

# VIII. *The Combining Volumes of Hydrogen and Oxygen.*

*By F. P. BURT, D.Sc., and E. C. EDGAR, D.Sc.,  
Senior Lecturers in Chemistry in the University of Manchester.*

*Communicated by Prof. H. B. DIXON, F.R.S.*

Received December 2, 1915,—Read February 24, 1916.

THE measurement of the combining weights of hydrogen and oxygen has been the subject of so many researches of a high order of excellence that any fresh investigation of this fundamental constant must be submitted with considerable diffidence. Nevertheless, it must be noted that the results obtained by various observers differ appreciably. According to CLARKE<sup>(1)</sup>, the values obtained by MORLEY and NOYES, by reason of the accuracy of their methods and the close concordance of the individual determinations, outweigh the results of all other investigators. The atomic weight of oxygen being 16, that of hydrogen, according to MORLEY<sup>(2)</sup>, is 1.00762, and according to NOYES<sup>(3)</sup>, 1.00787. (CLARKE, on NOYES' data, prefers the value 1.00783.) It is, further, a significant fact that the arithmetic mean of all determinations discussed by CLARKE, lies between these two values, which differ by 1 part in 4000. Both values are based on the gravimetric synthesis of water and are independent of a knowledge of the densities of the gases.

A physico-chemical method of determining the relative molecular weights depends on the knowledge of the ratio of the densities, together with that of the combining volumes.

The present uncertainty in the values of these two constants is probably greater in the case of the combining volumes. The classical researches of MORLEY have established the densities of hydrogen and oxygen within very narrow limits, and, according to CLARKE, writing in 1910, MORLEY's value for the ratio is to be preferred to any other. There are now, however, good reasons for believing the density of oxygen to be slightly greater than MORLEY's value, perhaps by 1 part in 28,000, though no subsequent work has advanced a more probable alternative to his value for hydrogen. Comparatively few investigations on the combining volumes have been made; of these, the two most important are due to SCOTT and MORLEY respectively. The historic researches of SCOTT<sup>(4)</sup> led to a value of 2.00245—this value being increased by him to 2.00285, when the necessary corrections (in calculating from room temperature to 0° C.) were made for the difference in the temperature coefficients of

the two gases. MORLEY<sup>(5)</sup>, by a less direct method, arrived at the value 2.00269. (CLARKE, on MORLEY'S data, gives 2.00274.) A few experiments by LEDUC<sup>(6)</sup> yielded a considerably higher figure, 2.0037, and later, 2.0034, whilst RAYLEIGH<sup>(7)</sup>, from compressibility measurements, obtained the slightly lower value 2.0026.

The agreement between the values of SCOTT and MORLEY is exceedingly close, but in view of the uncertainty of some necessary corrections in MORLEY'S work, there is some excuse for a further series of determinations in which the gases, before combination, are measured at 0° C. and 760 mm. pressure, that is to say, under the conditions of the density determinations. By adopting this procedure any errors due to uncertainty in the temperature and pressure coefficients are eliminated. This is the object of the present research.

The experience of previous workers shows that the chief difficulty presented by the problem is the preparation of the two gases in a state of purity. To ensure the absence of traces of foreign gases, in particular chemically inert gases such as nitrogen or paraffin hydro-carbons which cannot readily be removed by chemical re-agents, the most stringent precautions must be taken. In selecting a method for preparing a gas it is less important to secure a high initial state of purity than to avoid the introduction of substances that are afterwards difficult to separate; the presence of a trace of nitrogen may be much more troublesome than a considerable quantity of carbon dioxide. Treatment of gases by strongly heated solids is often unsatisfactory, because, although a particular impurity may be eliminated, some other impurity may be acquired.

In this investigation we have relied on physical rather than chemical methods for the ultimate purification of the gases. The case of hydrogen is peculiar in that it cannot conveniently be liquefied, but advantage may be taken of this very fact to separate impurities that are more readily condensible.

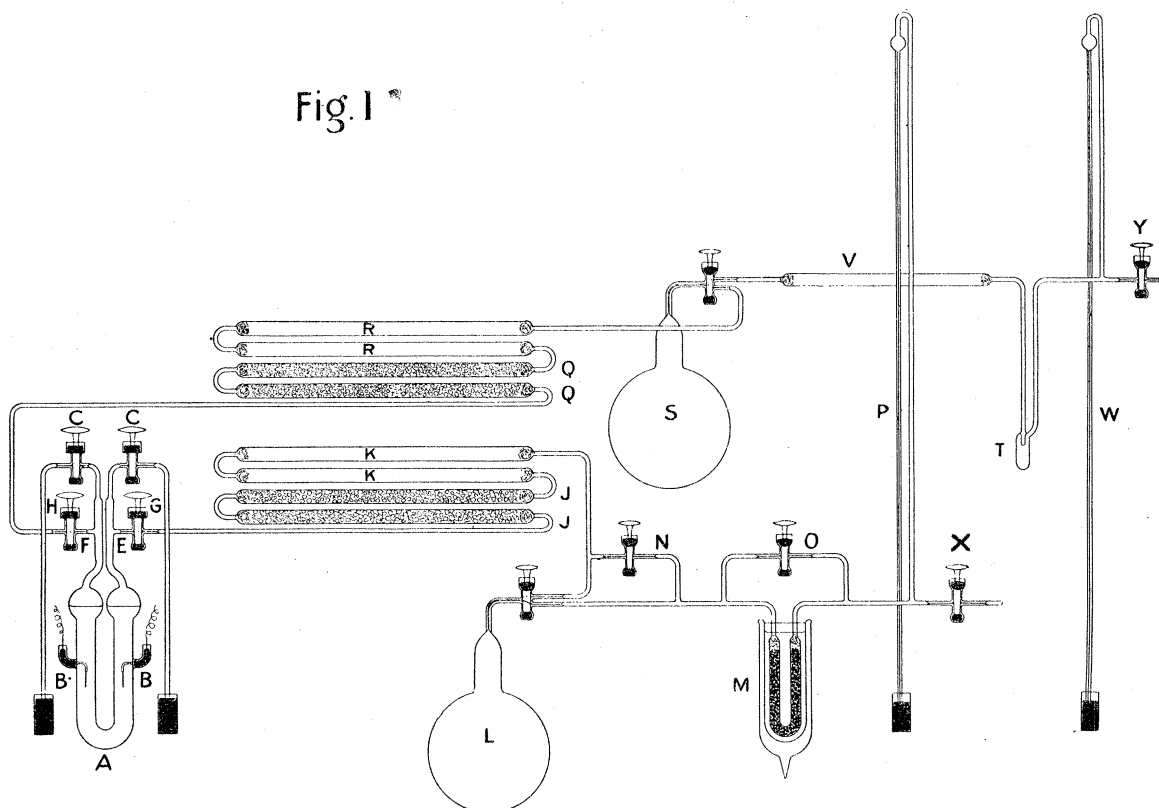
We began this investigation in July, 1911, and completed the experimental work in July, 1915. The apparatus was set up in an underground cellar below the Schunck Laboratory, and this room was reserved exclusively for our use.

### *Preparation of Hydrogen.*

The work of H. B. BAKER has shown that very pure gas is obtained by the electrolysis of an aqueous solution of barium hydroxide, and this is the method we have adopted throughout for generating hydrogen. The electrolysis was carried out in a U-tube constructed of boro-silicate glass (fig. 1, A), fitted with electrodes of stout platinum foil, about 27 mm. square. The platinum wire seals at B and B were mercury cupped. The two limbs of the U-tube were sealed to the soda glass connecting tubes by means of a glass of intermediate composition. The extension of each limb was bent over to form a short manometer which dipped into mercury; these manometers could be closed by the taps, C, C. T-pieces at E and F conducted the

gases through the taps, G and H, to the drying trains. Before one of the manometers was sealed on, a hot saturated solution of Kahlbaum's barium hydroxide, which had been four times re-crystallised by us, was filtered through glass wool into the U-tube; the manometer was immediately sealed on, and electrolysis started, and then the vessel was exhausted by a water pump until the solution boiled. Finally, both hydrogen and oxygen were allowed to run to waste through the gauges for a considerable time, so as to complete the elimination of air. A large proportion of the hydroxide crystallised out on cooling, and partially dissolved again when the temperature rose owing to passage of the current. No partition or diaphragm was

Fig. 1



employed in the U-tube, as the subsequent treatment of both hydrogen and oxygen was designed to remove traces of the other gas. A current of about 1.5 amperes was used for electrolysis, and the solution was not allowed to get very hot.

*Purification of Hydrogen: First Method.*

The hydrogen from the electrolysis vessel, after passing through two drying tubes filled with calcium chloride, J, J, and two filled with Merck's phosphoric oxide, K, K, entered the 2½-litre storage bulb, L, which was fitted with a 3-way tap. This bulb, after exhaustion by a water pump and a mercury pump, had had the last traces of air

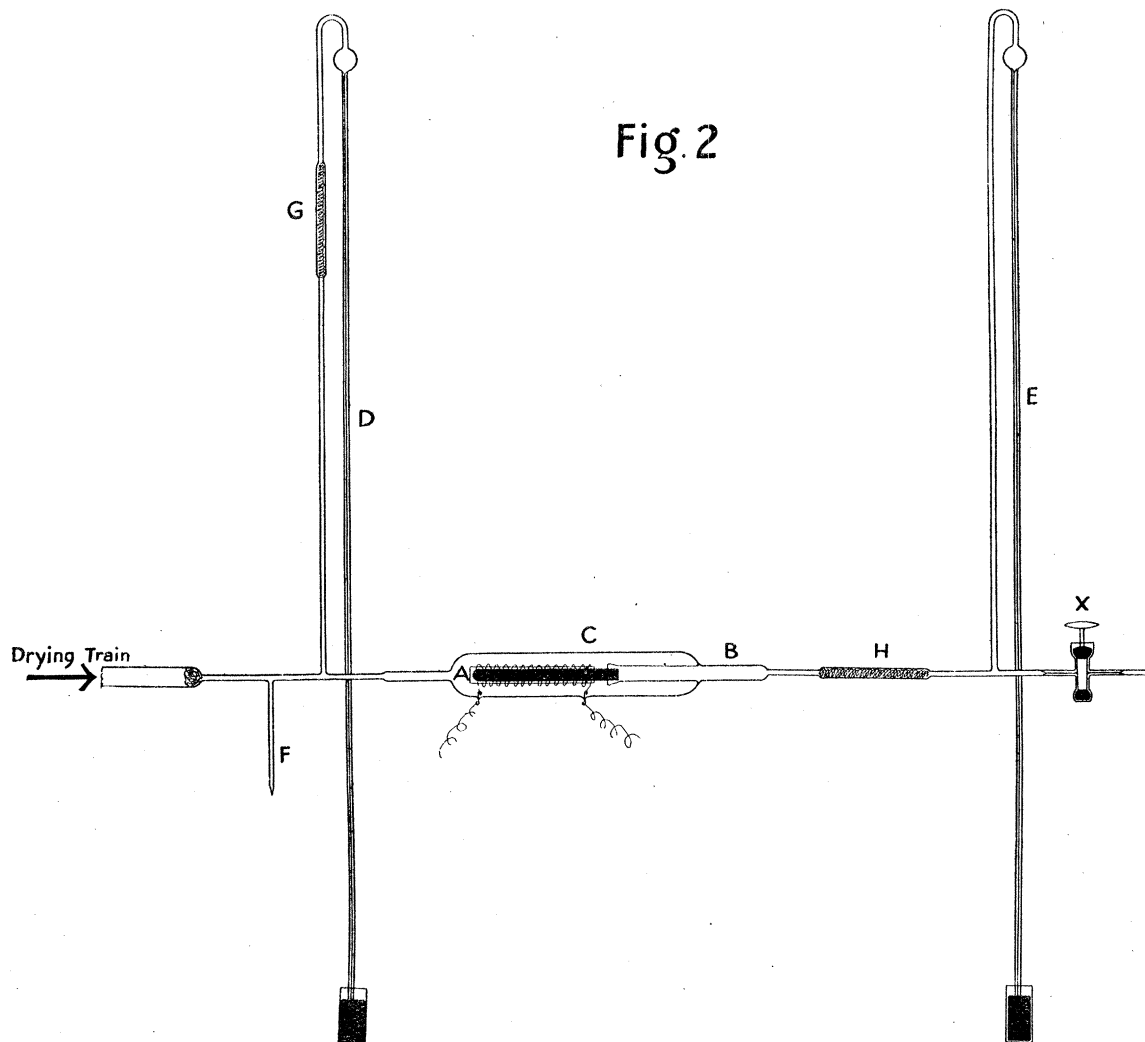
removed by four hours' exposure to charcoal cooled in liquid air. The storage bulb was connected to the U-tube, M, containing charcoal. This tube had been prepared in the following way: 11.5 gr. of charcoal, made from cocoa-nut shell, were introduced into the tube in fragments the size of a pea. The tube was exhausted by a water pump, and then heated in a glycerine bath to a temperature of  $240^{\circ}\text{C}$ . Dry hydrogen was next admitted and then pumped out again, and this operation was repeated several times. Finally, the tube was exhausted at  $240^{\circ}\text{C}$ . and sealed off. When cold, dry air was admitted, and the tube was immediately sealed to its connections on the apparatus. The observations of DEWAR<sup>(8)</sup> and, more recently, of CLAUDE<sup>(9)</sup>, indicate that, in the absence of helium and neon, exposure of hydrogen to charcoal at liquid air temperatures should prove a very efficient method of removing other gases. Hydrogen itself is absorbed to a considerable extent. According to the measurements of CLAUDE, 100 gr. of charcoal, cooled to  $-195^{\circ}.5\text{C}$ ., can take up about 20 c.c. of hydrogen before the pressure reaches a tenth of a millimeter of mercury. Five litres of nitrogen are required to produce a similar pressure, whilst oxygen is still more readily absorbed. When cooled in liquid air and put in connection with the  $2\frac{1}{2}$ -litre storage bulb, containing hydrogen at atmospheric pressure, the 11.5 gr. of charcoal in our U-tube reduced the pressure to about half an atmosphere. By closing the storage-bulb tap and admitting hydrogen from the electrolysis vessel and drying train through the cross-tube, N, the charcoal vessel was rapidly filled to atmospheric pressure. Electrolysis was then continued until sufficient hydrogen had been passed over the cooled charcoal to charge the measuring vessel. The liquid air vessel was then removed and part of the gas from the charcoal was allowed to return to the storage bulb. The later fractions were removed by the mercury pump, the train being exhausted at the same time. In this way impurities which had been retained by the charcoal were prevented from accumulating in the system. A cross-piece, O, carrying a tap connected the two limbs of the U-tube so that the train could be pumped out by another path in addition to that through the charcoal. A mercury gauge, P, recorded the pressure of gas in the system.

*Purification of Hydrogen: Second Method.*

The gas was dried, as before, over calcium chloride and phosphoric oxide, but, in some series of determinations, passed first through a tube containing palladium black to remove oxygen. After leaving the drying train the hydrogen was made to pass through the walls of a heated palladium tube (fig. 2, A). This tube, 10 cm. long, 1 cm. in external diameter, and having a wall thickness of about 0.6 mm., was welded to 3 cm. of platinum tube of similar dimensions. The platinum was sealed to a glass tube, B, which, in its turn, was fused as an inserted join into a wider tube, C, connected at its other end with the drying train. The wide tube thus formed a cul-de-sac into which the blind end of the palladium tube projected backwards. A short cylinder of quartz was slipped over the palladium tube and wound with a spiral of platinum wire, the

terminals of which made contact with stout platinum hooks sealed through the glass of the outer tube. By passing a current through the wire the palladium could be heated to any desired temperature.

The junction between the thick platinum tube and the glass was an excellent piece of workmanship carried out by Baumbach, the University glass-blower; it was quite free from air-bubbles and absolutely gas-tight. For a year and a half it has been constantly heated and cooled, and no sign of a crack has ever appeared.



The three palladium tubes used in this work were obtained from Messrs. Johnson and Matthey. The first tube was made from forged sponge; the second and third from fused metal. The third tube (the one figured in the diagram) contained 0.5 per cent. platinum and a trace of rhodium which were deliberately left in with the idea of increasing its mechanical rigidity. The weight of palladium in the second and third tubes was about 26 gr., but the third tube, the dimensions of which have already been stated, was made about twice the length and half the wall-thickness of the

second. The tube prepared from forged sponge showed a marked tendency to become crystalline and develop cracks, and for this reason was soon discarded. We have to express our indebtedness to Messrs. Johnson and Matthey for the great trouble they took in preparing tubes that would satisfy our requirements.

Before admitting hydrogen it was necessary to make certain that both the palladium itself and the glass-platinum junction were perfectly gas-tight. The palladium tube was evacuated by means of the mercury pump while the drying train was left full of air at atmospheric pressure, and the apparatus was allowed to stand overnight. In the morning the mercury gauges at D and E indicated no alteration in pressure on the two sides of the system, nor could any gas be obtained from the pump. After the palladium tube had been strongly heated, the vacuum still held. The drying train was now exhausted at the T-piece, F, and the palladium heated to a much higher temperature than was ever afterwards reached in the actual determinations. The train was then washed out with hydrogen, and this operation was repeated till all air was removed, when the T-piece, F, was sealed off.

Sometimes difficulty was experienced in "activating" the palladium. This could be effected by heating *in vacuo*, by heating in hydrogen, or, perhaps most surely, by heating in air. Once activated, the palladium remained in this condition throughout our experiments. The superficial film of oxide formed by heating in air disappeared when hydrogen was admitted. All the tubes used by us were permeable to hydrogen even in the cold, but the rate of passage of the gas was exceedingly slow. No movement of mercury in the gauges could be detected by eye, and equilibrium was only established after ten or twelve hours when the initial difference of pressure on the two sides of the system was as great as half an atmosphere.

In order to obtain hydrogen in the requisite quantities, the following procedure was adopted:—Electrolysis was continued until the pressure of hydrogen in the palladium was nearly atmospheric; if the palladium was heated at once, almost all the gas was evolved from the surface at which it had entered; if twenty-four hours were allowed to elapse before heating, hydrogen was evolved freely at both sides of the system. By keeping the metal at a temperature of  $100^{\circ}$  C. during charging, the process of diffusion was greatly accelerated. The required quantity of gas was obtained by heating to a temperature of  $180^{\circ}$  C.; after the expulsion of about 300 c.c., the metal was at once recharged at a lower temperature.

When the palladium was allowed to cool, the mercury in the gauge, E, rose rapidly to atmospheric height, and then fell very slowly till its level was the same as in the gauge, D. The life of the tube was certainly prolonged by keeping the palladium fully charged with hydrogen, and by using only a gentle heat to expel the gas. In order to obviate waste of gas through the gauge, D, a  $2\frac{1}{2}$ -litre storage bulb was attached to the train immediately after the electrolysis vessel. The palladium was protected from the action of mercury vapour by plugs of fine gold wire at G and H.

The last palladium tube used in this work was set up in January, 1914. During the following seventeen months, 20 to 30 litres of hydrogen passed through it. On June 1st, 1915, it was deprived of hydrogen as completely as possible by heating and pumping off the gas. Air was then admitted to the drying train by the T-piece, F, and the apparatus was left over a week-end. When examined again not a trace of gas could be found in the pump. The air in the train was next replaced by nitrogen and the palladium was heated for five and a half hours continuously by the maximum current used in the actual determinations, with the same negative result. Finally, after the apparatus had remained for six weeks with nitrogen at atmospheric pressure outside the tube, the interior was still vacuum.

*Preparation and Purification of Oxygen: First Method.*

Oxygen was first prepared by electrolysis of barium hydroxide solution in the U-tube already described. The gas, after being dried over calcium chloride (fig. 1, Q, Q), and phosphoric oxide, R, R, entered the 2½-litre storage bulb, S, till this was filled to atmospheric pressure. The storage bulb had been previously exhausted in the same manner as the hydrogen bulb. On immersing the small fractionating tube, T, in freshly made liquid air, more than a litre of oxygen could be withdrawn from the storage bulb over the phosphoric oxide in the tube, V, and condensed as a liquid. If desired, the storage bulb could then be re-charged by continuing the electrolysis, and a further quantity of gas could be condensed in T. About one-third of the liquid oxygen was allowed to escape into the air through the gauge, W, so as to eliminate traces of hydrogen or other low-boiling impurities. The next fraction was taken for the determination. A portion of the residue was returned to the storage bulb and the last fractions were boiled away into the air. The gas finally remaining in the apparatus was removed by the pump.

*Second Method.*

Oxygen as prepared above might possibly contain traces of hydrogen, though the solubility of this gas in boiling oxygen is certainly very small.

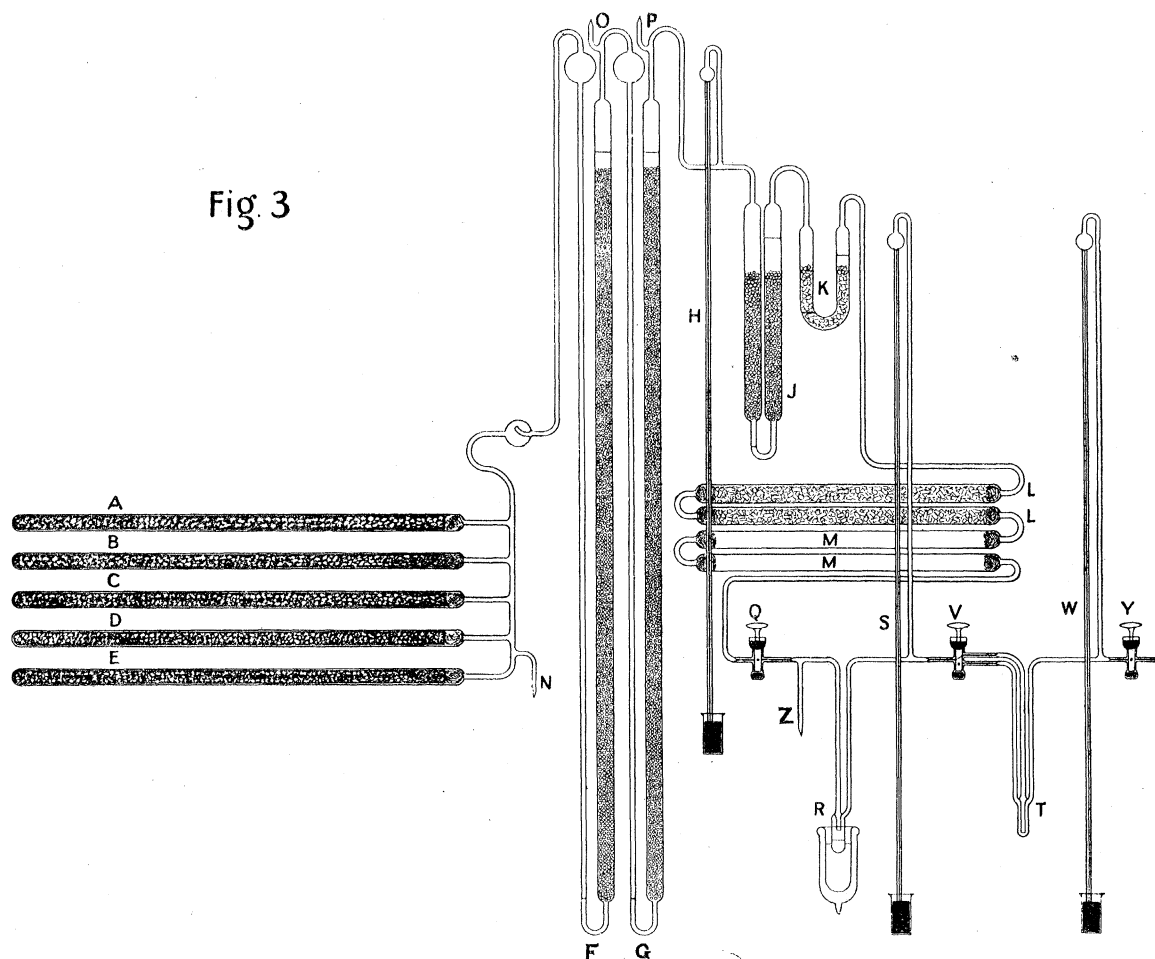
It was deemed advisable, therefore, to make oxygen by some other method which could not conceivably yield hydrogen as an impurity. Gas generated by heating potassium permanganate should fulfil this condition, and was consequently employed to check the results obtained with electrolytic oxygen.

Each of the four tubes, A, B, C, D (fig. 3), was charged with 250 gr. of finely powdered crystals of "pure" potassium permanganate in a dust-free atmosphere. The permanganate in the fifth tube, E, was three times re-crystallised from boiling water. The final crystallisation and subsequent drying were carried out in the decomposition tube itself. We may mention here that there was no difference in the results

whether oxygen was made by heating this tube or one of the other four. The mouths of the five tubes were plugged with carefully cleaned glass wool.

From the generating tubes the oxygen passed through a series of three washing towers filled with glass beads.

The first tower, F, contained a moderately strong solution of caustic potash; the second, G, a saturated solution of barium hydroxide. The column of liquid in each tower was over a metre in height. Between the barium hydroxide tower and the next washing vessel a manometer, H, was attached to the train. The short tower, J,



contained a stronger solution of potash, and the U-tube, K, a very concentrated potash solution on pumice that had previously been heated in a stream of oxygen. From the U-tube, K, the gas passed through two tubes, L, L, containing sticks of caustic potash, and finally through two tubes, M, M, containing phosphoric oxide.

The object of the two large alkaline towers was to retain oxides of manganese and carbon dioxide. The two tubes, J and K, containing potash of increasing concentration, served to diminish distillation of water from the towers to the stick potash tubes. After the apparatus had been in use for more than two years there was no sign of deliquescence either in the solid potash or in the phosphoric oxide.



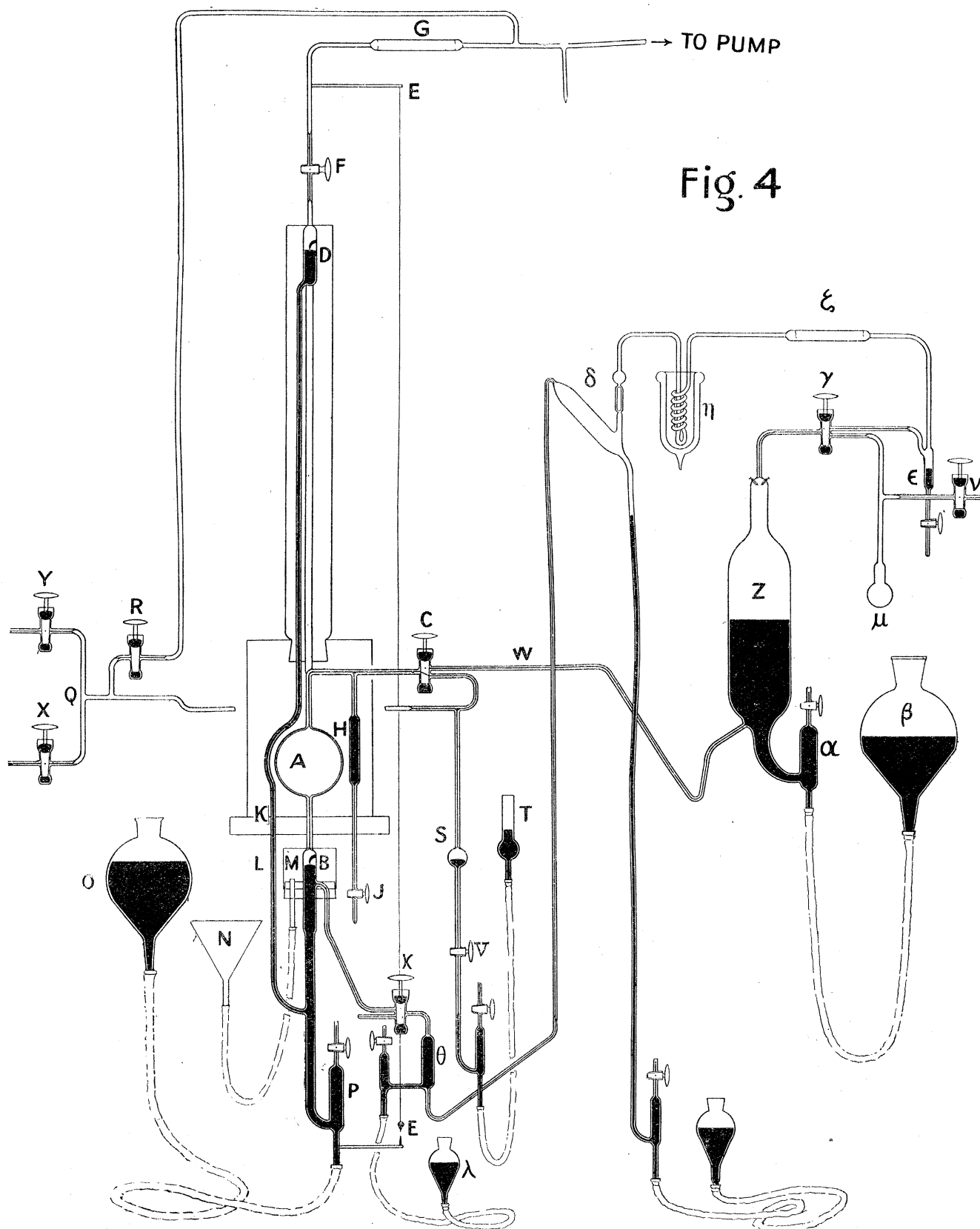
When the washing and drying train had been set up it was exhausted by a water pump from three T-pieces simultaneously at N, O and P. Each of the permanganate tubes was then heated in turn, the train being exhausted between each oxygen filling. When all air had been removed the T-pieces were sealed off. After leaving the drying train the gas passed through the tap, Q, to the fractionating tube, R, where it was liquefied. When a sufficient quantity of liquid had been condensed the tap, Q, was closed, and a portion of the liquid was allowed to boil off and escape through the gauge, S. The second fractionating tube, T, which had been previously exhausted, was now cooled in liquid air, and the 3-way tap, V, was opened. On lowering the liquid air vessel from R a small quantity of liquid oxygen soon condensed in T. The 3-way tap was then turned so that the gas bubbled through its liquid. The object of this was to prevent superheating so that any higher-boiling impurities would be more effectively retained. A quantity of gas, washed by its own liquid, was allowed to escape by the gauge, W, or was removed by the pump. The next fraction, bubbled in the same way through its own liquid, was taken for the determination, and the residue in both fractionating tubes was rejected.

*The Measuring Apparatus.*

It may be taken as established by earlier workers that the ratio of the combining volumes is slightly greater than 2 when the gases are measured at normal temperature and pressure. Our procedure, in brief, has been to explode one volume of oxygen with rather more than two volumes of hydrogen, the variable and carefully measured excess over two volumes being sufficient in quantity to ensure a residue of hydrogen being left after synthesis. The gases were measured consecutively in the same apparatus. By working with hydrogen in excess, the possibility of the formation of such substances as ozone, hydrogen peroxide, or oxide of mercury, should be diminished or eliminated.

The final operation was to estimate the hydrogen residue, when the combining volumes could be calculated.

For measuring the gases at 0° C., and 760 mm. pressure, the method was the same as that used by GRAY and BURT<sup>(10)</sup> for the volumetric analysis of hydrogen chloride. In fact, some parts of the original apparatus were kindly lent to us by Dr. GRAY. The measuring pipette (fig. 4) consisted of a thick-walled glass bulb, A, of about 300 c.c. capacity, sealed to capillary tubes at either end of its vertical diameter. The lower capillary expanded into the dead-space, B, which was furnished with a glass point. The upper capillary, after a right-angle turn, led to the 3-way tap, C. The pressure of gas in the bulb was registered by the vertical distance between the mercury surface in the dead-space and the mercury surface in the upper chamber, D, of the manometer, which communicated with the dead-space as shown in the figure. The upper chamber of the manometer, of the same diameter as the dead-space



(1.6 cm.), was also provided with a glass point. The vertical distance between the glass points was very nearly 760 mm., and this distance was maintained constant by means of a stout glass rod sealed at its upper end to the manometer chamber and at its lower to the elbow of the capillary connecting the bulb and the 3-way tap. The whole apparatus was rigidly fixed to a heavy iron bar with a tripod base, and the top of the bar was clamped to a staple driven into the ceiling. Any displacement from the vertical could be detected by the plumb-line, E, E, and corrected by means of levelling screws in the tripod base. The manometer head communicated with a mercury pump through the tap F, and the phosphoric oxide tube, G, so that the vacuum could be verified from time to time. Sealed to the capillary between the bulb and the 3-way tap was a capillary T-piece expanding into a tube of a few cubic centimetres capacity, H, which terminated at its lower end in another capillary, furnished with a tap, J. This tube, which was normally filled with mercury to the top, may be conveniently referred to as the volume-adjuster, since the capacity of the pipette could be increased to a small extent by withdrawing mercury from the tap, J.

The bulb, the volume-adjuster, and a portion of the manometer tube were enclosed in a tinned-iron bath with a stout brass base. The upper portion of the manometer was also enclosed in a bath constructed of a wide glass tube closed at the bottom by a rubber cork through which the glass rod and manometer tube passed. The lower bath somewhat overlapped the upper, so that by filling both baths with melting ice the whole system could be cooled to  $0^{\circ}\text{C}.$ , with the exception of the dead-space and a piece of the capillary above it and the short column of mercury in the manometer from K to L.

On account of the difficulty of seeing the point it was impracticable to surround the dead-space with ice. The small bath, M, was therefore filled with cooled brine by means of the funnel, N. It was found quite easy to secure a temperature within  $0^{\circ}.5\text{ C}.$  of zero when the final setting was made. Because of the small volume of the dead-space, (almost exactly 1 c.c.) a variation of this order did not affect the results. The mercury required for displacing gas from the bulb was contained in the reservoir, O. An air-catch, P, protected the pipette from any air leak at the rubber junction.

#### *Calibration of the Pipette.*

The volume of the bulb, dead-space, and connecting capillaries, from the tap, C, to the level of the glass point in the dead-space, was calibrated by means of mercury after the apparatus had been set up, but before the side tube leading to the manometer had been sealed on. For this purpose a stop-cock on capillary tubing was temporarily fused to the glass tubing below the dead-space.

The dead-space was calibrated separately. Mercury was introduced through the stop-cock until the meniscus was set to the point, the dead-space and tubing below it

being immersed in a water-bath so that the temperature of the mercury could be recorded satisfactorily. This mercury was run out and weighed. A mark was next made on the capillary just above the dead-space; mercury was introduced again to the level of the mark, and this quantity was run out and weighed.

| Weight of mercury from dead-space<br>point to end of stop-cock.  | Temperature.                 | Volume.                            |
|--|------------------------------|------------------------------------|
| gr.<br>(1) 192·14<br>(2) 192·17<br>(3) 192·20                    | ° C.<br>21·5<br>20·5<br>20·0 | c.c.<br>14·188<br>14·188<br>14·189 |
|  | Mean . . .                   | 14·188                             |
| Weight of mercury from mark on<br>capillary to end of stop-cock. |                              |                                    |
| gr.<br>(1) 205·76<br>(2) 205·84<br>(3) 205·90                    | 21·5<br>19·0<br>18·0         | 15·194<br>15·193<br>15·195         |
|  | Mean . . .                   | 15·194                             |
| Therefore volume of dead-space = 15·194 - 14·188 = 1·006 c.c.    |                              |                                    |

The pipette was now filled with mercury up to, but not including, the bore of the tap, C, and cooled to 0° C. with melting ice. Mercury was then run out from the tap to the mark on the capillary, care being taken that the initial and final temperatures of the warm mercury in the dead-space and tubing below it were the same.

| Weight of mercury from 3-way tap<br>to mark on capillary. | Temperature.   | Volume.                    |
|---|----------------|----------------------------|
| gr.<br>(1) 4160·03<br>(2) 4160·09                         | ° C.<br>0<br>0 | c.c.<br>305·986<br>305·990 |
|   | Mean . . .     | 305·988                    |
| Total volume of pipette = 305·988 + 1·006 = 306·994 c.c.  |                |                            |

This value was checked by running out mercury in a single operation from the 3-way tap to the dead-space point.

| Weight of mercury from 3-way tap<br>to dead-space point. | Temperature.                          | Volume.         |
|--|---------------------------------------|-----------------|
| gr.<br>4173·36   | ° C.<br>0 in bulb<br>21 in dead-space | c.c.<br>306·996 |
|  | Mean total volume                     | 306·995         |

For our purpose it was unnecessary to determine the volume of the pipette with very great exactness. Let the volume be represented by  $x$ , and let  $2x+y$  be the volume of hydrogen that unites with  $x$  of oxygen. Then the ratio of the combining volumes is  $\frac{2x+y}{x}$ , where  $x$  is more than three hundred times as great as  $y$ . A change of 0·5 c.c. in the value of  $x$  alters the ratio by only 1 part in 400,000.

No sensible error is introduced, therefore, by calling the volume of the pipette 307 c.c. in round numbers. Again, there was no need to reduce the mercury weighings to the vacuum standard, since the small volume increments (represented by  $y$ ) were also estimated by running out mercury which was counterpoised by the same set of weights. These weights were carefully compared with each other, but the deviations from their face values were far too small to involve a significant correction.

#### *Introduction and Measurement of the Gas.*

The exit tubes from the hydrogen and oxygen trains united beyond the taps, X and Y, at the T-piece, Q. The common channel then divided again, one branch leading to the mercury pump through the tap, R, and the other to the measuring bulb. After the large bath had been filled with powdered ice, gas was allowed to enter the pipette, displacing mercury into the reservoir, O, until the mercury surfaces in the dead-space and manometer chamber were approximately set to the two points. The tap, X or Y, as the case might be, was then closed. The ice in the large bath was pressed down and replenished, and the upper bath was also charged with ice. Finally, both baths were filled with ice-cold water, and the dead-space was cooled with brine. The fine adjustment was now made by means of the pressure-adjuster, S. By holding the small reservoir, T, at a suitable height and rapidly turning the tap, V, minute quantities of gas could be introduced into or withdrawn from the pipette. By the alternate manipulation of the pressure-adjuster and of the screws controlling a wooden clip which compressed the rubber tubing connecting the reservoir to the pipette, the

mercury meniscuses were set to their respective points. The tap, C, was then closed.

In this manner a definite volume of gas at a temperature of 0° C. and a pressure of 760 mm. could be obtained repeatedly.

### *Transference and Synthesis.*

By raising the reservoir, O, and opening the tap, C, the gas in the pipette was made to pass through the capillary tube, W, into the explosion vessel, Z, which was filled with mercury. The end of the capillary inlet tube was fused as an inserted joint through the base of the explosion vessel, and as the gas bubbled in, the mercury was displaced through the air-trap,  $\alpha$ , to the reservoir,  $\beta$ . The explosion vessel, about a litre in capacity, consisted of a wide glass cylinder, 22 cm. long and 8 cm. in diameter, drawn out at its upper end to a narrow neck, 6 cm. long and 18 mm. in diameter. Near the apex of the neck two platinum electrodes were sealed through the glass, the portions of wire inside the tube being glass-covered nearly to their tips. A capillary tube leading to the 3-way tap,  $\gamma$ , afforded exit from the explosion vessel. This tube remained full of mercury down to the top of the spark-gap during the entry and explosion of the gases.

The explosion vessel was supported by a wooden pedestal screwed on to the bench. The top of the pedestal was roughly shaped to fit the base of the cylinder, the pressure being evenly distributed by a packing of cotton wool.

When one measured volume of hydrogen had been transferred to the explosion vessel, the pipette was filled again and the operation repeated. In order to secure a small excess of hydrogen, a few cubic centimetres of mercury were withdrawn from the volume-adjuster during one of the fillings, so as to increase the volume of the pipette. By weighing this mercury the excess volume could be accurately estimated. When about half the gas had been expelled from the pipette, the tap, C, was closed and the reservoir, O, was lowered so as to reduce the pressure in the system. A crucible containing mercury was then brought up to submerge the capillary end of the volume-adjuster, and the tap, J, was opened until mercury rose to the level of the T-piece. The rest of the gas was then transferred.

The connecting tubes between the pipette tap and the gas trains were now exhausted and washed out with oxygen, after mercury had been taken through the lower bore of the tap, C, to expel the small quantity of hydrogen imprisoned there. The pipette was then filled with oxygen and the measured volume of gas was transferred to the synthesis vessel in successive portions, the addition of gas being continued until the passage of a spark caused an explosion. In practice we found that 600 c.c. of hydrogen and 300 c.c. of oxygen could be united conveniently by admitting the oxygen in seven fractions. The pressure in the explosion vessel was kept nearly atmospheric until six-sevenths of the oxygen had been fired, but, before the final explosion, the reservoir,  $\beta$ ,

was lowered, since the mixture now approximated to electrolytic gas, and there would have been some risk of shattering the vessel.

The small residue of wet hydrogen was compressed into the neck of the explosion vessel and sparked for a few moments. In order to collect any gas bubbles caught between the mercury and the glass, the reservoir,  $\beta$ , was lowered until most of the mercury had left the cylinder. A paper cone, mounted on a split cork, was fitted round the neck of the explosion vessel, and charged with a mixture of acetone and solid carbon dioxide. The water rapidly condensed as a film of ice on the walls of the neck, and, at the very low pressure in the vessel, the quantity of gas retained by the ice must have been negligibly small. When every trace of water had disappeared, mercury was allowed to rise to the bottom of the neck, and the dry hydrogen was sparked again for several minutes to eliminate any oxygen that might have escaped combination at the final explosion. Since any water vapour formed would at once be removed as ice, there was little chance of the reaction  $2\text{H}_2 + \text{O}_2 = 2\text{H}_2\text{O}$  being reversed.

*Measurement of the Hydrogen Residue.*

The tubing of the reservoir,  $\beta$ , was now clipped, and the tap,  $\gamma$ , turned to admit the dry hydrogen into the little pump,  $\delta$ . The mercury thread in the capillary was shot into the trap,  $\epsilon$ , and the gas passed to the pump through the tube,  $\xi$ , containing phosphoric oxide which had been distilled in oxygen, and the spiral,  $\eta$ , which was cooled in liquid air. Any impurities condensed in this spiral could be pumped out and examined after all the hydrogen had been removed. The delivery tube of the pump, made of very fine-bore capillary was turned up and sealed as an inserted join into the small collecting vessel,  $\theta$ .

This vessel carried a 3-way tap,  $\kappa$ , communicating on the one hand with the air, and on the other with the pipette by means of a capillary T-piece below the dead-space. The little pump was worked "tight," and any gas bubbles adhering to the turned-up end of the delivery tube were liberated by lowering the reservoir,  $\lambda$ . The pipette was now filled with hydrogen from the train, and a setting was made in the manner already described. As soon as the points were set the tap, C, was closed, and the hydrogen in  $\theta$  was driven over into the pipette by raising the reservoir,  $\lambda$ , and opening the tap,  $\kappa$ . The mercury in the dead-space was depressed, and the original pressure was recovered by withdrawing mercury from the volume-adjuster until both points were set again. From the weight of mercury taken out, the volume of the hydrogen residue could be calculated.

At first sight, this method of measuring a few cubic centimetres of gas may appear needlessly cumbrous, but in actual practice we found it both convenient and accurate. It had this great advantage, that no new pressure standard, with its possibly attendant errors, was introduced; the hydrogen residue was measured under precisely the same conditions as the gases before synthesis.

*Removal of the Water.*

After the hydrogen residue had been pumped out of the explosion vessel the tap,  $\gamma$ , was closed and the film of ice in the neck allowed to melt. On cooling the bulb,  $\mu$ , in liquid air and turning the tap,  $\gamma$ , the water distilled slowly from the neck to the bulb. When the removal of water was judged complete, the tap,  $\gamma$ , was closed and the clip on the tubing of the reservoir,  $\beta$ , opened to allow mercury to fill the vacuous neck of the explosion vessel. The click with which the mercury thread in the capillary met the tap-barrel bore witness to the absence of gas or water-vapour. After each experiment the bulk of the water collected in  $\mu$  was removed by exhausting with a water pump at the T-piece,  $\nu$ , while the bulb was warmed with a flame.

*First Series of Determinations.*

Both gases were made by electrolysis: the hydrogen was purified by exposure to charcoal cooled in liquid air; the oxygen was liquefied and fractionated as described on p. 399. To ensure the removal of moisture from the glass surfaces, the trains were left exhausted for a month and then washed out with hydrogen and oxygen respectively. The measuring pipette, explosion vessel, and small pump were also washed out with hydrogen, and the pentoxide tube,  $\xi$ , was warmed during passage of the gas.

To gain experience in manipulative technique, five preliminary determinations were carried out. Of the fourteen succeeding experiments, two (Nos. 8 and 9), were rejected. In these two experiments the normal procedure for purifying hydrogen was modified; instead of passing a stream of the gas through the cooled charcoal U-tube into the pipette, we allowed the saturated charcoal to warm up, and took the first fractions of the gas expelled. The results obtained were much higher than any others in the series.

The volume of oxygen taken for synthesis was 307 c.c. in all cases; the volume of hydrogen was 614 c.c. + a small, variable excess. Column 1 of the following table gives this excess as determined by the weight of mercury withdrawn from the volume-adjuster in one of the two hydrogen fillings. Column 2 gives the volume of the hydrogen residue after explosion, as determined by the weight of mercury withdrawn from the volume-adjuster in the final setting. Column 3 gives the difference between the volumes in the first two columns, representing the excess over 614 c.c. of hydrogen required to combine with 307 c.c. of oxygen. Column 4 gives the ratio of the combining volumes, and column 5, the atomic weight of hydrogen ( $O = 16$ ), computed from MORLEY's value for the density ratio  $\left(\frac{1.42900}{0.089873}\right)$ .

If  $R$  is the ratio of the combining volumes, and  $A$  the reciprocal of the density ratio, the atomic weight of hydrogen =  $8RA$ , so that any error in either ratio implies the same percentage error in the atomic weight.



TABLE I.

|                              | 1.<br>Hydrogen<br>excess. | 2.<br>Hydrogen<br>residue. | 3.<br>Difference. | 4.<br>Ratio of<br>combining<br>volumes. | 5.<br>Atomic weight<br>of<br>hydrogen. |
|------------------------------|---------------------------|----------------------------|-------------------|---|--|
|                              | c.c.                      | c.c.                       | c.c.              |   |  |
| 1                            | 4.316                     | 3.439                      | 0.877             | 2.00286                                 | 1.00771                                |
| 2                            | 4.072                     | 3.140                      | 0.932             | 2.00304                                 | 1.00780                                |
| 3                            | 4.755                     | 3.877                      | 0.878             | 2.00286                                 | 1.00771                                |
| 4                            | 4.271                     | 3.366                      | 0.905             | 2.00295                                 | 1.00776                                |
| 5                            | 1.670                     | 0.750                      | 0.920             | 2.00300                                 | 1.00778                                |
| 6                            | 5.717                     | 4.844                      | 0.873             | 2.00284                                 | 1.00771                                |
| 7                            | 2.962                     | 2.044                      | 0.918             | 2.00299                                 | 1.00778                                |
| 10                           | 2.202                     | 1.309                      | 0.893             | 2.00291                                 | 1.00774                                |
| 11                           | 2.565                     | 1.576                      | 0.989             | 2.00322                                 | 1.00790                                |
| 12                           | 2.605                     | 1.699                      | 0.906             | 2.00295                                 | 1.00776                                |
| 13                           | 2.015                     | 1.179                      | 0.836             | 2.00272                                 | 1.00765                                |
| 14                           | 3.231                     | 2.340                      | 0.891             | 2.00290                                 | 1.00774                                |
|                              |                           |                            | Mean . . . .      | 2.00294<br>$\pm 0.00002$                | 1.00775                                |
| Maximum deviation, 1 in 4000 |                           |                            |                   |   |  |

In the first few rejected experiments a small quantity of gas was condensed from the hydrogen residue in the spiral,  $\eta$ . This gas was measured in the calibrated capillary at the top of the collector,  $\theta$ . In the first experiment it amounted to about 10 c.mm., falling to 2 c.mm. to 3 c.mm. in the second. Throughout the rest of the series the quantity was less than 1 c.mm. This gas was most probably carbon dioxide, produced by combustion on the walls of the explosion vessel of traces of organic impurities which previous cleaning treatment had failed to remove. Since the capillary exit tube from the explosion vessel was always full of mercury while the gases were being combined, there was no possibility of the flame reaching the grease on the tap,  $\gamma$ .

*Second Series.*

Hydrogen, generated as in series 1, was purified by passage through the walls of a palladium tube.

Oxygen was made and purified as in series 1.

After four or five determinations, yielding somewhat discordant results, a crack was discovered in the palladium tube. A new tube, made from fused metal, was then set up. Of the following twelve experiments, two (Nos. 5 and 11), were rejected; No. 5, because, owing to an accident, the determination was interrupted in the middle, and only completed after an interval of several days; No. 11, because the

accuracy of one of the settings was suspected at the time on account of the light being bad.

The five columns of figures in Table II. correspond to those in Table I.

TABLE II.

|    | 1.<br>Hydrogen<br>excess. | 2.<br>Hydrogen<br>residue. | 3.<br>Difference.              | 4.<br>Ratio of<br>combining<br>volumes. | 5.<br>Atomic weight<br>of<br>hydrogen. |
|----|---------------------------|----------------------------|--------------------------------|---|--|
|    | c.c.                      | c.c.                       | c.c.                           |   |  |
| 1  | 2.026                     | 1.147                      | 0.879                          | 2.00286                                 | 1.00772                                |
| 2  | 3.331                     | 2.440                      | 0.891                          | 2.00290                                 | 1.00774                                |
| 3  | 3.687                     | 2.794                      | 0.893                          | 2.00291                                 | 1.00774                                |
| 4  | 2.233                     | 1.359                      | 0.874                          | 2.00285                                 | 1.00771                                |
| 6  | 5.641                     | 4.777                      | 0.864                          | 2.00281                                 | 1.00769                                |
| 7  | 3.871                     | 2.960                      | 0.911                          | 2.00297                                 | 1.00777                                |
| 8  | 4.738                     | 3.822                      | 0.916                          | 2.00298                                 | 1.00778                                |
| 9  | 3.926                     | 3.000                      | 0.926                          | 2.00302                                 | 1.00779                                |
| 10 | 2.835                     | 1.934                      | 0.901                          | 2.00293                                 | 1.00775                                |
| 12 | 2.958                     | 2.062                      | 0.896                          | 2.00292                                 | 1.00774                                |
|    |                           |                            | Mean . . . .                   | 2.00292<br>$\pm 0.000014$               | 1.00774                                |
|    |                           |                            | Maximum deviation, 1 in 10,000 |   |  |

Before the next series of determinations the palladium tube, which was showing some signs of weakness, was cut down and sent away to be repaired.

### *Third Series.*

Hydrogen was made and purified as in series 2, except that on leaving the electrolysis vessel it passed through a tube containing palladium black. Oxygen was obtained from potassium permanganate as described on pp. 399-401.

At this stage of the research we had a great deal of trouble owing to the appearance of condensible gas in the hydrogen left after explosion, accompanied by discrepant and much lower results. The quantity of gas condensed in the spiral,  $\eta$ , varied from 40 c.mm. to nearly 300 c.mm. in different experiments. It was completely soluble in a drop of potash or baryta solution, giving a white precipitate in the latter case. The source of the impurity was at first believed to be the oxygen generated from permanganate, since all other conditions were apparently the same as in series 2, but liquefaction and fractionation of much larger quantities of oxygen produced no improvement.

Any impurities accompanying the oxygen must have been sufficiently volatile to escape condensation in the fractionating tubes. To test whether oxygen could retain or acquire carbon dioxide, as such, after leaving the fractionating train, a considerable volume was pumped through the cooled spiral,  $\eta$ . Nothing was retained by the spiral. KAMMERLING ONNES<sup>(11)</sup> has shown that, at the boiling point of oxygen, the vapour pressure of carbon dioxide is about  $6 \times 10^{-6}$  mm. of mercury, so that little could escape condensation when exposed to a large surface of glass cooled in liquid air. It seemed just possible that oxidation of dust in the permanganate tubes might give rise to carbon monoxide, a gas about as difficult to separate from liquid oxygen by fractional distillation as nitrogen would be. Some experiments carried out by Mr. J. N. GREENWOOD indicate that if any carbon monoxide is present in permanganate oxygen, the quantity is less than 1 part in 40,000 by volume, even when no precautions are taken to avoid the presence of dust in the decomposition tube.

We next considered the possibility of impurities in the explosion vessel. There was no question of grease finding its way back from the tap,  $\gamma$ , because mercury and gas travelled always in the opposite direction. The pipette tap was separated from the explosion vessel by more than half a metre of capillary tubing in which there were several bends. Any grease carried by a mercury thread through a tap-bore is usually deposited in the first few centimetres of connecting tube. In order to obviate any possible risk of contamination in this way, the device illustrated in fig. 5

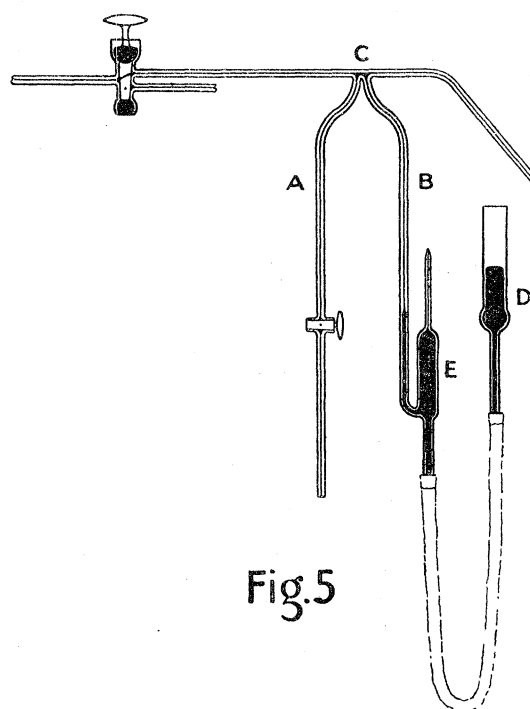


Fig. 5

was adopted. Two vertical capillary tubes, A and B, were sealed to the transference capillary at C, as close together as possible: A was provided with a tap, and B was connected with a mercury reservoir, D, through an air-trap, E. The tube, B, had no tap, but the flow of mercury through it was controlled by a screw-clip on the reservoir tubing.

All mercury that passed through the pipette tap was withdrawn by the tube, A. At the end of the process of transferring gas from the pipette to the explosion vessel, the mercury thread following the gas through the pipette tap and along the capillary was checked at C. The gas remaining in the capillary between C and the explosion vessel was then driven over by clean mercury from the reservoir, D.

To remove any grease that might have previously found its way there, the

explosion vessel itself was cut down and drastically cleaned by consecutive treatment with stannous chloride and strong hydrochloric acid, and a hot solution of chromic anhydride in fuming nitric acid. After the acid had been washed out, the final content of distilled water was replaced by dust-free air drawn in over cotton-wool. The vessel was then dried at room temperature in a stream of air passed over calcium chloride and filtered through cotton-wool.

On continuing the determinations, condensible gas was still found in the hydrogen residue. The only sources of impurity yet to be examined was the hydrogen. A glass spiral was inserted in the train between the palladium tube and the pipette, and cooled in liquid air during the filling. A small quantity of gas was condensed in the spiral, and the amount of impurity in the hydrogen residue was diminished, though not entirely eliminated, by this treatment; facts which at once suggested a flaw in the palladium tube. The tube was accordingly cut down and examined, and a crack was discovered. The phosphoric oxide in the drying trains had not been distilled in oxygen, and was probably the source of contamination. It is of interest to note that hydrogen passed over impure phosphoric oxide apparently contains some carbon compound which is not condensed at the temperature of liquid air; perhaps carbon monoxide. A new palladium tube, the third described in the preface, was procured and set up, and in the following series of determinations, the amount of condensible gas in the hydrogen residue was absolutely negligible. In some

TABLE III.

|    | 1.<br>Hydrogen<br>excess. | 2.<br>Hydrogen<br>residue. | 3.<br>Difference.              | 4.<br>Ratio of<br>combining<br>volumes. | 5.<br>Atomic weight<br>of<br>hydrogen. |
|----|---------------------------|----------------------------|--------------------------------|---|--|
|    | c.c.                      | c.c.                       | c.c.                           |   |  |
| 1  | 3·213                     | 2·323                      | 0·890                          | 2·00290                                 | 1·00773                                |
| 2  | 3·116                     | 2·221                      | 0·895                          | 2·00292                                 | 1·00774                                |
| 3  | 3·990                     | 3·092                      | 0·898                          | 2·00292                                 | 1·00775                                |
| 4  | 3·128                     | 2·240                      | 0·888                          | 2·00289                                 | 1·00773                                |
| 5  | 2·630                     | 1·754                      | 0·876                          | 2·00285                                 | 1·00771                                |
| 6  | 3·424                     | 2·521                      | 0·903                          | 2·00294                                 | 1·00776                                |
| 7  | 2·495                     | 1·584                      | 0·911                          | 2·00297                                 | 1·00777                                |
| 8  | 3·247                     | 2·341                      | 0·906                          | 2·00295                                 | 1·00776                                |
| 9  | 3·573                     | 2·655                      | 0·918                          | 2·00299                                 | 1·00778                                |
| 10 | 2·552                     | 1·675                      | 0·877                          | 2·00286                                 | 1·00771                                |
|    |                           |                            | Mean . . .                     | 2·00292<br>± 0·00001                    | 1·00774                                |
|    |                           |                            | Maximum deviation, 1 in 14,000 |   |  |

experiments in this series, a very large quantity of oxygen was liquefied and fractionated; in others, only just enough for the purpose. The concordance was better than in series 1 and 2, the maximum deviation among ten consecutive determinations being less than 1 part in 14,000.

The means of series 1, 2 and 3 differ by only 1 part in 100,000. The final mean, taking into account the probable error of each series, is 2.00292, with a probable error of less than  $\pm 4$  parts in 1,000,000. The corresponding atomic weight for hydrogen is 1.00775. Since the oxygen was obtained from two totally distinct sources, and the hydrogen, though always derived from the electrolysis of barium hydroxide, was purified by two essentially different methods, the close agreement of the means of the three series suggests that the purity of the gases reached a high standard. Before accepting these values, however, it was necessary to consider the possibility of systematic errors inherent in the methods employed. One such constant error had already been detected. When a measured volume of gas was displaced from the pipette by mercury, a small bubble was always trapped in the dead-space, at the region of insertion of the glass point. Since, after the expulsion of the second hydrogen filling, oxygen was admitted without first washing out the pipette, the oxygen was contaminated with this small quantity of hydrogen. This implied a corresponding deficit of oxygen, the nett result being an excess of hydrogen in the residue after explosion equal to three times the volume of the original bubble.\*

By closing the pipette tap after removal of the gas, and lowering the reservoir, O, this bubble escaped into the vacuum so formed, and could be measured in the pipette capillary which was calibrated for the purpose. From a number of measurements with both hydrogen and oxygen the volume of the imprisoned bubble proved to be remarkably constant. As a mean of six experiments, agreeing to within 1 c.mm., this volume was found to be 6.5 c.mm., when corrected to normal temperature and pressure. This implied an excess of 19.5 c.mm., in the hydrogen residue, which would make the ratio of the combining volumes (and the atomic weight of hydrogen) too low by 33 parts in 1,000,000. The alteration involved was much smaller than the variations among the individual determinations, but the correction was justifiable since it was constant both in magnitude and sign. The corrected values for the final means become 2.00299 and 1.00778.

#### *Fourth Series.*

To test the validity of this correction we proceeded to carry out a further series of determinations in which the imprisoned hydrogen bubble was removed before the introduction of the oxygen.

\* The final hydrogen filling, which was contaminated in a similar way with a trace of oxygen, was removed by the mercury pump at the end of each determination.

Hydrogen was prepared and purified as in series 3: oxygen was obtained both by electrolysis and by heating permanganate, so that large quantities of gas were rapidly available for fractionation. Electrolytic oxygen, accumulated from time to time in a  $2\frac{1}{2}$ -litre storage bulb, entered the main train at the T-piece (Z, fig. 3), after being dried over calcium chloride, and phosphoric oxide.

In this series, and in the preceding one, an attempt was made to measure the temperature of the mercury in the short exposed portion of the manometer column that projected below the bath (K to L, fig. 4). For this purpose, a small thermometer, graduated in tenths of a degree, was fastened by fine copper wire to the manometer tube, and the whole was wrapped in cotton-wool. The temperature registered by this thermometer was probably proportional to, if not identical with, the temperature of the mercury in this region of the manometer. The readings varied with the room temperature and length of time during which the system had been in ice. The main controlling factor was the temperature of the room. Since the distance between the

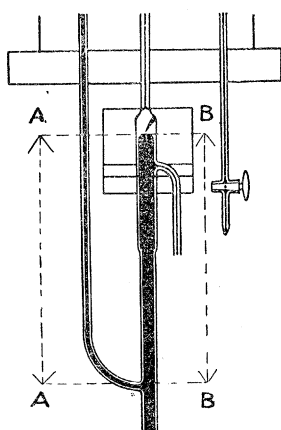


Fig 6

two glass points to which the mercury menisci were set was constant, any rise in temperature of the mercury in the manometer implied a diminution of pressure and corresponding increase in volume of the gas in the pipette. An empirical value for the temperature effect was obtained by filling the pipette with gas, making a setting and noting the temperature of the thermometer, and then repeating the measurement when the temperature was a degree or so higher. From the weight of the few drops of mercury that had to be withdrawn from the volume-adjuster to set the points on the second occasion, it was possible to estimate the increase in the volume occupied by the gas per unit rise of temperature as registered by the thermometer.

The mean of several very concordant results was 21 c.mm. per degree. Now the length of the exposed portion of the manometer was about 4 cm., and a change of  $1^{\circ}$  C. in the temperature of this length of mercury could not produce so large an effect. In fig. 6 the two columns of mercury, AA and BB, only equalise each other when their temperature is the same. All this region was packed in cotton-wool, the tubing below the dead-space being the more thickly coated. The mercury in A would be more sensitive to temperature changes than the larger bulk of better insulated mercury in B, so that part of the measured effect may have been due to relative temperature change in this part of the system.

In any case, the effect on the results is very small, since the room temperature seldom varied half a degree during a determination. The application of the correction to the results of series 3 improves the concordance a little without altering the mean.

In series 4 the temperature variations were greater. In order to protect the

apparatus from the warmth of the observer's body, a sheet of asbestos was fastened in front of the manometer and tubing below the dead-space, with the result that the cooling effect of the ice-baths above came more into play, and the temperature registered by the thermometer was lower the longer the system had been in ice. Consequently the hydrogen fillings, which were made first in the day, contained relatively too little gas. The result of applying the correction to series 4 was to lower the mean by 1 part in 50,000.

The following table gives the results of series 4: two additional columns, 6 and 7, give the values for the ratio and the atomic weight when the small correction is applied.

TABLE IV.

|                            | 1.<br>Hydrogen<br>excess. | 2.<br>Hydrogen<br>residue. | 3.<br>Difference. | 4.<br>Ratio of<br>combining<br>volumes. | 5.<br>Atomic<br>weight of<br>hydrogen. | 6.<br>Ratio of<br>combining<br>volumes. | 7.<br>Atomic<br>weight of<br>hydrogen. |
|----------------------------|---------------------------|----------------------------|-------------------|---|--|---|--|
|                            | c.c.                      | c.c.                       | c.c.              |   |  |   |  |
| 1                          | 2.443                     | 1.527                      | 0.916             | 2.00298                                 | 1.00778                                | 2.00300                                 | 1.00779                                |
| 2                          | 3.717                     | 2.827                      | 0.890             | 2.00290                                 | 1.00773                                | 2.00284                                 | 1.00771                                |
| 3                          | 2.846                     | 1.903                      | 0.943             | 2.00307                                 | 1.00782                                | 2.00299                                 | 1.00778                                |
| 4                          | 3.589                     | 2.614                      | 0.975             | 2.00318                                 | 1.00787                                | 2.00305                                 | 1.00781                                |
| 5                          | 3.453                     | 2.507                      | 0.946             | 2.00308                                 | 1.00783                                | 2.00309                                 | 1.00783                                |
| 6                          | 3.311                     | 2.410                      | 0.901             | 2.00293                                 | 1.00775                                | 2.00288                                 | 1.00773                                |
| 7                          | 3.895                     | 2.945                      | 0.950             | 2.00309                                 | 1.00783                                | 2.00306                                 | 1.00781                                |
| 8                          | 2.945                     | 2.015                      | 0.930             | 2.00303                                 | 1.00780                                | 2.00301                                 | 1.00779                                |
| 9                          | 2.015                     | 1.052                      | 0.963             | 2.00314                                 | 1.00785                                | 2.00307                                 | 1.00782                                |
| 10                         | 3.448                     | 2.521                      | 0.927             | 2.00302                                 | 1.00780                                | 2.00310                                 | 1.00784                                |
|                            |                           |                            | Mean. . . .       | 2.00304<br>$\pm 0.00002$                | 1.00781                                | 2.00301<br>$\pm 0.00002$                | 1.00779                                |
| Mean deviation, 1 in 7000. |                           |                            |                   |   |  |   |  |

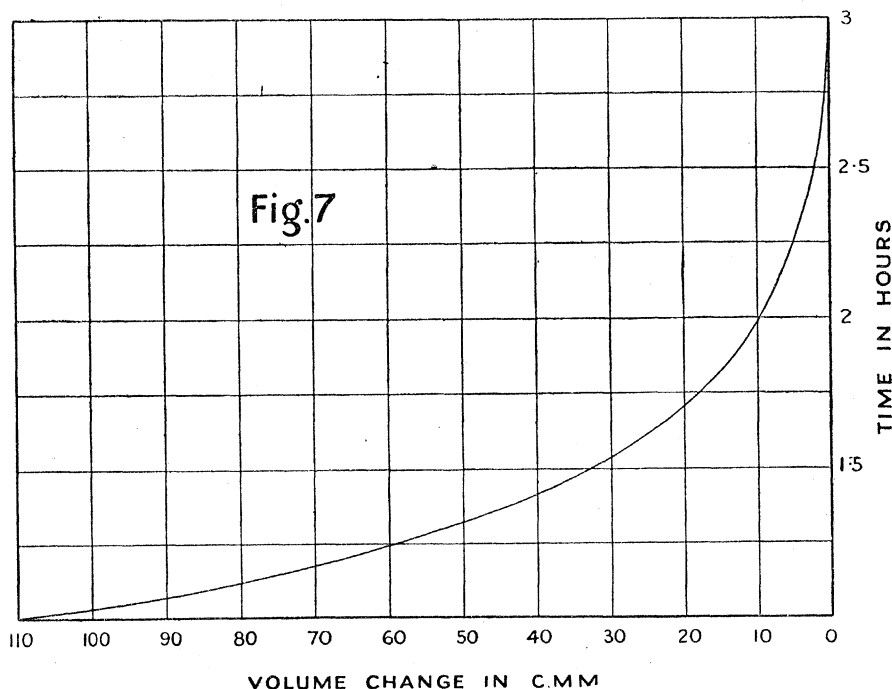
The mean value of the ratio in column 6 differs by only 1 part in 100,000 from the final mean of the first three series when this is corrected for the imprisoned bubble.

It may be noted in the above table that without experiments 2 and 6 the maximum deviation in column 4 is 1 part in 10,000, and in the corrected values in column 6, only 1 part in 18,000.

The explanation of the two low results is to be found in another temperature error which affects all four series. The final setting of a determination had sometimes been repeated on the following day, with the object of testing the accuracy of the measurement. On such occasions it was noticed that the volume of gas in the pipette had apparently increased, unless the bath had been iced for some time before the reading was made. It was therefore necessary to make a careful investigation of the time

needed for temperature equilibrium to be established after ice had been put in the pipette bath. The problem was attacked in two ways: in the first place, we made a series of measurements of the gas in the pipette on consecutive days, the interval of time between the introduction of ice and the setting being decreased from day to day. The volume expansion corresponding to these time intervals was obtained from the weight of mercury that had to be taken from the volume-adjuster in order to set the points.

In the second place, the pressure change of the gas in the pipette was measured at constant volume by making a setting a short time after the introduction of ice, and then, keeping the lower mercury meniscus set to the point in the dead-space, measuring the increase in distance between the upper meniscus and its point with



lapse of time. This was done with a reading telescope, fitted with a Hilger micrometer eye-piece. The two methods yielded concordant results which were checked at a later date by a large number of similar measurements made with a cathetometer. In fig. 7, volume change in cubic millimetres is plotted against the time, in hours, during which the bulb had been in ice, and the resulting curve indicates that nearly three hours were required to establish temperature equilibrium.\*

Now each complete determination occupied from twelve to fifteen hours and was carried through in two consecutive days. The normal procedure was to measure and

\* The unexpectedly long time taken by the gas to attain temperature equilibrium may have been due to the fact that the base of the bulb was supported by a small rubber cork which protected the glass over a small area from direct contact with the ice.



combine the gases on the first day and leave the wet hydrogen residue safely imprisoned between mercury surfaces in the explosion vessel over night. The residual hydrogen was measured on the following day. The order of operations at the beginning of each day was identical. First of all the pipette was cooled with ice; then hydrogen was admitted, the upper bath iced and a setting made. During the rest of the day the ice in the pipette bath was never removed, but was pressed down and replenished immediately before each reading. On the second day, as soon as the first hydrogen setting was accomplished, the residue in the explosion vessel was dried, sparked and transferred to the pipette; the ice in the baths was then replenished and the final setting was made. The last two measurements, therefore, were separated by a considerable interval of time. Of the five gas measurements required in each determination, only two, namely the first of each day, fell within the three-hour period preceding the establishment of equilibrium. Consequently, in both these measurements the quantity of hydrogen actually taken was less than the quantity assumed in the calculation. The error in each case makes the result too high.

The accurate evaluation of the correction involves a knowledge of the time interval between the introduction of ice and the completion of the setting. Although the time had always been noted when a setting was made, the same precaution had, unfortunately, seldom been taken at the moment of iceing the bulb. There was little variation, however, in the time occupied by the intermediate operations, which in series 3 and 4 had become almost mechanical. In series 3, the most uniform as regards method of procedure, and the most concordant in results, the time interval as actually measured in several determinations was one and three-quarter hours, and the mean time for the whole series was certainly within a few minutes of this. It may be seen from the curve (fig. 7) that when the bulb had been in ice for an hour and three-quarters, the volume of the gas was still 18 c.mm. in excess of its final value, so that had the measurement been delayed till contraction was complete, an additional 18 c.mm. of gas must have been introduced to achieve the setting. Since the calculation is based on this assumption, the nominal volume of hydrogen taken for synthesis must be diminished by 18 c.mm., and, by parity of reasoning, the nominal volume of the residue must be increased by the same amount. The net result is a diminution of 36 c.mm. in the volume of hydrogen required to combine with 307 c.c. of oxygen. This implies a reduction of 6 parts in 100,000 in the values for the ratio and the atomic weight.

In series 4, an attempt to estimate the above time intervals for each individual experiment led to the same average reduction. In experiment 6, for example, the oxygen measurement, instead of being made at the end of the first day when the bulb had been in ice for many hours, was made on the following morning. The temperatures of the oxygen and hydrogen were therefore more comparable, and the resulting correction was small. In several of the other determinations the correction was larger than in series 3. As regards series 1 and 2 a similar correction was necessary. The

time interval in question was in most cases rather greater, since the hydrogen took longer to obtain. On the other hand, the correction for the imprisoned bubble was probably a little smaller. The presence of this bubble had escaped observation in the early part of the research, owing, perhaps, to the fact that the mercury in the pipette was very clean and therefore trapped a smaller quantity of gas.\* With long continued use and contact with rubber tubing, inevitable slight fouling occurred.†

That the average volume of the imprisoned bubble was increasing very slightly during the later stages of the research, was proved by actual measurement. Both these opposing errors may therefore have been smaller in the earlier series. Taking into account the very close agreement of the means it seemed fairest to apply the same "contraction" correction throughout, and to reduce the means of all four series by 6 parts in 100,000. Collecting all the results we have:—

|                                       | Series 1. | Series 2.  | Series 3. | Series 4. |
|---------------------------------------|-----------|------------|-----------|-----------|
|                                       | 2·00294   | 2·00292    | 2·00292   | 2·00301   |
|                                       | ± 0·00002 | ± 0·000014 | ± 0·00001 | ± 0·00002 |
| Corrected for imprisoned bubble . . . | 2·00301   | 2·00299    | 2·00299   | 2·00301   |
| Corrected for "contraction" . . .     | 2·00289   | 2·00287    | 2·00287   | 2·00289   |

The arithmetic mean of the ratios in the last line is 2·00288, and the corresponding atomic weight of hydrogen is 1·00772.

#### *Fifth Series.*

Since the magnitude of the "contraction" correction was a little uncertain, a fifth series of determinations was undertaken. In this series no measurement was made until the pipette had been in ice for at least three hours. The gases were made and purified exactly as in series 4, and the trapped hydrogen bubble was removed before the oxygen filling. To eliminate variations in the temperature of the mercury in the exposed portion of the manometer, a small subsidiary bath, constructed of the two halves of a short brass cylinder, mounted on a split cork, was fitted to the manometer tube in this region. This bath was filled with powdered ice immediately before each reading was made. By a modification of procedure on the second day the two final settings were made one immediately after the other so that there was no need to re-ice the baths. As soon as the first setting was finished, the hydrogen residue, previously accumulated in the collector, was at once admitted, and the necessary adjustment made by running out mercury. Of the thirteen experiments in this series, one, No. 6, was

\* Before its introduction into the apparatus the mercury was purified from foreign metals by distillation and by washing with mercurous nitrate solution, and was finally dried by heating to 120° C.

† The tubing used was of a special kind designed to resist attack by mercury.

rejected. In this experiment, when the tap on the explosion vessel was opened to admit the hydrogen residue to the pump, the mercury thread in the capillary beyond the tap broke up into a series of globules which settled down and obstructed the passage of the gas. To remove them it was necessary to heat the capillary strongly with a flame, and since the glass in this region was contaminated with tap-grease, some chemical action may have occurred.

TABLE V.

|                                      | 1.<br>Hydrogen<br>excess. | 2.<br>Hydrogen<br>residue. | 3.<br>Difference. | 4.<br>Ratio of<br>combining<br>volumes. | 5.<br>Atomic weight<br>of<br>hydrogen. |
|--------------------------------------|---------------------------|----------------------------|-------------------|---|--|
|                                      | c.c.                      | c.c.                       | c.c.              |   |  |
| 1                                    | 3.428                     | 2.575                      | 0.853             | 2.00278                                 | 1.00767                                |
| 2                                    | 3.461                     | 2.585                      | 0.876             | 2.00285                                 | 1.00771                                |
| 3                                    | 3.080                     | 2.219                      | 0.861             | 2.00280                                 | 1.00769                                |
| 4                                    | 3.131                     | 2.242                      | 0.889             | 2.00290                                 | 1.00773                                |
| 5                                    | 3.078                     | 2.176                      | 0.902             | 2.00294                                 | 1.00775                                |
| 7                                    | 3.222                     | 2.351                      | 0.871             | 2.00284                                 | 1.00770                                |
| 8                                    | 3.855                     | 2.986                      | 0.869             | 2.00283                                 | 1.00770                                |
| 9                                    | 4.339                     | 3.429                      | 0.910             | 2.00296                                 | 1.00777                                |
| 10                                   | 3.160                     | 2.274                      | 0.886             | 2.00289                                 | 1.00773                                |
| 11                                   | 3.000                     | 2.090                      | 0.910             | 2.00296                                 | 1.00777                                |
| 12                                   | 3.155                     | 2.268                      | 0.887             | 2.00289                                 | 1.00773                                |
| 13                                   | 3.141                     | 2.276                      | 0.865             | 2.00282                                 | 1.00769                                |
| Mean . . . .                         |                           |                            |                   | 2.00287<br>$\pm 0.00001$                | 1.00772                                |
| Maximum deviation, 1 part in 11,000. |                           |                            |                   |   |  |

The mean is practically identical with the corrected mean of the first four series, so that the estimate of the "contraction" correction is satisfactorily confirmed.

Although, in this series, no uniformity of procedure was adopted as regards the distribution of the gas measurements over the two days, examination of the results reveals no discrepancies attributable to this cause.

In experiments 1, 3, 9, 11 and 13, for example, the oxygen was measured on the afternoon of the first day, whereas in experiments 2, 4, 5, 8, 10 and 12, it was measured on the morning of the second day; yet the mean result for each group is the same. Experiment 7 was completed in a single day.

Except for the longer interval between iceing and setting, the presence of the small subsidiary ice bath on the manometer tube and the juxtaposition of the two final measurements constituted the only difference from series 4. The lower results of series 5 cannot be attributed to the presence of the little ice bath since the volume

contraction curve was found to be the same whether this portion of the manometer was at room temperature or at  $0^{\circ}\text{C}$ . As the bath was used in every gas measurement, the effect of the resulting small increase in the quantity of gas required to fill the pipette cancels out.

The possibility of a small error, due to the difference of procedure in the two final measurements, was suspected on theoretical grounds. Before admitting the hydrogen residue to the pipette, the mercury in the dead-space was always lowered to the level of the capillary T-piece at which the gas entered. The mercury immediately below the dead-space and at the same level in the manometer was cold owing to the brine and the ice baths respectively. The result of lowering the pipette reservoir, therefore, was to bring cold mercury into the tubing below the dead-space and into the lower part of the manometer. The glass in these regions was cooled and if, on raising the mercury again, temperature equilibrium was established more rapidly in the manometer tube (see p. 414), the points would no longer be set. Moreover, if these assumptions are correct, the effect should be greater the higher the temperature of the room. Now the room temperatures at the determinations in series 5, ranged from  $11^{\circ}\cdot 5\text{ C}$ . to  $13^{\circ}\cdot 5\text{ C}$ ., and averaged about  $12^{\circ}\text{ C}$ . Examination of the experiments showed no connection between the temperature of the room and the value of the result.

A series of blank experiments was then undertaken when the temperature of the room was between  $17^{\circ}\text{ C}$ . and  $18^{\circ}\text{ C}$ . A setting having been made, the mercury was lowered for a period comparable to that required for admitting the hydrogen residue in an actual determination. On raising the pipette reservoir again it was found that mercury had to be taken from the volume-adjuster in order to set the points. The mean volume of mercury withdrawn in four very concordant experiments was 30 c.mm., so that actual determinations carried out at this room temperature would have been 1 part in 20,000 too low. The experiment was repeated at a room temperature of  $16^{\circ}\text{ C}$ ., when the volume of mercury withdrawn was only 10 c.mm. The inference is that, at the room temperatures obtaining in series 5, the correction would have been negligibly small, and this is confirmed by the above-mentioned fact that differences of  $2^{\circ}\text{ C}$ . in this temperature region had no detectable influence on the results. It was unfortunately impossible to make blank experiments at these lower temperatures, unless we had waited for the winter.

The error just discussed does not affect the first four series, where, after the hydrogen residue had been admitted, and a rough adjustment made by running out mercury, the ice in the baths was replenished before the final setting. During this time interval the normal temperature conditions of the mercury in the tubes below the dead-space level would have been established again.

For the reasons mentioned in the preface an excess of hydrogen had been taken in all our experiments. It does not seem probable that any constant error would be involved by this practice, but the point was tested by carrying out a few determinations with oxygen in excess.

The preparation and purification of the gases and all subsequent precautions were the same as in series 5.

First of all, exactly two volumes of hydrogen and one volume of oxygen were exploded and the small residue of oxygen measured. In three other experiments a slightly greater proportion of oxygen was taken. The volume of hydrogen was 614 c.c. in all cases. The oxygen residue was estimated in exactly the same way as the hydrogen residue. It would have been more logical to fill the pipette with oxygen instead of hydrogen, which was selected because it was more easily procurable. On mixing 1 or 2 c.c. of oxygen with 300 c.c. of hydrogen, the resulting volume is not strictly additive, but the deviation, though not exactly determinable from existing data, is probably very small.

In these four experiments a new phenomenon was observed. In each case, after the final explosion in which oxygen had been present in excess, brown stains were noticed on the walls of the explosion vessel. These stains were presumably oxide of mercury since they gradually disappeared when mixtures containing an excess of hydrogen were detonated in the vessel. If a significant quantity of oxygen was fixed in this way, the value of the ratio would be too low. It was a moot point whether it was advisable to spark the dried oxygen residue. COWARD <sup>(12)</sup> has shown that, when the pressure is low, traces of uncombined hydrogen and oxygen remain after detonating electrolytic gas. On the other hand, sparking might lead to the formation of ozone. In one case the result would be too high; in the other too low. The treatment in this respect was varied in the different experiments as follows:—

| Example 1.           | Example 2.   | Example 3.            | Example 4.         |
|----------------------|--------------|-----------------------|--------------------|
| 0·5 mins., sparking. | No sparking. | 0·75 mins., sparking. | 3 mins., sparking. |

It is significant that the result of experiment 2 was the highest. It should be mentioned here that nothing was condensed when the oxygen residue was pumped through the liquid-air-cooled spiral. In the following table columns 1 and 2 represent the surplus volume of oxygen taken and the residue of oxygen left after explosion, respectively. Column 3 gives the difference between the first two columns, representing the volume by which 307 c.c. of oxygen must be diminished to be chemically equivalent to 614 c.c. of hydrogen.

Without laying any particular stress on these results it may be claimed that they do not suggest the presence of a constant error in the earlier experiments. We therefore conclude that the ratio of the combining volumes of hydrogen and oxygen is represented with a high degree of probability by the figure

**2·00288** at 0° C., and 760 mm. pressure,

which differs from the value of SCOTT by only 3 parts in 200,000.

TABLE VI.

|                                 | 1.<br>Oxygen<br>excess. | 2<br>Oxygen<br>residue. | 3.<br>Difference. | 4.<br>Ratio of<br>combining<br>volumes. | 5.<br>Atomic weight<br>of<br>hydrogen. |
|---------------------------------|-------------------------|-------------------------|-------------------|---|--|
|                                 | c.c.                    | c.c.                    | c.c.              |   |  |
| 1                               | 0                       | 0.428                   | 0.428             | 2.00279                                 | 1.00768                                |
| 2                               | 1.533                   | 2.021                   | 0.488             | 2.00318                                 | 1.00788                                |
| 3                               | 1.084                   | 1.551                   | 0.467             | 2.00305                                 | 1.00781                                |
| 4                               | 0.508                   | 0.933                   | 0.425             | 2.00277                                 | 1.00767                                |
| Mean . . . .                    |                         |                         |                   | 2.00295                                 | 1.00776                                |
| Maximum deviation, 1 in 5000.   |                         |                         |                   |   |  |
| Omitting experiment 2, mean . . |                         |                         |                   | 2.00287                                 | 1.00772                                |
| Maximum deviation, 1 in 7000.   |                         |                         |                   |   |  |

The ratio may be calculated from compressibility measurements. If the compressibility coefficient of hydrogen at 0° C., between 0 and 1 atmospheres, is taken as +0.00054 (the mean of the values obtained by RAYLEIGH, JAQUEROD and SCHEUER, and CHAPPUIS) and the corresponding coefficient of oxygen as -0.000964 (GRAY and BURT), then the ratio of the volumes containing equal numbers of molecules at N.T.P. is  $\frac{1+0.00054}{1-0.000964}$  and the ratio of the combining volumes  $\frac{2(1+0.00054)}{1-0.000964} = 2.00303$ .

#### *Purity of the Gases.*

Provided that the source of the gas and the methods of purification are varied, the best criterion of purity is afforded by the concordance of the results.

Neither of the gases, in the condition in which they left the trains, yielded any residue when pumped through a spiral cooled in liquid air.

The liquefied oxygen left no residue on evaporation, and the results did not vary according to the fraction taken. Nitrogen might occur as an impurity owing to incomplete exhaustion of the trains, or to a faulty tap. In the first case the quantity would diminish throughout a series and, since the resulting error would not be constant, it could hardly escape detection. The taps on the apparatus were selected

with great care. They were mounted on capillary tube, and, in the case of the 3-way taps, had the two bores drilled diagonally and at right angles to each other. Experience has shown this to be the safest type for preventing leak. All taps through which gas passed were mercury cupped. The plugs were so finely ground that a very small quantity of grease sufficed to lubricate them, and they were kept well "home" in their barrels by means of rubber bands. When in use, the plug was turned through the smallest possible arc, a precaution which tends to prevent the appearance of striæ, particularly when the tap is in service for a long time. The grease used was the well-known rubber-paraffin-vaseline mixture, and, contrary to the experience of GERMANN<sup>(13)</sup>, we found that oxygen had no detectable effect on its appearance or properties. No leak between the interior of the apparatus and the air was ever observed, though the point was frequently tested. Nitrogen was tested for directly by exploding down about 1200 c.c., of hydrogen and 600 c.c. of oxygen, the quantities being adjusted so that hydrogen was in slight excess. The hydrogen residue, of about 3 c.c., was transferred to a small explosion eudiometer and mixed with 2 c.c. of oxygen. After passing a spark and introducing a small quantity of alkaline pyrogallol solution, about 1 c.mm. of gas remained unabsorbed. In other experiments hydrogen and oxygen residues were sparked over water or potash; in no case was any diminution in volume noticed.

The presence of nitrogen in either gas might give rise to traces of oxides of nitrogen, and eventually nitric acid, as a result of the explosions, or to ammonia as a result of the sparking. Oxides of nitrogen (except nitric oxide), nitric acid, and ammonia would remain with the ice in the explosion vessel. The water formed left no residue on the glass or mercury surfaces when evaporated; was odourless, tasteless, and neutral in re-action, and, when tested for nitric acid and ammonia, gave negative results. Traces of nitrogen, or other gases, in the hydrogen, provided that they were left unaltered by the explosions and sparking, would introduce no error, since they would be measured as part of the hydrogen residue. Any such impurity in the oxygen, on the other hand, would make the hydrogen residue too great by an amount equal to three times the volume of the original impurity.

The presence of carbon compounds in either gas would almost certainly lead to the formation of carbon dioxide in the explosion vessel. Since the vapour pressure of carbon dioxide, at the temperature of the acetone, solid carbon dioxide mixture used for freezing out the water, is more than 40 mm. of mercury, this gas would escape with the hydrogen from the explosion vessel to be retained and detected in the liquid-air-cooled spiral.

We have no direct proof of the completeness of synthesis, but the hydrogen residues were sparked at different pressures and for varying periods of time without affecting the results. The measured volume of hydrogen left in the pipette at the end of a determination was usually removed by the mercury pump, but in experiments 7, 8 and 9 of series 4, it was transferred to the explosion vessel and

constituted the first hydrogen filling of the succeeding experiment.\* The results show no indication of an accumulating impurity.

The successful removal of water from the hydrogen residue was proved by the fact that the small phosphoric oxide tube between the explosion vessel and the pump showed no signs of deliquescence after four years' use.

*Accuracy of Volume, Pressure, and Temperature Measurements.*

Owing to the fact that all gas measurements were made in the same vessel under the same conditions, various possible errors in this category tend to cancel out.

*Volume errors.*—Since all volumes were measured in terms of a weight of mercury, an accuracy greater than necessary was readily secured. The only operation in which special care was needed to prevent a volume error was the setting of the meniscus to the point in the dead-space. The final adjustment was always made with a rising meniscus, and cohesion effects were minimised by tapping the glass or pinching the reservoir tubing. The probable limits of variation may be estimated from the concordance of the values obtained in calibrating the dead-space at the beginning of the research.

*Pressure errors.*—The vertical distance between the two glass points of the manometer was measured with a cathetometer when the system was in ice. The accuracy attainable was not very great because of distortion by the small bath round the dead-space, but from two measurements giving values 760.35 and 760.32 mm., respectively, it may be concluded that the distance was within a third of a millimetre of the normal barometric height. A deviation of 1 mm. alters the density ratio only by 1 part in 500,000, so that a difference of the above order is quite negligible.

The precision with which the mercury menisci could be set to the two points was certainly very high. The order of accuracy attainable was tested in the following way: the upper chamber of the manometer was viewed through a telescope fitted with a Hilger micrometer eye-piece, and the cross-wire was set on the point. The meniscus was then adjusted until the cross-wire appeared exactly tangential to it. On examination with the pocket lens which was used in making the settings, a distinct gap was detectable between the point and its mirror image. Assuming the limit of accuracy with a micrometer to be 0.01 mm., it was estimated that adjustment by means of the lens should be within 0.002 mm.

The effect of capillarity on the pressure measurement can be neglected, since in tubes of the diameter of the point chambers (16 mm.), even the absolute depressions are vanishingly small.

*Temperature errors.*—These were undoubtedly the limiting factors in the accuracy of the work. Several have already been discussed in detail in the course

\* At this stage of the research the bubble trapped in the dead-space was removed after expulsion of each pipette-full of gas, so that the final hydrogen filling was not contaminated with oxygen.



of the paper. They may be tabulated here conveniently under five heads, as errors due to :—

- (1) Length of time required for the gas in the pipette to cool to  $0^{\circ}\text{C}$ .
- (2) Variation in the temperature of the iced system on different occasions.
- (3) Rise in temperature in parts of the iced system before completion of setting.
- (4) Variation in temperature of exposed portion of manometer column.
- (5) Relative temperature change in the mercury in the manometer and dead-space below the level of the point.

Comment on the nature of the error under each head may be made as follows :—

(1) Systematic error, which was estimated in the first four series and eliminated in the fifth.

(2) Probably very small errors : the point was frequently tested by repeating a measurement on the following day, when results agreeing to within a few cubic millimetres could be obtained, provided that the pipette had been in ice for a sufficient length of time.

(3) Negligible errors : experiments prove that the system remained at  $0^{\circ}\text{C}$ . for a much longer period than was actually required for the setting.

(4) Small hap-hazard errors, estimated and corrected for in series 3 and 4 and eliminated in series 5.

(5) Small hap-hazard errors, except perhaps in series 5.

A very large proportion of the time occupied by this research was spent in investigating errors of temperatures and, although we have no reason to regard our final result as seriously affected by such errors, we are inclined to believe that if the whole of the measuring apparatus down to the point where the manometer joins the tubing below the dead-space had been in direct contact with melting ice, a better concordance would have been obtained.

One further point suggested itself as worth examination. With the measuring apparatus used only a small variation was possible in the volume of hydrogen taken for synthesis. In the first three series, where this variation was greatest, there is no indication of any connection between the quantity of hydrogen taken and the result. Of the thirty-two experiments considered, the mean of those sixteen in which the hydrogen excess was greatest agrees to 1 part in 100,000 with the mean of the other sixteen.

#### *The Atomic Weight of Hydrogen.*

If the ratio of the combining volumes is 2.00288 the atomic weight of hydrogen is 1.00772, when MORLEY'S values for the densities, namely, 0.089873 and 1.42900, are taken

Comparing our result with those of MORLEY and NOYES, we have :—

MORLEY . . . . 1·00762,

NOYES. . . . . 1·00787,

or, as estimated by CLARKE from the same data,

1·00783,

BURT and EDGAR . 1·00772.

Our value, therefore, is very nearly the arithmetic mean of the other two.

In 1914, a paper was published by GERMANN<sup>(14)</sup> containing a series of measurements of the density of oxygen.

As a mean of fifteen experiments he obtained the value 1·42906 for the weight of a normal litre. The gas was made by heating potassium permanganate, and, after passing over potash and phosphoric oxide, was liquefied and fractionated. This last precaution entitles his results to special consideration. Collecting the results obtained by MORLEY, RAYLEIGH, and GERMANN, we have :—

MORLEY (41 experiments) . . . . 1·42900

RAYLEIGH (16 experiments) . . . . 1·42904

GERMANN (15 experiments) . . . . 1·42906.

The arithmetic mean is 1·42903, but GERMANN, attaching rather greater weight to his own result, partly because his oxygen was liquefied and fractionated, and partly because of special precautions taken in measuring the pressure, proposes the figure 1·42905 as the most probable value on existing data. Further confirmation of the higher value is afforded by the work of SCHEUER<sup>(15)</sup>, who has recently obtained a result identical with GERMANN'S. The substitution of this value (1·42905) for MORLEY'S in the density ratio alters our atomic weight to 1·00769. It seems unlikely that any probable future alteration in the density ratio would bring our value as low as MORLEY'S or as high as NOYES', and we may conclude that the true value of the atomic weight of hydrogen lies very close to

1·0077.

Part of the expense of this work was defrayed by a Royal Society Grant which we desire to acknowledge here. We are indebted to Prof. DIXON for his continued interest in the research and for a number of helpful suggestions.

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