The Determination of Atomic Weights by Means of the Microbalance, and the Values Obtained for Carbon, Nitrogen, and Fluorine

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III—The Determination of Atomic Weights by Means of the Microbalance, and the Values Obtained for Carbon, Nitrogen, and Fluorine

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1—Introduction

The chemical determination of atomic weights possesses one advantage over physical methods in that it gives the average atomic weight of an element as found naturally, whether that element be a simple one or a mixture of a number of isotopes. Thus, whilst the mass spectrograph method is capable of determining the mass of any isotope to a high degree of accuracy, the evaluation of the abundance ratios of each isotope present in a natural element is often a matter of considerable difficulty.

The method which we have used, namely, the microbalance method of limiting pressures, is not new, nor does it involve any new considerations or properties of the gas in question. The fundamental principle involved in the method is a variation of that originally put forward by Berthelot in 1898,* and known as the method of limiting densities. Berthelot showed that gases only obey Avogadro's Hypothesis at zero pressure, and consequently the extrapolation of the ratio of the *densities* of two gases, measured at a number of pressures down to zero pressure, would lead to the accurate ratio of their molecular weights. Hence, if the molecular weight of one of the gases was known, that of the other could be calculated with ease. In the microbalance method, the *pressures* of two gases are measured at which they have equal densities as shown by the deflexion of the balance. The ratio of the pressures so obtained would be equal to the inverse ratio of the molecular weights, if both the gases were perfect. In practice, however, owing to the deviations of gases from Boyle's Law, this is only true at zero pressure, and consequently a number of ratios are taken, corresponding to different densities. These, when plotted against the measured pressures of one of the gases, enable the extrapolation to zero to be carried out.

The microbalance has been used for determining gaseous densities by Whytlaw-Gray and Ramsay† in 1910, on the atomic weight of radium emanation, by Aston‡

* 'C.R. Acad. Sci. Paris,' vol. 126, p. 954 (1898).
† 'C.R. Acad. Sci. Paris,' vol. 151, p. 126 (1910) ; 'Proc. Roy. Soc.,' A, vol. 84, p. 536 (1910).
‡ 'Proc. Roy. Soc.,' A, vol. 89, p. 440 (1914).

in 1914 for testing the partial separation of the isotopes of neon by diffusion and refractionation, and by TAYLOR* in 1917 on the density of hydrogen.

In order, however, to carry out measurements with the precision required in modern atomic weight determinations, a much more elaborate technique has been evolved, which is the result of researches carried out in such widely different fields as, for instance, the meniscus depressions of mercury columns, the adsorption of gases on quartz, and the accurate temperature control of quite a large room. Many errors were found in the original method which, as will be seen later, were one by one either obviated entirely or corrected for accurately.

2—THEORETICAL CONSIDERATIONS

As the microbalance experiments are all carried out at pressures below one atmosphere, it is only the behaviour of the various gases over this pressure range that need be considered. It has been shown† that for all gases, except the exceedingly compressible ones, the $(pv - p)$ curve is linear within the limits of our experimental error, which is of the order of 1 in 20,000 on an individual density ratio. The isotherms can therefore be expressed by means of BERTHELOT's (*loc. cit.*) original formula :—

$$pv = p_0 v_0 (1 - Ap)$$

where p = pressure in atmospheres, and v = volume. This equation is only applicable to the range of 0–1 atmosphere and A, the deviation over one atmosphere of the gas from BOYLE's Law is called the compressibility.

As the Ap correction term is zero at zero pressure it follows that

$$p_0 v_0 = RT \frac{W}{M},$$

where W is the weight of gas under experiment, M is its molecular weight, R is the gas constant, and T is the absolute temperature.

Consequently,

$$pv = RT \frac{W}{M} (1 - Ap),$$

and

$$p = RT \frac{D}{M} (1 - Ap),$$

where D is the density of the gas in W/M units. In the microbalance method the pressures of two gases, one of known molecular weight, are measured, at which they

* 'Phys. Rev.,' vol. 10, p. 653 (1917).

† Cawood and Patterson, 'J. Chem. Soc.,' vol. 156, p. 619 (1933)

have equal densities, as shown by the deflexion of the balance due to the quartz buoyancy bulb suspended at one end of the beam.

Thus

$$p_1 = RT \frac{D}{M_1} (1 - A_1 p_1),$$

$$p_2 = RT \frac{D}{M_2} (1 - A_2 p_2),$$

therefore

$$\frac{p_1}{p_2} = \frac{M_2}{M_1} \cdot \frac{(1 - A_1 p_1)}{(1 - A_2 p_2)} = r. \quad \ldots \ldots \ldots \quad (1)$$

The ratio r of the two pressures measured under these circumstances will tend to be equal to the inverse ratio of their molecular weights when the pressures become infinitely small and the compressibility correction becomes negligible.

Now if r is plotted against p_1, a linear graph is obtained, as can be seen by differentiating the last equation,

$$i.e., \frac{dr}{dp_1} = (A_2 - \frac{M_2}{M_1} \cdot A_1) = \text{constant}.$$

Thus if the ratio r is measured at different densities of the gases, by changing the balancing point of the balance, a graph will be obtained, the linear extrapolation of which to zero pressure will give the limiting ratio, which is equal to the inverse ratio of the molecular weights of the two gases. It is important that r is plotted against p_1, as the curve $(r - p_2)$ is not straight but exhibits a slight curvature.

The compressibility of one of the gases may also be calculated if that of the other is known.

For from (1) we see that

$$\frac{M_2}{M_1} = r \frac{(1 - A_2 p_2)}{(1 - A_1 p_1)}.$$

This is true at whatever density the pressures are measured and therefore if two ratios r' and r'' are taken

then

$$r' \frac{(1 - A_2 p_2')}{(1 - A_1 p_1')} = r'' \frac{(1 - A_2 p_2'')}{(1 - A_1 p_1'')}.$$

Thus the only unknown is (say), A_1, all the other terms being experimental values.

It will be seen, therefore, that the microbalance method is a variation of the limiting density method, a better name for it being in this case the limiting pressure method. By means of the ratio measurements, the molecular weight of a gas and also its compressibility can be measured.

3—Experiments Leading to Improvement in the Accuracy of the Method

In the experiments already referred to of Whytlaw-Gray and Ramsay,* and Aston,† the microbalance was of the knife-edge type. That is, a quartz beam was constructed, onto which was fused a ground quartz knife edge, by means of a small oxy-coal-gas blow pipe. This rested on a small, polished quartz plate. Whilst this type of balance is satisfactory for certain purposes, it has two disadvantages which limit its application. Firstly, it is very sensitive to changes of position. That is, the zero alters if the knife edge rests on a different part of the quartz plate, or if the plate slightly changes its level. Secondly, the grinding and polishing of the knife edges is a matter of some considerable difficulty, and when finished they are fragile and easily chipped. Consequently the authors decided to use a quartz micro-balance of the torsion type, similar in principle to that of Taylor,‡ in which the
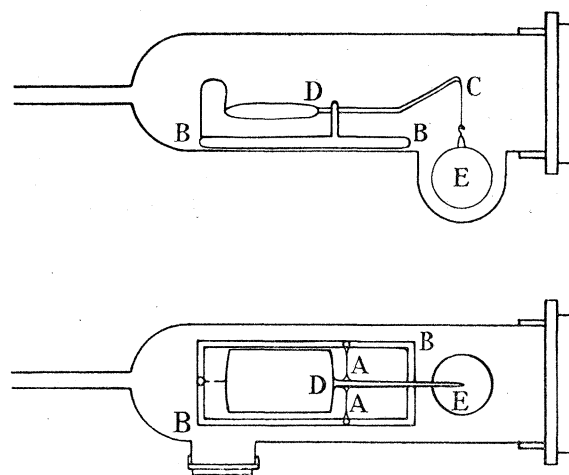

Fig. 1

beam is suspended by two tightly stretched quartz fibres at right angles to the motion of the beam. A balance of this type was constructed and used by the authors to determine the atomic weight of xenon.§ The balance and apparatus were fully described in the xenon paper, but as the design of the present apparatus is the outcome of various errors and difficulties met with in the initial apparatus, a short description is again necessary.

The microbalance was constructed from transparent quartz rod, about 1 mm. thick and 6 cm. long (fig. 1). It was suspended by the tightly stretched, fine quartz fibres AA at its mid-point from the stand B, which was made of rather thicker quartz rod. The end of the beam C carried another very thin quartz fibre and a

* 'C.R. Acad. Sci. Paris,' vol. 151, p. 126 (1910) ; 'Proc. Roy. Soc.,' A, vol. 84, p. 536 (1910).
† 'Proc. Roy. Soc.,' A, vol. 89, p. 440 (1914).
‡ 'Phys. Rev.,' vol. 10, p. 653 (1917).
§ Whytlaw-Gray, Patterson, and Cawood, 'Proc. Roy. Soc.,' A, vol. 134, p. 7 (1931).

hook from which was suspended the quartz buoyancy bulb, E. It is essential for accurate measurements that the bulb be suspended from the thinnest quartz fibre which will support it without breaking, rather than fused rigidly to the beam. In this latter design, the bulb is slightly distorted with change of pressure and consequently its centre of gravity shifts, relative to the balancing point, introducing a large, uncertain error. A balance of this type was used by WOODHEAD and WHYTLAW-GRAY* in the determination of the atomic weight of carbon from carbon monoxide, and these workers show how the inclusion of the error due to the shift of centre of gravity brought down the value of the atomic weight of carbon from $12 \cdot 015$ to $12 \cdot 011$. By suspending the bulb from a fibre, a knife-edge effect is obtained and the error is eliminated. Actually, there is another error due to this distortion of the bulb with pressure, which is present even when the fibre suspension is used, namely, the change of buoyancy between the balancing pressures of two gases of differing molecular weights. This, however, as will be shown later, is a second order correction and easily corrected for.

At the other end D of the beam is a fused quartz plate of equal area to that of the bulb. This is to compensate for any absorbed gas on the quartz bulb, and is fused onto the beam in such a position that the surface moments of the absorbed material are equal at both ends of the beam.

The microbalance, itself, was contained in a small glass tube of 30 cc. capacity, surrounded by a large brass casting which was heavily lagged with shredded asbestos and asbestos board. A microscope was focussed through an aperture in the casting onto the pointer of the balance, enabling the balancing position to be accurately adjusted. The glass balance case was connected to a manometer by a glass spiral to eliminate vibrations from the rest of the apparatus, and a small U-tube containing gold foil to prevent the entrance of mercury vapour. The manometer, which was surrounded by a water bath, consisted essentially of a U-tube of about $1 \cdot 7$-cm. bore, one limb being about 90 cm. long and evacuated by means of a Toepler pump, whilst the other limb was about 30 cm. long and was connected to the microbalance case. The lower end of the U-tube was connected by means of rubber tubing to a mercury reservoir. In addition, there was another capillary pressure gauge also connected to a mercury reservoir. By moving this reservoir upwards or downwards the pressure in the apparatus could be accurately adjusted until the balance beam pointer was exactly level with a similar pointer fused onto the framework of the balance. The pressure was measured by swinging a cathetometer telescope from the manometer to an accurate glass scale which was fixed vertically alongside the manometer in the water bath.

The gas of unknown molecular weight and the comparison gas, namely pure oxygen, were contained in 2-litre glass globes, and were connected to the microbalance and manometer by a system of glass tubes and mercury seal taps, in such a way that either might be independently let into the apparatus. Whilst the gas of unknown molecular weight could in general be frozen back into its flask by

* 'J. Chem. Soc.,' vol. 209, p. 846 (1933).

means of liquid air, the oxygen had to be pumped back by means of a circulating Toepler pump. A Hyvac oil pump was used to eliminate the last traces of either gas left in the apparatus. In addition an accurate McLeod gauge was connected, in order to test the tightness of the apparatus and to determine when the evacuation was complete.

With this apparatus, measurements were taken on methyl fluoride* which lead to a value of F = 19·01, which was thought at the time to be correct. In some respects, however, the apparatus as described above was unsatisfactory. At times large, inexplicable errors were found in the pressure measurements, and on certain days the temperature control was very erratic. It was therefore decided to rebuild the whole apparatus in a constant temperature room which could be kept at 21° C. to a high degree of accuracy, rather than to place the apparatus itself in a thermostat.

After some preliminary experiments in temperature control, in one of the cellars of the old Chemistry Department at Leeds, a room was placed at our disposal by Professor WHYTLAW-GRAY in the new Chemistry Department. This was about 20 feet square and was provided with double doors. Being in the basement it had the added advantages of having no windows, very thick walls, and being practically underground at one side. The existing steam radiators were turned off and the ventilators were permanently closed, it being thought sufficient to depend for oxygen on that obtained from the evaporating liquid air used in the apparatus, and the occasional opening of the doors. In each corner of the room was mounted an electric fan which was arranged to blow a stream of air on to a circular 700-watt electric heater. The heaters were wired in parallel to a mercury relay, which was actuated by a toluene-mercury thermometer. The thermometer was of a special design and consisted of a very thin-walled glass tube of 5-mm. bore, which ran round three sides of the room, terminating in a U-tube with 10-in. limbs. The tube was filled with toluene by partially evacuating several times and then the U-tube was filled with mercury. An adjustable platinum needle, which was mounted on the open side of the U-tube, when in connexion with the mercury, actuated the relay to cut out the heaters. By means of the adjustment, the temperature of the room could be varied from about 18° C. to 26° C. Whilst most of the work has been carried out at 21° C., it has been found necessary to raise the temperature to about 25° C. during very hot summer periods. It was found that any body of a fairly large thermal capacity, such as the block of brass round the balance case or a water bath, would keep at a temperature constant to a few hundredths of a degree for some days. Over the period of a reading, which was about a quarter of an hour, the difference of temperature was either nil or about 0·001° C.

When the apparatus was reconstructed in this room, it was found that irregularities were still present in the pressure readings which were obviously not due to temperature effects. The actual pressure readings themselves were therefore deemed suspect, although the cathetometer and the glass scale were undoubtedly

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* PATTERSON and CAWOOD, 'J. Chem. Soc.,' p. 2180 (1932).

accurate. This seemed to indicate that the capillary depressions due to the mercury meniscus in the manometer were probably in error, which seemed probable when it was found that the figures published in GLAZEBROOK's 'Physics' were purely theoretical calculations. A table of experimental values was deemed necessary and an apparatus was designed in order to measure them.* We immediately found, rather to our surprise, that it was impossible to take measurements accurate to $0 \cdot 01$ mm. through ordinary glass tubing of 17-mm. bore, owing to irregularities in the walls of the tubing. This error would also be largely magnified when the tubing was mounted in a water bath, as was the manometer which we used with the micro-balance. After some experiments with optically polished tubing it was found that the most satisfactory way of obviating these refraction errors was to use very thin walled tubing, the walls of 17-mm. tubing, for instance, being less than $0 \cdot 5$ mm. thick. With tubing of this description the capillary depressions of differing meniscus heights in differently sized tubes were measured, and a table formulated giving the depressions for meniscus heights varying from 0–2 mm. in tubes of 10–20-mm. bore (loc. cit.).

The results of this research showed that the design of the manometer must be radically changed, and that to use a water bath, with its consequent refraction errors, was quite impossible. A manometer was therefore constructed of the thin-walled tubing, with a metal jacket to keep the temperature constant. It consisted of a long tube A (fig. 2), and a short tube B, similar in shape to the old design, mounted in a teak case C, which was open on the side facing the cathetometer. The opposite side was closed with a piece of plate glass covered with tracing paper to give a diffused illumination. The tube B and the lower part of A were enclosed in a massive brass casting D, with slits to enable the middle part of the meniscus to be seen. The rest of A was enclosed between the two parts of a split aluminium tube G, arranged so that the middle of the mercury column was visible at any point. Thermometers were mounted in mercury cups at E. Although the walls of the manometer were very thin, in practice it was found to be quite strong, and would bear a sudden reduction of about an atmosphere on A with ease, although this meant, of course, the sudden rise of mercury up 760 mm. of the tube A. The glass scale F was mounted alongside the manometer as before. In order to read a pressure accurately, the top of the mercury meniscus must be illuminated by the narrow slit of light, and consequently dark shutters had to be arranged to slide

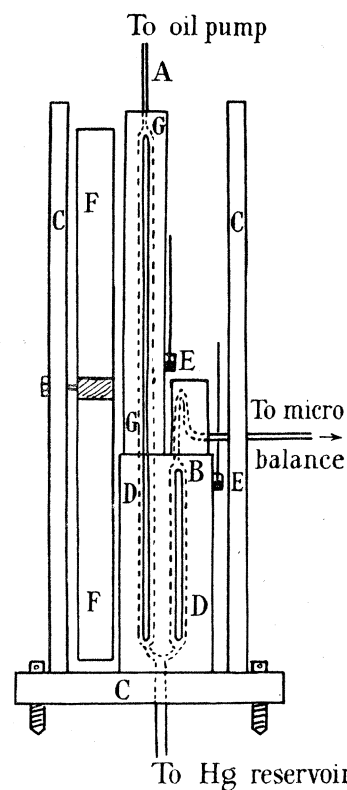To oil pump

To micro balance

To Hg reservoir

FIG. 2.

* CAWOOD and PATTERSON, 'Trans. Faraday Soc.,' vol. 29, p. 514 (1933).

up and down behind each tube. To measure the meniscus height for the capillary depression correction, front illumination was used.

With the aid of this manometer, measurements were taken with different fillings of pure oxygen. They were found to agree to $0\cdot01$ mm., and no variations were obtained when different parts of the tubes were used. This proved conclusively that errors due to temperature, refraction, and capillarity had been overcome and that the atomic weight measurements could be resumed.

As certain preliminary measurements* had given indications that the accepted atomic weight of carbon (C $=$ $12\cdot000$) was too low, pure carbon dioxide and ethylene were prepared. (The details of purification appear in § 4.) Pure oxygen was also prepared as a comparison gas, its molecular weight being taken as $32\cdot000$. The results obtained from these gases, whilst being perfectly satisfactory from the point of view of accuracy and freedom from zero alterations of the balance, led to values for the atomic weight of carbon of $12\cdot019$ in the case of ethylene and $12\cdot026$ in the case of carbon dioxide. These values were certainly too high, and it was decided to test the apparatus on nitrous oxide, as the atomic weight of nitrogen was known to be between $14\cdot007$–$14\cdot008$. Again satisfactory results were obtained with the apparatus, but the atomic weight of nitrogen came out at $14\cdot014$, proving that there was still some error left in the apparatus.

The only likely errors which appeared to be still present were those due to adsorption on the microbalance, and those due to the extrapolation of the ratios down to zero pressure.

To test the latter a series of separate experiments was carried out in an Andrews compression apparatus,† and the isothermals at 21° C. of carbon dioxide, ethylene, nitrous oxide, methyl ether, and sulphur dioxide were obtained. These were all strictly linear over a pressure range of about $0\cdot9$–3 mm. of mercury, and as there was no reason to doubt any sudden change in properties below this range down to zero pressure, this proved that the linear formula, $pv = p_0 v_0 (1 - Ap)$ was rigid, and consequently no error was introduced by the linear extrapolation of the microbalance ratios. In addition, when three or more microbalance ratios were measured at different pressures there was no evidence of any curvature of the r, p graph in either our work or that of WOODHEAD and WHYTLAW-GRAY.‡ We thus see that the most probable error of these preliminary results was that due to adsorption on the balance, despite the fact that the surface moments at each end of the beam were equal. This view was confirmed by a cross ratio between the carbon dioxide and nitrous oxide results. These two gases, having similar critical data, molecular weights, and compressibilities, would be expected to behave in a similar manner, and consequently the error due to adsorption should be either negligible or extremely small. The cross ratios were taken in the following way in order to eliminate the oxygen results with which the gases were originally compared.

* PATTERSON, WHYTLAW-GRAY, and CAWOOD, ' Nature,' vol. 128, p. 375 (1931).
† CAWOOD and PATTERSON, ' J. Chem. Soc.,' vol. 156, p. 619 (1933).
‡ ' J. Chem. Soc.,' pp. 209, 846 (1933).

Thus (from §2)

let

$$M_{CO_2} = M_{O_2} \cdot \frac{p_{O_2}(1 - A_{CO_2}\, p_{CO_2})}{p_{CO_2}(1 - A_{O_2}\, p_{O_2})},$$

and

$$M_{N_2O} = M_{O_2} \cdot \frac{p_{O_2}(1 - A_{N_2O}\, p_{N_2O})}{p_{N_2O}(1 - A_{O_2}\, p_{O_2})}.$$

As p_{O_2} is constant

therefore

$$\frac{M_{CO_2}}{M_{N_2O}} = \frac{p_{N_2O} \cdot (1 - A_{CO_2}\, p_{CO_2})}{p_{CO_2}(1 - A_{N_2O}\, p_{N_2O})}.$$

The extrapolation of $\left(\dfrac{p_{CO_2}}{p_{N_2O}}\right)$ against p_{CO_2} to zero pressure clearly leads to the limiting ratio.

Assuming that $N = 14 \cdot 008$ and inserting the forementioned results the cross ratios give the value $C = 12 \cdot 007$, which is in close agreement with the preliminary results, and with the value of WOODHEAD and WHYTLAW-GRAY.* It thus was obvious that an error was present which depended upon the physical properties of the gases themselves rather than inaccuracies in the pressure measurements, meniscus, or temperature corrections. This could only be due to unequal adsorption on the two ends of the balance, and it was therefore decided to correct for adsorption by trial and error with a very compressible gas of which the molecular weight was known to a fairly high degree of accuracy. Sulphur dioxide was the gas chosen because the atomic weight of sulphur appears to be established at $32 \cdot 06$. It is, moreover, absorbed by quartz about twenty times as much as any of the other gases used and has the added advantage of being about twice as heavy. Owing to this latter property, there is a further gain because of the actual weight of the molecules adsorbed, and the balancing pressure being low in comparison with that of oxygen. (The adsorption effect may be shown to increase relatively as the pressure is lowered.) The total error due to adsorption using sulphur dioxide is therefore about sixty times greater than any of the other gases used.

The method of compensating the balance was to alter the area of quartz on one end of the beam until a limiting ratio was obtained, leading to a value in close agreement with the accepted value for the molecular weight of sulphur dioxide. Eventually, after much laborious experimental work, the following results were obtained, which were deemed satisfactory :—

Ratio $\left(\dfrac{p_{O_2}}{p_{SO_2}}\right)$	p_{O_2}	
$2 \cdot 01154$	$417 \cdot 564$	(mean of four fillings)
$2 \cdot 00710$	$226 \cdot 940$	(,, ,,).

The extrapolation of these results leads to a limiting ratio of $2 \cdot 00182$ and therefore a molecular weight of $64 \cdot 058$, and an atomic weight of sulphur of $32 \cdot 06$. The

* 'J. Chem. Soc.,' pp. 209, 846 (1933).

error, therefore, is only of the order of 1 in 10,000 with sulphur dioxide, and with the gases such as carbon dioxide, nitrous oxide, ethylene, or any similar gas the maximum possible error due to adsorption would only be about 1 in 60,000 which is almost beyond the limit of working.

It is interesting to note, in connexion with the compensation of the balance by trial and error, that the actual measured area of the quartz surface appears to bear very little resemblance to the area of surface available for adsorption. The state of the quartz surface, that is, whether it is drawn, fused, or polished, is of very much greater importance. In the final microbalance, for instance, the ratio of the two surfaces at each end of the beam was about three to four, the larger surface being the blown buoyancy bulb and the smaller a fused quartz coverslip. This is probably due to the fact that the bulb has a more continuous surface than the coverslip, which had presumably been rolled, and was therefore slightly pitted or corrugated. Evidence in favour of this view was gained in the final compensation, when a number of bulbs of different sizes was tried. It was found in one case that a small, rather imperfectly blown bulb with a quite definite " bloom " on its surface adsorbed more sulphur dioxide than a bulb of larger radius with a smooth, clean surface. It is extremely important that all the quartz surfaces be clean and free from the white bloom which so easily appears on quartz when it is worked in the oxygen-gas blowpipe flame. Under working conditions the balance and its weights are taken down and washed in various organic solvents, then in concentrated nitric acid about every three weeks. The drying is carried out in a small tubular electric furnace.

If this procedure is not followed, variations occur in the readings, slight at first, but gradually getting larger until the results are worthless. This is probably due to the slow deposition of tap grease vapour on the quartz surfaces of the balance, although Apiezon grease of very low vapour pressure was always used.

We were thus led to the design of the final apparatus with which all the results in §5 were obtained. It is shown diagrammatically in fig. 3. All the glass connexions were blown, and the connecting tubes were kept as short as possible. They appear long in the diagram owing to the difficulty of clearly showing a three dimensional apparatus in a two dimensional diagram. The taps were of the mercury-seal type.

The manometer A was connected to the microbalance case E, through a U-tube B containing gold foil, a spiral C to damp out vibrations, and two deflectors D, which prevented the entering gas either blowing directly on the balance, or depositing particles on it. The balance case E was surrounded by a massive brass casting and the connexions to the manometer were heavily lagged with asbestos wool. The connexion to the gas storage flasks was made through the large tap F.

Whilst the gas of unknown molecular weight could be frozen back into its flask by means of the vessel H, a circulating Toepler pump G had to be used for the oxygen. The two gases were isolated from each other by means of the double taps I.

In practice the apparatus was first pumped down to about $0\cdot001$ mm. by means of the oil pump, a McLeod gauge being used as a test on the efficiency of the pump. Then oxygen was let into the balance case and manometer until the pointer on the balance beam was exactly level with a fixed pointer. A microscope, focussing through an aperture in the brass casting enabled this to be done with great accuracy. The apparatus was then closed by the tap F and left for about half an hour to get into equilibrium. Any slight alteration of the pointer was corrected by raising or lowering a mercury thread in the capillary tube J.

After reading the pressure, the oxygen was pumped back into its flask by the circulating pump, the last traces being removed by the oil pump. The same procedure was then carried out on the other gas, generally about five ratios being
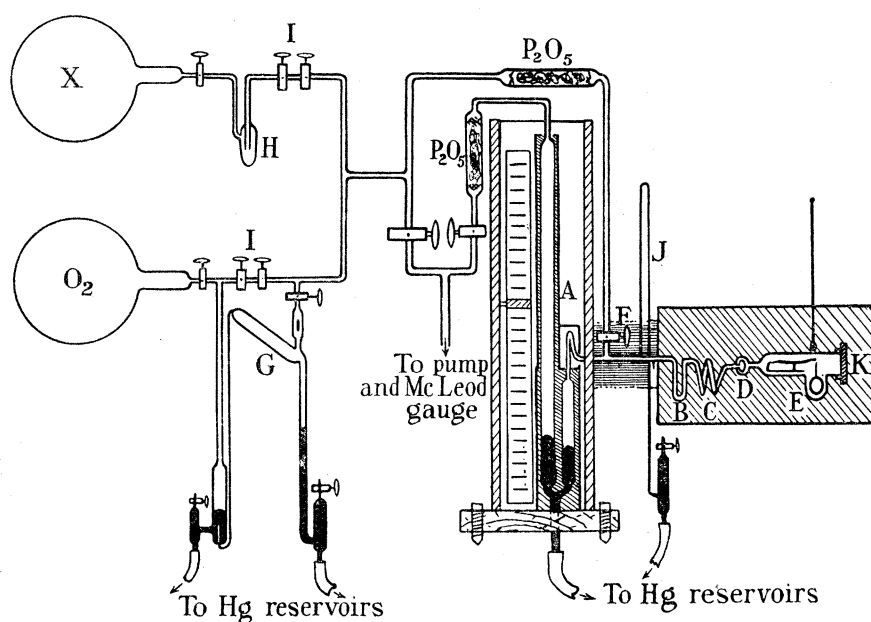

FIG. 3

possible at one run of the apparatus. The density at which the balancing point was obtained could be altered by taking the end plate K off the balance case and altering the weight.

4—PREPARATION OF PURE GASES

In any research on the atomic weights of elements by chemical methods, errors may be divided into two different classes, namely, those due to the apparatus which may be constant, systematic, or merely lack of accuracy, and those due to impurities in the compounds used in the experiments. The latter will be constant in any one particular set of observations, but in many cases they can be detected by a knowledge of the likely impurities. Thus the only likely impurity in carbon dioxide

as prepared below is air, and consequently if the results lead to too low a density for the gas it is fairly certain that all the air has not been pumped away from the solid carbon dioxide.

It is important, therefore, that any compound used for atomic weight determinations should be prepared in such a manner that all likely impurities are eliminated. Any errors or deviations then obtained are most probably due to the apparatus. When gaseous compounds are used, the problem of their preparation in a pure state is rather simpler than the corresponding case in stoichimetrical methods where solids are prepared. Thus, a reaction can generally be chosen where the gas required is the only gaseous product, and consequently it is possible to have impurities in the reacting compounds which will not affect the purity of the evolved
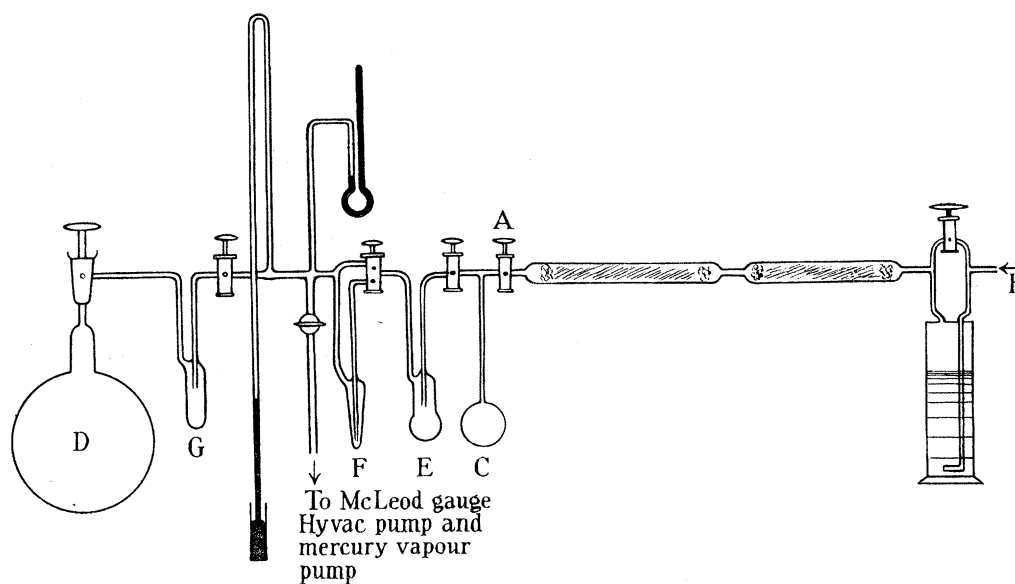

To McLeod gauge
Hyvac pump and
mercury vapour
pump

Fig. 4

gas in the least. In addition, the last traces of impurity may not only be removed by chemical means but also by physical methods which include fractionation, and solidification, etc. These latter, indeed, are probably the most important, for, by following the fractionation of the liquefied gas with gaseous density measurements, one is enabled to pick the purest fraction of what is initially an extremely pure sample, and so reduce the error due to impurities to a minimum.

The apparatus which was designed for the final purification of the gases used in these researches was similar for all the gases prepared and is shown in fig. 4. It is divided into two parts by the tap A, the part to the right being the ordinary chemical purification train containing the required reagents in wash bottles and tubes, whilst to the left the liquid air manipulations were carried out with the condensed gases. The whole apparatus was made of glass and all the connexions

were blown. There were no rubber connexions. The glass taps were all of the mercury sealed type.

In practice, the gas, prepared in a fairly pure form by specific methods described later, was allowed to enter the previously evacuated apparatus at B, and to pass over the various purifying chemicals, the last tube invariably being a metre long glass tube full of pure phosphorous pentoxide. It was then condensed in the bulb C by means of liquid air. The rest of the apparatus, including the storage flasks D, in the meanwhile had been evacuated by means of a mercury vapour pump, backed with an oil pump to a very low pressure about (0·001 mm.). This pressure is only obtained by washing out the apparatus a number of times with dry air, and the ultimate test is that the storage flasks should hold a vacuum of 0·001 mm. overnight as measured by a McLeod gauge. Having obtained all the gas in the liquid state in the bulb C, it was then solidified by liquid air where possible (oxygen being the only exception), and pumped down with the pumps. This process was repeated a number of times, the solid being allowed to melt between each, in order to eliminate the last traces of occluded air. The gas was then allowed to distil over into the vessel E by adjusting the Dewar flasks containing the liquid air, the first and last runnings being pumped off. Again the distillation was repeated, a number of times backward and forwards between C and E. The final process then consisted of condensing some of the gas in the bubbler F until a two-inch column was obtained, and allowing the rest of the gas to distil from E, bubble through its own liquid in F, and enter the storage flasks D. The process of bubbling the gas was rather a difficult manipulation, very careful adjustment of the liquid air levels being necessary. The flasks, which were filled to just under an atmosphere pressure, were then detached and sealed on to the microbalance apparatus.

A further refinement of this method was used with carbon tetrafluoride. It will be seen that as the flasks fill, the pressure at which the bubbling is carried out slowly rises to atmospheric pressure, and consequently the temperature of the liquid in the bubbler and the vapour pressure above the bubbler both rise. In order to carry out the process under constant conditions at a low pressure, a second bulb was sealed on to the apparatus at G, and after being bubbled the gas was condensed in this before being allowed to evaporate into the storage flasks.

In general the gases prepared in the above manner exhibited no signs of a gradual change of density between the various samples in the flasks. If any systematic change was detected the correct one was taken as that at which the density became constant in a number of samples.

The individual gases were prepared as follows :—

(a) Oxygen—A long glass tube containing the purest B.D.H. potassium permanganate was sealed on to the purification train at A. It was pumped down three or four times, the potassium permanganate being heated slightly between each. Then the oxygen was generated by stronger heating and was passed through liquid potassium hydroxide solution, over solid moist potassium hydroxide, and dried over phosphorus pentoxide. It was condensed in the bulb C by means of liquid air

with compressed air bubbling through it. A certain fraction was allowed to evaporate and be pumped away whilst the rest was bubbled through its own liquid to the flasks as previously described. During the course of the work the purity of the oxygen was tested periodically by burning phosphorus in it, and also by comparing the density of different samples, of which there were four.

(b) *Carbon Dioxide*—This gas was prepared from pure sodium bicarbonate which was previously pumped off in a similar manner to the potassium permanganate. It was passed through two phosphorus pentoxide tubes, frozen, pumped down, and then allowed to sublime into the flasks. In this case the bubbler could not be used. Four different samples were prepared, all of which had the same balancing pressure.

(c) *Ethylene*—Ethylene was prepared by the dehydration of ethyl alcohol with glacial phosphoric acid. It was passed through a strong solution of potassium hydroxide, over moist, solid potassium hydroxide, through a U-tube, immersed in a mixture of solid carbon dioxide and acetone, then dried over phosphorus pentoxide. The gas was then solidified, pumped free from air, refractionated four times and finally bubbled through its own liquid.

Another sample of ethylene was prepared by the action of zinc upon a mixture of equal volumes of ethylene dibromide and ethyl alcohol. The ethylene dibromide had previously been fractionated very carefully along a six pear fractionating column, and the constant boiling point fraction was used for the preparation.

Both samples had exactly the same density when compared with each other in the microbalance apparatus, but actually most of the results given in §5 were taken with the first sample.

(d) *Nitrous Oxide*—This gas was initially obtained from a dentist's cylinder of compressed nitrous oxide. It was purified in the same way as the ethylene except that in addition it was passed through three wash bottles of concentrated sulphuric acid. The solid and liquid nitrous oxide did not show any trace of blueness at any stage of the preparation. Altogether four 2-litre flasks of the gas were obtained, each having the same density.

(e) *Sulphur Dioxide*—The sulphur dioxide which was used for the absorption compensation of the balance as described in the previous section, was prepared by the action of concentrated sulphuric acid on mercury, the reaction being carried out in a high vacuum. The evolved gas was bubbled through concentrated sulphuric acid to eliminate sulphur trioxide and dried over phosphorus pentoxide. It then entered the purification apparatus and was purified by fractionation and bubbling as with the other gases.

(f) *Carbon Tetrafluoride*—This rather rare gas was prepared by the action of pure fluorine upon carbon in the form of Norit. The fluoride was obtained by the electrolysis of potassium hydrogen fluoride in a copper cell with a graphite anode.

The design of the cell was that of DENBIGH and WHYTLAW-GRAY,* and by means of it a steady stream of fluoride was produced with ease. The fluorine was purified from hydrofluoric acid by passing through a copper tube packed with sodium fluoride, and the issuing gas was led over a second tube packed with a mixture of Norit and sodium fluoride. As the reaction proceeded the tube became quite hot and the impure carbon tetrafluoride was condensed in a glass bulb by means of liquid air. About forty litres of the gas were condensed and then allowed to escape into a carboy. A certain amount of rather unvolatile impurity was neglected.

The gas in the carboy was then attached to a purification train consisting of moist potassium hydroxide, concentrated potassium hydroxide solution, phosphorus pentoxide, and finally molten potassium hydroxide to decompose any other carbon fluoride which might be present. The gas was passed backwards and forwards along this train five times, finally being led through a U-tube immersed in carbon dioxide and acetone, and condensed with liquid air in the bulb C of the fractionation apparatus. About 30 litres of the gas were obtained at this stage. The gas would not solidify when hydrogen was bubbled through the liquid air, showing that impurities were still present. The greater part of the impurities appear to be air dissolved in the liquid carbon tetrafluoride. After many fractionations and separations a fraction was obtained which would solidify with a very low vapour pressure, and at the temperature of ordinary liquid air had a vapour pressure of 15 mm., agreeing with other observations upon carbon tetrafluoride.† This fraction was bubbled through its own liquid, the pressure being kept at a cm. or so by means of the apparatus previously described. Three fractions of one litre were obtained. Two of these had exactly the same density and were used for the microbalance experiments.

(*g*) *Methyl Fluoride*—This gas was prepared by the action of heat on tetramethyl ammonium fluoride as previously described in our first publication‡ on the atomic weight of fluorine. The gas was the same as that used in the initial measurements except that it was refractionated and pumped down in order to eliminate any air which might have passed the taps into the storage flasks.

5—RESULTS

Nitrous Oxide—The measurements on nitrous oxide were taken at pressures of about 400 and 200 mm. To show how the various corrections were applied the following single pressure reading is given as an example.

> *Balancing pressure of nitrous oxide.*
>
> Temperature of balance case $= 21 \cdot 638°$ C.

* ' J. Soc. Chem. Ind.,' vol. 19, p. 139 (1934).
† RUFF, ' Z. anorg. Chem.,' vol. 192, p. 249 (1930).
‡ PATTERSON AND CAWOOD, 'J. Chem. Soc.,' p. 2180 (1932).

Pressure readings

Lower meniscus = 54·363 mm.
Upper   ,,   = 221·710   ,,
Lower   ,,   = 54·363   ,,

Upper meniscus height = 1·51 mm.
Lower   ,,   ,,   = 1·00   ,,

Upper meniscus + depression = 221·710 + 0·074 = 221·784 mm.
Lower   ,,   +   ,,   = 54·363 + 0·049 = 54·412   ,,

Difference of pressure uncorrected for temperature   167·372   ,,

Temperature of manometer column = 21·91° C. at top ; 21·82° at bottom.
Mean temperature of manometer column = 21·87° C.

Correction of column to 0° C. = 0·632 mm.
Therefore column at 0° C. = 166.740 mm.

Correction of gas pressure to 21° C.

$$= 166 \cdot 740 \times \frac{293 \cdot 109}{293 \cdot 747} = 166 \cdot 378 \; mm. = \textit{true balancing pressure.}$$

As all the measurements are taken in the neighbourhood of 21° C. and corrected to 21° C., any error in the value taken for the expansion coefficient is negligible. In all cases, however, we have taken the value given by what appears to us to be the most reliable published data.

The above example is typical of all the pressure readings, and each ratio given in the Tables is the mean of three separate fillings of the two gases (oxygen and nitrous oxide) and consequently the mean of nine actual pressure measurements. It will be seen that the oxygen balancing pressure alters slightly between each ratio owing to a slight shift of the zero of the balance. This, however, does not introduce any error so long as the mean ratio is plotted against the mean oxygen pressure, because the slope of the curve is so small that for the purpose of the extrapolation, the pressure need not be known to the accuracy required for the calculation of the ratios.

Table I

High Ratio

p_{O_2}	p_{N_2O}	$r = \dfrac{p_{O_2}}{p_{N_2O}}$
mm.	mm.	
418·579	303·772	1·37794
418·599	303·787	1·37794
418·624	303·801	1·37795
418·636	303·808	1·37796
418·636	303·814	1·37792

Mean r = 1·37794(2).
Mean p_{O_2} = 418·612 mm.

TABLE I—(continued)

LOW RATIO

p_{O_2}	p_{N_2O}	$r = \dfrac{p_{O_2}}{p_{N_2O}}$
mm.	mm.	
229·195	166·488	1·37681
229·206	166·485	1·37674
229·143	166·432	1·37680
229·081	166·378	1·37686
229·092	166·392	1·37682
229·103	166·405	1·37678

Mean $r = 1\cdot37680(1)$.
Mean $p_{O_2} = 229\cdot137$ mm.

The correction for the contraction of the buoyancy bulb between the nitrous oxide pressures and the oxygen pressures is in this case inappreciable, so that the two mean ratios given in Table I may be used for the extrapolation to zero pressure without any correction.
Consequently

$$\text{Limiting value of ratio} = r_0 = 1\cdot37680(1) - 0\cdot00114 \times \frac{229\cdot137}{189\cdot475}$$
$$= 1\cdot37542(3).$$
$$\text{Molecular weight of } N_2O = 1\cdot37542(3) \times 32$$
$$= 44\cdot0135.$$
$$\text{Atomic weight of N} = 14\cdot006(8).$$

Actually the purity of the gas is probably the limiting factor in the accuracy of the experiments and the atomic weight of nitrogen is consequently

$$N = 14\cdot007.$$

Carbon Dioxide—Carbon dioxide proved to be the most troublesome of any of the gases to work with at low pressures. It appeared to be adsorbed both by the balance and the walls of the balance case to a great extent, and the balance had to be cleaned out and baked frequently to obtain concordant readings. Indeed, it was found to be more difficult to work with carbon dioxide than sulphur dioxide, although the latter gas was considerably more adsorbed by the balance case and the tap grease, as was shown by observing the movements of the balance pointer when the two gases were allowed to stand in the case for some time. The difficulty appeared to be due to the fact that whilst the adsorbed sulphur dioxide could be readily pumped off, the carbon dioxide was difficult to remove. In consequence of these difficulties a very large number of low pressure ratios was taken, and as the balancing pressure altered slightly each time the balance was cleaned, three sets of ratios were obtained at oxygen pressures of about 229 mm., 237 mm., and 245 mm. The three sets, however, have been averaged to give one mean ratio and one mean oxygen

TABLE II

HIGH RATIO

p_{O_2}	p_{CO_2}	$r = \dfrac{p_{O_2}}{p_{CO_2}}$
mm.	mm.	
418·216	303·575	1·37764
418·239	303·588	1·37765
418·257	303·601	1·37765
418·281	303·640	1·37756
418·410	303·705	1·37769
Average 418·281	303·622	1·377638

LOW RATIO

p_{O_2}	p_{CO_2}	$r = \dfrac{p_{O_2}}{p_{CO_2}}$
mm.	mm.	
228·076	165·695	1·37648
228·137	165·747	1·37642
228·136	165·726	1·37659
229·131	166·446	1·37660
229·202	166·499	1·37659
229·172	166·482	1·37656
229·235	166·529	1·37655
229·245	166·547	1·37646
229·211	166·496	1·37667
229·049	166·388	1·37660
229·060	166·408	1·37650
229·063	166·416	1·37645
229·085	166·424	1·37652
229·094	166·423	1·37658
229·108	166·439	1·37653
229·120	166·453	1·37648
234·102	170·032	1·37681
234·101	170·029	1·37683
234·069	170·010	1·37680
236·855	172·090	1·37634
236·843	171·974	1·37720
236·822	171·974	1·37720
236·857	172·104	1·37624
236·785	171·948	1·37707
236·731	171·989	1·37643
236·766	171·991	1·37662
236·791	171·993	1·37675
236·807	172·015	1·37666
236·829	172·015	1·37679
236·851	172·028	1·37682
245·044	177·967	1·37690
245·062	178·029	1·37653
245·046	178·025	1·37647
245·073	178·059	1·37636
245·056	178·058	1·37627
245·094	178·057	1·37649
Average 234·464	170·3196	1·376618

pressure, as will be seen in Table II. The higher pressure results, on the other hand, present little difficulty.

Consequently

Limiting value of ratio $= 1 \cdot 376618 - 0 \cdot 001020 \times \dfrac{234 \cdot 464}{183 \cdot 817}$

$= 1 \cdot 375316 \pm 0 \cdot 000036.$

Hence molecular weight of carbon dioxide $= 44 \cdot 0101 \pm 0 \cdot 0020$
and the *Atomic weight of carbon* $= 12 \cdot 010(1) \pm 0 \cdot 0020.$

TABLE III—ETHYLENE

HIGH RATIO

p_{O_2}	$p_{C_2H_4}$	$r = \dfrac{p_{O_2}}{p_{C_2H_4}}$
mm.	mm.	
428·535	486·958	0·880025
428·356	486·801	0·879941
428·378	486·758	0·880064
428·088	486·439	0·880044
428·095	486·450	0·880039
428·082	486·447	0·879963
427·930	486·311	0·879951
427·974	486·396	0·879888
427·559	485·926	0·879885
428·225	486·845	0·879913
428·241	486·707	0·879874
Average 428·133	486·552	0·8799625

LOW RATIO

p_{O_2}	$p_{C_2H_4}$	$r = \dfrac{p_{O_2}}{p_{C_2H_4}}$
mm.	mm.	
233·543	265·886	0·878358
233·553	265·859	0·878484
233·550	265·832	0·878562
233·526	265·844	0·878508
233·564	265·856	0·878536
233·570	265·867	0·878521
233·581	265·905	0·878438
233·633	265·942	0·878511
233·631	265·934	0·878530
233·654	265·970	0·878498
239·374	272·474	0·878520
239·382	272·470	0·878562
239·376	272·465	0·878557
Average 234·918	267·408	0·8785065

O 2

Consequently, by linear extrapolation,

Limiting ratio $= 0 \cdot 8767352 \pm 0 \cdot 0000274.$

Molecular weight of ethylene $= 28 \cdot 0556 \pm 0 \cdot 00087.$

Atomic weight of hydrogen $\times 4 = 4 \cdot 0312.$

Therefore *Atomic weight of carbon* $= 12 \cdot 0122 \pm 0 \cdot 0004.$

Carbon Tetrafluoride—In addition to the usual corrections, with carbon tetrafluoride, the correction for the change in volume of the buoyancy bulb between the balancing pressures of oxygen and the carbon tetrafluoride was appreciable, for the molecular weight of the latter gas is almost three times that of oxygen. The correction, however, even in this case is not large enough to alter the value of the molecular weight of the carbon tetrafluoride, but slightly alters the slope of the $r - p$ curve, and consequently the compressibility.

TABLE IV

HIGH RATIO

p_{O_2}	p_{CF_4}	$r = \dfrac{p_{O_2}}{p_{CF_4}}$
mm.	mm.	
484·010	175·914	2·75140
484·180	175·993	2·75113
484·225	176·006	2·75119
484·250	176·019	2·75112
484·271	176·031	2·75106
484·271	176·031	2·75106
484·288	176·043	2·75096
484·309	176·033	2·75126
Average 484·225	176·009	2·75114(8)

LOW RATIO

p_{O_2}	p_{CF_4}	$r = \dfrac{p_{O_2}}{p_{CF_4}}$
mm.	mm.	
250·015	90·899	2·75047
250·015	90·899	2·75047
249·851	90·848	2·75021
249·839	90·831	2·75059
249·898	90·859	2·75039
257·459	93·602	2·75057
257·499	93·620	2·75045
257·506	93·626	2·75038
Average 252·760	91·898	2·75044(1)

The buoyancy bulb, which was used in the above experiments, was found to expand by $1 \cdot 372 \times 10^{-4}$ cc. per atmosphere decrease of pressure. The volume of the bulb itself was $1 \cdot 703$ cc.

Hence the fractional increase of the volume of the bulb, with the low pressure carbon tetrafluoride balancing pressures, over that at the oxygen pressures, is

$$\frac{1\cdot372 \times 10^{-4}}{1\cdot073} \times \frac{159}{760} = 1\cdot69 \times 10^{-5}$$

Hence r corrected $= \dfrac{2\cdot750441}{1\cdot0000169} = 2\cdot75039(5).$

Similarly for the high pressure ratio,

fractional increase $= \dfrac{1\cdot372 \times 10^{-4}}{1\cdot703} \times \dfrac{308}{760} = 3\cdot26 \times 10^{-5}$

and r corrected $= \dfrac{2\cdot751148}{1\cdot0000326} = 2\cdot75105(8).$

Hence the limiting ratio $= 2\cdot750395 - 0\cdot000663 \times \dfrac{252\cdot760}{231\cdot465}$

$$= 2\cdot74966(9).$$

Therefore, molecular weight of carbon tetrafluoride

$$= 2\cdot749669 \times 32$$
$$= 87\cdot989(4)$$

and if the atomic weight of carbon is taken as $12\cdot011$, the *Atomic weight of fluorine* $= 18\cdot995.$

TABLE V—METHYL FLUORIDE

HIGH RATIO

mm.	mm.	$r = \dfrac{p_{O_2}}{p_{CH_3F}}$
456·751	427·504	1·06841
456·751	427·504	1·06841
453·419	424·418	1·06834
453·438	424·418	1·06838
453·457	424·420	1·06842
Average 454·763	425·653	1·06839(2)

LOW RATIO

mm.	mm.	$r = \dfrac{p_{O_2}}{p_{CH_3F}}$
228·997	214·814	1·06602
229·034	214·885	1·06584
229·005	214·824	1·06601
228·989	214·832	1·06590
228·989	214·832	1·06590
229·027	214·841	1·06603
229·019	214·833	1·06603
Average 229·008	214·835	1·06596(1)

Hence, limiting ratio by linear extrapolation,

$$= 1 \cdot 06349(5).$$

Therefore molecular weight of methyl fluoride

$$= 1 \cdot 06349(5) \times 32$$
$$= 34 \cdot 0318,$$

and if the atomic weight of carbon is taken as $12 \cdot 011$ and that of hydrogen as $1 \cdot 0078$ then

Atomic weight of fluorine $= 18 \cdot 997$.

The compressibility measurements taken on the Andrews compression apparatus, in order to test the validity of the linear extrapolation of the microbalance results to zero pressure, afford a valuable check upon the microbalance values themselves. For, as has been shown in §2, the compressibility of the gas under examination may be calculated if that of the comparison gas is known. Therefore an agreement between the value so calculated and that directly measured with the compression apparatus is an additional proof that the microbalance observations are correct. The actual compressibility value, measured by the compression apparatus, is more accurate than that calculated from the microbalance results, for in the latter case the pressure range of the measurements is only about 200 mm. Further, this value depends upon the value of the compressibility assigned to oxygen. The value of the compressibility of oxygen is unfortunately not known at 21° C., but it may be deduced fairly accurately from the data at 0° C. Thus the most probable value of this temperature appears to be $0 \cdot 00094$ from the low pressure data. Now the Beatty-Bridgeman equation of state, when applied to the high pressure data, gives the value $0 \cdot 00101$, in fair agreement with the low pressure data. We have therefore used this equation to calculate the compressibility at 21° C. and obtained the value $0 \cdot 00079$. If we now assume that the ratio of the calculated to the experimental value is the same at 21° C. as at 0° C., we obtain for $A_{21° C.}$ the value $0 \cdot 00073$. The value of A for oxygen is so small that a slight error will not be appreciable in the above calculations.

The details of the experiments with the compression apparatus and also the values obtained for nitrous oxide, ethylene, carbon dioxide, and methyl fluoride have been published elsewhere.* Whilst, therefore, only the final values of A will be tabulated for these gases, the measurements upon carbon tetrafluoride which have not been published before are given in Table VI in full, that is, in the form of the isothermal.

The values in Table VI are the means of three sets of observations and within the limits of error they lie upon a straight line. Consequently, the equation of the line has been calculated by means of the method of least squares, and is

$$PV = (1 - 0 \cdot 005586p) \text{ in metres of mercury.}$$
$$PV = (1 - 0 \cdot 00423p) \text{ in atmospheres.}$$

* W. CAWOOD and H. S. PATTERSON, ' J. Chem. Soc.,' vol. 156, p. 619 (1933).

TABLE VI—CARBON TETRAFLUORIDE AT 21° C

p (in metres)	pv
0·9556	6·9880
1·5071	6·9658
1·9792	6·9504
2·8698	6·9145
3·4498	6·8899

The value of $A_{21° C.}$ is therefore $0·00423$. The value calculated from the microbalance ratios of carbon tetrafluoride is $0·00419$, which is in satisfactory agreement with the above value, which was measured separately on the compression apparatus. The complete table of the two sets of data is Table VII.

TABLE VII

	$A_{21° C.}$ micro- balance	$A_{21° C.}$ Andrews apparatus
Carbon dioxide	0·00522	0·00526
Nitrous oxide	0·00559	0·00567
Ethylene	0·00636	0·00612
Methyl fluoride	0·00900	0·00882
Carbon tetrafluoride	0·00419	0·00424

The values given in the first column are calculated from the microbalance ratios by means of the equation

$$A_{21° C.} = \frac{r''(1 - A_1 p_1') - r'(1 - A_1 p_1'')}{r''(1 - A_1 p_1')p_2'' - r'(1 - A_1 p_1'')p_2'}$$

where

r', r'' are microbalance ratios.

p_1' p_1'' are oxygen pressures.

p_2', p_2'' are comparison gas pressures.

A_1 is compressibility of oxygen at 21° C.

It will be seen that in each case the agreement is very satisfactory, considering the small range of pressure over which the microbalance results are taken. The small pressure range may lead to quite an appreciable error in the compressibility calculations without affecting the limiting value and hence the atomic weights.

In the case of methyl fluoride, the initial measurements on the old apparatus, which were referred to in § 3, led to a value for the compressibility of $A_{21°C.} = 0·0084$, and an atomic weight of fluorine of $19·01$. It will be seen that the new result with the adsorption errors eliminated is $0·0090$, which is in much better agreement with the value of $A_{21°C.} = 0·00882$ of the compression apparatus. The initial values were criticized by MOLES,* who had also taken measurements upon methyl

* 'Nature,' vol. 128, p. 966 (1931).

fluoride. At the time,[*] we emphasized that the microbalance results were only preliminary, but that as the compressibility had been measured on an independent apparatus in addition to that calculated from the microbalance, the value of $A_{21°C.}$ $= 0.0082$ was certainly of the right order of magnitude. The value of the compressibility calculated from the new microbalance results leads to a value of $A_{0°C.} = 0.0117$, whilst that actually measured on the Andrews apparatus at $0°$ C. is 0.0115. MOLES and BATEUCAS,[†] however, obtain from their measurements the value of $A_{0°C.}$ $= 0.019$, differing from our own value by about 65%. If the value of $A_{0°C.}$ $= 0.0116$, which we think to be correct, be applied to their normal density of methyl fluoride, a value of $F = 19.2$ is obtained. There seems little doubt, therefore, that the results of MOLES and BATEUCAS are incorrect, although they lead to an atomic weight of $F = 18.996$ when extrapolated. This is almost certainly due to some error which decreases with decrease of pressure, consequently giving the correct limiting density but an incorrect slope and normal density. We consider that our own previous criticisms of the work of MOLES and BATEUCAS not only still hold good but are confirmed by the data on methyl fluoride.

6—DISCUSSION OF THE RESULTS

In this section, where of necessity comparisons between chemical and physical atomic weights must be made, it is essential to reduce both sets of data to the same scale. Whilst the physical determinations are on the basis of $O^{16} = 16.000$, the discovery that oxygen is a mixture of the O^{16}, O^{17}, and O^{18} isotopes has shown that this is not the same as the chemical scale of $O = 16.000$ (where O is normal oxygen). The abundance ratio of the oxygen isotopes has been determined experimentally by a number of observers, but the value obtained by MECKE and CHILDE[‡] is generally regarded as being the most probable. These observers find the ratio of $O^{16} : O^{18} = 1 : 630$, the O^{17} isotope being negligible. In order to reduce the values given on the physical scale to the chemical scale, therefore, they must be divided by a factor of 1.00022. In the following paragraphs all atomic weights mentioned are on the chemical scale of $O = 16.000$, and if they have been measured by physical methods they have been reduced to this scale by the above factor.

Nitrogen—The value of the atomic weight of nitrogen, accepted by the International Atomic Weight Committee, is 14.008, being slightly higher than our own value of $N = 14.007$. The former value depends mainly upon the very accurate stoichimetrical work of HONIGSCHMID and SACHTLEBEN,[§] BAXTER and GREEN,[||] and

[*] PATTERSON and CAWOOD, ' Nature,' vol. 129, p. 794 (1932).

[†] ' J. Chim. Phys.,' vol. 18, p. 353 (1920).

[‡] ' Z. Physik,' vol. 68, p. 362 (1931).

[§] ' Z. anorg. Chem.,' vol. 178, p. 1 (1929).

[||] ' J. Amer. Chem. Soc.,' vol. 53, p. 604 (1931).

RICHARDS and FORBES,[*] all of whom have measured the silver-nitrate ratio, and upon the mass spectrograph value of ASTON. It must be pointed out, however, that the stoichimetrical determinations which depend upon the ratio of silver to silver-nitrate, therefore, depend upon the value of the atomic weight which is assigned to silver. The difference between $N = 14 \cdot 007$ and $N = 14 \cdot 008$ lies within the limits of the error on the atomic weight of silver.

There is, however a certain amount of evidence in favour of the rather lower value of $N = 14 \cdot 007$, for quite a number of physicochemical methods has led to this result. Thus MOLES and BATEUCAS,[†] by obtaining the limiting density of ammonia obtain $N = 14 \cdot 007$, and repetition of this work by MOLES and SANCHO,[‡] when an arithmetical error is corrected leads to exactly the same result. BATEUCAS,[§] using the same method on nitrous oxide, obtains $N = 14 \cdot 007$, but for the compressibility of the gas the value of $(1 + \lambda)_{0°C.} = 1 \cdot 000854$ was obtained. This is very different from all the other published values, including our own, and appears to us to show the presence of the same error as that pointed out in the previous section, on the methyl fluoride results of the same observer. That is, an error which tends to disappear at low pressures leading to a wrong slope and compressibility, but a correct limiting density and atomic weight.

As the difference between the two sets of values for the atomic weight of nitrogen is so small, it appears to be quite impossible to say without further data which is correct. In any case the accepted value of $N = 14 \cdot 008$ is probably correct within the limits of error imposed on chemical methods by the purity of the compounds used.

Carbon—Carbon occupies a rather unique position in the researches upon atomic weights, for where a discrepancy has occurred between physical or mass spectrograph methods, in the case of practically all the other elements more refined technique has confirmed the mass spectrograph value. In the case of carbon, however, we pointed out in 1931[||] that preliminary results had led us to the belief that a 13 isotope was present and that the atomic weight of carbon was of the order of $12 \cdot 01$. At this time ASTON's mass spectrograph value was $12 \cdot 001$. The higher value was also obtained by WHYTLAW-GRAY and WOODHEAD (*loc. cit.*), using the microbalance method, and also by JENKINS and ORNSTEIN[¶] who have measured the ratio of $C^{12} : C^{13}$ in the Swan spectra. Finally, ASTON[**] himself, by comparing the second order lines at positions 6 and $6 \cdot 5$ of C^{12} and C^{13} in an improved mass spectrograph apparatus with a greater resolution, has obtained the value $C = 12 \cdot 0093$. The higher result has also been obtained by VAUGHAN,

* 'Z. anorg. Chem.,' vol. 55, p. 33 (1907).
† 'An. Soc. esp. Fís. Quím.,' vol. 30, p. 876 (1932).
‡ 'An. Soc. esp. Fís. Quím.,' vol. 31, p. 172 (1933).
§ 'J. Chim. phys.,' vol. 28, p. 572 (1931) ; 'An. Soc. esp. Fís. Quím.,' vol. 29, p. 538 (1931).
|| PATTERSON, CAWOOD, and WHYTLAW-GRAY, 'Nature,' vol. 128, p. 375 (1931).
¶ 'Proc. Akad. Sci. Amst.,' vol. 33, p. 1,212 (1932).
** 'Proc. Roy. Soc.,' A, vol. 149, p. 396 (1935).

WILLIAMS, and TATE,* using a mass spectrograph apparatus of rather a different design. These observers find that the abundance ratio of $C^{13} : C^{12} = 1 : 91 \cdot 6$, and hence $C = 12 \cdot 0132$.

Our own values in the preceding section are $C = 12 \cdot 0101$ from carbon dioxide and $C = 12 \cdot 0122$ from ethylene. The atomic weight of hydrogen, $1 \cdot 0078$, which is the accepted chemical value, is probably too low because in all cases the hydrogen has been prepared electrolytically, a method which is known to effect a separation of the hydrogen isotopes. Consequently, the rather higher value obtained for the atomic weight of carbon from the ethylene results may be in part due to too low an atomic weight of hydrogen being used. The latest mass spectrograph value for the atomic weight of hydrogen is $1 \cdot 0081$ on the chemical scale, which leads to an atomic weight of carbon of $C = 12 \cdot 0116$ from the ethylene results, giving a much better agreement with the carbon dioxide values.

We thus see that the evidence in favour of an atomic weight of carbon higher than that of $C = 12 \cdot 00$ which is accepted by the International Atomic Weight Committee, is exceedingly strong and that the more correct value is $C = 12 \cdot 01$.

Fluorine—The value that we obtain for fluorine, namely $F = 18 \cdot 996$, is in agreement with ASTON's value of $F = 18 \cdot 996$ and shows that the presence of any higher isotope of fluorine is negligibly small. Here again we find indications of the higher value of the atomic weight of hydrogen, for if the mass spectrograph value of $1 \cdot 0081$ is used with the methyl fluoride results, a value for fluorine of $18 \cdot 996$ is obtained, which is in rather better agreement with the carbon tetrafluoride value. The work of SMITH and HAAGEN† on the ratio of borax to various other salts leads to a value for fluorine of $F = 19 \cdot 005$, from the cross ratios, but a value of the atomic weight of boron results, which is considerably different from the accepted value. It seems likely, therefore, that this latter work is in error, for no trace has been found of a higher isotope of fluorine in either the mass spectrograph, band spectra, or absorption spectra methods. Consequently the present accepted value of $F = 18 \cdot 996$ appears to us to be the most likely value within the limits of error of the various methods.

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* VAUGHAN, WILLIAMS, and TATE, ' Phys. Rev.,' vol. 46, p. 327 (1934) ; TATE, SMITH, and VAUGHAN, ' Phys. Rev.,' vol. 48, p. 525 (1935).

† ' Rep. Carnegie Trust.,' Pittsburgh, No. 267, p. 47 (1918).