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Freezing Points and Vapor Pressures of the System Potassium Fluoride–Hydrogen Fluoride[1]

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When one prepares fluorine by the electrolysis of a solution of potassium fluoride in anhydrous hydrofluoric acid, he is apt to become discouraged by one or more of several possible troubles. Perhaps the most obnoxious of these is that a part of the oxidation which takes place at the anode produces corrosion of the electrode itself, instead of the liberation of fluorine. In order to minimize this effect, which lowers the current efficiency of the generator, it is desirable to keep the temperature of the electrolyte as low as possible. Another difficulty is that the solution has a rather high vapor pressure of hydrogen fluoride. This not only requires the removal of the acid vapor from the fluorine which is produced, but also hastens the necessity of adding more solvent to keep the solution at the proper concentration. Because of these effects, it appears that a knowledge of the system potassium fluoride–hydrogen fluoride may enable one who prepares fluorine to economize both on time and materials.

Experimental Procedure

A diagram of the apparatus which was used is shown in Fig. 1. The cylindrical copper vessel, A, which had a capacity of about 250 cc., was equipped with a copper thermocouple well and a monel metal tube leading to brass pipe fittings near B. One arm of the mercury manometer was made from steel tubing and the other from glass. Since only one mercury surface could be observed, it was necessary to calibrate the manometer at several pressures. Silver solder was used for the fabrication of the apparatus except at a few points. The two steel tubes at C and the steel and glass tubes at D were held together with Piceïn cement. By means of lead and tin

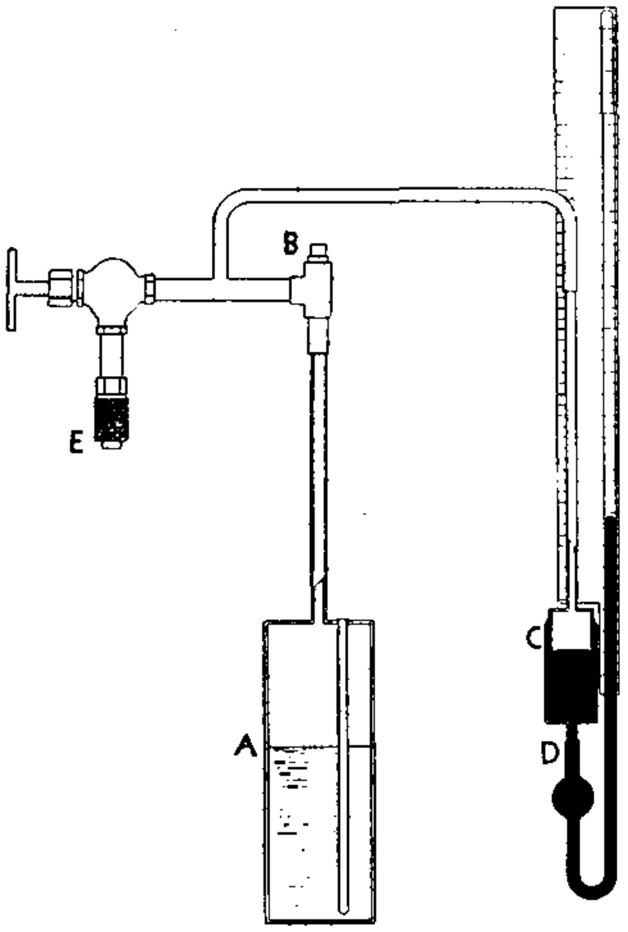

Fig. 1.—Apparatus used to study the system potassium fluoride–hydrogen fluoride.

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(1) Presented at the Chicago Meeting of the American Chemical Society, September 15, 1933.

solder placed on the threads, before screwing the parts together, the threaded connections were made vacuum tight.

Because the whole apparatus was small enough to be placed on the pan of a large balance, it was possible to make up solutions by weight in vessel A. After removing the pipe plug at B, pulverized anhydrous potassium fluoride of c. p. quality was poured in through the monel metal tube. The final dehydration of the salt was then accomplished by heating it under vacuum. Subsequently, hydrogen fluoride was distilled into the apparatus from a cylinder temporarily connected at E. Liquid distilled from a supply of anhydrous hydrofluoric acid, which was obtained from the Sterling Products Company, seemed to contain no water. Air was removed from the apparatus by a vaccum pump. When it appeared necessary, absorbed gases were expelled by repeated melting and freezing of the solution followed by evacuation of the apparatus. Between measurements the composition of the solution was changed by distilling away hydrogen fluoride.

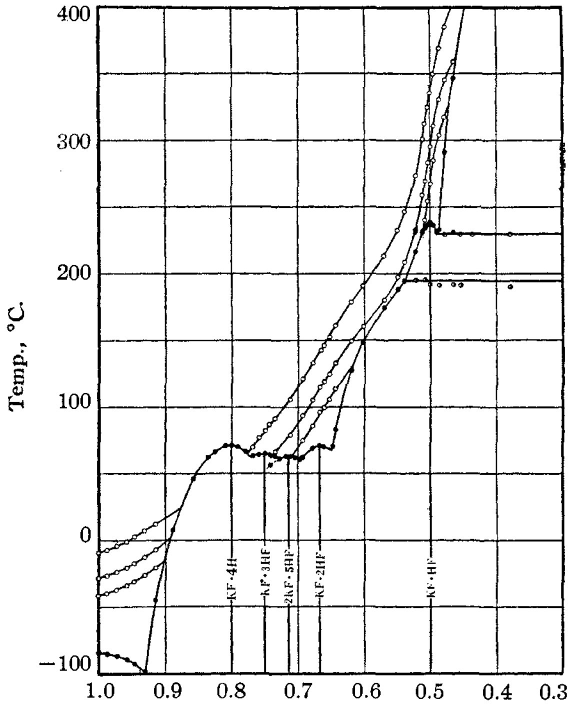

Fig. 2.—The system potassium fluoride–hydrogen fluoride: ●, freezing point; ◓, eutectic point; ◑, transition point; ○, vapor pressure. The highest vapor pressure curve is for a pressure of 25 cm., the middle for 10 cm. and the lowest for 5 cm. of mercury.

When observations were to be made, the vacuum line was disconnected, and A was placed either in a cylindrical heating unit or a Dewar flask. The whole assembly was then given a constant pendular motion about a point near B. This served to rapidly bring about an equilibrium between solution and vapor. Pressure measurements were made as the temperature passed slowly through either a maximum or a minimum. Since the two cases gave satisfactory agreement, it did not seem necessary to maintain a constant temperature for a long time. Freezing, eutectic and transition points were determined by cooling curves.

Two thermocouple thermometers were used. The one for temperatures below 15° was correctly calibrated to within 0.1°, but the high temperature thermometer probably was not quite as accurate. Electromotive force measurements were made with a Leeds and Northrup type K potentiometer.

Results

The data have been tabulated showing only significant figures which seem to have some value. It is probable, however, that in many cases the solution concentration is not correct to more than three figures and the fourth should be considered only as it influences the third. This is especially true for mole fractions of hydrogen fluoride below 0.750.

Completely shaded circles in Fig. 2 represent freezing points, while half shaded circles are in one case for a transition point and in another case for the eutectic temperature when both solid potassium fluoride and one form of KF·HF are forming. Other eutectic observations are not shown because they would make the drawing more confusing. Three vapor pressure curves pass through open circles. The highest of these curves corresponds to a vapor pressure of 25 cm., the middle to 10 cm. and the lowest to 5 cm. Points shown are not direct observations, but were obtained for each solution by plotting the logarithm of the vapor pressure against the reciprocal of the absolute temperature. Values taken from the lines obtained have been shown on the graph.

Discussion

Comparison with Previous Work.—Fredenhagen and Cadenbach[2] have measured the molecular boiling point rise produced by different solutes in liquid hydrogen fluoride and from their observations have calculated the vapor pressure lowering for dilute solutions. The measurements presented in this paper, while not made at as high pressures, agree with theirs by indicating an unusually great vapor pressure lowering.

The observed vapor pressures of pure hydrogen fluoride are about the same as those reported by Simons.[3] There is also an approximate agreement with his value of the freezing point, −83°, which compares very favorably with the tempera-

[2] Fredenhagen and Cadenbach, *Z. physik. Chem.*, **A164**, 201–208 (1933).

[3] J. H. Simons, This Journal, **46**, 2179–2183 (1924).

FREEZING POINTS AND VAPOR PRESSURES OF SOLUTIONS OF POTASSIUM FLUORIDE IN HYDROGEN FLUORIDE

Mole fraction of HF in soln.	F. p., °C.	Solid phase	Vapor pressure in mm. of mercury P	T	P	T	P	T	P	T
Satd. with KF		KF	29.9	302.3	45.4	320.9	72	343.9	97	359.5
0.4646	346	KF	79	348.0	119	366				
.4775	292	KF	40.3	309.9	71	331.7	82	337.3	181	370.3
.4860	229.5	Eutectic	27.5	283.9	52	306.4	94	328.5	148	346.4
.4947	236	β-KF·HF	24.9	258.9	62	292.0	145	326.1	239	348.0
.4996	238.8	β-KF·HF	33.4	253.3	79	286.0	149	312.3	263	338.0
(5000)	(239.0)	β-KF·HF								
0.5032	236.8	β-KF·HF	44.6	250.3	79	273.9	147	300.1	288	331.6
.5075	234	β-KF·HF	54.4	244.3	96	267.9	165	292.3	256	313.6
.5103	231	β-KF·HF	84	251.8	118	266.2				
.5218	217	β-KF·HF	83	224.8	121	240.1	197	262.0	255	274.5
.5382	195	α-KF·HF and β-KF·HF	86	202.6	114	213.4	167	228.6	288	252.1
.5488	189	α-KF·HF	91	194.6	128	207.1	160	215.6	260	235.2
.5695	175	α-KF·HF	122	187.7	161	197.4	207	205.6	233	211.1
.6014	148	α-KF·HF	77	152.6	124	167.3	180	179.3	274	194.3
.6197	128	α-KF·HF	49.4	129.3	69	139.1	131	158.1	240	177.8
.6435	84	α-KF·HF	25.3	96.8	45.4	111.5	90	130.4		
(.649)	68.3	Eutectic								
.6606	71.1	KF·2HF	43.5	95.6	113	122.2	208	140.9		
.6670	71.7	KF·2HF	56.0	98.7	111	118.2	158	128.6		
.6777	70.0	KF·2HF	48.3	86.1	65	93.5	109	108.0	221	129.1
.6932	62.4	KF·2HF	39.0	70.5	57	79.7	116	98.2	190	112.4
.6969	61.8	Eutectic								
.7040	63.4	2KF·5HF								
.7115	64.3	2KF·5HF	46.5	60.7	82.6	74.9	218	101.9		
(.714)	(64.3)	2KF·5HF								
.7173	64.0	2KF·5HF								
.725	62.7	2KF·5HF								
(.727)	62.4	Eutectic								
.7278	62.6	KF·3HF								
.7342	64.5	KF·3HF	92	65.0	116	70.9	157	79.2	233	90.0
.7438	65.5	KF·3HF								
.7490	65.8	KF·3HF	130	65.9	256	83.4	185	74.9		
(.7500)	(65.8)	KF·3HF								
.7583	65.4	KF·3HF	199	71.4	294	82.4				
.7676	64.4	KF·3HF	204	65.3	233	68.6				
(.771)	63.6	Eutectic								
.7783	67.8	KF·4HF	266	69.0	314	73.5				
.7901	71.0	KF·4HF								
.7993	72.0	KF·4HF								
(.800)	(72.0)	KF·4HF								
.8086	71.8	KF·4HF								
.8241	67.7	KF·4HF								
.8355	63.2	KF·4HF								
.8572	48	KF·4HF								
.8884	8	KF·4HF								
.9143	− 45	KF·4HF	44.1	−22.2	84	−10.3	135	− 0.8	260	13.7
.9311	− 97.0	Eutectic	59.9	−22.3	98	−12.7	143	− 4.9	259	8.4
.9466	− 92.8	HF	41.8	−33.6	93.3	−18.5	156	− 7.8	242	2.0
.9580	− 89.5	HF	21.6	−48.0	67.6	−27.8	115	−17.4	237.2	− 2.0
.9732	− 86.9	HF	50.0	−36.7	94	−25.0	163	−13.6	240	− 5.0
.9875	− 85.2	HF	35.4	−45.4	103	−25.8	178	−14.6	264	− 5.6
1.000	− 83.7	HF	24.4	−52.2	73	−34.0	165	−17.9	251	− 8.7

ture, −83.01°, found by Dahmlos and Jung.[4] The author feels that his figure, −83.7°, is not low because of the use of impure hydrogen fluoride, but, instead, that the difference lies in the thermometers which were used for the separate investigations. The freezing point as determined by this research was found easily reproducible to

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[4] J. Dahmlos and G. Jung, *Z. physik. Chem.*, **B21**, 317 (1933).

within 0.1°, and no change in the value was detected when half of the sample was allowed to boil away between measurements. Most of the time during which solid was melting it was observed that the temperature remained almost constant. Although the thermocouple was not calibrated at −83°, such a measurement was made at the subliming point of carbon dioxide.

The compounds KF·2HF and KF·3HF were discovered by Moissan,[5] who found the melting points to be about 105 and 65°, respectively. The corresponding temperatures reported by Lebeau[6] are about 70 and 56°. Values found in the present investigation are 71.7 and 65.8°. It was also noticed that a solution having a mole fraction of hydrogen fluoride near 0.75 was apt to supercool enough to allow one to obtain the freezing point of a metastable compound. This may account for the low freezing point given by Lebeau for KF·3HF.

The following temperatures for the melting point of KF·HF have been reported: (1) 227°,[7] (2) between 215 and 225°,[8] and (3) 217°.[9] The sharp maximum at 239° in the freezing point curve indicates the necessity of using a solution of just the correct composition and explains the wide variety of temperatures observed. Experiments of the author show that when a solution which contains as many moles of KF as HF is cooled, while being shaken, it freezes to a soft solid at about 239°, with the evolution of a rather small amount of heat. When this solid cools to about 195° it undergoes a transition to a relatively hard solid, with the evolution of a large quantity of heat. Measurements of the time of transition in the case of different solutions which were cooled at equal rates suggest that this solid is also KF·HF. We may call the form stable below 195° αKF·HF and the form stable at higher temperatures βKF·HF.

Morgen and Hildebrand,[10] while studying fused potassium acid fluoride, observed the coexistence of two liquid phases when the mole fraction of hydrogen fluoride in the molten salt fell below 0.48. This phenomenon, however, was not detected by Fredenhagen and Cadenbach,[8] who found that at 504° solid potassium fluoride was in equilibrium with a solution in which the mole fraction of hydrogen fluoride was 0.388. The present investigation not only failed to reveal the presence of two liquid phases, but also yielded different vapor pressure measurements from those given in the papers of Morgen and Hildebrand,[10] and of von Wartenberg and Klinkott.[11]

Suggestions Concerning the Preparation of Fluorine.—In Fig. 2 there are indicated three regions of solution concentration which, from the standpoint of vapor pressure, are particularly suitable to be used as the electrolyte for the preparation of fluorine. These are the areas on the diagram which are bounded by the freezing point curve and the line representing a vapor pressure of five centimeters. We may specifically recommend one of the following sets of conditions: (1) if the solution is cooled with subliming carbon dioxide, the mole fraction of hydrogen fluoride should not become less than 0.925; (2) if the solution is kept at 72°, the mole fraction should lie between 0.647 and 0.697; (3) if the temperature is kept at 240°, the mole fraction should lie between 0.485 and 0.508. Since many factors influence the success or failure of a fluorine generator, one may find that each of these types of electrolyte behaves very differently in his apparatus.

Summary

Freezing point and vapor pressure measurements have been made using potassium fluoride–hydrogen fluoride solutions in which the mole fraction of the acid was greater than 0.46. In addition to three acid salts already known KF·4HF and 2KF·5HF have been identified. It has also been found that there are two solid forms of KF·HF. The data suggest that some of the solutions studied are particularly suited to be used as the electrolyte for the preparation of fluorine.

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[5] H. Moissan, *Compt. rend.*, **106**, 547 (1888).

[6] P. Lebeau, *Bull. soc. encour. ind. nat.*, **139**, 15–35 (1927).

[7] Meyer and Sandow, *Ber.*, **54**, 759 (1921).

[8] Fredenhagen and Cadenbach, *Z. anorg. allgem. Chem.*, **178**, 289 (1929).

[9] Dennis, Veeder and Rochow, THIS JOURNAL, **53**, 3263 (1931).

[10] Morgen and Hildebrand, *ibid.*, **48**, 911–918 (1926).

[11] H. von Wartenberg and G. Klinkott, *Z. anorg. allgem. Chem.*, **193**, 409 (1930).