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

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On account of the prospect of being able to isolate fluorine by means of the action of chlorine, bromine, or iodine on argentic fluoride, I have in this investigation very fully examined the behaviour of those substances with that compound.

Behaviour with Chlorine (continued).—To ascertain more completely the nature of the compound formed by fluoride of silver with chlorine and platinum at a red heat, I passed a very slow current of pure chlorine over 24·62 grains of argentic fluoride in a platinum boat within a 20-inch platinum tube during nine hours at a very low red heat. A very minute amount of a vapour which corroded glass was continually evolved; and traces of a sublimate occurred, consisting chiefly of argentic chloride. On heating the boat and tube to redness after the experiment, a boiling sound was heard, a little fume and much chlorine escaped, and a loss of weight of 11·70 grains took place*. On weighing the cooled apparatus a gain of 6·49 grains upon the original weight still remained, theory requiring 6·88 grains if the whole of the fluoride took up its equivalent of chlorine without any fluorine being expelled. The thick platinum boat was powerfully corroded, and immoveably fixed to the tube, even at a red heat†. The residuary salt was easily fusible, tasteless, of a dark red colour, and contained much combined platinum; 3·38 grains of it fused with alkaline carbonates yielded 2·56 grains of metal (theory requiring 2·51 grains), of which by analysis 1·82 grain was found to be silver, and ·74 grain was platinum: ·63 grain of chlorine was also found in it, showing that the chlorine in it was chemically equivalent in amount to the silver. The deficiency of ·19 grain required to make up the quantity taken I have set down as fluorine. The red salt corroded glass in the presence of damp air, and contained only a few very minute particles of platinum.

	Found.	Calculated.
Silver	1·82	1·723
Chlorine	·63	·566
Platinum . . .	·74	·786
Fluorine	·19	·303
Total . .	3·38	3·378

The above calculation is made upon the assumption that the composition of the residue is in accordance with the equation $4AgF+4Cl+Pt=4AgCl, PtF_4$. The deficiency of

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* Melted chloride of silver absorbs much chlorine gas during the act of cooling; the resulting compound may perhaps be used as a means of getting liquid chlorine.

† Platinum articles are very liable to adhere together in chlorine at a red heat, occasioning much injury of apparatus.

fluorine is accounted for by the continuous minute escape of that body during the heating process. Some of the excess of silver found is explained by the presence of a rather large amount of free silver in the original fluoride. The platinum boat and short tube had lost 24·94 grains by corrosion, and the outer tube had gained 15·33 grains of platinum by vapour of a salt of that metal having been transferred to it and decomposed by the heat; ·80 grain of loose platinum was also found; the amount of platinum therefore chemically combined in the red salt was about 8·81 grains (the analysis gave 9·046 grains), theory requiring 9·55 grains. The following explanation closely agrees with the results obtained. The 24·62 grains of fluoride of silver (including a little free silver, and containing about 3·683 grains of fluorine) gained about 6·882 grains of chlorine, forming therewith about 27·818 grains of argentic chloride. The 3·683 grains of fluorine united with 9·551 grains of platinum to form tetrafluoride, which united with the argentic chloride to form 41·052 grains of a double salt, which only very slowly evolved a small portion of its fluorine in a current of chlorine at a red heat*. The results of this experiment agree with those obtained with boats of platinum and gold in chlorine, in the retort-and-receiver apparatus (see Phil. Trans. Roy. Soc. 1870, p. 240).

I heated some boats of cryolite and of fluor-spar very carefully to redness; they all became full of minute cracks, and melted fluoride of silver passed freely through them. By melting argentic fluoride in boats of previously ignited alabaster it was completely decomposed.

More than forty mixtures of the fluorides of glucinum, cerium, magnesium, calcium, strontium, lithium, and sodium, also cryolite and colourless fluor-spar, were made into boats by pouring them in a melted white-hot state into platinum boats immersed in red-hot gypsum, and either immersing a smaller platinum boat in the liquid and removing it after the mixture had solidified, to form the hollow part, or grinding out the hollow by the methods employed by lapidaries. Many of the cooled products formed beautiful enamel-looking substances, and might probably be used to form vessels for containing fluorides and for other technical purposes. The best mixtures were, 1st, the fluorides of calcium and magnesium in the proportion of their equivalent weights; 2nd, 300 parts of fluoride of calcium, 6 of fluoride of magnesium, and 3 of fluoride of lithium. The mixtures fused at a strong red heat to a clear liquid like water. Some of the mixtures of the fluorides of magnesium and lithium, and of the fluoride of magnesium with cryolite or fluoride of strontium, yielded crystals (probably double salts) on solidifying. On melting argentic fluoride in any of these boats, it passed over their edges by capillary action. Boats were also cut out of pieces of caustic lime, and heated repeatedly to redness in a current of anhydrous hydrofluoric acid, but they did not become wholly converted into calcic fluoride.

More than fifty boats were also made by moulding various fluorides in a state of wet paste and baking them: the fluorides tried were those of bismuth, copper, nickel, cobalt, lead, cadmium, zinc, manganese, uranium, chromium, cerium, magnesium, calcium,

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* The double salt absorbed about 11·70 grains of chlorine. See p. 321.

strontium, barium, lithium, and sodium; but, from various reasons, none of them could be used for the desired purpose.

To ascertain more definitely the behaviour of argentic fluoride with chlorine at 60° FAHR., I placed a platinum cup, containing 88·38 grains of the recently fused fluoride, in a dry glass bottle filled with 409·67 cub. centims. of perfectly dry and pure chlorine, the bottle being closed by a bung of vulcanized india-rubber coated with a mixture of paraffin and lampblack, and inverted in mercury during thirty-eight days. No mercury entered, and the bottle was not corroded. A partial diminution of colour of the chlorine was produced by absorption of one third of the gas by mercury around the bung; but the cup and silver-salt gained only ·17 grain in weight. The saline residue was not even superficially whitened, and was found to be almost entirely soluble in water. AIMÉ* passed chlorine over fluoride of silver at 60° Fahr. in glass vessels coated with caoutchouc; the caoutchouc was acted upon, and hydrofluoric acid produced.

To try the effect of a higher temperature, a stoppered glass bottle of 286·77 cub. centims. capacity (=13·38 grains of chlorine) was employed, its stopper being smeared with traces of very pure lampblack to make it more gas-tight. The platinum cup contained 70·77 grains of recently fused argentic fluoride, and was supported in the upper part of the bottle by a platinum wire. The mouth of the bottle was immersed in mercury, and the stopper secured. The bottle was kept at a temperature of 200° to 230° FAHR. during eleven days; the yellow colour of the gas was not then perceptible. It was further heated to the same temperature during four more days; no ingress of mercury or visible leakage took place, nor did the bottle become at all corroded. A crust of chloride of mercury formed around the stopper. After standing forty-eight hours at 60° Fahr., the neck of the bottle was broken under mercury, strong rarefaction was found, and the mercury rose rapidly until the bottle was about half full. The residuary gas was then yellow, and was wholly absorbable by mercury. The residue in the platinum cup was superficially white, and showed no appearance of containing chemically combined platinum. By heating the cup (loosely covered with a platinum lid) gradually to redness, no special odour or evolution of gas was perceivable; a trace of effervescence took place, such as always occurs with fluoride of silver on being fused in the air, and a loss of weight of ·39 grain occurred. The crust from the mouth of the bottle was found by analysis to contain 7·914 grains of chlorine, and no hydrofluoric acid. After dissolving the fluoride in the cup by hot water, and the metallic silver from the residue by dilute nitric acid, about ·80 grain of argentic chloride (=·2 grain of chlorine) was found. The cup after heating to redness had lost ·19 grain. From these results it is manifest that fluoride of silver heated to 230° Fahr. in a platinum vessel in dry chlorine during fifteen days, suffers only a minute superficial decomposition, and does not corrode the vessel as it does at a low red heat.

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* GMELIN's Handbook of Chemistry, vol. ii. p. 359; Annales de Chimie et de Physique (1833), vol. lv. p. 443; POGGENDORFF's Annalen, Leipzig, vol. xxxii. p. 576; Journal für praktische Chemie, vol. ii. p. 469; LIEBIG's Annalen (1835), vol. xvi. p. 174.

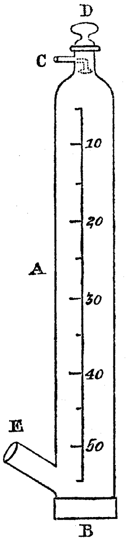
To ascertain if platinum vessels were corroded by chlorine in contact with argentic *chloride* at a red heat, a stream of the washed and dried gas was passed during half an hour over 166·67 grains of that substance in a melted state mixed with 10·30 grains of platinum filings, in a platinum boat within a roll of platinum foil in a glass tube. A gain of weight of 1·04 grain took place; a red-brown salt of platinum was formed; the boat was corroded, and had lost more than 1·58 grain in weight.

With regard to the behaviour of an aqueous solution of fluoride of silver with chlorine, PHIPSON states (Chemical News, vol. iv. p. 215), "When a solution of fluoride of silver is decomposed by a current of chlorine gas, the chloride of silver precipitated contains fluorine, and does not blacken under the influence of the solar rays; when exposed to the light it becomes of a light-brown tint, which is permanent even in sunlight. In this experiment a large portion of fluorine remains dissolved in the liquid; but it gradually decomposes the water, evolving large bubbles of oxygen gas, which appear to arise from the precipitate at the same time, and not before the glass becomes attacked by the hydrofluoric acid formed."

I passed an excess of chlorine through a dilute solution of argentic fluoride in a platinum cup; chloride of silver was freely precipitated; the mixture was then filtered in the dark, and boiled to expel the excess of chlorine; the clear liquid contained no silver, it was acid to test-paper, had no bleaching-power, contained a little hydrochloric acid and also hydrofluoric acid, the latter being shown by its giving a precipitate with a solution of chloride of barium. The silver chloride turned violet in daylight.

In some of these experiments I employed a graduated COOPER's receiver, A (fig. 8), 177·8 millims. high, 22·22 millims. diameter, and 60 cub. centims. total capacity, constructed of platinum, provided with a tightly fitting cap B to close its lower end, and a small exit-pipe C at its upper end, with an accurately fitting plug D, perforated in the direction of the dotted lines so as to act as a tap. The cap B having been cemented on air-tight by means of paraffin, the receiver was filled with washed chlorine. The tap D was then closed, and the lower end of the receiver immersed in an aqueous solution of argentic fluoride, with the arm E beneath the surface of the liquid. Rather rapid absorption of the gas took place, which ceased after about six hours. After standing twenty hours the lower opening of the vessel was closed, and the upper one momentarily opened; no odour of chlorine remained, and the vessel contained a gas which repeatedly and vigorously reinflamed a red-hot splint, it was therefore nearly pure oxygen. The bulk of this residuary gas was about 21·8 cub. centims. when corrected for difference of pressure*, the original volume of chlorine to the level of the arm E being about 52 cub. centims. A precipitate of chloride of silver was found freely in the vessel. In a second experiment I filled the same receiver with washed chlorine, introduced 20 grains of argentic fluoride, added 3·5 cub. centims. of distilled

Fig. 8.



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* It is probable that some atmospheric air entered unobserved.

water, closed the receiver and shook it; much heat was evolved: in this experiment also air got in and vitiated the measurement. In a third experiment the receiver was filled with washed chlorine, 15 grains (=about 5 grains excess) of the brown fluoride put in, then 6 cub. centims. of distilled water added without agitation, the vessel then securely closed and immersed in a glass bottle which was quite filled with distilled water, and frequently shaken during several hours, and stood all night; no leakage of any kind took place. On opening the lower arm E under a measured amount of distilled water, strong rarefaction was found; the vessel was then closed and again shaken, and reopened under water; about 42 cub. centims. of water ran in altogether, and the volume of the gas, after correction for deficient pressure, was 11·89 cub. centims. The gas did not cloud a drop of solution of argentic nitrate, and was found to be pure oxygen. In this experiment, therefore, 53 cub. centims. or 2·455 grains of chlorine was absorbed, and 11·89 cub. centims. or ·248 grain of oxygen evolved. The following equation agrees substantially with the results obtained:—

$$8AgF+8Cl+4H_2O=5AgCl+3AgClO+8HF+O,$$

or

$$7AgCl+AgClO_3+8HF+O.$$

With Hydrochloric Acid.—Two platinum boats, Nos. 1 & 2, containing respectively 48·25 and 63·33 grains of recently fused fluoride of silver, were placed whilst still warm in a horizontal platinum tube, and a slow current of dried hydrochloric acid gas passed over them during 2¼ hours. No. 1 boat was placed near the exit end of the tube and kept cool, and the end of the tube nearly closed by a platinum stopper; whilst No. 2 was enclosed within a short tube of platinum placed in the middle part of the longer tube, and heated to incipient redness during the whole of the time. The acid gas was dried by passing through two bottles containing strong sulphuric acid. Vapour was evolved, which powerfully corroded glass. The contents of the cold boat soon became moist, and also white with superficial formation of argentic chloride; no sublimate appeared. After the experiment the residue in the cold boat weighed 50·43 grains, it should have been 54·52 grains if wholly converted into chloride; and that of the heated boat 71·91, theory requiring 71·55 grains. The residue in the cold boat contained soluble silver-salt, whilst that in the heated boat was quite insoluble in water The tubes and boats were not visibly corroded, and suffered only minute alterations in weight. Thinking that the liberated hydrofluoric acid might possibly by its liquefaction have influenced the effects produced in the cold boat, I placed a platinum boat containing 34·00 grains of recently fused fluoride of silver, within a similar long platinum tube, and passed dried hydrochloric acid gas similarly over it during one hour without application of heat. It then weighed 34·10 grains, and had acquired only a very thin white coating of argentic chloride. The residue was freely soluble in water, and the boat was unaltered in weight. From these experiments I conclude that fluoride of silver at a low red heat is wholly decomposed by anhydrous hydrochloric acid gas and converted into argentic chloride, and that in the massive state, as after fusion and cooling, it is very slowly decomposed by that gas at 60° Fahr. with superficial formation of silver chloride.

With Chloric Acid.—A saturated aqueous solution of argentic fluoride manifested no signs of chemical change on the addition of aqueous chloric acid.

With Bromine.—The behaviour of argentic fluoride with bromine is generally similar to that with chlorine. 5·07 grains of earthy fluoride of silver in a closed glass bottle containing common liquid bromine, exposed during two days to sunlight, gained 1·15 grain in weight, theory requiring 2·43 grains if it had been wholly converted into bromide and its fluorine expelled.

A platinum cup containing 75·13 grains of recently fused argentic fluoride was placed in an inverted dry glass bottle; and within the cup was placed a small platinum crucible containing 42·16 grains of dry bromine which had been twice redistilled with fragments of fused chloride of calcium, and the last portions rejected. The stopper of the bottle having been firmly secured, the mouth of the bottle was immersed in mercury, and the whole set aside during thirty-six days at atmospheric temperature. Much free bromine still remained. The argentic salt had gained only ·38 grain in weight, and remained almost entirely soluble in water. In another similar experiment in which the liquid bromine was in contact with a larger surface of the silver-salt, similar results occurred. Bromine, therefore, has but little action on fused argentic fluoride at 60° Fahr.

To ascertain the effect of a higher temperature, two platinum cups were placed in a securely stoppered bottle inverted 3 inches deep in mercury with the mouths of the cups upwards. One cup contained 66·24 grains of the recently fused fluoride, and the other 28·64 grains of the redistilled and perfectly dry bromine. After standing six days at 60° Fahr., a gentle heat was applied; a small leakage of vapour occurred. After standing twenty-four more days at 60° Fahr., the bottle was again heated during two days to about 200° Fahr.; a small leakage again took place during the first few hours of heating. At the end of the twenty-four hours the colour of bromine had entirely disappeared, and the bottle was only slightly corroded. The bottle was again heated to 200° Fahr. during four days more and then cooled. Much bromide of mercury had formed around the outside of the stopper. The surface of the saline residue was yellow; and the cup and silver-salt had gained only 1·37 grain in weight. By digesting the residue in hot dilute nitric acid, about 3¼ grains of insoluble bromide was formed; the soluble portion yielded by analysis 71·83 grains of argentic fluoride=63·57 grains of fluoride of silver undecomposed. Bromine, therefore, acts slowly upon argentic fluoride at 200° Fahr., but less slowly than chlorine acts upon it.

Ordinary bromine, which had been rendered anhydrous, was passed during one hour over 51·88 grains of fluoride of silver at a low red heat in a platinum boat inside a short platinum tube within a longer one; a second platinum boat containing the bromine being placed near the first one, and the contiguous end of the long tube closed by a stopper of platinum, the heat extended to the bromine and produced a continuous supply of vapour. During the early part of the experiment a gas was evolved which corroded damp glass freely; only traces of sublimate appeared. After the process the excess of bromine was expelled by heat. The short tube and its contents had gained 27·37 grains in weight. Neither of the tubes was visibly corroded: the long one, after being cleaned, had lost ·5 grain, and the short one only ·05 grain in weight. The boat containing the silver-salt was much corroded, but only where the saline matter touched it, as in similar experiments with chlorine; after removing nearly the whole (or 93·17 grains) of the saline residue, and cleaning the boat, 14·30 grains of platinum was found to have been removed by corrosion. The residuary salt was red, and evidently contained chemically combined platinum; it also visibly contained a little metallic platinum; soluble undecomposed fluoride was also present in it. The gain of weight of 27·37 grains may be accounted for thus:—22·97 grains of bromine decomposed 36·46 grains of argentic fluoride, uniting with 31·00 grains of silver and displacing 5·455 grains of fluorine, which by uniting with 14·2 grains of the boat, formed 19·655 grains of tetrafluoride of platinum, which further united with the 53·968 grains of bromide of silver to form 73·623 grains of a stable double salt; a further amount of 5·78 grains of bromine decomposed 9·17 grains of argentic fluoride, uniting with 7·80 grains of silver to form 13·58 grains of argentic bromide, and expelling 1·37 grain of fluorine, either in the free state or united chemically with some of the excess of bromine—most probably the latter. According to this, 45·63 grains of argentic fluoride was decomposed, and 6·35 grains remained unchanged. I did not ascertain whether a portion of the 1·37 grain of fluorine was expelled in the form of hydrofluoric acid, in consequence of the presence of a very small amount of organic matter, which I afterwards found the ordinary bromine contained.

In a second similar experiment with highly pure and anhydrous bromine, 26·68 grains of the fluoride was employed. A vapour was freely evolved, which corroded glass in the presence of damp air. The boat and its contents gained 11·30 grains in weight, theory requiring 12·81 grains if all the fluorine was expelled. The saline residue contained some red-brown platinum salt, and by analysis it yielded 30·67 grains of argentic bromide, 6·50 grains of undecomposed argentic fluoride, and 2·17 grains of metallic platinum. The boat and short tube lost 3·12 grains by corrosion; the remaining ·95 grain of platinum passed into solution, probably as 1·316 grain of tetrafluoride. I consider, from the results of these two experiments, that bromine gradually expels a portion of the fluorine (probably in the form of pentafluoride of bromine) from argentic fluoride in platinum vessels at a red heat, whilst the remainder of the fluorine corrodes and unites with the platinum of the vessels to form a red salt, as it does when chlorine is employed.

The vapour of ordinary bromine was also passed over fused argentic fluoride in a boat of Siberian graphite, which had been partially purified (see Phil. Trans. Roy. Soc. 1870, p. 242) but was not heated immediately before use. The silver-salt weighed after fusion 47·62 grains, and was slightly reduced to metal upon its surface in consequence of impurities, or of moisture, in the boat. The boat was heated to incipient redness in the vapour of bromine during 1½ hour, in the same manner as in the last experiment, and the excess of bromine then expelled by heat; no sublimate occurred. The boat and its contents had increased in weight 22·39 grains, theory requiring 22·87 grains if all the salt was converted into argentic bromide and its fluorine expelled. The platinum tube was not corroded, nor altered in weight. The boat had lost 2·52 grains, apparently partly by corrosion; say, 2·25 by corrosion and ·27 by moisture (as found in a similar experiment). The saline residue was translucent, somewhat malleable, insoluble in water, and weighed 71·58 grains, theory requiring 70·49 grains of argentic bromide, the slight excess of weight being accounted for by the fused fluoride having contained a little reduced silver. By fusing 5·85 grains of it with an excess of alkaline carbonates, 3·36 grains of silver, entirely soluble in dilute nitric acid, was obtained, theory requiring exactly that amount. I consider that in this experiment the whole of the argentic fluoride was converted into bromide, the fluorine escaping in chemical union with the carbon of the boat as in similar experiments with chlorine (see Phil. Trans. Roy. Soc. 1870, pages 243, 244). The bromine used in this experiment was not quite pure.

I repeated the experiment with perfectly pure and anhydrous bromine, and a boat of Spanish graphite which had been perfectly purified by the process already referred to (page 327), the boat being heated nearly to redness immediately before the experiment. The boat after heating weighed 88·48 grains, and the fused fluoride 77·63 grains. The experiment lasted six hours, and much vapour, which corroded glass in damp air, was evolved. After expelling the excess of bromine, the boat was found slightly corroded, and, with its contents, weighed 201·82 grains. The saline residue adhered to the boat and could not be separately weighed; its weight, however, must have been about 115 grains, on account of the loss of weight of the boat; it contained scarcely perceptible traces of soluble silver-salt. The results of this experiment perfectly agree with those of the previous one.

It may be here remarked that gaseous fluoride of carbon does not corrode dry glass, and that the corrosive action of vaporous fluorine compounds upon glass is variable, and is caused in some cases by the compounds assuming the liquid state, and in others by the presence of traces of moisture.

On adding liquid bromine to a saturated aqueous solution of argentic fluoride, an abundant precipitate was produced, but no gas was evolved; on further adding fragments of the fluoride and stirring, effervescence occurred rather freely, and much heat and acid odour and a little oxygen were evolved.

The reaction may be represented by the following equations:—

$$8AgF + 8Br + 4H_2O = 5AgBr + 3AgBrO + 8HF + O,$$

or

$$7AgBr + AgBrO_3 + 8HF + O.$$

I now perfectly dried the yellow precipitate in a nearly covered platinum cup, and heated a portion of it with sulphuric acid in a glass test-tube; bromine was liberated freely, but the glass was not corroded. With dilute hydrochloric acid the yellow powder effervesced freely and evolved much chlorine. The dried powder changed to a dirty grey colour in sunlight. I also heated 26·56 grains of the dry powder gradually to gentle redness in a deep platinum cup; much effervescence occurred, and an odourless gas, proved to be oxygen, was evolved; the residue was argentic bromide. The loss of weight was ·80 grain; theory requires a loss of 1·095 grain if the reaction took place according to the following equation:—

$$5AgBr + 3AgBrO, \text{ or } 7AgBr + AgBrO_3 = 8AgBr + 3O.$$

The deficiency of loss is accounted for by the oxygen previously expelled by the heat of the reaction, and that expelled by the heat applied in drying the mixture.

26·76 grains of earthy fluoride of silver was dissolved in a small amount of water in a deep platinum cup, an excess of bromine mixed with it, and repeatedly evaporated to dryness with water and an excess of bromine each time, and finally fused at a low red heat; the weight of argentic bromide found was 39·25 grains, theory requiring 39·39 grains; the deficiency was due to moisture in the fluoride.

With Hydrobromic Acid.—An aqueous solution of fluoride of silver was instantly and completely precipitated by an excess of aqueous hydrobromic acid.

With Bromic Acid.—Aqueous bromic acid produced a copious white precipitate in a dilute aqueous solution of argentic fluoride.

With Iodine.—KÄMMERER[*] has already made an experiment of heating fluoride of silver with iodine. He introduced iodine into a perfectly dry tube of glass along with a small stoppered glass tube filled with an excess of the fluoride[†].

After expelling all the air by vapour of iodine, he broke the inner tube, and heated the apparatus to about 70° to 80° C. (=158° to 176° Fahr.) for twenty-four hours. The contents of the glass tube were then colourless, the iodine had disappeared, and the glass was transparent. The tube was then opened under mercury, the gas transferred to a eudiometer, and rapidly absorbed by a fragment of potash. After this absorption no trace of silica or iodine could be found in the potash; the oxygen (of the potash) displaced by the fluorine had combined either with potash or water to form peroxide of potassium or of hydrogen. The tube was not at all attacked. He considered he had isolated fluorine in this experiment, and mentioned Sir HUMPHRY DAVY'S statement that fluorine does not attack glass, and may be transferred over mercury. He also proposed to try bromine instead of iodine.

To ascertain the effect of iodine upon argentic fluoride at moderately elevated temperatures I made several experiments.

A platinum cup containing 32·75 grains of pure and recently fused iodine was inverted within a second platinum cup, containing 34·26 grains of recently fused and still hot

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[*] Phil. Mag. 1863, vol. xxv. p. 213; Chemisches Centralblatt, August 1862, p. 523; MILLER'S 'Chemistry,' 3rd edition, vol. ii. p. 159.

[†] In all those of my preliminary experiments in which fluoride of silver was heated in contact with glass, serious interferences occurred; and if the silver-salt was not thoroughly fused it contained moisture, which acted upon glass, and also greatly promoted the absorption of the iodine.

argentic fluoride[*], and the two cups placed in a glass bottle, the air of which had been dried by a stick of caustic potash[†]. The bottle, with its stopper well secured, was inverted in mercury, with the mouth of the larger cup upwards, and kept at a temperature of 150° to 200° Fahr. during eight days. A small leakage of air took place during the first hour. The bottle was further heated during three weeks to a temperature between 200° and 300° Fahr., and was then somewhat corroded. After a third heating to between 300° and 450° Fahr. during two more weeks, until the colour of iodine had entirely disappeared, and during one day more, the corrosion was rather considerable[‡], and no mercury had entered the bottle. On opening the bottle under mercury, no contraction or rarefaction was found, and the bottle contained some fluoride of silicon; 3·53 grains of alkaline silico-fluoride was scraped off the bottle. The two cups (and their contents) had lost ·58 grain in weight and were not corroded. On heating them to low redness in a long platinum tube retort provided with a long exit-tube, the outer end of the retort being kept cold, a boiling sound occurred and iodine sublimed freely; tetrafluoride of silicon also escaped and deposited silica around the orifice; the loss of weight, including only a small portion of the free iodine, was 3·44 grains. No signs were observed of a condensed liquid. By further careful heating of the whole retort, 3·30 grains of free iodine (apparently containing some fuming vapour) was expelled, and a small amount of argentic iodide sublimed. I rubbed 22·89 grains of the very easily fusible residue to fine powder in plenty of boiling water[§] until all soluble silver-salt was extracted, and precipitated the filtered solution; 3·00 grains of argentic chloride was obtained =6·909 grains of argentic fluoride[||], in the total 59·70 grains of saline residue freed from excess of iodine. If we assume 6·0 grains of unchanged fluoride of silver to have been present in the fused residue after expulsion of the free iodine, and the original fused silver fluoride to have contained 6 per cent. of free silver, the results may be approximately explained thus:—2·41 grains of iodine united with the 2·05 grains of free silver to form 4·46 grains of AgI; 26·21 grains of iodine decomposed 26·21 grains of AgF, forming 48·5 grains of AgI, and took the place of 3·92 grains of fluorine, only a small portion of which was expelled by the heat employed to effect the reaction.

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[*] The fluoride probably contained about 6 per cent. of free silver.

[†] It was absolutely necessary in these experiments to exclude the least trace of moisture; otherwise the iodine was rapidly absorbed.

[‡] It is astonishing how much corrosion of glass the most minute amount of watery vapour will under such circumstances produce; the moisture probably acts in such a way that a series of chemical reactions take place, attended by continued reproduction of a portion of water.

[§] A mixture of argentic iodide and fluoride melts to a thin black oily looking liquid under a *small* quantity of boiling water.

[||] This number is too great; I have found by experiment that iodide of silver dissolves in a strong aqueous solution of argentic fluoride, and is reprecipitated on diluting the liquid.

Approximate Composition of the Saline Residue.

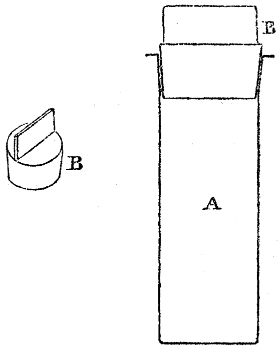
Before expulsion of Fluorine and Iodine.			After expulsion of Fluorine and Iodine.	
Loosely united fluorine	3·92	=6·74		
Loosely united iodine	2·82			
AgF	6·00		AgF	6·00
AgI	53·70		AgI	53·70
Loss	·57		Total	59·70
Total	67·01			

These numbers show some disagreements; but more accurate ones could not be obtained.

In a second similar experiment with 35·98 grains of the fluoride, the results were generally similar: the vapour expelled by fusing the residue extinguished red-hot charcoal. The residue, after expulsion of loosely united fluorine and iodine, weighed 63·62 grains, and doubtless consisted of 60·23 grains of iodide of silver and 3·48 grains of argentic fluoride. In a third experiment 57·55 grains of iodine and 80·85 grains of fluoride were employed; the results were again similar. The yellow residue weighed 137·28 grains. Crystals of silicon heated to redness in the vapour expelled by melting the saline residue, were quickly corroded, but did not visibly incandesce. The sublimed iodine fumed strongly in the air. After expulsion of all the free iodine, the residue had lost 14·12 grains and weighed 123·16 grains = a gain of weight of 42·31 grains by the silver-salt =49·753 grains of fluoride decomposed = 49·753 grains of iodine combined =7·443 grains of fluorine liberated. In a fourth experiment the argentic fluoride was in a thick layer at the bottom of the cup; and after heating the substances to about 250° Fahr. during ten weeks, more than half the iodine and fluoride remained unchanged.

From the results of these experiments, I conclude that iodine slowly displaces fluorine from argentic fluoride at temperatures between 200° and 500° Fahr., without corroding platinum vessels, and forms a loosely combined compound of fluorine, argentic iodide and iodine, from which the loosely combined fluorine and ineffective iodine are expelled at a red heat.

Fig. 9.



As the results were somewhat interfered with by the formation of fluoride of silicon, I employed instead of a glass bottle a platinum one of the form A, fig. 9, 76·2 millims. deep, and 25·4 millims. diameter, provided with a hollow stopper (B) ground into it as air-tight as possible.

Two platinum cups were placed inside the bottle, one within the other—the outer and deeper one containing 64·80 grains of pure and fused iodine, and the other 80·46 grains of recently fused fluoride. The bottle, with its stopper secured, was inverted its whole depth in mercury at about 200° to 250° Fahr. during thirty-six days and then cooled. On opening, its gaseous contents exhibited no tension; it was full of a vapour of an intensely dusty odour, which fumed very strongly in the air, was heavy, and might be poured. The iodine cup was empty, the other contained the usual yellow residue, most of which had been fused by heat applied in extracting the stopper. On heating the cups gradually to redness, the fuming vapour and free iodine were expelled. The saline residue after fusion weighed 126·73 grains =8·14 grains of fluorine expelled. The cups were not corroded.

To try the effect of a higher temperature, I employed a platinum retort of the form A, fig. 10, 153 millims. long and 22 millims. diameter, with an air-tight stopper B, and a thick platinum bottle C with a wide mouth, to contain the fluoride, and an arrangement (fig. 11) to secure the stopper. 29·83 grains of fluoride and 35·33 grains of iodine were taken; and nearly half the retort was placed horizontally in a hole in a block of cast iron, and kept at 600° Fahr. during ten hours, with frequent rotation. The temperature was partly determined by means of a bit of cadmium placed upon the block. No leakage occurred; and no tension of vapour was found on opening the cooled retort. The results were similar to those of the last experiment. By fusing the saline residue it lost 18·36 grains, and then weighed 46·80 grains =2·98 grains of fluorine expelled. The bottle was slightly corroded and had lost ·35 grain in weight.

Fig. 10.

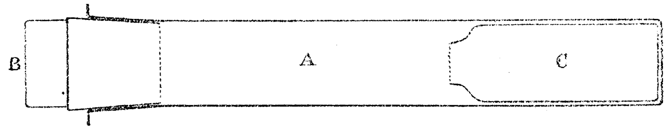
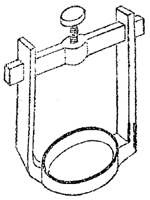


Fig. 11.



In a second experiment with this retort, 46·73 grains of fluoride and 34·98 grains of iodine were taken, and the retort heated to about 720° Fahr. during fifteen hours. The results were again similar. All the free iodine had been absorbed by the saline residue. The silver-salt after fusion weighed 67·81 grains =3·708 grains of fluorine expelled. The bottle lost 1·20 grain in weight. After a third experiment, with much larger quantities of materials at a still higher temperature, much fuming iodine remained, and a platinum boat containing the fluoride had lost 9·63 grains in weight.

From these experiments it is evident that platinum is corroded by contact with iodine and argentic fluoride at a temperature of 700° Fahr.

I also passed vapour of recently fused iodine during two hours over 135·29 grains of previously melted fluoride in the same apparatus and manner as in the experiments with bromine (see page 326). An acid odour was evolved, and a vapour which corroded glass quickly, but no sublimate except iodine appeared; the sublimed iodine fumed strongly in the air. After heating the platinum apparatus to redness the gain of weight was 89·62 grains, =104·568 grains of the fluoride decomposed and its fluorine expelled, if we allow 4·65 grains of iodine taken up by 3·96 grains of free silver in the original fused fluoride (see analysis of fluoride of silver, Phil. Trans. Roy. Soc. 1870, p. 229).

The platinum boat was corroded and had lost 6·08 grains in weight. The total weight of the residue, including platinum in it, was 230·55 grains; it showed no visible colour of chemically combined platinum. 5·17 grains of it, digested with a strong solution of iodide of potassium, left ·03 grain of platinum. A second portion, weighing 49·06 grains, digested with a hot solution of mercuric nitrate, left 2·99 grains of platinum in large fragments. A third portion, of 8·60 grains, exhausted of soluble matter by hot water, lost 1·53 grain (including a small amount of dissolved argentic iodide, see note ‖, page 330); and the filtered liquid gave by precipitation 1·37 grain of argentic chloride, =31·80 grains of undecomposed fluoride (including a little iodide) in the whole of the residue: ·04 grain of platinum was found in the clear filtered liquid. The insoluble part of the 8·60 grains was a pale-yellow powder, easily fusible, and weighed 7·07 grains; by twice fusing it with an excess of pure alkaline carbonates, 3·23 grains of metallic silver, entirely soluble in dilute nitric acid (except ·01 grain of platinum), was obtained, pure argentic iodide requiring 3·23 grains. The composition of the total saline residue was about as follows:—

	grains.
Iodide of silver	195·00
Fluoride of silver	30·72
Metallic platinum	5·01
Combined platinum	1·07
Total	231·80

I repeated this experiment with perfectly pure iodine, passing the vapour of the iodine over 29·83 grains of the fluoride during four hours at a low red heat: similar results occurred. A colourless vapour was evolved. The saline residue appeared to contain traces of a red platinum salt. The gain of weight of the boat and its contents was 23·14 grains =27·21 grains of the fluoride converted into iodide. By analysis, as in the last experiment, 4·22 grains of argentic chloride was obtained, =3·73 grains of undecomposed fluoride (this number is too high, for the reason already stated); the other ingredients were also similarly determined. The boat was slightly corroded and had lost ·43 grain.

Composition of Residue.

	grains.	
Iodide of silver, about . . .	50·35	=52·97
Fluoride of silver, about . .	2·62	
Platinum	·43	
Total	53·40	

It is evident that, in these experiments at a red heat, iodine expelled fluorine freely from argentic fluoride, either in a free state or united with some of the excess of iodine.

Several other kinds of platinum apparatus besides those described were devised and employed for effecting the reaction of iodine with argentic fluoride, but were found less effective.

To ascertain the effect of a carbon vessel, a boat of Siberian graphite weighing 48·36 grains was employed; it had been partially purified in the manner already described (Phil. Trans. Roy. Soc. 1870, p. 242), and was heated to incipient redness in a nearly closed vessel immediately before use. It contained 48·91 grains of recently fused argentic fluoride slightly reduced to silver by impurities in the graphite. A gentle current of pure iodine vapour was maintained over the red-hot salt during two hours in the same apparatus and manner as in the experiment with bromine (see p. 327); a vapour apparently heavy was evolved, which fumed in the air, and was strongly acid to litmus paper without first bleaching it. After expelling the excess of iodine by a red heat, the tube and its contents had gained 40·00 grains, theory requiring 41·55 grains if all the fluorine was expelled and the boat had suffered no loss. The sublimed iodine was dry, and did not fume in the air. The boat and its contents weighed 137·18 grains =a gain of 39·91 grains; and one end of the boat was a little corroded; the salt adhered to the boat, and could not be separately weighed. The platinum articles were not corroded, but ·38 grain of the silver-salt had been transferred to them. By melting the salt out of the boat, the latter was found corroded beneath. The salt was evidently argentic iodide. 9·30 grains of it fused with an excess of alkaline carbonates yielded 4·295 grains of metallic silver, =9·345 grains of the iodide. A second portion, weighing 36·50 grains, digested with boiling water until all soluble salt was extracted, and the filtered solution precipitated, gave ·24 grain of argentic chloride =·212 grain of argentic fluoride, or ·523 grain of undecomposed fluoride in the total 90 grains of residue. I consider that in this experiment, as in similar ones with a graphite boat in bromine and chlorine, the fluorine of the salt was expelled in chemical union with the carbon of the boat. It did not appear to me necessary to repeat this experiment with a perfectly purified boat.

On adding iodine to a saturated aqueous solution of argentic fluoride the mixture become yellow, and evolved some heat, but no visible bubbles of gas were liberated; by adding fragments of the fluoride to the mixture and stirring, a strongly acid odour was ultimately evolved. The reaction was probably similar to those with chlorine and bromine, and according to the following equation:—

$$8AgF + 8I + 4H_2O = 5AgI + 3AgIO + 8HF + O, \text{ or } 7AgI + AgIO_3 + 8HF + O.$$

With Hydriodic Acid.—An aqueous solution of argentic fluoride was instantly and completely precipitated by a brown solution of hydriodic acid, with evolution of heat.

With Iodic Acid.—Aqueous iodic acid produced a copious white precipitate with a dilute solution of argentic fluoride.

I am now examining the substance produced by the reaction of iodine and argentic fluoride under the influence of heat.

Added June 3rd, 1871.—I have since determined the chemical composition of the volatile substance evolved by the action of argentic fluoride and iodine at red heat.