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THE ACCURATE ANALYSIS OF GASEOUS MIXTURES

By BERTRAM LAMBERT AND DOUGLAS JOHN BORGARS

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The gas-analysis technique described in this paper has been developed for the accurate determination of the percentage content of one constituent of a gaseous mixture when only small quantities of the mixture are available for analysis.

When about 10 c.c. of gaseous mixture are used for an analysis, it has been found possible to obtain values (for the percentage content of one constituent) which are accurate to $\pm 0.02\%$; when using only 1–2 c.c. of gaseous mixture, values accurate to $\pm 0.1\%$ have been obtained.

The technique can be used for the determination of more than one constituent in the same sample of a gaseous mixture, but, of course, the accuracy decreases with each determination subsequent to the first.

The technique is based on the principle of removing from a measured volume of the gaseous mixture, the constituent of which the percentage content is required, followed by the measurement of the volume of the residual gas.

In order to determine the percentage content of a constituent X in 10 c.c. of gas mixture—and obtain a value reliably accurate to $\pm 0.02\%$ —it is essential,

(a) that the required volume measurements should be made under comparable conditions so far as the pressure, temperature and water-vapour content are concerned, and, further, that they should be accurate to 0.001 c.c.;

(b) that X should be removed by a process which definitely proceeds to completion and which *does not alter by more than 0.001 c.c. the volume of the other gases originally present in the measured volume of gaseous mixture.*

A satisfactory apparatus for the purpose must therefore provide:

I. *A gas-measuring system* which allows the measurement of gas samples (of about 10 c.c.) in strict accordance with the requirements stated in (a) above;

II. *A removal system* which allows the complete elimination from the gaseous phase of one constituent of a measured volume of gaseous mixture in strict accordance with the requirements stated in (b) above;

III. *A manipulatory system* which provides for the collection and introduction of a sample of gas into the apparatus and for its transference from I to II, and vice versa, without the slightest risk of contamination or loss.

1. THE GAS-MEASURING SYSTEM

The principles underlying the volume measurement of successive samples of gas under comparable conditions (of temperature, pressure and water-vapour content) are simple and well known. They may be summarized as follows: The water-vapour content of each sample of gas is brought to the same value by having a little normal sulphuric acid on the top of the mercury in the measuring limb of the gas burette; the volume of each sample of gas is read after its pressure has been exactly balanced against that of a confined volume of air which is also kept in contact with normal sulphuric acid—the gas burette and the pressure-balancing (“compensator”) device being maintained at the same temperature.

Experience shows that the most careful manipulation is essential if the volume error—under the comparable conditions required—is to be kept with certainty within 0.001 c.c. when using a 25 c.c. burette; and particular attention must be paid to (a) the construction, calibration and reading of the gas burette, (b) the exact setting of the mercury at the zero mark of the burette, and (c) the sensitivity and reliability of the pressure-adjusting and pressure-balancing devices.

The gas-measuring system used in this work is shown in section in fig. 1, and in the following description attention is directed to those details of construction and manipulation which have been found necessary to ensure a uniformly high accuracy.

The gas burette *R* is of the type generally employed for the measurement of gas volumes at atmospheric pressure. It consists of a graduated measuring limb (the lower, ungraduated part of which is widened to form a cylindrical bulb of about 20 c.c. capacity) alongside a balancing limb of the same internal diameter (about 8 mm.); the two limbs are joined at the bottom end and connected, by means of capillary tubing, the three-way stopcock (2) and a ground flange joint,* to the mercury reservoir *S* (capacity about 100 c.c.) and a coarse-adjustment pressure regulator *T*. The arrangement is clearly shown in fig. 1 and requires no further description.

The upper end of the balancing limb is joined by a capillary tube to the three-way stopcock (3) which allows it to be opened either to the air *or* to the fine-adjustment pressure regulator *V*; at the upper end of the graduated measuring limb there is a

* Unless it is stated otherwise, the capillary tubing used in all parts of the gas-analysis apparatus has an internal diameter (bore) of 1–1.2 mm. and an external diameter of 7–8 mm. All the stopcocks have their limbs made of this capillary tubing and their stoppers are solid and drilled with holes of the same diameter as the bore of the connecting capillary tubing. The stopcocks must be accurately made so that no gas is trapped in the bores when mercury passes through them.

The type of ground capillary flange joint used throughout the apparatus allows a junction to be made in the capillary tubing without producing a change in the bore. The two parts of the flange joint are ground flat and are held firmly together by means of a special screw clip; when lubricated with a thin layer of Apiezon Grease “L”, the joint is vacuum-tight and mercury passes through it without trapping gas bubbles. This excellent type of *interchangeable* capillary flange joint is made by Messrs J. C. Cowlshaw Ltd., Bridge St, C.-on-M., Manchester; the gas burette and the stopcocks used throughout the apparatus were also made by this firm.

three-way stopcock (1) which allows it to be connected *either* to the "compensator" *W* or to the fine-adjustment zero-setting device *X* and the rest of the apparatus. Details of *V*, *W* and *X* are given later. It is important that the tube connecting the graduated part

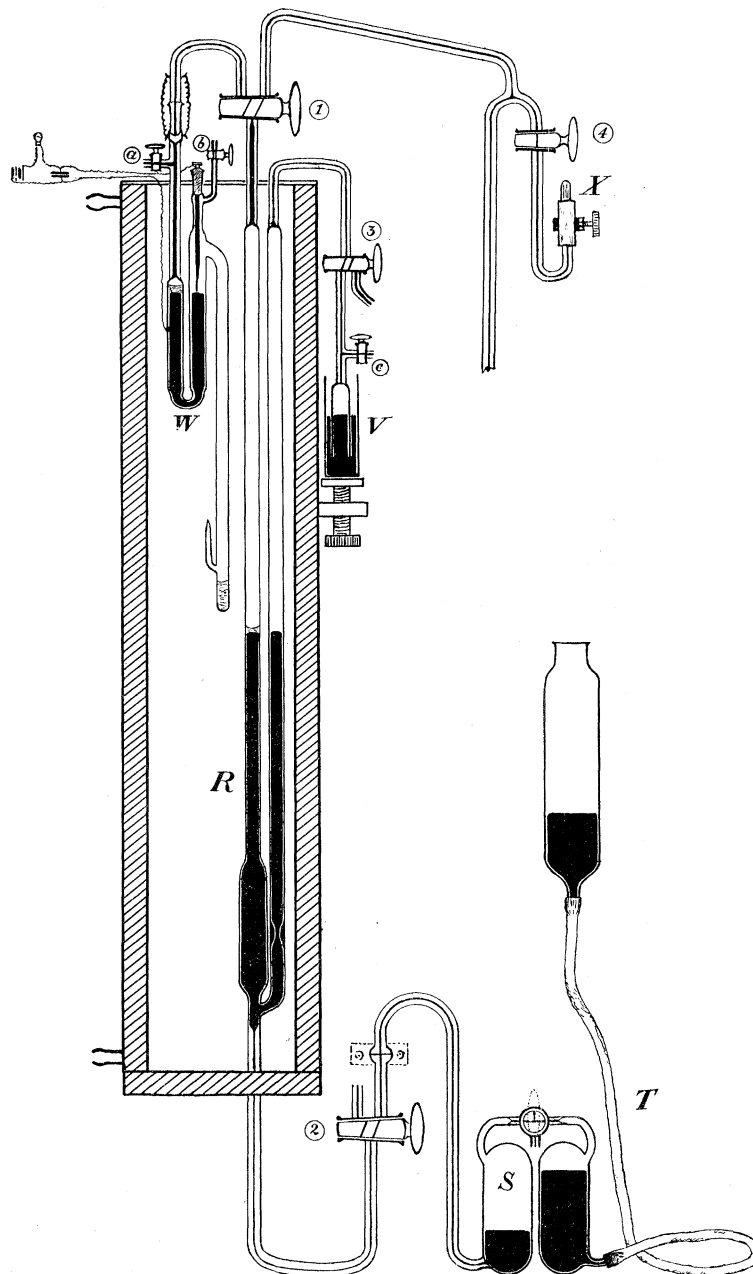


FIG. 1

of the measuring limb to the capillary stopcock (1) should be of internal diameter 2 mm., the bore being contracted to about 1 mm. just before it enters the barrel of the stopcock; the reason for this is explained in the section dealing with the calibration of the burette.

The gas burette R and the “compensator” W are set up vertically in a water-jacket made with the sides and bottom of accurately machined sheet Bakelite (25 mm. thick) and having plate-glass windows back and front. The water-jacket has side tubes near the bottom and top and is maintained at a constant temperature ($20 \pm 0.01^\circ \text{C}$) by pumping through it a rapid stream of water from a thermostatically controlled water-bath.

The burette is read by means of a reading microscope mounted on a carriage which moves vertically up and down an accurately machined phosphor-bronze bar bolted to the front of the water-jacket. This bar is shaped like a lathe-bed, the hand-driven mechanism for moving the microscope carriage being similar to that of a precision lathe and having a coarse and fine motion. The microscope has its own focusing movement which moves the whole microscope horizontally along its own axis. If this precision-reading device is well made it is much superior to a cathetometer.

The reading microscope is provided with a micrometer scale in the eyepiece and the magnification is adjusted (and fixed) so that 25 micrometer scale divisions exactly cover the space (about 1 mm.) between the centres of any two adjacent graduation marks in focus. There is a graduation mark for each 0.05 c.c.; one micrometer scale division therefore represents 0.002 c.c., and readings to 0.001 c.c. can be carried out with reasonable certainty. The finely etched graduation marks are alternately 2 and 1 mm. in length; they all begin on an imaginary vertical line slightly to the right of the front of the burette, while the figures (marked every 0.1 c.c., opposite the longer graduation marks) are small, *inverted* and etched slightly to the left of the front of the burette. This method of graduation leaves a clear space about 1 mm. wide—free from etched lines or figures—vertically down the front of the burette between the graduation marks and the figures. A clear, undistorted image of the tip of the gas-confining meniscus can thus be focused in the reading microscope and made to coincide exactly with the centre mark of the micrometer scale in the eyepiece; and, when the microscope is subsequently focused on the corresponding graduation marks, the significant figures are brought into view *erect* and the volume can be read with ease and certainty.

Suitable illumination of the gas-confining meniscus (formed by normal sulphuric acid on top of the mercury in the measuring limb) is a most valuable aid to accuracy and is obtained as follows: An illuminated screen is made to move behind (and close to) the water-jacket in the line of vision of the reading microscope. This screen, which is the full width of the water-jacket, is made of translucent tracing paper mounted on a light wooden frame; it is attached firmly to (and moves with) the microscope carriage by means of a bent brass tube. The lower half of the screen is blackened and a small 4.5 V electric light bulb is fixed behind this part. When the lamp is switched on, the upper translucent half of the screen transmits a soft diffused light which affords a suitable illumination of the gas-confining meniscus and forms an excellent background for focusing it sharply in the microscope.

Since there is normal sulphuric acid on top of the mercury in the measuring limb of the gas burette the walls are wetted when gas is introduced. Uniform accuracy of volume measurement can, of course, only be attained if care is taken to eliminate all possibility of error arising out of irregularities in the drainage of the wetting liquid from the walls of the burette. Careful experiment (using the full capacity of the burette) showed that no significant movement of the gas-confining meniscus took place during the 21st minute after the introduction of gas into the burette. *In the calibration of the burette and in its subsequent use, volume readings are therefore always made 20 minutes after the introduction of gas into the burette.*

It is most important that the burette be accurately calibrated and this must be done before the apparatus is assembled.

The calibration of the burette. The graduated measuring limb of the burette, with its three-way stopcock (1), is cut off (below the graduation marks) from the balancing limb and a length of fine (about 0.3 mm.) bore capillary tubing sealed on temporarily. The stopcock is lubricated with Ramsay grease and it is essential that the grease which collects in the bores of the stopcock during this operation be completely removed. This is done by drawing through the bores (by means of a water pump) warm carbon tetrachloride followed in turn by air, warm sulphuric-chromic acid mixture, warm water, pure alcohol and finally dry air.

Note. This procedure is always followed after the lubrication of the stopcocks in the apparatus or when the walls of the burette show the slightest sign of greasiness. The whole apparatus has been designed so that the gas burette, capillary connecting tubes and stopcocks can be freed from grease, *in situ*, as and when required, by this method. After the bore of a stopcock has been cleaned the stopper must not be turned until the bore is quite dry and then it should be turned gently backwards and forwards through a small arc, until there is complete optical contact between the stopper and the barrel.

Uniformly high accuracy can only be obtained if the walls of the gas burette are kept free from grease and the wetting film consequently smooth and even.

The clean burette is set up vertically in the water-jacket, the temporary extension passing through a cork in the bottom of the jacket; a small fine-bore capillary stopcock is then sealed on just below the water-jacket. The water-jacket is maintained at a constant temperature of $20 \pm 0.01^\circ \text{C}$.

The burette is now ready for calibration by the weighed mercury method. Clean dry mercury is forced into the burette from the bottom until it overflows from the right-hand open limb of stopcock (1) into normal sulphuric acid covering the end of this open tube and contained in a glass sleeve temporarily fixed round this limb. Sufficient mercury is then run out from the burette to cause about 0.1 c.c. of the sulphuric acid to enter the burette. After turning stopcock (1) so as to open the burette to the air, mercury is run out into a tared weighing bottle and the position of the gas-confining meniscus read (to 0.001 c.c., as described above) after a lapse of 20 min. This whole procedure is followed in detail for each separate point determined in the

calibration of the burette; the burette is therefore calibrated in precisely the same way as it is used and errors due to irregularities in drainage are eliminated. It is advisable to calibrate the burette at small volume intervals throughout its whole length and construct a calibration chart.

The stopcock (1) must necessarily be outside the constant-temperature jacket, and the tube connecting it to the graduated limb of the burette should therefore have the smallest possible capacity; but, as pointed out above, the bore of this tube must not be less than 2 mm. or the sulphuric acid will not drain from it satisfactorily.

The fine-adjustment zero-setting device X

Since the calibration chart of the burette shows the volume to the nearest 0.001 c.c. between the gas-confining meniscus and the entrance to the right-hand bore of the stopcock (1), it is necessary, when gas is brought into the burette for measurement, to adjust the position of the mercury which follows the gas so that the mercury *completely* and *exactly* fills the right-hand bore of the stopcock. This important and delicate operation cannot be carried out easily by the use of the coarse-adjustment pressure regulator *T*. The simple device shown at *X* enables the operation to be done quickly and accurately. The device is essentially a tiny compressible mercury reservoir (made from thick-walled rubber pressure tubing closed with a glass rod); it is actuated by a screw-clip which allows a very fine adjustment of the amount of mercury contained in it. The device is connected by capillary tubing and the stopcock (4) to a side-arm of the apparatus as shown in fig. 1. The stopcock is opened after the mercury has been roughly adjusted near the zero mark and the final accurate adjustment is then readily obtained by the turning of the screw-clip. The device has another use in the manipulation of the apparatus (see later in section on general manipulation of the apparatus, p. 558).

The compensator W

The accurate volume measurement of successive samples of gas under comparable conditions (of pressure, temperature and water-vapour content) requires that the volume of *each* sample should be read after its pressure has been exactly balanced against that of a confined volume of air—both gas sample and confined volume of air being in contact with the same aqueous solution (normal sulphuric acid) and maintained at the same temperature; the pressure-balancing device used for this operation is called a compensator.

Since the gas being measured in the burette and the confined volume of air in the compensator must be at the same temperature, the gas burette and the compensator are housed alongside one another in the constant temperature water-jacket as shown in fig. 1.

In its simplest form the compensator is essentially a U-tube mercury manometer with the mercury confining, on one side of the manometer, a volume of air (at approximately atmospheric pressure) in contact with normal sulphuric acid, the other side

of the manometer being attached to the gas burette and capable of being put into contact with it by the appropriate turning of the three-way burette stopcock. Each gas sample brought into the burette for measurement is in contact with normal sulphuric acid and, before the volume is read, the pressure on the gas is adjusted so that it is exactly equal—as shown by the mercury manometer—to that of the confined volume of air in the compensator. In carrying out a pressure-balancing operation with this simple type of compensator (in which the confined volume of air is at an arbitrary pressure) it is obviously difficult (if not impossible) to avoid contamination of the measured gas sample with the gas in the tube connecting the measuring burette to the compensator.

A modified type of compensator has been devised which allows the difficulty to be overcome; a reliable and sensitive indication of pressure balance is also provided in this improved form of compensator.

The design and scheme of assembly of the compensator are clearly indicated at *W* in fig. 1. The U-tube manometer is made of tubing of internal diameter not less than 10 mm., the tube containing the confined volume of air in contact with normal sulphuric acid having the same internal diameter (8 mm.) as the measuring limb of the gas burette; this tube is provided with a small side arm, as shown, for the introduction of the normal sulphuric acid. The connexion to the burette—through the left-hand limb of the three-way stopcock (1)—is made of capillary tubing with a tapered ground joint (provided with hooks and springs); it is advisable to have the bore of the lower part of the connexion (between the ground joint and the U-tube) 2–2.2 mm. in order to facilitate the filling and adjustment. The ground joint allows the compensator to be detached from the burette, when required, for cleaning or adjustment; and, when the compensator is detached, the removal of grease from the left-hand bore of stopcock (1) is made possible.

Small stopcocks (*a*) and (*b*), to open to the air, are fitted on each side of the manometer U-tube.

A platinum wire is sealed through the side of the left-hand limb of the U-tube and a thick pointed platinum-iridium wire (fitted through a ground joint) is centred in the right-hand limb of the U-tube as shown. These two wires are connected to the terminals of a 4 V battery with a switch and a 4.5 V lamp in series; an efficient, large-capacity condenser is connected across the circuit. This electrical circuit is closed—and the lamp lighted—when the mercury in the U-tube makes contact with the platinum-iridium point; a sensitive and visible indication (of pressure balance on the two sides of the U-tube manometer) is thus made possible and, when a really efficient condenser is used—to eliminate the spark produced at the breaking of the contact between the mercury and the platinum-iridium point—the pressure-balancing device remains reliable over long periods of use.

After the compensator has been carefully cleaned and dried, normal sulphuric acid is introduced through the small side-arm (provided for this purpose) which is then sealed.

The assembled compensator, with the stopcocks (*a*) and (*b*) open to the air, is clamped vertically in a constant-temperature bath (maintained at $20 \pm 0.01^\circ \text{C}$) and clean dry mercury introduced through the left-hand side of the U-tube until a gap of about 0.5 mm. is left between the platinum-iridium point and the mercury surface in the right-hand limb; normal sulphuric acid is then added to the mercury in the left-hand limb until this gap has been almost—but not quite—closed and the indicator lamp flickers in and out when the compensator is *gently* tapped.

The compensator, thus delicately adjusted, is then attached to the burette, the small stopcocks (*a*) and (*b*) being left open to the air until the attachment is completed.

Manipulation of the compensator

A sample of gas mixture having been introduced into the burette for measurement (*vide infra* for details of this operation) and the mercury accurately adjusted at the zero mark, stopcock (1) is closed. By using the coarse-adjustment pressure regulator *T*, with stopcock (3) open to the air, *the gas enclosed in the measuring limb of the burette is next brought to a pressure slightly above atmospheric*—as shown when the mercury level in the balancing limb is about 10 mm. higher than that in the measuring limb; stopcock (2) connecting the burette to the pressure regulator *T* is then closed.

After the lapse of about 18 min. from the time of introducing the gas into the burette, the small compensator stopcocks (*a*) and (*b*) are opened to the air and the burette stopcock (1) is then turned so as to connect the gas burette to the compensator. The gas in the measuring limb of the burette (which *was* at a pressure slightly higher than atmospheric) automatically adjusts itself to atmospheric pressure and, at the same time, the gas in the capillary tube connecting the burette to the compensator is replaced by some of the gas mixture being measured; the danger of any contamination of the measured gas sample is thus eliminated.

The small compensator stopcocks (a) and (b) are then closed and kept closed in all further operations with the sample of gas under investigation.

The pressure is now the same as that of the atmosphere on the two sides of the compensator manometer and the two sides of the gas burette; and, if the compensator is *gently* tapped, the indicator light flickers on and off. Since a knowledge of the exact pressure within the compensator is required at a later stage, the barometer must be read and noted.

A more certain and definite “end-point” (than one requiring the tapping of the compensator) for the pressure-balancing operation is, however, desirable and so the pressure on the gas in the burette is finally adjusted until the compensator lamp just remains definitely alight without tapping. This final small adjustment of the pressure—prior to reading the volume during the 21st minute after the introduction of the gas into the burette—is made by the fine-adjustment pressure regulator shown at *V*. If the compensator has originally been adjusted with sufficient delicacy, this final small-pressure adjustment produces no measurable alteration in the volume of the gas in the burette.

The fine-adjustment pressure regulator, V , is essentially a small air buffer capable of being connected to the balancing limb of the gas burette by the appropriate turning of the three-way stopcock (3). The pressure on the air (over mercury) in the buffer is adjustable within fine limits by movement of the screw-actuated platform on which stands a mercury reservoir surrounding the lower (open) end of the buffer; the air in the buffer can, at any time, be brought to atmospheric pressure by opening (and then closing) the small stopcock (c).

The construction of this device is clearly shown in fig. 1 and further details of its manipulation are unnecessary; it is, of course, only used in the final stage of pressure adjustment.

The compensator technique described above is obviously not applicable to the volume measurement of the residual gas after the removal of a constituent from the original measured gas sample. Since it is often necessary (even when the percentage proportion of one constituent only is required) to check the completeness of a removal operation by repetition, with volume measurements after each such operation, it is essential that there should be no contamination of the *residual* gas during these measurements. The gas in the capillary tube between the burette and compensator has not the same composition as the residual gas requiring measurement, and the "sweeping out" process used (to eliminate the possibility of contamination) in the measurement of the original sample is no longer possible. In order to avoid contamination during the pressure-balancing operation in all volume measurements subsequent to the first, it is therefore necessary—*before turning stopcock (1) and so connecting the burette with the compensator*—to adjust the pressure of the gas in the burette so that it is equal to that of the confined volume of air within the compensator.

Since the compensator is kept at a constant temperature the pressure within it remains constant and this is known (*vide supra*). It is possible, with care and practice, to adjust the pressure of the gas in the burette to a value so nearly equal to that within the compensator that any detectable contamination due to pressure inequality (when the burette and compensator are connected for the final pressure-balancing operation) is avoided.

The barometer is read and the difference noted between this reading and that made at the time of the original volume measurement; the height of the sulphuric acid layer on the mercury in the measuring limb of the burette is determined by means of a millimetre scale made to slide on the front of the water-jacket; it is then possible—with the aid of the scale—to adjust the pressure on the gas in the measuring limb of the burette so that it is equal (within 0.2 mm.) to that within the compensator.

The possibility of contamination by *diffusion*, during the short time necessary for effecting the final pressure-balancing operation, has been found to be negligible.

2. THE REMOVAL SYSTEM

The removal from the gaseous phase of one constituent of a gas mixture—by a process which definitely proceeds to completion and which does not measurably (to

0.001 c.c.) affect the volume of the other gases present—is the most difficult problem in accurate gas analysis.

The processes used for the purpose in this work are:

- (a) chemical absorption;
- (b) explosion with oxygen;
- (c) combustion with oxygen.

Processes (b) and (c) are applicable only to gases which combine with oxygen and they are frequently followed by an absorption process. A completely satisfactory absorption process is therefore a necessary part of the technique.

It is, of course, essential that any absorbent used for the removal of one constituent of a gas mixture should be capable of removing the absorbable gas *completely* and *permanently* from the gaseous phase and that it should have no chemical action whatever on the other gases present in the mixture.

The use of chemical absorbents in the solid form is unsatisfactory because of the length of time taken for the *complete* removal of the absorbable gas. A chemical absorbent in the liquid form is very much quicker in reaching completion provided that there is a large gas-liquid interface and that this is constantly renewed.

There is, however, a serious difficulty connected with the employment of any liquid absorbent in accurate gas analysis since *all* gases are soluble in liquids in amounts which vary with the temperature and pressure. It is therefore obvious that the use of a liquid absorbent, for the removal of *one* constituent of a gaseous mixture, involves the strict fulfilment of the following requirements in order to ensure that the process has no measurable effect on the volume of the other gases present:

- (i) The liquid absorbent must be completely saturated, *before use*, with “the other gases present” in the gas mixture under exactly the same conditions (of temperature and pressure) as obtain in its actual use.
- (ii) The liquid absorbent must be effectively shielded from contact with the air and maintained at a constant temperature throughout its use.

A long experience of the analysis of gaseous mixtures has shown that a uniformly high standard of accuracy can only be attained by the use of a gas-absorption system which provides for the strict fulfilment of the requirements stated above. A system has been devised which meets these requirements and which provides the large and constantly renewed gas-liquid interface necessary for completing the absorption process in the shortest possible time. The apparatus is shown in fig. 2 and is described in detail below.

The gas-absorption system (fig. 2)

The gas pipette consists of a wide cylindrical glass tube *A*, open at the lower end and sealed at the upper end to the central limb of a three-way capillary stopcock *B*; the second limb of the stopcock terminates in a ground capillary flange joint *C*, for connexion to the rest of the apparatus (*vide infra*), while the third limb is bent round

and attached, by means of a cork, to a small overflow vessel *D* which has a side tube open to the air. The dimensions of *A* (suitable for use with a 25 c.c. gas-measuring system) are: length 120–124 mm., internal diameter 30–32 mm.

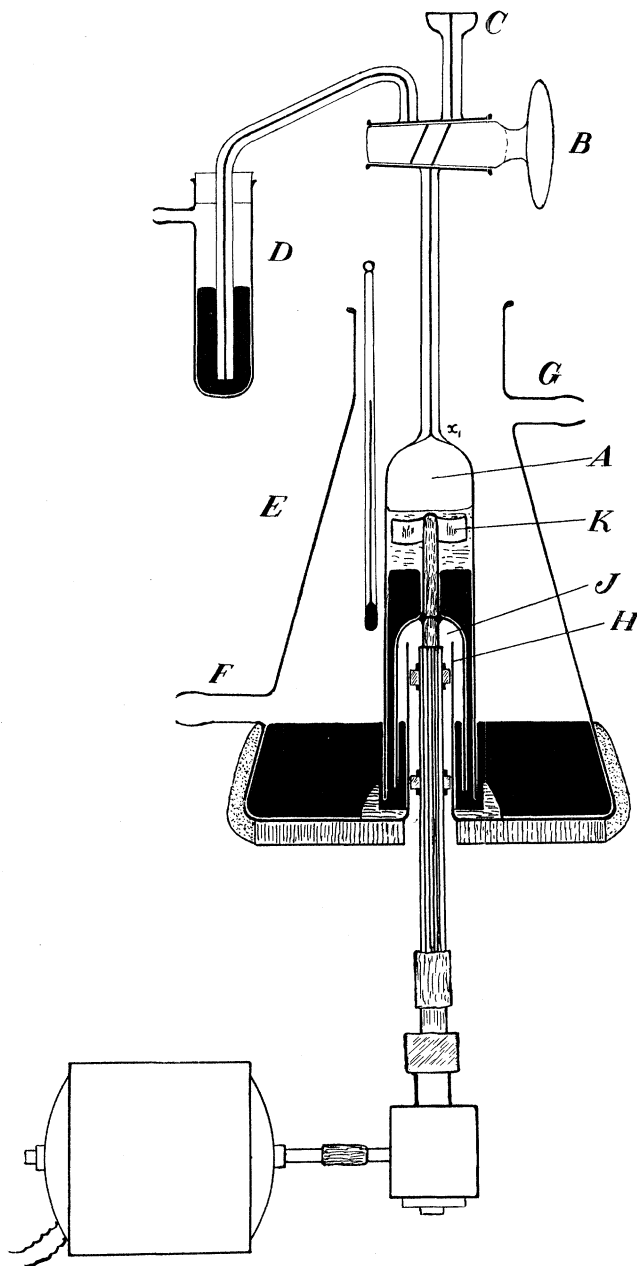


FIG. 2

The open end of *A* dips into mercury contained in a 750 c.c. wide-mouthed conical flask *E* made of Pyrex glass. The flask is provided with two horizontal side tubes *F* and *G* (internal diameter 8–10 mm.) and a vertical tube *H* (length 72–75 mm. and internal diameter 14–15 mm.) which is sealed centrally in the bottom of the flask;

this vertical tube, which is open at both ends, serves as a bearing for the stem of the motor-driven stirrer K . The stirrer is made of Pyrex glass and has propeller-shaped blades (about 10 mm. high) made from a flat strip and fused to the end of a rod which is sealed centrally through the closed end of a tube J (internal diameter 20–22 mm. and length 64–66 mm.); the lower open end of J dips into the mercury contained in the flask and forms a mercury seal for the stirrer. The lower part of the stem of the stirrer is cemented inside a thin metal sheath on which are built two felt washers with vertical slots cut in them; the felt washers are impregnated with vaseline and made to fit in the central bearing tube H . This construction allows the stirrer to be driven at high speeds without setting up excessive vibration. For the purpose of driving the stirrer a $\frac{1}{50}$ h.p. high-speed motor is used in conjunction with a 4–1 reduction gear. The vertical stem of the reduction gear is provided with a chuck holding a short steel rod which is connected to the stirrer stem by means of a piece of thick rubber tubing; the horizontal stem of the reduction gear is connected directly to the shaft of the motor—also by thick rubber tubing. Flexibility is thus provided in the connexion between motor and stirrer and the position of the stirrer in the gas pipette can also be readily adjusted.

The open end of the gas pipette is kept centrally in position by sliding loosely into a circular Bakelite “shoe” which fits round the “bearing” tube H and is cemented on the bottom of the flask E ; the side of the “shoe” is cut away in two places (for about 5 mm.) so as to allow the free flow of mercury to and from the gas pipette.

The flask E is filled with mercury up to the level of the lower side tube F and water from a thermostatically controlled water-bath is pumped rapidly through the upper part of the flask, returning to the bath by the upper side tube G . The lower part of the flask (below the mercury level) is well “lagged” by cementing a cork ring (12 mm. thick) on the bottom and moulding asbestos pulp around the outside of the flask up to the level of the side tube F . Such a construction makes it possible—given an efficient water circulating pump and constant temperature bath—to keep the whole absorption system at a temperature of $20 \pm 0.01^\circ \text{C}$, over long periods, provided that the temperature of the room does not fluctuate more than 2°C on either side of this temperature.

Care must be taken to provide a strong and stable mounting for the whole system.

The manipulation of the gas pipette. The pipette, the left-hand bore of the stopcock and the capillary tube connecting to the overflow vessel, are freed from air and filled with mercury by applying suction at the side tube of D ; the right-hand bore of the stopcock and the capillary tubes leading to the rest of the apparatus are next freed from air and filled with mercury by means of the “distributor” (see later, fig. 5), the stopcock being turned appropriately for these operations and then closed; the liquid absorbent (12–14 c.c.) is now introduced from D and followed by mercury until the mercury has passed through the bore of the stopcock which is then turned; the measured volume of gas is finally brought into the pipette from the “distributor” and followed by mercury

until the mercury reaches the bottom (x_1) of the capillary tube when the stopcock is closed.

After adjusting the height of the stirrer so that the top edge of the blades is just below the surface of the liquid absorbent (the bottom edge of the blades then being about 7 or 8 mm. above the level of the mercury in the pipette) the stirrer is put into action.

The above procedure makes it possible to bring the *whole* of a measured volume of gas for analysis into contact with the *whole* of the liquid absorbent to be used in a vessel where they are effectively protected from contact with the air and maintained at a constant temperature. The mercury-sealed stirrer, driven at a rate of 500–600 r.p.m., provides a very large and constantly renewed interface between the gas and the liquid absorbent so that equilibrium between the liquid and gaseous phases is reached in the least possible time.

The liquid absorbent can be completely saturated, before use, with the unabsorbable gases of the mixture, under exactly the same conditions of temperature and pressure as obtain in its use if attention is paid to one important point concerning the pressure. Assuming there are only insignificant barometric fluctuations during the course of an analysis, the gas pressure inside the pipette is determined by the volume of the gas enclosed and it is therefore essential that *the volume of residual gas left after the "saturation" of the liquid absorbent should be closely the same as the volume of the residual gas left after the removal of the absorbable gas in the actual analysis*; this ensures, since the temperature is kept constant throughout, that there is no change, during the course of the analysis, in the amount of the residual (unabsorbed) gas dissolved in the liquid absorbent. A simple method of carrying out this important operation—"saturating the liquid absorbent with the unabsorbed gases"—is to use a volume of the gas under examination approximately equal to that which is to be used, subsequently, for the actual analysis; when equilibrium has been reached in the gas pipette and the gas removed—through *D* or via the "distributor"—the liquid absorbent will be left saturated with the residual, unabsorbable gases under the exact conditions obtaining for its use in the subsequent analysis. The normal amount of liquid absorbent used (12–14 c.c.) is usually sufficient for several analyses and so this procedure has no serious effect on its absorptive capacity.

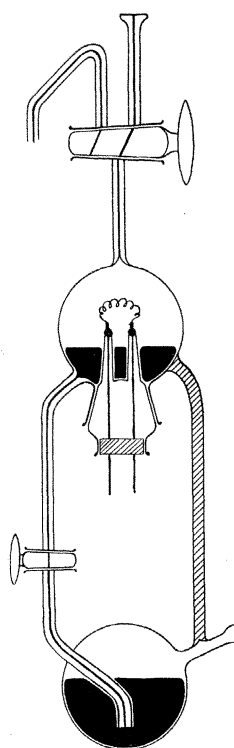
The explosion pipette (fig. 3). The combustion pipette (fig. 4)

The design and construction of these parts, M_1 and M_2 , of the removal system are clearly shown in the figures. In each pipette the (gas) chamber has a capacity of about 50 c.c. and the lower (mercury) reservoir a capacity of about 100 c.c. There is a stopcock between the upper and lower chambers so that the pressure on the gas contained in the upper chamber can be adjusted. The mercury is lowered by opening the stopcock and raised by the application of pressure (by means of rubber hand bellows) at the open side tubes on the lower (mercury) reservoirs.

The pipettes are connected by flange joints to the same point on the apparatus (see fig. 5) and so it is advisable that their over-all length should be the same.



M_1
FIG. 3



M_2
FIG. 4

3. THE MANIPULATORY SYSTEM

A diagram showing the complete gas-analysis apparatus is given in fig. 5. The measuring system is shown at the left of the diagram and the removal system towards the right; they are designated by the same letters as those used in figs. 1–3. The manipulatory system is shown as the connecting link between them.

A satisfactory manipulatory system must provide means (*a*) for collecting a gas sample for analysis, (*b*) for introducing it (in portions) into the measuring system, and (*c*) for transferring the gas to and from the removal and measuring systems as required. There must be no risk of loss or contamination during the performance of any of these operations and it is therefore necessary to ensure that no bubbles of gas are left behind in the bores of the stopcocks or on the sides of the connecting tubes. When gas is transferred from one part of the apparatus to another it is always

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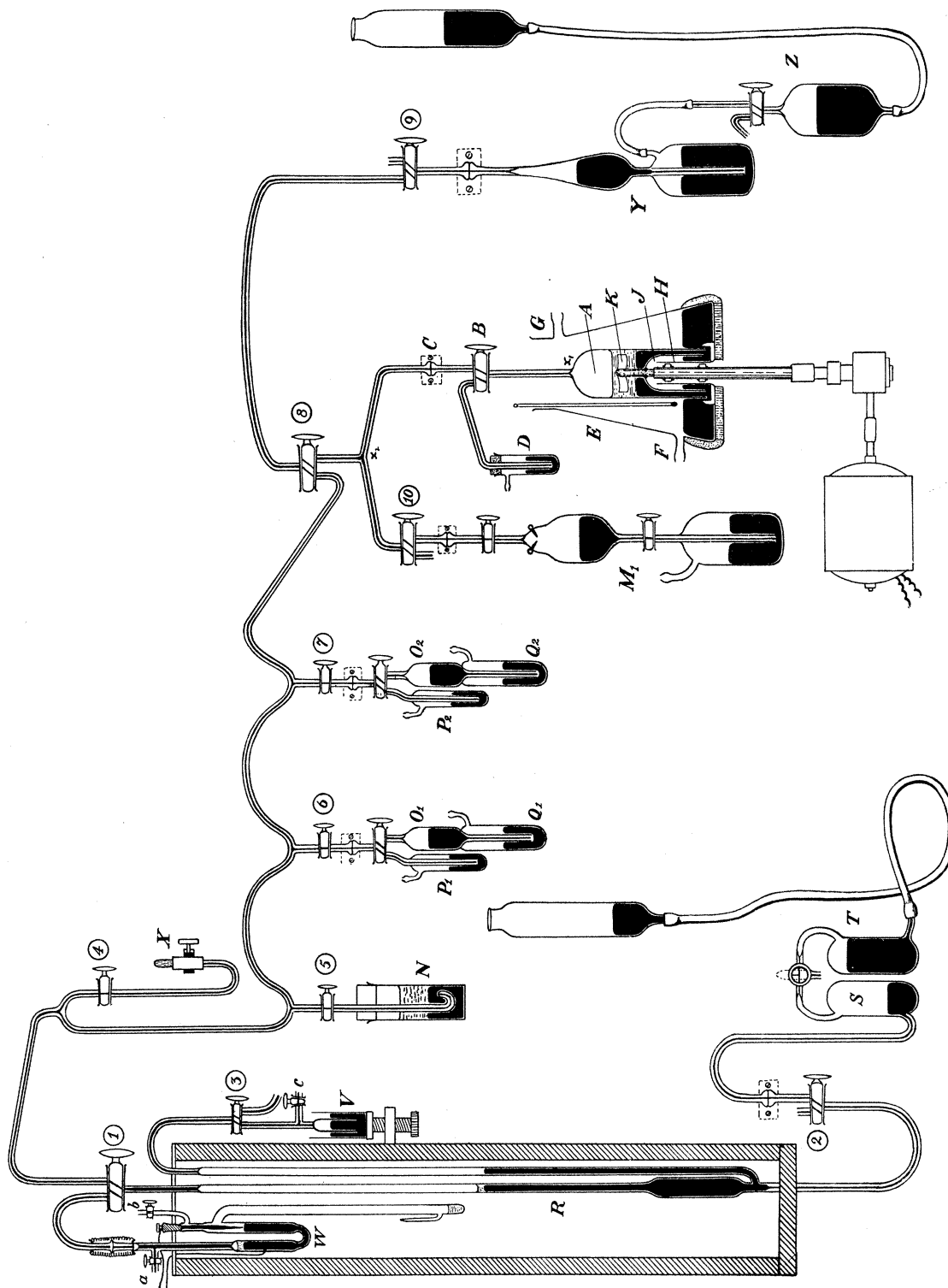


FIG. 5

“followed” by a liquid and the “sweeping” action of the liquid on the gas must be completely effective on all occasions; the use of capillary connecting tubes with a bore not greater than 1.2 mm. diameter and the avoidance of all horizontal parts in the manipulatory system are important aids to efficiency in carrying out such operations. These considerations explain the shape and “lay-out” of the manipulatory system shown in fig. 5. All junctions (except flange joints) are fused and it is important that the bore of the capillary tubing should show no marked alteration in diameter at the fused junctions.

The manipulatory “main” has attached to it:

- (1) Two gas collectors (and storage vessels) $O_1P_1Q_1$, $O_2P_2Q_2$.
- (2) The “distributor” Y with its pressure adjustor Z .
- (3) The device N which is used for the introduction of the small quantity of normal sulphuric acid required in the gas burette.

(1) *The gas collectors (and storage vessels)*

It is desirable to have two of these vessels; the design, construction and method of attachment to the manipulatory main are clearly shown in fig. 5.

There is a flange joint on the central limb of the three-way capillary stopcock; this is used to connect the gas collector to the manipulatory main or, alternately, to the source of supply from which the gas for analysis is to be collected.

The upper (gas) reservoir (O_1 or O_2) which is sealed to the second limb of the three-way stopcock, has a capacity of about 35 c.c. and a small auxiliary (mercury) reservoir (P_1 or P_2) is sealed to the third limb of the stopcock. The lower (mercury) reservoir (Q_1 or Q_2) has a capacity of about 50 c.c.; there is an open side tube on this reservoir and also on the small auxiliary mercury reservoir, so that pressure can be applied to either of these mercury reservoirs, as and when required, by attaching rubber hand-bellows to the side tube.

The lower (mercury) reservoir is filled with pure dry mercury and the small auxiliary (mercury) reservoir is about half-filled.

Collection of a sample of gas for analysis. Pressure is applied to the side tube of the lower (mercury) reservoir and, with the three-way stopcock turned appropriately, the air in the upper gas reservoir and the right-hand bore of the stopcock is removed, and replaced by mercury; the stopcock is then closed and the collector attached, by means of the flange joint, to the apparatus from which the sample of gas for analysis is to be withdrawn. The air in the capillary connecting tube between the collector and the source of supply is removed and replaced (by pure sample) by applying suction at the side tube of the auxiliary mercury reservoir. When the three-way stopcock is subsequently opened to the upper (gas) reservoir, the mercury falls into the lower (mercury) reservoir and allows the collection of an uncontaminated supply of gas for analysis in the gas reservoir and the right-hand bore of the three-way stopcock. The three-way

stopcock is then closed and the collector attached to the gas-analysis apparatus. The introduction of this gas (in portions) into the gas burette is described later.

(2) *The “distributor” Y*

This device, with its pressure adjustor *Z*, is shown at the extreme right of fig. 5; it might be described as the pivot of the manipulatory system.

It is a mercury-sealed gas collector and distributor located in the manipulatory main between the measuring system and the removal system and it is capable of being put into direct contact (by the appropriate turning of stopcocks) with

- (a) the gas burette *R*;
- (b) the fine-adjustment zero-setting device *X*;
- (c) the gas collectors $O_1P_1Q_1$ and $O_2P_2Q_2$;
- (d) the device for introducing normal sulphuric acid *N*;
- (e) the absorption pipette *A*;
- (f) the explosion (or combustion) pipette M_1 or M_2 ;
- (g) the atmosphere.

The design of the distributor is clearly shown at *Y* in the diagram. The upper (gas) reservoir has a capacity of 40–50 c.c. and the lower (mercury) reservoir a capacity of 60–80 c.c. The lower (mercury) reservoir has a side tube to connect it—by thick-walled rubber tubing—to its pressure adjustor *Z*. The pressure adjustor permits of the application of a wide range of positive and negative pressures to the mercury in the distributor.

The distributor is attached to the manipulatory main by means of a flange joint since it is necessary that it should be detachable, for cleaning purposes, from time to time.

Its functions and use are described later in the section on general manipulation of the apparatus.

(3) *The device for the introduction of 0.1 c.c. of normal sulphuric acid into the gas burette*

The device is shown at *N* in fig. 5. An open capillary tube (bent upwards at the lower end, as shown) dips into a cylindrical reservoir and is connected, through stopcock (5), with the manipulatory main. The reservoir contains normal sulphuric acid over mercury and it is supported on a platform which has two “rest” positions; in one position the open end of the capillary tube is covered by the sulphuric acid while, in the other position, it is immersed in the mercury. The use of the device is explained later.

In setting up the apparatus it is important that adjustable platforms should be provided to support the weight of the distributor, explosion (or combustion) pipette and gas collectors, and so remove the strain from the flange joints connecting them to the manipulatory main. In the case of the absorption pipette it is advisable to have a stable fixed platform for a support.

If the back of the capillary tubing constituting the manipulatory main is painted with white cellulose paint, the transference of gas from one part of the apparatus to another can be seen and followed very easily.

General manipulation of the apparatus. After the collection of the gas for analysis and the attachment of the gas collectors $O_1P_1Q_1$ and $O_2P_2Q_2$ to the apparatus, the following operations—in the order given—are necessary for carrying out a complete analysis:

(a) Air is removed (and replaced by mercury) from the gas burette, the removal system, the manipulatory main and all connecting tubes, by reducing the pressure in the distributor Y and drawing the air—“followed” by mercury—into it. The pressure on the distributor is now raised and the air, thus collected, is swept out by mercury through the limb of stopcock (9) which connects to the atmosphere.

Notes: (i) It is necessary to raise the pressure in the gas burette during this operation.

(ii) The air in the tubes connecting the gas collectors to the respiratory main is “followed” by mercury from the auxiliary mercury reservoirs P_1 and P_2 .

(b) Normal sulphuric acid (approximately 0.1 c.c.) is introduced into the measuring limb of the gas burette from N and “followed” by mercury. The operation is carried out by lowering the pressure in the gas burette and opening stopcocks (1) and (5) appropriately. The volume of sulphuric acid can be judged by the length of the capillary connecting tube filled by it.

(c) With the pressure in the gas burette still lowered, a sample of gas is drawn into the measuring limb from one of the gas collectors $O_1P_1Q_1$ or $O_2P_2Q_2$. After the approximate adjustment of the volume of gas in the burette (at atmospheric pressure) to 10 c.c. the gas remaining in the connecting tubes and manipulatory main is swept into the burette by mercury from the auxiliary mercury reservoir P_1 or P_2 ; this procedure allows successive samples to be taken from the gas collectors or storage vessels. The mercury having been adjusted at the zero mark of the burette, by the use of the fine-adjustment device X , the volume of the gas is read as described earlier.

Note. If the first sample of gas is to be used only for saturating the liquid absorbent used in the removal system, an approximate volume measurement only is required.

(d) The liquid absorbent is introduced into the gas pipette (and “followed” by mercury) as described earlier.

(e) The gas is next transferred from the gas burette R to the distributor Y ; it is “followed” by the sulphuric acid and mercury and it is important that the gas *only* and not the sulphuric acid should enter the distributor. The separation of the sulphuric acid from the gas is effected at stopcock (8) as follows: The pressure in the gas burette having been raised and that in the distributor lowered, stopcocks (1), (8) and (9) are opened so that the gas is slowly drawn into the distributor; when the sulphuric acid “following” the gas has reached a position just short of stopcock (8) the burette stopcock (1) is closed. Using the fine-adjustment zero-setting device X , the sulphuric

acid is pushed towards the distributor until the left-hand bore of stopcock (8) is just completely filled, after which the stopcock is turned.

(*f*) The pressure in the distributor is now raised and the gas transferred to the gas pipette; it is followed by mercury until the mercury has reached the point x_1 . The procedure described above enables the whole of the gas to be brought into contact with the liquid absorbent.

(*g*) The gas and liquid absorbent are then kept intimately mixed, as described earlier, for a period of 45 min. at constant temperature ($20 \pm 0.01^\circ \text{C}$) when equilibrium is usually attained. It is advisable, however, to check the completeness of a removal (or saturation) operation by repetition and the necessary accurate volume measurements.

(*h*) A period of 5 min. is allowed, after the gas pipette stirrer is stopped, to ensure the complete separation of the gas from the liquid absorbent. The gas is then transferred to the distributor and it is important that no liquid absorbent should enter the distributor. The complete separation of the gas from the liquid absorbent is effected at the Y-junction above the pipette stopcock *B*. The pressure in the distributor is lowered and the stopcocks *B*, (8) and (9) opened appropriately so that the gas is *very slowly* drawn into the distributor followed by the liquid absorbent. When the liquid absorbent has reached the point x_2 at the Y-junction, the pipette stopcock *B* is closed. The gas is then swept through stopcock (8) by means of mercury from the explosion (or combustion) pipette.

(*i*) Details for the transference of the gas from the distributor to the gas burette are unnecessary as also are details of the method of transferring gas to and from the explosion and combustion pipettes; when the latter are used one of the gas collectors is employed as a storage vessel for pure oxygen.

4. EXPERIMENTAL RESULTS

(i) *Determination of the oxygen content of gaseous mixtures*

The technique described above has been employed with marked success in determining the exact oxygen content of gaseous mixtures, the oxygen being removed by a liquid absorbent.

The liquid absorbent normally used is an alkaline solution of sodium hydrosulphite containing Fieser's catalyst (the sodium salt of anthraquinone β -sulphonic acid—"silver salt"). It is made up, as follows, immediately before introduction into the absorption pipette: 1.7 g. of sodium hydrosulphite are dissolved in 12.5 c.c. of a cold saturated aqueous solution of "silver salt"; 2.5 c.c. of caustic soda solution (containing 28% NaOH) are then added and the dark red solution filtered.

(a) *The oxygen content of air (freed from carbon dioxide)*

A sample of air was taken out of doors after being drawn slowly through soda-lime to remove the carbon dioxide.

Results of three separate analyses:

	Volume of air taken	Volume of residual gas after removal of oxygen	Oxygen content %
(1)	8.205	6.487	20.94
(2)	8.244	6.518	20.94
(3)	8.048	6.364	20.92

Volumes are given in c.c. throughout.

(b) *The oxygen + carbon dioxide content of air*

Two samples, A and B, of air were taken directly into the gas collectors out of doors.

Results of the analyses:

Sample A. Three separate analyses

Sample B. Two separate analyses

	Volume of air taken	Volume of residual gas after removal of oxygen and carbon dioxide	Content of oxygen + carbon dioxide %
A (1)	9.270	7.327	20.96
(2)	8.785	6.944	20.96
(3)	8.855	6.999	20.96
B (1)	6.922	5.469	20.99
(2)	7.696	6.082	20.97

The difference between the results of experiments (a) and (b) gives a value of 0.04% for the carbon dioxide content of the air. That a result so close to the accepted value is obtainable by the analysis of less than 10 c.c. of air is an indication of the degree of precision obtainable with the apparatus.

(c) *“Micro” analyses of air*

Three separate analyses of the oxygen + carbon dioxide content of air were carried out using less than 2 c.c. of air for each analysis. In these analyses a measured volume of residual gas (used in saturating the liquid absorbent with the unabsorbed constituents) was taken, and the small samples of air added, so that a manageable total volume of gas was available for use.

The results were as follows (all volumes in c.c.):

	Volume of residual gas taken	Total volume after addition of air sample	Volume of air sample	Total volume after removal of O ₂ + CO ₂	Volume (by difference) of residual gas from air sample	Oxygen + carbon dioxide content %
(1)	4.207	5.978	1.771	5.607	1.400	20.9
(2)	4.050	5.111	1.061	4.888	0.838	21.0
(3)	4.047	5.059	1.012	4.846	0.799	21.0

The apparatus has been employed chiefly for determining the exact composition of binary mixtures of pure gases used in the study of gas-solid equilibria, and all these mixtures contained approximately equal proportions of the two constituents. The gases used—all of the highest purity—were hydrogen, oxygen, nitrogen, argon and carbon

monoxide. Binary mixtures containing oxygen were analysed by the method given above, but a modification in the liquid absorbent was found necessary in analysing oxygen-carbon monoxide mixtures (*vide infra*).

Test analyses were first carried out on mixtures made from accurately determined volumes of the pure dry gases; these analyses served as a useful check on the purity of the gases used. In the subsequent analyses of the mixtures of unknown composition (withdrawn from the adsorption experiments) duplicate analyses were made and the close concordance between the results of the two independent analyses is an indication of the reliability of the technique.

(d) *The oxygen content of oxygen-hydrogen mixtures*

Test analysis: A mixture of the pure dry gases was made up containing 50.46% oxygen.

Results of three separate analyses of this mixture:

	Volume of mixture taken	Volume of residual gas after removal of oxygen	Oxygen content found %
(1)	13.873	6.873	50.46
(2)	14.133	7.004	50.44
(3)	13.475	6.675	50.46

Duplicate analyses of six different oxygen-hydrogen mixtures:

Mixture	1st analysis % oxygen	2nd analysis % oxygen
(1)	50.11	50.11
(2)	49.66	49.66
(3)	48.38	48.38
(4)	48.23	48.23
(5)	49.72	49.73
(6)	49.75	49.75

(e) *The oxygen content of oxygen-carbon monoxide mixtures*

The determination of the *exact* composition of mixtures of these two gases presented an unexpectedly difficult problem.

The normal method of determining the oxygen content—by the removal of this gas with alkaline hydrosulphite and the subsequent measurement of the “residual gas”—was found to be inaccurate owing to the fact that carbon monoxide combines slowly, even at ordinary temperatures and pressures, with caustic alkali solutions. Careful experiments made with simple aqueous (dilute) caustic soda solutions showed that carbon monoxide was absorbed at the rate of about 0.1 c.c./hr. under the conditions obtaining in the absorption pipette; qualitative tests on the product showed the presence of formate in the alkali solution.

The determination of the carbon monoxide content by burning this gas, with a measured excess of oxygen (in the combustion pipette), removing the carbon dioxide by absorption, and measuring the volume of oxygen unused, was found to be unreliable because of the impossibility of preventing traces of tap-grease from reaching the

platinum spiral. The determination of the carbon monoxide content—by removing it with a liquid absorbent—was not possible because absorbents for carbon monoxide also absorb oxygen.

Attempts were made to remove oxygen by acid solutions of (*a*) chromous salts, (*b*) vanadous salts, but these absorbents were useless owing to the fact that they decompose slowly with the evolution of hydrogen. Acid solutions of titanous chloride were found to be unsatisfactory because of their slowness in action.

A satisfactory liquid absorbent for oxygen was finally obtained by substituting trisodium phosphate (Na_3PO_4) for caustic soda in the normal oxygen absorbent. The absorbent is made in the way described above except that a saturated solution of Na_3PO_4 is used in place of the NaOH . This liquid absorbent is somewhat slower in its action than the normal oxygen absorbent, but it has no measurable effect on carbon monoxide and its use led to satisfactory results being obtained in the analysis of oxygen-carbon monoxide mixtures.

Test analysis: A mixture of the pure dry gases was made up containing 50·09% oxygen. Results of two separate analyses of the mixture:

	Volume of mixture taken	Volume of residue after removal of oxygen	Oxygen content found %
(1)	8·588	4·286	50·09
(2)	4·726	2·359	50·08

Duplicate analyses of six different oxygen-carbon monoxide mixtures:

Mixture	1st analysis % oxygen	2nd analysis % oxygen
(1)	50·76	50·76
(2)	50·42	50·40
(3)	50·44	50·44
(4)	50·19	50·19
(5)	50·08	50·08
(6)	49·74	49·74

(ii) *Determination of the hydrogen content of gaseous mixtures by explosion with a measured excess of oxygen and subsequent determination of the decrease in volume*

Mixtures containing approximately 50% of hydrogen with (*a*) argon, (*b*) nitrogen, were analysed. The amount of pure oxygen added, before explosion, was such that there was about 50 vol. of combustible gas ($2\text{H}_2 + \text{O}_2$) for 100 vol. of non-combustible gas; this is in accordance with Bunsen's recommendations and results.

The explosion was done under reduced pressure (about half an atmosphere) and the gas mixture was allowed to stand in the explosion pipette for half an hour before being exploded.

The hydrogen content was taken to be two-thirds of the decrease of volume produced by explosion.

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(a) *The hydrogen content of hydrogen-argon mixtures*

Test analyses: Two mixtures were made up from the pure dry gases.

Mixture A contained 50.29% hydrogen.

Mixture B contained 49.50% hydrogen.

Two analyses of each mixture were made:

	Volume of mixture taken	Volume of oxygen added	Volume of residual gas after explosion	Percentage of hydrogen found	Correct percentage of hydrogen
A (1)	10.127	12.325	14.816	50.27	50.29
(2)	9.980	12.671	15.128	50.25	50.29
B (1)	10.419	13.003	15.690	49.48	49.50
(2)	10.232	12.918	15.557	49.47	49.50

Duplicate analyses of six different hydrogen-argon mixtures:

Mixture	1st analysis % hydrogen	2nd analysis % hydrogen
(1)	50.76	50.72
(2)	51.15	51.11
(3)	51.97	52.02
(4)	51.88	51.84
(5)	50.80	50.84
(6)	47.09	47.07

(b) *The hydrogen content of hydrogen-nitrogen mixtures*

Test analysis: A mixture was made up from the pure dry gases and contained 49.53% hydrogen.

Two analyses of the mixture were made:

	Volume of mixture taken	Volume of oxygen added	Volume of residual gas after explosion	Percentage of hydrogen found	Correct percentage of hydrogen
(1)	10.345	12.572	15.233	49.52	49.53
(2)	10.186	12.232	14.857	49.49	49.53

Duplicate analyses of six different hydrogen-nitrogen mixtures:

Mixture	1st analysis % hydrogen	2nd analysis % hydrogen
(1)	51.42	51.42
(2)	52.09	52.12
(3)	51.54	51.57
(4)	50.32	50.32
(5)	49.89	49.94
(6)	50.58	50.59

The results obtained by the explosion technique do not show the high degree of accuracy and reproducibility obtained by the absorption technique and the results on mixtures of known composition all give a slightly low value for the hydrogen content.

(iii) *Determination of the carbon monoxide content of gaseous mixtures*

The accurate analysis of simple binary mixtures of carbon monoxide and oxygen can be carried out, as described above, by a method involving the removal of the

oxygen. In most cases, however, the determination of the exact carbon monoxide content of a gaseous mixture demands a technique for the *complete removal of the carbon monoxide*.

In ordinary gas-analysis methods carbon monoxide is removed by liquid absorbents such as ammoniacal cuprous chloride solution; the removal depends on the formation of rather unstable addition complexes, an equilibrium being set up between the complex in aqueous solution and the carbon monoxide in the gaseous phase. The reaction does not proceed to completion and our experience shows that absorption processes (all the known processes have been investigated) for the removal of carbon monoxide are not suitable for use in accurate gas analysis.

The only really effective method of removing carbon monoxide from the gaseous phase is to oxidize it to carbon dioxide and then absorb the latter.

Difficulties unexpectedly arise, however, in bringing the oxidation process to completion. Carbon monoxide cannot be *completely* oxidized by explosion with excess of oxygen. Scherb (1924 *Gas u. Wasserfash.* **67**, 391) states that carbon dioxide seems to retard the oxidation of carbon monoxide (by hot copper oxide) and that the reaction is only complete when the carbon dioxide is simultaneously absorbed by alkali. Careful experiments made on the oxidation of carbon monoxide (mixed with excess of pure oxygen) at the surface of a red-hot platinum spiral, have convinced us that *the reaction does not go to completion in one operation*; and increasing the time of "burning" has no appreciable effect on the amount of carbon monoxide left unoxidized.

The oxidation of the carbon monoxide to dioxide can, however, be made to go to completion by three successive "burning" operations with oxygen if the carbon dioxide is removed and the platinum spiral effectively "degassed" between the operations.

The manipulative procedure can best be explained by reference to an actual analysis of a carbon monoxide and nitrogen mixture of known composition.

The analysis is performed by "burning" a measured volume of the gas mixture with excess of pure oxygen (in the combustion pipette) at the surface of a red-hot platinum spiral, removing the carbon dioxide produced together with the excess oxygen by the alkaline hydrosulphite (in the absorption pipette) and measuring the volume of the residual nitrogen. The use of the combustion pipette in association with the absorption pipette and distributor needs no further explanation.

The liquid absorbent is, of course, saturated with the residual gas before use and the platinum spiral is thoroughly "degassed" by heating to a red heat *in vacuo* and, after cooling, the gas set free is removed through the open limb of the three-way stopcock at the top of the combustion pipette. The "degassing" operation must be repeated until no more gas is evolved.

After the "burning" operation is completed (this requires a maximum time of 5 min. with the platinum spiral at red heat) the gas is transferred, via the distributor, to the absorption pipette. The platinum spiral is then thoroughly "degassed", the gas removed

from it being added to that in the absorption pipette. In subsequent "burning" operations a further supply of pure oxygen must, of course, be added.

Details are given below to show how the oxidation of the carbon monoxide proceeds to completion. The results of two separate analyses are given of a mixture (made up from pure nitrogen and carbon monoxide) containing 51.92% nitrogen and 48.08% carbon monoxide.

Analysis 1

Volume of gas mixture taken 9.498 c.c.

	Residual volume of nitrogen c.c.	Carbon monoxide content %
(a) After 1st "burning"	4.967	47.71
(b) " 2nd "	4.940	47.99
(c) " 3rd "	4.931	48.08
(d) " 4th "	4.931	48.08

Analysis 2

Volume of gas mixture taken 8.748 c.c.

	Residual volume of nitrogen c.c.	Carbon monoxide content %
(a) After 1st "burning"	4.578	47.67
(b) " 2nd "	4.551	47.98
(c) " 3rd "	4.542	48.08
(d) " 4th "	4.541	48.09

Duplicate analyses of four different carbon monoxide and nitrogen mixtures:

Mixture	Ist analysis % carbon monoxide	2nd analysis % carbon monoxide
(1)	49.18	49.17
(2)	49.17	49.16
(3)	49.51	49.51
(4)	49.36	49.37

We have to thank Messrs H. S. Heaven and C. R. Oswin for valuable help in carrying out this work. Grateful acknowledgement is also made of a grant towards the cost of the work by Messrs Imperial Chemical Industries, Ltd.

SUMMARY

An apparatus is described for the accurate analysis of small volumes of gas mixtures.

It has been found possible to obtain results accurate to $\pm 0.02\%$ for the determination of the percentage content of one constituent of a gaseous mixture using about 10 c.c. of gas. The apparatus is also suitable for "micro-analyses" of gaseous mixtures using 1–2 c.c. of gas mixture and results accurate to $\pm 0.1\%$ are obtainable.

Difficulties associated with the accurate determination of carbon monoxide in gaseous mixtures are discussed and methods for overcoming them are described.