3. The critical temperature is approximately 144°K. and the critical pressure is about 55 atmospheres.

4. The heat of vaporization at the boiling point is 1600 cal. per mole, as calculated by the Clausius–Clapeyron equation, or, allowing for deviations from the gas laws, 1540 cal.

BERKELEY, CALIFORNIA

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

FREEZING POINTS OF THE SYSTEM WATER–HYDROGEN FLUORIDE

BY G. H. CADY AND J. H. HILDEBRAND

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The highly polar nature of both water and hydrogen fluoride suggested that an especial interest would attach to a determination of the solid compounds they might form with each other. We wished particularly to learn whether any of these might be regarded as resulting from the partial substitution of water in the polymer $(HF)_6$, which Simons and Hildebrand[1] assumed to explain the vapor densities of hydrogen fluoride over a considerable range of pressure and temperature. In spite of the excellent agreement of the assumption with the data, it is quite possible that the association actually involves more numerous molecular species, one of which might be $(HF)_4$, which has been proposed by Berliner and Hann.[2] They point out that the hydrofluorides of amines have the general formula $B \cdot 4HF$ in which B stands for the molecular formula of the base. Other compounds such as $KF \cdot 3HF$ and $MgF_2 \cdot 2NaF$ may be regarded as derivatives of the hypothetical acid H_4F_4. If water behaves in a manner similar to the amines, one compound formed should be $H_2O \cdot 4HF$.

Although no complete study of the system $HF–H_2O$ has previously been made, the freezing points of hydrogen fluoride,[3] of the compound $H_2O \cdot HF$,[4] and of dilute hydrofluoric acid solutions in concentrations ranging up to 4.140 molal[5] have been known for several years. Mr. L. Clark, working in this Laboratory during 1928, made a partial investigation of the system, but his work was considered of too preliminary a nature to warrant publication

Experimental Part

The apparatus used is illustrated in Fig. 1. The equilibrium mixture was contained in a gold cup of about 175-cc. capacity. This was surrounded by a taller copper cup

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[1] Simons and Hildebrand, THIS JOURNAL, 46, 2183 (1924).

[2] J. F. T. Berliner and R. M. Hann, *J. Phys. Chem.*, **32**, 1142–1162 (1928).

[3] Simons, THIS JOURNAL, **46**, 2179 (1924).

[4] R. Metzner, *Compt. rend.*, 119, 682 (1894).

[5] Paterno and Peratoner, *Atti Accad. Lincei*, **6**, 306 (1890); Kendall, Booge and Andrews, THIS JOURNAL, **39**, 2303 (1917); Anthony and Huddleston, *J. Chem. Soc.*, **127**, 1122 (1925).

which fitted closely into a small Dewar cylinder, thereby partially protecting the glass against attack by hydrofluoric acid vapor. To afford still further thermal insulation, the small Dewar was placed within a one-gallon vacuum jar. Both vessels had covers of light wood provided with suitable holes for the introduction of the gold-plated stirrer, the platinum pipet for removing samples for analysis, and the thermocouple, which was encased in a platinum tube. The pipet had a capacity of about 10 cc. and was equipped at the bottom with a filter of platinum gauze and spongy platinum.

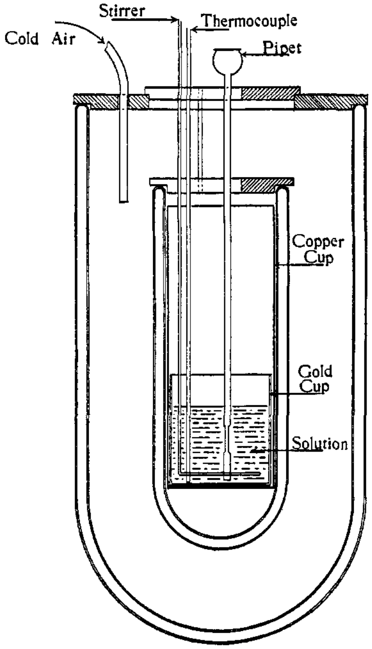

Fig. 1.—Apparatus for determining freezing points of aqueous hydrogen fluoride solutions.

For solutions of smaller concentration than 0.51 mole fraction of HF, Baker and Adamson's c. p. hydrofluoric acid was used. To obtain more concentrated acid, it was necessary to decompose KHF_2 by heating.[8]

The following simple procedure was found to give reproducible freezing points over most of the range. To about 100 cc. of solution in the gold cup, enough liquid air was added to partially freeze the solution. After stirring continually for about fifteen minutes to allow the attainment of equilibrium between solid and solution, the temperature was read, and immediately afterward a sample of the liquid phase was removed in the pipet. This sample, usually from 1 to 5 cc., was dissolved in water contained in a paraffin bottle and its weight determined by difference. A titration of the acid in this dilute solution with sodium hydroxide then gave the composition of liquid in equilibrium with the frozen solid at the observed temperature. Following the suggestion of Haga and Osaka,[6] phenolphthalein was used as the indicator.

For mole fractions of hydrofluoric acid between 0.68 and 0.89, the above treatment did not give very reproducible results. The crystals of solid seemed to be so small that they clogged the filter in the pipet and prevented the removal of large enough samples of solution. It was, therefore, found necessary to determine warming curves and to take the final sudden change in slope as the freezing point. An analysis of the completely liquid solution then became an easy matter.

Table I gives the experimental points, and they are plotted in Fig. 2.

Table I

Freezing Points of the System $HF-H_2O$

Mole fraction, HF	Temp., °K.	Solid phase	Mole fraction, HF	Temp., °K.	Solid phase
0.00777	272.10	Ice	0.698	197.6	$H_2O \cdot 2HF$
.0564	266.7	Ice	.710	197.3	$H_2O \cdot 2HF$
.0809	263.2	Ice	.743	191.3	$H_2O \cdot 2HF$
.1565	250.0	Ice	.762	181.9	$H_2O \cdot 2HF$
.216	231.6	Ice	.776	171.7	Eutectic
.265	213.0	Ice	.786	172.3	$H_2O \cdot 4HF$

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[6] Haga and Osaka, *J. Chem. Soc.*, **67**, 251–255 (1895).

TABLE I *(Concluded)*

Mole fraction, HF	Temp., °K.	Solid phase	Mole fraction, HF	Temp., °K.	Solid phase
0.276	202.9	Eutectic	0.796	172.7	$H_2O\cdot4HF$
.307	210.3	$H_2O\cdot HF$	(.800)	(172.8)	$H_2O\cdot4HF$
.321	213.6	$H_2O\cdot HF$	.817	172.4	$H_2O\cdot4HF$
.371	224.1	$H_2O\cdot HF$	.864	167.6	$H_2O\cdot4HF$
.403	229.5	$H_2O\cdot HF$	.883	162.2	Eutectic
.478	236.9	$H_2O\cdot HF$	.894	166.1	HF
(.500)	(237.7)	$H_2O\cdot HF$	.913	173.3	HF
.515	237.2	$H_2O\cdot HF$	.939	179.4	HF
.575	231.5	$H_2O\cdot HF$	.961	184.1	HF
.627	222.0	$H_2O\cdot HF$	.974	186.1	HF
.675	204.9	$H_2O\cdot HF$	.982	187.6	HF
.685	197.9	$H_2O\cdot HF$ and $H_2O\cdot2HF$	1.000	190.1[3]	HF

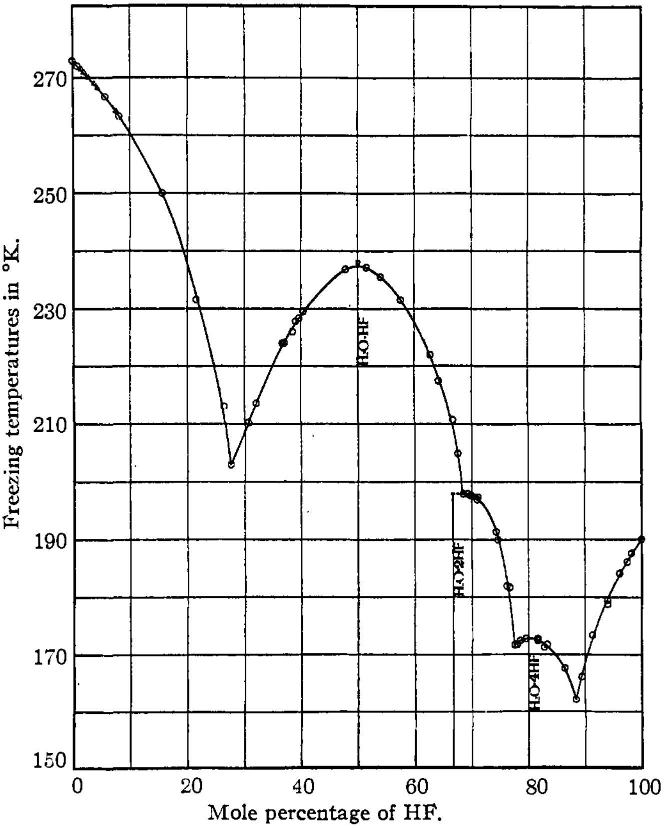

Fig. 2.—Freezing points of aqueous solutions of hydrogen fluoride. Circles refer to this research, the square to Metzner[4] and the triangles to Anthony and Huddleston.[5]

Three distinct addition compounds are indicated by the curve: $H_2O \cdot HF$, $H_2O \cdot 2HF$ and $H_2O \cdot 4HF$. The second does not quite melt congruently, but the shape of the curve hardly leaves any doubt that it has the composition given. The first of these has been prepared by Metzner[4] by freezing it from hydrofluoric acid solutions. He reports its melting point to be −35°, which is not far from our value, −35.4°.

Before anything very definite can be said concerning the configuration of these compounds, it will be desirable to have data bearing upon their crystal structures. We will merely call attention to the fact that the observations of Berliner and Hann[2] are extended by the discovery of the compound $H_2O \cdot 4HF$ and that the existence of two compounds with an excess of HF, while there are none with an excess of H_2O, harmonizes with the view that HF tends to assume a more complex polymerization than water.

Summary

The freezing point–composition diagram for the system water–hydrogen fluoride has been studied over the entire range. In addition to the solid compound $H_2O \cdot HF$, previously known, we have discovered the compounds $H_2O \cdot 2HF$ and $H_2O \cdot 4HF$.

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[COMMUNICATION NO. 430 FROM THE KODAK RESEARCH LABORATORIES]

MEASUREMENTS OF THE FLUORESCENCE OF CELLULOSE ACETATE, CELLULOSE NITRATE AND GELATIN IN ULTRAVIOLET LIGHT

BY JAMES G. MCNALLY AND WALDEMAR VANSELOW

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The fluorescence of cellulose in ultraviolet light was first noted by Hartley[1] in 1893 but no further attention seems to have been given the subject until Judd-Lewis began a series of experiments in 1918. In his first communication, Judd-Lewis[2] described the appearance of various cellulosic derivatives when held where the photographic plate is normally placed in a quartz spectrograph. Cellulose acetate, viscose, filter paper and "normal" paper showed strong fluorescence in the ultraviolet region while nitrocellulose and paper treated with ethyl malonate showed very little fluorescence.

A method of photographing the fluorescent spectrum was devised by this author[3] in which a camera was mounted in the back of the spectrograph arm and the spectrum photographed by reflected light, a procedure necessi-

[1] W. N. Hartley, *J. Chem. Soc.*, **63**, 243 (1893).

[2] S. Judd-Lewis, *J. Soc. Dyers Colourists*, **34**, 167 (1918).

[3] S. Judd-Lewis, *ibid.*, **37**, 201 (1921).