XII. *On Fluoride of Silver.* *By* George Gore, *F.R.S.*

Received October 5, 1869,—Read January 13, 1870.

*Formation**.

Anhydrous or gaseous hydrofluoric acid had no visible action on metallic silver; by electrolysis of the aqueous acid with a silver anode, the metal was dissolved and argentic fluoride formed; by electrolysis of anhydrous hydrofluoric acid also, a silver anode was rapidly corroded. Metallic silver in contact with platinum, in a mixture of dilute hydrofluoric acid and aqueous nitrate of potassium, was not corroded even with the aid of heat. A solution of nitrate of silver, mixed with dilute hydrofluoric acid, did not yield fluoride of silver on evaporation to dryness; nor did it show any signs of decomposition on the addition of solutions of any of the soluble fluorides, except stannous fluoride, or a saturated solution of fluoride of potassium. The effects of anhydrous hydrofluoric acid upon oxide, peroxide, nitrate, chloride, iodide, and carbonate of silver have been already briefly described (Phil. Trans. Roy. Soc. 1869, pages 191 and 192).

Preparation.

I prepared the salt as follows:—A solution of pure nitrate of silver was precipitated by pure carbonate of sodium, and the well-washed carbonate dissolved in dilute hydrofluoric acid; a little heat was absorbed. The clear liquid was heated to boiling, filtered, evaporated, and heated to incipient fusion; transferred whilst hot to a bottle of platinum, and when partly cool retransferred to a gutta-percha bottle.

The earthy-brown salt thus prepared contains a small amount of free silver (especially if it has been stirred when nearly dry), some water, and traces of hydrofluoric acid. To remove the water and acid, I have sometimes heated it in a platinum cup covered with layers of filtering-paper kept cold by a vessel of water placed upon them. When nearly dry it had a greenish metallic lustre, due to the free silver; and when made perfectly anhydrous, by heating nearly to its point of softening, it was black, with a grey satin metallic lustre.

Analysis.

To determine the amount of silver, I passed hydrogen, steam, or ammonia over the gently fused salt, or I precipitated the aqueous solution by hydrochloric acid. To find the amount of fluorine, I precipitated the solution by nitrate of lime; I also employed the following process, and found it much more accurate and satisfactory. About 50 or 100 grains of the salt was weighed in a narrow closed cup of platinum, the cup then

---

* All the operations upon fluorine compounds described in this paper were conducted in platinum vessels, unless otherwise stated.

placed in a platinum tube-retort about 150 millims. long, and the salt heated to fusion to expel all moisture; the retort was then closed by a tube containing fragments of chloride of calcium and cooled. The cup was removed, instantly closed, and reweighed. The salt was then dissolved in hot water, the solution filtered in the dark into a two-ounce platinum bottle, the washed filter burned, and the residuary silver weighed. The well-washed cup was also heated to faint redness, and its gain of weight of silver ascertained. By deducting these weights from that of the fused fluoride, nearly the true weight of soluble fluoride was found. For every single grain of soluble fluoride, there was now added to the contents of the bottle ·22047 grain of perfectly pure caustic lime in powder (prepared as described, Phil. Trans. Roy. Soc. 1869, p. 179), which had just been heated nearly to whiteness until it ceased to lose weight. The bottle was now placed in a large platinum dish, with a small inverted platinum funnel supported above its mouth, and the mixture continuously evaporated to perfect dryness, the products of combustion from the gas-flame being deflected on one side (see page 232). The bottle was then heated to incipient redness until it ceased to lose weight. This method is capable of yielding very accurate results when sufficient care is exercised.

The reaction upon which this method is based is represented by the following equation:—

$$2\mathrm{Ag\,F} + \mathrm{Ca\,O} = \mathrm{Ca\,F_2} + 2\mathrm{Ag} + \mathrm{O}.$$

Two molecules, or 254 parts, of the silver salt, and one molecule, or 56 parts, of caustic lime lose 16 parts of oxygen, and leave a mixture of 78 parts of fluoride of calcium and 216 parts of metallic silver. The 16 parts of oxygen lost by the above weights of materials equal 38 parts of fluorine present; a *greater* proportion of loss would occur if the silver salt contained *less* fluorine and an equal weight of oxygen or water was present to supply the deficiency, because the lime prevents the expulsion of the fluorine by heat, but not that of any oxygen or water.

The following are the particulars of an analysis of this kind:—100·92 grains of the brown fluoride was fused in the cup and retort; it effervesced, and a little silver was set free upon the surface of the cup; the loss of weight was 1·08 grain =1·070 per cent., consisting of acid watery vapour, and some oxygen produced by the action of that vapour upon the heated salt. On dissolving the salt and filtering, 2·80 grains of silver was found upon the filter, and ·13 grain upon the cup. The quantity of salt dissolved therefore was 96·91 grains =21·366 grains of CaO; 21·39 grains of the lime was then added, and the mixture evaporated and ignited; the process occupied about nine hours. The residue was perfectly neutral to test-paper, and weighed 112·20 grains = a loss of 6·10 grains, theory requiring 6·104 grains.

The contents of the bottle was now dissolved by warm dilute nitric acid, the solution filtered and precipitated; 108·545 grains of argentic chloride, =81·692 grains of silver, was obtained, theory requiring 82·411 grains*.

To determine the amount of silver more accurately I made the following experiment:—

---

* Platinum vessels heated to low redness in contact with finely divided silver from fused argentic fluoride show an increase of weight even after having been cleaned by nitric acid (see page 229).—Added April 1870, G. G.

55·44 grains of the brown fluoride was put into a platinum boat and heated to fusion in the retort-tube; it lost ·91 grain =1·641 per cent. The boat and contents was then put into a tube of platinum 114 millims. long, in the middle part of another platinum tube 508 millims. long, and heated to low redness during 55 minutes in a slow current of gaseous ammonia previously dried by caustic lime. A very bulky white and deliquescent sublimate of fluoride of ammonium, having the appearance of down, was produced, and the silver salt crept over the edge of the boat at the exit end. The heat was continued some time after the sublimation ceased, and the boat was cooled in the current of gas. The whole of the salt was reduced to metal, and the amount of silver found was 46·09 grains. A small amount, ·305 grain, had been carried forward into the long tube during the process, thus making a total of 46·395 grains, theory requiring 46·610 grains, viz. 1·599 grains[*] of free silver, and 45·011 grains of combined silver, in the salt after fusion. After thoroughly digesting the boat in warm dilute nitric acid and washing, it was jet-black (whilst wet) in those parts which had been in contact with the fused salt, and when dry those parts were grey and rough with finely divided platinum (see page 234); the boat had also increased 1·14 grain in weight, probably by absorption of metallic silver: igniting the boat did not alter this weight. The short tube enclosing the boat had, after similar cleaning, lost ·05 grain in weight. The reaction which occurred in this case was probably in accordance with the following equation:—

$$4H_3N + 3AgF = 3(H_4NF) + 3Ag + N;$$

the twelve atoms of hydrogen lose one atom of trivalent nitrogen and gain three atoms of monovalent fluorine by substitution.

To ascertain the amount of free silver in a specimen of the brown fluoride, 43·04 grains of the salt was dissolved in cold water, and the solution filtered in the dark; a little grey powder of silver separated. The residue was well washed, ignited, and weighed; ·575 grain of silver was found after deducting the weight of filter ash.

The foregoing results show that 100 grains by weight of the brown fluoride contained 1·336 grain of silver, ·795 grain of aqueous hydrofluoric acid, and 97·869 grains of pure fluoride. By fusing this quantity (*i. e.* 100 grains) of the brown salt in a nearly closed platinum vessel it loses 1·070 grain[†], consisting of water and hydrofluoric acid. The fused residue contained 2·903 grains of free silver, of which 1·336 grain was in the salt when first taken, and 1·567 grain was set free during the fusion; it also contained 96·027 grains of pure fluoride of silver.

	Dried salt.		Fused salt.				
AgF	97·869	AgF	96·027	or	Silver . . .	82·544	=97·066 AgF.
Free silver about	1·336	Free silver about	2·903	„	Fluorine . . .	14·522	
Aqueous H F. .	·795		98·930		Free silver about	2·934	
	100·000	Loss by fusion . .	1·070			100·000	
			100·000				

---

[*] This number is necessarily variable owing to the salt suffering different amounts of decomposition in the process of drying.

[†] This number is also variable.

All these numbers, especially those representing the amounts of free silver and of water, are slightly variable, owing to the extreme deliquescence of the salt and its easy decomposability by heated aqueous vapour*.

According to M. PRAT (Comptes Rendus, No. 9, August 26th, 1867), ordinary fluoride of silver in the anhydrous state is composed of oxygen, fluorine, and silver, its composition being represented by the formula AgF, AgO; and true fluoride of silver, prepared by him in a different way, and possessing very different properties from the ordinary fluoride, has the following composition,—

Silver, 1 equiv. or . . .	108·0	0·785
Fluorine, 1 equiv. or . .	29·6	0·215
AgF	137·6	1·000

He considers the equivalent or atomic weight of fluorine to be 29·6; and he represents the composition of fluor-spar as follows:—

Calcium, 2 equivs. or	40·0
Fluorine, 1 equiv. or	29·6
Oxygen, 1 equiv. or	8·0
	77·6

The results obtained by me in the foregoing analytical experiments, as well as those obtained in determining the molecular volume of anhydrous hydrofluoric acid in the gaseous state (Phil. Trans. Roy. Soc. 1869, pages 179–183), do not agree with the view that ordinary fluoride of silver in the anhydrous state, prepared in the way I have described, contains oxygen.

Physical Properties.

The salt is a troublesome one to prepare, vessels of silver or platinum are essential for the evaporation of its solution. The solution must be heated and filtered before evaporating. When its solution was nearly concentrated by evaporation skin-like films formed upon its surface, and the liquid beneath was filled with very minute silky fibres, probably crystals of the salt. When heated nearly to dryness it became a tenacious sticky mass, requiring a rigid and sharp-edged spatula to remove it. The dried salt was in brown earthy fragments, which rapidly attracted moisture and deliquesced. In a fused state it formed a highly lustrous, mobile, and jet-black liquid, which on cooling became hard and tough†. On dissolving the cooled salt in hot water, filtering, and evaporating the clear solution by heat, some jet-black crystalline powder separated. On several oocasions a clear solution of the pure salt, containing free hydrofluoric acid, became blackish with separation of a little black powder on heating.

The salt is very soluble, and evolves a small amount of heat whilst dissolving in the minimum amount of water. 103·58 grains of its aqueous solution (saturated at 15°·5 C.),

---

* (Added April 1870.)—I have since made numerous analyses and quantitative experiments relating to fluoride of silver, and they have all confirmed the above composition of the salt.—G. G.

† In a state of fusion it corrodes silver. See page 233.

placed in a platinum cup 51 millims. deep and 16 millims wide, and evaporated to dryness and heated to gentle fusion, left 66·16 grains of solid residue. After allowing ·34 grain for the fluorine set free during the fusion, the result shows that 66·5 parts of it dissolved in 37·08 parts of water, or 1 part of water dissolves about 1·79 part of the salt at 15°·5 C., or 1 part of the salt is soluble in ·55 part of water at that temperature. The aqueous solution is strongly alkaline to litmus-paper. On adding distilled water to a hot saturated solution, a white cloud appeared which afterwards dissolved; it probably consisted of a basic salt. On several occasions I have had reason to suspect a slight degree of solubility of finely divided metallic silver in a strong solution of the salt, similar to that of lead and silver in strong aqueous solutions of their respective nitrates. The salt is nearly insoluble in anhydrous alcohol.

By weighing a known amount of the brown salt in a specific-gravity bottle filled up with tetrachloride of carbon, the specific gravity of it was found to be =5·852 at 15°·5 C.

The saturated solution of it at 15°·5 C. was very heavy, its specific gravity being =2·61. I have not obtained crystals from it at that temperature*, but by placing it in a covered platinum cup in a freezing-mixture at −23°·5 C. it solidified to a mass of needle-shaped crystals, radiating towards the centre of the cup, and finally to a solid mass of colourless salt with deep fissures in its surface produced by contraction. In another similar experiment the solution became a mass of crystalline plates at −2°·25 C., very similar to those of the acid fluoride of potassium. During the formation of these crystals a yellowish-brown sediment formed at the bottom of the vessel, and on dissolving the crystals by means of gentle heat the sediment remained. The crust was now broken to pieces, and a little cold water added; this caused it to cohere to a rather hard mass, which soon dissolved to a colourless liquid, leaving only a few blackish particles. There was no impurity present, and the probable explanation of the formation of the crust is that there was not sufficient water in the original solution to form the crystalline hydrate, and when the hydrate crystallized it withdrew the water from the remaining portion of salt, and left it in the anhydrous state as a heavy powder which sank to the bottom. This result is remarkable if we consider the great degree of attraction for water which the anhydrous salt possesses, and shows that its tendency to form a crystalline hydrate is even more powerful. I have not experimentally determined the composition of the crystals, but from several circumstances I consider them likely to prove *penta*-hydrated. A saturated solution of the salt chilled to −18° C. exhibited the phenomenon of supersaturation on immersing a platinum wire in it. Melted fluoride of silver which had been gradually cooled was covered with crystalline markings.

A fragment of the brown salt in a well-stoppered colourless glass bottle, exposed to daylight and sunlight during ten weeks, showed no signs of decomposition. A saturated solution of the salt in a platinum cup in a similar bottle similarly exposed during fourteen days evolved traces of hydrofluoric acid, but liberated no silver.

---

* According to Fremy, 'Chemist,' New Series, vol. i. pp. 556 & 557; Comptes Rendus, February 27, 1854, a concentrated solution of the salt yields very regular crystals.

Fluoride of silver in a platinum crucible within a heated cast-iron muffle with a bar of zinc near the crucible, melted at a temperature much below redness, and at exactly the same time as the zinc; its fusion-point therefore is about 434° C.

50 grains of the salt was melted in a platinum crucible; 20 grains of scraps of platinum was now added, and the lower end of the retort (enclosed within a glass test-tube) heated in a bath of melted zinc during half an hour to a temperature varying both above and below its fusion-point, the exit-tube of the retort being connected with a glass receiver over mercury. Only a trace of gas was evolved, and the retort and its contents lost only ·05 grain in weight. The salt therefore is not decomposed by heat alone at the temperature of melting zinc. According to Fremy also (Chemist, New Series, vol. i. pp. 556 & 557) the anhydrous salt is undecomposable by heat.

In some cases of evaporation of fluorides I have used the following arrangement to prevent the products of combustion from the gas-flame coming into contact with the substances. It consists of a triangular sheet-iron cap, fig. 1, without a bottom, fitting over the top of a common iron tripod. In the upper surface of the cap is a large hole A, to receive the evaporating dish. The cap has a short chimney, B, and two flaps of sheet iron, C, C, with hinges to admit of a gas-burner being placed beneath.

In other experiments in which tubes were heated to redness, I have employed a row of Bunsen's burners (fig. 2), with a moveable table A A of sheet iron fixed to them at any desired height by the screws B, B. The table was for the purpose of supporting the tube, which lay in two notches in its edges in the direction C C; it was also used for supporting notched plates of fireclay to increase the heat. To fix the tube securely to the table, two peculiar hooked-shaped pieces of iron, provided with screws, were employed, as shown in fig. 3.

Fig. 1.

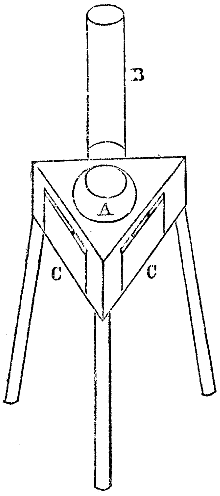


Fig. 2.

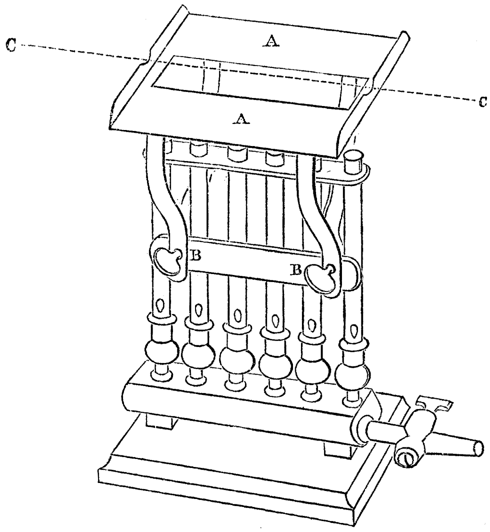
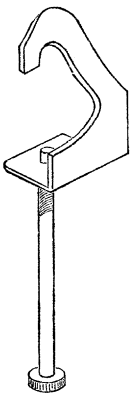


Fig. 3.



In numerous experiments requiring the fusion of fluorides &c., I have employed a thin platinum cup or muffle (fig. 4), made without solder, heated by means of a furnace (fig. 5), in which the substances could be raised to a high temperature without exposing them to contact with the products of combustion. A (fig. 5) is an open clay cylinder,

Fig. 4.

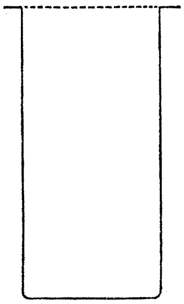
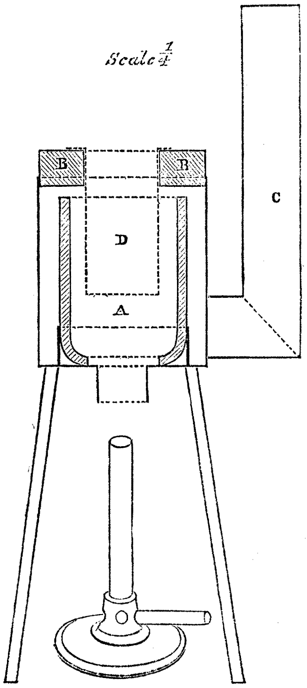


Fig. 5.



B B is a perforated clay plate to receive the cup D. With the aid of this arrangement and a corrugated gas-burner, I have been able to electrolyze substances at the temperature of melted cast iron, and observe the phenomena taking place at the electrodes, and by means of additional arrangements have also collected the gases evolved at those temperatures without admission of air.

On cooling melted fluoride of silver in an open platinum vessel, it effervesced on every occasion whilst solidifying; and on remelting it out of contact with the gases of the burner, more gas was evolved as soon as it acquired a dull red heat. 100 grains of the brown salt, alternately heated to redness and cooled nearly to solidifying, thus, repeatedly during thirty-five minutes, lost 3·86 grains in weight; and the residue, on solution in water, left 17·04 grains of silver, chiefly as a fine powder. A second 100 grains, kept at a dull red heat in an open crucible within the covered muffle during forty-five minutes, lost 2·47 grains, and yielded 12·22 grains of free silver. In a third experiment, 50 grains kept at just visible redness in a closely covered crucible in the closely covered muffle during $1\frac{1}{2}$ hour, lost only ·62 grain, and yielded 3·18 grains of free silver. In a fourth similar experiment, in which the silver-salt was partially exposed to the air during one hour, the quantity of silver set free was equivalent to about five-sixths of the total amount of fluorine present. The losses in all these experiments were due, 1st, to the watery vapour expelled from the brown salt itself, and 2nd, to that of the outer air; the more the air was excluded the less was the percentage of loss. In each experiment some of the silver was set free in a coherent deposited state upon the crucible, chiefly at the junction with the surface of the liquid, and the crucible was slightly corroded. On dissolving this silver by nitric acid, jet-black powder of platinum appeared beneath; this always occurs in such cases.

A current of dried air was passed over 20 grains of argentic fluoride at a gentle red heat in a platinum boat within a glass tube during half an hour; the fluoride was not decomposed. A current of undried air was also similarly passed over the salt in a state of fusion; a little silver was set free at the ingoing end of the boat, and where the salt was not kept perfectly fused effervescence occurred, which caused the salt to creep up the sides of the boat.

Electrolysis.

A number of experiments were made of electrolyzing argentic fluoride in a fused state, with platinum electrodes and six SMEE'S elements, in a covered platinum cup. In each case conduction commenced before the salt had fused. When the salt was liquid the conduction was *perfect*, so that on closing the circuit by a copper wire no additional action could be detected in the battery. No gas was evolved at the cathode, and only a little from the anode, most on each occasion at the first moment of conduction. The anode exhibited no more signs of corrosion than the cathode, nor than what always occurs when argentic fluoride is fused in contact with platinum. Metallic silver was set free in each case, but apparently only by the usual influence of moisture of the air. No film of coherent silver was deposited upon the cathode. I have met with similar results of perfect conduction without manifest electrolysis whilst passing electric currents through certain other metallic fluorides in a state of fusion.

In one of these experiments, supposing that fine fibres of silver might have stretched across and united the electrodes, as actually does occur in some cases, I frequently stirred the liquid around the anode by means of a platinum wire, but no alteration of conduction was thereby produced, and no fibres of silver could be seen. Had such fibres been formed they would probably have been highly heated by the electric current and rendered visible.

On electrolyzing the fused salt with an anode composed of a rod of highly ignited charcoal of lignum-vitæ and ten SMEE'S elements, only a small amount of conduction took place in consequence of the resistance offered by the charcoal. Gas was evolved from the anode, and the anode was corroded, but no special odour besides that of hydrofluoric acid was perceived. According to FREMY (Chemist, New Series, vol. ii. p. 548; Comptes Rendus, April 25, 1855), who electrolyzed the fused salt in a platinum vessel, it decomposed easily, but the liberated silver perforated the platinum vessel in a few minutes.

A special investigation is necessary to determine the amount of conduction which occurs without electrolysis in this and certain other fluorides in a state of fusion.

Various aqueous solutions of the salt were also electrolyzed. In two of these experiments a saturated solution, not containing free acid, in a platinum dish as the cathode, and a slightly immersed thick platinum wire as the anode, was electrolyzed by means of six large GROVE'S cells. Free conduction occurred. No gas or odour was evolved. A thick, hard, and strongly adherent crust quickly formed upon the anode, and a rapid deposit of loose brilliant yellow scales of silver upon the cathode. The crystals soon extended upwards and united the electrodes. By still less immersion of the anode sufficient heat was evolved to boil the liquid and set free metallic silver. In another experiment with a large platinum anode suspended inside an inverted funnel of gutta percha to collect evolved gas, no gas was evolved and a similar crust was formed. The black crust, after washing with water, effervesced with ozone-like odour in strong nitric acid, and formed a deep brown opake solution. With strong hydrochloric acid it effervesced and evolved an odour like that of an oxide of chlorine. In concentrated sulphuric acid it evolved gas and an odour of ozone. It also evolved gas in strong aqueous ammonia. Probably, therefore, it was a peroxide of silver, such as occurs in the electrolysis of a solution of argentic nitrate. 13·2 grains of it (which had been kept a long time in a glass bottle with but little corrosive effect upon the glass, and contained scales of free silver) was heated gradually to redness in a narrow platinum tube-retort; much acid fume was evolved at first, and then a gas which repeatedly reinflamed a red-hot charcoal splint explosively. The loss of weight was 1·9 grain. If the substance was peroxide of silver, $Ag_2 O_2$, the loss should have been 1·7 grain. Metallic silver was left. By the electrolysis of a more dilute solution a similar crust was formed, but gas was also evolved at the anode.

Anhydrous hydrofluoric acid, artificially chilled, was electrolyzed by means of ten SMEE'S elements with a silver anode. The acid conducted more freely than with an anode of palladium, and still more so than with one of gold (see Phil. Trans. Roy. Soc. 1869, p. 189). The anode corroded rapidly, and became covered, first with a little black powder upon its edges, and then with a grey powder (probably metallic silver) which contained only a trace of soluble silver-salt.

The following is the order of electrical relation of several metals in the fused salt at a barely visible red heat, the most positive being named first:—silver, platinum, charcoal of lignum-vitæ, palladium, gold. The silver was rapidly corroded and apparently dissolved. The charcoal emitted much gas when first immersed. Silicon could not be tried because it decomposes the salt rapidly, setting free silver; it is not, however, necessarily electro-positive to silver on that account, for I have met with substances which are electro-negative to silver in argentic solutions from which they liberate silver rapidly. For a similar reason the base metals could not be tried.

Magnesium was rather strongly electro-positive, and silver, palladium, and a rod of charcoal of lignum-vitæ weakly positive to platinum in a saturated solution of the salt at 16° C.

The following is the order of electrical relation found with a moderately dilute solution of the salt at ordinary temperature:—aluminium, magnesium, silicon, *iridium*, *rhodium*, and *carbon of lignum-vitæ* nearly equal, platinum, palladium, tellurium*, gold. The iridium was much more strongly positive if it was covered with a film of oxide.

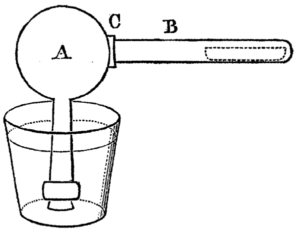
Chemical Behaviour.

In many of the experiments great corrosion and injury of the vessels was caused by reduced silver alloying with the platinum; and the products of the reactions were very difficult and tedious to remove. The solvents employed for cleaning the vessels were usually dilute nitric or hydrochloric acids, strong aqueous ammonia, or saturated solutions of iodide of potassium or nitrate of mercury†. In some cases the residue of silver-salt had to be reduced to metal at a red heat by means of hydrogen or alkaline carbonates.

With Hydrogen.—The reduction of the salt by hydrogen has been already described (Phil. Trans. Roy. Soc. 1869, p. 183). Fragments of the brown salt in hydrogen in a colourless glass vessel at 60° Fahr., exposed to sunlight during two days, exhibited no chemical change. A solution of the salt in a platinum vessel at 60° Fahr., containing a little free hydrofluoric acid, was not decomposed by passing a stream of hydrogen through it.

With Nitrogen.—A globe of glass of the form A, fig. 6, was filled with pure nitrogen; the platinum retort B enclosing a platinum boat, containing a weighed amount of the previously fused salt, was now fixed on air-tight by means of a washer of vulcanized india-rubber at C, and its outer end heated to redness during half an hour, the mouth of the vessel being closed air-tight by a bung of vulcanized india-rubber, and immersing it in a basin of mercury. On opening the mouth of the cooled vessel under mercury, no alteration of volume of the gas was found, and the loss of weight of the boat and its contents was only ·26 grain. The residual gas was found by proper tests to be nitrogen. Nitrogen, therefore, is not absorbed by, and does not decompose, argentic fluoride at a low red heat.

Fig. 6.



With Ammonia.—A fragment of the brown salt, weighing 10½ grains, was fixed in an iron clip and introduced into a colourless 4-ounce bottle filled with dry ammonia gas over mercury, a stick of caustic potash having been previously placed in the gas; the bottle was then exposed to sunlight. In a few minutes the salt became darker in colour, and a slow absorption of the gas continued during about twenty-six days; a slight odour of ammonia then remained, and the salt had absorbed about 98·3 cub. centims. or 1·0914 grain, or about 844 times its volume of the gas. Light was not necessary, as the absorption was observed to occur during the night. The ammoniated salt was odourless, and was probably analogous to the corresponding compound of argentic chloride and

---

* The tellurium contained traces of copper.

† The most convenient plan I have employed for recovering noble metals from the acid liquids used in cleaning the pieces of apparatus, has been to immerse a plate of zinc in them in a vessel of ebonite.

ammonia. The behaviour of argentic fluoride in a state of fusion in a current of dry gaseous ammonia has been already described (see p. 229). A saturated aqueous solution of argentic fluoride was instantly decomposed with powerful action by the strongest aqueous ammonia, but no precipitate was observed.

With Oxygen.—24·6 grains of oxide of silver previously heated to 600° Fahr. was introduced into a platinum tube-retort containing 49·86 grains of the previously fused salt, and 20 grains of platinum scraps, and the retort (enclosed in a test-tube) heated in a bath of melted zinc to an incipient red heat during fifteen minutes until evolution of gas ceased. The loss of weight was 1·8 grain, and about $5\frac{1}{2}$ cubic inches of gas was collected over mercury. The gas was proved to be oxygen, and the residue contained soluble undecomposed fluoride. Fluoride of silver therefore is not decomposed by heating with oxide of silver. A globe (see fig. 6) was filled with pure and dry oxygen. The platinum retort B, containing the residue of the last experiment, was fixed air-tight on the tubulure C, and the outer end of the retort heated to low redness during half an hour, the open neck of the receiver being immersed in mercury. No alteration of volume or properties of the gas took place, and the loss of weight was only ·16 grain. This result, therefore, confirms the previous one. The effect of dry air upon the salt in a state of fusion has been already described (see p. 234).

With Water.—The behaviour of the salt with liquid water has been already described (see p. 231). 20 grains of the brown salt was heated to fusion in a platinum boat within a glass tube, and a current of steam passed over it; rapid decomposition took place; the salt lost its fluidity and became of a brown colour for a short time, as if converted into oxide of silver; abundance of hydrofluoric acid was set free and the glass corroded powerfully; soon, however, by more heat the whole of the salt was changed into white silver. The loss of weight was 4·45 grains, consisting no doubt of fluorine (united to hydrogen), substance carried away mechanically by the violence of the action, and a small amount of acid moisture originally contained in the brown salt. This confirms the results obtained by heating the salt to fusion in undried atmospheric air (see p. 233).

With Nitrous Oxide.—71·64 grains of the recently fused salt in a platinum boat inside a platinum tube within a platinum tube-retort at a low red heat was subjected to a current of previously dried nitrous oxide during one hour. No chemical change took place, and the loss of weight was only ·27 grain. Argentic fluoride, therefore, is not decomposed by nitrous oxide at a low red heat.

With Nitric Oxide.—A current of dried nitric oxide from a mixture of nitre, sulphuric acid, water, and ferrous sulphate, was passed during forty-five minutes over 75·2 grains of the previously fused salt in a platinum boat within a short platinum tube placed in the middle of another platinum tube 508 millims. long, the salt being kept at an incipient red heat. Traces only of hydrofluoric acid were set free, and the salt lost only ·5 grain in weight; the loss might have been due to traces of moisture still remaining in the gas. Argentic fluoride, therefore, is not decomposed by nitric oxide at a low red heat.

With Nitrous Anhydride.—Nitrous anhydride from a mixture of starch and partly diluted nitric acid, perfectly dried by passing through a LIEBIG'S condenser and then over burnt chloride of calcium, was passed during two hours over a weighed amount of the previously fused salt at a low read heat in platinum vessels. The salt was wholly converted into chloride, evidently in consequence of my having employed chloride of calcium as the drying agent.

With Peroxide of Nitrogen.—Highly dried and hot nitrate of lead in powder in a glass retort was heated until the retort was full of a red-brown vapour; the vapour then passed over 69·68 grains of *gently warmed* fluoride of silver (which had been previously fused) in a platinum boat within the long platinum tube (used in the nitric oxide experiment) during seventy minutes. The salt gained 4·70 grains in weight, but exhibited no signs of decomposition; by heating the residue to near redness it freely evolved brown fumes of peroxide of nitrogen. Gently warmed argentic fluoride, therefore, is not decomposed by peroxide of nitrogen, but only absorbs it. The residuary salt of this experiment was now heated just to redness in the same apparatus, and the vapour similarly prepared passed over it during 1½ hour. During the whole of the first hour fumes were evolved which corroded dry glass freely; the corrosive action then ceased. After the process the boat was empty of silver-salt, and much reduced silver (more than 24 grains) was found in the boat and tube. The undecomposed portion of the salt had passed out of the boat by capillary action. The results were probably due to moisture still remaining in the nitrate of lead.

Fluoride of silver dissolved in hot concentrated nitric acid.

With Hydrofluoric Acid.—The behaviour of the brown salt with liquid anhydrous hydrofluoric acid has been already described (Phil. Trans. Roy. Soc. 1869, p. 191). 41·14 grains of the recently fused salt in a platinum boat within a short tube of platinum was placed in the middle part of the long platinum tube, and near the exit end of the tube was placed a second boat containing 37·88 grains of similar fused fluoride, that end of the tube having a very small exit-tube of platinum. Near the opposite end of the tube was placed a third platinum boat containing pure and anhydrous acid fluoride of potassium, and that end closed by a stopper of platinum. A red heat being now applied to the middle boat, and also gentle heat to the third boat very gradually, a current of anhydrous hydrofluoric acid vapour passed over the two boats during 1¾ hour, the second boat being kept below 16° C. When the current of vapour had ceased, the cold boat contained a large quantity of liquid anhydrous hydrofluoric acid, which was then expelled by application of a gentle heat. The boats were transferred to a closed platinum tube and separately reweighed. The residue in the cold boat was of a grey-white colour, and in micaceous scales, totally unlike ordinary fluoride of silver; a large portion of the fluoride, however, remained unchanged. The weight of this residue was 41·48 grains; had it all been converted into a salt of the formula AgF, HF the weight would have been 43·54 grains. The heated boat and its contents had lost only ·08 grain; the residue consisted of unaltered fluoride, and showed no signs of free silver as it would have done if any moisture had been present. No special corrosion of any of the vessels occurred. From these results, supported by other reasons, I consider that a double fluoride of hydrogen and silver exists, similar to the corresponding salt of hydrogen and potassium, but more easily decomposable by heat. The non-reduction of any of the heated salt to metal affords further confirmation of the fact that the liquid expelled by heat from the acid fluoride of potassium is quite free from water (see Phil. Trans. Roy. Soc. 1869, pp. 184 & 185).

With Chlorine.—Several investigators have subjected argentic fluoride to the action of chlorine. AIME[*] passed chlorine over the salt at 60° Fahr. Sir H. DAVY[†] heated perfectly dry fluoride of silver in a glass vessel filled with chlorine; the salt was converted into chloride, the retort was violently corroded, much chlorine was absorbed, fluoride of silicon and free oxygen was produced, but no new gas was discovered.

The brown fluoride, in the proportion of 6 grains to each ounce of chlorine, was exposed to the sun's rays in a bottle full of that gas in the dry state; the yellow colour of the gas disappeared, and strong rarefaction was found on opening the vessel.

A glass receiver A (see p. 236), of 262 cub. centims. capacity, was filled with dry chlorine. A stout tube B of refractory glass (lined within its outer half with a sheet of platinum), containing a platinum boat with an equivalent quantity of recently fused argentic fluoride, was fixed to the globe air-tight by a washer of vulcanized india-rubber coated with paraffin[‡]. The neck of the globe was closed by a cork coated with paraffin and immersed in mercury. A gentle red heat was applied to the boat, and the tubulure was kept cold by a stream of water. The yellow colour of the gas disappeared in less than one hour, and the heat was continued $3\frac{3}{4}$ hours. The receiver was then opened under mercury, on doing which the mercury entered with force until it filled about $\frac{5}{6}$ of the vessel. The mercury acquired a slight film as if a little free chlorine still remained. The level of the mercury was not lowered by now applying a low red heat to the boat. No leakage of gas took place, and the bottle was comparatively but little corroded.

In a second similar experiment the retort was of platinum constructed without solder. 59 grains of the fused fluoride was employed, and a red heat applied during one hour and twenty-two minutes. The colour disappeared in three quarters of an hour, and no leakage of gas took place. On admitting the mercury it immediately filled the apparatus within 41 cub. centims. of its capacity at standard pressure. The boat was much corroded, and the contents of the tube had gained 9·5 grains in weight, the missing chlorine being 221·2 cub. centims.=10·3 grains. By heating the retort to redness its contents lost 1·06 grain; and an acid fuming vapour (probably fluoride of silicon) was evolved, which extinguished a red-hot splint.

To exclude the interferences caused by corrosion of the glass, I have employed an apparatus composed entirely of platinum, its parts being constructed without solder; it

---

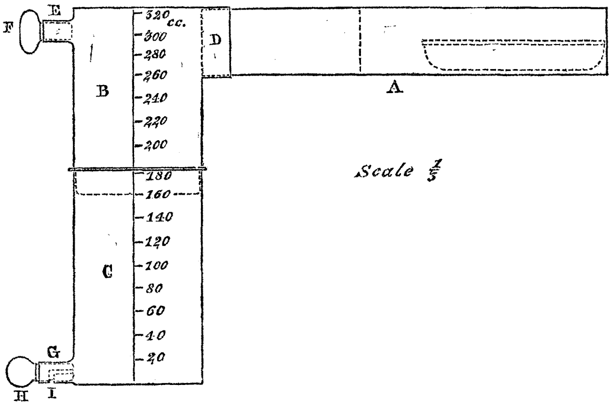
[*] GMELIN's Handbook of Chemistry, vol. ii. p. 359; Annal. de Chimie, vol. lv. (1833) p. 443; LIEBIG's Annal. vol. xvi. (1835) p. 174; POGGENDORFF's Annalen, vol. xxxii. (1834) p. 576.

[†] Sir H. DAVY's Works, v. p. 416.

[‡] Paraffin protects vulcanized india-rubber bungs very effectually from injury by chlorine.

is represented by the annexed sketch, fig. 7. A is a tube-retort $6\frac{1}{2}$ inches (=165·1 millims.) long and 1 inch (=25·4 millims.) wide. B and C are the two halves of a cylindrical receiver 2 inches (=50·8 millims.) diameter and 6 inches (=152·4 millims.) high, the upper half, B, being 3 inches (=76·2 millims.) high, and fitting very accurately and tightly to about $\frac{1}{2}$ an inch (=12·7 millims.) of its height within the part C; it has a tubulure D, into which the end of the retort A has been ground nearly air-tight to a distance of about $\frac{1}{2}$ an inch (=12·7 millims.); and also a smaller tubulure E, $\frac{1}{4}$ of an inch (=6·35 millims.) diameter, with a plug F, also ground nearly air-tight; the lower half, C, has a tubulure G, $\frac{1}{4}$ of an inch (=6·35 millims) diameter, with a small hole I, 0·1 inch (=2·54 millims.) diameter in its lower surface; it has also a plug H ground in nearly air-tight, which is perforated with a hole about $\frac{1}{8}$ of an inch (=3·17 millims.) diameter in the direction of the dotted lines, so as to serve the purpose of a tap.

Fig. 7.



The receiver was graduated as shown in the figure, its contents being 19·77 cubic inches (=324 cub. centims.), and the contents of the retort 4·943 cubic inches (=81 cub. centims.), or total contents of the apparatus 24·7 cubic inches (=405 cub. centims.) =18·895 grains of chlorine, or 67·578 grains of argentic fluoride=10·11 grains of fluorine. The total weight of the apparatus was about 5650 grains. The junctions of its different parts were made gas-tight by the mixture of melted paraffin and lampblack.

One experiment made with this apparatus was as follows:—Closed the receiver portion with sticks of potash in it during sixteen hours. Reheated to near redness the retort, containing a boat with 69·71 grains of recently fused argentic fluoride, and (after having removed the potash) at once fixed the retort on the receiver, and cemented the junction. Inserted a horizontal glass exit-tube, about 8 inches (=203 millims.) long, in the tubulure E, with its inner end close to the boat. Passed a stream of pure chlorine into the apparatus by the opening G, and out by the exit-tube during about thirty or forty minutes, until I knew for certain (by means of a separate special experiment I made) that not more than $\frac{1}{50}$ of the total contents of the apparatus consisted of atmospheric air. Removed the exit-tube and inserted the plugs F and H, and cemented the junctions very carefully. Supported the receiver vertically with its lower end in mercury; placed a wet rag upon the retort and tubulure at D, and kept it cold by a constant stream of water. Heated about 3 inches of the outer end of the retort to gentle redness during seventy-six minutes. Allowed the apparatus to cool, and slightly opened the lower tap of the receiver (which was in an inclined position to prevent the mercury rising into contact with the boat) under the surface of a large and measured bulk (600 cub. centims.) of mercury in a graduated glass vessel; great rarefaction was found, and about 315 cub. centims. of mercury rushed in during four or five minutes; the bulk of gas which had disappeared was 326·37 cub. centims. (=15·236 grains of chlorine) when corrected for difference of pressure.

The tap H was now closed, and the retort separated from the receiver; the residuary gas had a strong odour of chlorine, filmed mercury powerfully, and fumed in the air; the reaction was evidently not complete. The stout platinum boat had a large hole corroded in it, and with the stout sheet platinum surrounding it, and saline residue, showed an increase of 16·46 grains in weight. The weight of the salt alone could not be definitely ascertained. The saline matter was red-brown, and contained much dissolved platinum; traces of it (weighing ·15 grain) were found upon the retort. It was a little deliquescent and contained a small quantity of undecomposed fluoride, but consisted nearly wholly of a double salt in which chloride of silver was united to tetrafluoride of platinum. After cleaning the apparatus the following losses of weight were found:—retort, 1·67 grain; sheet platinum, ·64 grain; boat, 20·58 grains; total, 22·89 grains (=16·754 grains of chlorine). This includes some particles of metallic platinum imbedded in the salt. These results show that the chlorine was absorbed without liberating much (if any) fluorine, and that 1·67 grain of platinum had been transferred from the retort to the saline mass.

Thinking that the platinum boat may have conduced to the formation of the double salt, I made another similar experiment, using, however, a boat of pure gold and 70·16 grains of recently fused fluoride. In this experiment the outer end of the retort became concave (indicating rarefaction) long before the end of the heating process. On opening the apparatus under mercury powerful rarefaction was found, and 300 cub. centims. of mercury rapidly ran in, and more would have entered but was prevented. Much free chlorine was again found, the gas fumed in the air, and the retort and its contents had gained 16·20 grains in weight. The gold boat and sheet platinum were powerfully corroded where the saline matter touched them. The saline residue contained very little soluble matter. After cleaning the apparatus the losses of weight were as follows:—retort, 1·13 grain; sheet platinum, 14·59 grains; boat, 11·36 grains; total, 27·08 grains. After dissolving the chloride of silver by aqueous ammonia, and the salts of gold and platinum by hydrochloric acid, 6·32 grains of fragments and dust of those metals was found, thereby reducing the total loss by corrosion to 20·76 grains. The general and numerical results of this experiment closely agree with those of the preceding one*.

---

* A number of other experiments were also made with this apparatus, but with its lower half composed of glass; in each instance the glass was more or less corroded, and there was less rarefaction than with the receiver formed wholly of platinum; I have not described the results obtained because of the interference produced by this corrosion.

I conclude, therefore, that chlorine does not set free fluorine from fluoride of silver at a low red heat in vessels of gold or platinum, but unites chemically with that salt and with the metal of the vessel to form a compound from which fluorine is not set free at a low red heat.

I now tried a method of getting boats of pure carbon in order to repeat the foregoing experiment. The method consisted in making boats of lignum-vitæ, baking them very gradually until they were quite black and evolved no visible liquid, then heating them with extreme slowness in a nearly closed copper tube, with frequent turning until the tube was quite red-hot, and cooling them very slowly. On heating fluoride of silver in one of them inside a platinum tube-retort, it became nearly wholly reduced to metal, probably in consequence of the presence of hydrogen in the boat. To purify the boats from that substance, a number of them were heated to redness in a porcelain tube with a current of chlorine passing over them during three hours; nearly the whole of them fell to pieces during the process.

I also obtained a large variety of specimens of native graphite, and made many boats from the purest and hardest varieties*, and also from selected pieces of gas-carbon†. To purify them, they were digested about six days in hot concentrated hydrochloric acid until soluble matter ceased to come out, then in boiling water, then in cold and pure aqueous hydrofluoric acid during six days, and again in boiling water until all acid was removed. They were now dried and ignited to expel sulphur; and to remove hydrogen they were heated to redness in a platinum tube-retort in a current of bromine‡ vapour during more than one hour; and to remove any remaining silica they were similarly heated in vapour of pure aqueous hydrofluoric acid during one hour; then finally heated to redness in an open platinum tube. Boats thus prepared had no chemical effect upon melted fluoride of silver at a low red heat, provided they were heated to redness immediately before use.

The following kinds of native graphite were tried. Ceylon graphite; the hardest specimens were too fragile. Graphite from Iceland; much too impure. Compressed Cumberland graphite; fell to powder when heated in hydrochloric acid. Graphite from Greenland; split into layers in the process of carving. SIDOROFF'S graphite from the Lower Tongooska River, Siberia§; boats made of it cracked when heated with fluoride of silver in chlorine. Graphite from "Marbella, Andulasia," also a specimen of "Siberian graphite"||; formed good boats, but were rather soft. Excellent boats were made from a specimen of "Graphite from Spain;" but the best were made from ALIBERT'S graphite from Irkoutsk, and that from Borrodale. Many specimens contained veins and nodules of quartz.

---

* The best I have found have been the purest varieties of ALIBERT'S Siberian plumbago, obtained from Messrs. FABER, of Stein, near Nuremberg; and also selected pieces of Borrodale graphite.

† Boats of this substance have been made for me in a satisfactory manner by Mr. J. THORP, 3 Charles Street, Wandsworth Road, London.

‡ If chlorine was used the boats became covered with minute spangles of platinum.

§ Given to me by Mr. BRANDT, Palmerston Buildings, Bishopsgate Street, London.

|| Given to me by the Plumbago Crucible Company, Battersea, London.

Pure chlorine was passed in a slow stream during 1½ hour over 30·66 grains of previously fused argentic fluoride in a boat of purified gas-carbon in a short platinum tube within a long one at a barely visible red heat; a fuming vapour, which corroded glass freely, was evolved during the earlier part of the process, and a small amount of platinum salt sublimed. The saline residue weighed 35·14 grains, theory requiring 34·82 grains of argentic chloride, if the correction be made for the amount of free silver in the original fluoride. The residue was non-deliquescent, and had the physical properties of argentic chloride slightly coloured by traces of platinum salt. After cleaning the two tubes by means of aqueous ammonia and by hydrochloric acid, the short one had lost 3·58 grains, and the long one 1·31 grain by corrosive action of the gas. In this experiment I consider the fluorine passed away in chemical union with the carbon of the boat, and that the corrosive action upon the platinum was due to the chlorine.

69·59 grains of recently fused fluoride in a partly purified and recently ignited boat of Siberian graphite, was heated to incipient redness in the graduated platinum receiver apparatus during 3¼ hours, and then stood all night. No leakage occurred. On opening the receiver under mercury less powerful rarefaction occurred than when a boat of platinum or gold was employed, and about 260 cub. centims. (=12·1 grains of chlorine) of mercury ran in. A slow absorption of gas then took place, after which the residuary gas was 130 cub. centims. at ordinary pressure and temperature. On opening the receiver free chlorine was found, and the gas fumed in the air. A film of brown sublimed salt of platinum was spread over the inside of the vessel. The saline residue weighed 76·18 grains (=14·11 grains or 302·27 cub. centims. of effective chlorine); it consisted of argentic chloride containing some undecomposed fluoride. After cleaning the platinum articles by suitable solvents, they were found to have lost 4·81 grains=3·467 grains, or 74·3 cub. centims. of chlorine taken up by them and rendered non-effective. Some chlorine was also absorbed by the mercury on its admission. The carbon boat was slightly corroded around the silver-salt, and its weight was increased 2·07 grains; by heating it to low redness in a nearly closed platinum retort, it evolved a strong acid odour and a vapour which corroded glass rapidly, and lost 1·57 grain in weight. I consider that the residuary gas was a compound of fluorine and carbon containing free chlorine, and that there were interferences in the results caused by several circumstances.

To obtain a more accurate result with the same apparatus, I took *an excess*, or 117·11 grains, of recently fused fluoride in a very pure boat of Borrodale graphite (weighing 119·4 grains) which had just been heated nearly to redness. A slight leakage took place, and the receiver had to be refilled with gas, thereby causing the silver-salt to take up ·4 grain of chlorine. The end of the retort containing the boat was heated to low redness during four hours, and the apparatus then set aside thirty-six hours at 60° Fahr. On opening the receiver under mercury, 282 cub. centims. ran in under ordinary pressure=123 cub. centims. of residual gas. Warming the receiver did not much expand the enclosed gas, showing thereby the absence of any highly volatile liquid. On separating the retort from the receiver no chlorine remained, and the mercury was not filmed; the excess of silver-salt employed had made the reaction complete. The enclosed gas was colourless, heavy, fumed in the air, had no odour of chlorine, but a peculiar characteristic dusty odour very distinctly, similar to that evolved when bisulphide of carbon is digested with iodine and a large excess of dry argentic fluoride. The gas did not attack mercury or *dry* glass. It was freely absorbed by purified plumbago; the boat of graphite absorbed 2·88 grains of it at 60° Fahr. The retort and contents had gained 12·90 grains (including the 2·88 grains of gas absorbed by the boat). The saline residue weighed 125·62 grains=8·11 grains gain of weight=17·448 grains, or 379·27 cub. centims. of *effective* chlorine=9·338 grains of expelled fluorine; it contained undecomposed fluoride of silver freely. The boat was corroded all over its inner surface only, and smelt strongly of the residuary gas. By heating it nearly to redness in a nearly closed platinum tube during half an hour, the gas was expelled, and it lost 2·88 grains in weight. Its final weight was 117·72 grains=1·68 grain lost by the heating in chlorine. The platinum apparatus was less corroded than in previous experiments, owing to the more rapid absorption of the chlorine by the excess of argentic fluoride, and had lost only 1·33 grain =·958 grain, or 20·53 cub. centims. of chlorine rendered non-effective.

The general results of this experiment may be approximately explained as follows:—The apparatus, when ready for heating, contained 394·5 cub. centims. or 18·406 grains of chlorine, and 10·5 cub. centims. (or a little less) of air, and about 117·5 grains of silver-salt. Of this quantity of chlorine, about ·958 grain was rendered non-effective; the remaining 17·448 grains united with the silver of the fluoride and expelled 9·338 grains of fluorine, which united with 1·474 grain of carbon of the boat and produced 10·812 grains of tetrafluoride of carbon, of which 2·88 grains was in an absorbed state in the boat when the gas was measured, and the remaining 7·932 grains occupied about 123 cub. centims. in the apparatus.

To obtain a still more accurate result I employed a still larger excess of the fluoride, and diminished the heated platinum surface by discarding a boat and cup I had previously employed to contain the carbon boat, and also heated a less length of the retort. The same boat was used; it contained 153·1 grains of the fused salt. The boat and contents was heated during three hours, and then cooled during $1\frac{1}{2}$ hour. On opening the receiver under mercury about 162 cub. centims. of residuary gas (=a loss of about 1·48 grain of carbon from the boat) was found; it contained no free chlorine. On applying a red heat to the outer end of the retort the gas was considerably increased in volume, and returned only partly to its original bulk on cooling, showing that the boat or its contents absorbed some of the gas. Some of the gas was transferred to a glass vessel over mercury; it was colourless, clear, and did not corrode mercury or glass in twenty days. On taking the retort off the receiver the gas exhibited the same properties as in the last experiment, and contained no free chlorine. The amount of sublimed platinum salt was now very small, only ·49 grain=·20 grain of chlorine rendered non-effective. The total gain of the retort and its contents was only 7·35 grains, chiefly in consequence of the boat and outer end of the retort having been heated to redness before disconnecting them from the receiver. The saline residue weighed 161·17 grains=a gain of 7·87 grains=16·93 grains, or 362·8 cub. centims. of effective chlorine. After heating the boat to just below redness for half an hour in a nearly closed platinum retort, it was found to weigh 1·63 grain less than after heating to redness immediately before the experiment. The results are substantially the same as those of the last experiment, and may be explained in a similar manner.

In another experiment made for the purpose of collecting some of the gas, the same boat, containing 177·2 grains of the fused fluoride, was employed, and the retort was heated 2½ hours. About 156·4 cub. centims. of gas was found*, and the properties of the gas were the same as those previously found. Three separate small portions of it were mixed with an equal volume of hydrogen in one instance, and with twice its volume in the other instances, and a light applied; combustion only, without explosion, took place, hydrofluoric acid was formed, and the glass became corroded on the entrance of atmospheric air. The gas therefore was not free fluorine. The odour of the gas was the same as that observed in other experiments in which fluoride of carbon was formed by different reactions.

---

* The true volume of gas could not be accurately determined in these experiments on account of its absorption by the carbon boat, and also on account of the opacity of the receiver.