Fluorine, Hydrogen Fluoride

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Fluorine

$\text{F}_2$

Fluorine is produced at present either by electrolysis of molten KHF$_2$, being liberated at a graphite anode between 200 and 300°C (slight contamination by CF$_4$), or from molten KF·3 HF at a Ni anode at approximately 100°C, according to the method of Lebeau (if the melt contains water, contamination by O$_2$). The latter method is the most tractable and has been tested extensively. The only suitable vessel materials are Fe (which develops a rust coating on the surface), Cu and Mg. The salt is available in a pot made entirely of brazed Cu with about 2-mm. wall thickness (Fig. 104). The cover rests lightly on three pieces of CaF$_2$, placed in the upper trough, and held in place by a layer of cement. Alternatively, the cover rests on a gasket cut from 5-mm.-thick soft rubber sheet, which in turn rests on the flat lip of the pot. To slow down the penetration of humid air into the trough, the latter is also packed with CaF$_2$ powder. The anode, made of 3-mm. nickel wire, is attacked only at its extreme end. Therefore, greater service life is obtained by coiling the electrode or attaching to it a 1-cm. nickel rod. Thus, the useful life of an electrode may be extended to the electrolysis of approximately two complete salt batches. After that, a new anode can easily be inserted into the connecting copper adapter. The melt usually spatters and creeps up the walls. This is the reason for placing the insulation so high in the thick-wall Cu adapter, which is cemented into the upper tube with litharge-glycerol. This adapter should preferably be taken out with strong pliers at the end of each electrolysis cycle and thoroughly washed. The sturdy fluorite stopper is secured with the same cement. It is even simpler to use a one-hole rubber stopper, coated with polytrifluorochloroethylene oil. The anode is surrounded by a copper or, better, a nickel tube. Three struts extend downward from the tube and are attached, by keyed copper connections, to a Cu plate. This plate acts as protection against
the \( \text{H}_2 \) rising from the wall of the pot. The pot serves as the cathode. This is the best arrangement since it leaves a large free cross section for the electrolyte salt. The \( \text{Cu} \) tube may become coated with an insulating layer of fluoride, which, however, sometimes dissolves if the temperature rises too high, making it necessary to replace the tube from time to time. The tube cannot be replaced with sintered alumina, which dissolves in the melt. This inconvenience is unfortunately encountered with all apparatus for production of fluorine. In order to generate the \( \text{F}_2 \) under a pressure of about 10 cm. of water, the pot is intentionally made tall. The outlet tubing must be at least 6 mm. inside diameter, since some electrolyte particles are always entrained with the gas. A single electrolysis batch requires 1.2 kg. of difluoride of the highest purity and 300 g. of freshly distilled, anhydrous HF. The apparatus is put on a hot plate which is placed on an ordinary platform scale, making it easy to determine from the loss in weight (300 g.) whether refilling is necessary and to avoid unnecessary overshooting of the temperature. At the beginning of the preparation a horizontally directed Bunsen flame is used as auxiliary heat, so that the salt is melted and heated to 70°C in half an hour (attach a thermometer). No heat is applied during the electrolysis, which proceeds at about ten volts and about 4-5 amp. (with Ni rod anodes, 6 amp. yields 40 ml. of \( \text{F}_2/\text{min.} \)). The hot plate serves only to keep the contents of the pot in the liquid state during interruptions in the run. After electrolyte depletion, the cover is removed and the residual salt is allowed to solidify while the container is being rotated, thus creating a cavity (work under a hood, wearing goggles; \( p_{\text{HF}} \) at 150°C is 130 mm.). Fresh HF is added to the cavity, the vessel is covered with a piece of \( \text{Cu} \) sheet, and the HF is left to be absorbed by the salt overnight. After heating to 90°C, the cover with the anode can be replaced. In order to remove the small amounts of HF, the product gas is first led through a 10 x 50 mm., Dry Ice-cooled \( \text{Cu} \) bottle brazed to a tube of poorly heat-conducting nickel-silver alloy (\( p_{\text{HF}} \sim 1 \text{ mm.} \)) and then through a \( \text{Cu} \) tube filled with granular NaF and provided with copper plug valves. Detection of \( \text{F}_2 \) in the exit stream (as well as at leaks) is easy. A jet of illuminating gas or a rag soaked in machine oil and attached to a wire will ignite on contact with \( \text{F}_2 \). If the salt mass has been well dried, the traces of water disappear completely after the first hour of electrolysis. Any \( \text{O}_2 \) which may be formed cannot be
separated from the $F_2$; it may be determined, although not con-
veniently, by shaking with Hg [2].

With the packing materials now on the market, for example,
Teflon, it is easy to build similar equipment made of somewhat
thicker sheet copper or of cast magnesium by using Teflon-
insulated gaskets and tightening the apparatus with screws. When
a Cu pot with 5-mm.-thick walls, 35 cm. high and 15 cm. in
diameter, containing 5 kg. of KHF$_2$, is used, a current of 5 amp.
may be applied. The HF gas can then be fed almost continuously
to the outer chamber, thus replacing the raw material as it is
consumed.

PROPERTIES:

Atomic weight 19.00. M.p. -223°C, b.p. -187°C; d (liq.) 1.11,
d (gas) 1.31 (air = 1). Fluorine does not attack quartz and very dry
glass. For heating in a $F_2$ atmosphere, Pt tubes are used, or even
better, sintered alumina tubes (up to 600°C), while Cu tubes are
useful up to 350°C and Ni to 600 or 700°C. Teflon or Kel-F is used
as gasketing material and Kel-F grease is used for lubrication of
stopcocks and ground joints.

For commercial apparatus, see [3, 4].

REFERENCES:

1. H. v. Wartenberg. Z. anorg. allg. Chem. 193, 409 (1930);
244, 337 (1940).
2. H. v. Wartenberg. Z. anorg. allg. Chem. 242, 408 (1938);
H. Schmitz and H. J. Schumacher. Z. anorg. allg. Chem. 245,
221 (1940).

Hydrogen Fluoride

HF

Precautionary measures: Since hydrogen fluoride solutions,
particularly when concentrated, cause extremely painful and pro-
tracted burns, a paste made of magnesium oxide with a little
glycerol should be kept on hand when working with larger quantities.
The eyes must be protected and rubber gloves must be worn.

I. CRUDE HYDROFLUORIC ACID [1]

Laboratory preparation of this material will almost never be
undertaken. To obtain 0.25 kg. of HF, 1 kg. of finely pulverized
fluorite or, even better, cryolite (for Si-free HF) is vigorously
heated with 2.25 to 2.5 kg. of 97.5% As-free H$_2$SO$_4$ in a small autoclave placed on an air bath. A lead tube 1.5 meters long and 2 cm. in diameter, with an attached Liebig condenser, is soldered to the cover. Run duration, 4 hours. The product is collected in a copper flask cooled with ice-salt mixture. Impurities: H$_3$SiF$_6$, HCl, H$_2$SO$_3$, H$_2$SO$_4$, HSO$_3$F, Pb.

II. PURE, 35% HYDROFLUORIC ACID

This solution is commercially available in polyethylene bottles and is already quite pure. For further purification, it is distilled from a NaF-containing Pt retort into a Pt receiver, leaving behind the SO$_4^{2-}$ and SiF$_6^{2-}$ ions. A little PbCO$_3$ is added to remove the Cl$^-$. This yields PbClF, which is insoluble in concentrated HF. An excess of PbCO$_3$ does no harm, even in the presence of H$_2$SO$_4$. Organic material is removed only when KMnO$_4$ is added (dropwise).

Vessel materials: Pt, Ag, Cu, Mg (but not Pb), celluloid (may be easily shaped in warm water), polyethylene, paraffin, metal dishes coated with Bakelite, Teflon, etc. See also section on F$_2$.

Boiling points of various H$_2$O/HF mixtures are given in [4].

III. ANHYDROUS HYDROGEN FLUORIDE

Distillation of 1.2 kg. of anhydrous KHF$_2$ at 500°C yields 250 g. of HF. Technical grade KHF$_2$ is dissolved in warm water, some PbCO$_3$ is added to eliminate Cl$^-$, the K$_2$SiF$_6$ and PbClF are allowed to settle, and the clear solution is evaporated in Cu or Mg dishes until crystallization occurs. Alternatively, a quantity of hydrofluoric acid is divided into two equal parts, one of which is neutralized with K$_2$CO$_3$, mixed with the other part and evaporated. Filter hot through a Cu funnel. The crystals which separate on cooling are allowed to drain and are dried initially on filter paper, at 100°C. Further drying must be carried out with great care at 130 to 140°C. A thin layer of crystals is placed on a Mg or Cu sheet turned up 1-2 cm. along the edges, and the sheet is placed on a large hot plate. After 2-3 days the crystals are ground in a coffee mill and dried for another day, after which they are stored in paraffin-coated glass bottles. The dust from the salt is disagreeable. The compound can be obtained more readily by decomposition of NaHF$_2$, but the decomposition starts already drying, and NaHF$_2$ is therefore not recommended as a raw material.

Distillation is carried out in a Cu flask, 24 cm. high, provided with a conical ground stopper, 4 cm. in diameter, held in place with screw clamps (Fig. 105). The cone is lubricated with graphite-paraffin oil or Kel-F grease to prevent freezing of the joint. The 1-m.-long Cu tube must be 2-2.5 cm. in diameter, since salt is carried over and inconvenient plugging can occur in the middle of
the run. The glass condenser is gasketed with a piece of rubber hose, and to slow down the decomposition, a few turns of water-cooled tin tubing are wound on it. The Cu tube is allowed to stand in HCl/Br\(_2\) until it is bright, or the initial HF fraction will be brown. The retort should be provided with a Cu thermowell, projecting upward for 5 cm. from the bottom and externally brazed in place, to accommodate a copper-constantan thermocouple. The retort is heated either on a multiple burner in an iron jacket or, preferably, in an electric furnace. Before filling it should be cleaned with HCl until bright and dried carefully in a stream of CO\(_2\). The Cu receiver (250 ml.) is connected by a special coupling (Fig. 106) and must be cleaned with HCl until bright. It is then dried and reduced in a stream of H\(_2\) at 300°C. During distillation, use an ice-salt mixture (−10°C) for cooling. A second container provides protection against overflow. The retort is first heated slowly for approximately 3/4 hour to about 400 to 500°C, that is until HF begins to drip into a Pt dish below (leave the screw coupling at \(E\) open). Vapor pressures of KF and HF are given in \[6\]. After about 10 ml. has been collected, a test is made to determine whether a strip of filter paper gelatinizes immediately. If so, the acid is anhydrous. Now the coupling at \(E\) is tightened (use pliers and rubber gloves) and the freezing bath is put in place. Raising of the temperature to 500°C must be accomplished with great care, since at that temperature KF begins to separate from the melt and violent evolution of HF also occurs [\[2\]]. The operation is decidedly more convenient if a thick-walled Cu capillary (shown with dotted lines) is brazed to the Cu tube. The capillary should dip about 2 cm. into a Hg pool in a Pt dish. If this is done, the couplings on the receivers may be tightened before the run and the first few milliliters allowed to drip from the capillary until the paper test shows the absence of water. The capillary may then be sealed off simply by raising the level of the mercury. Should the evolution of HF be too violent, excess HF can escape through the capillary, accompanied, of course, by noxious fumes.

![Fig. 105. Distillation of anhydrous hydrofluoric acid.](image)

- distillation retort (Cu); \(B\) condenser (inner tube of Cu); \(C\) receiver (Cu), −10°C; \(D\) second receiver, −10°C; \(E, F\) conical screw couplings.
The evolution subsides after about 3 hours and the heating is discontinued. Loosen \( E \) and \( F \) and close them off with Cu cones. If the distilled acid is to be stored, the tubes can be closed off at \( E \) and \( F \) with solid Cu cones equipped with screw caps. After cooling, the contents of the retort may be dissolved in boiling water and regenerated with aqueous HF.

![Diagram of conical copper coupling](image)

**Fig. 106.** Details of the conical copper coupling. The cones are interchangeable.

For regeneration, the solution is treated in a large Cu or Mg dish with sufficient pure, commercial (35-40%) HF to turn litmus completely red. The solution is then evaporated over an open flame but not to the point where spattering occurs. The salt mass is then crushed and dried as described previously.

The resultant HF still contains traces of entrained KF and can be redistilled at 30-35°C into the second receiver. For very pure HF, silver equipment should be used [2]. Since organic substances are immediately decomposed by HF vapor, joints can be made tight only by means of the Cu cones described. Alternatively fused sulfur may be used, with picein or a like substance covering cracks in the sulfur mass. As a temporary expedient, resulting in not quite anhydrous acid, the seal can be made with well-dried litharge-glycerol cement.

Liquid HF is available in steel tanks or cylinders. (Heat gently with flame to make it flow.)

In order to render the liquid HF completely anhydrous, fluorine may be bubbled through using a silver capillary. The \( F_2 \) gas decomposes traces of water. Thus a cylinder HF can be partially dried by somewhat loosening the main valve with a wrench in a cold room and then putting the cylinder in a container of appropriate height, filled with ice-salt mixture; after the cylinder has cooled down, the valve is removed completely and \( F_2 \) is bubbled through or half an hour from a fluorine cylinder through a silver capillary; the valve is then screwed back on and tightened with the wrench. The fluorine pressure produced in the usual laboratory generators is not sufficient for the HF cylinders. For all practical purposes, \( F_2 \) does not dissolve in liquid HF. Instead of using fluorine, the water may be removed by dropwise addition of thionyl chloride, which liberates gaseous HCl, SO\(_2\) and SOF\(_2\), all insoluble in HF [K. Wiechert, Z. anorg. Chem. 261, 314 (1950)].
Pure HF for very small scale experiments be easily obtained (together with hydrogen) by placing a copper boat with well-dried PbF$_2$ in a platinum or copper tube in front of the compound to be reacted with the nascent HF. The boat is heated to red heat in a stream of hydrogen.

Conduits for HF gas are made of well-dried copper tubes provided with conical copper joints. In such tubes HF gas may be heated to 1000°C (of course, protection from the atmosphere must be provided). Sintered alumina tubes may be used up to 500°C. Copper caps, temporarily cemented on with litharge-glycerol, may serve as closures, but it is better to solder them onto the alumina tube. To accomplish this, the alumina tube is electrolytically coated with copper, and soft solder is used for attaching the caps. Completely anhydrous HF does not attack quartz. Lead and organic substances are destroyed, except for polymerized tetrafluoroethylene (Teflon) [5]. Copper (not brass) stopcocks or, preferably, platinum valves (Bodenstein design) serve to shut off the flow. It is advisable to make the stopcock body of copper and to turn out the plug from a Teflon block on a lathe. Such a plug turns easily and needs no lubrication.

PROPERTIES:

Formula weight 20.01. B.p. 19.5°C; for b.p. at various pressures see [3]; m.p. -85°C; d (liq.) 0.987. t$_{cr}$ 188°C, p$_{cr}$ 66.2 kg./cm.$^2$, d$_{cr}$ 0.29.

REFERENCES: