the graphite electrode. The former is easily and completely removed by passing the gas through dry sodium fluoride, while the latter, according to Meyer and Sandow, are present in extremely small amounts.

Summary

The fluorine generator described by Argo, Mathers, Humiston and Anderson has been improved. The technique for the regeneration of the electrolyte and for the continuous generation of large quantities of fluorine has been developed.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION, FREEZING POINT AND VAPOR PRESSURE OF HYDROGEN FLUORIDE

BY JOSEPH SIMONS

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The Preparation of Anhydrous Hydrofluoric Acid

Frémy[1] was the first to make anhydrous hydrofluoric acid, distilling it from potassium acid fluoride. Later Gore[2] prepared the material in the same manner and studied many of its properties. We have found that heating the acid fluoride to fusion, as done by Gore and others[3] does not suffice to dehydrate it completely. Argo, Mathers, Humiston and Anderson[4] recommend the use of the sodium salt in place of the potassium salt and enumerate certain advantages, but it is quite evident that the complete dehydration of the sodium salt would involve the same difficulty.

In the preceding paper a method is given for the preparation of the anhydrous potassium salt by electrolyzing out the last traces of water. This gave a material from which anhydrous hydrofluoric acid could be prepared, and the next step was to develop an apparatus for the distillation. Argo and his associates encountered difficulties in this process due to the obstruction of the exit tube by the solidification of foam therein. We have been able to construct an apparatus (Fig. 1) which avoids this difficulty as follows.

A heavy copper retort is heated by a large blast ring burner so as to apply the heat near the surface of the molten charge. The lid is clamped on with "C" clamps, and the joint made tight by means of a copper washer with annular corrugations. The exit tube leading from the lid is 1 meter long and 2.5 cm. in diameter. It has a chamber

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[1] Frémy, *Ann. chim. phys.*, [3] **47**, 6 (1836).

[2] Gore, *J. Chem. Soc.*, **22**, 368 (1869).

[3] Thorpe and Hambly, *ibid.*, **55**, 163 (1889). Ruff and Plato, *Ber.*, **37**, 673 (1904).

[4] Argo, Mathers, Humiston and Anderson, *Trans. Am. Electrochem. Soc.*, **35**, 335 (1919).

near its upper end tightly packed with copper wire to remove any salt spray that the acid may carry with it. Above this is a side tube, and two brass cocks as shown in Fig. 1, one leading to the apparatus in which the acid is to be condensed, the other as an outlet for the discharge of the first fraction. The acid can be distilled from this apparatus very smoothly and rapidly.

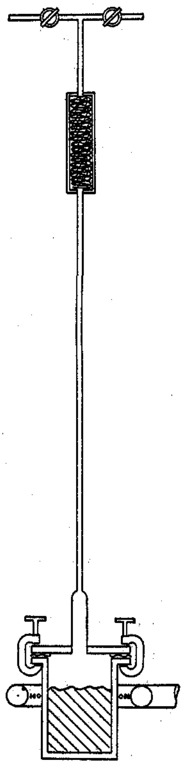

Fig. 1.—Still for preparation of hydrogen fluoride.

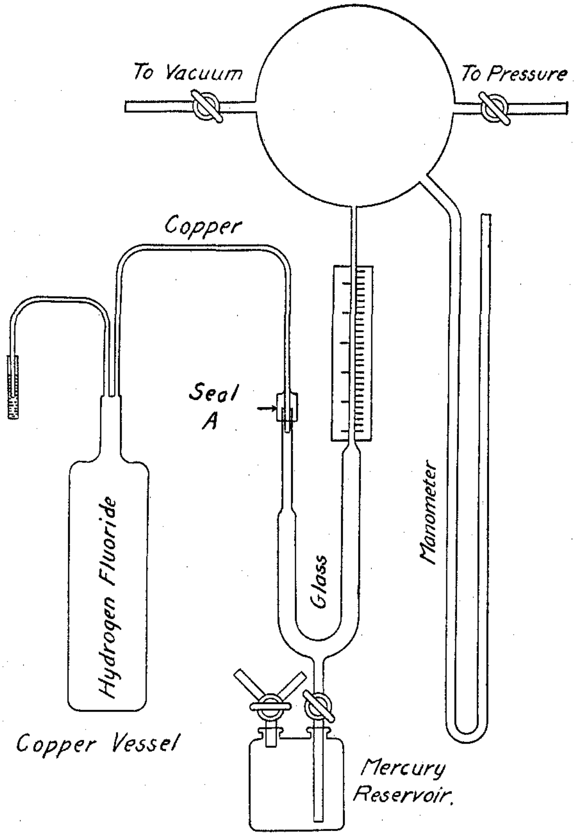

Fig. 2.—Apparatus for measuring the vapor pressure of hydrogen fluoride.

The Freezing Point

For this determination about 25 g. of the acid was condensed in a gold-plated, cylindrical copper vessel. The single opening to this vessel was at the top and was connected to a copper tube that terminated in a brass cock. The tube was bent so that the open end pointed downwards to prevent any corroded material which might form on the cock from dissolving in the liquid acid. A thermocouple was enclosed in a small thin-walled copper tube on the inside of the vessel extending from the top nearly to the bottom. All joints were made with silver solder. Air was removed by boiling out some of the acid. The acid was then frozen with liquid air, the apparatus placed in a tall, cold Dewar vessel, and a time-temperature curve taken as the material was allowed to warm slowly. The flat portion of the curve indicated the freezing point.

The value of the freezing point thus determined was 190° K. or —83°C. No single determination deviated from this by more than 0.5°. This value is 10° higher than that given by Olszewski[5] but his determination was made with the material exposed to the air of the laboratory, and the acid is very hygroscopic.

The Vapor Pressure

Fig. 2 shows the apparatus used for determining the vapor pressure of the acid.

The acid container was made of copper and had two small copper tubes connected to it. One of these was sealed off with a tube containing solder; on the other was a sleeve, as shown in the figure, to enable it to be sealed to the glass part of the apparatus with de Khotinski cement. The glass part of the apparatus was connected to a standard vacuum bench containing a McLeod gage, mercury manometer and diffusion pump. The copper portion could be trapped off from the glass by means of mercury from the reservoir below. A thermocouple junction (not shown in the figure) was tied to the outside of the heavy-walled copper vessel with copper wire.

The procedure of making a determination was as follows. The end "A" of the copper tube was connected to the acid still; the end of the other tube was open to the air. A freezing mixture was used to condense the acid as it came from the still. The acid was then frozen with liquid air, the open tube sealed with a tube of molten solder, and the tube "A" connected to the glass apparatus with de Khotinski cement. The air was removed by pumping while allowing the acid to warm slowly to above its melting point. The copper vessel was immersed in liquid air again and the pumps were run until a pressure 10^{-5} mm. of mercury was obtained. Mercury from the reservoir was allowed to enter the small copper tube and its companion glass tube to a noted mark on the scale behind the glass tube. The acid was now allowed to warm very slowly by being kept in a cold Dewar vessel. The mercury in the glass tube was kept at the same level by means of air pressure in the glass portion of the apparatus. The quantity of mercury being constant, the level of the mercury inside the copper tube was therefore constant. At intervals readings were taken of the temperature of the acid and the pressure of the air above the mercury.

The thermocouple was of copper-constantin and was calibrated against the thermocouple standardized by Eastman and Rodebush.[6] It was read on a Leeds and Northrup Type K potentiometer.

The experimental data are given in Table I. These values represent

[5] Olszewski, *Monatsh.*, **7**, 371 (1886).

[6] Eastman and Rodebush, THIS JOURNAL, **40**, 389 (1918).

two separate series of measurements taken with two different samples of the acid but they show, when plotted, no systematic deviation from each other.

TABLE I

VAPOR PRESSURE OF HYDROGEN FLUORIDE

	P, mm. of Hg			P, mm. of Hg			P, mm. of Hg	
T, °K.	Exptl.	Calcd.	T, °K.	Exptl.	Calcd.	T, °K.	Exptl.	Calcd.
192.0	1.5	3.3	265.0	257	257	290.7	697	708
201.5	5.5	6.9	265.5	259	263	291.5	719	724
205.7	5.5	9.5	267.5	281	282	292.7	752	759
218.0	18	22	268.0	290	288	292.7	755	759
223.0	25	29	270.0	327	316	295.0	816	813
228.5	32	42	271.5	335	339	295.3	841	832
236.0	60	63	272.0	337	347	296.5	863	871
238.5	73	72	274.0	373	372	298.5	911	933
242.5	87	89	275.0	388	389	299.5	958	955
243.0	93	91	275.5	400	398	302.5	1042	1047
246.5	104	110	277.0	426	417	304.7	1152	1122
247.0	117	112	278.0	433	436	305.5	1165	1175
249.5	122	126	279.0	451	457	307.5	1263	1230
250.7	139	135	280.0	472	468	309.3	1303	1318
252.7	143	148	280.7	483	490	311.0	1400	1380
253.3	160	151	282.5	512	525	312.0	1429	1445
255.0	160	162	283.5	531	537	313.3	1518	1479
257.0	186	178	284.5	559	562	315.0	1539	1585
258.0	184	186	286.5	597	603	315.7	1643	1622
260.0	202	204	286.5	600	603	316.0	1625	1622
260.5	215	209	288.7	646	646	317.7	1698	1698
263.0	230	234	289.0	650	661	318.5	1759	1738
						320.0	1827	1820

The relation between temperature and pressure as given by these data is $\log P = 7.37 - \frac{1315}{T}$, where P is pressure in millimeters of mercury and T is temperature in °K. This equation holds very well, as shown by the agreement between the observed and calculated values in the table, except for a slight deviation at the lower end. Comparing the above equation with the integrated form of the Clausius-Clapeyron equation, $\log P = \frac{-\Delta H}{RT} + \text{const.}$, we may equate the terms containing temperature and calculate $\Delta H = 2615$ cals. per mole of hydrogen fluoride. However, the fact that the gas under these conditions does not obey the gas laws robs this figure of any such simple physical significance, and renders the linear relationship given by the above equation rather surprising.

Summary

1. A method is described for the preparation of anhydrous hydrogen fluoride.

2. The freezing point was found to be —83 °C.

3. The vapor-pressure curve was established from the melting point, 192 °K., to 320 °K. and a pressure of 25 atmospheres.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE DENSITY AND MOLECULAR COMPLEXITY OF GASEOUS HYDROGEN FLUORIDE

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The Density of Hydrogen Fluoride Vapor Below its Boiling Point

Thorpe and Hambly[1] have shown that the apparent molecular weight of hydrogen fluoride vapor is 51.18 at 26.4° and 745 mm. This corresponds to a higher polymerization than the H_2F_2 often stated in the textbooks, and indicated to us the desirability of pushing the measurements to lower temperatures in order to determine the degree of complexity which this interesting substance may be capable of assuming.

The "dynamic" method of measuring vapor density was adopted with the following procedure. Nitrogen gas, freed from oxygen by passage through a cuprous ammonia reducing tower and thoroughly dried, was bubbled through anhydrous liquid hydrofluoric acid. It was then passed through copper tubes containing dry sodium fluoride, which absorbed the hydrogen fluoride, the quantity of which could be ascertained by weighing the tubes. Knowing the vapor pressure of the liquid from the data in the preceding paper and the weight of the acid carried off by a known quantity of nitrogen, the density and apparent molecular weight of the gas can be calculated from the perfect gas law.

A diagram of the apparatus is shown in Fig. 1.

The volume of the nitrogen was obtained by weighing the 2-liter bottle in which it was contained, displacing the gas with water and weighing again. The water contained a small amount of ferrous sulfate in solution to prevent its containing oxygen. The reason for the precautions to remove oxygen is that it would oxidize the copper vessel in which the acid was contained and so contaminate it. The nitrogen was passed through sulfuric acid and phosphorus pentoxide to dry it and then into the copper vessel containing the acid; twice in its passage it was forced to bubble through the liquid. It then passed through the train of sodium fluoride tubes which removed the hydrogen fluoride. The vessel was made of thin-walled copper tubing, silver soldered throughout. It was inserted in a Dewar vessel in which was placed the constant-temperature bath. The connections of the copper part of the gas train that had to be broken between every two runs were made of tightly fitting sleeves of copper tubing covered with pure gum rubber tubing. Two small auxiliary cells, containing mercury at the bottom and to which small glass tubes were connected with outer sleeves to aid in sealing, served

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[1] Thorpe and Hambly, *J. Chem. Soc.*, **55**, 163 (1889).