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On the Composition of Water by Volume

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IX. *On the Composition of Water by Volume.*

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In a preliminary note, "On the Composition of Water by Volume," presented to the Society in June, 1887, I remarked that up to that time we had no direct measurements of this important constant, except those of Gay-Lussac and Humboldt. The value they deduced from their experiments corresponded so far with the number I then gave as the most probable one, in that it required rather less than two volumes of hydrogen to one volume of oxygen. The results of my experiments, in spite of this coincidence, astonished me, for it was to be expected that as oxygen is more compressible than hydrogen (to say nothing of its coefficient of expansion), it would contain more molecules per unit volume than hydrogen, and, therefore, necessarily require more than two volumes of hydrogen for one volume of oxygen.

In a short note, published in "Nature," of March 8th, 1888, I announced that I had detected a most important, and hitherto unsuspected, source of error which had led to the consumption of oxygen, and this naturally accounted for the relatively small number for the hydrogen. This source of error lay in the use of a lubricant of a combustible nature, not because of its volatility, but because of its tending to form a greasy layer on the surface of the eudiometer, and which was, to a certain extent, burnt with each explosion in the eudiometer.

In the 'American Journal of Science,' for March and April, 1891, E. W. Morley gives an account of twenty experiments made with a very elaborate apparatus for preparing his gases, and with a measuring apparatus practically the same as I described in my former paper, except that he explodes his gases in his measuring vessel, which is a wide cylindrical tube, thus necessitating microscopical readings of levels and heights, which he claims he *can* make with accuracy to $\frac{1}{500}$th of a millimetre, and that they actually were made to $\frac{1}{200}$th in his experiments. How this can be done satisfactorily after the explosion and the accumulation of water as the result of it, must astonish all who have tried to measure heights of mercury in glass tubes with accuracy. No mention is made as to where the water was expelled to, or how it could be got rid of.

28.8.93

Throughout I have endeavoured to use the simplest apparatus possible and to prepare the gases themselves from only the purest materials, and those of the simplest composition that I could find, so that no purification should be required and all unnecessary contact with other chemical substances avoided, to work with an apparatus of glass throughout, so that no diffusion could take place, and, finally, so to work, that with a given amount of materials, I might compare the gas given off in the first fractions continuously to the last fractions, and thus endeavour to detect any possible impurity, either by variation of the ratio, or by actual observation from the residual gas.

My new experiments are divided primarily into two series, as two different forms of measuring vessel were used, one of the type described in my former paper in which both pressure and volume had to be measured, in the later form the pressure only required measurement, the volume being kept constant. This tended greatly to increase the accuracy of measurements, both because it lessened the number required, and, also, even if the total volume were as much as one cubic centimetre wrong, it would make no appreciable error in the ratio found, as all were measured in the same vessel. This will be obvious on slight consideration of the conditions.

The hydrogen required was obtained from the following sources :—

1. Electrolysis of dilute sulphuric acid
2. ,, ,, hydrochloric acid

Using in both cases a platinum electrode for the hydrogen to be evolved from, and amalgamated zinc for the absorption of the oxygen.

3. Action of steam on sodium.
4. Palladium hydride, formed by passing hydrogen from sources 2 and 3 over palladium at the ordinary temperature.

The oxygen was prepared from—

1. Re-crystallized potassium chlorate, sometimes with the addition of a little pure sodium hydrate (from sodium).
2. Mercuric oxide.
3. Silver oxide.
4. Silver oxide and barium sulphate.

Before using either the sulphuric or hydrochloric acid, after the necessary dilution it was boiled with some zinc amalgam for an hour or an hour and a-half to get rid of all dissolved gases, and then added to the generating vessel while hot.

The sodium used was such as had never been at any time in contact with paraffin or naphtha, and was obtained direct from the manufacturers. It was, before use, fused in a clean iron ladle and cast in an iron mould. It was always heated up till the anhydrous oxide fused so that the metal could be poured quite free from all scum.

The palladium was used in the form of thin sheets and was ignited in a current of pure air for some time to a full red heat, to remove all traces of greasy matter which it might have acquired during the rolling.

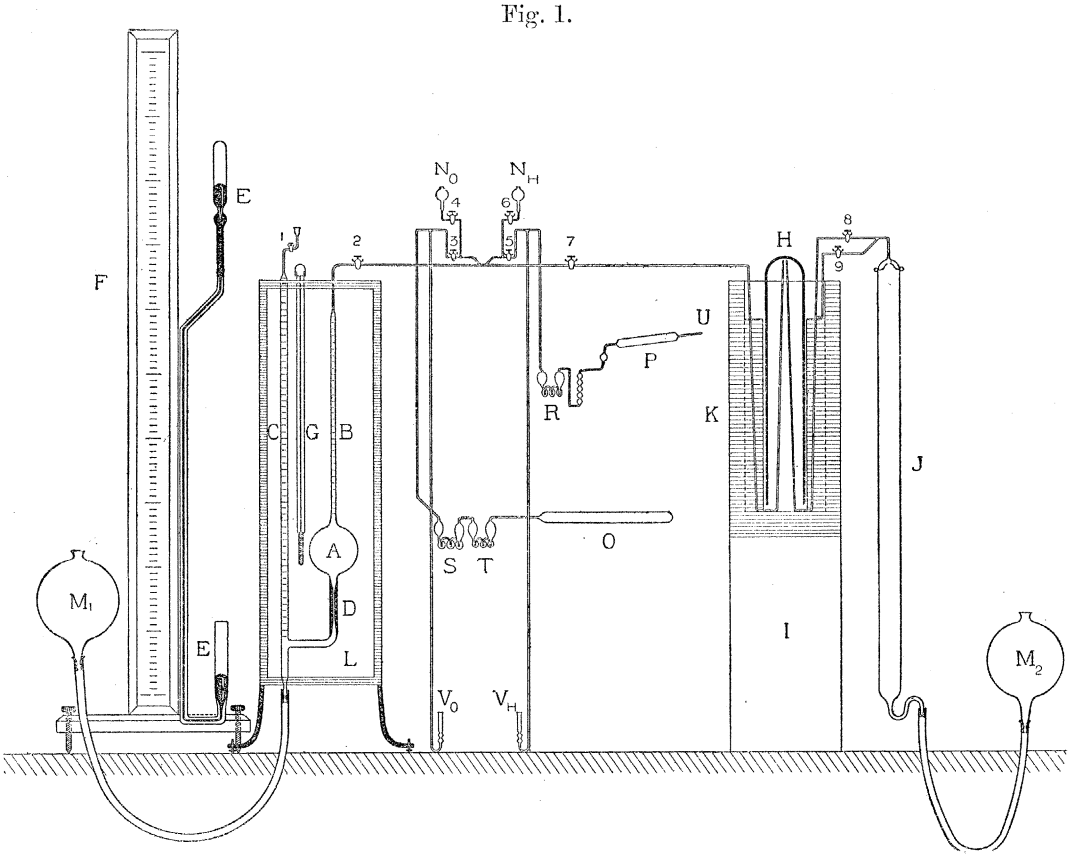
The potassium chlorate was very carefully recrystallized and fused in a platinum dish before use, and in the later experiments a small quantity of pure sodium hydrate made from the metal was added, to prevent, if possible, the evolution of small quantities of chlorine.

Very few experiments were made with mercuric oxide as the temperature required for its decomposition was rather high for soft German glass to stand with safety. Two samples were used, the first of which at first gave off some carbon dioxide, so a sample was prepared with great care from the metal, by first converting it into mercurous chloride, then into mercuric chloride, and finally into the oxide which, after thorough washing, was moistened with pure soda solution and dried. The soda effectually retained any carbon dioxide in this sample, but the repeated fractures of the tubes containing the mercuric oxide led me to abandon its use. Silver oxide seems to be by far the most convenient source of pure oxygen, and has been used in all the later experiments. It was made at first by precipitating silver nitrate solution by means of pure barium hydrate, washing free from barium nitrate, and then drying rapidly on the water bath. The first sample prepared had absorbed so much carbon dioxide from the air during its drying that it rendered worthless several experiments. The second sample was, therefore, prepared by the same reaction, but was very carefully washed with thoroughly boiled water in closed flasks, and dried, *in vacuo*, in vessels with ground glass stoppers, free from all grease. Thinking that nitrates might still adhere to the precipitate as STAS showed they were so prone to do, a quantity of silver sulphate was precipitated with barium hydrate, so that a mixture of silver oxide and barium sulphate was obtained and used after drying as above, and worked extremely well. The silver oxide used in the last experiments, and which has given gas in which no impurity, however small, can be detected, was prepared from silver sulphate and excess of pure potassium hydrate, and after washing, giving another treatment with some fairly dilute potassium hydrate solution by boiling for half an hour or so, again washing with water well boiled and just coloured with potassium permanganate, till free from sulphates, then allowed to settle, and the clear liquid decanted and a little pure soda added (as was done always with the silver oxide) and the oxide dried, *in vacuo*, at 110° C.

Fig. 1 shows the apparatus as used in the later series of experiments, and is drawn to scale as regards the size of the principal parts; the tubes are merely elongated so as to show their connection clearly. The scale F, which is 1 metre in length, indicates the size of the various parts.

The constant volume is contained between a mark on the narrow tube above B, and a similar mark about the middle of the tube D. The internal diameter of these tubes, which are of strong Sprengel tubing, is almost exactly 2 millims., as they

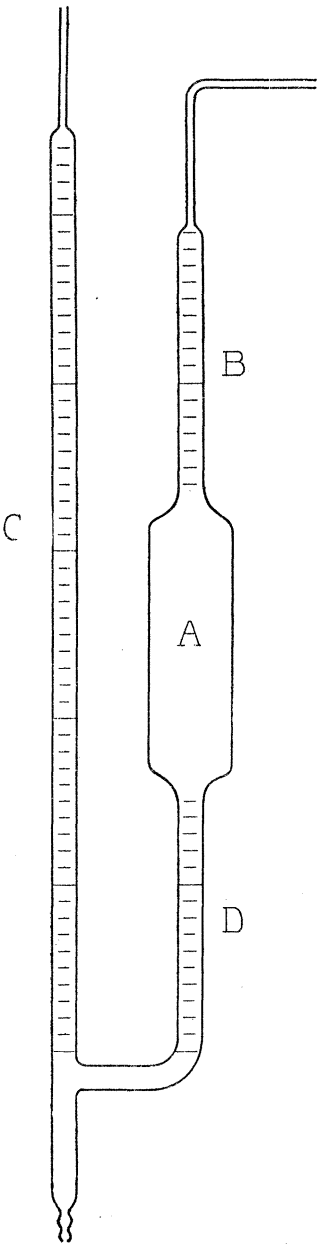
Fig. 1.



A, Bulb for measuring volume of gas.
B, Graduated tube calibrated for measuring residual volumes.
C, Manometer tube.
D, Narrow tube with mark.
EE, Barometer.
F, Standard metre scale divided into millimetres.
G, Thermometer graduated in $\frac{1}{50}^{\circ}$ C.
H, Jar for mixing gases before explosion.
I, Wooden block to support mercury trough.
J, Tube for exploding gases under diminished pressure.
K, Mercury trough of wood, varnished.
L, Water tank, for maintaining temperature steady, with stirrer and levelling screws (contents = about 14 litres).
M_1, M_2, Mercury reservoirs.
N_0, N_H, Small mercury reservoirs for driving gases out of tubes into A and B.
O, Tube, with silver oxide.
P, Tube, with palladium.
R, S, Geissler's bulbs, with pure water.
T, Geissler's bulbs with pure sodium hydrate (from sodium and water).
U, Tube for hydrogen to pass in at from generating vessel, but sealed up when palladium hydride is used.
V_0, V_H, Gauges and safety valves with mercury covered with water for oxygen and hydrogen.
1, 2, 3, 4, 5, 6, 7, 8, and 9, safety taps with syrupy phosphoric acid.

contain ·0395 grm. of mercury per millim. length. The capillarity correction, due to the difference in diameter between the manometer tube C and the tube D, amounted to 3·9 millims., and between B and C to ·1 millim. Temperatures were read to

Fig. 2.



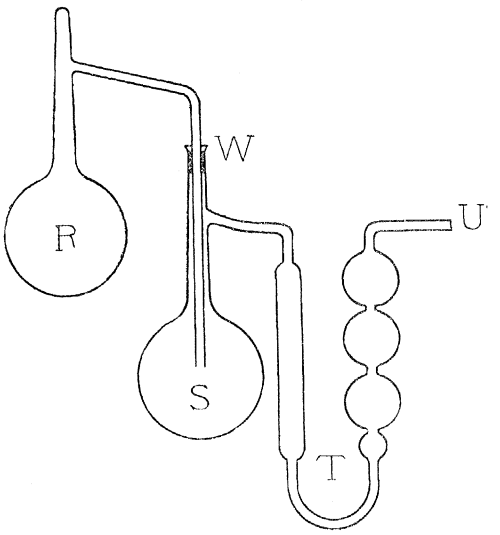
A, Bulb for measuring gases.
B, Tube for measuring residues.
C, Manometer tube.
D, Calibrated tube.

$\frac{1}{100}$th of a degree centigrade in the later series of experiments, but only to $\frac{1}{10}$th previously, by means of the thermometer G, after thorough mixture by means of a stirrer not shown in the figure. All heights were referred to the standard scale F,

both those of the barometer EE, as well as those in C and D, by means of a catheto-meter Z (fig. 4) constructed specially for the purpose. This consisted essentially of a vertical steel axis carrying two horizontal telescopes with cross wires, which were set one at each level, and then the axis rotated to the scale F, and the heights registered to ·1 millim. This method was necessitated from the want of steadiness in the floor of the room in Durham School Laboratory, where the majority of the experiments were carried out. The same arrangement (which is very convenient as well as accurate) was also used in the later experiments which were carried out under more favourable conditions in the gas analysis room of the Cambridge University Chemical Laboratory.

Fig. 2 shows the earlier form of measuring vessel used when the varying pressures and volumes were both measured. The tubes B, C, and D were all of the same diameter, so that no capillarity corrections were required.

Fig. 3.

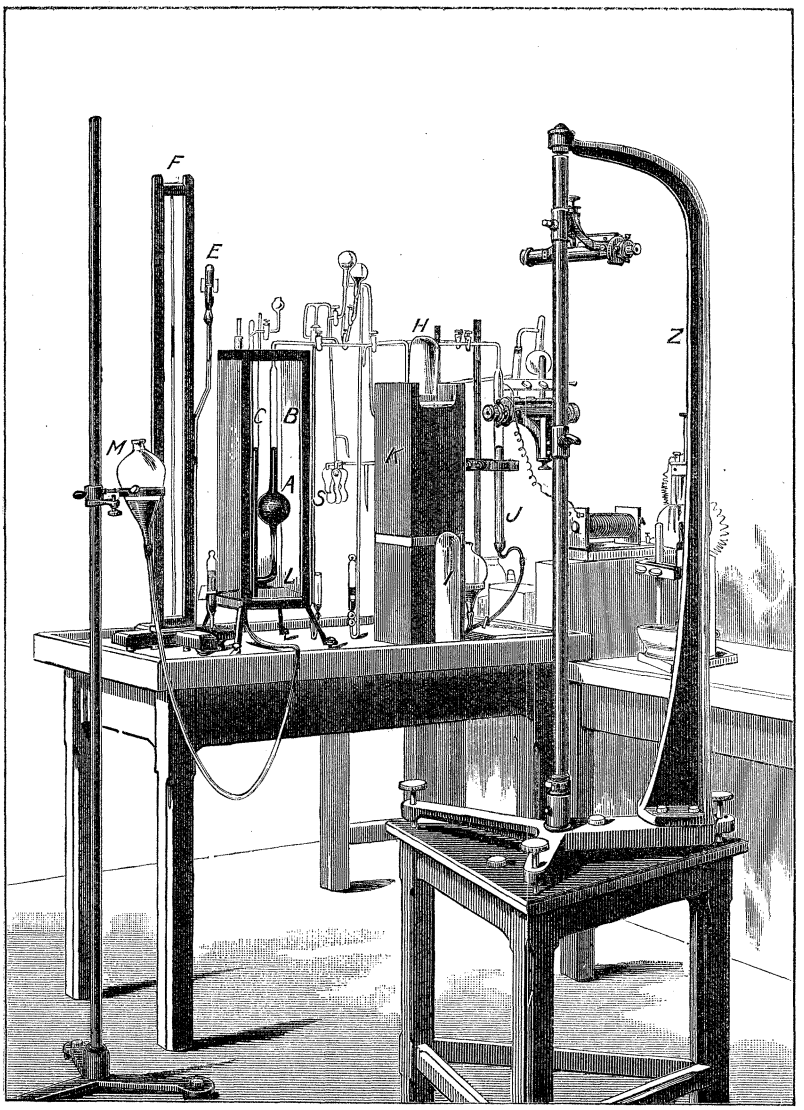


R, Flask for water to be boiled.
S, Flask for sodium.
T, Washing tube, with *very dilute* hydrochloric acid.
U, Exit tube for hydrogen, sealed to U (fig. 1) when in use.
W, Small india-rubber stopper.

Fig. 3 shows the simple apparatus employed for the preparation of hydrogen from sodium by acting on it with steam. When it was used the end of the tube U was sealed to the tube U (fig. 1), which contained palladium in its wider part, P. The only india-rubber connection is at W, where there is a stopper of that material, but diffusion through this was practically impossible to any injurious extent, as the space between the tubes was very narrow and the stopper was 6 to 8 millims. long, and after setting up the apparatus it was sealed over with paraffin containing enough vaseline to prevent its cracking, whilst it allowed of its being easily shaken.

Before beginning a series of experiments the apparatus was carefully exhausted by filling A, B, and C with mercury, as well as the tubes leading to the bulbs N_0 and N_H, by having the taps open, and by raising the reservoir M_1, closing all the taps 1, 3, 4, 5, 6, and 7, then lowering M_1 and opening tap 5, which opened communication with the

Fig. 4.



General view of apparatus from front, showing cathetometer.

hydrogen generating apparatus, M_1 being lowered until the mercury fell to D. Then tap 5 was closed and M_1 raised till the air was under more than atmospheric pressure, tap 6 opened and the air inside the apparatus expelled by forcing mercury up into the bulb N_H. This was repeated till no more air could be thus pumped out. A little hydrogen was now generated and pumped out, and the process repeated twice,

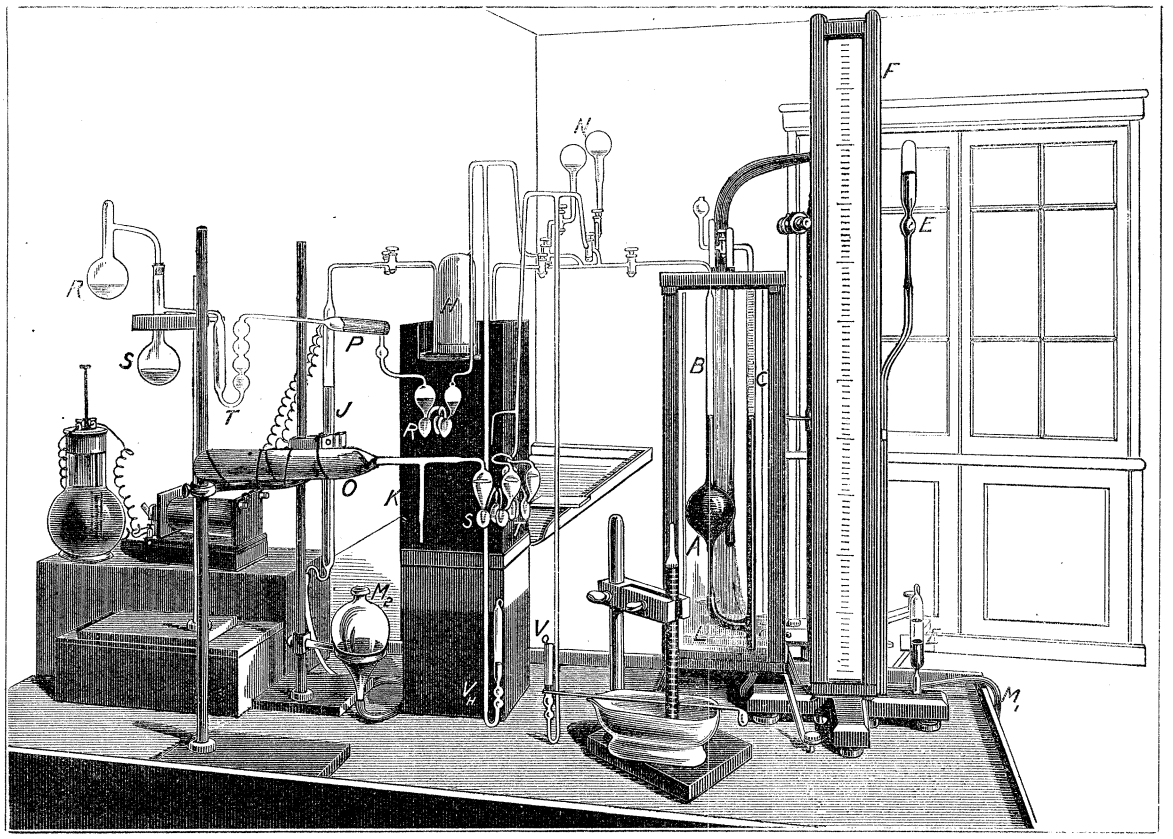
when the gas now generated might be regarded as absolutely free from admixed air. The same was repeated with the oxygen apparatus. It was easy to arrange before raising the reservoir M_1, so that there was no "untraversed space" by filling the tubes with mercury from the bulbs N_H and N_0.

The mode of using the apparatus will be best understood by the description of an actual experiment.

Oxygen was evolved from the oxide of silver in O by heating till it was almost equal in pressure to that of the external atmosphere, as indicated by the gauge and safety valve V_0, when taps 3 and 2 were opened, M_1 being about the level indicated, and the heating continued till B and A were almost filled to the mark on D, when the flame was extinguished and tap 2 shut, and then mercury was run into the fine tubes from N_0, so that it passed the tap 4 a short distance, that tap was then closed, and 2 opened carefully, so that the gas in the tube was driven into the calibrated space, and the mercury was stopped at the mark by closing taps 2 and 4. Tap 1 on the manometer was opened generally before filling the volume with gas, as one could judge better of the exact pressure by so doing. All being now ready for the final adjustments the mercury reservoir M_1 was raised or lowered by a fine screw on its holder till the mercury came exactly to the mark on D, and, after thorough stirring of the water in L, left for a quarter of an hour, and the adjustments looked to, and then repeatedly stirred, and readings taken in about half an hour after filling if the volume was quite steady. The temperature and barometric pressure were then read. Closing tap 1 on the manometer, and opening taps 2 and 7, the oxygen was next expelled into the jar H (which had been completely filled with mercury) by raising M_1 sufficiently. When all the gas has been thus driven over into H, tap 7 is closed, M_1 is returned to its former position, tap 1 opened again, and the same operation repeated twice for the hydrogen. By opening tap 8 quantities of the mixed gases are drawn over into the explosion-tube J, and there caused to combine under diminished pressure by passing a spark, and this continued till nearly all has combined, when what remains in the explosion-tube is passed back into the jar H, and mixed and drawn back again, and exploded as before. A small residue of one or other gas in excess now remains. This was now passed into H, but the water formed was expelled by closing tap 8 and opening tap 9 when the water flowed out on to the surface of the mercury; it was easy to arrange so that nothing but the gaseous residue was driven into H, from which it was now drawn into B, and its volume accurately determined. After measurement it was again expelled into H, and, if hydrogen, some oxygen in excess was drawn into B, and measured as before, passed into H, and the mixture exploded, and the new residue, measured as before, again passed back into H, and then into J, and expelled into an absorption-tube, measured and treated first with pure potassium hydrate solution to estimate any carbon dioxide, and then with solution of pyrogallol to absorb the oxygen and determine the amount of impurity, if any, present. The final residue gave thus a *maximum* value for any impurity which

existed as permanent gas, and might be either nitrogen, carbon monoxide, or hydrogen which had escaped combination in the relatively large excess of oxygen which usually was present in the final explosion. In all probability this is the real explanation of the permanent gas found, as the apparent impurity was almost always larger when the excess of oxygen was large than when it was small and was roughly in proportion

Fig. 5.



General view of apparatus from back, with barometer turned round.

to it. This will be easily seen on inspection of the table of results. Taking a few examples in Series IIc, we have

Residue.	Impurity.
10·2	·3
28·9	·5
41·1	·8

There are, no doubt, exceptions to this, but it seems to hold generally that the larger the oxygen residue the larger the impurity found as shown above. The other explanation which might account for the same thing is, that carbon monoxide might be given off easily (from the pyrogallol) to the small extent usually found,

·3 corresponding to an impurity of about $\frac{1}{34,000}$.

1·0 ,, ,, ,, $\frac{1}{10,000}$.

The impurity was called 0 when the impurity was less than ·1 = about $\frac{1}{140}$ of a cubic centimetre, or = $\frac{1}{100,000}$ of the volume of the gases used.

The gases were measured moist, and the surface of the measuring vessel was kept thoroughly moist by washing the apparatus with distilled water in the evening and expelling the water, and then leaving it full of mercury and expelling what had risen through the night, so that no appreciable error was introduced from water present as such in the vessel. One advantage of working with moist gases and vessels with moist surfaces is that the gases can be so completely got rid of, none remaining as a film. When both manometer and measuring vessel were completely filled with mercury and the reservoir lowered so as to produce a Torricellian vacuum in both, it was usual for the mercury to remain for some time 300 to 400 millims. higher in the measuring vessel than in the manometer, the mercury not leaving the moist glass till a trace of gas from the stopcock 2 set it off.

The following experiments taken at random show the modes of measurement and calculation adopted.

August 24th, 1889. Experiment XXXIV., Series If. Apparatus with Variable Volume.

Oxygen from mercuric oxide—

Volume 50·0 = 3881·0. Temperature = 15·4° C.

	millims.		millims.
Height of mercury in manometer tube on scale =	71·3	on cathetometer =	10·0
,, ,, volume tube on scale . =	71·6	,, =	10·3
Correction . . . . . =	−0·3	=	−0·3

	millims.
Barometer 777·1 − 26·0 . . . . . =	751·1
Pressure of aqueous vapour . . . . =	13·0

∴ Pressure of oxygen = 751·1 − ·3 − 13·0 . . = 737·8

Hydrogen from electrolysis of dilute hydrochloric acid—

Volume 45·3 = 3819·6. Temperature = 15·35° C.

	millims.
Height of mercury in manometer tube on scale	118·5
,, ,, volume tube on scale	118·5
Correction . . . . . =	·0
Barometer 777·4 − 25·8 . . . . . =	751·6
Pressure of aqueous vapour . . . . . =	13·0

∴ Pressure of hydrogen = 751·6 − 13·0 . . . . . = 738·6

Hydrogen as before—

Volume 45·6 = 3823·5 Temperature = 15·4° C.

	millims.	millims.
Height of mercury in manometer tube on scale	= 115·8	on cathetometer = 7·1
,, ,, volume tube on scale .	= 115·5	,, = 6·8
Correction	= + 0·3	+ 0·3

millims.

Barometer 777·6 − 25·7 . . . . . = 751·9
Pressure of aqueous vapour . . . . = 13·0

Pressure of hydrogen = 751·9 + ·3 − 13·0 . = 739·2

Residue (of oxygen)—

Volume 8·6 = 56·5 Temperature = 15·4° C.

	millims.	millims.
Height of mercury in manometer tube on scale	= 491·9	on cathetometer = 10·0
,, ,, volume tube on scale .	= 484·7	,, = 2·8
Correction	+ 7·2	+ 7·2

millims.

Barometer = 777·7 − 25·4 . . . . = 752·3
Pressure of aqueous vapour . . . . = 13·0

Pressure of gas = 752·3 + 7·2 − 13·0 . . . = 746·5

On analysis of residue ·6 of unabsorbable gas remained after treatment with potassium hydrate and pyrogallol; no carbon dioxide being detected.

Total oxygen volume reduced to 0° C. and 760 millims. pressure, becomes

millims.

$$3881{\cdot}0 \times \frac{737{\cdot}8}{760{\cdot}0} \times \frac{273{\cdot}0}{288{\cdot}4} \quad . \quad . \quad . \quad . = 3566{\cdot}4$$

Residual volume

$$56{\cdot}5 \times \frac{746{\cdot}5}{760{\cdot}0} \times \frac{273{\cdot}0}{288{\cdot}4} \quad . \quad . \quad . \quad . = 52{\cdot}5$$

·6

Oxygen in residue . . . = 51·9

Hydrogen volumes become

$$3819{\cdot}6 \times \frac{738{\cdot}6}{760{\cdot}0} \times \frac{273{\cdot}0}{288{\cdot}35} \quad . \quad . \quad . \quad . = 3514{\cdot}4$$

$$3823{\cdot}5 \times \frac{739{\cdot}2}{760{\cdot}0} \times \frac{273{\cdot}0}{288{\cdot}4} \quad . \quad . \quad . \quad . = 3520{\cdot}2$$

Total hydrogen volume . = 7034·6

Assuming the impurity to be equally distributed between the two gases we have

7034·2 of hydrogen unite with 3514·3 of oxygen,

or

2·0016 ,, ,, 1 ,,

If all impurity be in oxygen, we get the ratio

2·0019 : 1,

and if all in the hydrogen,

2·0014 : 1.

For the experiment with the apparatus arranged as in fig. 1, I have chosen an experiment in which the hydrogen measured is in excess of the oxygen. The constant volume of the apparatus = 3826·3 grms. of mercury.

April 7th, 1892. Experiment XXXIII., Series IIE.

Oxygen from silver oxide (from silver sulphate and potassium hydrate)—

	millims.
Height of mercury in manometer tube	= 154·5
,, ,, volume tube	= 145·4
Correction	+ 9·1
Pressure of aqueous vapour	= 13·4
Capillarity correction	= 3·9
	− 17·3
Barometer 790·6 − 29·1	= 761·5
Pressure of oxygen = 761·5 + 9·1 − 17·3	= 753·3

Temperature = 15·92° C.

Hydrogen from palladium hydride—

	millims.
Height of mercury in manometer tube	= 154·6
,, ,, volume ,, ...	= 145·3
Correction	+ 9·3
Pressure of aqueous vapour	13·5
Capillarity correction	3·9
	− 17·4
Barometer, 790·7 − 29·0	= 761·7
Pressure of hydrogen = 761·7 + 9·3 − 17·4	= 753·6

Temperature = 15·97° C.

Hydrogen, second volume—

	millims.
Height of mercury in manometer tube.	= 155·0
,, ,, volume ,, ...	= 145·5
Correction	+ 9·5
Pressure of aqueous vapour	= 13·2
Capillarity correction	= 3·9
	— 17·1
Barometer, 791·7 — 28·0.	= 763·7
Pressure of hydrogen = 763·7 + 9·5 — 17·1	= 756·1

Temperature, 15·70° C.

The oxygen volume and the first hydrogen volume were measured in the afternoon, the second hydrogen volume in the evening. This is why there is such a difference in the temperature and barometric pressure in the latter case.

Volume of residue, 6·5 = 15·3.

	millims.
Height of mercury in manometer tube	= 127·1
,, ,, volume ,, ...	= 562·7
Correction	— 435·6
Pressure of aqueous vapour	= 13·3
Capillarity correction	= ·1
	= — 13·4
Barometer, 791·4 — 28·2.	= 763·2
Pressure of hydrogen = 763·2 — 435·6 — 13·4 . . .	= 314·2

Temperature, 15·80° C.

These volumes, when reduced to 0° C. and 760 millims. pressure, become—

For the oxygen	$3826{\cdot}3 \times \frac{753{\cdot}3}{760} \times \frac{273{\cdot}0}{288{\cdot}92} = 3396{\cdot}4$
,, hydrogen	$3826{\cdot}3 \times \frac{753{\cdot}6}{760} \times \frac{273{\cdot}0}{288{\cdot}97} = 3397{\cdot}0$
,, ,, . . .	$3826{\cdot}3 \times \frac{756{\cdot}1}{760} \times \frac{273{\cdot}0}{288{\cdot}70} = 3411{\cdot}5$
Total hydrogen volume	6808·5
For the residue (hydrogen)	$15{\cdot}3 \times \frac{314{\cdot}2}{760} \times \frac{273{\cdot}0}{288{\cdot}80} = 5{\cdot}98 = 6{\cdot}0$
Hydrogen used	= 6802·5

In order to analyse the residue it was passed into the jar H, and a quantity of oxygen drawn from the oxygen apparatus and measured in B, in exactly the same way as the residue; then both were mixed and again measured, giving the corrected volume 14·8 for the volume before explosion. After explosion 5·9 remained, and on treatment as in the other experiment described above, first with potassium hydrate and then with pyrogallol, no carbon dioxide could be detected, and all the gas was absorbed with the exception of a minute bubble of as nearly as possible 1 millim. in diameter. The residue of 5·98 was therefore pure hydrogen, being confirmed by the analysis $\frac{2}{3}(14{\cdot}8 - 5{\cdot}9) = 5{\cdot}93$.

The combining volumes are therefore—

$$6808{\cdot}5 - 6{\cdot}0 = 6802{\cdot}5 \text{ of hydrogen with } 3395{\cdot}8 \text{ of oxygen,}$$

or—

$$2{\cdot}0028 \quad ,, \quad ,, \quad 1{\cdot}0 \quad ,,$$

In order to determine the degree of accuracy with which the volumes of the gases might be determined, the same volume of gas was repeatedly measured during a fortnight, so as to have it under much greater variations of temperature and pressure than ever occurred during any experiment. The following corrected values were found :—

3279·4	3279·7
3280·3	3279·4
3280·6	3279·8
3280·1	

giving as a mean 3279·9, with the probable error on a single observation of $\pm$ ·3.

These are highly satisfactory when one remembers that ·1 millim. in pressure corresponds to about ·5 in volume, and ·01° C. to rather more than ·1.

In the following experiments the volumes of the gases measured and the residues are given reduced to 0° C. and 760 millims. pressure. They are divided into two primary series, corresponding to the two forms of measuring vessel employed; and these are again divided into sub-series, according to the sources of the oxygen and hydrogen.

All experiments are given which were completed, except a very few, which were contaminated by such large quantities of impurity, such as carbon dioxide (as in the first experiments with oxygen from mercuric and argentic oxide), which rendered the determination of the ratio impossible or very unsatisfactory. The first seven experiments of Series Ia were also omitted, as they were rendered practically valueless, as were all those formerly published, owing to the use of vaseline as a lubricant for the glass taps. Experiments VIII. and IX. show how this source of error was detected, and on using syrupy phosphoric acid as the lubricant, and safety taps with cups,

carbon dioxide vanished as an ordinary impurity, and the total impurity fell away to a very small amount indeed.

In the following Tables the following data are given :—

Column A gives the number of the experiment.
" B " " date on which it was performed.
" C " " hydrogen volume as measured and corrected to 0° C + 760 millims.
" D " " oxygen " " " " "
" H " " hydrogen in residue.
" O " " oxygen " "
" N " " impurity, determined by potash and pyrogallol.
" R " " ratio of combining volume of hydrogen to that of oxygen when the impurity was assumed to be equally distributed in both gases.
" S " " ratio of combining volume of hydrogen to that of oxygen when the impurity was supposed to be all in the hydrogen.
" T " " source of the hydrogen.
" W " " " " oxygen.

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Series Ia.

A.	B.	C.	D.	H.	O.	N.	R.	S.	T.	W.
	1887									
VIII.	August 30 . .	6909·4	3451·2	38·9	..	7·9 CO_2 7·2 CO ·7 N_2	..	..	Electrolysis of H_2SO_4	$KClO_3$
IX.	,, 30 . .	6882·2	3414·2	74·9	..	5·3 CO_2 2·6 CO 3·6 N_2	..	..	Electrolysis of H_2SO_4	$KClO_3$

Series Ib.

	1888									
X.	January 11 . .	Lost some hydrogen after exploding some.								
XI.	,, 16 . .	Burst eudiometer								
XII.	,, 17 . .	7657·2	3798·7	63·3	..	·8	1·9991	1·9989	Electrolysis of H_2SO_4	$KClO_3$
XIII.	,, 17 . .	7561·4	3777·9	19·9	..	·7	1·9962	1·9961		
XIV.	,, 18 . .	Burst eudiometer								

Series Ic.

XV.	April 30 . . .	Oxygen flask cracked and much air in oxygen.								
XVI.	,, 30 . . .	7177·4	3609·7	..	19·0	·8	1·9989	1·9987	Electrolysis of H_2SO_4	$KClO_3$
XIX.	May 2	7042·7	3605·8	..	83·0	1·2	1·9992	1·9989		

Series Id.

XX.	May 2	6946·8	3582·9	..	111·8	1·2	2·0013	2·0010	..	Old $KClO_3$
XXI.	,, 5	7144·0	3657·1	..	83·4	2·4	1·9990	1·9984	Electrolysis of HCl	New $KClO_3$
XXII.	,, 5	7247·2	3654·1	..	27·1	·6	1·9981	1·9980		
XXIII.	August 31 . .	7171·1	3613·0	..	19·4	·5	1·9958	1·9956		

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Series Ie.

A.	B.	C.	D.	H	O.	N.	R.	S.	T.	W.
	1889.									
XXV.	August 8 . .	6875·5	3533·0	..	93·5	1·7	1·9990	1·9985	..	$KClO_3$
XXVI.	,, 13 . .	7014·7	3558·0	..	49·6	3·2	1·9994	1·9985		
XXVII.	,, 14 . .	6964·9	3535·6	..	56·8	1·7	2·0021	2·0016		
XXVIII.	,, 14 . .	6972·3	3544·6	..	61·6	3·2	2·0018	2·0009	Electrolysis of HCl	$KClO_3$+NaHO
XXIX.	,, 15 . .	7028·0	3562·9	..	53·8	·8	2·0028	2·0025		
XXX.	,, 16 . .	6989·7	3528·1	..	35·9	·4	2·0015	2·0013		

Series If.

XXXI.	August 22 . .	6963·1	3490·9	28·9	..	16·3 CO_2 19·9 CO 3·2 N_2	2·0014	2·0005		
XXXII.	,, 23 . .	7004·3	3569·7	..	70·2	·8	2·0015	2·0013	Electrolysis of HCl	HgO
XXXIII.	,, 23 . .	6981·8	3538·8	..	48·8	·8	2·0006	2·0003		
XXXIV.	,, 24 . .	7034·6	3566·4	..	51·9	·6	2·0016	2·0014		
XXXV.	,, 24 . .	7041·6	3603·5	..	86·2	·8	2·0019	2·0017		
XXXVI.	,, 27 . .	7070·1	3609·7	..	74·0	·9	1·9996	1·9994	Pd_2H	HgO
XXXIX.	,, 30 . .	6968·2	3622·9	..	144·3	1·1	2·0032	2·0028	Pd_2H	Ag_2O

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Series IIA.

A.	B.	C.	D.	H.	O.	N.	R.	S.	T.	W.
	1890.									
I.	January 20 . .	6883·7	3461·4	..	25·3	·3	2·0033	2·0033		
II.	„ 20 . .	6860·4	3513·6	..	88·6	·4	2·0030	2·0029	Pd_2H	Ag_2O
III.	„ 21 . .	6940·1	3523·4	..	54·5	·3	2·0007	2·0006		
IV.	„ 21 . .	6741·6	3433·8	..	66·6	·2	2·0021	2·0021		
VI.	May 26 . . .	6821·9	3499·5	..	93·9	·9	2·0031	2·0028	$Na+H_2O$	New Ag_2O
VII.	June 3	6750·8	3431·7	..	58·3	1·2	2·0012	2·0008	„	
VIII.	„ 5	6760·6	3393·2	..	20·3	·3	2·0043	2·0043	„	Ag_2O
IX.	„ 7	6833·6	3449·2	..	35·8	·2	2·0019	2·0019	Pd_2H	
X.	„ 9	6734·6	3399·4	..	38·2	·5	2·0036	2·0035		
	1891.									
XII.	August 11 . .	6745·3	3388·7	..	16·4	·5	2·0003	2·0001	Pd_2H	
XIII.	„ 11 . .	6793·9	3425·3	..	25·7	·5	1·9985	1·9983		
XIV.	„ 13 . .	6792·8	3429·2	..	36·1	·3	2·0019	2·0019		
XV.	„ 13 . .	6726·2	3430·8	..	70·45	·35	2·0017	2·0016	$Na+H_2O$	
XVI.	„ 14 . .	6746·4	3404·1	..	35·8	·3	2·0029	2·0028		Ag_2O
XVII.	„ 14 . .	6724·4	3378·4	..	23·7	·3	2·0044	2·0044		
XVIII.	„ 15 . .	6669·0	3342·8	..	13·9	·1	2·0033	2·0033		
XIX.	„ 15 . .	6660·0	3330·8	..	3 3	·0	2·0015	2·0015	Pd_2H	
XX.	„ 17 . .	6835·0	3421·4	..	4·3	·1	2·0002	2·0002		
XXI.	„ 17 . .	6821·4	3414·2	..	3·5	·3	2·0000	2·0000		

Series IIB.

I.	November 21 .	6691·5	3371·1	..	36·5	·9	2·0067	2·0064		
II.	„ 21 .	6643·8	3335·2	..	26·0	1·2	2·0076	2·0073		
III.	„ 24 .	6721·1	3378·7	..	22·9	·7	2·0028	2·0026		
IV.	„ 26 .	6717·2	3369·1	..	13·0	·4	2·0015	2·0014	$Na+H_2O$	$Ag_2O+BaSO_4$
V.	„ 26 .	6677·1	3365·0	..	32·2	·7	2·0034	2·0032		
VI.	„ 28 .	6715·1	3373·6	..	17·9	·4	2·0011	2·0010		
VII.	December 5 . .	6665·5	3328·7	..	2·0	·2	2·0036	2·0036		

PHILOSOPHICAL TRANSACTIONS OF THE ROYAL SOCIETY A MATHEMATICAL, PHYSICAL & ENGINEERING SCIENCES

Series IIc.

A.	B.	C.	D.	H.	O.	N.	R.	S.	T.	W.
	1891.									
VIII.	December 7 . .	6475·8	3247·0	..	7·6	·5	1·9991	1·9989	Pd_2H	$Ag_2O+BaSO_4$
X.	„ 8 . .	6714·2	3367·0	..	2·5	6·3	1·9993*	..		
	1892.									
XII.	February 23 . .	6647·4	3329·2	..	4·7	·3	1·9995	1·9994	Pd_2H	$Ag_2O+BaSO_4$
XIII.	„ 24 . .	6715·0	3379·6	..	28·9	·5	2·0040	2·0039		
XIV.	„ 27 . .	6805·3	3409·7	..	10·2	·3	2·0019	2·0018		
XV.	March 1 . . .	6784·7	3418·1	..	30·6	·3	2·0029	2·0028		
XVI.	„ 2 . . .	6803·3	3420·5	..	24·4	·4	2·0032	2·0031		
XVII.	„ 3 . . .	6873·5	3453·2	..	18·0	·4	2·0009	2·0008		
XVIII.	„ 4 . . .	6848·2	3462·0	..	41·1	·8	2·0019	2·0016		
XIX.	„ 10 . . .	6853·5	3429·0	..	5·9	·7	2·0021	2·0019		

Series IId.

XX.	March 28 . . .	6655·0	3344·4	..	23·2	·3	2·0038	2·0037	$Na+H_2O$	New Ag_2O
XXI.	„ 30 . . .	6905·2	3461·7	..	15·7	·1	2·0038	2·0038	New $Na+H_2O$	
XXII.	„ 30 . . .	6890·5	3455·9	..	15·0	·0	2·0025			
XXIII.	„ 31 . . .	6871·4	3452·2	..	20·8	·0	2·0025			
XXIV.	„ 31 . . .	6855·7	3430·2	..	6·5	..	2·0024			

Series IIe.

XXV.	April 1 . . .	6863·8	3443·8	..	15·4	·3	2·0020	2·0019	Pd_2H	Ag_2O
XXVI.	„ 1 . . .	6870·0	3432·9	..	2·1	·0	2·0024			
XXVII.	„ 2 . . .	6870·1	3439·7	..	9·2	·0	2·0026			
XXVIII.	„ 4 . . .	6848·7	3422·1	..	2·9	·0	2·0030			
XXIX.	„ 4 . . .	6792·5	3386·6	13·5	..	·0	2·0022			
XXX.	„ 5 . . .	6809·2	3399·5	1·5	..	·0	2·0025			
XXXI.	„ 5 . . .	6793·9	3399·6	..	7·7	·0	2·0029			
XXXII.	„ 6 . . .	6789·6	3389·5	2·9	..	·0	2·0023			
XXXIII.	„ 7 . . .	6808·5	3396·4	6·0	..	·0	2·0028			
XXXIV.	„ 8 . . .	6793·1	3395·8	..	2·1	·0	2·0017			
XXXV.	„ 8 . . .	6786·5	3395·0	..	5·4	·0	2·0022			
XXXVI.	„ 9 . . .	6814·8	3411·9	..	9·3	·0	2·0028			

* Impurity all in oxygen.

The experiments in Series I. were all made in the apparatus with variable volume.

Series Ia.

Only two experiments are given of this series, and these two the last that were done with taps lubricated with a very stiff mixture of vaseline and paraffin. The ratios of the volumes of carbon dioxide and carbon monoxide to one another are interesting, being almost 1 : 1, when the excess of hydrogen is rather small, and 2 : 1 when the excess of hydrogen is much larger, recalling the results of Bunsen's experiments on limited oxidation of carbon monoxide.

Series Ib.

These show how experiments failed frequently. They also led to the discovery that the fracture of the eudiometer was generally due to its being allowed to become too hot from the number of explosions following one another too rapidly, and then the cold mercury cracked the glass. The temperature at which they were performed was about 4° C. The ordinary glass taps were lubricated with syrupy phosphoric acid.

Series Ic.

These experiments were made with the apparatus fitted with safety taps, and lubricated with phosphoric acid.

Series Id.

These experiments were the first made with dilute hydrochloric acid instead of dilute sulphuric acid, and it will be noticed that the ratio gradually falls from the first to the last of the four experiments, pointing out clearly that either the hydrogen is not the same or that the oxygen is not the same throughout, and that the impurity tends to increase or to diminish as the materials get used up. The first experiment of this series is the first in which the ratio exceeds 2 : 1.

Series Ie.

The experiments in this series, especially the later ones, seem to indicate clearly that the low values found for the ratio were due to traces of chlorine escaping with the oxygen, even after passing through Geissler's bulbs filled with pure soda, as the value rises except in the first case, after which potassium chlorate mixed with a little pure soda was used as the source of the oxygen.

Series If.

Oxide of mercury was used instead of potassium chlorate as the source of oxygen when the value found is practically the same as in the later experiments of the last

sub-series. It is plain that the source of the hydrogen ought to be varied. This was done by passing the hydrogen over palladium, and getting the hydrogen from the hydride formed by heating it.

Finally silver oxide was substituted for mercuric oxide, as it decomposes at a more convenient temperature.

The fracture of the measuring vessel rendered a new apparatus necessary, and one or two improvements were now introduced, the chief being the use of a constant volume, so that pressures only required to be measured for the large volumes, and the use of a narrower tube for measuring the residues.

One interesting point about the fracture of the measuring vessel is that, while surrounded by water and full of mercury, it broke in exactly the same way that a spare one which was kept ready for fear of accidents broke *at the same time*. The one in use was found fractured on a Wednesday morning, and the spare one had been handled and put on a shelf on the Monday afternoon just preceding. On going on the Wednesday to take it down to replace the other which had broken, it was found to have broken in such a similar manner that the pieces had to be fitted to each other to find out to which apparatus they belonged. The spare one had never been used, and not even calibrated.

In Series II. the oxygen was always got from oxide of silver, and the hydrogen from sodium and water or from palladium hydride, the hydrogen for which was furnished by sodium and water, with the exception of the first four experiments in Series IIa., when the hydrogen charge in the palladium was what was left in it from Series If., the hydrogen for which was obtained by the electrolysis of dilute hydrochloric acid. The 93 grms. of palladium absorbed usually somewhat over 6 litres of hydrogen, enabling twelve experiments to be done consecutively from one charge.

In Series IIa. the only two experiments which perhaps ought to be rejected are Nos. XII. and XIII., which were the first two performed after the apparatus had stood unused for over a year. Why these results should be so low I can offer no suggestion, but they differ notably from those of the same charge both before and after them.

Series IIb.

The results in this series vary remarkably, two of the ratios being very high and the mean of the whole being high, but with a large probable error. The oxygen from the mixture of silver oxide and barium sulphate seemed to be very pure.

Series IIc.

The hydrogen from the palladium hydride at first behaved in a peculiar way, and some air seemed somehow to have got in with the oxygen, and in two of the experi-

ments the residues were very large, so large that the results were absolutely valueless, the non-absorbable residue amounting to many cubic centimetres in Experiments IX. and XI. It is therefore advisable to neglect also Experiments VIII., X., and XII., the results of which are somewhat abnormal. No reason can be given for the abnormal behaviour of all five experiments, but being all consecutive there is no doubt that some common source of impurity infected all five.

Series IID.

The first experiment was made with the last lot of hydrogen from a charge of sodium; fresh sodium was added, and the second experiment was made with the hydrogen at first given off. Both these results are high. The next three agree wonderfully with one another and are, as it were, made with the purest hydrogen obtainable from sodium, any impurity which would come off first being used in Experiment XXI., and any which tended to remain being left behind, and was rejected as not quite enough sodium remained to give hydrogen for another experiment. The gases were in the last three experiments also perfectly pure as far as residual gas was concerned. The silver oxide in this series and the next was the same sample and prepared from silver sulphate and potassium hydrate.

Series IIE.

This series as a whole is the best which has been done, the gases being throughout pure, with the exception of very small impurity in the first experiment. They agree remarkably with one another, whether the hydrogen or the oxygen was in excess. The whole twelve experiments were successful without exception, and were all that could be performed with one charging of the palladium.

The values deduced from the various series are given below and together so that they may readily be compared. The equations employed in their reduction are the following well known ones :—

1. For the probable error of the arithmetical mean

$$\text{probable error} = \pm \cdot 6745 \sqrt{\left(\frac{s}{n(n-1)}\right)}$$

where n = number of observations,

s = sum of squares of the variations of the individual results from the mean.

2. For the probable value of the result from several series of experiments

$$M = \frac{\frac{A}{a^2} + \frac{B}{b^2} + \frac{C}{c^2} \&c.}{\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \&c.}.$$

M = general mean.
A, B, C, &c., being the mean results as above.
a, b, c, &c., being the probable error of each.

3. For the probable error of this general mean = m

$$m = \frac{1}{\sqrt{\left(\frac{1}{a^2} + \frac{1}{b^2} + \frac{1}{c^2} \&c.\right)}}.$$

These mean values are for

Series I.

	Number of experiments in each sub-series.	Impurity equally in both gases.	Number of experiments.	Impurity all in hydrogen.
IB.	(2)	1·9976 ±·001	(2)	1·9975 ±·001
IC.	(2)	1·99905 ±·0001	(2)	1·9988 ±·00006
ID.	(4)	1·9985 ±·0007	(4)	1·9982 ±·0007
IE.	(6)	2·00011 ±·0004	(6)	2·00055±·0005
IF.	(5)	2·0014 ±·00005	(5)	2·00104±·00018
		General mean for Series I.		
	(19)	2·000903±·00004	(19)	1·99925±·00005

Series II.

	Number of experiments in each sub-series.	Impurity equally in both cases.	Number of experiments.	Impurity all in hydrogen.
IIA.	(19)	2·0020 ±·00024	(19)	2·0019 ±·00024
IIB.	(7)	2·0038 ±·0062	(7)	2·0037 ±·0060
IIC.	(10)	2·0015 ±·00036	(9)	2·0016 ±·00036
IID.	(5)	2·0030 ±·00022	(5)	2·0030 ±·00022
IIE.	(12)	2·00245 ±·00007	(12)	2·00245 ±·00007
		General mean for Series II.		
	(53)	2·002435±·00006	(52)	2·002431±·00006

If we omit experiment XIII., Series IIA.
,, ,, VIII., X., XII., Series IIC.
,, ,, XX., XXI., Series IID.

we get for

	Number of experiments in each sub-series.	Impurity equally in both gases.	Number of experiments.	Impurity all in hydrogen.
IIA.	(18)	2·0022 ±·00022	..	2·0021 ±·00022
IIC.	(7)	2·0024 ±·00024	..	2·0023 ±·00026
IID.	(3)	2·00247 ±·0000033	..	2·00247 ±·0000033
	which with the values above for IIB., IIE., gives the general mean for Series II.			
	(47)	2·002466±·000003	(46)	2·002466±·000003

Neglecting altogether Series I., as in all probablity (as pointed out above) the oxygen was contaminated by chlorine, we have the values—

2·002433,
2·002466,

as the extreme values for the number of volumes of hydrogen uniting with 1 volume of oxygen to form water. As Series D was a small one, especially when the two first experiments in it are omitted, the second value is unduly weighted by the extremely small probable error in the remaining three, I think that the value—

2·00245,

may be taken as the true value for the ratio sought.

It is highly satisfactory to note that this is exactly the value found in the last series of twelve experiments made with the purest gases, and the advantage of prolonged experience in the manipulation of these difficult and tedious experiments. Although the last of the experiments was performed in April of last year, I have refrained from publishing the results till I could feel certain that I was unable to detect any further source of error, and until I felt assured that all the possible sources of error which have been suggested to me by various friends who have taken an active interest in my work, had been successfully overcome or did not apply to my methods of manipulation and measurement.

With regard to the results published by MORLEY, I think I may fairly claim that the simplicity of my apparatus for measuring and preparing my gases, the fact that they were never transferred from one mercury trough to another, that they were always saturated with water in the same way, and that the water formed by the

union was never admitted to my measuring vessel, amongst other advantages, render my results more worthy of confidence than his. The means adopted by him for detecting any impurity are unable to detect such small amounts of foreign gas as were not only easily detected but measured by my method. As long as the bubble could be seen it could be measured, and this, as measured, was always a maximum. His excess over 2 volumes is just one-tenth part of what I find.

The value for the ratio found by LEDUC* from his determinations of the densities of hydrogen, oxygen, and the detonating gas from the electrolysis of strong potassium hydrate solution, agrees far more nearly with my value, which it exceeds somewhat, being—

2·0037.

I do not think, however, that this method can compare in accuracy with a direct method, even if it be proved that the detonating gas so prepared unites completely without any residue whatever of either oxygen, hydrogen, or foreign gas.

There is but little doubt that the carbon in MORLEY'S hydrogen is due to acetates in his potassium hydrate giving ethane on electrolysis, some of which, although evolved at the opposite pole, being soluble to a certain extent in water, will find its way into the hydrogen. It is well known that potassium hydrate, purified by alcohol, is useless for gas analysis.†

The values for the ratio of the volumes are, therefore,

MORLEY	2·00023 : 1,
LEDUC	2·0037 : 1,
SCOTT	2·00245 : 1,

and for densities—

Lord RAYLEIGH	15·882,
LEDUC	15·905.

Combining my value with that of Lord RAYLEIGH, we get for the atomic weight of oxygen—

15·862,

a number almost identical with that of—

DITTMAR . . . . . = 15·866,

and with

COOKE and RICHARDS . . . = 15·869.

Combining LEDUC'S two values, we get for the same—

15·876.

* 'Compt. Rendus,' August 8, 1892.

† HEMPEL'S 'Gas Analysis,' DENNIS' Translation, p. 115.

The value 2·00245 is for temperatures about 14° to 18° C. If, however, the values for the coefficients of expansion of oxygen and hydrogen be taken as $\frac{1}{272\cdot16}$ and $\frac{1}{273\cdot13}$ respectively, we have for the ratio at 0° C., 2·00285.

In conclusion, I have only to say that *every measurement in all the experiments* was made by me, and that all the solutions required were made up, and cleansings of the apparatus, &c., were carried out by my own hands, so that no ambiguity could arise without my being in the position to elucidate any possible error at any time.

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