Studies on Fluorine at Low Temperatures. III. Dissolution of Chlorine in Liquid Fluorine.

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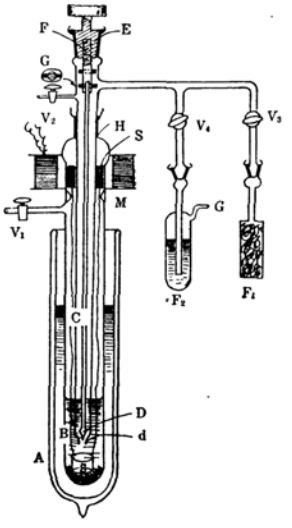
Merck's potassium bifluoride contains 0.17% chlorine. When it is electrolysed, chlorine of the chloride in the molten salt is expelled by fluorine and the produced fluorine gas is contaminated with chlorine gas, and sometimes traces of chlorine can be found in liquid fluorine. Of course, such occurs only while the salt is fresh, and no chlorine exists in the salt which has been subjected to electrolysis for a long time.

It is unusual that a solution of crystals exists at such a low temperature as that of liquid fluorine. The present authors carried out measurements as to this interesting case.

I. Apparatus. A special apparatus as shown in the accompanying figure was devised for the purpose of taking a sample for analysis, and used in the analysis of liquid air and a solution of chlorine in liquid fluorine. A is a Dewar vessel to keep liquid nitrogen, B a glass pipe 30 mm. in diameter, where fluorine entering at V_2 is condensed, C a Pyrex glass sampler for the solution, 10 mm. in diameter, D a valve spindle made of Pyrex glass, the top of which is connected with the lower end of the copper rod. F has a screw-thread cut on it and the spindle goes up and down as cap E in the upper part with ground glass surface is turned, and thus the ground glass surface joint between D and d at the lower end is opened or closed. Two copper pieces are attached to the lower part of F as shown in the figure. The cross-section of the pipe at this point is made elliptical (G), so that F does not rotate but only goes up and down when E rotates. S is a stirrer, M an electric magnet for working the stirrer S, F_1 a silver-plated copper vessel filled with many small coils of silver filament and acts as an absorber of fluorine, and F_2 a glass vessel in which an aqueous solution of silver nitrate is placed to absorb fluorine and chlorine.



II. Operation. Fluorine or chlorine is introduced at V_2. V_1 is an opening for evacuating the apparatus in advance. The interior of F_1 is also previously evacuated. When a proper amount of solution is condensed on the bottom of B, the stirrer S is moved up and down by operating M and the liquid is made homogeneous. The valve D is closed by turning E and the sample of liquid is accumulated in C.

By turning H, B and C are disconnected at the ground glass surface junction. C is drawn up slightly from the liquid fluorine and the solution is gradually vaporized. When V_3 is opened and F_1 is heated to 200°C., the sample in C is vaporized and the fluorine, acting on the silver, is absorbed. Care must be taken so that sudden boiling may not take place at the time of vaporization and the crystals of the segregated solute and a small quantity of the solution may finally remain. Then V_3 is closed and V_4 is opened. In this way the remainder of fluorine and the crystals of the segregated chlorine are vaporized and the vapour produced is passed through the solution of silver nitrate in F_2.

The solution of silver nitrate is first made ammoniacal, and is acidified with nitric acid after the halogens have been passed through it. To make ammoniacal is intended for preventing a part of chlorine from becoming soluble $AgClO_3$.

The gas in C is drawn by working a pump at G and by introducing air at V_2. All the gas in C is passed through F_2.

III. **Quantitative determination of fluorine and chlorine.** (1) The greater part of fluorine, apart from chlorine, is acted on by the silver filament in F_1, and makes silver fluoride. The quantity of fluorine is determined by weighing F_1.

(2) The solution of silver nitrate, the deposits of silver fluoride and silver chloride are carefully poured from F_2 into a bakelite beaker and are acidified with nitric acid, whereby the silver fluoride is dissolved. Then the solution is filtered and the residue of silver chloride is weighed. Thus, the quantity of chlorine can separately be determined.

(3) The filtrate contains silver fluoride and silver nitrate. With an addition of aqueous solution of NaCl, it is precipitated as silver chloride. Then by removing the deposit a filtrate of NaF can be obtained. This filtrate is made alkaline by adding an aqueous solution of Na_2CO_3 to it. Then deposits of $CaCO_3$ and CaF_2 are formed by adding a solution of $CaCl_2$ to this alkaline filtrate. When $CaCO_3$ alone is dissolved by acetic acid, CaF_2 remains as deposit. This deposit is filtered and weighed, and the quantity of fluorine is determined from CaF_2.

IV. **Results of measurements.** (1) Fluorine obtained from a new electrolyte of potassium bifluoride. Fluorine as AgF in F_1 1.0524 g., as CaF_2 in F_2 0.1155 g., total 1.1679 g. Chlorine as AgCl in F_2 0.0075 g. Thus, the percentage of chlorine in the mixture was found 0.64.

(2) The percentage of chlorine in fluorine produced from an old electrolytic salt was 0.09%.

(3) Quantity of chlorine in liquid fluorine saturated at −195°C. Chlorine was separately introduced, condensed, and precipitated. After stirring, the solution was analysed with the result as follows: Fluorine as AgF in F_1 0.7145 g., as CaF_2 in F_2 0.1227 g. Chlorine as AgCl in F_2 0.0088 g. The quantity of chlorine in the solution saturated at −195°C. was 1.04%.

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