Iodide, and the other halides as well, behaves in a similar manner in isobutyronitrile as solvent.[17] For both solvents we attribute the formation of the two anodic waves of iodide ion to the successive electro-reactions

$$Hg + 3I^- - 2e^- \rightleftharpoons HgI_3^-$$

and

$$Hg + 2HgI_3^- - 2e^- \rightleftharpoons 3HgI_2$$

It can be shown that a plot of the potential of the dropping mercury electrode as a function of the quantity $\log [i/(i_d - i)^3]$ (for the first wave), and $\log [i^3/(i_d - i)^2]$ (for the second wave), should be linear with a slope of 30 mv. in each case for a reversible process. Excellent linear plots were indeed obtained, with slopes of 34 and 32 mv. and half-wave potentials of −0.37 and +0.20 v., respectively.

The anodic waves of halide ions and the stability of mercury(II) halide complexes in various solvents will be discussed elsewhere.[17]

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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The System Ammonium Fluoride–Hydrogen Fluoride–Water at 0 and −20°

BY JOHN P. BUETTNER AND ALBERT W. JACHE[1]

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The system NH_4F–HF–H_2O has been investigated at 0 and at −20°. The solid phases at 0° are NH_4F, $NH_4F \cdot HF$ and $NH_4F \cdot 3HF$, while at −20°, $NH_4F \cdot HF$, $NH_4F \cdot 3HF$, and H_2O were found.

Introduction

The system ammonium fluoride-hydrogen fluoride-water (NH_4F–HF–H_2O) provides an interesting study for the interaction of three compounds which are quite similar in some respects and in others show quite different properties. The binary phase diagrams of all combinations of the three compounds have been reported.[2–4] Recently, studies of the solid solution of ammonium fluoride in ice have been reported.[5]

We have studied the ternary system at 0 and −20°, using Schreinemakers' wet residue method.[6]

Experimental

Whenever possible, solutions with solid phases were made up from distilled water, reagent grade aqueous HF, and ammonium bifluoride ($NH_4F \cdot HF$). For very low HF concentrations it was necessary to use NH_4F. It was not used for higher HF concentrations since it tends to carry along some water. The solution of $NH_4F \cdot HF$ in solutions of high HF concentration is much less exothermic than that of NH_4F. For very high HF concentrations anhydrous HF was used along with the aqueous HF. The anhydrous HF was the middle fraction obtained from a commercial cylinder. This was distilled from the cylinder into a polyethylene collection bottle and redistilled through an all-polyethylene system. The first and last fractions of each distillation were discarded. The liquid HF could be saturated with $NH_4F \cdot HF$ to reduce its vapor pressure and stored until needed.

Samples of appropriate composition were made up in 1-oz. or 2-oz. narrow-mouthed polyethylene bottles and placed in ethylene glycol–water baths whose temperatures were controlled to +0.02° in the case of the 0° bath and ±0.10° for the −20° bath. Samples were agitated periodically in the bath but were not analyzed for at least 4 days. After that, the liquid phase of one sample out of a given set was analyzed daily until analysis indicated a constant composition. After this, the rest of the samples in the set were analyzed. Usually, at least 5 days was required at 0° and 7 days at −20° for a set of samples to come to equilibrium.

Liquid phase samples were withdrawn from the bottles with a 10-ml. polyethylene syringe fitted with a hypodermic needle, and immediately placed into a tared polyethylene weighing bottle and weighed. Wet residue samples were obtained by decanting most of the liquid phase and removing some of the residue with a thin-bladed spatula. They also were weighed in a tared polyethylene bottle. After the sample weights were obtained, the samples were washed carefully with distilled water into a glass volumetric flask containing excess NaOH solution. Aliquots could be taken for analysis.

All samples were analyzed for nitrogen using the Winkler[7] modification of the standard Kjeldahl technique. Total fluoride was determined by titration in aqueous solution with standard $Th(NO_3)_4$ solution. It was not possible to determine HF directly by a simple acidity titration since the sample solutions provide considerable buffering action.

Discussion and Results

The results of the analyses of the solutions and their wet residues are given in Tables I and II and representative points have been plotted in Fig. 1 and 2. Table III gives the results for one set of samples indicating the existence of $NH_4F \cdot 2HF$ as a solid phase. We were not able to reproduce these results. We assume that these points are not properly part of the equilibrium phase diagram, but rather represent a state of pseudo-equilibrium.

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TABLE I

ANALYSES OF SAMPLES AT 0°

Liquid phase, weight %		Wet residues, weight %		Comp. of solid phase
HF	NH_4F	HF	NH_4F	
0.00	41.69	0.00	51.26	NH_4F
1.64	42.84	1.48	57.24	NH_4F
2.63	42.78	2.99	51.76	NH_4F
3.54	43.56	2.92	57.87	$NH_4F \cdot HF$
3.97	43.15	14.79	50.48	$NH_4F \cdot HF$
4.61	39.95	16.22	48.80	$NH_4F \cdot HF$
4.25	39.05	16.48	47.33	$NH_4F \cdot HF$
4.53	31.90	13.70	42.28	$NH_4F \cdot HF$
4.92	29.18	13.96	39.52	$NH_4F \cdot HF$
5.71	25.59	17.86	42.57	$NH_4F \cdot HF$
7.65	21.57	17.51	35.87	$NH_4F \cdot HF$
10.10	18.72	20.18	35.98	$NH_4F \cdot HF$
13.13	17.67	21.01	33.44	$NH_4F \cdot HF$
15.59	17.28	22.84	33.92	$NH_4F \cdot HF$
19.62	18.43	26.01	36.62	$NH_4F \cdot HF$
25.33	19.96	29.58	34.21	$NH_4F \cdot HF$
31.27	22.02	24.62	42.42	$NH_4F \cdot HF$
34.22	23.30	34.40	40.00	$NH_4F \cdot HF$
35.43	23.20	34.51	40.56	$NH_4F \cdot HF$
35.64	23.98	35.04	40.45	$NH_4F \cdot HF$
37.13	25.20	35.71	40.29	$NH_4F \cdot HF$
40.05	28.03	37.38	44.36	$NH_4F \cdot HF$
41.98	30.10	38.23	43.51	$NH_4F \cdot HF$
43.18	29.11	39.79	42.67	$NH_4F \cdot HF$
44.48	32.66	40.33	45.61	$NH_4F \cdot HF$
46.58	34.18	43.50	44.46	$NH_4F \cdot HF$
46.88	35.68	42.26	46.11	$NH_4F \cdot HF$
47.48	35.27	43.77	45.26	$NH_4F \cdot HF$
48.58	37.37	43.47	47.13	$NH_4F \cdot HF$
51.97	39.42	46.91	48.32	$NH_4F \cdot HF$
51.15	41.33	47.70	46.46	$NH_4F \cdot HF$
53.01	40.39	47.90	47.56	$NH_4F \cdot HF$
53.38	40.35	48.42	47.08	$NH_4F \cdot HF$
53.00	41.98	47.98	48.59	$NH_4F \cdot HF$
53.62	41.42	48.87	48.37	$NH_4F \cdot HF$
54.37	42.53	48.55	49.65	$NH_4F \cdot HF$
55.03	43.99	50.33	48.97	$NH_4F \cdot HF$
55.81	42.81	59.14	40.25	$NH_4F \cdot 3HF$
56.15	42.02	59.93	39.14	$NH_4F \cdot 3HF$
55.87	41.02	58.66	39.36	$NH_4F \cdot 3HF$
55.51	39.76	59.36	38.17	$NH_4F \cdot 3HF$
55.42	37.49	61.31	37.46	$NH_4F \cdot 3HF$
56.53	36.07	58.17	36.32	$NH_4F \cdot 3HF$
57.29	35.98	60.57	36.66	$NH_4F \cdot 3HF$
57.01	34.55	60.57	36.47	$NH_4F \cdot 3HF$
58.40	32.75	60.60	35.02	$NH_4F \cdot 3HF$
59.05	30.68	61.08	34.85	$NH_4F \cdot 3HF$
60.02	29.69	61.93	34.25	$NH_4F \cdot 3HF$
60.61	27.98	61.49	33.66	$NH_4F \cdot 3HF$
61.90	26.72	61.05	32.83	$NH_4F \cdot 3HF$
62.67	26.61	61.95	33.65	$NH_4F \cdot 3HF$
64.79	26.83	62.97	34.02	$NH_4F \cdot 3HF$
66.32	27.47	63.48	34.55	$NH_4F \cdot 3HF$
68.09	27.24	65.59	33.42	$NH_4F \cdot 3HF$
69.88	29.04	67.09	32.70	$NH_4F \cdot 3HF$

One of the referees has kindly pointed out that the results of the previous investigation on the binary system $NH_4F–H_2O$ indicate that below 0° there must be a range of unsaturated solutions, originating in the system $NH_4F–H_2O$ and extending for some (possibly small) distance into the ternary diagram on addition of HF. The boundaries of this region should be experimentally determined in the −20° diagram. Unfortunately, we are not able to do it at this time.

TABLE II

ANALYSES OF SAMPLES AT −20°

Liquid phase, weight %		Wet residues, weight %		Comp. of solid phase
HF	NH_4F	HF	NH_4F	
14.58	0.00	13.01	0.00	H_2O
14.10	2.06	13.13	1.90	H_2O
13.97	3.58	11.21	3.61	H_2O
14.81	4.68	12.16	4.80	H_2O
14.07	8.66	9.74	6.11	H_2O
13.01	11.72	10.78	10.23	H_2O
13.57	11.83	20.88	29.98	$NH_4F.HF$
16.92	13.32	22.61	30.92	$NH_4F \cdot HF$
22.38	13.78	25.83	32.40	$NH_4F \cdot HF$
27.66	15.78	30.81	38.08	$NH_4F \cdot HF$
31.94	16.89	33.07	40.32	$NH_4F \cdot HF$
34.63	19.14	34.70	34.17	$NH_4F \cdot HF$
39.36	23.63	36.34	40.09	$NH_4F \cdot HF$
43.00	27.33	40.64	39.19	$NH_4F \cdot HF$
46.15	31.39	40.76	44.44	$NH_4F \cdot HF$
47.84	33.10	45.62	42.84	$NH_4F \cdot HF$
47.98	35.24	43.47	44.29	$NH_4F \cdot HF$
48.25	35.81	43.32	45.30	$NH_4F \cdot HF$
50.44	36.58	47.08	42.85	$NH_4F \cdot HF$
52.17	37.57	47.67	43.43	$NH_4F \cdot HF$
52.46	37.23	48.70	43.56	$NH_4F \cdot HF$
51.99	37.46	48.04	44.61	$NH_4F \cdot HF$
54.74	37.02	47.31	46.78	$NH_4F \cdot HF$
55.92	37.10	47.79	48.29	$NH_4F \cdot HF$
58.18	36.16	59.11	38.28	$NH_4F \cdot HF$ + $NH_4F \cdot 3HF$
59.16	35.42	60.47	36.31	$NH_4F \cdot 3HF$
55.51	34.48	57.78	35.91	$NH_4F \cdot 3HF$
53.94	33.18	56.95	34.30	$NH_4F \cdot 3HF$
53.76	31.41	56.28	33.34	$NH_4F \cdot 3HF$
53.89	30.45	59.11	33.48	$NH_4F \cdot 3HF$
54.01	27.46	57.77	31.38	$NH_4F \cdot 3HF$
54.27	24.68	57.15	29.76	$NH_4F \cdot 3HF$
55.85	22.79	60.93	30.04	$NH_4F \cdot 3HF$
57.29	20.88	60.23	32.62	$NH_4F \cdot 3HF$
59.99	19.11	62.02	29.22	$NH_4F \cdot 3HF$
62.36	18.87	62.89	26.14	$NH_4F \cdot 3HF$
66.68	19.83	64.51	29.51	$NH_4F \cdot 3HF$
69.49	21.36	65.81	29.61	$NH_4F \cdot 3HF$
71.57	23.81	66.34	32.12	$NH_4F \cdot 3HF$
70.88	26.79	65.55	33.58	$NH_4F \cdot 3HF$
72.45	26.02	66.75	32.76	$NH_4F \cdot 3HF$
72.93	26.19	67.52	32.09	$NH_4F \cdot 3HF$
73.07	26.87	69.12	30.86	$NH_4F \cdot 3HF$

TABLE III

UNCOMFIRMED ANALYSES OF SAMPLES AT −20°

Liquid phase, weight %		Wet residues, weight %		Comp. of solid phase
HF	NH_4F	HF	NH_4F	
62.96	20.40	60.33	29.01	$NH_4F \cdot 2HF$
67.08	23.49	62.95	29.62	$NH_4F \cdot 2HF$
69.02	24.69	64.29	30.71	$NH_4F \cdot 2HF$
71.50	25.08	65.94	31.30	$NH_4F \cdot 2HF$
71.37	25.86	66.15	31.31	$NH_4F \cdot 2HF$
71.88	26.47	67.08	32.06	$NH_4F \cdot 2HF$

Among the solid phases found at 0 and −20° were $NH_4F \cdot HF$ and $NH_4F \cdot 3HF$. NH_4F was found at 0°, but not at −20°, while H_2O can exist as a solid phase at −20° but not at 0°. The spreading tie lines near the water corner at −20° seem consistent with the recent reports of solid solutions of NH_4F with ice. No hydrated acid fluorides were found.

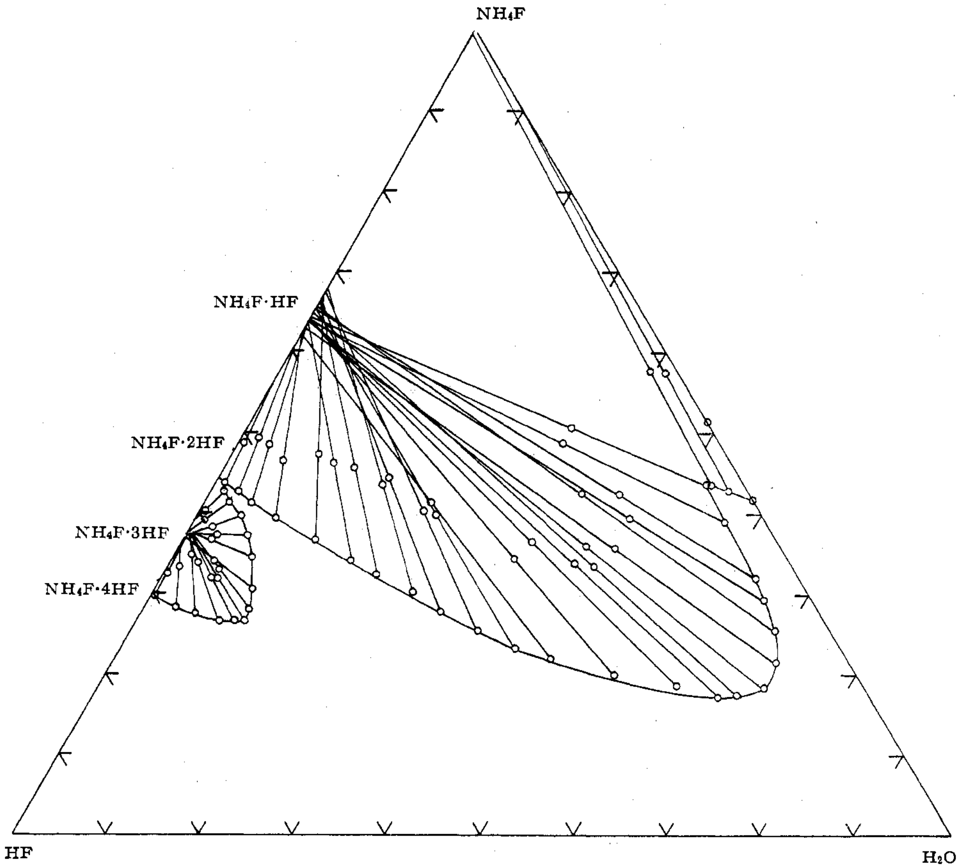

Fig. 1.—NH_4F·HF·H_2O at 0°

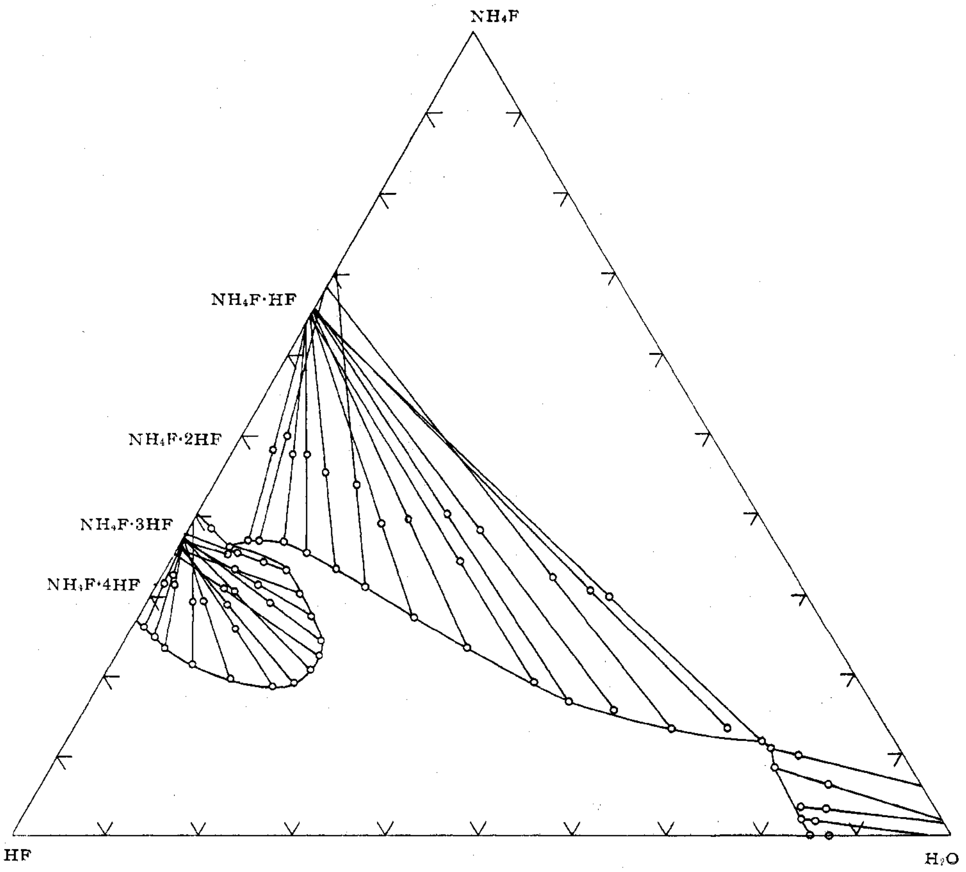

Fig. 2.—NH_4F·HF·H_2O at −20°.

No $NH_4F\cdot 4HF$ was detected. However, its existence has not been definitely disproved at $-20°$. A change in slope of the tie line of less than 0.10% would produce an indication of the tetra-HF compound because the line is so close to the 0% H_2O axis. At 0°, however, a change of slope of nearly 5% would be required. Here the possibility of the existence of $NH_4\cdot 4HF$ seems less. The only solid phase which was less dense than the liquid with which it was in equilibrium was H_2O.

The solid phases exist as the stated compounds over the following HF concentration ranges: at 0°, NH_4F from 0 to 3.7%, $NH_4F\cdot HF$ from 3.5 to 55.5% HF, and $NH_4F\cdot 3HF$ from 55.5 to 70.0% HF. At $-20°$, the solid H_2O phase exists from 13.0 to 14.8% HF, the NH_4F from 13.5 to 57.0%, and the $NH_4F\cdot 3HF$ from 53.7 to 73.0% HF. The reason for the overlap becomes evident on examination of the phase diagrams; at $-20°$ in the HF concentration range 53–58%, the effect of both NH_4F and H_2O on the saturated solution line is more pronounced than that of HF itself.

In general, the solubility of NH_4F in $HF-H_2O$ mixtures is somewhat lower at the lower temperatures. There are marked changes in solubility associated with changes in the solid phase.

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Vitreous Phosphorus

BY RAY C. ELLIS, JR.

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A vitreous allotrope of phosphorus has been prepared by two different methods. This form is compared with the other modifications of phosphorus. The chemistry of vitreous phosphorus has been studied briefly, and the relationship of the various forms of phosphorus is discussed.

Introduction

Phosphorus appears to have more allotropic forms than any other element. Reported are about 12 forms, most of which exist at room temperature and pressure. They have been summarized by Van Wazer.[1]

Experimental

Preparation of Black and Vitreous Phosphorus by Pressure.—Black Phosphorus I was first prepared by Bridgman[2,3] in 1914. Jacobs[4] later showed that the black powder obtained when white phosphorus is transformed by this technique is actually another form, the amorphous black.

Our first method of preparing black phosphorus followed that of Bridgman. As expected, the charge was transformed to an ingot of crystalline black phosphorus I, surrounded by a layer of powdery, amorphous black phosphorus. In two experiments where the initial pressure had been over 7 kilobars and the temperature was above 250° during the high pressure cycle, no usual sudden pressure drop was observed. An examination of the charge from these runs revealed an unexpected vitreous product. This vitreous form in one charge surrounded a core of the crystalline black form and in the other it composed nearly all of the ingot, which was about 1 cm. in diameter by 4 cm. long. The outer layers of the ingots consisted of amorphous black and some red phosphorus. The vitreous material could be separated from the rest of the ingot by breaking or sawing.

Catalytic Preparation of Black and Vitreous Phosphorus.—In 1955 a catalytic method for the preparation of black phosphorus I was reported by Krebs, Weitz, and Worms.[5] Following this method, equal weights of white phosphorus and mercury were sealed in an evacuated tube and heated to 380°. The temperature then was increased to 450° over a period of 4 days. The product is polycrystalline black phosphorus which appears to be the same as the material from the pressure method. It contains up to 30% by weight of mercury, nearly all of which may be removed by heating in a sealed tube with lead or gold.

The catalytic reaction proceeds through a vitreous form, for if the reaction is stopped after reaching a temperature of 380°, the charge is found to be converted entirely to this vitreous form. Tubes opened at various stages show a progressive conversion from the vitreous to the black form. There is always a sharp demarcation between the forms, the black being grainy where cut, broken, or etched, while the vitreous is smooth. The vitreous phosphorus, except for the mercury content, appears to be the same as the vitreous material prepared using high pressure.

The formation of vitreous phosphorus proceeds exothermically and if the charge is heated rapidly or is large, explosion may result. The vitreous phosphorus forms with the exclusion of the red except for an occasional skin on the charge.

In separate experiments it was confirmed that red phosphorus is not converted to the vitreous or the black using the catalytic method described.

Results and Discussion

Properties of Vitreous Phosphorus.—This form of phosphorus is a dark gray, hard, brittle solid exhibiting conchoidal fracture. X-Ray examination gives no lines or rings and the material therefore is completely amorphous. Its density was found to be 2.26 ± 0.01.

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