

# The Atomic Weight of Chlorine: An Attempt to Determine the Equivalent of Chlorine by Direct Burning with Hydrogen

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V. *The Atomic Weight of Chlorine: An Attempt to determine the Equivalent of Chlorine by Direct Burning with Hydrogen.*

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PART I.—GENERAL.

SOME apology seems needed in presenting a new research on the atomic weight of an element already measured with a precision which the highest living critic has emphasised as “the magnificent accuracy of STAS’ determination.”\* Moreover, the present experiments cannot claim an accuracy to be compared with any individual series of STAS’ ratios. But, on the other hand, STAS’ atomic weight of chlorine is derived indirectly from oxygen by a series of operations which include the determination of (1) the oxygen in potassium chlorate, (2) the silver equivalent to the molecule of potassium chloride, and (3) the composition of silver chloride. STAS himself has assigned different values to these ratios at different times; *e.g.*, in 1860 he found that 100 parts of silver were equal to 69·103 of potassium chloride, in 1882 he

\* F. W. CLARKE, ‘A Recalculation of the Atomic Weights.’ New edition. 1897, p. 57.

found 100 of silver equal to 69·119, and in his latest work to 69·123 of potassium chloride. Therefore, although STAS' value 35·457 ( $O = 16$ ) is in satisfactory agreement with CLARKE'S value 35·447 re-calculated from all the best determinations, it is possible that some constant error may occur in some part of the long chain connecting the value of hydrogen with that of chlorine, an error which would be repeated from link to link, and would become evident only when the two ends of the chain were connected up.

A direct comparison between hydrogen and chlorine might not only serve to detect any systematic error in this chain of ratios, but such a comparison, inasmuch as it does not involve the probable error of other ratios, would be *ceteris paribus* more exact. Again, the closing of the chain between hydrogen and chlorine with reasonable accuracy would permit the accidental errors to be distributed and prevent their accumulation at the unconnected end. The accumulated "probable error" in CLARKE'S recalculated value for chlorine is  $\pm 0048$ ; the "probable error" of our nine experiments is  $\pm 0019$ .

The suggestion to carry out this work was made to us by Professor EDWARD W. MORLEY, who happened to visit our laboratories when pure chlorine was being prepared by the electrolysis of fused silver chloride. He suggested that we should burn weighed hydrogen and chlorine in a closed vessel, just as he had burnt weighed hydrogen and oxygen. After some discussion we decided to make the attempt—an attempt which was rendered possible by the fact that one of us was enabled, by a research scholarship, to devote his whole time to the investigation.

A year was spent in designing, making and testing the several parts of the apparatus. In the second year we put together the pieces and carried through preliminary experiments, which led to some modifications and further trials. In the third year the apparatus was got into working order and the determinations made. After the three years' work we are painfully aware how far our attempt falls short of the precision of Professor MORLEY'S own determination, but the relation we have found between hydrogen and chlorine seems worthy of record on account of the directness of the method of comparison.

Our method was, briefly, as follows:—Chlorine prepared by the electrolysis of fused silver chloride (with purified carbon poles in a Jena-glass vessel) was condensed and weighed as a liquid in a sealed glass bulb. This was attached to a vacuum "combustion globe" and the chlorine allowed to evaporate slowly into the globe. The hydrogen prepared by the electrolysis of barium hydrate was dried and absorbed by palladium in a weighed vessel. The palladium on being warmed gave off the hydrogen, which was ignited by a spark and burnt at a jet in the combustion globe previously filled with chlorine. The gases were regulated so as to maintain the hydrogen flame until nearly all the chlorine had been combined; then the palladium was allowed to cool and the hydrogen was turned off just before the flame died out. The hydrogen chloride, as it was formed in the flame, was dissolved by water standing

in the globe, which was kept cool by ice. A little hydrogen chloride was formed by the action of the water-vapour on the chlorine in the flame, a corresponding amount of oxygen being liberated. This oxygen was determined in the analysis of the residual gases, which contained, besides traces of air, the small quantity of hydrogen which filled the capillary tube between the tap and the jet when the flame was extinguished, and any that might escape unburnt from the flame.

The chlorine remaining in the globe unburnt, as gas and in solution, was determined by breaking a thin glass bulb containing potassium iodide. The residual gases having been pumped out (and any iodine vapour caught by a wash-bottle), the liberated iodine was determined by standard thiosulphate in an atmosphere of carbonic acid. In calculating the unburnt chlorine from the iodine, the atomic weight of chlorine was assumed to be 35·195 and the atomic weight of iodine 126·015.\* In each experiment we burnt about 11 litres of hydrogen and 11 litres of chlorine. The volume of chlorine left unburnt was about 2 per cent. of the volume burnt.

The balance (by OERTLING) was fixed on a stone pedestal in an underground cellar. The vibrations of the pointer were read by a telescope, GAUSS' method of reversals being used. The chlorine and the hydrogen bulbs were counterpoised on the balance by bulbs of the same glass and of nearly the same displacement, and the small weights used in the weighings were reduced to a vacuum standard.

In the following table are given the corrected weights of hydrogen and of chlorine burnt in the several experiments—the weights of hydrogen being rounded off to ·1 milligramme :—

TABLE I.

	Hydrogen burnt, in grammes.	Chlorine burnt, in grammes.	Atomic Weight of Chlorine.
1	·9993	35·1666	35·191
2	1·0218	35·9621	35·195
3	·9960	35·0662	35·207
4	1·0243	36·0403	35·185
5	1·0060	35·4144	35·203
6	·9887	34·8005	35·198
7	1·0159	35·7639	35·204
8	1·1134	39·1736	35·184
9	1·0132	35·6527	35·188
Mean . . . .			35·195 ± ·0019

In the whole of these experiments 9·1786 grammes of hydrogen combined with 323·0403 grammes of chlorine; hence the atomic weight of chlorine, calculated in mass, is 35·195.

\* G. P. BAXTER, 'Proc. Amer. Acad.,' xl, 419.

The percentage composition of hydrochloric acid according to these determinations is:—

Chlorine . . . . .	97·237
Hydrogen . . . . .	2·763
	100·000

The number we have obtained for the atomic weight of chlorine is appreciably higher than that calculated by F. W. CLARKE from the previous determinations, and is slightly higher than STAS' value:—

CLARKE'S calculation.	STAS.	DIXON and EDGAR,	
35·179	35·189	35·195	H = 1
35·447	35·457	35·463	O = 16

After our experiments were completed, we heard that Professor T. W. RICHARDS was engaged on a revision of STAS' work on the composition of silver chloride. G. P. BAXTER quotes the value 35·467 as having been obtained by RICHARDS and WELLS for the atomic weight of chlorine, a number slightly higher than our own.\*

It would not be difficult to extend our experiments, using larger quantities of the gases, if in the judgment of chemists it were thought desirable.†

## PART II.—DETAILS OF EXPERIMENTS.

### 1. *Preparation of Hydrogen.*

For the preparation of hydrogen we employed the electrolysis of a solution of barium hydrate, first proposed by BRERETON BAKER,‡ as a means of preparing hydrogen free from traces of hydro-carbons.

Since barium carbonate is quite insoluble in a solution of barium hydrate, any slight action of the carbonic acid of the air on the dissolved hydrate during its unavoidable exposure while filling the electrolytic apparatus might be safely neglected. We have to thank Mr. BRERETON BAKER for kindly supplying us with some of his highly purified barium hydrate. It had been re-crystallised fifteen times and was not radio-active. It still contained a very small trace of barium carbonate.

The arrangement of the hydrogen apparatus is shown in fig. 1. Three preliminary

\* Professor RICHARDS writes (February 13, 1905) that he finds 100,000 parts of silver yield 132,867 of silver chloride, whereas STAS considered 132,850 the most probable result. This new determination, combined with our value for chlorine, would give silver an atomic weight 107·90.

† As further experiments have shown that chlorine can conveniently be burnt in an atmosphere of hydrogen, one of us proposes to make a fresh set of determinations in this way and to condense and weigh the hydrochloric acid formed.—*July, 1905.*

‡ 'Jl. Chem. Soc.,' 1902, vol. 81, p. 400.

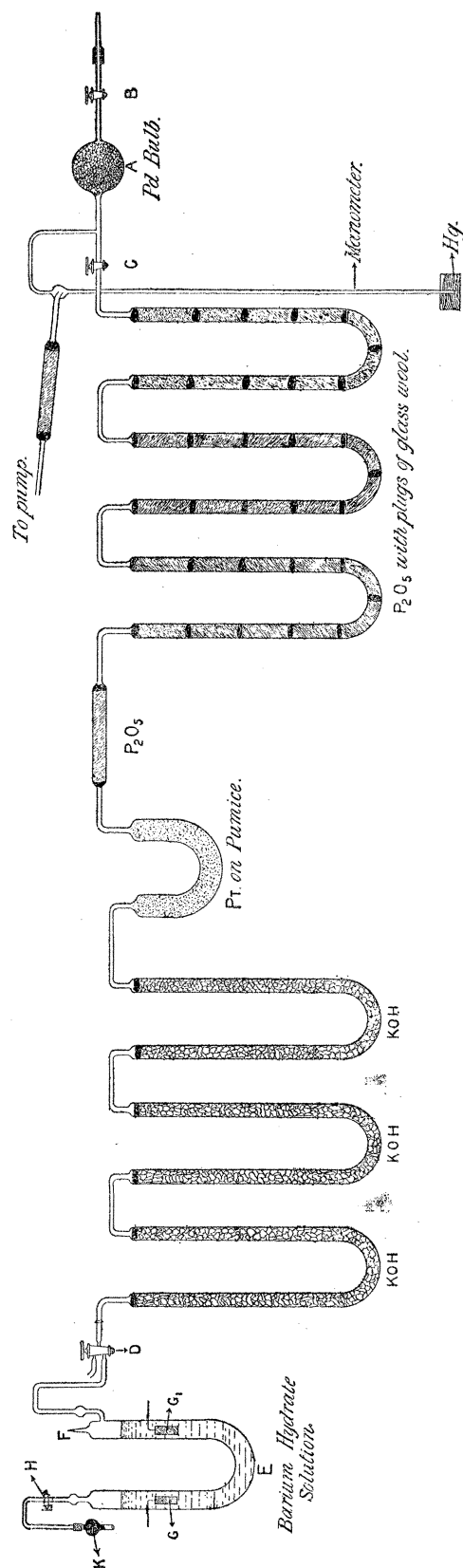


Fig. 1. Hydrogen apparatus.



drying tubes were employed, each 1 metre in length and 2·5 centims. in diameter, filled with small pieces of purified potassium hydrate. The gas then passed through a **U**-tube containing platinised pumice, kept at a temperature of 220° C., in order to remove any oxygen diffusing from the + electrode, and then through a short horizontal tube and three long **U**-tubes filled with pure phosphorus pentoxide. As recommended by COOKE, the phosphorus pentoxide was packed closely into the drying tubes and was alternated at frequent intervals with plugs of clean glass-wool. To ensure efficient drying, the current of hydrogen was passed through these drying tubes at a rate not greater than 2 litres an hour. At the end of our experiments the last layers of phosphorus pentoxide had picked up so little moisture that a slight tapping of the tube threw the powder into a cloud.

The drying tubes, when filled, were fused together, and to the last phosphorus pentoxide tube was fused the tap C. This, in turn, was fused to one limb of a **T**-piece, to the other two limbs of which were fused the bulb containing the palladium foil and the Toepler pump. To the first potassium hydrate drying tube at the other end of the apparatus was fused a three-way tap. The **U**-tube E, in which the electrolysis of barium hydrate was carried out, was also fused to D, whilst the third arm of D opened into the air.

When the current was passed through the warm barium-hydrate solution between the platinum electrodes G and G<sub>1</sub>, the evolved gases were allowed to escape into the atmosphere until the air, which was originally contained in the two arms of the **U**-tube, had been replaced by hydrogen and oxygen respectively. Connection with the atmosphere was then cut off by closing the tap H and by fusing off the capillary portion of the opening F. During our experiments the solution showed no signs of milkiness and no precipitate settled at the bottom of the tube; we believe, therefore, that no carbonate was present.

The preparation and occlusion of hydrogen was carried out as follows:—Before the fusion of the palladium bulb to the apparatus, the tubes on the right-hand side of the tap D were exhausted as far as possible by means of the pump. The **U**-tube, containing the solution of barium hydrate, was raised to a temperature of 60° C. in a water-bath (in order to dissolve the hydrate which had crystallised out from the solution) and the electrolysis commenced. The evolved oxygen escaped into the air through the tap H and the tube K, filled with a dried mixture of CaO and Na<sub>2</sub>SO<sub>4</sub>, while the hydrogen was admitted, by very cautiously opening the tap D, to the evacuated part of the apparatus. The stream of hydrogen was continued until the bubbling of the gas through the manometer tube showed that the previously evacuated portion of the apparatus was now full. The electrolysis was discontinued, the tap D closed and the drying tubes again evacuated. This operation of filling and exhausting was repeated twelve times in order to get rid of all traces of air. The taps C and D were then closed and the electrolysis stopped.

The bulb A containing the thin palladium foil was then fused to the apparatus.

The palladium was raised to a very low red heat and the apparatus on the right-hand side of the tap C evacuated, and then allowed to cool to the ordinary temperature. The tap C was cautiously opened, the electrolysis resumed, and hydrogen admitted to the palladium until it was saturated, care being taken that the pressure on the left-hand side of the tap C was always kept slightly above the atmospheric. This last precaution was easily effected by opening the tap D fully and regulating the admission of the gas to the palladium by means of the tap C. C was now closed, the temperature raised to a very low red heat, and the evolved gas sucked out by the pump. The operation of alternately filling the palladium with hydrogen and evacuating the bulb at a high temperature was repeated four times, when it was considered that all traces of nitrogen or other gases had been removed from the palladium bulb and the connecting tubes on the right-hand side of C. The palladium after the final exhaustion was maintained at a low red heat whilst hydrogen was admitted to it through C.

When the pressure throughout the apparatus had become a little more than atmospheric—this was easily attained by so adjusting the tap H of the electrolysis tube that the rate of escape of the evolved oxygen through it was slightly less than its actual rate of evolution—the tap B was slightly opened and the current of hydrogen was passed through the palladium, the gas finally escaping through a capillary tube dipping under mercury. The palladium was now allowed to cool very slowly, the current of hydrogen passing through it all the time. Great care was taken that the rate of entry of hydrogen to the palladium was always greater than its rate of occlusion, or, in other words, that an excess of hydrogen was constantly escaping through the capillary tubing during the occlusion.

At the temperature of maximum absorption of hydrogen from  $97^{\circ}$  to  $100^{\circ}$  C., the cooling of the palladium was interrupted and the temperature kept constant for one hour. The cooling was then allowed to continue, hydrogen passing through the apparatus all the while, until the temperature of the room was reached. The taps B, C, D, and H were then finally closed and the electrolysis discontinued. The palladium bulb was fused off from the rest of the apparatus, the outside cleaned and dried, and the whole was then ready for weighing.

## 2. *The Palladium Bulb.*

The palladium vessel A (fig. 2) was a bulb of hard Jena glass of about 180 cub. centims. capacity, fitted on the one side with a tap B, the inner portion of a ground glass joint M, and a glass jet J, at which the combustion of hydrogen in chlorine was carried out; and on the other with a capillary tube by which it could be attached to the rest of the hydrogen apparatus and afterwards separated by fusion with the blowpipe flame.

Since the date when Professor E. W. MORLEY defined a tap as “a contrivance for



lessening the flow of gas through a tube," improvements have been made which seemed to us to justify the use of one for regulating the flow of hydrogen from the palladium bulb. The tap B, fig. 2, was made with a long barrel with its bearings

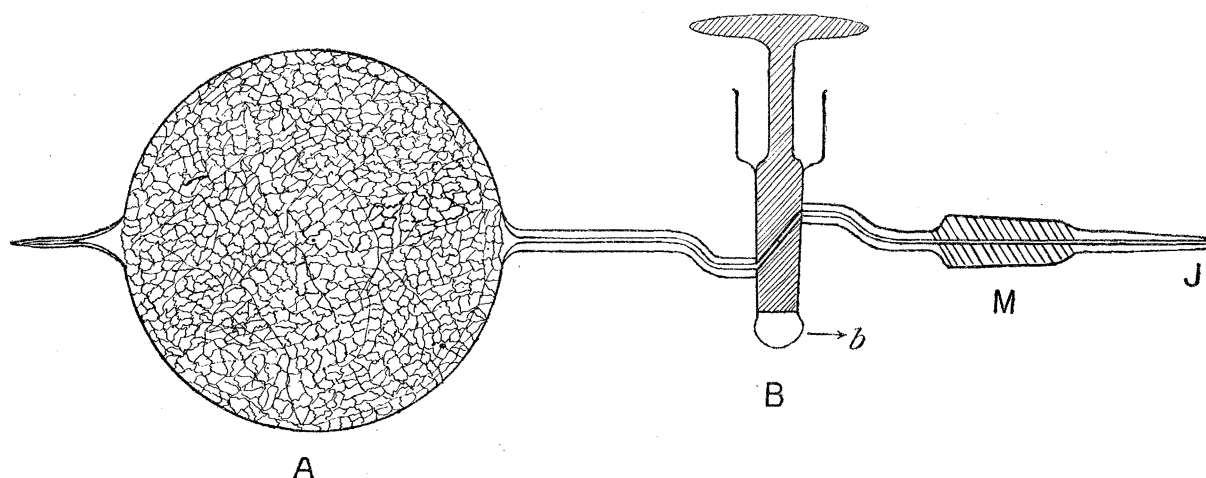


Fig 2. The palladium vessel.

ground to the sheath for a length of 30 millims. The barrel forms a portion of an elongated cone, its diameter at the wider end being 10 millims., and at the narrower end 8 millims. The bore of the tap is inclined so that one opening is 10 millims. above the other. The sheath of the tap ends in a closed bulb below and a cup above.

The method of lubricating and fixing the tap was as follows:—After thorough cleaning and drying, the bulb *b* of the tap was filled with dry mercury to such a height that the barrel of the tap, when placed in position, just touched its surface. The mercury was then gently heated until it filled the whole bulb. The lubricant glacial phosphoric acid was melted and carefully rubbed over the barrel, which was placed in position, turned several times to ensure equal distribution of the lubricant, and then pressed firmly into the sheath whilst the bulb *b* containing the mercury was cooled. The bulb now contained no air, but the cooling resulted in the production of a partial vacuum, which kept the tap firmly fixed. We have tested this tap by a pump and found it to remain perfectly gas-tight. All the other taps used in the apparatus with the exception of the chlorine tap were made and used in the same way. We are indebted to the skill of the University glass-blower, OTTO BAUMBACH, for the accurate grinding of these taps, and for the joints by which he succeeded in fusing hard Jena to soft glass.

It was of course essential that the weight of the palladium bulb should be most accurately determined before and after the combustion of its charge of hydrogen. To avoid change of volume the bulb was made of a hard Jena glass which preliminary hydrostatic weighings showed not to alter when heated to dull redness and cooled. The charged palladium bulb was heated and cooled alternately to

determine its change of volume, if any. When immersed in water to a mark on the stem the bulb weighed—

Before heating . . . . .	230·314 grammes.
After heating for two hours to a dull red heat . . . . .	230·311 „
After a second heating . . . . .	230·307 „
After a third heating . . . . .	230·308 „

The alteration in volume of the bulb, after heating to dull redness, was therefore so slight that the difference in its displacement of air was negligible. In the actual experiments the bulb was never heated beyond 550° C.

The palladium was used in the form of thin foil. We are indebted to Messrs. JOHNSON and MATTHEY for kindly supplementing our stock for the purpose of this investigation. The bulb contained sufficient palladium foil (360 grammes) to absorb about 1½ grammes of hydrogen. When the bulb A had been detached from the rest of the hydrogen apparatus and had been cleaned, it was suspended by platinum wire from one arm of the balance, from the other was suspended a counterpoise (of the same Jena glass) which had nearly the same displacement as the palladium bulb. It was then weighed by GAUSS' method of reversals. The balance case, after each reversal, remained closed at least half-an-hour before a new weighing was started. The air displaced by the small weights added to secure equilibrium was allowed for. By equalising the volumes of the systems suspended from the arms of the balance, errors due to variations of temperature in the balance case and to any deposition of moisture on the bulb were avoided.

### 3. *Preparation of Chlorine.*

SHENSTONE,\* in 1893, first proposed the electrolysis of fused silver chloride in a vacuum as the best means of obtaining pure chlorine. He stated that his chief difficulty was the rapid formation of silver trees, which eventually made contact between the electrodes and thus prevented any further decomposition of the fused chloride. In 1901, MELLOR and RUSSELL† substituted for SHENSTONE'S tube a V-tube of the hardest Jena glass, so that the silver tree had to travel along the two limbs of the V before making contact, and thus the decomposition of silver chloride could be carried on to a greater extent than in SHENSTONE'S apparatus. They fastened their carbons to glass tubes (ground into the necks of the V) by means of a plaster of Paris joint.

We have modified their apparatus by drawing out the upper portion of each arm of the U, and melting it on to the carbon electrode for a length of about 2·5 centims. We fused a little silver chloride round the top junction of glass and carbon. A mercury cup completed the joint, and served for making electrical contact with the carbon. Such a joint, even with a vacuum in the interior of the tubing, is quite impervious.

\* 'Journ. Chem. Soc.,' 71, 471 (1897).

† 'Journ. Chem. Soc.,' 82, 1272 (1902).

The arrangement of the apparatus is shown in fig. 3. A was the U-tube of Jena glass, having two delivery tubes B and B<sub>1</sub> which united at C; its capacity was such as to admit of the fusion of 800 grammes of silver chloride introduced through the side tube F. The carbon electrodes D and D<sub>1</sub>, of 2 millims. diameter, were specially made for us by the Acheson Graphite Company, Niagara. Before being fixed in position they were heated to redness for twelve hours in a current of chlorine, and

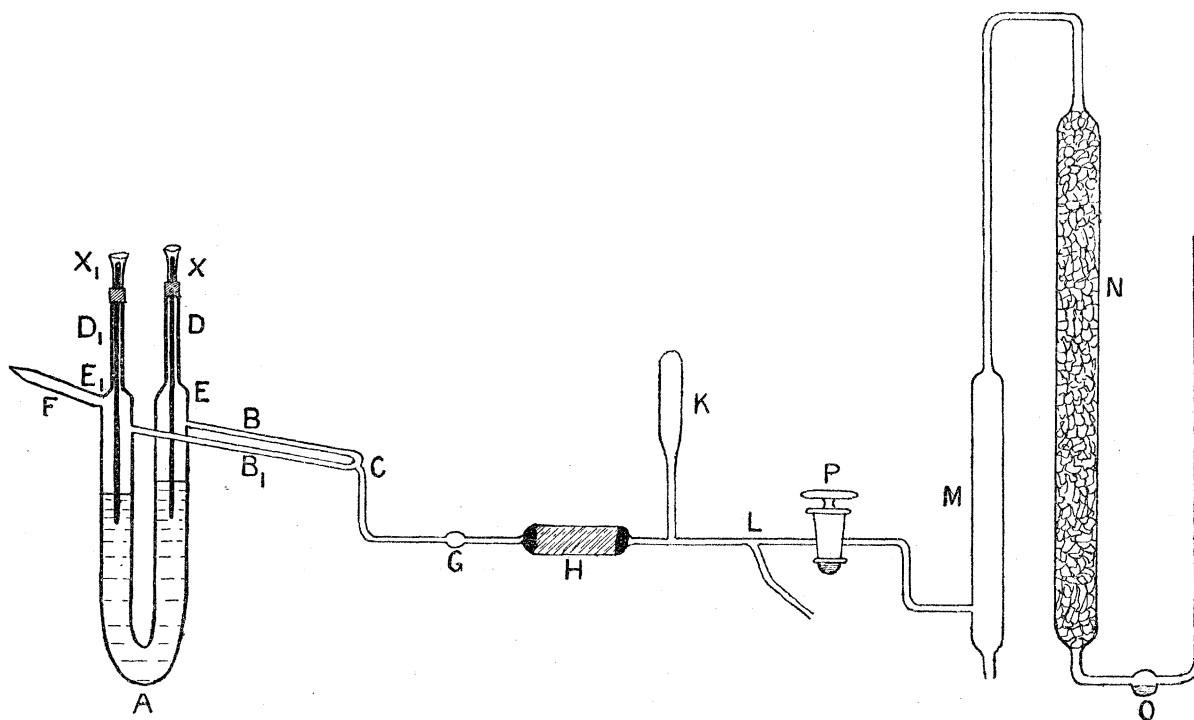


Fig. 3. Chlorine apparatus.

were then kept *in vacuo* in a porcelain tube for three hours at a bright red heat. A special glass joint at G permitted the junction of the U-tube to the other portion of the apparatus, which was constructed of soft glass. This joint was made by fusing together a series of twelve very short pieces of tubing which varied by small gradations from hard Jena to soft glass. H was a small drying tube containing pure phosphorus pentoxide, which was kept in position by two plugs of clean glass-wool. K was a glass tube (capacity 25 cub. centims.) in which a sample of the prepared chlorine could be collected to test its purity. L was a T-piece, one limb of which was fused to the chlorine generator; another led, viâ the absorption tubes M and N, to the mercury pump, whilst the third was fused to the "chlorine bulb."

To prevent any residual chlorine reaching the pump, it was passed through the tube M (which could be filled with mercury to a suitable height by raising a reservoir), and then through a tube N, 1 metre in length and 4 centims. in diameter, packed closely with pure potassium hydrate. A little mercury, contained in the cavity O, acted as a *témoin*. The dulling of its bright surface would have indicated

that the absorption of chlorine had not been complete, but, at the end of our experiments, its lustre was unimpaired.

*Preparation of Silver Chloride.*—Commercial silver nitrate was purified by re-crystallisation twice from water. A strong solution of hydrochloric acid was prepared by cautiously distilling the pure concentrated acid, washing the evolved gas with a little water and then dissolving it in re-distilled water, kept cool by means of an ice and salt freezing mixture.

A strong solution of re-crystallised sodium chloride was prepared, and into it was passed the acid gas evolved by heating the solution of hydrochloric acid previously made. The precipitated sodium chloride was washed with a little ice-cold water, dissolved in fresh re-distilled water and again re-precipitated by means of hydrochloric acid gas. This re-precipitation was carried out three times. Silver chloride was then prepared by adding a dilute solution of the re-crystallised silver nitrate to excess of a dilute solution of the purified sodium chloride.

The precipitation of the silver chloride and all subsequent operations were carried out in the absence (as far as possible) of actinic light. The supernatant liquors were decanted as soon as possible and the silver chloride washed repeatedly with boiling distilled water, until a test portion of the washings gave no cloudiness with silver nitrate. The silver chloride was then frequently agitated with more hot distilled water and allowed to stand in contact with it for some time. Then the final washings were decanted and the silver chloride was dried as completely as possible in large porcelain dishes on a water-bath. It was then cautiously fused in deep porcelain crucibles and kept in the molten state for twenty-four hours, care being taken to prevent contact, during the prolonged heating, between the acid gases of the flame and the molten chloride. The chloride was then poured into a clean silver trough so as to form thin sheets. These, on cooling, were easily detachable, and were cut into small fragments. The silver chloride prepared in this way was a colourless, horn-like, translucent substance, which could be easily broken or cut into small pieces.

The operation of fusing the requisite amount of silver chloride in the **U**-tube **A** was carried out as follows:—The **U**-tube (filled through the side tube **F** with the solid pieces of silver chloride up to the level of the carbon electrodes) was gradually raised in temperature by heating the cast-iron box in which it was closely packed round with asbestos. A high-range thermometer, with its bulb resting on the bend of the **U**-tube, indicated the temperature of the chloride. When the contained silver chloride had fused, more was slowly added until the calculated amount, 800 grammes, had been completely reduced to the molten state. The side tube **F** was then sealed and the whole apparatus was exhausted by the pump. When the tubes were thoroughly evacuated the tap **P** was closed, and the current from one storage cell was passed through the silver chloride for a short time. The current was then increased by the addition of another cell, and chlorine was steadily evolved until the whole of the apparatus on the left-hand side of the tap was filled with chlorine at a



pressure slightly above atmospheric. Then the current was discontinued, the tap P cautiously opened, and the gas allowed to escape, first through mercury contained in the tube M and then through solid potassium hydrate. Any gas other than chlorine was then sucked out by the automatic pump, which, during the first part of the electrolysis, was kept constantly working.

The operation of filling the apparatus with chlorine and exhausting was repeated four times. The gas from the first two fillings was not completely absorbed. In preparing chlorine for our determinations we filled the apparatus five times, and tested the fifth by fusing-off the side tube K and opening it under mercury. The absorption was so complete as to leave no visible gas residue. This test assured us that no air was left in our chlorine. The fact that the chlorine first evolved was allowed to escape was a safeguard against the possible presence of bromine or iodine, for any bromide in the silver chloride would have been decomposed by the chlorine, and the evolved bromine would have been carried over with the chlorine first escaping.

The chlorine bulb (immersed in a cooling mixture of solid carbonic acid and ether contained in a silvered Dewar tube) was then filled with liquid chlorine. The current was increased and the condensation allowed to proceed until the liquid reached the level of a circular line etched on the bulb, when the current was stopped. About 37 grammes of liquid chlorine were collected in each experiment. Finally the chlorine bulb was separated by fusion.

Irregularities, arising in the electrolytic cell, were shown by an ammeter placed in the electrical circuit. We found it advisable, as SHENSTONE says, to prevent these irregularities by frequently reversing the current for a short interval of time, thus shattering any incipient silver tree.

#### 4. *The Chlorine Bulb.*

Chlorine, prepared by the electrolysis of fused silver chloride *in vacuo*, and dried by phosphorus pentoxide, was condensed by means of a freezing mixture of solid carbonic acid and ether, or by liquid air, in an apparatus shown in fig. 4. The chlorine vessel, which was made of soft glass, consisted of a stout glass bulb, A, holding about 40 cub. centims. To this was attached one limb of a T-piece, made of capillary tubing; another limb could be fused to the source of chlorine, whilst the third ended in a *cul-de-sac* (B).

B was a contrivance by means of which we got over a difficulty, which threatened at one time to bring our work to a premature end. For a long time we were unable to discover any means by which liquid chlorine could be safely weighed, and, at the same time, be under such complete control as to admit of its subsequent regular entry to the combustion globe. The pressure of liquid chlorine at ordinary temperatures is from 6 to 8 atmospheres, and the difficulties of successfully controlling such a pressure by means of a tap were found very great.



After many failures we finally designed the vessel shown in fig. 4. The chlorine weighed in the bulb A could only reach the tap when the sealed end of the inner tube B was broken off by the rod of glass C falling on it. The tap D was an inversion of the ordinary form of tap, that is, its smallest diameter is at the top of the tap; so that instead of the key having to be pushed into its socket, it has to be pulled into it to fit. Internal pressure, instead of tending to loosen the key, only made it fit more tightly. Of course, if the internal pressure became too great, the key was so firmly driven into its socket that it stuck, and then became useless. However, the taps we used, when lubricated with viscid phosphoric acid, withstood a pressure of four atmospheres without sticking. Their chief disadvantages lay in the difficulties of cleaning and lubricating them, and in the fact that it was necessary to affix to them weights, suspended from a pulley, when carrying out exhaustions of vessels to which they were attached. We are not aware that such taps have been used before in scientific research work; they were made for us by the University glass-blower.

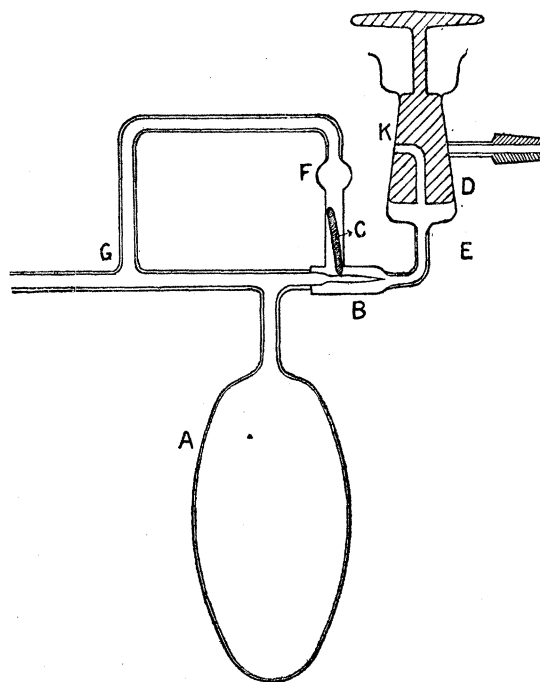


Fig. 4. Chlorine bulb.

The small space E (less than .5 cub. centim.) immediately below the key of the special tap D, and the glass tubes connected with it, were first evacuated and then filled with pure chlorine from the silver chloride through the tube F, which was sealed off while the apparatus was cooled by immersion in a freezing mixture. On the removal of the freezing mixture, the gas trapped between E and F (about 4 cub. centims.) tended to expand, and thus held the tap D firmly in position.

The chlorine condensation bulb, filled with approximately 37 grammes of liquid chlorine, was weighed in a precisely similar manner to that detailed for the palladium bulb.

##### 5. Preparation of Reagents.

*Iodine.*—Pure iodine was prepared by the first of the two methods proposed by STAS. A strong solution of potassium iodide was saturated with resublimed commercial iodine. To this, sufficient water was added to precipitate one half of the dissolved iodine. The supernatant liquid was decanted and the precipitated iodine repeatedly washed with small quantities of distilled water. It was then divided into two portions. The iodine, in the first, was distilled in steam, the solid distillate

collected and dried *in vacuo* over solid calcium nitrate, which was frequently changed. The iodine was then intimately mixed with 5 per cent. of its weight of purified barium oxide, and distilled to remove the last traces of water and hydrogen iodide. The wet iodine, in the second portion, was dissolved in a strong, cold solution of purified potassium hydrate until the solution had acquired a permanent light yellow tinge. The solution was then evaporated to dryness on a water bath. The mixture of potassium iodide and iodate so obtained was then placed in a large platinum crucible, fitted with a platinum hood, and heated to dull redness for six hours. The resultant potassium iodide was recrystallised five times from water and dried *in vacuo* over calcium nitrate, which was frequently changed. It was pure white in colour, and contained no trace of potassium iodate; its solution in water was neutral and remained colourless when exposed to light.

*Standard Solution of Iodine in Potassium Iodide.*—In a small weighing bottle, carefully cleaned and dried, iodine, purified as described, was placed. This was kept in a desiccator until ready for weighing. The details of the weighing are given below:—

Temperature at start 16°·5 C.,	Barometer at start 759·8 millims.,
Temperature at end, 15°·5 C.,	Barometer at end 757·0 millims.,
Weight of bottle and iodine . . . . .	52·28137 grammes.
Weight of bottle . . . . .	23·70084 „
	<hr/>
	28·58053 „
Vacuum correction + . . . . .	·00279 „
	<hr/>
	28·58332 „
	<hr/>

The weight of iodine dissolved was therefore 28·58332 grammes.

This iodine having been dissolved in a solution of potassium iodide, the iodine solution was brought into a 2-litre flask through a drawn out funnel, and the residual solution carefully washed in.

The flask was calibrated by means of a burette previously calibrated, the neck of the flask being drawn out in the blowpipe flame. After cleaning and drying, the flask was filled with pure water from the burette, at the same temperature as that at which the burette had been calibrated. The last drops were allowed to run into the flask by contact with the glass surface immediately above the water, which stood in the constricted part of the neck. A circular line was etched on the glass to mark the exact level of the liquid in the constriction.

The iodine solution was brought up to the etched mark by slowly adding pure water, the solution being shaken after each addition of water. The final temperature of the solution was almost identical with the temperature at which the volume

of the 2-litre flask was determined. It was assumed that no loss in weight of the iodine had occurred during its solution in the potassium iodide solution. We had then 28.58332 grammes of iodine dissolved in 2033.68 of our units of volume, which gives .014055 gramme of iodine in one of our units of volumes. The solution was kept in the tightly stoppered 2-litre flask.

*Potassium Hydrate.*—Potassium hydrogen carbonate was twice re-crystallised from water. The crystals were heated in a platinum crucible, fitted with a platinum hood, to a dull red heat for six hours. The potassium carbonate so obtained was dissolved in water, and silver carbonate added, and the mixture thoroughly agitated for three hours. The precipitate, composed chiefly of silver carbonate but probably containing traces of silver chloride and other substances, was allowed to settle and the supernatant liquid filtered into a silver dish through a filter filled with clean pieces of broken marble.

The solution in the silver dish contained one part of potassium carbonate in twelve of water. It was heated to the boiling-point, and two parts of lime (prepared by heating calcium carbonate to bright redness in a platinum crucible, and previously slaked in ten parts of water) were added by degrees, the liquid being boiled for a few minutes after each addition of lime to ensure its complete conversion into calcium carbonate. The addition of lime completed, the solution was boiled for half-an-hour and allowed to clarify by standing. The clarified solution was then filtered through another marble filter into a silver dish and boiled down until the hydrate commenced to evaporate. The semi-solid mass was then poured into a silver dish and allowed to cool *in vacuo* over calcium chloride. It was then divided into four portions, the first was broken into small fragments and introduced as rapidly as possible into the potash drying tubes; the second was broken into larger pieces with which the chlorine absorption tube (fig. 3) was filled; the third was dissolved in pure distilled water and the solution employed in the preparation of potassium iodide, whilst the remainder was used in the purification of water.

*Pure Water.*—The water used in these experiments was prepared by rectifying hot distilled water from the laboratory still. This was distilled over potassium hydrate (purified as described) and potassium permanganate, twice re-crystallised from water. The retort employed was made of hard Bohemian glass, the condensing tube and receiver of Geräte glass. Immediately before use these were cleaned and steamed. 100 cub. centims. of this water, when slowly evaporated in a small platinum retort, gave no solid residue.

*Phosphorus Pentoxide.*—KAHLBAUM'S purest pentoxide, contained in Jena hard glass tubes, was distilled, at a bright red heat, in a current of pure dry oxygen through spongy platinum, kept in position by two platinised asbestos plugs. The distilled oxide condensed as a fine white crystalline powder in the cooler part of the Jena-glass tubes. It was kept in a tightly stoppered bottle until its introduction into the drying tubes. It answered all the tests recommended by SHENSTONE and

BECK for the identification of pure phosphorus pentoxide: (1) it did not reduce a 10-per cent. solution of silver nitrate; (2) it did not reduce mercuric chloride when boiled with it; and (3) on evaporating an aqueous solution of it to dryness and igniting moderately, no odour of phosphine was detected.

*Palladium Foil.*—The palladium, which was used in the form of thin foil cut into very small pieces, was heated to dull redness in a current of pure dry air for twenty-four hours, in order to eliminate any grease which might have been acquired during rolling. It was then heated in glazed porcelain tubes to a bright heat, *in vacuo*, for six hours.

*Sodium Thiosulphate.*—The sodium thiosulphate used was re-crystallised from water four times and was dried, *in vacuo*, over calcium chloride; it was pure white in colour and its solution was neutral to litmus.

*Sodium Hydrogen Carbonate.*—The sodium hydrogen carbonate used for the preparation of carbonic acid, in an atmosphere of which the titration of the iodine contained in the combustion bulb was carried out, was purified by exposing the solid, at 70° C., to the action of a slow stream of carbonic acid gas passing through it. The carbonic acid was prepared by the action of hydrochloric acid on marble, and, before reaching the carbonate, was washed thoroughly with water. When the current of gas had been passing for three hours, the carbonate was allowed to cool in it until the ordinary temperature had been reached. Sodium hydrogen carbonate so prepared had no effect in impairing the accuracy of titrations of thiosulphate by means of the standard solution of iodine in potassium iodide. The gas obtained on heating the acid carbonate was completely absorbed by potassium hydrate.

*Starch Solution.*—The solution of starch, used as an indicator, was prepared by adding soluble starch, in very small quantities at a time, to boiling water which had been purified. When the solution commenced to assume a faint opalescent blue, the addition was discontinued. The solution, on cooling, was preserved in a tightly stoppered bottle, and to prevent any fermentation, a little mercuric iodide was added and dispersed through the solution by vigorous shaking.

*Platinised Pumice.*—Pumice stone was ground into small fragments and sifted through two sieves—the first of 2 sq. millims. mesh, the second 1 sq. millim.; the part remaining on the second was transferred to a porcelain basin and washed thoroughly with aqua regia. After decanting the supernatant acid, the mass was washed with water until the washings were no longer acid. It was then dried in a porcelain crucible contained in an air-bath at 120° C. The dried product was saturated with a concentrated solution of platinic chloride, excess of ammonium hydrate added, and the mass stirred until the yellow colour of the platinic chloride had disappeared from the supernatant liquid, which was then decanted and the platinised pumice carefully dried. It was then heated in a deep porcelain crucible until fumes were no longer evolved. A lid was placed on the crucible and the whole heated to a dull red heat for twelve hours. On cooling, the platinised pumice was



packed into the small U-tube B (fig. 1), which was then fused to the apparatus for the preparation of hydrogen.

*Purification of the Mercury used in the Pumps.*—The mercury was frequently cleaned as follows:—It was placed in a suction flask, and on to its surface was poured a weak solution of nitric acid. The side tube of the flask was attached to the water pump, which drew air through the mercury by means of a glass tube held in position by a cork in the neck of the flask.

This stream of air, coupled with the intimate mixing of the mercury and the nitric acid, resulted in the rapid oxidation and solution of all metallic impurities contained in the metal. When this had been accomplished, the mercury was thoroughly washed with water, dried with filter paper, and filtered, by means of very fine holes, through clean white paper.

*Cleaning of Glass Apparatus.*—Before use, all glass apparatus was filled with a hot mixture of potassium dichromate solution and concentrated sulphuric acid and allowed to stand for six hours. It was then washed out with boiling distilled water, and filled with hot concentrated nitric acid and allowed to stand overnight. The next morning the vessel was emptied, thoroughly washed out with hot distilled water, and steamed for three hours. Finally, a current of hot air, filtered through cotton-wool and dried through sulphuric acid, was passed through it until it was completely dried.

#### 6. *Weighing the Bulbs.*

The balance, made specially for atomic weight determinations, was placed on a stone pedestal in a cellar, situated in the basement of the chemical laboratories. Observations with a maximum and minimum thermometer showed that the temperature in this cellar varied but little. Three filter funnels filled with calcium chloride were kept inside the balance case; the air in it was assumed to be half dried. The doors of the balance case were closed and half-an-hour allowed to elapse before a weighing was made.

The vibrations of the pointer over the scale were viewed through a mirror by means of a telescope. Assuming the number of divisions on the scale to be 1000, and the average zero at no load 500, then the range of the zero variations, during our experiments, was 9 divisions, between 496 to 505.

The sensibility of the balance, during the weighings of the chlorine bulb, was approximately 206 divisions for 1 milligramme, with a range of variation of 8 divisions. During the weighings of the hydrogen bulb, the sensibility was approximately 198 divisions for 1 milligramme, with a range of variation equal to 10 divisions. The method of weighing adopted was GAUSS' method of reversals. Generally, five weighings were taken on one side and four on the other. The concordance of the individual weighings showed that their mean could be relied on to 4 divisions or  $\cdot 00002$  gramme.



The weights employed were a brass hectogramme and its subdivisions to a gramme, and, for the submultiples of a gramme, small platinum weights. The hectogramme was taken as the unit and the separate weights were carefully compared with it. Since all our measurements of mass were relative and not absolute, it was not necessary to determine the absolute mass of our unit. In comparing the gramme of platinum with the brass gramme marked Z, a correction was applied for the different weights of air displaced by them. The values of all the weights are given below:—

## VALUES of the Brass Weights.

Nominal value.	Value found.
100 grammes (unit)	100·00000 grammes
50    "    "	50·00005    "
20    "    "	19·99973    "
10    "    (A)	10·00002    "
10    "    (B)	9·99986    "
5     "    "	4·99991    "
2     "    "	1·99994    "
1     "    (I)	1·00025    "
1     "    (Z)	·99998    "
1     "    (H)	·99993    "

## VALUES of the Platinum Weights.

Nominal value.	Value found.
·5 gramme	·49998 gramme
·2    "    "	·19994    "
·1    "    (1)	·09996    "
·1    "    (2)	·09992    "
·05   "    "	·04995    "
·02   "    "	·02001    "
·01   "    (1)	·01001    "
·01   "    (2)	·01000    "
Pt rider	·01007    "

The palladium bulb, when charged with hydrogen and sealed off, varied in weight from about 419 grammes to 425 grammes. It was counterpoised by a vessel made of the same glass and of approximately the same volume, weighing 400·00097 grammes. The brass and platinum standardised weights were used to complete the equilibrium. The only vacuum corrections necessary to apply to the weighings were—(i.) that for the difference in volume between the small weights used before and after the combustion, *i.e.*, the volume occupied by (approximately) 1 gramme of brass, and (ii.) for possible changes in the buoyancy of the bulb.

The glass counterpoise was made the same volume as the bulb when first used in Experiment I. It was not considered necessary to alter it so as to make it exactly

the same volume as the bulb in the subsequent experiments, since the maximum variation in the displacement of the bulb did not exceed 1.3 cub. centim. This variation in volume, caused by differences in sealing off the thick-walled capillary tube, may be assumed to be due to the solid glass drop at the sealed end. When the density of the air altered between the first and second weighings of the bulb, a difference between the displacement of the bulb and the counterpoise might affect the apparent weight of the bulb, but in only one experiment (No. 8) was a correction necessary, and that only a unit in the fifth place of decimals.

The weighings of the chlorine bulb were carried out in the same manner, with a similar glass counterpoise. It was not, of course, necessary to obtain the same degree of accuracy in weighing the chlorine as in weighing the hydrogen, since a unit in the fourth place of decimals is insignificant. Variations in the displacement of the chlorine bulb, caused by sealing-off, though considerably larger than those of the hydrogen bulb, did not affect the determination of the "chlorine taken."

In illustration of the method of weighing we may refer to Experiment V. The palladium bulb (charged with hydrogen) required the following weights to be added to the opposite pan:—

Weights used.	Value.
Brass 20 grammes	19.99973 grammes
Pt .5 "	.49998 "
.02 "	.02001 "
.01 " (1)	.01001 "
.01 " (2)	.01000 "
Pt rider on 2nd division	.00201 "
	<hr/> 20.54174 grammes

Five weighings with the weights in the right-hand pan gave a mean zero of 398.2 divisions on the scale. Four weighings with the weights reversed gave a mean zero of 597. With no load the mean zero was 497. The two differences are:

$$\text{Right } 98.8. \quad \text{Left } 100.0. \quad \text{Mean } 99.4.$$

The sensibility under this load was found to be 202 divisions of the scale for a difference of 1 milligramme. The mean displacement of the zero was, therefore, equal to a weight .00049 gramme to be subtracted.

Adding these weights together

$$\begin{array}{r} \text{Counterpoise} + 400.00097 \text{ grammes} \\ \text{Weights + rider} + 20.54174 \quad \text{"} \\ - \quad .00049 \quad \text{"} \\ \hline 420.54222 \quad \text{"} \end{array}$$

In this experiment the palladium bulb has a volume below that of the counterpoise by rather less than  $\cdot 5$  cub. centim. The mean barometric pressure at the first weighing was 766.1 millims., and the mean temperature was  $14^{\circ}5$  C. At the second weighing, after the combustion, the mean barometric pressure was 761.2 millims., and the temperature was  $12^{\circ}1$  C. The difference in weight of  $\cdot 5$  cub. centim. of air measured under these conditions is only  $\cdot 001$  milligramme, and is therefore negligible.

Subjoined are the details of the weighings of the palladium bulb in Experiment V

#### EXPERIMENT V. Before Combustion.

Temperature of balance (at start of weighing)  $14^{\circ}5$  C.

„ „ „ (at end „ „ )  $14^{\circ}6$  C.

Barometric height (at start of weighing) 766.7 millims.

„ „ (at end „ „ ) 765.5 „

Weights used were:—20,  $\cdot 5$ ,  $\cdot 02$ ,  $\cdot 01$  and  $\cdot 01$ . Rider on 2nd division on beam.

Zero at no load . . . . 498.

„ (weights in right pan) 393.

„ ( „ „ left „ ) 609.

„ ( „ „ right „ ) 390.

„ ( „ „ left „ ) 591.

„ at no load . . . . 496.

„ (weights in right pan) 404.

„ ( „ „ left „ ) 599.

„ ( „ „ right „ ) 408.

„ ( „ „ left „ ) 589.

„ ( „ „ right „ ) 396.

„ at no load . . . . 498.

Mean zero at no load 497.

Zero (weights in right pan, mean of 5) 398.2.

„ ( „ „ left „ „ 4) 597.

Sensibility 202.

Weight of bulb (before experiment) 420.54222 grammes.

#### EXPERIMENT V. After Combustion.

Temperature of balance (at start of weighing)  $11^{\circ}8$  C.

„ „ „ (at end „ „ )  $12^{\circ}4$  C.

Barometric height (at start of weighing) 760.5 millims.

„ „ (at end „ „ ) 761.9 „

Weights used were:—10 (A), 5, 2, 1 (I), 1 (Z),  $\cdot 5$ ,  $\cdot 02$ ,  $\cdot 01$  (1), and rider on 5th division.

Zero at no load . . . . 503.

„ (weights in right pan) 480.

„ ( „ „ left „ ) 514.

„ ( „ „ right „ ) 488.

„ at no load . . . . 501.

„ (weights in left pan) 513.

„ ( „ „ right „ ) 496.

„ ( „ „ left „ ) 509.

„ ( „ „ right „ ) 492.

„ ( „ „ left „ ) 515.

„ ( „ „ right „ ) 491.

„ at no load . . . . 499.

Mean zero at no load 501.

Zero (weights in right pan, mean of 5) 489.4.

„ ( „ „ left „ „ 4) 512.8.

Sensibility 201.

Weight of bulb after experiment 419.53605 grammes.

7. *Method of Carrying Out the Combustion.*

The weighings of the palladium bulb and the chlorine condensation bulb completed, the next step was to set up the combustion apparatus (fig. 5). This consisted of a stout glass globe A, the "combustion globe" made of Jena glass. Its capacity was about 750 cub. centims., and it was provided with three ground-glass tubulures. In order to ignite the hydrogen at the jet, two platinum-iridium wires\* (totally enclosed, save for their extreme tips, in glass covers) were fused into the combustion globe on each side of the hydrogen tubulure. By the passage of electric sparks between their tips, the jet of hydrogen was easily ignited.

Into the combustion globe was run sufficient water to absorb all the hydrochloric acid gas formed during the combustion, and to leave dilute acid of a not greater strength than one-seventh concentrated. Then two very thin glass bulbs (capacity of each about 6 cub. centims.), which had been previously filled with a hot, concentrated solution of potassium iodide and sealed, were cautiously slid into this water through one of the tubulures. The palladium bulb B, the chlorine condensation bulb C, and the three-way tap D were then, respectively, fitted to the tubulures E, F, and G, care being taken that none of the lubricant (phosphoric acid) was squeezed into the combustion globe through the interstices of the ground-glass joints. To one limb of the three-way tap D, a generator of carbonic acid in an atmosphere of which the subsequent titration of residual iodine was carried out, was attached by a short length of thick-walled indiarubber tubing; to the third limb was fused the apparatus H, through which any residual gases from the combustion were drawn. It consisted of a wash-bottle which could be taken to pieces by means of the ground-glass joint J. The tap K controlled the passage of the gases through the liquid, an alkaline solution of sodium thiosulphate, contained in the wash bottle.

The tube L was attached to the mercury pump by a short piece of thick-walled indiarubber tubing.

These two short lengths of indiarubber tubing were employed so as to enable us to give a jerking motion to the combustion globe and the bulbs when fitted together: (i.) to break the drawn-out *cul-de-sac* of the chlorine bulb, and (ii.) to break the potassium iodide bulbs after the combustion. The only danger arose from a possible in-leakage of air through the tube connecting the wash-bottle with the pump, by which the residual oxygen, nitrogen, and hydrogen were withdrawn from the globe. This tube was wired on to the glass when hot, and was well "drowned" before being used to evacuate the globe. We found that no readable volume of air had leaked through into the highest vacuum attainable during three days.

The different parts of the combustion apparatus having been fitted together, the strength of a neutral solution of sodium thiosulphate was determined by titrating a

\* The position of these wires is shown by the dotted lines P and P<sub>1</sub>; they lie in a plane at right angles to the vertical section shown in fig. 5.

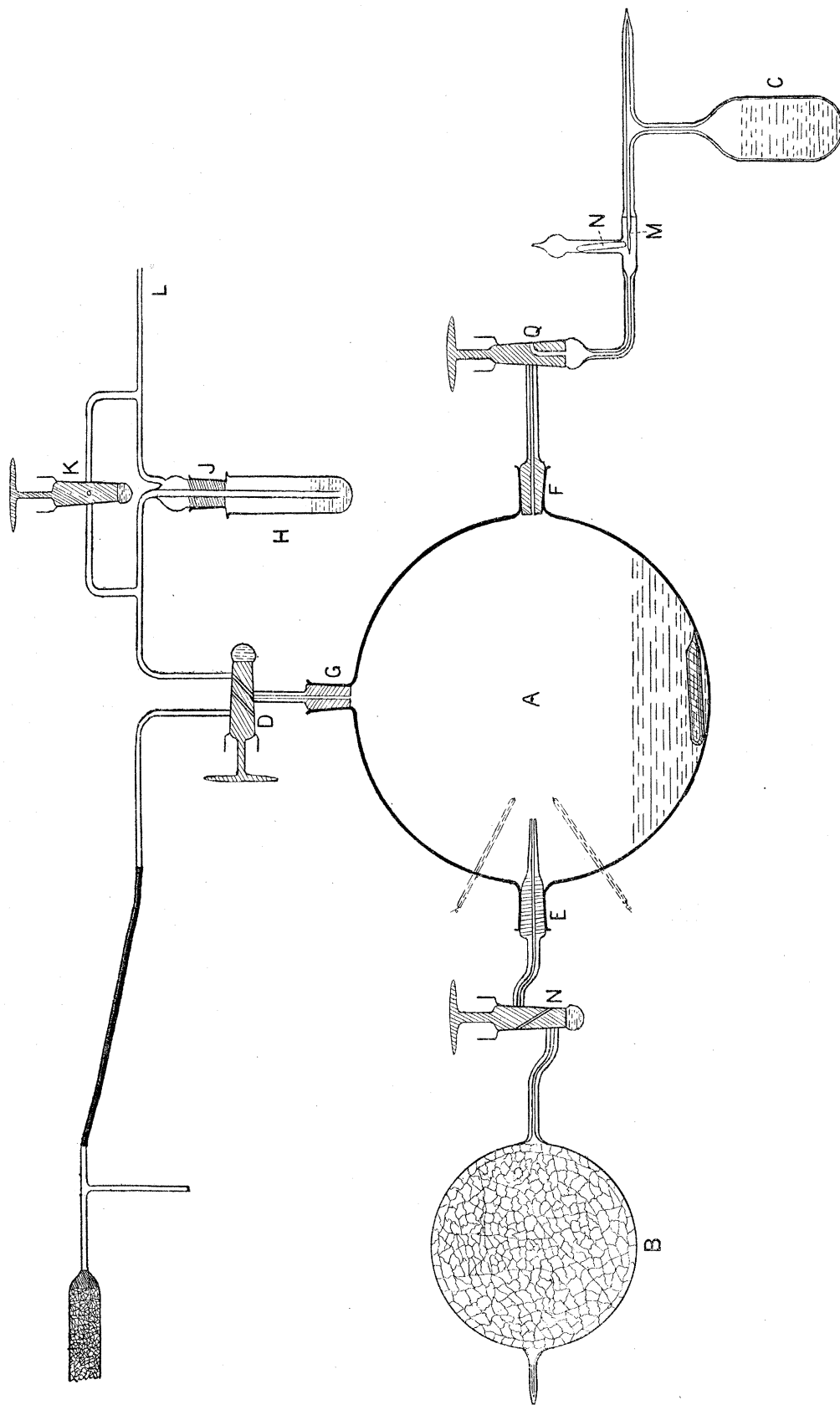


Fig. 5. Combustion apparatus.



measured volume against the standard solution of iodine in potassium iodide. A measured amount (about 6 to 7 cub. centims.) of the sodium thiosulphate solution was run into the wash-bottle and made alkaline by the addition of sodium hydrogen carbonate. The taps D and K were now opened, and the combustion apparatus evacuated (in a stream of water-vapour) as far as possible by the pump. A rapid stream of water-vapour was produced by immersing a large condenser, fused to the pump, in a freezing mixture of ice and salt, and by gently warming the lower part of the combustion globe with warm water. This was done to facilitate the removal of traces of air and nitrogen, and that this was accomplished we concluded from the small amount of nitrogen discovered in the subsequent gas analysis. During the last period of the exhaustion, the calcium chloride and ice freezing mixture, in which the bulb containing liquid chlorine was immersed during the combustion, was prepared, placed in a wide-necked, unsilvered Dewar tube, and packed well round the liquid chlorine bulb.

The evacuation completed, the taps D and H were closed, and the glass *cul-de-sac* M broken by jerking the glass rod N against it.

The heating of the palladium bulb, enclosed in a stout copper box covered with asbestos sheet, was next started, the temperature being noted by means of a mercury-nitrogen thermometer.

The temperature of the liquid chlorine was now between  $-25^{\circ}$  C. and  $-30^{\circ}$  C., and the pressure on the special tap Q was therefore not greatly above atmospheric. Q was slightly turned so as to admit chlorine slowly into the combustion globe. When the pressure of gas in the globe had become nearly atmospheric, the tap Q was closed. This point was determined by the change in the faint hissing noise which attended the entry of chlorine into the vacuum. When the palladium bulb had reached a suitable temperature, all lights were turned out.

Next came the ignition of the jet of hydrogen. Whilst a rapid succession of sparks was passed between the platinum-iridium tips, the tap N was very cautiously opened so as to admit the hydrogen slowly into the combustion globe. The moment the jet of hydrogen had ignited the sparks were discontinued, and all attention was centred on the flame. To cool the globe during the combustion, ice was packed round the lower portion, while that part which was immediately above the flame was cooled by a stream of cold water.

To avoid, as far as possible, any diffusion of hydrogen through the flame, the combustion was carried out at a pressure only slightly below atmospheric. The atmosphere of chlorine was constantly replenished through the tap Q, whilst the tap N regulated the admission of hydrogen to the flame.

The combustion of hydrogen in chlorine at a glass jet is an interesting phenomenon. The flame can be divided into two zones—an inner zone of a light apple-green colour, with an outer zone of less pronounced hue. We learnt by experience that three points in connection with the flame were important for our purpose. Firstly, the

gradual elongation of the outer zone, together with a lessening of the luminosity of the inner zone, indicated that the atmosphere of chlorine was not being renewed quickly enough. Secondly, when the flame became smaller and more luminous, we knew that the pressure of chlorine was in excess, and that the gas was being admitted into the globe too quickly. Lastly, a gradual shrinking in the size of the flame, unattended by any change of luminosity, indicated that the supply of hydrogen was failing. This was, of course, remedied by raising the temperature of the palladium bulb.

When the combustion had been carried to such a point that only a drop of liquid chlorine was left in the condensation bulb, the tap Q was finally closed and the flame made very small. As the atmosphere became rarefied, the outer zone of the flame became elongated and less luminous; the inner zone changed also, but to a less extent. In one experiment (IV.), the flow of hydrogen not being reduced as the chlorine-atmosphere became rarefied, a flame passed through the whole globe. Just before the point of extinction the tap N was closed and the combustion was ended. The duration of the combustion was about three hours, during which constant watching was necessary. The palladium bulb was now allowed to cool to the ordinary temperature.

The two small bulbs, containing concentrated solution of potassium iodide, were then broken by dashing them against the interior of the combustion globe, when the residual chlorine was absorbed with precipitation of iodine. The precipitated iodine, however, soon dissolved in the excess of potassium iodide. The tap D was opened and the residual gases were sucked out of the combustion globe in a current of water-vapour through the alkaline solution of sodium thiosulphate contained in the wash-bottle H, in which the vaporised iodine was absorbed. The residual gases were collected in the gas analysis apparatus.

During this exhaustion the long glass tube R connected with the three-way tap D, and containing  $\text{NaHCO}_3$ , had been heated. The evacuation completed, D was turned and  $\text{CO}_2$  admitted until the combustion globe was full. This was indicated by the escape of gas through the manometer. The tubulure G was now opened, cleaned from adhering phosphoric acid, and the residual iodine titrated in the atmosphere of carbonic acid by means of the sodium thiosulphate solution of known strength contained in a calibrated burette.\* As sufficient potassium iodide was originally contained in the thin glass bulbs to dissolve easily the precipitated iodine, the titration was quickly and accurately carried out, five drops of starch solution being added towards the end of the titration.† One drop of the standard solution of iodine restored the blue starch-iodide colour to the decolourised liquid in the combustion

\* The two burettes employed were carefully calibrated by means of an Ostwald calibrator of 2 cub. centims. volume. The mean results of two calibrations were tabulated and used in determining the volumes.

† Owing to the action of hydrochloric acid on a solution of sodium thiosulphate, we were unable to add excess of the sodium thiosulphate solution and titrate back with the standard solution of iodine.

globe, so it was evident that the error in our volumetric determinations of iodine must have been small. The alkaline sodium thiosulphate solution in the wash-bottle was exactly neutralised with very dilute hydrochloric acid, and the residual thiosulphate estimated with the standard iodine solution.

The determination of the residual gases was effected as follows :—Fig. 6 is a sketch of the gas-analysis apparatus employed.\* It consisted of a graduated pipette A attached to a bent capillary tube, with stopcocks C and D and a graduated tube B. The weight of the apparatus, filled with mercury from the tap C to the end of the capillary tube E, having been determined, the whole was filled with mercury and placed in the trough. The gases, sucked out by the pump from the combustion globe, were collected in B and passed into A. It was assumed that the gases consisted of hydrogen, oxygen, and nitrogen.

When the residual gases had been collected, the whole was transferred to the balance room and allowed to reach the temperature of the room. During this time the taps C and D (fig. 6) were, of course, left open; they were then closed. In order to maintain the gases during analysis at not only constant temperature but constant pressure, it was necessary that the height of the mercury in the limb A of the gas-analysis apparatus above the surface of the mercury in the trough should be kept constant. With the aid of the two etched scales on A and B, the divisions of which were 1 millim. apart, this constant pressure could be easily attained by raising or depressing the apparatus in the trough until the mercury in the limb A stood the same height as before above the level of the mercury in the trough.

When the gases had reached the temperature of the balance room, and the difference in level of the mercury in the limb A and of the mercury in the trough had been noted, the taps C and D were closed, B was emptied and the apparatus was then ready for weighing. The difference in the weights of the apparatus (i.) full of mercury, and (ii.) containing the residual gases of the combustion (corrected for the weight of these residual gases) gave, by an obvious process, their volume.

After being weighed, the gas apparatus was transferred to the mercury trough, the platinum spiral F was then cautiously heated by an electric current so as to bring about the combination of all the hydrogen with the oxygen. Sometimes the oxidation was attended by an explosion; this, of course, occurred when the percentage of hydrogen was relatively great.

As can be seen from Table II., the oxygen was always in excess of that required

\* This form of gas-analysis apparatus was first used by D. L. CHAPMAN and E. HOPKINSON.

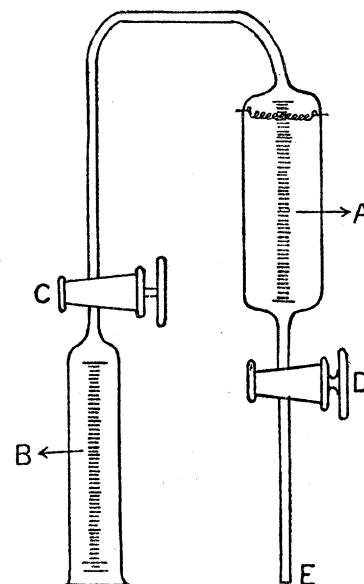


Fig. 6. Gas-analysis apparatus.

for the complete combustion of the hydrogen. After B had been re-filled with mercury and the apparatus inverted in the trough, the taps C and D were opened, and consequent upon the contraction in volume of the gases, mercury rose in the two limbs A and B. When the whole had cooled to the temperature of the room, and the pressure had been equalised, C and D were closed and the apparatus again weighed as before. The difference between the second weighing and this last one gave the volume of contraction, *i.e.*, gave the volumes of hydrogen and oxygen which had combined.

The apparatus was again transferred to the mercury trough, C and D opened, and hydrogen admitted to the apparatus, sufficient to burn up the residual oxygen. The mercury levels were again adjusted, C and D were closed, and the apparatus again weighed. From weighings three and four the volume of the added gas was easily calculated. The gases were fired by heating the platinum spiral, and, on cooling, the apparatus was weighed as before. The final weighing, coupled with weighing four, gave the volume of contraction, *i.e.*, gave the volume of residual oxygen. From the data thus obtained the composition of the residual gases of the combustion, assuming them to have been hydrogen, oxygen, and nitrogen, was easily calculated.\*

The analysis of the residual gases from Experiment 2 is given below in illustration :—

Mean temperature of balance room . . . . .	13°·8 C.
„ barometric height . . . . .	768·5 millims.
Difference in level between mercury in limb A and mercury in trough . . . . .	198·5 „
Weight of gas apparatus full of mercury . . . . .	489·029 grammes.
„ „ „ and residual gases . . . . .	413·756 „
„ „ „ after combustion . . . . .	440·846 „
„ „ „ „ addition of H <sub>2</sub> . . . . .	309·846 „
„ „ „ „ combustion . . . . .	450·838 „

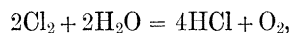
From these weights the composition of the residual gases was calculated to be as follows :—

4·12 cub. centims. of oxygen	} at 13°·8 C. and 768·5 – 198·5 millims. pressure.
1·33 „ „ hydrogen	
·09 „ „ nitrogen	
	} Gases saturated with aqueous vapour.

These volumes gave, on reduction to N.T.P.,

2·87 cub. centims. of oxygen from steam	} at 0° C. and 760 millims.
·93 „ „ hydrogen	
·08 „ „ air	
	} Gases dry.

Now, in accordance with the equation



2·87 cub. centims. of oxygen were produced by the action on aqueous vapour of 5·74 cub. centims. of chlorine.

Weight of 5·74 cub. centims. of chlorine is  $5·74 \times \cdot 00317 = \cdot 0182$  gramme.

Weight of ·93 cub. centim. of hydrogen = ·00008 gramme.

\* In preliminary experiments, carried out in the same way, we failed to detect any trace of CO<sub>2</sub> in the products of combustion.



8. *Results of the Experiments.*

In the following tables we have put together the results obtained in the nine experiments. Table II. contains the volumes of the several residual gases, reduced to normal temperature and pressure, as determined by the gas-analysis.

We have assumed that the nitrogen found at the end of the experiments is due to residual air left in the evacuation of the large combustion globe. It is conceivable that a trace of this nitrogen came from the palladium bulb and was weighed as hydrogen. If that were so, the atomic weight of chlorine we have found would be *too low*. The total volume of nitrogen found in the nine experiments was  $\cdot 8$  cub. centim. To make an extreme supposition—if *all* this nitrogen had been introduced from the palladium bulb, and weighed as hydrogen, and therefore all the oxygen had come from the steam, the atomic weight of chlorine found by us would be  $\cdot 005$  too low.

In Table III. we have put together the several portions of residual chlorine not combining with the weighed hydrogen :—(i.) that calculated from the iodine found in the globe ; (ii.) that calculated from the iodine vapour drawn over with the residual gases and caught in the wash-bottle ; and (iii.) that calculated from the oxygen found in the residual gases *less* the oxygen assumed (from the nitrogen) to be present as air.

In Table IV. the weights of the bulbs before and after the combustion are given, with the corrections for buoyancy and for the unburnt gases. We set out the hydrogen weighings to five places of decimals, although it is not, of course, suggested that the *absolute weight* of the palladium bulb can be determined to this degree of accuracy. The fifth figure does not affect the mean atomic weight deduced from the experiments.



TABLE II.—Determination of Volumes of Residual Gases, cub. centims. at N.T.P.

Experiment. . . . .	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Volume of oxygen liberated from steam. . . . .	3·39	2·87	5·07	2·91	4·30	3·41	3·65	3·11	4·80
Volume of hydrogen unburnt. . . . .	1·51	·93	2·02	·08	·40	·74	1·04	3·61	2·45
Volume of residual air . . . . .	·11	·08	·06	·11	·16	·06	·18	·13	·12

TABLE III.—Determination of the Weight of Chlorine uncombined with the Weighed Hydrogen (in grammes).

Experiment. . . . .	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Unburnt chlorine calculated from iodine in globe. . . . .	·6941	·6603	·7865	·6238	·6767	·5981	·6838	·7222	·7260
Unburnt chlorine calculated from iodine vapour . . . . .	·0005	·0006	·0004	·0003	·0007	·0005	·0005	·0006	·0005
Chlorine corresponding with oxygen liberated. . . . .	·0215	·0182	·0321	·0185	·0273	·0216	·0231	·0197	·0304
Total excess of chlorine . . . . .	·7161	·6791	·8190	·6426	·7047	·6202	·7074	·7425	·7569

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TABLE IV.

Experiment . . .	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Weight of H bulb (i) . . .	421·70013	424·95423	421·54520	419·43291	420·54232	421·97791	420·68473	423·44677	421·57693
" " (ii) . . .	420·70057	423·93222	420·54884	418·40843	419·53605	420·98896	419·66861	422·33286	420·56339
Difference . . . . .	·99956	1·02201	·99636	1·02448	1·00617	·98895	1·01612	1·11391	1·01354
Correction for density of air								·00001	
Vacuum correction for weights . . . . .	·00015	·00015	·00015	·00015	·00015	·00015	·00015	·00015	·00015
Weight of H taken . . .	·99941	·02186	·99621	1·02433	1·00602	·98880	1·01597	1·11375	1·01339
" " unburnt . . .	·00014	·00008	·00018	·00001	·00004	·00007	·00009	·00032	·00022
" " burnt . . .	·99927	1·02178	·99603	1·02432	1·00598	·98873	1·01588	1·11343	1·01317
Weight of Cl bulb (i) . . .	87·7687	85·3040	83·0760	93·9105	88·1273	84·7047	83·4678	92·1924	90·6115
" " (ii) . . .	51·8807	48·6573	47·1853	57·2220	52·0029	49·2787	46·9908	52·2704	54·1964
Difference . . . . .	35·8880	36·6467	35·8907	36·6885	36·1244	35·4260	36·4770	39·9220	36·4151
Vacuum correction for weights . . . . .	·0053	·0055	·0055	·0056	·0053	·0053	·0057	·0059	·0055
Weight of Cl taken . . .	35·8827	36·6412	35·8852	36·6829	36·1191	35·4207	36·4713	39·9161	36·4096
Excess of Cl . . . . .	·7161	·6791	·8190	·6426	·7047	·6202	·7074	·7425	·7569
Weight of Cl burnt . . .	35·1666	35·9621	35·0662	36·0403	35·4144	34·8005	35·7639	39·1736	35·6527
Ratio $\frac{\text{Cl}}{\text{H}}$ . . . . .	35·192	35·196	35·206	35·184	35·204	35·197	35·205	35·183	35·189

Mean ratio, 35·195 ± ·002.

## APPENDIX.

1. *The Action of Chlorine on Glass.*

The following experiments were made to determine the action, if any, of pure, dry chlorine on soft glass. Two glass bulbs of approximately equal volume and weight were made. To one of these, A, was fused the inner portion of a ground glass joint; it was then cleaned and dried. The two bulbs were then suspended from different pans of the balance and small weights added to one pan to bring them to equilibrium. A was then fitted to the apparatus for generating chlorine, and the whole was evacuated and filled with pure dry chlorine. The bulb was separated from the rest of the apparatus by fusion beyond the ground-glass joint and was then kept for one week. At the end of that time the ground-glass joint was taken to pieces, and the chlorine sucked out and replaced by dried air. It was then weighed, the other bulb acting as a counterpoise.

Weight to counterpoise the bulb (before exposure to chlorine)	. . .	1·32468	grammes.
"    "    "    (after    "    "    )	. . .	1·32464	"

The experiment was repeated with two similar bulbs, but the chlorine was left in contact with the glass for a fortnight.

Weight to counterpoise the bulb (before exposure to chlorine)	. . .	2·67931	grammes.
"    "    "    (after    "    "    )	. . .	2·67925	"

Two more bulbs were subjected to similar treatment, the time of contact, in this case, being a month.

Weight to counterpoise the bulb (before exposure to chlorine)	. . .	1·12884	grammes.
"    "    "    (after    "    "    )	. . .	1·12879	"

These weighings show that on allowing chlorine to remain in contact with soft glass for a considerable period of time, the latter loses weight very slightly.

The bulb used in Experiment 1 was again filled with chlorine, which was allowed to remain in contact with the glass for a week.

Weight of bulb before exposure . . . . .	1·32464	grammes.
"    "    after    "    . . . . .	1·32465	"

An exposure for a further period of two weeks gave :—

Weight of bulb before exposure . . . . .	1·32465	grammes.
"    "    after    "    . . . . .	1·32463	"

If any action of chlorine on the soft glass bulb may be assumed to have taken place, it must have occurred during the first week, as further exposure to chlorine gave a constant result.

The solvent action of liquid chlorine, if any, on soft glass was also examined. The same bulb was employed. After its weight had been determined as above, 10 cub. centims. of liquid chlorine were condensed in it by means of a freezing mixture of solid carbonic acid and ether. The bulb was then separated from the chlorine apparatus by fusion between the ground-glass joint and the bulb, and was laid aside for a week. The ground-glass portion was cleaned and dried, a mark was cut with a clean glass cutter in the glass capillary tubing attached to the bulb, and a clean fracture effected. When the chlorine in the bulb had been totally replaced by air, the three parts of the original apparatus, *i.e.*, the bulb, the piece of glass broken off from it, and the inner portion of the ground-glass joint were weighed, the companion bulb acting as a counterpoise.

Weight of bulb before exposure . . . . .	1·32464 grammes.
"    "    after    "    . . . . .	1·32466    "

A similar apparatus was constructed, and, after being subjected to the action of pure dry gaseous chlorine for a week, the last experiment was repeated, the time of exposure being a month.

Weight of bulb before exposure . . . . .	3·49842 grammes.
"    "    after    "    . . . . .	3·49839    "

There seemed to be no appreciable action of liquid chlorine on soft glass.

Though the combined effect of gaseous and liquid chlorine on soft glass was so exceedingly small, the bulb of the chlorine condensation bulb was subjected, before use, to the action of pure dry gaseous chlorine for a fortnight.

## 2. *The Reaction between Iodine and Sodium Thiosulphate in Presence of Carbonic Acid and of Hydrochloric Acid.*

Titration of sodium thiosulphate by iodine in potassium iodide, carried out in an atmosphere of carbonic acid, showed that the gas had no influence on the accuracy of the residual iodine determinations. A known volume of sodium thiosulphate solution was run into a small Erlenmeyer flask and titrated with the standard solution of iodine in potassium iodide. An equal volume was run into another flask and pure carbonic acid (from sodium hydrogen carbonate) was passed through the solution for ten minutes, it was then titrated as usual. No difference in the volumes of iodine in potassium iodide solution required to combine with the thio in the two flasks could be detected. Several repetitions gave similar results.

S. U. PICKERING\* has shown that iodine in potassium iodide solution can be correctly titrated by thiosulphate in presence of hydrochloric acid, if allowance is made for the slow oxidation of the liberated hydrogen iodide by the oxygen from the

\* 'Journ. Chem. Soc.,' 1880, p. 134.



air. We have confirmed these experiments with different strengths of hydrochloric acid and found that practically no iodine was liberated in the oxygen free solutions employed.

Approximately equal volumes of iodine in potassium iodide solution were run into small Erlenmeyer flasks X and Y from the calibrated burette B. The iodine in X was then titrated by means of thiosulphate solution from burette A; hydrochloric acid of known strength was then added to Y and the titration immediately completed.

The experiments were repeated several times with the addition of hydrochloric acid of  $\frac{1}{5}$  concentration :

#### EXPERIMENT I.

120 cub. centims. of  $\frac{1}{10}$  concentrated HCl were added to the solution in flask Y.

Volumes of iodine in K 1 taken.

Burette B. Flask X, 25·04 cub. centims. Flask Y, 25·04 cub. centims.

Volumes of thio required by above

Burette A. Flask X, 25·13 cub. centims. Flask Y, 25·16 cub. centims.

#### EXPERIMENT II.

120 cub. centims. of  $\frac{1}{5}$  concentrated HCl were added to the solution in flask Y.

Volumes of iodine in K 1 taken.

Burette B. Flask X, 25·08 cub. centims. Flask Y, 25·10 cub. centims.

Volumes of thio required by above

Burette A. Flask X, 25·21 cub. centims. Flask Y, 25·20 cub. centims.

#### EXPERIMENT III.

120 cub. centims. of  $\frac{1}{5}$  concentrated HCl were added to the solution in flask Y.

Volumes of iodine in K 1 taken.

Burette B. Flask X, 25·23 cub. centims. Flask Y, 25·19 cub. centims.

Volumes of thio required by above

Burette A. Flask X, 25·31 cub. centims. Flask Y, 25·29 cub. centims.

#### EXPERIMENT IV.

120 cub. centims. of  $\frac{1}{5}$  concentrated HCl were added to the solution in flask Y.

Volumes of iodine in K 1 taken.

Burette B. Flask X, 25·05 cub. centims. Flask Y, 25·06 cub. centims.

Volumes of thio required by above

Burette A. Flask X, 25·14 cub. centims. Flask Y, 25·17 cub. centims.

Since hydrochloric acid of  $\frac{1}{6}$  concentration has then no influence on the titration of iodine in potassium iodide solution by sodium thiosulphate solution, we felt justified in using, in our experiments, such volumes of water as never permitted of the acid solution attaining a greater strength than  $\frac{1}{7}$  concentrated.