The Determination of Gaseous Densities

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THE DETERMINATION OF GASEOUS DENSITIES

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CONTENTS

The microbalance technique for the determination of gaseous densities is examined and the requirements stated for its use as a method of high precision and reliability.

A detailed description is given of the construction of a sensitive and stable quartz microbalance and of the precautions necessary to obtain reproducible gas-pressure measurements of high precision.

The improved technique is used for the determination of the atomic weights of carbon and nitrogen by the comparison of the pressure ratios at 'limiting density' of the pure gases nitrogen, methane and oxygen; the values obtained are:

nitrogen 14·0078 (±0·0003)
carbon 12·0112 (±0·0005)

Nitrogen prepared by heating pure, dry sodium azide is shown to contain traces of hydrogen (either in the free state or combined with nitrogen as ammonia), and a new method is described of purifying nitrogen made by this method.

Part I. The construction of a sensitive and stable quartz microbalance and its use in the determination of gaseous densities

Principle of the method

The operation of a quartz microbalance for the determination of gaseous densities depends upon the change of buoyancy produced in a sealed quartz bulb by a change in the density of the surrounding gaseous medium, the bulb being suspended from the end of a beam which is pivoted and adjusted so as to balance in gas of a certain density. When used as a null-point instrument, in association with a manometer, it thus affords a means of comparing the pressures at which different gases have the same density.

If the microbalance is made sufficiently sensitive to changes of pressure in the surrounding gaseous medium and measurements of gas pressure can be carried out with certainty and high precision, the technique provides the basis of a convenient and accurate method of determining the densities of gases by comparison with a standard gas; and if, further, the comparison can be effected at a number of densities—by appropriate adjustments of the null-point—the method of 'limiting densities' (which requires the measurement of pressure ratios at more than one density) can be employed.

No serious difficulty arises in making a quartz microbalance that is sensitive to the smallest measurable alteration of pressure in the surrounding gaseous medium, but it has not hitherto been found possible to make one sufficiently stable to preclude a 'wandering' or 'drift' of the zero-point within the time required (necessarily several days, as shown later) for carrying out a series of measurements, viz. (i) balancing pressure at zero of gas A, (ii) balancing pressure at zero of gas B, (iii) repetition of balancing pressure at zero of gas A. In calculating the pressure ratio A/B it has therefore been necessary to allow for this 'drift' of the zero-point by taking the average of the first and last measurements of the balancing pressure at zero of gas A. Further, the methods hitherto employed for the measurement of gas pressures have been lacking in precision and reliability.

It has now been found possible to remedy—if not entirely to eliminate—these drawbacks and, consequently, to increase the accuracy and dependability of density determinations made by the use of the microbalance technique.

Requisites for accurate measurement

The conditions requisite for the use of the microbalance, in association with a mercury manometer, in a high-precision and dependable technique for the determination of gaseous densities may be summarized briefly as follows:

I. *The microbalance*

The beam of the balance must show a definite and accurately measurable deflexion for the smallest measurable alteration of pressure in the surrounding gaseous medium; in actual practice, using a mercury manometer, this means a pressure change of the order of 0·001 mm. of mercury.

The balance must have a null-point or zero which is sufficiently stable to show no measurable 'drift' over a period of several weeks.

The balance must be housed in a metal case in order to eliminate static electricity effects and be maintainable (along with its surrounding gaseous medium) at a constant temperature which does not fluctuate more than ±0·01° C. The case must protect the balance effectively from accidental shock and external vibrations and be provided with means for viewing and accurately measuring the deflexion of the beam.

II. *The mercury manometer*

This must be so constructed, housed and operated that measurements of gas pressure can be made with dependable accuracy and *reproducibility* to ±0·01 mm. (or less) of mercury; it must be maintainable at exactly the same temperature as the microbalance and be provided with means for adjusting the gas pressure so that the microbalance beam pointer can readily be brought to (or near) its zero position.

The mercury must be 'earthed' so as to eliminate frictional electricity effects arising from the movement of mercury in a dry gas over a dry glass surface.

III. *The manipulatory system*

This must provide a connexion between the manometer and balance case that is maintainable at the same temperature as they are; it must provide means for the thorough evacuation of the whole apparatus and for the satisfactory introduction of the pure gases under investigation without any possibility of their contamination by impurities; it must, further, be provided with means for preventing the passage of mercury vapour from the manometer to the balance case.

The technique described below has been found to meet all these requirements satisfactorily.

The microbalance

Because of its lightness, its low adsorptive capacity, its high resistance to corrosion and chemical action and its ease of working in the oxy-hydrogen or oxy-coal-gas flame, transparent fused quartz is undoubtedly the most satisfactory material for the construction of a microbalance, especially when a fibre suspension is to be used for the beam and buoyancy bulb; it lends itself admirably to the drawing of very fine, elastic and strong fibres which are essential in the construction of a reasonably robust and yet highly sensitive balance of this type.

Other methods of suspension, namely, polished quartz knife-edges, rounded points and needle points have been used in the construction of microbalances, but they have no advantage over a fibre suspension; they are much more difficult to make and set up in the laboratory and, moreover, they seem to be subject to unavoidable 'drift' in their zero-points.

The framework

The design of the framework, which carries the beam on its fibre suspension, is of much importance in providing a sufficient degree of robustness to allow of a sensitive microbalance being handled and cleaned without risk of fracture. The framework shown in figure 1 is made entirely of transparent quartz rod; it has been found to provide an adequate degree of robustness and, at the same time, to afford good conditions for drawing the fibre suspensions, for attaching the beam suspensions to the framework and for rendering them taut.

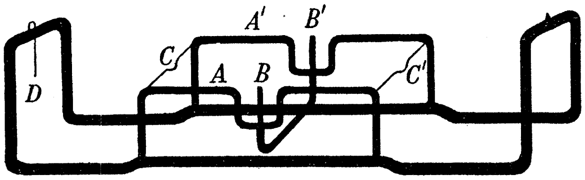

FIGURE 1

The main outer frame is made of rod of about 3 mm. diameter; the 'bridges' AA' and the 'pegs' BB' (to which the suspensory fibres are fused) are about 2 mm. diameter. The beam arrests CC', fused across the 'bridges' as shown, are about 1 mm. diameter. D is a fixed pointer used to mark the zero position of the beam pointer.

After the frame has been made it is advisable to give it the accelerated ageing treatment described below and then, after it has stood for some weeks, to grind the base flat on a sheet of plate glass using fine carborundum powder and water. This procedure produces a strong and stable framework for the microbalance.

Small 'jigs' (conveniently made of Bakelite and cork and attachable by light binding screws across the 'bridges' AA') enable the beam of the balance to be held firmly in position while the suspensory fibres are drawn, sealed to the 'pegs' BB', and made taut (by bending the pegs outwards) and while the sensitizing operations described below are carried out. The rigidity of the assembly allows the frame to be clamped firmly in the best position for carrying out these operations.

The beam

The example of Whytlaw-Gray and his co-workers has, in general, been followed in the design of the beam which, in its simpler form, is shown in figure 2.

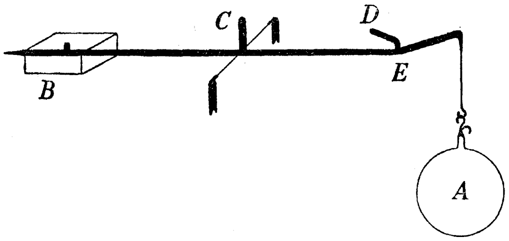

FIGURE 2

The buoyancy bulb A is suspended from one end of the beam by a hook formed at the end of a very fine fibre which is drawn from a point as nearly as possible in line with the main axis of the beam; this makes it possible to adjust the zero point—and thus enable pressure ratios to be determined at more than one density—by the addition of quartz riders to the hook from which the buoyancy bulb is hung, without producing any very significant effect on the sensitivity of the balance.

A counterpoise B is sealed on a peg positioned on the other side of the beam as shown. The counterpoise is made from very thin-walled tubing of about 15 mm. diameter and is formed into a rectangular shape so as to produce the maximum damping effect and to economize in space for its movement. The surface area of the counterpoise and its position on the beam are such that it provides a surface adsorption moment equal to that of the buoyancy bulb. The counterpoise is 'flamed' inside and out, and the external surface of the buoyancy bulb is similarly treated so that equal *specific* adsorption surfaces are provided on each arm of the beam. It is essential that all traces of 'bloom' which has a high adsorptive capacity, should be removed from the beam, buoyancy bulb and counterpoise; this can usually be done—although it may require time and patience—by 'flaming' with a soft (and therefore not very hot) oxy-coal-gas flame.

Attachments C and D, fused on the beam as shown, are used in the sensitization of the balance which is described below.

The buoyancy bulb is provided with two hooks—one to hang it on its fibre suspension and the other for use in handling.

The suspensory fibres are drawn from rod, of about 0·4 mm. diameter, which must be quite free from dust or grease.

Note. The drawing of quartz fibres of a definite length is an operation which requires considerable practice and patience with particular attention paid to (*a*) *the drawing weight* (conveniently a glass rod weighing about 1·5 g. hooked to the end of the quartz rod from which the fibre is being drawn and sliding freely in a vertical glass sheath) and (*b*) *the type of flame* which should be very small and not too hot.

Dimensions of the balance

The dimensions of the balance are:

diameter of buoyancy bulb	18·5 mm.
weight (in air) of buoyancy bulb	0·2904 g.
internal volume of buoyancy bulb	3·054 ml.
weight (in air) of counterpoise	0·3192 g.
length of beam	10 cm.
diameter of beam	1·4 mm.
length of framework	12·8 cm.
breadth of framework	2·7 cm.

Sensitization of the balance

The vertical adjustment of the centre of gravity of this type of beam, which is necessary to bring the balance to the point of maximum sensitivity, is usually a long and tedious task. The progress of the operation is conveniently followed by the determination (after each stage of the operation) of the period of oscillation of the beam with the aim of getting the longest possible period of oscillation.

Note. While the period of oscillation of the beam is a useful indication of the sensitivity of the balance, this can only be considered satisfactory when the balance shows, on testing under actual experimental conditions, a measurable deflexion of the beam for the smallest measurable alteration in the pressure of the surrounding gaseous medium. It is very difficult to obtain a sensitivity represented by a period of oscillation of more than 20 sec. with this type of beam, but a much longer period of oscillation—and, consequently, a greater sensitivity—can be achieved with the modified type of beam described later.

After equalization of the weight moments on the two sides of the beam, the earlier stages of the sensitization can be carried out by bending the beam slightly up or down at E, or bending the attachment D, or increasing (or decreasing) the length of the attachment C; this procedure is continued until the beam becomes *just top-heavy and just refuses to swing*. Before the final stages of sensitization are carried out it is necessary to anneal the balance and so relieve, as far as possible, the gross strains set up in the quartz by the high temperatures to which it has been subjected in making the balance. This annealing or accelerated 'ageing' treatment is carried out by heating the balance for several hours at a temperature of 200° C in a stream of dry nitrogen; the treatment should not be applied to a fully sensitized balance since it usually has a very profound affect on the sensitivity.

The final stages of sensitization are best carried out by confining the heating to the tip of the attachments C or D—adding or removing minute quantities of quartz until the beam is just top-heavy and then very slowly lowering the centre of gravity by volatilization of quartz from the tip until the required sensitivity is attained. Since the final sensitization of this type of beam involves heating a part of it to a very high temperature, some degree of strain must inevitably be left in the quartz, and this can only be removed or rendered negligible by lapse of time. It is therefore not surprising that a quartz microbalance sensitized in this way should tend to be unstable and be liable to show 'drift' in its zero-point. It is advisable to allow such a balance to stand at least 3 weeks—and preferably very much longer—before it is put into use.

Note. An interesting analogy is offered by the behaviour of a thermometer in this laboratory. A fine standard thermometer (range 0 to 50° C) had its ice-point checked at intervals over a period of 15 years, the ice being made from freshly distilled water; the ice-point showed a measurable and slowly decreasing annual rise for 10 years and then remained dead steady. Its original certified ice-point was 0·02° above the zero graduation mark, and it rose finally to 0·08° above the zero graduation mark. It was only after this long period of natural ageing that the contraction of the bulb was reduced to a value which had no further measurable effect on its ice-point although the thermometer had, presumably, been annealed after the bulb was blown.

If, after the completion of the preliminary stages of sensitization and the subsequent easing of all gross strains by the accelerated ageing treatment, *the final sensitization could be effected without further heating of the beam*, it should clearly be possible to produce a more stable balance with a greatly decreased tendency for the zero-point to 'drift' or 'wander'.

A modification of the design of the beam has made it possible to do this and to produce a highly sensitive microbalance in which the zero-point shows no measurable 'drift' over a period of several weeks. The zero-point can be adjusted for use in the measurement of balancing pressures at a number of densities, and the sensitivity adjusted to its maximum value for each zero setting, by the simple addition of small quartz riders. It is only necessary that the preliminary sensitization processes should, after completion of the accelerated ageing treatment and a subsequent rest of 3 weeks, give a beam which swings smoothly in air at low pressure.

The design of the modified beam is shown in figure 3. It differs from the simpler form of beam (figure 2) in the arm which carries the buoyancy bulb. In addition to the vertical fibre suspension A which carries the buoyancy bulb on a hook and which is drawn from a point as nearly as possible in line with the main axis of the beam, there is a second vertical fibre suspension B (with a hook at the end) drawn from an attachment to the beam at a point about 4 mm. *above* the line of the main axis and hanging freely through a loop in the beam as shown.

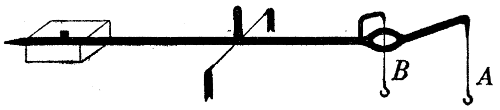

FIGURE 3

Since a weight hung on a fine fibre suspension acts at the point from which the fibre is drawn (just as the weight on the pan of an ordinary balance acts as if it were at the point of suspension of the pan), it is clear that a rider hung on A will have very little effect on the vertical position of the centre of gravity of the beam—and hence on the sensitivity of the balance—while a rider hung on B will *raise* the vertical position of the centre of gravity of the beam and thus have a marked effect on the sensitivity of the balance.

The following typical figures show how the balancing pressure at zero and the sensitivity (as judged by the period of oscillation) were affected, in a balance with this type of beam, by riders hung on A and B. Since riders hung from both A and B increase the balancing pressure it is necessary, as pointed out above, that the beam should be so adjusted, before this final sensitization, that it swings freely in air at low pressure.

wt. of rider hung from B (mg.)	wt. of rider hung from A (mg.)	balancing pressure in air (mm. of mercury)	period of oscillation (sec.)
0	14·3	60	20
3·4	11·9	60	28
8·6	5·3	—	top-heavy
4·6	8·1	90	35
5·3	7·7	110	42
6·1*	7·3*	135	62
6·1*	7·1*	85	67
6·4	6·95	85	110
6·9*	6·6*	—	top-heavy
6·9*	6·9*	130	120

Note. It is clear from the figures marked * that the fibre A was drawn from a point slightly below a horizontal line passing through the centre of gravity of the beam.

The complete balance with this modified type of beam is shown in figure 4.

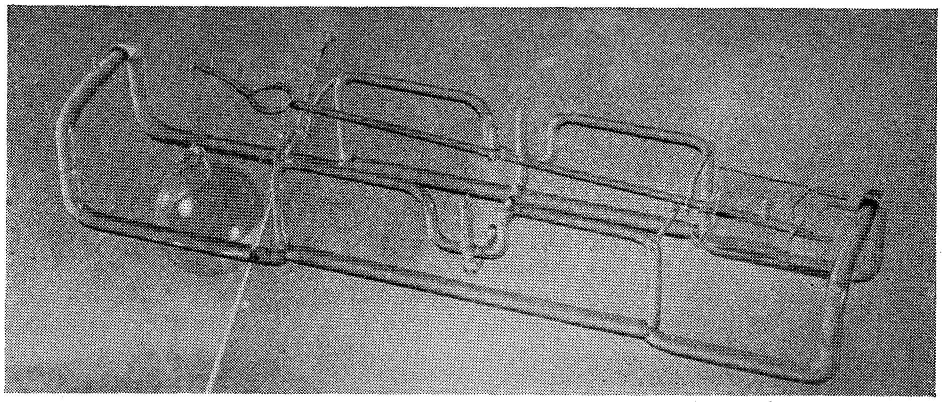

FIGURE 4

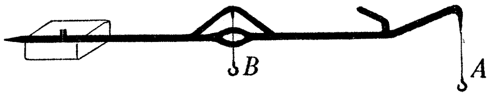

FIGURE 5

The ideal design for a beam of this type would be as shown in figure 5, with the vertical fibre B drawn from a point about 4 mm. above the centre of the beam so that riders hung from it would affect *only* the vertical position of the centre of gravity of the beam and have no effect on the balancing pressure. The adjustment of the zero setting to obtain a balance at different densities could then be made by riders hung from A and the adjustment of the sensitivity, for each zero setting, effected by the appropriate rider hung from B. It is obviously impossible to ensure that fibre A is drawn from a point accurately in line with the axis passing through the centre of gravity and so entirely eliminating any effect on the vertical position of the centre of gravity of riders hung from it.

A beam of this design, besides offering considerable difficulties in construction, requires a wider framework; it could not be used in our experiments since the balance case would not accommodate a wider framework.

The balance case

The successful use of a microbalance which is sensitive to alterations of pressure of the order of 0·001 mm. of mercury in the surrounding gaseous medium clearly requires that it should be maintainable within temperature limits sufficiently narrow to have no effect on this degree of sensitivity; it is essential also that the equilibrium position taken up by the beam pointer should remain dead steady.

It has been found possible to maintain the temperature of the balance (with its surrounding gaseous medium) constant at 20 ± 0·005° C by working in a well-insulated room kept at 19·3 ± 0·2° C, by housing the balance in a water-jacketed balance case and by circulating water through the jacket from a large thermostatically controlled water-bath.

Vibrational effects were rendered negligible—and the beam pointer made to remain dead steady at its equilibrium position—by mounting the balance case on a vibrationless platform and by 'smoothing' the water flow (*a*) by using a high-speed, smooth-running centrifugal pump immersed in the water-bath, (*b*) by careful adjustment of the speed of circulation and (*c*) by passing the water, just before it entered the balance case, through a perforated porcelain plug taken from the 'anti-splash' device used on a domestic water tap.

The position of the beam pointer in relation to the fixed zero-point was viewed through optically flat and parallel windows in the balance case by means of a reading microscope with a scale in the eyepiece; the pointers were illuminated, from behind, by the light from a 4 V torch-battery bulb, the light being filtered through an aqueous solution of potassium chromate.

Gas-pressure measurement

Since a microbalance can be made with a stable zero-point, sensitive to alterations of gas pressure of the order of 0·001 mm. of mercury, and it can be housed and operated under conditions which do not interfere with this degree of sensitivity, it is clear that its use in a dependable technique for the determination of gaseous densities depends, ultimately, on the accuracy and certainty with which measurements of gas pressure can be made. It is *this* operation which has hitherto been the least satisfactory part of the technique, and great care has therefore been taken to find means of improving its accuracy and dependability.

The most suitable instrument at present available for the measurement of gas pressures over the range normally employed in density determinations is the mercury manometer; its operation involves the apparently simple measurement of the vertical distance between the tips of two mercury menisci in a U-tube—one meniscus being exposed to the gas whose pressure is being measured and the other to a vacuum; the distance is normally measured, in relation to a millimetre scale, by means of a cathetometer. A long experience has shown that gas-pressure measurements which are dependably accurate to ± 0·01 mm. (or less) of mercury can only be obtained by taking the most meticulous care to eliminate all possible sources of error and, where elimination is not possible, to correct for the errors by calibration or otherwise. The sources of error and the methods adopted for dealing with them are discussed in the following description of our manometer assembly.

The scale

The scale was made of plate glass 10 mm. thick and 800 mm. in length and was graduated in millimetres. The graduation marks were diamond-ruled by the Société Genevoise and guaranteed accurate at 20° C to 5μ over the whole length.

Examination under a travelling microscope showed no detectable error throughout, *provided that the measurements were made between the centres of the graduation marks*. The graduation marks were about 0·035 mm. wide, but the width was not quite constant and it was therefore necessary to ensure that the scale was illuminated from behind by a parallel beam of diffused light which was normal to the scale so that the graduation marks were illuminated equally at the two edges and their centres thus clearly defined. Refraction errors were also eliminated by this method of illumination which is described below.

The U*-tube manometer*

The two limbs of the U-tube manometer were made from glass tubing of exactly the same diameter (15 mm.) and of wall thickness about 0·3 mm.; the tubing was selected so as to be straight, of uniform diameter and free from air-lines and irregularities. Refraction errors which, as pointed out by Cawood & Patterson (1933) may be serious in a manometer made from thick-walled tubing, become negligible when the limbs of the manometer are made from very thin—so-called 'egg-shell'—tubing.

The scale and manometer were firmly mounted in a water-jacketed casing and maintained at the same temperature (20 ± 0·005° C) as the balance case, and kept equally free from vibrational effects, by the method described above.

The manometer casing was made with sides and bottom of accurately machined, thick Bakelite with back and front of plate glass. Care was taken to ensure that the scale, manometer and the plate-glass back and front of the casing were parallel throughout their whole length and that the casing was firmly set up vertical; by taking these precautions it was found possible to eliminate the refraction errors which might be expected to arise from the use of a water-jacketed manometer construction. It was, however, found to be essential (1) to illuminate the scale and manometer by a parallel beam of diffused light which was truly normal to the scale, manometer and to the plate-glass back and front of the casing and (2) to use a reading microscope which was *at all times truly perpendicular to the manometer assembly*. The latter condition made it impossible to use an ordinary type of cathetometer and a special reading microscope assembly was therefore necessary.

The reading microscope assembly

The reading microscope was specially made and the magnification adjusted (and fixed) so that, when focused on the manometer scale, 25 eye-piece scale divisions exactly fitted the space (1 mm.) between the centres of adjacent graduation marks. Scale readings could readily be made to one-tenth of an eyepiece scale division—that is to 0·004 mm.—and were reproducible to this accuracy; it is, however, convenient to record readings to the nearest 0·001 mm.

The reading microscope was mounted on a carriage which moved vertically along a heavy, accurately machined and hand-finished phosphor-bronze bar fixed to the right-hand side of the manometer casing; the bar was shaped like a lathe bed, the hand-driven mechanism for moving the carriage being similar to that of a precision lathe. The design of the carriage provided for the microscope being moved horizontally across the face of the manometer casing and focused on the mercury menisci and scale while the axis of the microscope remained at all times perpendicular to the manometer, the scale and the plate-glass back and front of the casing.

Although the reading microscope assembly was very well made it was not found possible to ensure that the movements necessary for focusing the microscope on the scale and the mercury menisci were truly horizontal for all possible vertical positions of the instrument, and so the errors (which, while they were very small, were nevertheless significant) were corrected by calibration; a precision spirit level made by Troughton and Simms was used for this purpose.

This method of calibration only allowed relative measurements of the divergence of the microscope movements from the true horizontal. Absolute values were, in addition, obtained by measuring the apparent divergence in height between the two mercury menisci when both sides of the manometer were evacuated. The difference between the absolute and relative values is a measure of the divergence of the whole manometer assembly from the true vertical, i.e. the 'tilt' of the manometer; this difference was determined at a large number of vertical positions of the reading microscope and was found to be constant to ±0·001 mm. The measurements served as a confirmation of the calibration and of the satisfactory performance of the microscope assembly. The 'tilt' of the manometer was checked from time to time; it was found to remain effectively constant over the period required for the density measurements described in part II.

The method of illumination

The method of illumination of the manometer assembly was found to be a very important factor in high-precision manometry under the conditions of experiment described above. In order to achieve completely satisfactory illumination of the scale graduations and to render refraction errors negligible in the whole assembly it was found necessary, as pointed out above, to use a parallel beam of diffused light which was truly normal to the scale, manometer and to the plate-glass back and front of the casing.

A parallel beam of light, directed vertically downwards, was reflected by a plane mirror through the back of the manometer casing, and satisfactory diffusion was obtained by covering the back of the casing with thick tracing paper; the mirror was mounted on an arm of the microscope carriage, and its inclination to the manometer assembly could be controlled and adjusted so that the scale graduation marks were equally illuminated at the two edges—a simple and effective method of adjusting the beam of light to the required normality.

This method of illumination was also found satisfactory for viewing the mercury menisci and for setting their tips accurately on the centre line of the eyepiece scale of the reading microscope. It was, however, necessary, in order to obtain a well-defined image of a mercury meniscus, to shade it by means of a 'shroud' placed above and very close to it so as to cut out all overhead illumination. The position of the meniscus which is observed and measured depends upon its distance from the shroud so that *the shroud must always be set at exactly the same distance from the tip of the mercury meniscus*. The shrouds are conveniently made of thin-walled ebonite cylinders tapered at the lower edges and fitting closely to the manometer limbs; they are moved up and down by long stainless steel rods passing through sleeves at the top of the manometer casing.

The mercury reservoir

The manometer assembly is shown in figure 6, which also depicts the manipulatory system to be described later.

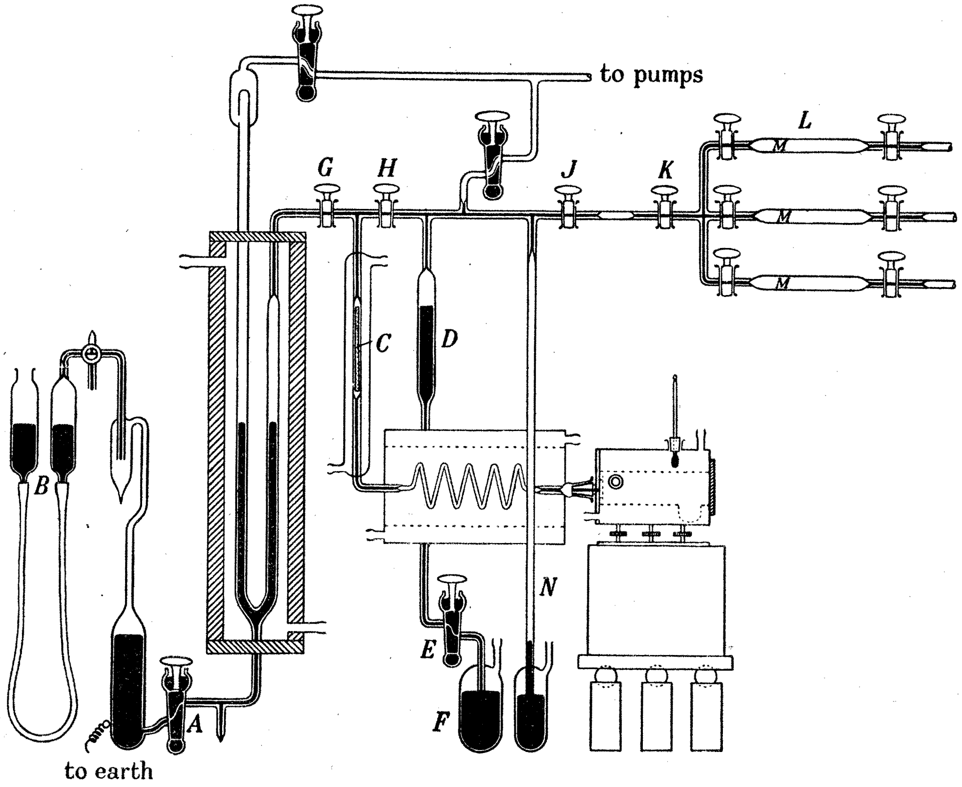

FIGURE 6

The mercury reservoir is fixed and is connected to the manometer by capillary tubing (which passes through a cork in the bottom of the manometer casing) and a mercury-sealed stopcock *A*. The alterations of pressure required to work the reservoir are obtained by compressing or rarefying the air in contact with the mercury by means of the external mercury compressor *B*. The compressor-reservoir is carried in a cradle which moves in a long vertical slide with coarse and fine adjustments for height; it is thus possible to adjust the pressure of gas in the apparatus and to bring the balance pointer to (or very near) its zero-point; the stopcock *A* is then closed so that the manometer is cut off from its mercury reservoir while a pressure measurement is actually being made. The mercury (carefully purified and distilled three times *in vacuo*) is earthed through a platinum wire sealed into the reservoir so as to eliminate frictional electricity effects produced by the movement of dry mercury on a dry glass surface in a dry gas.

The form of the mercury meniscus

Whytlaw-Gray has stated in a recent publication (1948) that, when mercury is used in gasometric operations, 'the form of the mercury meniscus should be taken into account if results of high accuracy are to be obtained', and our experience fully confirms the vital importance of this statement so far as it applies to gas-pressure measurements.

Even when both limbs of a U-tube manometer are of exactly the same diameter, the vertical distance between the tips of the two mercury menisci, one exposed to the gas and the other to a vacuum, is not a true measure of the gas pressure unless the depths of the two menisci are equal. Failure to measure meniscus depths and correct for any difference between them—a difference which may amount to several tenths of a millimetre, unless the manometer is made of very wide tubing—may lead to errors of great significance in high-precision manometry.

The theoretical treatment of this problem is made difficult by the fact that the relation between capillary depression and meniscus depth is sensitive to meniscus *shape*, and the theoretical tables are consequently somewhat discordant. In correcting for the meniscus capillary depression we have found it much more satisfactory to use the admirable experimental results of Cawood & Patterson (1933); their results are given to the nearest 0·001 mm., although they only claim an accuracy to the nearest 0·005 mm. Since, however, the experimental relation between meniscus depth and capillary depression proves to be a linear one, the net depression for a difference between two similar meniscus depths will be given with much greater accuracy than is given by each individual expression. In our measurements the depth of the meniscus exposed to the gas was always rather greater than that of the meniscus exposed to a vacuum; no measurements were recorded when the difference between the two meniscus depths was greater than 0·2 mm.

We have found that uniformly consistent and reproducible results can only be obtained if the bottom of the meniscus (in contact with the glass) is both horizontal and even; this condition can usually be brought about by moving the mercury several times up and down the manometer limbs or sometimes, more simply, by tapping gently, but, whichever method is used, the meniscus must subsequently be allowed to settle down over a period of at least 10 min. before a reading of its position is made. When neither of the above methods proves effective the manometer tubes should be cleaned and the mercury replaced with a freshly distilled supply.

The effect of oxygen on a mercury meniscus

Exploratory work carried out during the early stages of this investigation showed that *reproducible* results of high precision could not be obtained in gas-pressure measurements if oxygen was allowed to come into contact with the mercury in the manometer. If oxygen is left in contact with mercury in a manometer the convex meniscus gradually flattens and it may, after some time, become actually concave; the mercury sticks to the glass and, although the convexity of the meniscus is restored by moving the mercury or by gentle tapping, it becomes more and more difficult to get a meniscus the bottom of which is horizontal and evenly in contact with the glass. This effect is presumably due to the formation of a film of mercury oxide, and it is remarkable that attention has not been drawn by earlier workers to this very disturbing effect of oxygen since this gas is generally used as a standard in gas-density determinations.

This difficulty has been overcome, when determining the balancing pressure at zero of oxygen, by the use of pure nitrogen as a buffer gas between the oxygen (in the balance case) and the manometer. The success of the procedure is dependent on the interdiffusion of the gases being slow in comparison with the time taken for a balancing pressure measurement. The manipulatory system was designed with this operation in view, and it was found that the effect of the interdiffusion on the position of the balance pointer was only detectable after 40 min. when connexion was made between the oxygen in the balance case and the nitrogen in the manometer, while a reading of the balancing pressure at zero for the oxygen could be completed in from 15 to 20 min.

The manipulatory system

This provides the connexion between the balance case and the manometer and, in addition, a volume-adjustor and a gas-inlet manifold, together with connexions to the vacuum pumps; it is shown in figure 6.

The connexion between the balance case and the manometer is made of tubing of about 3 mm. bore and is sufficiently long—about 1500 cm.—to prevent any effect of the diffusion of the buffer gas (pure nitrogen in the manometer) being shown in the balance case while the balancing pressure of oxygen is being determined (see above, p. 426). It is maintained at the same temperature as the manometer and balance case by the method described above, and that part of it which is adjacent to the balance case is made of thin-walled tubing, in the form of a wide spiral, so as to protect the balance from the effects of any accidental knock on the rest of the apparatus. The passage of mercury vapour from the manometer to the balance case is prevented by a long (15 cm.) closely fitting tube of pure gold with an internal diameter of 2 mm., shown at *C*.

The volume-adjustor

This is a vessel of about 80 ml. capacity, shown at *D*, which is connected through the stopcock *E* and narrow-bore capillary tubing to a mercury reservoir *F*. It provides a convenient means of altering the internal volume system so that:

(1) pressure readings can be repeated with the mercury at different positions in the manometer tubes,

(2) when the balancing pressure of oxygen is being determined (and the manometer contains pure nitrogen) the balance pointer can be brought to its zero position before connexion is made between the balance case and the manometer, and

(3) the beam of the balance can be brought gently down on to its arrests before evacuating the system.

Note. Any sudden shock to the balance suspension, such as that produced by allowing the beam to come suddenly down on its arrests, may affect the zero-point of the balance. A similar shift of the zero-point—quite distinct and different from the 'drift' of the zero-point referred to earlier—may also result from cleaning the balance with a mixture of nitric and chromic acids—an operation which is necessary from time to time. A shift of the zero-point from both these causes was experienced in the course of the measurements given in part II.

Since the volume-adjustor is cut off from the manometer and balance case, by closing the stopcock *H*, when a balancing pressure is being determined, there is no need for the accurate control of its temperature.

The gas-inlet manifold

This is shown at *L*. It allows the gases under examination to be introduced into the apparatus by a controlled and step-wise method so that sudden shocks to the balance are avoided. The volume of the tubes *M* is about 12 ml., and that between stopcocks *J* and *K* about 1 ml. The manometer *N* is used to show the approximate pressure of gas in the apparatus. The connexions to the vacuum pumps are as shown.

Experimental procedure

The setting of the balance pointer accurately in line with the fixed zero pointer on the framework is a difficult and tedious operation, and it is much more convenient to adjust the pressure so as to bring the beam pointer close to the fixed zero-point and then measure its deviation from the true zero in the eyepiece scale of the reading microscope; the sensitivity of the balance having been determined, the necessary correction can then be made in the pressure reading. If a number of balancing pressures at zero for the same gas is determined in this way and the pressures plotted against the deviation (in eyepiece scale divisions) from true zero, the plot is linear, as would be expected; such a plot made for the standard gas, during a series of measurements, is useful in showing whether the balance is functioning properly and its zero is steady and free from 'drift'.

A plot of this kind is shown in figure 7 for nitrogen which was the 'bracketing' gas used in the determination of the atomic weights of carbon and nitrogen described later. The plot

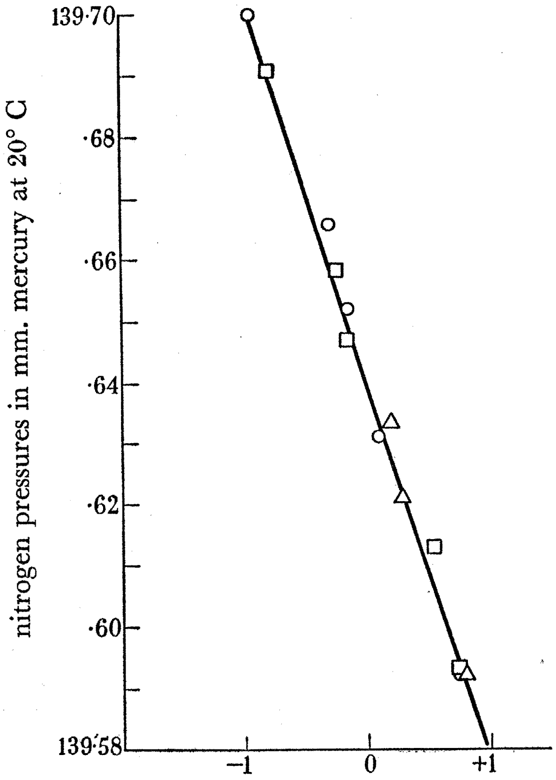

FIGURE 7. Deviation of beam pointer from zero position (in eyepiece scale divisions). ○, before methane measurements; □, after methane and before oxygen measurements; △, after oxygen measurements.

shows clearly the steadiness of the zero-point of the balance during a period of about 3 weeks required to carry out a series of measurements at one density; it shows also the high degree of precision and reproducibility which can be achieved in gas-pressure measurements.

In determining the ratio of the balancing pressures at zero of two gases care must be taken to ensure, beyond any doubt, that the purity of the gas being measured is not affected by traces of the gas previously used—and therefore adsorbed on the quartz, glass and metal surfaces—in the apparatus.

The apparatus is such that it cannot be heated, and therefore the adsorbed gas cannot be completely removed even by repeated evacuation. We have found that when, after thorough evacuation, a different pure gas is introduced into the apparatus, it becomes contaminated by traces of the previous gas—presumably owing to an exchange between the molecules of the entering gas and those in the adsorbed gas layer—to an extent which has a significant effect on its balancing pressure at zero. This difficulty, which is inherent in the technique, can only be overcome by the establishment of a stable adsorption layer of the new gas under examination—so that no further significant contamination takes place—before any balancing pressure measurements are made. The following series of operations has been found to overcome this difficulty:

(1) very thorough evacuation after measurements have been completed with the first gas,
(2) leaving the apparatus overnight filled with the second gas at a low pressure,
(3) thorough evacuation,
(4) filling the apparatus with a fresh supply of the second gas *at a pressure a little higher than its balancing pressure and leaving for several hours*,
(5) thorough evacuation,
(6) filling the apparatus with a fresh supply of the second gas for measurement.

After the gas for measurement has been introduced into the apparatus, and at least 1 hr. allowed for its temperature to become constant, the pressure is adjusted so as to bring the beam pointer near to zero. Attention is then given to the forms of the mercury menisci and, after a lapse of 10 min., readings are taken in the following order:

(*a*) deviation of the beam pointer from its fixed zero,
(*b*) position of the upper meniscus in the manometer in relation to the scale,
(*c*) depth of the upper meniscus,
(*d*) repetition of (*a*),
(*e*) position of the lower meniscus in the manometer in relation to the scale,
(*f*) depth of lower meniscus.

These readings are repeated until constant values have been obtained, and the necessary corrections are then applied to (*b*) and (*e*).

Similar measurements are then made with the mercury at different positions in the limbs of the manometer, the volume-adjustor being used for this purpose.

The whole apparatus is then evacuated and filled with a fresh supply of the same gas and the operations repeated; this procedure is continued until consistent results are obtained with at least two successive fillings of the gas under examination.

The procedure has to be somewhat modified for the determination of the balancing pressure at zero of oxygen. Unless nitrogen has been the gas previously under examination, this gas is introduced after the apparatus has been evacuated; stopcock *G* is then closed and the pressure of the nitrogen enclosed in the manometer adjusted as nearly as possible to the value expected for the balancing pressure of oxygen. Operations (1) to (6) are now carried out on the rest of the apparatus and pure oxygen thus brought into it; after the lapse of 1 hr. the pressure of the oxygen is adjusted (by using the volume-adjustor) so that the balance beam pointer is brought near to its zero; the volume-adjustor is then cut off by closing stopcock *H*. After connexion has been made between the balance case and the manometer, by opening stopcock *G*, operations (*a*) to (*f*) are carried out. It is, of course, only possible to obtain one balancing pressure measurement for each filling of oxygen.

By following this experimental procedure and observing strictly *all* the precautions described above, it has been found possible to make gas-pressure measurements on pure gases which are reliably reproducible to less than ±0·01 mm. of mercury and so to obtain results of dependably high accuracy for gas-density determinations from a much smaller number of measurements than has hitherto been considered necessary. This is shown clearly in the results obtained by the use of this improved technique in the determination of the atomic weights of carbon and nitrogen described in the second part of this paper.

PART II. A DETERMINATION OF THE ATOMIC WEIGHTS OF CARBON AND NITROGEN BY THE MICROBALANCE TECHNIQUE

Using the technique described in part I, values have been obtained for the atomic weights of carbon and nitrogen from determinations of the balancing pressure ratios of the pure gases nitrogen, methane and oxygen at three different settings of the zero-point of the balance and the subsequent use of the method of 'limiting densities'. The balancing pressure measurements thus fall into three series: a high-pressure series, a medium-pressure series and a low-pressure series, which are tabulated below. The preparation of the pure gases is described in an appendix.

Nitrogen was used as the 'bracketing gas' in each series, the order of balancing pressure measurements being nitrogen-methane-nitrogen-oxygen-nitrogen. The measurements in the high- and medium-pressure series were carried out with a balance having the simpler type of beam (figure 2); a balance having the modified type of beam (figure 3) was used for the measurements in the low-pressure series. All measurements were carried out at the temperature 20±0·005° C.

In the tables shown below, *gas pressures* are given in mm. of mercury at 20±0·005° C, *deviations of the beam pointer* (from the fixed zero) are given in scale divisions in the eyepiece of the reading microscope, and *balance sensitivities* are expressed as pressure changes in mm. of mercury for a deviation of one scale division in the eyepiece of the reading microscope.

It is interesting to note that the measured sensitivities correspond very closely with those calculated from the relative molecular weights of the three gases.

TABLE 1. HIGH-PRESSURE SERIES

gas	corrected pressure reading	deviation of beam pointer	pressure at zero balance	balance sensitivity
nitrogen	230·680	+1·1	230·728	0·044
	230·811	−1·9	230·727	
	230·714	+0·35	230·729	
	230·734	−0·2	230·725	
	230·792	−1·5	230·726	
	230·744	−0·3	230·731	
	230·714	+0·45	230·734	
		average	230·729	
methane	402·610	−1·75	402·477	0·076
	402·462	+0·1	402·470	
	402·392	+1·15	402·479	
	402·448	+0·35	402·475	
	402·617	−1·85	402·476	
	402·388	+1·2	402·479	
		average	402·476	
nitrogen	230·705	+0·7	230·736	0·044
	230·814	−1·8	230·735	
	230·736	−0·15	230·729	
	230·649	+1·8	230·728	
		average	230·732	
		average of all nitrogen values	230·730	
oxygen	202·039	−0·8	202·009	0·038
	202·046	−0·95	202·010	
	201·976	+0·9	202·010	
	201·962	+1·1	202·004	
		average	202·008	
nitrogen	230·821	−1·3	230·764	0·044
	230·790	−0·7	230·759	
	230·758	+0·1	230·762	
	230·815	−1·2	230·762	
		average	230·762	
oxygen	202·045	−1·1	202·003	
		average of all oxygen values	202·007	

In evacuating the apparatus before taking the first oxygen measurements, the balance beam was unfortunately brought rather suddenly down on to its arrests, and it was suspected that the shock might have affected the beam suspension. This suspicion was strengthened when the subsequent measurements of the balancing pressure of nitrogen gave values which were consistently 0·03 mm. higher than those obtained earlier in the series. The alteration might have been due to a gradual 'drift' of the zero during the time taken for the oxygen measurements and for the two changes of gas in the apparatus, but this explanation seemed unlikely in view of the consistency of the oxygen values obtained. A further oxygen measurement, which gave a value in close agreement with those taken earlier, finally confirmed the suspicion that the beam suspension had been affected by the shock and that a definite shift of the zero had been caused by allowing the balance beam to come suddenly down on to its arrests. The shift of the zero was not accompanied, in this case, by any measurable change in the sensitivity of the balance.

TABLE 2. MEDIUM-PRESSURE SERIES

gas	corrected pressure reading	deviation of beam pointer	pressure at zero balance	balance sensitivity
nitrogen	139·666	−0·3	139·648	0·061
	139·652	−0·15	139·643	
	139·700	−0·95	139·642	
	139·631	+0·1	139·637	
	139·592	+0·75	139·638	
			average 139·642	
methane	243·537	+1·5	243·693	0·104
	243·636	+0·6	243·698	
	243·691	−0·1	243·681	
	243·712	−0·2	243·691	
	243·630	+0·6	243·692	
			average 243·691	
nitrogen	139·647	−0·15	139·638	0·061
	139·613	+0·55	139·647	
	139·691	−0·8	139·641	
	139·593	+0·75	139·639	
	139·658	−0·25	139·643	
			average 139·642	
oxygen	122·231	+0·3	122·249	0·060
	122·262	−0·25	122·247	
	122·269	−0·35	122·248	
			average 122·248	
nitrogen	139·621	+0·3	139·639	0·061
	139·633	+0·2	139·645	
	139·592	+0·8	139·641	
			average 139·642	

TABLE 3. LOW-PRESSURE SERIES

gas	corrected pressure reading	deviation of beam pointer	pressure at zero balance	balance sensitivity
nitrogen	85·659	+0·1	85·669	0·105
	85·614	+0·4	85·656	
	85·722	−0·55	85·664	
	85·650	+0·15	85·666	
	85·732	−0·7	85·659	
	85·562	+0·95	85·662	
	85·598	+0·6	85·661	
			average 85·662	
methane	149·528	0·0	149·528	0·197
	149·616	−0·45	149·527	
	149·430	+0·5	149·529	
	149·455	+0·35	149·524	
	149·606	−0·4	149·527	
			average 149·527	
nitrogen	85·627	+0·35	85·664	0·105
	85·725	−0·6	85·662	
	85·563	+0·95	85·663	
	85·650	+0·1	85·660	
			average 85·662	

Owing to an accident, several months elapsed between the measurements taken for the methane/nitrogen pressure ratio and those (given below) taken for the nitrogen/oxygen pressure ratio in this series. The lapse of time and the necessary cleaning of the balance resulted in a definite shift of the zero and a slight alteration in the sensitivity of the balance. The sensitivity of the balance for the oxygen measurements was, in this case, calculated from the value determined for the nitrogen measurements.

Table 4. Low-pressure series (continued)

gas	corrected pressure reading	deviation of beam pointer	pressure at zero balance	balance sensitivity
nitrogen	85·565	+0·2	85·584	0·095
	85·526	+0·65	85·588	
	85·551	+0·35	85·584	
	85·600	−0·2	85·581	
	85·612	−0·3	85·583	
			average 85·584	
oxygen	74·908	+0·2	74·925	0·083
	74·907	+0·2	74·924	
	74·907	+0·2	74·924	
			average 74·924	
nitrogen	85·569	+0·2	85·588	0·095
	85·566	+0·2	85·585	
	85·569	+0·15	85·583	
	85·604	−0·2	85·585	
	85·521	+0·65	85·583	
			average 85·585	
			average of all nitrogen values 85·584	

Pressure ratios

The pressure ratios derived from the values obtained in the three series are:

high-pressure series: $\frac{\text{methane}}{\text{nitrogen}} = \frac{402{\cdot}476}{230{\cdot}730} = 1{\cdot}74436$, $\frac{\text{nitrogen}}{\text{oxygen}} = \frac{230{\cdot}762}{202{\cdot}007} = 1{\cdot}14235$.

medium-pressure series: $\frac{\text{methane}}{\text{nitrogen}} = \frac{243{\cdot}691}{139{\cdot}642} = 1{\cdot}74511$, $\frac{\text{nitrogen}}{\text{oxygen}} = \frac{139{\cdot}642}{122{\cdot}248} = 1{\cdot}14228$.

low-pressure series: $\frac{\text{methane}}{\text{nitrogen}} = \frac{149{\cdot}527}{85{\cdot}662} = 1{\cdot}74555$. $\frac{\text{nitrogen}}{\text{oxygen}} = \frac{85{\cdot}584}{74{\cdot}924} = 1{\cdot}14228$.

Atomic weights

Extrapolation of the pressure ratios obtained in the three series (figures 8 and 9)—effectively straight line plots, since all the gases involved are ‘permanent’—leads to the following values for the ‘limiting ratios’:

$$\frac{\text{nitrogen}}{\text{oxygen}} = 1{\cdot}14222\ (\pm 0{\cdot}00002),$$

$$\frac{\text{methane}}{\text{nitrogen}} = 1{\cdot}74626\ (\pm 0{\cdot}00004).$$

Taking oxygen as 16·0000 and hydrogen as 1·0080, this leads to the following values for the atomic weights of nitrogen and carbon:

nitrogen	14·0078 (±0·0003)
carbon	12·0112 (±0·0005)

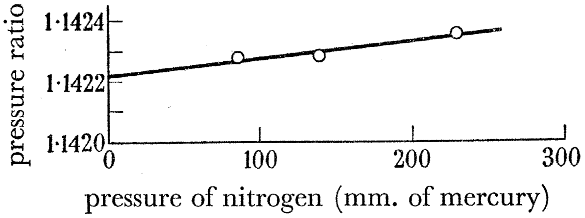

FIGURE 8

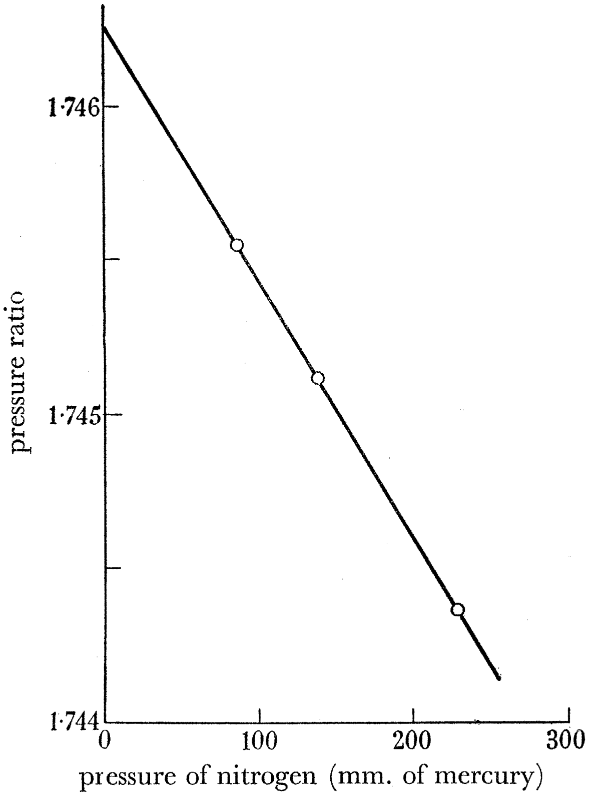

FIGURE 9

Compressibilities

The compressibilities of nitrogen and methane have been calculated from the slopes of the extrapolation plots. If the compressibility be defined by the equation

$$PV/P_0V_0 = 1 - ap,$$

where p is measured in atmospheres, then, assuming $a = 0{\cdot}00068$ for oxygen at 20° C, the following values are obtained:

nitrogen	$a = 0{\cdot}00026$ (±0·00005)
methane	$a = 0{\cdot}00219$ (±0·00007)

The values calculated from the Landolt-Börnstein Tabellen for these gases are:

nitrogen $a = 0{\cdot}00026$

methane $a = 0{\cdot}00218$

No correction has been made, in these calculations, for the contraction of the buoyancy bulb with pressure; this correction is probably negligible in its effect on the compressibility of nitrogen and small in its effect on the compressibility of methane (where the pressure ratio—and hence the correction—is larger). Since the correction is proportional to the density at which a pressure ratio is determined, the 'limiting ratios'—and hence the atomic weights—are not affected by it.

Computation of errors

In our calculations we have assumed that the experimental errors are completely random Equal weight has been given to each measurement in a series. The values recorded are standard (root mean square) errors.

Appendix. Preparation of pure gases

The preparation of pure nitrogen

When pure dry sodium azide crystals are heated *in vacuo* to 320° C, and care is taken to avoid any possibility of local overheating, the crystals decompose slowly and smoothly, *without melting*, nitrogen being given off and metallic sodium formed. In the early stages of the reaction—while the pressure of the nitrogen is low—some sodium vaporizes and condenses on the cooler parts of the reaction vessel.

A striking change in the colour of the crystals—from white to deep red—takes place very soon after the decomposition begins, and this colour change has been attributed to the possible formation of sodium nitride; that sodium nitride is actually present can be proved by cautiously adding some of the cooled, partially decomposed product to water when a distinct and unmistakable smell of ammonia is produced.

Since metallic sodium and sodium nitride are formed, along with nitrogen, when sodium azide crystals are decomposed by heat, the nitrogen must inevitably be contaminated with hydrogen and ammonia unless all traces of water are removed from the crystals before the decomposition takes place—a requirement which probably cannot be fulfilled since the crystals are decomposed without melting. In his classical researches on atomic weights, Richards (1910) has stressed the great importance of recognizing that traces of water are almost invariably retained within the structure of crystals and that this water cannot be removed until the crystal structure is destroyed either by decomposition or by a change of phase.* In view of these considerations, it seems to be very probable that nitrogen of the

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* A very striking instance of the strong retention of water within a crystal structure was encountered in the course of preparing helium from thorianite in this laboratory. Crystals of the mineral were ground in an agate mortar, passed through a 100-mesh sieve and dried over phosphorus pentoxide in a vacuum desiccator; about 500 g. of the dry powder were then heated in a quartz tube attached to an apparatus set up for purifying and storing the helium. After thorough evacuation of the apparatus, the thorianite was heated to 500° C and maintained at that temperature until a good vacuum could be maintained; when the temperature was subsequently raised to 900° C, the helium which was evolved was accompanied by so much water that *several grams of it* were collected in a cooled trap which formed part of the apparatus.

highest possible purity cannot be obtained by the decomposition of sodium azide unless effective measures are employed for the purification of the gas from traces of hydrogen and ammonia.

The nitrogen used in this investigation was made by the decomposition of pure dry sodium azide in an apparatus (shown in figure 10) which was designed to meet this requirement. It has been found possible by using this apparatus:

(*a*) to show that the nitrogen undoubtedly contains hydrogen as an impurity, and

(*b*) to remove the hydrogen whether it is present in the free state or in combination with nitrogen as ammonia.

The sodium azide used in the preparation was purified by repeated recrystallization, the crystals being separated from the mother-liquors in dust-free air and finally dried for several months over pure phosphorus pentoxide in a vacuum desiccator.

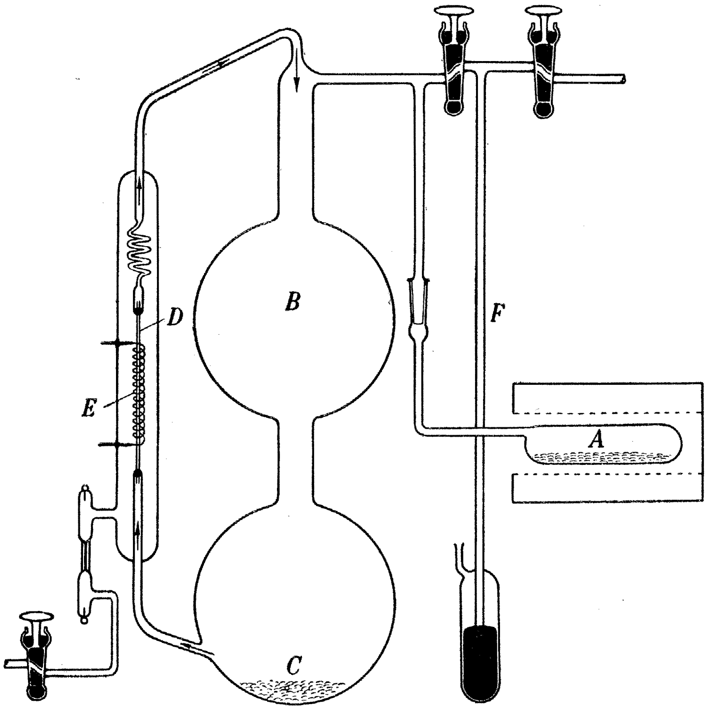

FIGURE 10

Figure 10 shows the complete apparatus which serves for the preparation, storage and purification of the nitrogen.

The generating vessel A is made of transparent, fused quartz and contains about 25 g. of pure sodium azide. It is heated by an electric tube-furnace which surrounds the vessel but does not touch it at any point so that the possibility of local overheating of the sodium azide is precluded. The quartz vessel is joined to the glass parts of the apparatus by means of a long ground joint which is sealed with black Apiezon wax.

The storage reservoir BC has a capacity of about 6 l.; it contains pure phosphorus pentoxide which is distilled (in a current of oxygen) directly into the lower part *C* before the apparatus is assembled.

The manometer F, with its open end in a mercury reservoir, serves to show the pressure of nitrogen in the apparatus and acts, in case of necessity, as a 'blow-off'.

Connexion to the evacuating system is made through the mercury-sealed stopcocks shown in the diagram.

The purifier (shown on the left of figure 10), which also acts as a circulator, is essentially a hydrogen filter. It consists of a palladium tube *D*, which forms part of a by-pass linking the top and bottom of the storage reservoir, and is enclosed in a jacket which is evacuated through the discharge tube shown in the diagram. The palladium tube is heated by radiation from an electrically operated platinum wire spiral *E* which is supported by sealing through the wall of the jacket and which can be maintained at a bright red heat for long periods. When the purifier is in operation, the nitrogen in the storage reservoir is slowly and continuously circulated in the direction shown by the arrows; hydrogen is removed by diffusing through the palladium tube into the surrounding evacuated space, while ammonia is catalytically decomposed at the hot palladium surface into nitrogen and hydrogen.

Note. (i) The palladium tube is 7 cm. long and its internal diameter is 2 mm. At each end it has a platinum extension (gold-soldered to the palladium) so that vacuum-tight seals can be made where it is joined to the glass tubing.

(ii) A thin walled glass spiral, which is sufficiently flexible to 'take up' the expansion and contraction of the palladium tube is an essential part of the purifier.

The whole apparatus was thoroughly evacuated and washed out many times with dry cylinder nitrogen; during these operations the generating vessel *A* was heated to 200° C, the platinum wire spiral *E* was maintained at a bright red heat and the walls of the storage vessel heated from time to time. This procedure was continued until a high vacuum could be maintained and no discharge could be produced in the discharge tube.

The temperature of the generating vessel *A* was then raised to 320° C and maintained there until the manometer showed a pressure of about 1 cm. of nitrogen in the storage reservoir when the heating was cut off and the apparatus left overnight. At this stage the sodium azide had become deep orange-red in colour. When the purifier was brought into operation no discharge could be obtained in the discharge tube until about half an hour had elapsed when, following on a green fluorescence, a bright discharge was obtained which showed a pure hydrogen spectrum; definite evidence was thus produced that the nitrogen contained hydrogen and that the purifier was effective in removing the impurity.

The whole apparatus was then thoroughly evacuated and nitrogen generated until the pressure reached 2·5 cm.; this gas was again found to contain hydrogen, as was a further supply generated until the pressure reached 5 cm. When it had thus become clear that all the impurity was not produced in the early stages of the decomposition of the sodium azide, the reaction was allowed to proceed until there was a pressure of about 65 cm. of gas in the storage reservoir.

The purifier was now brought into operation and the jacket evacuated continuously except for occasional periods required to test whether hydrogen was still being removed. Nearly 200 hr. of intermittent operation of the purifier were necessary before hydrogen could no longer be found in the jacket surrounding the purifier. After a further 50 hr. operation of the purifier it was considered that all traces of impurity—hydrogen *and* ammonia—had been removed from the nitrogen stored in the reservoir.

The preparation of pure methane

The methane was prepared by the action of water on magnesium methyl iodide. The starting material was methyl alcohol which was carefully purified from all traces of ethyl alcohol before being converted into methyl iodide; this, in turn, was purified and then used to prepare the magnesium methyl iodide in dry ether solution.

The methane was freed from water vapour and ether by a succession of traps cooled to −80° C and was then liquefied; the liquid was fractionated and the middle fraction allowed to evaporate into a large storage vessel containing pure phosphorus pentoxide. After several days the dry gas was condensed as a solid in a vessel cooled by liquid nitrogen and again fractionated by sublimation of the solid, the middle fraction only being retained. The final purification was carried out in a modified form of the fractionating apparatus described by Clusius & Riccobini (1938), the gas collected being only that which came off at a constant pressure. The gas was stored in a glass reservoir over pure phosphorus pentoxide.

The preparation of pure oxygen

The oxygen was prepared by the decomposition, *in vacuo*, of pure dry potassium permanganate. The gas was stored over an aqueous solution of caustic potash through which a strong stream of cylinder oxygen had been bubbled for several hours; after 3 days it was dried by passing slowly through drying towers and an efficient double-walled trap cooled in liquid air and then liquefied in a vessel surrounded by liquid nitrogen. The liquid oxygen was fractionated several times, the middle fraction only being collected and liquefied on each occasion. It was finally purified in the fractionating apparatus of Clusius & Riccobini, the gas collected being only that which came off at a constant pressure. The pure oxygen was stored in a glass reservoir containing pure phosphorus pentoxide and was protected from contact with stopcock grease until it was required for use.

All stopcocks employed throughout this investigation were lubricated with vapourless Apiezon grease. The phosphorus pentoxide used for drying the gases was distilled, in a current of oxygen, directly into the storage vessels, by a method which had been shown to remove all detectable traces of the lower oxide.

A grant towards the cost of this investigation by Messrs Imperial Chemical Industries is gratefully acknowledged, and thanks are also due to Messrs F. F. Ross, C. L. Bibby and S. R. Epton for valuable assistance in the early stages of the development of the microbalance technique.

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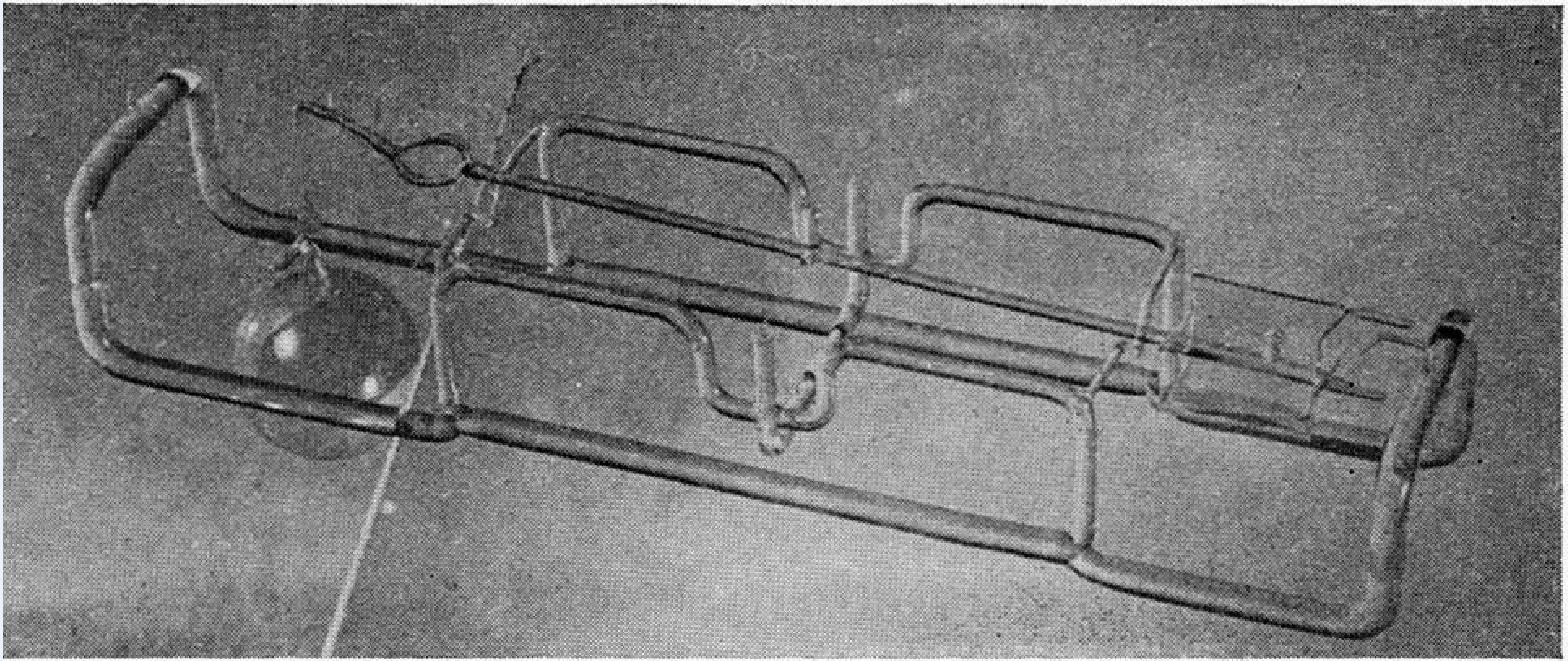

FIGURE 4