressures of different specimens prepared and purified in different ways. To quote one instance taken from the data recorded in Series II (p. 851), the mean value of the balancing pressure of six fillings of the case with oxygen from permanganate was found to be 182·339 mm., whilst five fillings with chlorate oxygen gave a mean of 182·336 mm.

Two methods were used for the preparation of carbon monoxide, *viz.*, the action of sulphuric acid on (*a*) formic acid, (*b*) potassium ferrocyanide. Highly purified reagents were used, and the reactions were carried out in a low vacuum. In method (*a*) the volatility of the formic acid was controlled by cooling the reaction vessel, and in some experiments by the use of a low-temperature reflux condenser. The crude gas was first passed through a vessel cooled in liquid air, then through tubes containing liquid and solid potash and phosphoric anhydride, and finally it was liquefied and fractionated.

In order to reach a sufficiently low temperature to do this, we found Stock's device of passing a stream of hydrogen through the liquid air refrigerant very convenient. The finally purified carbon monoxide and also the oxygen were stored in a series of one- and two-litre bulbs. These were previously cleaned, baked, evacuated with the mercury and the Hyvac pump, washed out with the pure gas, and finally pumped out to the lowest possible vacuum.

The most likely impurity which would affect the density of carbon monoxide appreciably and might not be eliminated by the treatment described, is oxygen derived from traces of air. A trace of nitrogen would be of no consequence since its density lies so close to that of carbon monoxide. In some experiments, therefore, the gas was passed over molten yellow phosphorus and then through a spiral cooled in liquid air. No difference could be detected in the samples prepared and purified in various ways. Successive fractions, too, taken from the liquefied gas were also found to agree closely in density and to show no evidence of a change in one direction.

Indeed, taking all the data into consideration, we find strong evidence for the homogeneous character of the various specimens.

As the work developed and a number of consistent measurements were obtained, it was seen that the ratios led to a very high value for the atomic weight of carbon—in the vicinity of 12·015.

Accordingly, a careful search was made for the presence in the gas of a heavy impurity. The carbon monoxide was tested with baryta water to see if a trace of carbon dioxide was present, but not the slighest indication of its presence was ever found. At one time it was suspected that a trace of a metallic carbonyl was formed when the gas came in contact with mercury, but special experiments devised to test this always gave negative results. The apparatus was carefully examined for air leaks, and the number of stopcocks was reduced to a minimum, only those being employed which were above suspicion. The possibility, too, of a trace of water in the balance case which might have made the balancing pressure of the oxygen too high was investigated, but again the results were entirely negative.

Finally, the apparatus was taken down and rebuilt to an improved design, and with this the final results were obtained.

The course of an experiment can now be described shortly.

After making sure that the thermostatic arrangements were working satisfactorily, the balance case, lower manometer chamber and connexions were pumped down to as low a vacuum as possible with a mercury-vapour pump backed by a Hyvac pump. The final vacuum was tested by a Töpler pump, which was in the circuit and served as a McLeod gauge. One of the gases was then run in very slowly through a U-tube cooled in liquid air until the balance was seen to float.

The gas supply was then shut off, and the balance pointer adjusted closely to the reference point, a coarse adjustment being made by a slight alteration of the mercury level in the lower manometer chamber, and a fine adjustment by changing the level of mercury in a capillary manometer (pressure adjuster) in the same circuit.

The gas was usually allowed to stand for 20—30 minutes before pressure readings were taken. Each balancing pressure recorded in the tables of results is the mean of three and sometimes four pressure measurements, between each of which the balance pointer was reset to its reference point by changing the mercury level in the manometer and making a fresh setting with the pressure adjuster. By working in this way, the position of the meniscus in the manometer with reference to the walls of the tube varied in each reading, and possible errors due to irregular refraction would in the mean tend to cancel out. Moreover, by arresting and resetting the balance it was thought that any change in zero due to imperfect elasticity in the fibre would be partially eliminated.

The pressure readings were corrected (*a*) for errors in the scale (irregularity in ruling and total length), (*b*) to 0°. They were also corrected to what they would have been had the balance been set exactly to the reference point instead of to a small distance either above or below this position. It may be noted that the balance was observed with a long-focus microscope through a plane-glass window, and the position of the pointer measured by a screw micrometer reading directly to 0·005 mm. Finally, a slight correction had to be made for the variation of the temperature of the gas in the balance case from the mean temperature.

Had corrections (*a*) and (*b*) been omitted, this would have had very little effect on the ratios, and none at all if the ruling of the scale was perfectly regular.

However, since the setting of the manometer thermostat was occasionally adjusted, a correction had often to be applied when comparing different specimens of the same gas, and in order to make the balancing pressures strictly comparable it was found convenient to reduce them to 0° and express them in terms of true millimetres.

A typical record of the data from which a single balancing pressure is calculated is shown below. These are as they were recorded and have not been reduced from 20·21° to 0° or corrected for the scale length.

| | | | | | Manometer height. | | | |
|---|---|---|---|---|---|---|---|---|
| Expt. No. | Balance temp. | Manom. temp. | Lower meniscus reading. | Upper meniscus reading. | Uncorr. | Corr. to value for gas at 19·80°. | Balance setting. | Manom. height (corr.). |
| 1 | 19·74° | 20·21° | 142·59 | 557·27 | 414·68 | 414·77 | −0·01 | 414·77 |
| 2 | 19·74 | 20·21 | 142·43 | 557·12 | 414·69 | 414·78 | +0·03 | 414·76 |
| 3 | 19·73 | 20·21 | 142·45 | 557·15 | 414·71 | 414·80 | +0·005 | 414·80 |
| 4 | 19·72 | 20·21 | 141·58 | 556·25 | 414·68 | 414·79 | +0·02 | 414·78 |
| | | | | | | | Mean | 414·77(7) |

Correcting to true millimetres and to 0°, we get 413·44(5), which is the balancing pressure of the carbon monoxide in Expt. 5, Series III (p. 851).

After the pressure of one of the gases, usually oxygen, had been determined in this way, the balance case, manometer, and connecting tubes were again evacuated completely, the other gas introduced, and its pressure determined in the same way. When sufficient ratios of the pressures had been determined for one density, the balance was withdrawn from its case, and by fusing on a small piece of silica to the solid sphere the beam was made to balance at a lower pressure, and another series of ratios was determined, and if desired a third.

It will be noted that the concordance of the pressures in any series is not as good as the measurements would lead one to expect. Often the final corrected readings differed by 0·03 mm. although the balance was easily sensitive to a pressure change of 0·005 mm. and the error in the actual measurement of the position of the mercury surfaces did not exceed 0·01 mm. Slight temperature fluctuations could not be correlated with these variations, nor were they caused by impurities in the gases, for even with the same sample, they appeared when the readings were taken at different points in the manometer tube. It was suspected that irregular refraction through the walls of the tube was responsible for these variations in the pressure readings. Recent work by Cawood and Patterson has proved definitely that this is the case, and has shown how refraction errors can be largely avoided by the use of manometer tubing of very thin wall (*Trans. Faraday Soc.*, 1933, **29**, 514). In the experiments described here, the errors in the pressure measurements set a limit to the accuracy of the final ratios, but to some extent the errors have been reduced, though not completely eliminated, by the method employed in taking the readings.

The experimental results obtained in this investigation are given in the following tables. In Series I the pressures of the two gases were compared at 0°, and in the remaining series at 19·8°.

*Series* I. *Preliminary Results.*

*Balance at* 0°.

| Expt. | Description of oxygen. | Balancing press. of $O_2$ corr. to 0°. | Description of CO. | Balancing press. of CO corr. to 0°. | Ratio of balancing press., $O_2$/CO. |
|---|---|---|---|---|---|
| 1 | $KMnO_4$, $A_1$ | 383·43 | Formic acid, X | 438·17 | 0·87507 |
| 2 | ,, ,, | 383·45 | ,, ,, | 438·12 | 0·87522 |
| 3 | ,, ,, | 383·55 | ,, ,, | 438·14 | 0·87541 |
| 4 | ,, ,, | 383·45 | ,, ,, | 438·09 | 0·87528 |
| 5 | ,, $A_2$ | 383·44 | ,, ,, | 438·15 | 0·87513 |
| 6 | ,, A | 383·49 | ,, ,, | (438·15) | 0·87525 |
| 7 | ,, $B_1$ | 383·45 | ,, ,, | 438·09 | 0·87528 |
| 8 | ,, $A_1$ | 383·47 | ,, ,, | (438·09) | 0·87532 |
| | | | (Balance cleaned.) | | |
| 9 | $KMnO_4$, $B_1$ | 383·06 | Formic acid, $X_1$ | 437·67 | 0·87523 |
| 10 | ,, ,, | 382·77 | ,, ,, | 437·27 | 0·87536 |
| 11 | ,, ,, | 382·67 | ,, ,, | 437·27 | 0·87513 |
| 12 | ,, ,, | 382·67 | ,, ,, | (437·27) | 0·87513 |
| 13 | ,, ,, | 382·69 | ,, $X_1$ | 437·22 | 0·87528 |
| 14 | ,, ,, | 382·69 | ,, ,, | 437·20 | 0·87532 |
| 15 | ,, ,, | 382·70 | ,, $X_2$ | 437·13 | 0·87548 |
| | | | (Balance cleaned and apparatus adjusted.) | | |
| 16 | $KMnO_4$, $B_1$ | 381·96 | Formic acid, $X_2$ | 436·36 | 0·87533 |
| 17 | ,, ,, | 381·89 | ,, $X_3$ | 436·36 | 0·87517 |
| 18 | ,, ,, | 381·97 | ,, $X_3$ | 436·39 | 0·87530 |
| 19 | ,, ,, | 381·96 | ,, $X_2$ | 436·36 | 0·87533 |
| 20 | ,, ,, | 381·98 | ,, $X_5$ | 436·44 | 0·87522 |
| 21 | ,, ,, | 381·84 | ,, $X_4$ | 436·24 | 0·87530 |
| | | | | Mean | 0·87526(4) |

In the table, the different samples of the two gases used are distinguished by letters. Thus for oxygen:

A denotes oxygen obtained by heating permanganate and not liquefied.

$A_1$ ,, ,, from same source, bubbled through its own liquid and then reliquefied and collected from middle fraction.

$B_1$ ,, ,, from permanganate, liquefied and collected from middle fraction, not bubbled through its own liquid.

For carbon monoxide:

X is gas prepared from formic acid and sulphuric acid in the manner described on p. 848.

$X_1$, $X_2$, $X_3$, $X_4$, $X_5$ are successive fractions collected from the distillation of the liquefied gas.

In Expts. 6, 8, and 12 the balancing pressure of oxygen only was determined; the carbon monoxide pressure in brackets used in calculating the ratio is that from the previous experiment.

In this series the maximum deviation from the mean is 2·5 parts in 10,000, but most of the ratios show a much closer concordance.

In this set of measurements the balance showed a tendency to change its zero and was not as constant in its behaviour as in the later series.

*Series* II. *Low Pressures.*

*Balance at* 19·8°.

| Expt. | Description of oxygen. | Balancing press. of $O_2$ corr. to 0°. | Description of CO. | Balancing press. of CO corr. to 0°. | Ratio of balancing press., $O_2/CO$. |
|---|---|---|---|---|---|
| 1 | $KMnO_4$, $B_1$ | 182·342 | Ferrocyanide, Y | 208·319 | 0·87530 |
| 2 | ,, ,, | (182·342) | Formic acid, $X_6$ | 208·319 | 0·87530 |
| 3 | ,, ,, | 182·342 | Ferrocyanide, Y | 208·321 | 0·87529 |
| 4 | ,, ,, | 182·338 | ,, ,, | (208·321) | 0·87527 |
| 5 | $KClO_3$, C | 182·345 | Formic acid, $X_6$ | 208·288 | 0·87545 |
| 6 | ,, ,, | 182·343 | Ferrocyanide, Y | 208·272 | 0·87550 |
| 7 | $KMnO_4$, $B_1$ | 182·338 | Formic acid, X | 208·287 | 0·87542 |
| 8 | ,, ,, | 182·332 | Ferrocyanide, Y | 208·273 | 0·87545 |
| 9 | $KClO_3$, C | 182·314 | ,, ,, | 208·288 | 0·87530 |
| 10 | ,, ,, | 182·356 | ,, ,, | 208·329 | 0·87533 |
| 11 | ,, ,, | 182·324 | Formic acid, X | 208·286 | 0·87535 |
| 12 | $KMnO_4$, $B_1$ | 182·344 | ,, ,, | 208·312 | 0·87534 |
| | | | (Balance removed and cleaned.) | | |
| 13 | $KMnO_4$, $B_1$ | 181·420 | Formic acid, X | 207·260 | 0·87533 |
| 14 | ,, ,, | 181·435 | ,, ,, | 207·264 | 0·87538 |
| 15 | ,, ,, | 181·432 | ,, ,, | 207·262 | 0·87538 |
| | | | (Balance set to lower zero.) | | |
| 16 | $KMnO_4$, $B_1$ | 180·012 | Formic acid, X | 205·663 | 0·87528 |
| 17 | ,, ,, | 180·017 | ,, ,, | 205·647 | 0·87537 |
| | | | | Mean | 0·87535(5) |

In this set of results the zero of the balance was more constant. The maximum deviation from the mean ratio was 1·7 parts in 10,000, and the mean probable error 0·14 part in 10,000.

*Series* III. *Intermediate Pressures.*

*Balance at* 19·80°.

| | | | | | |
|---|---|---|---|---|---|
| 1 | $KMnO_4$, $B_1$ | 361·895 | Formic acid, X | 413·482 | 0·87524 |
| 2 | ,, ,, | 361·898 | ,, ,, | 413·456 | 0·87530 |
| 3 | ,, ,, | 361·890 | ,, ,, | 413·475 | 0·87524 |
| 4 | ,, ,, | 361·887 | ,, ,, | 413·480 | 0·87522 |
| 5 | ,, ,, | 361·875 | X, re-treated KOH | 413·445 | 0·87527 |
| 6 | ,, ,, | 361·866 | Formic acid, X | 413·462 | 0·87521 |
| | | | | Mean | 0·87524(7) |

Maximum deviation from the mean, 0·41 part in 10,000 parts.
Mean probable error, 0·1 in 10,000.

*Series* IV. *High Pressures.*

| | | | | | |
|---|---|---|---|---|---|
| 1 | $KMnO_4$, $B_1$ | 572·266 | Formic acid, Z | 653·897 | 0·87516 |
| 2 | ,, ,, | 572·291 | ,, ,, | 653·965 | 0·87511 |
| 3 | ,, ,, | 572·261 | ,, ,, | 653·961 | 0·87507 |
| 4 | ,, ,, | (572·261) | ,, $Z_1$ | 653·979 | 0·87505 |
| 5 | ,, ,, | (572·306) | ,, $Z_2$ | 653·995 | 0·87509 |
| 6 | $KMnO_4$, $B_1$ | 572·306 | ,, $Z_3$ | 653·985 | 0·87511 |
| | | | | Mean | 0·87509(8) |

Maximum deviation from the mean, 0·75 part in 10,000.
Mean probable error, 0·15 part in 10,000.

The oxygen samples were the middle fractions taken from the liquefied gas and prepared from potassium permanganate ($B_1$) and from potassium chlorate (C). The carbon monoxide samples were obtained from ferrocyanide (Y) and also from formic acid (X) and (Z). The gas after purification in the manner described was liquefied, and the samples collected from the middle fraction. In some cases, *i.e.*, $Z_1$, $Z_2$, and $Z_3$, the gas was collected in successive fractions. The pressures in brackets denote values taken from a previous experiment and used in calculating the ratio. In Expt. 5 in Series IV the oxygen pressure used is that obtained in Expt. 6, since there was evidence of a zero shift in the balance between Expts. 4 and 5.

Before the mean ratios in the four sets of results can be used to compute the molecular weight of carbon monoxide, two corrections must be applied: (1) for the slight decrease in volume of the buoyancy bulb when oxygen is replaced by carbon monoxide and the consequent increase in gas pressure; (2) for the shift of the centre of gravity of the buoyancy bulb occasioned by this shrinkage in volume. (1) This is the usual Rayleigh correction, and for this pair of gases is small even at the highest pressures compared (Series IV), where it reaches a maximum of 0·4 part in 10,000. Careful measurements were made on this particular silica bulb by Mr. Whitaker in this laboratory, and he found as a mean of a number of concordant determinations that the contraction per atmosphere change in pressure was 3·3 cub. mm. (2) This source of error was first pointed out to us by Dr. W. Cawood (Ramsay Fellow), and we are much indebted to him for calling our attention to it.

Apparently this error has not been noticed before by workers with this type of balance, and Stock and Ritter (*loc. cit.*) do not mention it in their investigation on the relative densities of oxygen and ethylene. (It does not apply, however, to results obtained with a microbalance carrying a suspended bulb instead of a fixed one as was the case with xenon.) Now, if we assume that the silica bulb is perfectly symmetrical and of even wall thickness, the shift of its centre of gravity as it contracts with increase of external pressure is easily calculated.

On this assumption it was found to be $1{\cdot}53 \times 10^{-3}$ mm. per atmosphere. Measurements of the diameter along three axes at right angles to one another showed the bulb to be very closely spherical in form, but in spite of this it could not be assumed that the shrinkage would be even and that the bulb would still remain a sphere on contraction. It seemed possible that an alteration in volume might occur without a corresponding change in the position of the centre of gravity. To test this point, Mr. Whitaker kindly undertook to measure the actual wall displacement of the bulb at various points when a vacuum was produced in its interior. By an ingenious method, he was able to measure these small displacements with sufficient accuracy (Whitaker, *J. Sci. Instr.*, 1931, **8**, No. 8, 251). When examined in this way, one segment of the bulb showed considerably less contraction than the rest of the surface. The points on the surface at which displacement measurements had been made were then marked, the bulb broken, and the wall thickness of the marked and also of other portions carefully measured.

It was found that the displacements corresponded closely with thickness of wall, and that the segment showing the smallest contraction was more than twice as thick as the rest of the bulb. From a knowledge of the displacement and thickness of wall over the surface of the bulb, Mr. Whitaker was able to calculate the mean displacement per atmosphere of the centre of gravity of the bulb along the balance beam.

This was found to be $1{\cdot}33 \times 10^{-3}$ mm. per atmosphere.

Since the thicker portion of the bulb was at the extremity of a diameter at right angles to the balance beam, it is evident that the shift of the centre of gravity with shrinkage will not be strictly along the axis of the balance, and hence its effective component along the axis will be smaller than if the bulb had been perfectly uniform. The figure just given was therefore taken in preference to the former as being a more reliable value from which to calculate the correction.

With the balance used, the distance from the centre of the bulb to the axis of the beam, *i.e.*, the fibre suspension, was 38·2 mm., and its weight without stem was 0·349 g. The change in weight produced by a pressure difference of one atmosphere was therefore $1{\cdot}33 \times 10^{-3} \times 0{\cdot}349/38{\cdot}2 = 1{\cdot}215 \times 10^{-5}$ g. On application of this to Series IV, where the difference in balancing pressure of the carbon monoxide and oxygen was 81·7 mm., the corresponding weight change becomes $1{\cdot}312 \times 10^{-6}$ g.

Now the upward displacement of the bulb (volume = 8·435 c.c.) when balanced in oxygen at 572·3 mm. at 19·8° is equal to $8{\cdot}46 \times 10^{-3}$ g. Hence the total buoyancy necessary to float the balance suffers a fractional increase of $1{\cdot}312 \times 10^{-6}/8{\cdot}46 \times 10^{-3} = 1{\cdot}55 \times 10^{-4}$ on account of the centre of gravity shift, and the mean ratio in Series IV must therefore be decreased by this fraction, *i.e.*, by $0{\cdot}8751 \times 1{\cdot}55 \times 10^{-4} = 1{\cdot}357 \times 10^{-4}$.

The Rayleigh correction, which allows for the contraction in volume of the bulb itself with rising pressure, alters the buoyancy in the opposite sense. For the same pressure range the fractional change in volume of the bulb is $3{\cdot}3 \times 81{\cdot}7/8435 \times 760 = 0{\cdot}422 \times 10^{-4}$, so that the ratio (Press. $O_2$)/(Press. CO) must be increased by $0{\cdot}875 \times 0{\cdot}422 \times 10^{-4} = 0{\cdot}37 \times 10^{-4}$. The total correction to be applied to the ratio is therefore $(-\,1{\cdot}36 + 0{\cdot}37) \times 10^{-4} = -\,0{\cdot}000099$.

It can be shown that, whilst the Rayleigh correction gets smaller as the balance is set to equilibrium at lower densities, the centre of gravity correction remains constant, for although the actual centre of gravity shift becomes less, the weight of gas displaced by the bulb is diminished in the same ratio, so that the weight change from this cause is always the same fraction of the total buoyancy. For the pair of gases in question and this particular balance, the maximum correction due to centre of gravity change is 1·4 parts in 10,000; but with gases differing widely in density, especially with a shorter beam balance, the error may be much greater.

The final mean ratios, corrected and uncorrected, are shown in the following table.

| | Approximate pressures. | | Ratio, uncorr. | Corrections (1) and (2). | Corrected ratio. |
|---|---|---|---|---|---|
| | $O_2$. | CO. | | | |
| Series I, 0° | 382·8 | 437·2 | 0·87526 | −0·00010 | 0·87516 |
| Series II, 19·8° | 181·9 | 207·8 | $0{\cdot}87535_5$ | −0·000123 | 0·87523 |
| Series III, ,, | 361·9 | 413·5 | $0{\cdot}87524_7$ | −0·000112 | 0·87514 |
| Series IV, ,, | 572·3 | 654·0 | $0{\cdot}87509_8$ | −0·000099 | 0·87500 |

From the corrected mean ratios of Series II, III, and IV the limiting ratio can be calculated by a linear extrapolation. The assumption made by this treatment is that the *pv–p* graphs for each gas are strictly linear over the pressure range considered, for it can be shown that the ratios must be a linear function of pressure if the isothermals for each gas are straight lines. As a matter of fact, the graph obtained by plotting the ratios against the corresponding pressures for either oxygen or carbon monoxide was found to be a straight line within the limits of experimental error. From the three series, three values for the limiting ratio can be obtained in this way and are tabulated below.

| | Limiting ratios. | Mol. wt. of carbon monoxide. |
|---|---|---|
| From Series II and III | 0·87533 | 28·010(6) |
| II and IV | 0·87534 | 28·011(0) |
| III and IV | 0·87537 | 28·011(8) |
| Series I | 0·87534 | 28·011 |

The mean value from Series I is not considered to be as reliable experimentally as the values obtained later in Series II, III, and IV. To calculate the limiting value of this ratio, we must use the values of $1 + \lambda$ for oxygen and for carbon monoxide at 0° which have been found experimentally. The result for the molecular weight obtained from this series set forth in the table has been calculated by assuming for carbon monoxide the $1 + \lambda$ value found by Batuecas, Maverick, and Schlatter (*loc. cit.*), *i.e.*, 1·00048, and for oxygen the mean value 1·00094 given by Wild (*loc. cit.*). The agreement is certainly remarkable.

The mean atomic weight of carbon calculated from all these data is C = 12·011, which is considerably higher than the accepted chemical value for carbon but is in close agreement with Rayleigh's value obtained from carbon monoxide.

By using the above compressibility coefficients, the weight of a normal litre of carbon monoxide can be calculated. Taking 1·42894 as the weight of a normal litre of oxygen, we have $L_{CO} = L_{O_2} + R_{lim.} \times \frac{(1+\lambda)CO}{(1+\lambda)O_2} = 1{\cdot}42894 \times 0{\cdot}875345 \times \frac{1{\cdot}00048}{1{\cdot}00094} = 1{\cdot}25024$, where $R_{lim.}$ is the limiting value of the ratio of the balancing pressures. This value is in very close agreement with Rayleigh's, *viz.*, 1·25027, but about 1 part in 10,000 higher than the value obtained by Pire and Moles, and by Moles and Salazar (*Ann. Soc. Fis. Quim.*, 1932, **30**, 182), *i.e.*, 1·25011.

The ratios of Series II, III, and IV can be used in conjunction with the limiting ratio to calculate the relative compressibility coefficients of carbon monoxide and oxygen. Using the Berthelot notation for the compressibilities of gases, which, as Cawood and Patterson (this vol., p. 619) have emphasised, is stricter than that of Guye when we are dealing with pressures which are fractions of an atmosphere, it can be shown that $R = M_1(1 - A_2p_2)/M_2(1 - A_1p_1)$, where $R$ is the ratio of the balancing pressures $p_1$ and $p_2$ of two gases at the same density, $A_1$ and $A_2$ are the compressibility coefficients as defined by Berthelot, *i.e.*, $A = 1 - p_1v_1/p_0v_0$ for one atmosphere, and $M_1$ and $M_2$ the molecular weights.

In the limit ($p = 0$), $R_{lim.} = M_1/M_2$, so that $R/R_{lim.} = (1 - A_2p_2)/(1 - A_1p_1)$, and if the compressibility of oxygen is known at 20°, that of carbon monoxide can be calculated. Taking for oxygen at 20°, $1 + \lambda = 1{\cdot}00075$, we get for carbon monoxide at the same temperature 1·00020 as a mean from the three ratios. The value for oxygen was calculated by Cawood and Patterson and is probably a close approximation; that for carbon monoxide appears to be somewhat low in the light of the high-pressure data obtained recently for carbon monoxide by Scott (*Proc. Roy. Soc.*, 1929, *A*, **125**, 330) and by Townend and Bhatt (*ibid.*, 1931, **134**, 502) and extrapolated to low pressures. The data of those observers give a value of $1 + \lambda$ at 20° of approximately 1·00045, but the value at 0° obtained by Townend and Bhatt, *viz.*, 1·00073, is very probably too large by about 1 part in 5000. From Bartlett's data (*J. Amer. Chem. Soc.*, 1930, **52**, 1374), $1 + \lambda$ at $20° = 1·00023$, but his value at 0°, *viz.*, 1·0004, is slightly too small when compared with recent direct determinations at low pressure, Batuecas, Maverick, and Schlatter (*loc. cit.*) having found $1 + \lambda = 1·00048$. From the Beattie–Bridgman equation, using the constants for nitrogen, which is closely similar to carbon monoxide, we have $1 + \lambda_{20°} = 1·0003$. The evidence, then, though not very conclusive, favours a slightly higher figure than the one calculated from our results, and it is of interest to see whether the substitution of such a value in our ratios would affect the atomic weight of carbon appreciably. Assuming for carbon monoxide at 20°, $1 + \lambda = 1·00035$ instead of 1·0002, the mean atomic weight from the three ratios is found to be 12·009—a reduction which is inconsiderable.

Pire and Moles in their work on the density of carbon moxonide, and also Moles and Salazar in an extended investigation on the same subject recently published (*loc. cit.*), calculate the molecular weight of the gas from the expression

$$M = \frac{RL}{1 + \lambda} = \frac{22·414 \times 1·25010}{1·00050}, \text{ whence C} = 12·006.$$

If, instead of using the limiting molar volume 22·414, we compare the density of carbon monoxide with the density of oxygen determined under the same experimental conditions by Moles and Gonzales (*loc. cit.*), a procedure which appears to us sounder, and use for $1 + \lambda$ for oxygen the mean value 1·00094 calculated by Wild (*loc. cit.*), the value for C becomes 12·008.

It may be noted that the microbalance method involves no measurements in absolute measure nor independent determinations of compressibility. Moreover, the higher value for carbon which we find is confirmed by the determinations of the compressibilities of carbon dioxide and ethylene recently published by Cawood and Patterson (*loc. cit.*).

A further confirmation of the higher value for carbon is obtained by comparing the normal densities of nitrogen and carbon monoxide. These two gases show very nearly the same deviation from Boyle's law over a large pressure range, so that the ratio of the normal densities is very nearly identical with the ratio of the limiting densities. Moreover, any uncertainty in the atomic weight of nitrogen is very small. If we take for the normal density of nitrogen 1·25046, a general mean of the best established data (Moles, *Z. anorg. Chem.*, 1927, **167**, 49), and the mean value 1·25020 for the normal litre of carbon monoxide based on the results of Rayleigh, Moles, and ourselves, and assume N = 14·0082, we get for carbon 12·011.

We conclude therefore that 12·011 is a close approximation to the atomic weight of carbon on the chemical scale, and that the values accepted hitherto are too low. If this conclusion is correct, the proportion of the $C^{13}$ isotope must be as high as 1%, which is in close agreement with the results obtained recently by band-spectrum methods by Jenkins and Ornstein (*Proc. K. Akad. Wetensch. Amsterdam*, 1932, **33**, 1212).

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THE UNIVERSITY, LEEDS.

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