chlorite. Within five to fifteen minutes one mole of cyanogen chloride is destroyed in this rapid reaction for each mole of hypochlorite present.

Summary

The kinetics of hydrolysis of cyanogen chloride in alkaline, bicarbonate-buffered and phosphate-buffered solutions appear to be in satisfactory agreement with the following expression.

$$-d[\mathrm{ClCN}]/dt = 6 \times 10^{2}[\mathrm{ClCN}][\mathrm{OH}^-] + 3 \times 10^{-2}[\mathrm{ClCN}][\text{phosphate}]$$

Cyanogen chloride reacts with hypochlorite stoichiometrically corresponding to the oxidation of the nitrogen it contains to gaseous nitrogen. Since the reaction is markedly more rapid than hydrolysis under the same conditions, there must be a rapid direct reaction between cyanogen chloride and hypochlorite. This was shown to be even more rapid than subsequent disappearance of "active chlorine."

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Thermodynamics of Aqueous Hydrofluoric Acid Solutions

BY HERMAN H. BROENE[1] AND THOMAS DE VRIES

Two instances are recorded in scientific literature in which a hydrogen electrode has been used in hydrofluoric acid solutions. Wynne-Jones and Hudleston[2] measured the e. m. f. at 25° of the cell H_2, HF (*N*), KCl (sat.), Hg_2Cl_2, Hg, where *N* varied from 0.03 to 1.55. Jahn-Held and Jellinek[3] measured the potential of the cell Pb (5% amalgam), PbF_2(s), HF(1 *N*), H_2 at 15, 25 and 35°.

Ivett and De Vries[4] have made a study of the cell Na(amalgam), NaF(*m*), PbF_2(s), Pb(amalgam), and have determined the standard potential of the lead amalgam–lead fluoride electrode. In the present investigation use was made of this standard value to determine thermodynamic properties of hydrofluoric acid solutions. The activity coefficients of hydrofluoric acid were calculated from measurements made on cells of the type: I Pb(5% amalgam), PbF_2(s), HF(*m*), H_2(g); and the equilibrium constants from cells of the type: II, Pb(5% amalgam), PbF_2(s), HF(m_1), NaF(m_2), H_2(g).

Experimental

Materials.—Lead amalgam, lead fluoride and sodium fluoride were prepared in the manner described by Ivett and De Vries.[4]

Hydrogen from a commercial cylinder was bubbled through a chromous (II) sulfate[5] or chromous chloride[6] solution to remove traces of oxygen, and through a solution of copper sulfate to remove any hydrogen sulfide which might have been formed in the first solution.[7] The hydrogen was bubbled twice through distilled water, and finally through a hydrofluoric acid solution of the same concentration and temperature as that used in the cell.

A few of the hydrofluoric acid solutions were prepared by diluting Baker and Adamson Reagent 48% hydrofluoric acid with conductivity water. Most solutions, however, were made from a stock solution prepared by bubbling Harshaw anhydrous hydrogen fluoride into conductivity water.

Analysis of Hydrofluoric Acid.—A measured amount of hydrofluoric acid was placed in an Erlenmeyer flask and phenolphthalein added. Sodium hydroxide was run in from a buret until the acid was almost neutralized. The mixture was heated to boiling and the titration finished while hot. The sodium hydroxide solution remaining in the buret was used to titrate a sample of standard hydrochloric acid in the same manner. The results of three or more analyses were averaged. All volumetric ware was carefully calibrated and a correction made to each titration for carbon dioxide dissolved in the acids and wash water. While the titration in bare Pyrex flasks involves the formation of some fluosilicic acid, this will not interfere if the solution is kept above 60°.[8]

The molality of each solution was calculated from the normality using the density data of Winteler.[9]

In order to prepare mixed solutions of hydrofluoric acid and sodium fluoride, the acid solution was first prepared and standardized. To a known weight of this solution, a weighed amount of dry sodium fluoride was added and the molality calculated.

Apparatus and Procedure.—The apparatus used was of conventional design. The anode and cathode were, however, in two separate compartments connected by a bridge containing the electrolyte. This was necessary to prevent poisoning of the platinized platinum electrode by lead ions. The electrodes were sealed in place with paraffin wax to make the cell air tight. Hydrogen escaped through a trap containing distilled water.

The cell was placed in a water thermostat which held the temperature to ±0.02°. Hydrogen was allowed to ow slowly past the platinized platinum electrode, and after three to five hours the e. m. f. became constant. When changed to another temperature, readings became constant after about an hour and a half. Measurements were made on a Rubicon, type B, potentiometer, using a carefully calibrated standard cell.

A fresh platinized platinum electrode was used for each cell assembled. Platinization was done in two ways: one using chloroplatinic acid only, and one using acid containing a trace of lead acetate. Both methods gave satisfactory electrodes which agreed very closely in e. m. f. readings. Platinization, however, took longer without lead acetate, and it gave a dull gray deposit instead of a black one.

The cell apparatus was constructed of Pyrex glass. The interior was coated with a special lacquer[10] and then with ceresin wax. Before a satisfactory coating of this kind was developed, considerable trouble was experienced.

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(1) Abstract of the Ph. D. dissertation of H. H. Broene whose present address is Eastman Kodak Co., Rochester, N. Y.

(2) Wynne-Jones and Hudleston, *J. Chem. Soc.*, **125**, 1031 (1924).

(3) Jahn-Held and Jellinek, *Z. Elektrochem.*, **42**, 401 (1936).

(4) Ivett and De Vries, THIS JOURNAL, **63**, 2821 (1941).

(5) Stone and Beeson, *Ind. Eng. Chem., Anal. Ed.*, **8**, 188 (1936).

(6) Stone and Skavinski, *ibid.*, **17**, 495 (1945).

(7) Branham, *J. Research Natl. Bur. Standards*, **21**, 45 (1938).

(8) Swinehart and Flisik, *Ind. Eng. Chem., Anal. Ed.*, **16**, 419 (1944).

(9) Winteler, *Z. angew. Chem.*, **15**, 33 (1902).

(10) S-988, Stoner–Mudge. Inc., Pittsburgh, Pa.

Apparently a platinized platinum electrode is very sensitive to poisoning by substances formed in the attack of hydrofluoric acid on glass. This poisoning resulted in a potential which jumped several millivolts as each bubble of hydrogen passed over the electrode. The combination of a lacquer and wax coating, however, usually afforded adequate protection.

Measurements were made on approximately 60 cells of Types I and II. The experimental results are given in Tables I and II. All readings were corrected to 760 mm. partial pressure of hydrogen.

TABLE I

ELECTROMOTIVE FORCE OF CELLS

$Pb(Hg), PbF_2(s), HF(m), H_2(g)$

m	15°, v.	25°, v.	35°, v.
0.985	0.15497	0.15458	0.15415
.3174	.12636	.12491	.12381
.1006	.09710	.09493	.09297
.03047	.0677	.0649	.0625
.00957	.0406	.0379	.0355
.00295	.0163	.0133	.0107
.000986	−.0061	−.0087	−.0113

TABLE II

ELECTROMOTIVE FORCE OF CELLS

$Pb(Hg), PbF_2(s), HF(m_1), NaF(m_2), H_2(g)$

m_1	m_2	15°, v.	25°, v.	35°, v.
0.0921	0.1000	0.09112	0.08848	0.08538
.0921	.3015	.08088	.07783	.07367
.01299	.06028	.04393	.03944	.03480
.01299	.13388	.03891	.03431	.02891

Calculations

Equilibrium Constants of Hydrofluoric Acid.—It seems to be generally agreed[11] that aqueous hydrofluoric acid contains H^+, F^-, HF and HF_2^-. From the results in Table II (cells containing sodium fluoride), it is possible to determine the equilibrium constants K_1 and K_2 for the reactions (1) $HF = H^+ + F^-$ and (2) $HF + F^- = HF_2^-$. It was assumed that in any solution of this series the solubility of lead fluoride was negligible, and that the mean activity coefficient of sodium fluoride in the hydrofluoric acid solutions was the same as that found by Ivett and De Vries[4] for solutions of sodium fluoride only. Both of these assumptions were later found to be justifiable. For example, in a solution of 0.0921 m HF and 0.3015 m NaF, the concentrations of the H^+, F^- and HF_2^- ions are 1.21×10^{-4}, 0.2559 and 0.0457 m, making the ionic strength 0.3016 (HF concentration is 0.0463).

The equations were set up as

$$\begin{array}{ccccc} HF & = & H^+ & + & F^- \\ m_1 - q - r & & q & & m_2 + q - r \\ HF & + & F^- & = & HF_2^- \\ m_1 - q - r & & m_2 + q - r & & r \end{array}$$

where m_1 = total molality of HF, m_2 = total molality of NaF, q = actual molality of H^+ ion, r = actual molality of HF_2^- ion. The e. m. f. of the cell will be given by $E = E^0 + 2.303\, RT/nF \log k$, where $k = q(m_2 + q - r)f^2$. The activity coefficient, f, represents activity divided by *ionic* molality. It was assumed to be the same for all ions present. The E^0 value of Ivett and De Vries[4] was used in the above equation. The two equilibrium constants may be obtained in the forms

$$K_1 = \frac{k}{\left(m_1 - m_2 - 2q + \frac{k}{qf^2}\right)} \qquad (1)$$

$$K_2 = \frac{m_2 + q - \frac{k}{qf^2}}{\left(m_1 - m_2 - 2q + \frac{k}{qf^2}\right)\left(\frac{k}{qf^2}\right)} \qquad (2)$$

For each acid–salt solution we obtain two equations like (1) and (2), but three unknowns: K_1, K_2 and q. The results from two or more solutions may be combined to find K_1 and K_2. This was done by a graphical method. Various values of q were inserted in equations (1) and (2), and the corresponding values of K_1 and K_2 determined. These were plotted against each other as shown in Fig. 1 for the calculations at 25°. We thus obtain one line for each of the four solutions studied. These lines are seen to intersect in a point within the limits of experimental error. The values of K_1 and K_2 corresponding to the intersections are

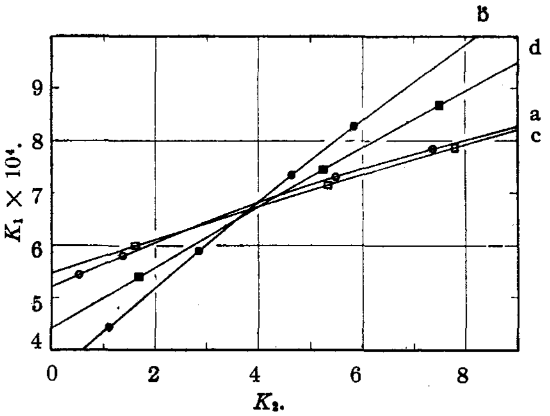

Fig. 1.—Graphical solution at 25°.

TABLE III

EQUILIBRIUM CONSTANTS OF HYDROFLUORIC ACID

	15°	25°	35°
$K_1 \times 10^4$	7.93 (±0.10)	6.71	5.64
K_2	3.94 (±0.20)	3.86	4.32

TABLE IV

EQUILIBRIUM CONSTANTS OF HYDROFLUORIC ACID AT 25°

$K_1 \times 10^4$	K_2	Reference
7.4	4.7	Anthony and Hudleston[a]
1.67	..	Aumeras[b]
7.4	4.7	Davies and Hudleston[a]
7.2	5.5	Pick[a]
5.5	..	Roth, *et al.*[c]
6.71	3.96	This work

[a] Ref. 11. [b] Aumeras, *Compt. rend.*, **184**, 1650 (1927). [c] Roth, Pahlke, Bertram and Borger, *Z. Elektrochem.*, **43**, 350 (1937).

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[11] Anthony and Hudleston, *J. Chem. Soc.*, **127**, 1122 (1925); Davies and Hudleston, *ibid.*, **125**, 260 (1924); Pick, "Nernst's Festschrift," W. Knapp, Halle, 1912, p. 360.

taken to be the actual values. The graphs at 15 and 35° were similar to the one shown for 25°. Results are listed in Table III. They compare favorably with values found by other workers, Table IV.

Ionic Activities.—The activities of the various ions in any hydrofluoric acid soluton may be determined from the data in Table III by means of the equations

$$a_{\mathrm{H}^+}a_{\mathrm{F}^-} = K_1 a_{\mathrm{HF}} \quad (3)$$

$$a_{\mathrm{HF}_2^-} = K_2 a_{\mathrm{F}^-} a_{\mathrm{HF}} \quad (4)$$

$$a_{\mathrm{H}^+} = a_{\mathrm{F}^-} + a_{\mathrm{HF}_2^-} \quad (5)$$

$$m = a_{\mathrm{HF}} + a_{\mathrm{H}^+}/f + a_{\mathrm{HF}_2^-}/f \quad (6)$$

where a = activity, m = total molality of HF, f = activity coefficient of H^+, HF_2^- or F^- ion, *i. e.*, activity divided by *ionic* molality. These four equations were solved for each hydrofluoric acid solution used in cells of Type I. The value of f in equation (6) was approximated until a value was found which satisfied both this equation and the equation $\log f = -A'\sqrt{\mu}/(1 + \sqrt{\mu})$, where A' is the Debye–Hückel constant and μ is the ionic strength.

As has been mentioned, the cells were assembled in two parts, connected by a bridge containing the electrolyte. It was assumed that at the hydrogen electrode the activities could be obtained by solving equations (3) to (6). At the lead amalgam–lead fluoride electrode, however, the solution was assumed to be saturated with lead fluoride; hence one more activity enters, that of lead ion, and one more equation, the activity product of lead fluoride. The value of the latter quantity was calculated from solubility measurements made by Kohlrausch, by Dundon, and by Carter.[12] The Debye–Hückel limiting law was used to estimate the activity coefficient of lead fluoride in water. The value of the activity product was taken to be 3.66×10^{-8} at 15°, 4.37×10^{-8} at 25° and 5.17×10^{-8} at 35°. When considering lead fluoride, equation (5) should be modified to

$$a_{\mathrm{H}^+} + 2a_{\mathrm{Pb}^{++}} f_+/f_{++} = a_{\mathrm{F}^-} + a_{\mathrm{HF}_2^-} \quad (5')$$

where the activity coefficient of the lead ions can be given by $\log f_{++} = -A'4\sqrt{\mu}$ and for the univalent ions by $\log f_+ = -A'\sqrt{\mu}$.

Liquid Junction Potential.—The Nernst equation for cell I may be written

$$E_{\mathrm{obs.}} = E^0_{\mathrm{electrodes}} + \frac{RT}{nF} \ln a_{\mathrm{H}^+_x} af_{\bar{y}} + E_{\mathrm{L}} \quad (7)$$

The subscript x refers to concentration at the hydrogen electrode (no lead fluoride present); the subscript y to concentration at the lead amalgam–lead fluoride electrode. The term E_{L} represents the potential due to the liquid junction between the two hydrofluoric acid solutions, one saturated with lead fluoride and one free from it. The term $E^0_{\mathrm{electrodes}}$ is the sum of standard *electrode* potentials of the cell, using data of Ivett and De Vries.[4]

The activities called for in equation (7) were obtained by solving the equations 1 to 6 in the preceding section. Equation (7) then led to the values for E_{L} given in Table V. The values at 25° calculated from ionic activities by means of the Henderson equation[13] are shown for comparison. The agreement is good considering that both methods are but approximations.

TABLE V

LIQUID JUNCTION POTENTIAL

m	15°, v.	25°, v.	35°, v.	25°, v. Calcd. with Henderson eq.
0.985	+0.0013	+0.0011	+0.0014	−0.0004
.3174	+ .0004	.0000	− .0002	− .0006
.1006	− .0014	− .0020	− .0030	− .0019
.03047	− .0049	− .0066	− .0085	− .0064
.00957	− .0111	− .0131	− .0152	− .0113
.00295	− .0162	− .0184	− .0207	− .0143
.000986	− .0200	− .0216	− .0237	− .0157

Activity Coefficients.—The activity coefficients of hydrofluoric acid in aqueous solution were calculated from the ionic activities of equations (3) to (6) with the equation $\gamma = (a_{\mathrm{H}^+}a_{\mathrm{F}^-})^{1/2}/m$. The values determined in this way were plotted on a large graph from which the values listed in Table VI were taken. It must be noted that these are stoichiometric activity coefficients with reference to H^+ and F^- ions; *i. e.*, the molality m is the total molality of the hydrofluoric acid, not corrected for incomplete dissociation.

TABLE VI

ACTIVITY COEFFICIENTS OF HF

m	15°	25°	35°
1.00	0.026	0.024	0.022
0.50	.034	.031	.028
.30	.048	.044	.042
.10	.083	.077	.070
.05	.115	.106	.097
.03	.148	.136	.125
.01	.241	.224	.208
.005	.320	.300	.280
.003	.395	.371	.347
.001	.573	.544	.515

Summary

From potentials of the cells

$$\mathrm{Pb(Hg),\ PbF_2(s),\ HF}(m_1)\mathrm{,\ NaF}(m_2)\mathrm{,\ H_2(g)}$$

it has been possible to calculate the equilibrium constants at 15, 25 and 35° for the reactions

$$\mathrm{HF} = \mathrm{H}^+ + \mathrm{F}^-$$

$$\mathrm{HF} + \mathrm{F}^- = \mathrm{HF}_2^-$$

Stoichiometric activity coefficients for hydrofluoric acid were determined from measurements made on cells of the type

$$\mathrm{Pb(Hg),\ PbF_2(s),\ HF}(m)\mathrm{,\ H_2(g)}$$

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[12] Kohlrausch, *Z. physik. Chem.*, **64**, 129 (1908); Dundon, THIS JOURNAL, **45**, 2658 (1923); Carter, *Ind. Eng. Chem.*, **20**, 1195 (1928).

[13] Henderson, *Z. physik. Chem.*, **59**, 118 (1907); **63**, 325 (1908).