CCCXXX.—*The Determination of the Atomic Weight of Silver by the Direct Ratio of Silver to Oxygen in Silver Oxide.*

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1. *The Stability of Silver Oxide.*

THERE is considerable difference of opinion as to the stability of silver oxide. According to Rose (*Pogg. Ann.*, 1852, **85**, 314; *Chem. Gazz.*, 1852, **10**, 182), silver oxide decomposes in light at the ordinary temperature and suffers slight loss of oxygen at 100°. He advises 80° as the maximum temperature at which it is safe to dry the substance. Carey Lea (*Amer. J. Sci.*, 1892, **43**, 249) dried silver oxide to constant weight at 160—165°; the product had lost a small amount of oxygen. From the colour of the chloride obtained by dissolving the oxide in hydrochloric acid, he assumed that even drying at the ordinary temperature causes slight decomposition. The silver oxide, even after drying for 20 hours at 100°, still contained about 0·5% of moisture. Colson (*Compt. rend.*, 1898, **127**, 961; 1900, **130**, 330) states that the temperature can be taken to 200° without decomposition of the silver oxide. None of these workers, however, collected the oxygen evolved, their conclusions being drawn from the percentage loss in weight of the substance on ignition.

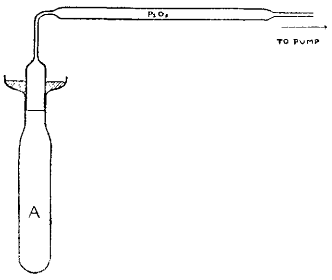
The reaction $2Ag_2O \rightleftarrows 4Ag + O_2$ has been shown by le Chatelier (*Bull. Soc. chim.*, 1887, **48**, 342; *Z. physikal. Chem.*, 1887, **1**, 516) and Lewis (*ibid.*, 1905, **52**, 310) to be reversible. The latter (*J. Amer. Chem. Soc.*, 1906, **28**, 139) measured the decomposition pressures of silver oxide (dried at 240°) at 302°, 325°, and 445° and found them to be 20·5, 32, and 204 atm. respectively. From these results he calculated the decomposition pressure of the oxide at 25° to be

5×10^{-4} atm. or approximately 0·4 mm. Hg. If this value be correct, it should be possible to dry silver oxide at the ordinary temperature and pressure without any fear of decomposition.

Madsen (*Z. anorg. Chem.*, 1913, **79**, 200) concludes that it is impossible to remove all the water from silver oxide without slight decomposition. Von Kohlschütter and Eydmann (*Annalen*, 1913, **398**, 1) report very slow decomposition at 300°. Mixter (*Amer. J. Sci.*, 1911, **32**, 202) dried silver oxide at 280°; the sample obtained, which was slightly carbonated, on analysis, showed 92% Ag (Ag_2O requires 93·1%). Hardin (*J. Amer. Chem. Soc.*, 1896, **18**, 994) mentions an attempt to determine the ratio of silver to oxygen in silver oxide, but he abandoned the experiments owing to loss of oxygen on drying the oxide.

The importance of the atomic weight of silver renders it highly desirable that it should be determined by a direct ratio of silver to oxygen in silver oxide. The ratio is not ideal, being of the order 13·5 : 1, but this disadvantage would be outweighed by the simplicity of the experimental determination of the ratio if it were possible to prepare silver oxide in the pure condition. It was therefore decided to reinvestigate its stability.

FIG. 1.



Freshly-prepared silver oxide was placed in the silica tube A (Fig. 1) and the apparatus was quickly evacuated with a Fleuss pump followed by a Sprengel pump. The gas extracted by the Sprengel pump was analysed (CO_2, 0·045 c.c.; O_2, 0·020 c.c.; N_2, 0·080 c.c.) and deemed to be a mixture of carbon dioxide and air. The apparatus was then kept for 4 days to allow the oxide to dry. No depression of the mercury in the pump manometer was noticed, but on starting the pump a very small quantity of gas, about 0·01 c.c., too small for separate analysis, was collected. The tube containing the oxide was therefore immersed in a water-bath at 100° and kept at that temperature for 5 days and nights. The gas pumped off after this time was analysed, with the following result: CO_2, 0·073 c.c.; O_2, 0·008 c.c.; N_2, 0·037 c.c. Thus at 100° the gas evolved was mainly carbon dioxide, the remainder being a little air, probably from the walls of the tube. The pump was again started and kept working for a further period of 7 hours, the silica tube and contents being kept at 100°. A small bubble of gas collected which was completely absorbed by caustic potash and was therefore free from oxygen.

During the drying at the ordinary temperature, the oxide was exposed to diffused daylight, yet the oxygen and nitrogen found in the gas pumped out of the apparatus were in the ratio normally obtaining in air, thus showing that there was no excess of oxygen. Hence it seems that, contrary to previous statements, silver oxide is not decomposed to any appreciable extent by light or by drying over phosphorus pentoxide at the ordinary temperature. Moreover, since no oxygen was evolved at 100°, in a vacuum, it should be possible to dry silver oxide at 100° without any fear of decomposition. To make sure that the phosphorus pentoxide (prepared by a method described later) was not absorbing any oxygen, dry carbon dioxide-free air was admitted into the apparatus. No alteration in pressure was observed after 3 days.

The moist silver oxide placed in the apparatus, on treatment with dilute hydrochloric acid, gave a perfectly white chloride, but the chloride obtained from the oxide after drying was brownish-pink. Carey Lea (*loc. cit.*) states that this pink chloride is the photochloride. If so, then the above experiment indicated that it was formed with very slight loss of oxygen.

Experiments carried out in a similar manner at higher temperatures showed that silver oxide decomposed extremely slowly at 165°. It was also found possible to heat the oxide for several hours at 250° without any oxygen being evolved. Once the decomposition had started, however, it accelerated and soon became fairly rapid.

The above experiments indicated that it was possible to dry silver oxide over pure phosphorus pentoxide at the ordinary temperature or in a vacuum at 100° without the loss of any appreciable amount of oxygen. It seemed, however, that some very small amount of oxygen was lost, because the dried oxide always gave a pink chloride on treatment with hydrochloric acid. The pink chloride was not the photochloride as stated by Carey Lea, because experiments showed that light had nothing to do with its production. Silver oxide prepared and dried in absolute darkness also gave this pink chloride. It was thought, nevertheless, that the pink colour of the chloride might be due to a negligible loss of oxygen from the oxide and it was therefore decided to prepare silver oxide as pure as possible and analyse it with " atomic weight " accuracy.

Preparation of Pure Materials.

Water. The water used was prepared by distilling ordinary laboratory distilled water from a weakly alkaline (potassium hydroxide) solution of potassium permanganate in a copper still, through a block-copper condenser. After simmering over-night, the middle portion of each distillate was collected in resistance glass bottles (Durosil) after the distillate had been shown to be free from ammonium compounds.

Nitric acid. Ordinary pure nitric acid (Hopkin and Williams) was distilled over silver nitrate and potassium nitrate in a Jena glass retort, and the distillate discarded until free from halogen. This acid was finally transferred to a platinum still, the middle portion of the distillate from the platinum being used. The acid was always distilled immediately before use into a small platinum flask. The strength of the acid so obtained, as determined by its density, is about 65%, this being the composition of the constant-boiling mixture.

Silver nitrate. Silver nitrate was recrystallised five times from acid solution, the crystals being dried on a porcelain centrifuge. After the fifth recrystallisation the nitrate was dissolved in water and reduced with a slight excess of pure ammonium formate, freshly prepared. When the violent ebullition and evolution of gas had subsided the spongy grey silver was broken up with a glass rod and then washed repeatedly with hot water until free from ammonia. The finely powdered amorphous silver was finally dissolved in a slight excess of freshly distilled nitric acid and crystallised once more.

All crystallisations were carried out in Austrian hard-glass vessels. Conductivity water was used throughout. In order to avoid waste of silver nitrate and also to promote quicker crystallisation, thereby reducing occlusion, the silver nitrate solution was evaporated to an oily consistency and then excess of pure nitric acid was added with continual stirring until no more crystals of silver nitrate were thrown down. In this way, each crystallisation could be carried out with a loss of 8% of nitrate.

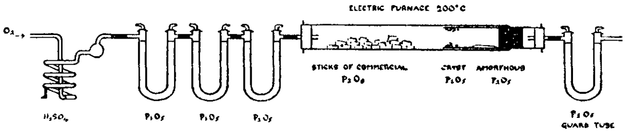
It was found impossible to test the wash-water from the silver directly with Nessler's reagent, as the dissolved silver was sufficient to give a yellow coloration, due to the formation of silver iodide. When testing, therefore, the wash-liquors were boiled with caustic potash and the distillate was tested with Nessler's reagent. An all-glass distillation apparatus was employed. The process of washing took 2—3 days.

Ammonium formate. Kahlbaum's pure formic acid (*d* 1·2) was distilled in platinum and neutralised with ammonia, freshly prepared by boiling the concentrated solution (*d* 0·880) and leading the gas into conductivity water. The solution was tested for halogens by first neutralising it with pure nitric acid and then adding silver nitrate solution.

Baryta. To avoid the presence of silica, crystallisations were carried out in a pure silver flask and a large pure silver basin. One pound of baryta (Hopkin and Williams's "pure recrystallised") was dissolved in 200 c.c. of distilled water contained in the silver flask, the flask being gently heated to effect solution. The solution was poured into the silver basin, which was surrounded by cold water and protected from dust. The finely crystalline baryta so formed was centrifuged and the crystals were damped with distilled water, recentrifuged, and again damped and centrifuged. The recrystallisation was repeated three times, after which conductivity water was used. Nine crystallisations were necessary. The baryta was then free from chloride but contained a little carbonate, which was subsequently removed.

Phosphorus pentoxide. Pellets of "pure" phosphorus pentoxide were distilled at a low temperature (180—210°) in a slow stream of oxygen, the apparatus shown in Fig. 2 being employed. The product, which consisted of fairly large crystals and a finely-divided powder, was stored in a stoppered bottle in a desiccator over phosphorus pentoxide. Owing to the unavoidable formation of the vitreous variety on the surface of the crude pentoxide, not more than 10% distilled over.

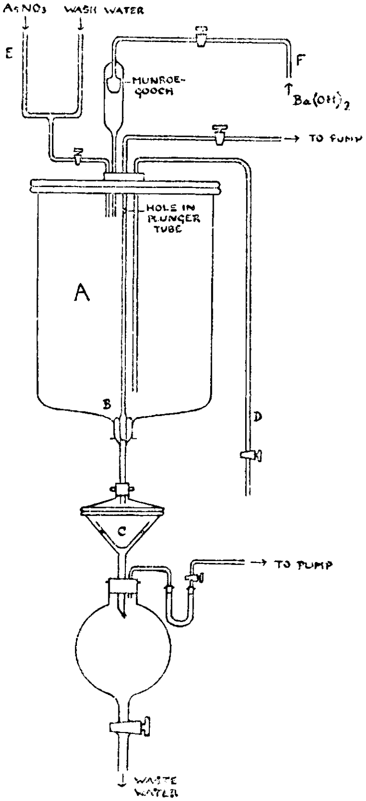
FIG. 2.



Silver oxide. An attempt to prepare pure silver oxide was made in the apparatus shown in Fig. 3. It consists of a large inverted bell-jar, A, which, by raising the plunger, B, may be put in communication with the filter C. The bell-jar is closed with a ground glass plate held firmly in position by means of wooden clamps. The glass plate is bored centrally and carries a large rubber stopper through which pass the plunger, a syphon tube, and tubes to permit the entry of silver nitrate and baryta solutions and wash-water. The lower part of the apparatus consists of a funnel and ground glass cover, held firmly together by means of a wooden clamp. The lower part of the funnel is connected to a large tap-funnel.

The preparation of silver oxide in this apparatus was carried out as follows: All parts of the apparatus were thoroughly cleaned with a mixture of chromic and nitric acids. The apparatus was then assembled, all rubber stoppers being protected by means of paraffin wax. The precipitation vessel A was completely filled with filtered distilled water and after standing over-night was emptied by means of the syphon tube D. The process was repeated with distilled water and then with conductivity water. A current of carbon dioxide-free air was drawn through the apparatus by way of E and D until the issuing air, on bubbling through baryta solution for 6 hours, gave no precipitate. This required about 80 hours. Conductivity water was freed from carbon dioxide by bubbling a current of carbon dioxide-free air through it for 3 days at the rate of three bubbles a second.

FIG. 3.



In carrying out the precipitation a slight excess of silver nitrate was used to minimise any risk of the introduction of silica through the action of the alkaline baryta on the glass. A quantity of silver nitrate, sufficient to form about 70 g. of silver oxide, was dissolved in boiled-out conductivity water, drawn over into the precipitation vessel by way of E, and diluted to 2 litres. The equivalent quantity of pure baryta was dissolved in 2 litres of conductivity water in a silver soup tureen and drawn over into the precipitation vessel by way of F. Before entering A the baryta solution passed through a Munroe-Gooch platinum crucible sealed directly on to the glass syphon tube, all traces of carbonate being thus removed.

The precipitated silver oxide was allowed to settle over-night and the supernatant liquid decanted off through the syphon tube D. The precipitate was washed by decantation until the wash-liquors gave no turbidity with dilute sulphuric acid. It was then transferred completely to the filter. This consists of a pure silver cone with a perforated bottom. To the bottom of the cone are firmly clamped, by means of a small silver nut and bolt, two discs of pure silver gauze and a perforated silver plate. This device was quite efficient in filtering the rather coarse granular precipitate of silver oxide.

The precipitate was washed several times on the filter until free from barium, and a current of carbon dioxide-free air was drawn through it to remove as much water as possible. The filter and precipitate were then quickly transferred to a desiccator containing solid caustic potash. After a fortnight the oxide was sufficiently dry to permit rough powdering. The drying was continued in a desiccator over pure phosphorus pentoxide for a further month. It was deemed advisable not to accelerate the drying by raising the temperature in order to make quite sure that no loss of oxygen took place.

Three samples of silver oxide were prepared, each of 60—70 g. Sample A was prepared from pure silver oxide made during the preliminary experiments and subsequently converted into nitrate. The source of sample B was pure silver nitrate, also made during the preliminary experiments. Sample C was made from the nitrate prepared from 8 oz. of Johnson and Matthey's purest assay silver.

The method adopted for the analysis of the three samples of oxide was essentially the same as that described later. The following results were obtained:

	Ratio O : Ag.		
	Sample A.	Sample B.	Sample C.
Experiment 1	8 : 108·08	8 : 108·64	——
,, 2	8 : 108·07	8 : 108·64	8 : 108·03
,, 3	8 : 108·08	8 : 108·71	8 : 108·08

In spite of the fairly good agreement of the results of the A and C series of experiments, the great divergence of the B results and the fact that all the results are considerably higher than the accepted value for the atomic weight of silver indicated that the compound analysed must have lost some oxygen during the drying process. This was supported by the fact that all samples, on being treated with dilute hydrochloric acid, gave a pink chloride. This result was contradictory to that obtained in the preliminary experiments on the stability of the oxide. A careful repetition of these experiments gave the same result, *viz.*, that it was possible to heat silver oxide for long periods at 100° without being able to detect any oxygen in the gases pumped out of the apparatus containing the oxide.

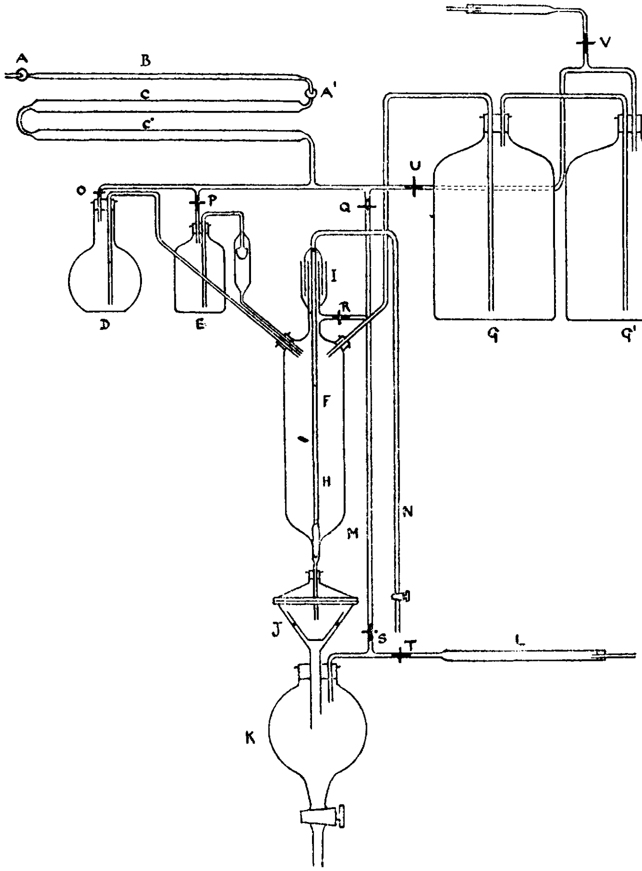
The gravimetric results indicated that some slow reaction was taking place during the drying process which resulted in a small amount of reduction. In order to find if it were possible to speed up this reaction and also the extent to which the reduction would go, it was decided to dry the oxide at a higher temperature and then analyse the product gravimetrically. Air from a compressed-air cylinder, after bubbling through phosphoric acid and passing through a tube 4 feet long, half of which was packed with solid caustic soda and half with phosphorus pentoxide, passed into a hard-glass tube heated electrically at 80°, containing a porcelain boat filled with freshly-prepared silver oxide. After the air had passed over the oxide for 5 days and nights, small white specks of metallic silver were observed on the oxide nearest the air inlet. After a further week, the half of the oxide nearer the inlet had become perfectly white, but the other half was still black. On taking the boat out of the tube it was found that only a very thin surface film of the oxide had been reduced, the remainder being quite black. This suggested that the reduction of the silver oxide was not due to any instability of the oxide, but that it was being reduced by the small amount of organic matter which passed through the drying tubes. A tube containing copper oxide, heated electrically to dull redness, was inserted between the compressed-air cylinder and the bubbler and the experiment repeated. No visible reduction took place during a fortnight. The temperature was raised to 120°; after a further week no white specks of metallic silver had appeared.

This sensitivity of silver oxide to reduction by small traces of organic matter explained the apparent contradiction between the results of the gravimetric and volumetric experiments and it can be stated with certainty that silver oxide is quite stable at the ordinary temperature and suffers no decomposition on being dried. The statements of Rose (*loc. cit.*), Carey Lea (*loc. cit.*), and Hardin (*loc. cit.*) and our own volumetric results are all explained by the ease with which silver oxide is reduced by small traces of organic matter. No details are given in the papers mentioned as to the methods of preparing the silver oxide, but it is almost certain that at some stage in the preparation, either through the use of impure water or through contact with the atmosphere, some small trace of organic matter would be introduced. It was found later that the most scrupulous care is necessary in the exclusion of organic matter from the silver oxide in order to prepare a sample which, after drying, will give a white chloride on treatment with dilute hydrochloric acid. In the volumetric experiments the oxygen from the silver oxide was given off as carbon dioxide.

2. *The Preparation of Pure Silver Oxide.*

From the foregoing it will be seen that in order to prepare silver oxide of atomic weight purity, an apparatus is necessary in which precipitation, washing, and filtration can be carried out in an atmosphere entirely free from organic matter and the slightest trace of carbon dioxide. With this object in view, the apparatus shown in Fig. 4 was erected. A, B, and C constitute a system of purification tubes. A and A′ are bubblers containing syrupy phosphoric acid. A is connected to a hard glass tube, B, by means of a piece of rubber pressure tubing. B is filled with copper oxide and may be heated electrically to dull redness. The other end of B is connected by tubing to another bubbler, A′, which is sealed on to the soda-lime tube, C. C is sealed on to another similar tube, C′, which is half filled with soda-lime and half with purified, strongly ignited asbestos. Each of the three tubes is about 18 inches long; C and C′ are 1 inch in diameter and B ½ inch. The bubbler A is connected by means of a piece of pressure tubing to a compressed-air cylinder, the flow of air from the cylinder being regulated by an "Endurance" valve. C′ connects through a four-way piece of glass tubing with the silver nitrate vessel, D, the baryta vessel, E, the precipitation

FIG. 4.



vessel, F, and the water bottles, G and G′. Connexion is made with each of these by means of a piece of pressure tubing carrying a screw clip, so that any one of them singly may be put into communication with the supply of pure air. The silver nitrate vessel, D, is a litre Jena-glass flask fitted with a syphon tube which communicates with the precipitation vessel. The baryta vessel, E, is a pure silver flask of about 800 c.c. capacity. This also is fitted with a syphon tube, which carries a filter. The filter is a Munroe-Gooch platinum crucible sealed directly to the glass syphon tube and serves to filter the baryta solution immediately before entering the precipitation vessel. The wash-bottles are of Durosil resistance glass, each of about 10 litres capacity. Each is fitted with syphon tubes whereby G′ communicates with G and G with the precipitation vessel. The syphon tubes enter the precipitation vessel through rubber stoppers fitted in two tubuli in the upper part of F. The precipitation vessel is of about 2½ litres capacity and is of Durosil resistance glass. The lower tubulus of F is closed by a ground glass plunger. The mercury-water seal, I, permits the plunger to be raised without admitting air, so that the precipitation vessel may be put into communication with the filter funnel, J. This consists of a glass funnel and ground glass top held together by a wooden clamp. The funnel stem passes through a rubber stopper in the tubulus of the large separating funnel, K. Resting on a rubber ring in the filter funnel is the silver filter previously described. The large 2-litre separating funnel, K, may be put in communication with the atmosphere through the soda-lime guard-tube, L, or with the supply of pure air by means of the tube M.

About 2 cm. from the bottom of the plunger-tube H is a small hole so that liquid may be syphoned out of the precipitation vessel by way of the tube N.

The procedure in preparing pure silver oxide by means of this apparatus was as follows : All glass parts of the apparatus were thoroughly cleaned, first with ordinary water, followed by strong sodium hydroxide solution, distilled water, chromic and nitric acids, strong nitric acid, distilled water, and finally conductivity water. Whilst the cleaning and erection were in progress the two wash-bottles were filled directly from the still with conductivity water. As soon as they were full, the bottles were placed in position and quickly connected with the rest of the apparatus, the water being exposed to the atmosphere for only 2 or 3 seconds. With the screw clips O, P, R, V, and Q open, and S, T, and U closed, the " Endurance " pressure regulator on the compressed-air cylinder was opened so that a slow stream of purified air passed by way of the purifying tubes, through D, E, and F, and bubbled through the water in G and G′, passing out of the apparatus by way of the soda-lime guard-tube at V. In this way it was possible to remove the last trace of carbon dioxide present in the wash-water and at the same time any introduction of organic matter into the conductivity water was avoided. After the air had been bubbling through the water for 3 days and nights it was found to be free from carbon dioxide by bubbling the issuing air through baryta solution for 6 hours, after which time no turbidity had developed.

The screw slips O, P, Q, and V were then closed and U was opened. Water was forced from G′ into G and from G into F. As soon as the syphon had started, the supply of air was cut off and Q and R were opened. Under these conditions the syphon continues to function. When F was almost full of water, U was closed and the supply of air turned on, thus immediately stopping the syphon. The plunger tube was then raised slightly and, with a slow stream of air passing into F by way of Q and R, the water was allowed to trickle through the filter into K, the air in K being driven out through the guard-tube, L. When K was full the remainder of the water was drawn off through the syphon, N. The water in K was withdrawn slowly, pure air entering *via* Q and S, and T being closed. The apparatus was now filled with pure, carbon dioxide-free air.

With all the clips closed save Q and R, the air valve was opened and the flasks D and E disconnected, the ends of the syphon tubes being placed in beakers of water through which a fairly rapid stream of air was bubbled. In the meantime, exactly equivalent quantities of pure silver nitrate and pure baryta, sufficient to form about 25 g. of silver oxide, had been weighed out. The silver nitrate was dissolved in 750 c.c. of pure water in the Jena flask, and the solution was boiled out and allowed to cool in an atmosphere free from carbon dioxide. The baryta was dissolved in 750 c.c. of pure water in the silver flask, the whole being heated to effect solution and then allowed to cool in an atmosphere free from carbon dioxide. The baryta contained a small amount of carbonate for which allowance was made when weighing the substance. When both solutions were cold, their respective syphon tubes were washed down with pure water and the flasks replaced in position, a stream of pure air being passed down the syphon tubes during the operation.

About 500 c.c. of pure water were syphoned over into the precipitation vessel. With all screw clips closed, except O, P, R, S, and T, the air valve was opened so that the silver nitrate and baryta solutions were forced over into the precipitation vessel. The clips O and P and the air valve were so adjusted that the solutions entered the precipitation vessel at a slow and, as nearly as could be judged, an equal rate. It was found after a little preliminary practice with this apparatus that this could be done fairly accurately when syphon tubes of the same diameter were employed. This procedure was devised to minimise any risk of occlusion. The precipitated oxide was allowed to settle for about 6 hours and the supernatant liquid syphoned off by way of N. The precipitation vessel was then filled with wash-water. The apparatus was sufficiently flexible to permit a slight rocking motion being given to the precipitation vessel. By this means a swirling motion was imparted to the wash-water. This brought about mixing but, owing to the heavy nature of the precipitate, was not as efficient as could be desired. After standing for ½ hour in contact with the precipitate and being agitated at intervals, the wash-water was withdrawn *via* the syphon tube. The silver oxide was allowed to drain by raising the plunger very slightly so that the last traces of wash-water dripped through into the funnel. Washing was repeated several times with large quantities of water so that the walls of the precipitation vessel were completely washed down each time. The amount of water was then reduced to one, a half, and finally, a quarter of a litre of water at each washing. The quarter-litre washings were continued until 20 c.c. of the wash-liquor, after standing in contact with the precipitate for ½ hour, gave no turbidity with dilute sulphuric acid on standing in the nephelometer tube for 4 hours. The precipitate was then washed on to the filter and washing continued (the funnel being filled and allowed to drain completely each time) until 200 c.c. of the wash-liquor, acidified with dilute hydrochloric acid and filtered to remove the silver, on evaporation to 20 c.c. showed no precipitate after standing over-night in the nephelometer tube with dilute sulphuric acid. The precipitated silver oxide was allowed to drain while a current of pure air was passed through the apparatus to remove as much water as possible. The filter was then removed from the funnel and quickly transferred to a desiccator containing fused potash. After 3 to 4 weeks the oxide was sufficiently dry to permit of its being roughly powdered. Drying was continued for a further period of 3 weeks over fresh potash, when the oxide was ready for analysis.

The purity of the sample was tested as follows : A small quantity of the oxide was suspended in water and a few drops of dilute hydrochloric acid were added. The production of a white chloride showed that no reduction of the oxide had taken place during drying. The oxide was tested for barium by extracting 2 g. with dilute hydrochloric acid, filtering, and adding to the hot filtrate a few drops of dilute sulphuric acid. After standing over-night, the liquid was examined in the nephelometer. The absence of any turbidity showed the oxide to be free from barium.

The silver nitrate used in the preparation of the pure silver oxide was from four sources :

A. The silver resulting from the A series of preliminary experiments.

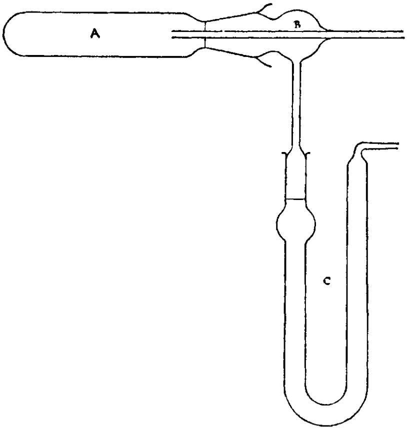
B. The silver resulting from the B series of preliminary experiments.

C. The silver resulting from the C series of preliminary experiments.

D. Pure atomic weight silver prepared by the late Sir Edward Thorpe.

The pure silver was, in each case, after a preliminary etching, dissolved in pure nitric acid. The solution was filtered through a Munroe-Gooch crucible and recrystallised in the manner previously described. Each sample was between 50 and 60 g. in weight.

Fig. 5.

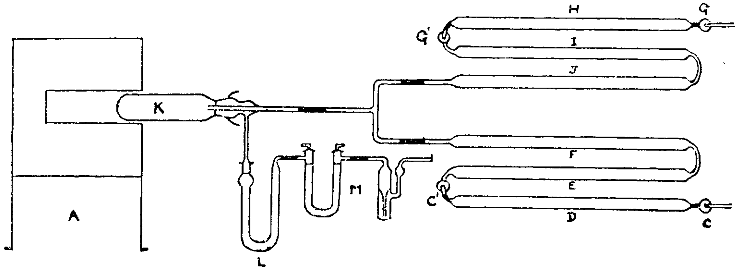


3. *Determination of the Ratio Silver : Oxygen in Silver Oxide.*

Preliminary investigation had shown that it is impossible to remove all the water from precipitated silver oxide by drying at the ordinary temperature. In determining the ratio of silver to oxygen it is therefore necessary to make a correction for the amount of moisture left in the oxide. The apparatus used is shown in Fig. 5. It consists of a thin-walled, transparent silica tube, A, weighing about 50 g. The neck of this tube has been strengthened by thickening the silica and it is ground to fit a glass stopper and a Jena glass adapter, B. The adapter carries a side-arm which connects, through a ground glass joint, with the U-tube, C. The left limb of the U-tube is half filled with fused potash, the bend packed with purified asbestos, and the right limb filled with purified phosphorus pentoxide. Besides the adapter side-tube, the left limb of the U-tube is ground to fit a glass stopper, and a ground glass cap fits the narrowed end of the right limb. As it is impossible to use any lubricant on these ground joints, they were hand-polished until optical contact was made. Under these conditions, the unavoidable small leak was reduced to negligible proportions. Owing to the greater coefficient of expansion of glass, the silica-glass joint between the silica tube and the adapter becomes gas-tight as soon as heating is commenced.

The method of carrying out a determination of the above ratio is briefly as follows. The silver oxide is weighed in the silica tube and decomposed in a current of pure dry air at 350—400°. The water and any small amount of carbon dioxide in the oxide are retained by the potash and phosphorus pentoxide in the U-tube. The loss in weight of the silica tube and contents (oxygen) may thus be corrected by subtracting the gain in weight of the U-tube. The weight of the residual silver is determined by first displacing the air in the tube by pure hydrogen and then melting the amorphous silver in the atmosphere of hydrogen, cooling, replacing the hydrogen by air and finally weighing.

Fig. 6.



The apparatus is shown in Fig. 6. A (shown in detail in Fig. 7) is the electric furnace used for heating the silica tube. The thin-walled silica tube is wound with seven turns of thin platinum foil about $\frac{1}{8}$ inch in width. This is lagged with heavy magnesia and a thick-walled silica tube. Ten turns of nichrome wire are wound round the thick-walled silica tube and connected in series with the platinum ribbon. The whole is placed in an asbestos box and well lagged with woolly asbestos. The furnace could be safely run at 1200°; it then consumed about 700 watts.

At B is an electrolytic cell (shown in detail in Fig. 8) for the preparation of pure hydrogen. It consists of three glass U-tubes connected in parallel. The electrolyte is a solution of pure barium hydroxide and the electrodes are of platinum foil.

The current of air in which the oxide is decomposed is purified by passing through the bubbler C (containing syrupy phosphoric acid), over copper oxide heated electrically to dull redness in the hard glass tube D, through another phosphoric acid bubbler, C′, and finally through the drying tubes E and F, E containing fused potash and F pure phosphorus pentoxide. The source of air is a cylinder of compressed air and the flow is regulated by means of an " Endurance " valve. A similar series of purifying tubes is used for the hydrogen. G and G′ are phosphoric acid bubblers. H is a hard glass tube containing copper gauze heated electrically to dull redness. This removes the small amount of oxygen which is carried over with the hydrogen from the baryta cell. I and J are potash and phosphorus pentoxide drying tubes respectively. K is the silica tube and L the U-tube. The ground joints between the adapter and the silica tube and between the adapter and the U-tube are heated electrically to 100° to prevent moisture condensing anywhere but in the U-tube. M is a guard arrangement, consisting of a pentoxide tube and a phosphoric acid bubbler.

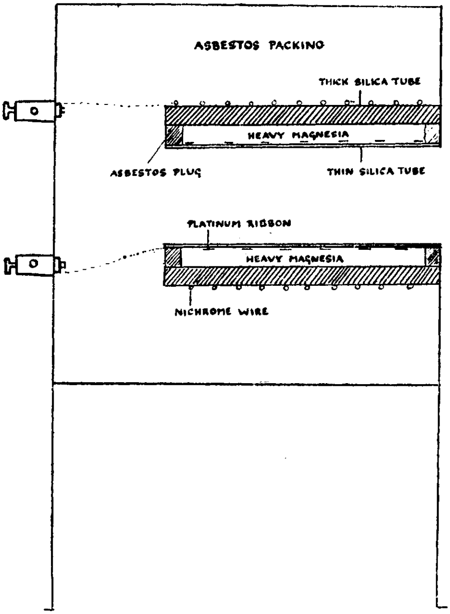


FIG. 7.

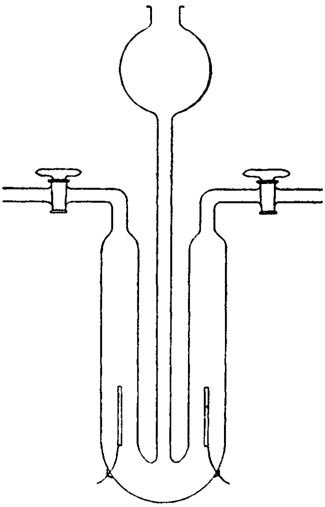


FIG. 8.

All weighings were carried out on a long beam (No. 5) Oertling balance, kept specially for atomic weight work and previously used in the determination of the atomic weights of tellurium and mercury. The sensitivity of the balance increased slightly with load and was in the neighbourhood of 250 (*i.e.*, a change of load of 0·1 mg. shifted the zero 2·5 divisions of the pointer scale). To cut down any vibration to a minimum the balance-case feet were supported on pads of filter-papers. The weights used were of brass (platinum-plated), the fractions being pure platinum. They were carefully calibrated, by the method due to Richards (*J. Amer. Chem. Soc.*, 1900, **22**, 144), both before and after the determinations. No appreciable change had taken place. All weighings were made against a counterpoise, and the weights corrected to vacuum by the formula: Buoyancy correction $= M\sigma(1/\Delta - 1/\rho)$, where $M =$ mass on balance pan; $\sigma =$ density of air; $\Delta =$ density of substance weighed; and $\rho =$ density of weights employed. The following densities were used: Brass 8·26, platinum 21·5, silver 10·5. That of desiccated silver oxide was measured and found to be 7·10.

Before commencing the determinations a series of blank experiments was performed. These were carried out in an exactly similar manner to the determinations proper and it was found that there was a constant increase in weight of the U-tube after each blank experiment. The mean gain in weight in twelve experiments was 0·24 mg., no single experiment differing from the mean by more than 0·05 mg.

The actual determinations were carried out as follows: The silica tube was heated in the electric furnace to 1100°, the air having been previously displaced by hydrogen. After the tube had cooled, the hydrogen was displaced by air, the adapter removed, and the tube heated to 400° while a current of air was passed through it. The tube was placed while still hot in a desiccator over phosphorus pentoxide and again allowed to cool. It is necessary to remove the adapter before heating for the second time because the silica-glass joint is quite tight at temperatures above normal owing to the greater expansion of the glass. After remaining in the desiccator for ½ hour, the silica tube was removed, stoppered, and placed in the balance case along with another silica tube which had been similarly treated (the counterpoise). The atmosphere in the balance case was kept dry by means of phosphorus pentoxide and potash. After remaining in the balance case for ½ hour, the stoppers were eased, thus adjusting the pressure in each tube to atmospheric. The tubes were then suspended from the arms of the balance and carefully weighed after another ½ hour. Before being placed in the balance-case the silica tubes were lightly dusted with a piece of silk. It was found that only by keeping strictly to the above procedure could the silica tube be kept constant in weight. Any variation in the length of time in the desiccator, heat treatment before weighing, etc., altered the weight in some cases by as much as 0·25 mg.

After being weighed the tube and counterpoise were again heated to 400° and allowed to cool for ½ hour in the desiccator. Before stoppering the silica tube, about 20 g. of pure silver oxide were quickly introduced through a wide-stemmed funnel. The silica tube containing the oxide was now weighed with precautions similar to those employed in weighing the empty tube.

The absorption U-tube, which along with its counterpoise had been placed in the balance-case, was now suspended from the balance arm after the stopper had been eased momentarily in order to adjust the pressure. After ½ hour the U-tube was weighed.

The silica tube and the absorption U-tube were then quickly connected to the hard glass adapter, the heating coils placed in position, and a slow current of air was turned on. The electric furnace was moved carefully over the silica tube, care being taken that the furnace walls did not touch it, and the current was switched on. The rate of evolution of oxygen was controlled by means of a variable resistance and also by sliding the furnace backwards and forwards; it was not allowed to exceed four bubbles per second.

The silver oxide, which was originally decidedly brown, gradually became darker until it was black. As the temperature increased, white specks of metallic silver appeared at the far end of the tube and these grew, as the decomposition progressed, until all the oxide had been converted into white, amorphous silver. This was accompanied by considerable shrinkage, the residual amorphous silver occupying about one-quarter of the original volume of the oxide and still retaining the shape of the silica tube. When decomposition was complete (in about 3 hours) the apparatus was disconnected and the absorption U-tube re-weighed, with all the previous precautions. The gain in weight was noted and, after correction, was subtracted from the weight of silver oxide, thus giving the weight of pure oxide.

The apparatus was then reassembled and the air displaced by pure hydrogen from the baryta cell. In the meantime the electric furnace was switched on and, by the time the air had been displaced, it had acquired the temperature necessary to melt the silver. The furnace was moved up carefully over the silica tube. It was necessary to protect the ground joint between the silica tube and the glass adapter because if this became too hot a fracture resulted. The protection was effected by a piece of asbestos board and by fanning the joint. In about 20 minutes the silver had melted to a bead. The heating was discontinued and the tube allowed to cool slowly. Too rapid cooling cracked the tube owing to the greater contraction of the silver bead, which adhered to the fused quartz surface. When the apparatus was cool the hydrogen was displaced by air. The adapter was then disconnected and the tube heated to 400° in a current of pure air and, while still hot, placed in the desiccator to cool. It was weighed under similar conditions to those employed in the initial weighing.

The silver bead in some cases was found to be coated with a very thin film of dross. This proved to be silica. It was shown, however, that the weight of this silica, which was always of the order of a fraction of a milligram, was equal to the loss in weight of the silica tube. Apparently the molten silver, or the hot silver oxide, attacks the tube somewhat, and the silica is deposited on the surface of the bead as it cools.

From the loss in weight of the silver oxide and the weight of the residual silver, the value of the ratio silver to oxygen can easily be calculated.

The following are the results of the experiments :

Experiment.

Weights (g.).	1 A.	1 B.	2 B.	1 C.	2 C.	2 D.
$Ag_2O + H_2O$	20·20674	19·43588	21·82606	20·03207	19·47189	21·31387
H_2O	0·06607	0·04469	0·06330	0·07361	0·05963	0·05989
Ag_2O	20·14067	19·39119	21·76276	19·95846	19·41226	21·25398
Ag_2O (vac.) ...	20·14133	19·39186	21·76351	19·95910	19·41287	21·25468
Ag	18·75106	18·05341	20·26123	18·58147	18·07284	19·78749
Ag (vac.)	18·75067	18·05298	20·26076	18·58107	18·07242	19·78708
Oxygen	1·39066	1·33888	1·50275	1·37803	1·34045	1·46760
Ratio O : Ag = 8 :	107·866	107·869	107·861	107·870	107·859	107·861
Mean			107·864 ± 0·0013			

4. *The Action of Light on Silver Oxide.*

The desiccated silver oxide, prepared as previously described, has a decided brown colour, quite free from the purplish-black colour usually associated with the compound. A sample of the oxide exposed to daylight in a closed glass vessel over a period of several weeks showed no alteration in colour. The oxide used in the atomic weight determination was prepared in a darkened room and only exposed to red light in order to be quite sure that no decomposition took place, but it is doubtful whether this precaution was necessary. A sample of the oxide exposed to daylight in an open vessel darkened slowly and in the course of a day or two became almost black. This darkening was probably due to the reduction of the oxide by the organic matter in the atmosphere.

Some of the preliminary work on this subject was carried out in conjunction with Messrs. E. Skelton, T. T. H. Verschoyle, and R. W. Farnell, to whom the authors express their sincere thanks. We are also indebted to Messrs. Brunner Mond and Co., a grant from whom covered a large part of the expense of this research. One of us (H. L. R.) wishes to place on record his thanks to the Trustees of the Beit Scientific Research Fellowships for election to a Fellowship which enabled him to participate in this investigation.

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