Summary

The general effect of adding sodium iodide to a solution of sodium in liquid ammonia is a decrease in the miscibility over the range of sodium iodide concentration studied. The sodium iodide is found to be more soluble in the conjugate solution having a lower concentration of sodium. A portion of the phase diagram for the ternary system Na–NaI–NH_3 is given.

ITHACA, N. Y. RECEIVED MARCH 12, 1949

[CONTRIBUTION FROM THE CHEMICAL RESEARCH SECTION, CHEMICAL ENGINEERING DIVISION, TENNESSEE VALLEY AUTHORITY]

Thermodynamics of Aqueous Hydrogen Fluoride at 25°

BY KELLY L. ELMORE, JOHN D. HATFIELD, CHARLES M. MASON[1] AND ARTHUR D. JONES

In research on the recovery of by-product hydrogen fluoride from the processing of phosphate rock, a need arose for certain calculations that could be made only through a knowledge of the thermodynamic properties of hydrogen fluoride in aqueous solution. The present paper describes the calculation of the activity, free energy, enthalpy, entropy and molal heat capacity of the system hydrogen fluoride–water at 25°.

Activity in Dilute Solution

Hydrofluoric acid is a weak electrolyte which exists in simultaneous equilibrium with ions and "triple ions"[2,3] as shown by the relations

$$HF = H^+ + F^-;$$
$$K_1 = a_{H^+}a_{F^-}/a_u = m_{H^+}m_{F^-}\gamma_{H^+}\gamma_{F^-}/m_u\gamma_u \qquad (1)$$
$$HF + F^- = HF_2^-;$$
$$K_2 = a_{HF_2^-}/a_ua_{F^-} = m_{HF_2^-}\gamma_{HF_2^-}/m_um_{F^-}\gamma_u\gamma_{F^-} \qquad (2)$$

where a, m and γ represent the activity, molality and practical activity coefficient, respectively, of the designated ions or the undissociated acid, u. Wooster[2] has applied the principle of "unilateral triple ion formation," as developed by Fuoss and Kraus,[3] to the conductance data of Deussen[4] for aqueous hydrogen fluoride, and the same treatment was used as a basis for the present calculations in the dilute range.

In Table I the values of m_{F^-}/m and $m_{HF_2^-}/m$, where m is the total molality, at the concentrations given by Deussen[4] were calculated through the constants of Wooster[2] ($K_1 = 6.89 \times 10^{-4}$ and $K_2 = 2.695$), the activity coefficients of Kielland[5] for γ_{H^+} and γ_{F^-} (assuming that $\gamma_{HF_2^-} = \gamma_{F^-}$), the determination of m_{H^+}/m by means of the Shedlovsky[6] refinement, the elimination of γ_u and m_u by taking the ratio K_1/K_2, and the solution of the resulting quadratic for m_{F^-}/m. Subtraction of m_{F^-}/m from m_{H^+}/m gives $m_{HF_2^-}/m$.

TABLE I

VALUES OF COMPUTED FUNCTIONS FOR HYDROGEN FLUORIDE SOLUTIONS

C	m	γ_{H^+}	γ_{F^-}	m_{F^-}/m	$m_{HF_2^-}/m$
1.0	1.0158	0.8332	0.7744	0.01655	0.04987
0.5	0.50466	.8618	.8272	.02872	.04061
.25	.25153	.8847	.8650	.04628	.03156
.125	.12557	.9066	.8910	.07031	.02297
.0625	.062733	.9213	.9104	.1024	.0161
.03125	.031355	.9326	.9269	.1438	.0106
.01563	.015674	.9447	.9392	.1972	.0068
.007813	.0078367	.9540	.9499	.2646	.0041
.003906	.0039177	.9614	.9579	.3510	.0024
.001953	.0019588	.9682	.9660	.4530	.0013
.0009766	.00097948	.9730	.9730	.5736	.0008

The quantity $a_{H^+}a_{F^-}$ was calculated from the values in Table I and compared with the values calculated from the e.m.f. measurements of Broene and DeVries[7] as shown in Fig. 1. Whereas the two sets of calculated values are in substantial agreement at the higher concentrations, there is a marked difference in very dilute solutions, possibly because of the inherent lack of reliability of e.m.f. measurements in very dilute solutions.

Equations for the Activities of Hydrogen Fluoride and Water in Dilute Solution.—The molar concentrations given by Deussen[4] were converted to molal concentration by means of an equation that was derived from the density of hydrogen fluoride solutions as given in the "International Critical Tables."[8] Where necessary data at other temperatures were extrapolated to 25°. The equation

$$\rho = 0.99707 + 0.00369\,w \qquad (3)$$

where ρ is the density and w is the percentage of hydrogen fluoride by weight, proved applicable at values of w from 0 to 10%. Table I shows the molar and molal concentrations.

Values of a_u, calculated from equation 1 and the conductance data of Deussen[4] by means of values in Table I, were expressed as a function of m over

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[1] Present address: Explosives Branch, Bureau of Mines, U. S. Department of the Interior, Bruceton, Pennsylvania.

[2] C. B. Wooster, THIS JOURNAL, **60**, 1609-1613 (1938).

[3] R. M. Fuoss and C. A. Kraus, *ibid.*, **55**, 2387-2399 (1933).

[4] E. Deussen, *Z. anorg. Chem.*, **44**, 303-331 (1905).

[5] J. Kielland, THIS JOURNAL, **59**, 1675-1678 (1937).

[6] T. Shedlovsky, *J. Franklin Institute*, **225**, 739-743 (1938). The constants calculated by Wooster were obtained from the conductance data of Deussen by means of a derived equation in which it was assumed that the undissociated fraction of HF in solution was represented by $1 - \Lambda/\Lambda_0$. The Shedlovsky refinement for evaluating m_{H^+}/m, when applied to a calculation of K_1 and K_2, gives values which agree with those of Wooster within experimental error, and it is concluded that no significant error is introduced by using the refinement in the calculation of m_{F^-}/m and $m_{HF_2^-}/m$.

[7] H. H. Broene and T. DeVries, THIS JOURNAL, **69**, 1644-1646 (1947).

[8] "International Critical Tables," Vol. III, p. 54.

the concentration range from 0.001 to 1 molal, as given in the equation

$$\log a_u = A + B \log \frac{1 + m^{1/4}}{m^{1/2}} + Cm^{-1/4} \sin (D \log m + E) \quad (4)$$

where $A = 0.83078$, $B = -2.65196$, $C = -0.00725$, $D = 2.19937$ and $E = 3.12661$. The average error through use of equation 4 was ±0.48% in a_u. The last term in equation 4 was introduced to offset variations of ±2% or less in $\log a_u$ when expressed as a function of the first two terms only.

The substitution of equation 4 into the Gibbs–Duhem equation in the form developed by Van Rysselberghe[9]

$$-\mathrm{d} \log a_1 = m/M \, \mathrm{d} \log a_u \quad (5)$$

and integration yield

$$-\log a_1 = A'[1/4m + 1/3m^{3/4} - 1/2m^{1/2} + m^{1/4} - \ln (1 + m^{1/4})] + B'm^{3/4}[\sin (D \log m + E) + C' \cos (D \log m + E)] + I \quad (6)$$

where D and E have the same values as in equation 4, $A' = 0.020749$, $B' = -0.000012108$ and $C' = 1.31773$. The integration constant, I, can be ignored as it can be proved to equal zero.

Activity in Concentrated Solution

The data of Brosheer, Lenfesty and Elmore[10] for the vapor pressure of hydrofluoric acid were used in an evaluation of the activity of water and of undissociated acid over the range from 1 to 20 molal. The activity of the water, a_1, was calculated from the measured partial pressure of water vapor and fitted, by the method of least squares, to an equation of the form

$$-\log a_1 = A_1 m^{-1/2} + B_1 m + C_1 m^{3/2} + D_1 m^2 \quad (7)$$

where $A_1 = 0.00020892$, $B_1 = 0.00806007$, $C_1 = -0.00032638$ and $D_1 = 0.00026745$. Equation 7 fitted the experimental data over the range from 1 to 20 molal with an average error of ±0.4% in a_1. Substitution of equation 7 into equation 5 and integration give

$$\log a_u = 0.0038655m^{-3/2} + 1.030139 \log m - 0.054348m^{1/2} + 0.029690m + 0.05314 \quad (8)$$

The integration constant, 0.05314, in equation 8 was evaluated from the value of $\log a_u$ as calculated at 1 molal from equation 4.

For concentrations greater than 20 molal (about 30% hydrogen fluoride) the only available data were those of the General Chemical Company,[11] which give the vapor pressure of hydrogen fluoride over aqueous solutions containing 30 to 100% hydrogen fluoride. Simons and Hildebrand[12] have shown that gaseous hydrogen fluoride can be treated as an equilibrium mixture of a monomer and a hexamer, with a heat of association of 6670 cal. per mole of monomer. Since at equilibrium the partial molal free energy of the gaseous monomer is equal to the partial molal free energy of the liquid monomer in solution, and since that quantity must be used in equation 5, it was necessary that the activity of monomeric hydrogen fluoride in the vapor phase be calculated. This calculation was made by the equation derived by Simons and Hildebrand[12] to calculate the degree of polymerization, from which the partial pressure of monomeric hydrogen fluoride was calculated at each concentration.

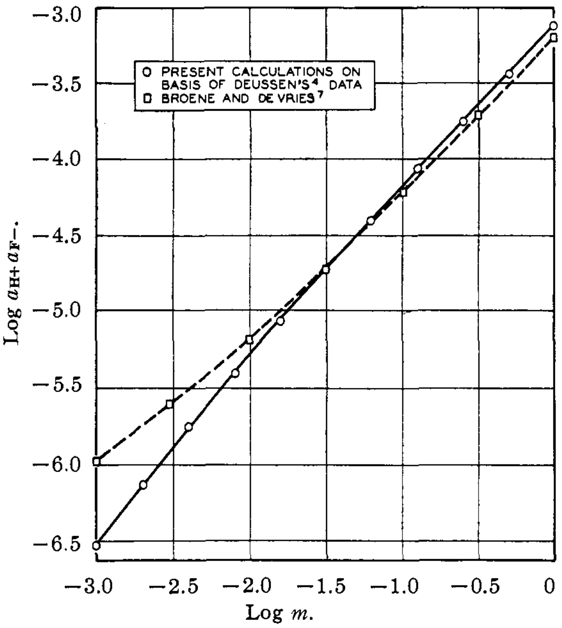

Fig. 1.—Comparison of $a_{H^+}a_{F^-}$ as calculated from conductivity and e. m. f. data.

The activity of undissociated acid, a_u, is based upon a hypothetical 1-molal solution in which the ratio a_u/m is unity as m approaches zero. However, a_u is a function of the pressure of monomeric hydrogen fluoride through the relationship

$$a_u = hP_{\text{mono}} \quad (9)$$

where h is the constant in Henry's law. The value of h was determined for hydrogen fluoride solutions through equation 9, P_{mono} being known from the data of Brosheer, Lenfesty and Elmore,[10] and a_u being calculated by means of equation 8. The average value of h was 27.604.

Equation 9 then was used to determine the values of a_u over the range 30 to 100% hydrogen fluoride. The activity of water over this concentration range was determined through graphical integration by means of equation 5.

Partial Molal Free Energy

The relative partial molal free energies of water and hydrogen fluoride are given by the equations

$$\bar{F}_1 - \bar{F}_1^0 = RT \ln a_1 \quad (10)$$

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(9) P. Van Rysselberghe, *J. Phys. Chem.*, **39**, 403–414 (1935).

(10) J. C. Brosheer, F. A. Lenfesty and K. L. Elmore, *Ind. Eng. Chem.*, **39**, 423–427 (1947).

(11) General Chemical Company, *Tech. Service Bull.*, **30A**, 13 (1945).

(12) J. Simons and J. H. Hildebrand, THIS JOURNAL, **46**, 2183–2191 (1924).

and

$$\bar{F}_2 - \bar{F}_2^0 = RT \ln a_u \qquad (11)$$

where $\bar{F}_1^0$ and $\bar{F}_2^0$ are the free energies of formation of water and a hypothetical 1 molal solution, respectively. These quantities were calculated from values of a_1 and a_u as determined by previous equations. Table II lists the relative partial molal free energies, $\bar{F}_1 - \bar{F}_1^0$ and $\bar{F}_2 - \bar{F}_2^0$, as functions of m. The absolute partial molal free energies, $\bar{F}_1$ and $\bar{F}_2$, may be calculated readily from the relative quantities, the values of $\bar{F}_1^0$ and $\bar{F}_2^0$ being

$$\begin{aligned} \bar{F}_1^0 &= -56{,}693 \text{ (ref. 13)} \\ \bar{F}_2^0 &= -70{,}390 \text{ (ref. 14)} \qquad (12) \end{aligned}$$

Table III lists the relative partial molal free energies of water and hydrogen fluoride for solutions containing from 30 to 100% hydrogen fluoride. The accuracy of the values in Table III cannot be computed because of the lack of sufficient information concerning the accuracy of the original measurements of vapor pressure.[11]

The calculated value of $\bar{F}_2$ for 100% hydrogen fluoride (Table III) represents the free energy of formation of liquid hydrogen fluoride, however, and may be used in a calculation of its entropy at 25° on the basis of the formation of the liquid from either the hypothetical 1 molal aqueous solution or the gas. Thus, through use of the value of $\bar{F}_2$ for 100% hydrogen fluoride, the thermodynamic values of the hypothetical 1 molal solution, and the calculations which Kelley[15] made on the liquid–gas equilibrium through the use of the data of Simons and Hildebrand,[12] the following quantities were derived for the respective equilibria at 25°:

TABLE II

RELATIVE AND ABSOLUTE PARTIAL MOLAL FREE ENERGY OF HYDROFLUORIC ACID SOLUTIONS AT 25° (CALORIES)

m	$-(\bar{F}_1 - \bar{F}_1^0)$	$(\bar{F}_2 - \bar{F}_2^0)$	m	$-(\bar{F}_1 - \bar{F}_1^0)$	$(\bar{F}_2 - \bar{F}_2^0)$
0.001	0.0173	−4567	0.6	6.767	− 265
.002	.0312	−4034	.7	7.851	− 171
.003	.0437	−3732	.8	8.929	− 90
.004	.0565	−3523	.9	10.00	− 19
.005	.0703	−3364	1.0	11.07	+ 44
.006	.0820	−3235	2.0	22.39	+ 473
.007	.0945	−3129	3.0	34.12	+ 739
.008	.1074	−3037	4.0	46.40	+ 933
.009	.1196	−2957	5.0	59.25	+1092
.01	.1315	−2885	6.0	72.68	+1227
.02	.2543	−2426	7.0	86.71	+1347
.03	.3750	−2162	8.0	101.3	+1455
.04	.4946	−1977	9.0	116.6	+1555
.05	.6133	−1833	10.0	132.4	+1648
.06	.7307	−1716	11.0	148.9	+1735
.07	.8482	−1618	12.0	166.1	+1818
.08	.9649	−1533	13.0	183.8	+1897
.09	1.0815	−1457	14.0	202.2	+1972
.1	1.197	−1390	15.0	221.2	+2045
.2	2.341	− 950	16.0	240.9	+2116
.3	3.466	− 695	17.0	261.2	+2184
.4	4.576	− 515	18.0	282.2	+2250
.5	5.676	− 377	19.0	303.8	+2315
			20.0	326.1	+2379

TABLE III

RELATIVE AND ABSOLUTE PARTIAL MOLAL FREE ENERGY OF HYDROFLUORIC ACID SOLUTIONS AT 25° (CALORIES)

HF, %	$-(\bar{F}_1 - \bar{F}_1^0)$	$(\bar{F}_2 - \bar{F}_2^0)$
30	358.7	2352
35	530.0	2745
40	813.0	3266
45	1129.0	3739
50	1394	4062
55	1688	4357
60	2023	4630
65	2370	4859
70	2751	5061
75	3174	5238
80	3673	5396
85	4169	5510
90	4761	5600
95	5433	5653
100		5693

$$\begin{array}{llll} & & \text{HF(aq.)} = \text{HF(l)} & \\ \Delta H^0: & -75{,}662 & -71{,}460; & \Delta H = 4202 \\ \Delta F^0: & -70{,}390 & -64{,}697; & \Delta F = 5693 \quad (13) \\ S^0: & 22.22 & 17.22 & \Delta S = -5.00 \end{array}$$

and

$$\begin{array}{llll} & & \text{HF(g)} = \text{HF(l)} & \\ \Delta H^0: & -64{,}000 & -71{,}460; & \Delta H = -7460 \\ \Delta F^0: & -64{,}496 & -64{,}697; & \Delta F = -201 \quad (14) \\ S^0: & 41.53 & 17.18; & \Delta S = -24.35 \end{array}$$

When computed through equations 13 and 14, the agreement in the entropy of liquid hydrogen fluoride at 25° indicates that the values of the free energy functions of aqueous hydrogen fluoride are reasonably accurate (± 15 calories).

Heat Content and Entropy of Hydrogen Fluoride Solutions

The calculation of the heat content of aqueous solutions of hydrogen fluoride was made by the method of Vogt[16] after increasing the pressure to 1140 mm., a change for which ΔH is negligible.

$$400\text{H}_2\text{O (l, 20°)} \longrightarrow 400\text{H}_2\text{O (l, 32°)} \qquad \Delta H_1 = 86{,}388 \text{ cal.}$$

$$\text{HF (l, 20°)} \longrightarrow \text{HF (l, 32°)} \qquad \Delta H_2 = 217 \text{ cal.}$$

$$\text{HF (l, 32°)} \longrightarrow [\text{HF} + (\text{HF})_6] \text{ (g, 32°)} \qquad \Delta H_3 = 2{,}102 \text{ cal.}$$

$$[\text{HF} + (\text{HF})_6] \text{ (g, 32°)} \longrightarrow \text{HF (g, 32°)} \qquad \Delta H_4 = 5{,}214 \text{ cal.}$$

$$\text{HF (g, 32°)} + 400\text{H}_2\text{O (l, 32°)} \longrightarrow \text{HF (400 aq, 32°)} \qquad \Delta H_5 = -11{,}560 \text{ cal.}$$

$$\text{HF (400 aq, 32°)} \longrightarrow \text{HF (400 aq, 20°)} \qquad \Delta H_6 = -86{,}197 \text{ cal.}$$

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(13) F. D. Rossini, *J. Research Natl. Bur. Standards*, **22**, 407–414 (1939).

(14) National Bureau of Standards, "Tables of Selected Values of Chemical Thermodynamic Properties," 1947, Series I, Table 9-1.

(15) K. K. Kelley, "The Free Energies of Vaporization and Vapor Pressures of Inorganic Substances," U. S. Bur. Mines Bull. 383, 1935, p. 54.

(16) E. G. Vogt, *Trans. Am. Inst. Chem. Eng.*, **43**, 39–40 (1947).

The steps were added to yield, at 20°

$$\mathrm{HF(l)} + 400\ \mathrm{H_2O(l)} \longrightarrow \mathrm{HF(400\ aq)} \qquad \Delta H_{293.16} = -3.836\ \mathrm{cal}$$

which then was combined with the heat of dilution data of Roth and co-workers[17] to construct the diagram shown in Fig. 2 for the integral heat of solution at 20°.

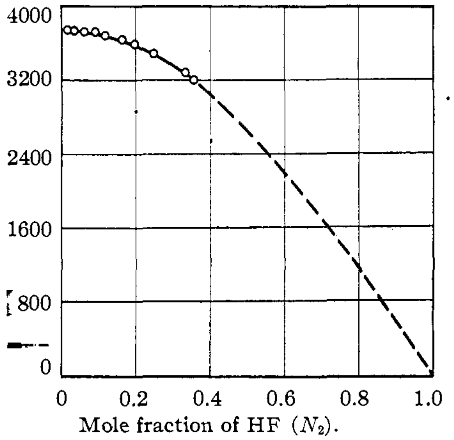

Fig. 2.—Integral heat of solution of hydrogen fluoride at 20°.

From the integral heat of solution at 20°, the data of Thorvaldson and Bailey[18] for specific heat c, and dc/dT as given by Vogt,[16] the integral heat of solution at 25° was calculated. The relative heat content per mole of solution over the range from 0 to 100% hydrogen fluoride was calculated from the integral heat of solution at 25°, and the partial molal heat contents of solute and solvent, $\bar{H}_2 - \bar{H}_2^0$ and $\bar{H}_1 - \bar{H}_1^0$, respectively, were evaluated by the method described by Wenner.[19] The partial molal entropies were calculated from the partial molal free energies and the partial molal enthalpies, the reference solutions being the pure components. Table IV shows the calculated values of enthalpy and entropy; it is believed that these values are correct within 1%.

TABLE IV

PARTIAL MOLAL ENTHALPY AND ENTROPY OF HYDROGEN FLUORIDE SOLUTIONS AT 25°

HF, %	$-(\bar{H}_1 - \bar{H}_1^0)$, cal.	$-(\bar{H}_2 - \bar{H}_2^0)$, cal.	$(\bar{S}_1 - \bar{S}_1^0)$ (E.u.)	$(\bar{S}_2 - \bar{S}_2^0)$ (E.u.)
0	0.00	....	0.000	....
5	1.42	3770	.095	4.24
10	6.54	3700	.202	2.80
15	19.5	3600	.316	1.91
20	53.9	3430	.405	1.52
25	106.0	3230	.496	1.31
30	185	3000	.584	1.15
35	312	2710	.732	0.802
40	498	2370	1.06	.207
45	694	2070	1.46	−.383
50	919	1790	1.59	−.542
55	1220	1490	1.57	−.525
60	1560	1220	1.56	−.516
65	1950	961	1.42	−.425
70	2410	716	1.16	−.280
75	2950	488	0.748	−.109
80	3410	339	.884	−.141
85	4040	190	.449	−.023
90	4600	100	.524	−.022
95	5270	44.4	.555	−.013
100	..	0.0	...	0.000

The relative free energy, enthalpy and entropy per mole of solution are defined by the equations

$$F - F^0 = N_1(\bar{F}_1 - \bar{F}_1^0) + N_2(\bar{F}_2 - \bar{F}_2^0) \quad (15)$$

$$H - H^0 = N_1(\bar{H}_1 - \bar{H}_1^0) + N_2(\bar{H}_2 - \bar{H}_2^0) \quad (16)$$

$$S - S^0 = N_1(\bar{S}_1 - \bar{S}_1^0) + N_2(\bar{S}_2 - \bar{S}_2^0) \quad (17)$$

in which the reference solutions are the pure components. These quantities are shown in Fig. 3 as functions of the mole fraction of hydrogen fluoride.

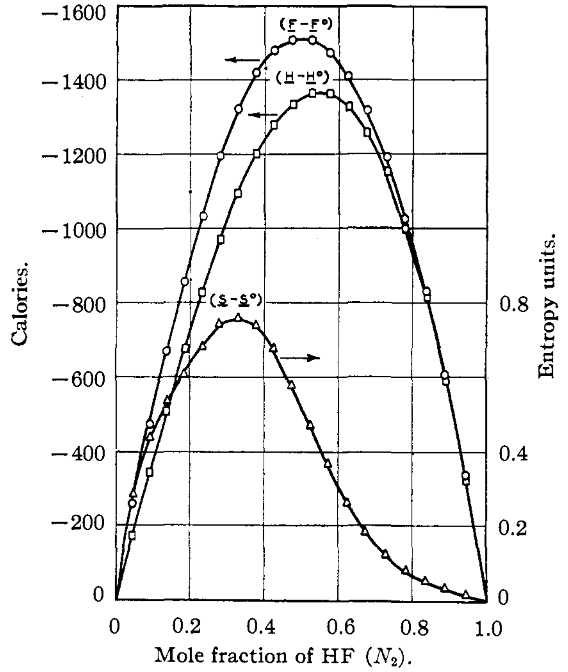

Fig. 3.—Relative thermodynamic quantities for solutions of hydrogen fluoride.

Heat Capacities

The specific heat data of Thorvaldson and Bailey[18] were used in a calculation of the partial molal heat capacities of water and hydrogen fluoride, $\bar{C}_{p_1} - C^0_{p_1}$ and $\bar{C}_{p_2} - \bar{C}^0_{p_2}$, respectively, by the method described by Wenner.[19] The relative heat capacity per mole of solution was calculated from the equation

$$C_p - C^0_p = N_1(\bar{C}_{p_1} - \bar{C}^0_{p_1}) + N_2(\bar{C}_{p_2} - \bar{C}^0_{p_2}) \quad (18)$$

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[17] W. A. Roth, H. Pahlke, A. Bertram and E. Börger, *Z. Elektrochem.*, **43**, 350–355 (1937).

[18] T. Thorvaldson and E. C. Bailey, *Can. J. Research*, **24B**, 51–56 (1946).

[19] R. R. Wenner, "Thermochemical Calculations," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, pp. 28-40.

The values of the functions in equation 18 for various concentrations of hydrogen fluoride are given in Table V.

TABLE V

HEAT CAPACITY FUNCTIONS FOR AQUEOUS HYDROGEN FLUORIDE AT 25° (CALORIES/MOLE/°C.)

HF, %	$-(\bar{C}p_1 - \bar{C}^0p_1)$	$-(\bar{C}p_2 - \bar{C}^0p_2)$	$-(\bar{C}p - \bar{C}^0p)$
5	0.065	12.6	0.632
10	.111	11.6	1.16
15	.172	11.4	1.71
20	.246	10.9	2.20
25	.352	10.5	2.69
30	.492	10.1	3.17
35	.825	9.26	3.58
40	1.34	8.31	3.95
45	2.25	6.98	4.26
50	3.10	5.96	4.45
55	3.96	5.03	4.52
60	5.10	4.07	4.51
65	6.27	3.32	4.42
70	7.70	2.56	4.22
75	9.18	1.94	3.90
80	11.1	1.30	3.43
85	13.5	0.737	2.83
90	15.0	0.423	2.02
95	17.0	0.176	1.11

Summary

The activities of water and undissociated hydrogen fluoride at 25° have been calculated over the entire range of hydrofluoric acid solutions, and relationships were obtained to express these activities as a function of molality. The partial molal quantities, free energy, enthalpy, entropy and heat capacity, were calculated from available experimental data, and the relative thermodynamic functions per mole of solution were evaluated for the two-component system water and hydrogen fluoride.

WILSON DAM, ALABAMA RECEIVED MARCH 3, 1949

[CONTRIBUTION FROM BALLISTIC RESEARCH LABORATORIES, ABERDEEN PROVING GROUND, MD.]

The Mutual Habit Modification of Sodium Chloride and Dipolar Ions

BY CHARLES P. FENIMORE AND ARTHUR THRAILKILL

A number of more or less detailed mechanisms have been suggested for the habit modification of growing crystals by added substances.[1] The effect must depend on preferential absorption, and Bunn has proposed a condition for strong absorption: that the atomic arrangement in the absorbing face of the host crystal must correspond to that in a face in crystals of the habit modifying substance. That is, the absorbed particles must lie on the crystal surface in nearly the same way as would be stable if these particles were to crystallize alone. A consequence of this view is that habit modification should generally be reciprocal. If substance A modifies the habit of B, one anticipates that the converse will occur unless the atomic arrangement of A which is similar to that of a plane in B exists on a face already prominent in A, in which case it would be impossible to tell whether the prominence of the face has or has not been affected by the presence of B.[2]

The work described in this paper was undertaken to see whether dipolar ions as a class would modify the habit of ionic crystals. In virtue of their dipolar character, the amino acids, for example, interact with dissolved sodium chloride and without regard to detailed mechanism, one might have thought that an interaction between growing sodium chloride crystals and dipoles dissolved in the saturated aqueous solution of sodium chloride would lead to crystal habit modification by almost any amino acid. This expectation was not realized. On the contrary, two of the three new habit modifiers found for sodium chloride appear to provide additional evidence for the absorption criterion stated above.

Results and Discussion

Under conditions of rapid crystallization (a drop of solution on a microscope slide) a solution of 10 g. of glycine in 100 g. of water, saturated with sodium chloride, deposits sodium chloride crystals showing the cube and the dodecahedron in approximately equal development instead of the cube only as is characteristic of sodium chloride grown from pure water. A 15-g. solution of glycine gives dodecahedra only. Since the aliphatic amino acids, almost entirely dipolar in neutral aqueous solution, are at the same time fairly strong acids and fairly strong bases, it is possible to show that the habit modification is due to the free dipoles. For glycine

$$H_3N^+CH_2COO^- + H^+ \rightleftharpoons H_3N^+CH_2COOH \qquad \log K = 2.31$$

$$H_2N^+CH_2(COO^- + OH^- \rightleftharpoons H_2NCH_2COO^- + H_2O \qquad \log K = 4.18$$

the ratio of dipolar to monopolar molecules drops from 5×10^4 to 10^{-1} when the *p*H decreases from 7.0 to 1.3 or increases from 7.0 to 10.8. If the 15 g. glycine solution, saturated with sodium chloride, is adjusted to *p*H 1.3 with hydrochloric acid, only cubes are observed. If it is adjusted to *p*H 10.8 with sodium hydroxide, cubes with an occasional very small octahedral face are obtained. That the effect of *p*H is not directly to cause reversion of growing sodium chloride to cubes, but to des-

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(1) For references, see Wells, "Annual Repts. of Chem. Soc.," **43**, 62 (1946).

(2) Bunn, *Proc. Roy. Soc. (London)*, **141A**, 567 (1933).