

Vapor-Liquid Equilibrium of the Binary System HF-H₂O Extending to Extremely Anhydrous Hydrogen Fluoride

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ABSTRACT

The vapor-liquid equilibrium of the binary system HF-H₂O was determined, especially in the range of low water concentrations. The purity of anhydrous hydrogen fluoride used in this work was 9N (99.999999%) with a conductivity of $0.7 \times 10^{-6} \text{ Scm}^{-1}$ (water concentration of 0.033 ppm). We elucidated that the vapor-liquid equilibrium of the binary system HF-H₂O obeyed Raoult's law below $1 \times 10^{-3} \text{ mol dm}^{-3}$ (18 ppm) water concentration. We determined the activity coefficients of HF and H₂O at the boiling point of the binary system HF-H₂O.

Munter *et al.* (1, 2) reported the vapor-liquid equilibrium of the binary system HF-H₂O at atmospheric pressure over a considerable range of composition. The boiling points and vapor-liquid compositions of the binary system HF-H₂O determined by them are now utilized as the standard for hydrofluoric acid. Figure 1 shows their boiling points and vapor-liquid compositions for the binary system HF-H₂O. They only measured the equilibrium up to 89% hydrogen fluoride (HF) concentration, and the equilibrium has not yet been measured in the range below 10% water concentration. Vieweg (3) has reviewed and unified the available data on vapor pressure over HF-H₂O mixtures for the range of composition of 5-80% HF. It is important for promoting a technology of dehydration of HF that the equilibrium of the binary system HF-H₂O is determined in the range of trace amounts of water. Here we have determined the binary system equilibrium, especially in the range of low water concentrations, using the conductivity method developed by ourselves (4, 5). We have calculated the activity coefficient of HF and H₂O at the boiling point for the entire binary system HF-H₂O.

Experimental

Principle of measurement.—Anhydrous hydrogen fluoride exhibits a hygroscopic nature, so measurements of the equilibrium were carried out under the following two conditions: (i) an apparatus consisting of a closed circulating system and (ii) measuring instruments set in the system.

Figure 2 shows the principle of the closed circulating system. This system consists of a vaporization part and a condensation part, with conductivity cells for measuring water concentrations set in both parts. In this work, the closed conductivity cells used were entirely made of fluorocarbon polymer with two bright platinum electrodes.

Materials.—The purity of anhydrous hydrogen fluoride used is 9N level (1 ppb max for every anion impurity and 0.1 ppb max for every cation impurity), and its conductivity is $0.7 \times 10^{-6} \text{ Scm}^{-1}$ (at 0°C), that is, the water concentration is below $1.85 \times 10^{-6} \text{ mol dm}^{-3}$ (0.033 ppm). Anhydrous hydrogen fluoride was charged into the apparatus from an ultrapurifying process which is based on a new chemical distillation principle (6). The new chemical distillation principle consists of ultra dehydration and a fluorine oxidation process. The complexity of the chemical formulas of the impurities converges to simple anhydrous structures due to the extreme dehydration of the hydrogen fluoride, and the various valences of the impurities converge to the highest oxidation state by the fluorine oxidation. Consequently, all of the impurities having various chemical formulas are simplified to structures removable from hydrogen fluoride, which can be purified perfectly by the distillation.

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Composition of the binary system HF-H₂O.—Figure 3 shows the relation between conductivities and water concentrations determined by known additions of water and by the Karl Fischer method. The conductivity of anhydrous hydrogen fluoride in the closed system attained the level of $0.7 \times 10^{-6} \text{ Scm}^{-1}$ for continuous flowing anhydrous hydrogen fluoride. In the range of water concentrations below $1 \times 10^{-2} \text{ mol dm}^{-3}$ (180 ppm), a definite quantity of water was added to the anhydrous hydrogen fluoride, and the conductivity was measured. In the range of water concentrations over $1 \times 10^{-2} \text{ mol dm}^{-3}$ (180 ppm), the water concentrations were measured using the Karl Fischer method. The calibration curve was obtained from both results (4, 5). For the vapor-liquid equilibria, measured water contents less than 1 mol dm^{-3} (18,000 ppm) by the conductivity method using the calibration curve and greater than 1 mol dm^{-3} (18,000 ppm) using a neutralization titration method.

Measurement of Vapor-Liquid Equilibrium

Figure 4 shows the measurement apparatus for the vapor-liquid equilibrium. First, anhydrous hydrogen fluoride was introduced into the vessel A from the ultra puri-

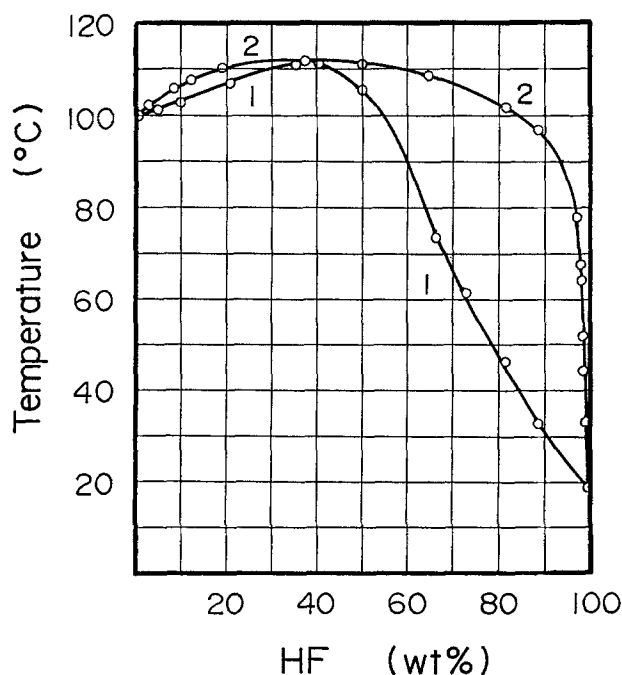


Fig. 1. Boiling points and vapor-liquid composition of the binary system HF-H₂O. 1, Liquid phase; 2, vapor phase.

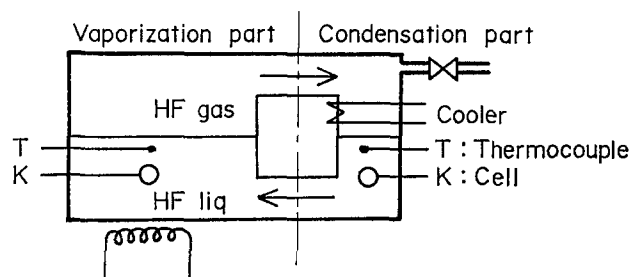


Fig. 2. Schematic diagram of the closed-circulating system for vapor-liquid equilibrium.

fying process, after which a definite quantity of water was added from injection hole I. At this time, the water concentration was measured using conductivity cell K_1 . The hydrogen fluoride was then heated to increase its vapor pressure and exhausted from the point F in Fig. 4 by reduced pressure to eliminate the air in the system. Subsequently, hydrogen fluoride was statically vaporized, and then the vapor of hydrogen fluoride was condensed by condenser G to return to the vessel A. The key point for this experiment is the static vaporization method, because vigorous boiling disturbs the vapor-liquid equilibrium. Circulation was continued until temperatures T_1 , T_2 , and T_3 and conductivities k_1 and k_2 reached constant values.

Results and Discussion

The vapor-liquid equilibrium of the binary system HF-H₂O has been determined at atmospheric pressure, especially in the range of low water concentrations. Table I and Table II present the liquid and vapor compositions and related boiling points determined for the binary system HF-H₂O.

Figure 5 shows the relation between the boiling points and vapor-liquid composition for the low water concentrations in the binary system HF-H₂O, using the data in Table II. The binary system in the region of low water concentrations has been accurately determined in this work. The conventional boiling points have been demonstrated to coincide well with our data for hydrogen fluoride concentrations up to 89%. On the other hand, in the region of very low water concentrations, the vapor composition (line 2) is completely different from the previously reported data (1, 2). It is considered that this difference is caused by the analytical method. The previous workers sampled the condensate, diluted with ice, and analyzed for hydrogen fluoride by titration. It is considered likely that the samples ab-

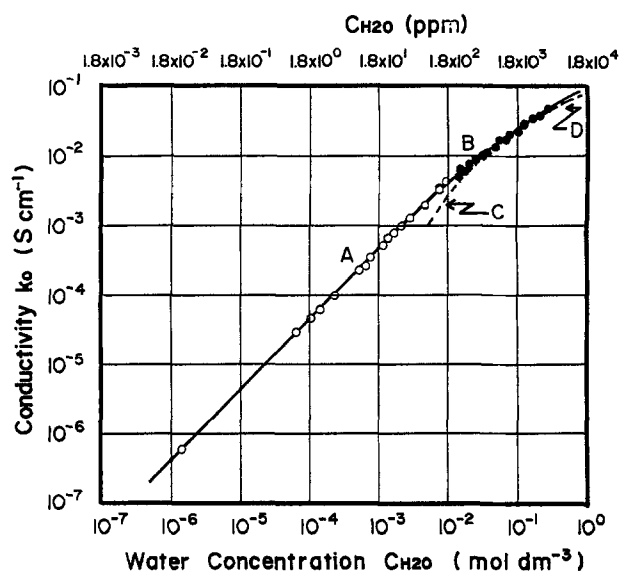


Fig. 3. The relation of water concentration and conductivity of hydrogen fluoride. (A, \circ) (0°C) this work; (B, \bullet) (0°C) this work (Karl Fischer's method); (C, ---) (15°C) Ref. (11); (D, - - -) (15°C) Ref. (7).

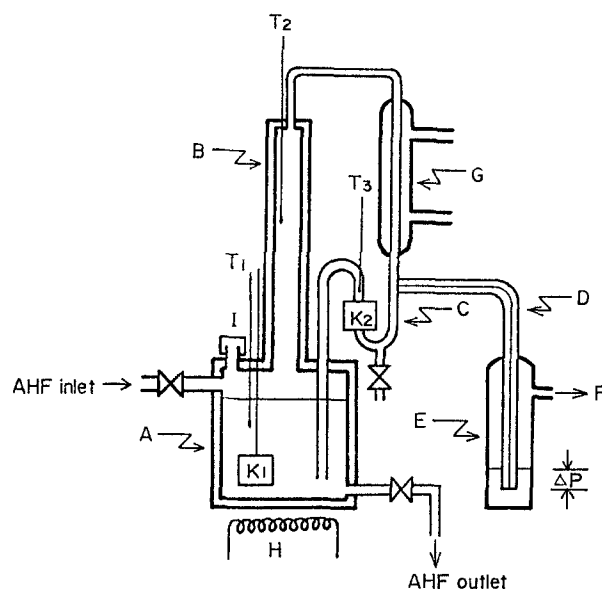


Fig. 4. Measurement apparatus for vapor-liquid equilibrium: A, vessel; B, tower; C, condensed hydrogen fluoride, D, capillary; E, control vessel for pressure; F, vacuum system; G, condenser; H, heater; I, injection hole with fluoro-polymer rubber; T_1 , T_2 , T_3 , thermocouple; K_1 , K_2 , cell.

sorbed moisture in the course of the analysis process, which resulted in higher concentrations of water. The conventional method is not able to measure accurately a trace amount of water in HF because of its open system configuration and the accompanying absorption of water from the environment due to external leakage of the measuring system and back diffusion of water from the open end of the system. In this work, the measuring system was

Table I. Composition in liquid and vapor phase at boiling point of the system HF-H₂O

Liquid			Vapor			
T_1 (°C)	k_1 (0°C) ($\times 10^{-6}$ S cm $^{-1}$)	C_{H_2O} (ppm)	T_2 (°C)	T_3 (°C)	k_2 (0°C) ($\times 10^{-6}$ S cm $^{-1}$)	C_{H_2O} (ppm)
108.5	—	754000 ^a	108.3	15.5	—	932800 ^a
113.7	—	580000 ^a	113.6	15.6	—	481000 ^a
113.2	—	563000 ^a	113.0	15.6	—	389500 ^a
101.5	—	454000 ^a	101.4	15.4	—	52900 ^a
76.0	—	340000 ^a	75.8	15.4	41000	4600
57.1	—	259000 ^a	57.0	15.3	28000	2700
35.5	—	125000 ^a	35.4	15.3	13500	1000
29.8	—	84000 ^a	29.8	15.2	8700	570
20.3	46800	5570	20.2	14.8	2022	89
19.8	25500	2390	20.0	15.1	1081	46
19.5	9041	600	19.8	15.1	350	12
19.5	947	44	19.5	15.2	20	0.84
19.5	502	20	19.5	15.0	10	0.45

^a Neutralization titration.

Table II. Activity coefficients in the binary system HF-H₂O

HF (weight Percent)		Boiling point (°C)	Vapor pressure (mmHg)		Activity coefficient	
Liquid	Vapor		P_o (HF)	P_o (H ₂ O)	γ_1 (HF)	γ_2 (H ₂ O)
24.6	6.72	108.5	9614	1021.5	0.02	0.90
42.0	51.90	113.7	10810	1215.2	0.09	0.52
43.7	61.05	113.2	10690	1195.3	0.10	0.45
54.6	94.71	101.5	8175	801.6	0.18	0.12
66.0	99.54	76.0	4321	301.4	0.27	0.04
74.1	99.73	57.1	2554	129.8	0.41	0.06
87.5	99.90	35.5	1311	43.4	0.67	0.14
91.6	99.943	29.8	1090	31.5	0.77	0.17
99.443	99.9911	20.3	787	17.9	0.97	0.68
99.761	99.9954	19.8	768	17.3	1.00	0.86
99.940	99.9988	19.5	760	17.0	1.00	0.90
99.9956	99.999916	19.5	760	17.0	1.00	1.00
99.9980	99.999955	19.5	760	17.0	1.00	1.00

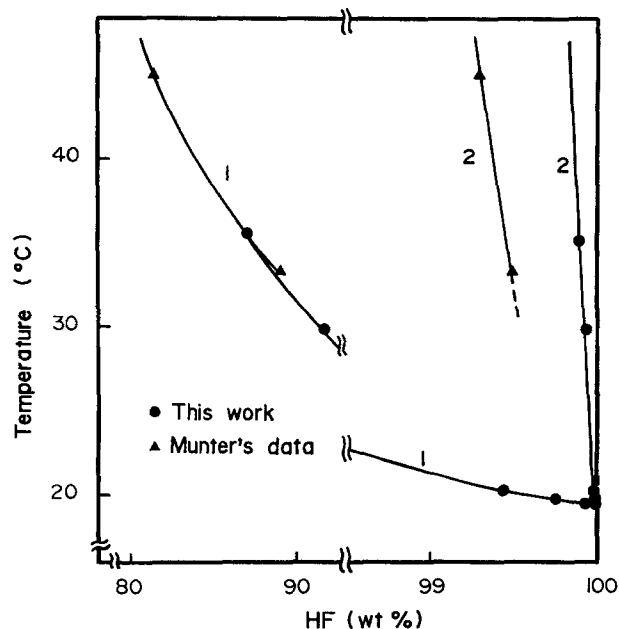


Fig. 5. Boiling points and vapor-liquid composition for low H₂O concentrations in the binary system HF-H₂O 1, liquid phase; 2, vapor phase.

closed, as shown in Fig. 4 and, moreover, the system was completely covered by a nitrogen environment in order to suppress the incursion of water through external leakage.

Figure 6 shows the relation between the water content in the vapor and liquid phases in the binary system HF-H₂O. The concentration of water in the vapor phase in this work is different from the value obtained by Munter and Vieweg over the range of 60-90% HF concentration in the liquid phase.

Every partial pressure in the vapor-liquid equilibrium of the binary system HF-H₂O generally obeys Henry's law [1]

$$p_n = \gamma_n P_n^\circ X_n \quad \text{at } t^\circ\text{C} \quad [1]$$

- p_n = partial pressure of nth component
- P_n° = vapor pressure of nth component at $t^\circ\text{C}$
- γ_n = activity coefficient of nth component
- X_n = mole fraction of nth component in liquid

The dashed line in Fig. 6 indicates the relation between the water concentrations in the vapor and liquid phases obtained by calculation using $\gamma_{\text{H}_2\text{O}} = 1$. It is recognized that

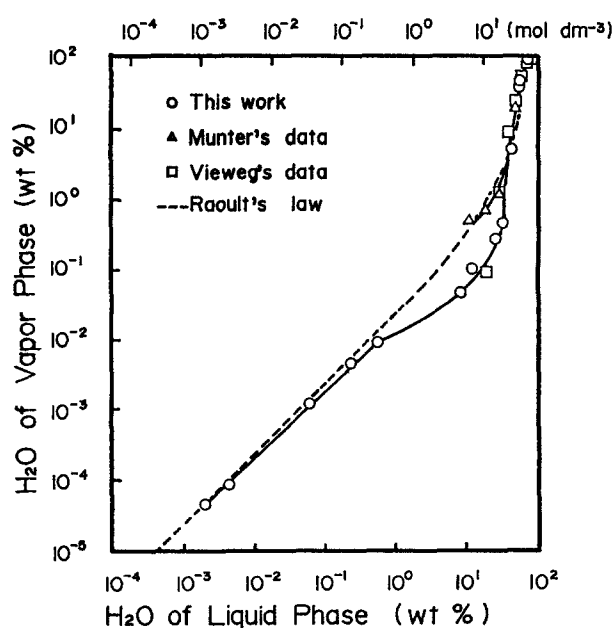


Fig. 6. Vapor-liquid equilibrium of the binary system HF-H₂O

Table III. Activity coefficients in the binary system HF-H₂O from the data of Munter and Vieweg

HF (weight percent)	Boiling point (°C)	Vapor pressure (mmHg)		Activity coefficient		
		P_o (HF)	P_o (H ₂ O)	γ_1 (HF)	γ_2 (H ₂ O)	
Munter (1)						
10	2.0	102.8	8433	836	0.02	0.98
20	7.1	106.6	9183	950	0.03	0.91
30	19.4	110.3	10046	1087	0.05	0.80
50	80.0	106.2	9120	939	0.14	0.33
70	98.8	65.5	3250	192	0.34	0.12
81	99.3	44.9	1769	71	0.54	0.40
89	99.5	33.3	1224	38	0.70	0.82
Vieweg (3)						
10	2.01	102.8	8433	836	0.02	0.98
20	6.78	106.6	9184	950	0.03	0.91
30	19.26	110.3	10046	1087	0.05	0.80
40	43.52	111.7	10337	1136	0.08	0.63
50	74.25	106.2	9120	939	0.13	0.43
60	90.99	87.0	5743	469	0.21	0.38
70	98.73	65.5	3250	192	0.34	0.17
80	99.91	47.6	1923	82	0.50	0.04

the experimental data coincide with the theoretical line below 1×10^{-3} mol dm⁻³ (18 ppm) of water. The slope of the relation between the water concentrations in liquid and in vapor became 1 in the range below 1×10^{-3} mol dm⁻³ (18 ppm) water in hydrogen fluoride. This result led to the conclusion that the vapor-liquid equilibrium of the binary system HF-H₂O obeys Raoult's law below 1×10^{-3} mol dm⁻³ (18 ppm) water concentration.

The activity coefficient of H₂O ($\gamma_{\text{H}_2\text{O}}$) in HF has not been reported previously. Activity coefficients of HF and H₂O have been determined over a wide range of composition at the boiling points at atmospheric pressure in the binary system HF-H₂O, as calculated from the following equation [2] (8, 9). Table III shows the activity coefficients calculated from the data of Munter *et al.* and Vieweg (2, 3).

$$\gamma_i = \frac{P y_i}{p_i x_i} \quad \text{at } t^\circ\text{C} \quad [2]$$

- γ_i = activity coefficient of ith component
- p = total pressure of system
- p_i = vapor pressure of ith component at $t^\circ\text{C}$
- x_i = mole fraction of ith component in liquid
- y_i = mole fraction of ith component in vapor

The results are shown in Table II and Fig. 7. The values of $\gamma_{\text{H}_2\text{O}}$ calculated from the reported data (1-3) are different

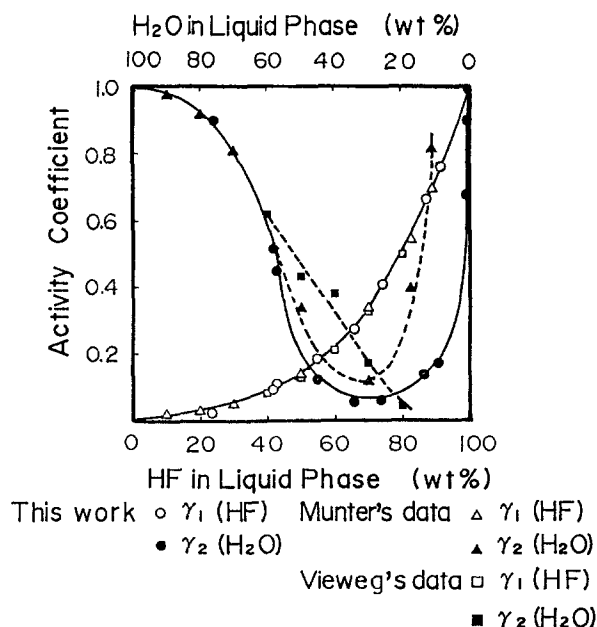


Fig. 7. Activity coefficients of the binary system HF-H₂O

from those calculated from our data, particularly at low water concentrations in HF, though the reported values of γ_{HF} coincide well with our data in the binary system HF-H₂O with decrease of water. The activity coefficient for HF (γ_{HF}) monotonically increases and approaches 1 with a decrease of water concentration, while the activity coefficient for H₂O ($\gamma_{\text{H}_2\text{O}}$) exhibits a minimum value at about 70% HF in the binary system HF-H₂O. The existence of the minimum value of $\gamma_{\text{H}_2\text{O}}$ is explained as follows. The liquid structure of the HF-H₂O system has already been demonstrated to exhibit a minimum ¹H chemical shift at about 70% HF by NMR measurement, due to a maximum formation of H₃O⁺F(HF₅)⁻ (10), and, moreover, the density of HF solutions is well known to exhibit a maximum value at about 70% HF because of the strong hydrogen bond (10). In the extremely anhydrous region of the binary system HF-H₂O, the value of $\gamma_{\text{H}_2\text{O}}$ approaches 1, where water molecules ideally dissociate.

Conclusion

The vapor-liquid equilibrium of the binary system HF-H₂O has been determined, especially in the range of low water concentrations.

It has been demonstrated experimentally that the vapor-liquid equilibrium of the binary system HF-H₂O obeys Raoult's law below 1×10^{-3} mol dm⁻³ (18 ppm) water concentration. We have determined the activity coefficients of HF and H₂O at the boiling point of the binary system

HF-H₂O. It has been shown that the activity coefficient of H₂O has a minimum value at a concentration of about 70% HF and approaches 1 with a decrease of water concentration.

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REFERENCES

1. P. A. Munter, O. T. Aeppli, and R. A. Kossatz, *Ind. Eng. Chem.*, **39**, 427 (1947).
2. P. A. Munter, O. T. Aeppli, and R. A. Kossatz, *ibid.*, **41**, 1504 (1949).
3. R. Vieweg, *Chem. Tech. (Berlin)*, **15**, 734 (1963).
4. N. Miki, M. Maeno, and K. Maruhashi, *Jpn Anal.*, **29**, 88 (1980).
5. N. Miki, M. Maeno, T. Ohmi, *This Journal*, **137**, 790 (1990).
6. N. Miki, U. S. Pat. 4,668,497 (1987).
7. R. Ukazi and I. Kageyama, *Jpn Anal.*, **9**, 604 (1960).
8. R. L. Jarry, and W. Davis, Jr., *J. Phys. Chem.*, **57**, 600 (1953).
9. *Chemical Handbook*, Japan Chemical Association (1984).
10. M. F. A. Dove and A. F. Clifford, "Chemistry in Nonaqueous Ionizing Solvents," Vol. II, Part I. pp. 212-218, Pergamon Press (1971).
11. Draft, International Standard ISO/DIS 3700-2 (1978).

Conductivity and Dissociation Equilibrium of Extremely Anhydrous Hydrogen Fluoride

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ABSTRACT

We have studied the conductivity of extremely anhydrous hydrogen fluoride (AHF) and obtained a minimum conductivity of 0.7×10^{-6} S cm⁻¹ at 0°C. We have recognized that water in AHF at concentrations below 1×10^{-3} mol dm⁻³ shows an ideal dissociation and that the limiting equivalent conductance of AHF is 436 S cm² mol⁻¹ at 0°C. The ideal relationship between the conductivity and water concentration obtained in this work was extrapolated to the ultra-micro water concentration region. The conductivity of 0.7×10^{-6} S cm⁻¹ corresponds to a water concentration of 1.85×10^{-6} mol dm⁻³ (0.033 ppm) in the above relationship; however, this conductivity is not due to the dissociation of water but to that of hydrogen fluoride. We recognized that the relationship between the conductivity and water concentration of AHF coincides completely with that of ultra-pure water in the ultra-micro conductivity region (10^{-8} S cm⁻¹).

The relationship between the dissociation of water and the conductivity in anhydrous hydrogen fluoride is important for the electrochemical theory, the analytical technology of water, and the dehydration technology of hydrogen fluoride.

Freundhagen *et al.* studied conductivities over the range from 0.013 to 0.5N water in hydrogen fluoride and obtained a conductivity of 1.4×10^{-5} S cm⁻¹ for anhydrous hydrogen fluoride at 15°C (1-4).

Kilpatrick *et al.* improved the methods for the purification of anhydrous hydrogen fluoride, which yielded acid with much lower conductivity, 1.6×10^{-6} S cm⁻¹ at 0°C, than reported previously (5-7).

Rogers examined the dehydration of hydrogen fluoride by CoF₂ and Hyman tried the fractional distillation of hydrogen fluoride, but their conductivities for anhydrous hydrogen fluoride were only at the 10^{-4} S cm⁻¹ level (8, 9).

Ukazi *et al.* analytically studied conductivities over the range from 0.1 to 5% water in anhydrous hydrofluoric acid

with a conductivity of 10^{-2} S cm⁻¹, which was distilled after heating a mixture of HF and F₂ to 200°-300°C (10).

Netzer *et al.* described a modified fractionation system from which they obtained hydrogen fluoride with a conductivity of about 1×10^{-6} S cm⁻¹ at 25°C (11).

The International Organization for Standardization (ISO) has presented a conductometric method for determination of water concentrations in industrial anhydrous hydrogen fluoride over the range of 0.01-0.4% water (12).

We have reported previously the conductivities below 0.01% water concentration in anhydrous hydrogen fluoride (13). We now report that we have measured the conductivity of anhydrous hydrogen fluoride with lower water concentrations and studied theoretically the dissociation of water in extremely anhydrous hydrogen fluoride.

Experimental

Materials.—Hydrogen fluoride was purified by an ultra purifying process to reach a very low level of impurities as shown in Table I. The ultra purifying process, which is based on a new chemical distillation principle, consists of

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