is more limited than the range of the D.M.E. because of the greater sensitivity of the former electrode. For example, the reduction of 0.1 *M* potassium ion at the R.M.E. would be expected to begin at a potential about 140 mv. *less* negative than the potential of the same reduction at the D.M.E. because the R.M.E. is 200 times more sensitive than the D.M.E. Likewise, the anodic dissolution of mercury at the R.M.E. would occur at a *more* negative potential than at the D.M.E. The range of potentials of the R.M.E. would therefore be expected to be less by several tenths of a volt. In practice it was found that the range was even more restricted, and that the residual current became large, presumably due to the reduction of water, at potentials more negative than -1.2 v. *vs.* S.C.E. unless (1) the surface of the groove of the electrode was highly polished, and (2) vibration of the electrode was minimized. In addition it was found that the range B was increased if the chemical and physical nature of the surface of the groove was such that the interfacial tension between plastic and mercury was as small as possible and the interfacial tension between plastic and electrolyte was as large as possible.

The residual current (Fig. 9) of the R.M.E., at its present stage of development, is such that analysis for the alkaline earth ions and the alkali ions is not possible.[17] Aluminum ion can be reduced but the analysis for aluminum at low concentrations is not practical. Most of the other metal ions that can be determined with the D.M.E. can probably be determined with the R.M.E., although this expectation has not yet been put to an exhaustive test.

Applications.[3]—The current–voltage curves of the R.M.E. can be used for the qualitative and quantitative analysis of electro-reducible substances at concentrations as low as 10^{-7} *M*. Metal ions at concentrations down to 5×10^{-9} *M* can be determined by a combination of coulometric and voltammetric techniques. The R.M.E. is also useful for amperometric titrations and "derivative" analysis.[18]

Acknowledgment.—The author is indebted to Professor I. M. Kolthoff, University of Minnesota, for interesting discussions and valuable suggestions.

Part of this study was aided by a grant from the Shell Oil Company.

[17] The surface of the groove of the R.M.E. of Fig. 9 was coated with a thin layer of "Lubriseal," a high molecular weight saturated hydrocarbon. See reference 3.

[18] O. H. Müller, ref. 1e, p. 132.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Electrode Potentials in Liquid Hydrogen Fluoride

BY GEORGE G. KOERBER[1] AND THOMAS DE VRIES

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The values of the electromotive force of cells of the type $M,MF_2(s)/HF(NaF)/Hg_2F_2(s)/Hg$ where M represents cadmium, copper or lead were found at 10 and 0°. These were used to evaluate the standard free energies of formation of mercurous, cupric and lead fluorides. A study of the vapor pressures of the systems mercurous fluoride–hydrogen fluoride, cadmium fluoride–hydrogen fluoride, and lead fluoride–hydrogen fluoride was made at 0°. Lead fluoride was found to form an addition compound with hydrogen fluoride with the formula $PbF_2 \cdot 2^1/_2HF$. The cell $Hg,Hg_2F_2(s)/NaF(\text{in HF})//NaF,H_3OF,$-$AgF$ (in HF)/Ag was studied at 0° over a range of concentrations of the electrolytes. The data fron this were used to calculate activity coefficients of silver fluoride in liquid hydrogen fluoride. An ion size parameter of 1.9 Å. was found for silver fluoride in the solutions studied. The standard free energy of formation of $AgF \cdot HF$ from silver, fluorine and hydrogen fluoride was calculated.

It has been known for a long time that liquid hydrogen fluoride is a good ionizing solvent medium. With the exception of the work by O. T. Krefft,[2] who evaluated the standard free energy of formation of liquid hydrogen fluoride at 0° by measuring the potential of the cell $H_2(Pt)/HF(KF)/F_2(Pt)$, the use of electrode potentials in liquid hydrogen fluoride as a means of studying the thermodynamics of solutions in hydrogen fluoride, and of evaluating thermodynamic properties of metal fluorides has been neglected.

In this research, cells of the type $M,MF_2(s)/HF(NaF)/Hg_2F_2(s),Hg$ where M represents cadmium, copper and lead, were measured in order to evaluate the standard free energies of formation of the metal fluorides and the cell $Hg,Hg_2F_2(s)/NaF(\text{in HF})//NaF,H_3OF,AgF(\text{in HF})/Ag$ was studied in order to investigate the thermodynamics of solutions in hydrogen fluoride. Vapor pressure measurements were made of the systems metal fluoride–hydrogen fluoride in order to determine whether any of the metal fluorides formed addition compounds with hydrogen fluoride.

Experimental

Materials.—Harshaw "Anhydrous" hydrogen fluoride of a purity of 99.5% was used directly from the cylinder. The water content of this material was less than 0.2%.

Lead, cadmium and mercurous fluorides were prepared by treating the carbonates with hydrofluoric acid, Baker Reagent Grade. Cupric fluoride was prepared by passing hydrogen fluoride over the basic carbonate at 200°.

Copper and cadmium amalgams were prepared by electrolysis and lead amalgam was prepared by mixing the proper proportions of spectroscopically pure lead and triple distilled mercury. Two-phase amalgams were used throughout this research.

Silver oxide was prepared by precipitation of the oxide from a solution of silver nitrate with potassium hydroxide.

Silver and lead stick electrodes were made by inserting silver wire or lead sticks into Teflon plugs that screwed into the base of the cell. These were made reversible by etching

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[1] Abstract from the Ph.D. dissertation of George G. Koerber whose present address is Bell Telephone Laboratories, Murray Hill, New Jersey.

[2] O.T. Krefft, "Inaug. Diss.," Greifswald Institut für Physikalische Chemie, Greifswald, Germany, 1939.

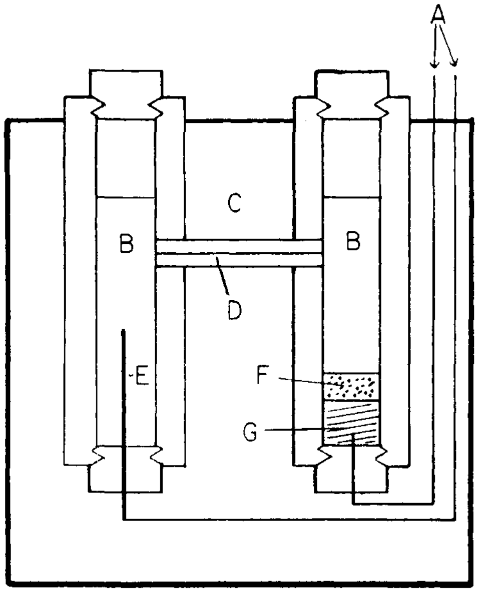

Fig. 1.—Diagram of cell: A, lead wires; B, liquid hydrogen fluoride; C, paraffin; D, liquid junction capillary; E, silver electrode; F, mercurous fluoride; G, mercury.

the electrode under a mixture of the metal nitrate and nitric acid.

Apparatus and Procedures.—The cell design is shown in Fig. 1. The hollow tube connecting the two arms of the cell was replaced with a solid Teflon tube with a pin-hole through it for the cell Hg,Hg_2F_2(s)/NaF(in HF)//NaF, H_3OF,AgF(in HF)/Ag. The liquid junction was formed in the pin-hole.

The thermostat was the conventional water-bath type controlled to 0.1°. Potentials were measured with a Leeds and Northrup Student Potentiometer calibrated with an Eppley Standard Cell.

Solutions of a solute in hydrogen fluoride were prepared by condensing hydrogen fluoride into a weighed Teflon bottle to which the desired amount of solute was then added. The cell Hg,Hg_2F_2(s)/NaF(in HF)//NaF,H_3OF,AgF(in HF)/Ag had solutions of equal ionic strength on each side of the liquid junction. The solution in contact with the silver electrode was made by adding a mixture of silver oxide and sodium fluoride to hydrogen fluoride. The proportions of sodium fluoride and silver fluoride in the mixture were such that the concentration of the silver fluoride in the resulting solution was equal to $^2/_{13}$ of the total concentration of all the electrolytes. Water dissolved in hydrogen fluoride is a strong electrolyte ionizing to form H_3O^+ and F^- ions.[3] Solutions and the cell were placed separately in the thermostat for an hour prior to filling the cell in order that the cell would reach equilibrium before the liquid junction lost its spherical symmetry.

Vapor pressure measurements of the systems metal fluoride–hydrogen fluoride were made by use of the apparatus shown in Fig. 2. Measurements were made at 0°. The calculations were based upon the weight of hydrogen fluoride absorbed in an absorption tube through which a certain volume of air saturated with hydrogen fluoride had been passed. The air saturated with hydrogen fluoride was displaced from the apparatus by introducing a measured volume of mercury into the apparatus. The molecular weight of the hydrogen fluoride in the vapor phase was assigned the value 92.4 by interpolating the results of vapor density measurements made by Simons and Hildebrand.[4]

Experimental Results

Vapor Pressure Measurements of the Systems Metal Fluoride–Hydrogen Fluoride.—Lead fluoride was found to form an additional compound with hydrogen fluoride under the experimental conditions (see Table I). The formula of the compound is $PbF_2 \cdot 2^1/_2HF$ and the vapor pressure of the system PbF_2–$PbF_2 \cdot 2^1/_2HF$ was found to be 0.014 atmosphere. From this the free energy change for the reaction

$$PbF_2(s) + 2^1/_2HF(l) \longrightarrow PbF_2 \cdot 2^1/_2HF(s)$$

was computed to be −4.5 kcal. at 0°.

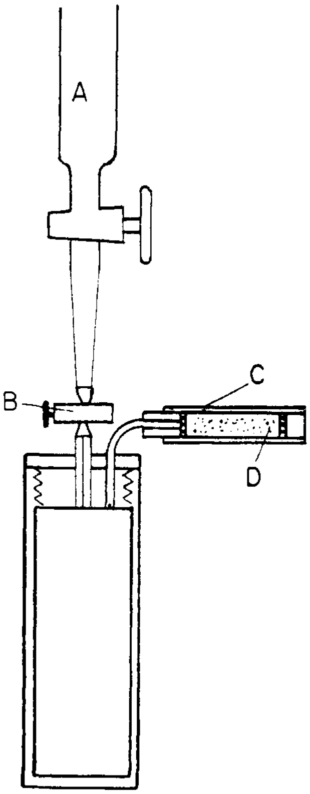

Fig. 2.—Vapor pressure apparatus: A, buret; B, clamp; C, adsorption tube; D, broken pellets of sodium hydroxide.

TABLE I

THE VARIATION OF VAPOR PRESSURE OVER MIXTURES OF HF AND PbF_2 WITH CHANGES IN THE RATIO OF HF TO PbF_2

Ratio of moles HF to moles PbF_2	Vapor pressure, atm.
0.6	0.047
1.40	.013
2.49	.015
2.71	.467
3.43	.447
Pure HF	.495

No evidence was found for the existence of an addition compound between cadmium or mercurous fluorides and hydrogen fluoride.

The Cell Pb(het. amal.), $PbF_2 \cdot 2^1/_2HF$(s)/HF (NaF)/Hg_2F_2(s),Hg.—For this cell the reaction is

$$\text{Pb(het. amal.)} + 2^1/_2HF(l) + Hg_2F_2(s) \longrightarrow PbF_2 \cdot 2^1/_2HF + 2Hg(l);\ E_{273} = 1.0637 \pm 0.0008 \text{ volt},\ \Delta F_{273} = -49.09 \text{ kcal.}$$

From Gerke's[5] value of the potential of the cell Pb(het. amal.)/Pb^{++}/Pb(s), the following free energy change is calculated

$$Pb(s) \longrightarrow \text{Pb(het. amal.)},\ \Delta F_{273} = -0.20 \text{ kcal.}$$

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[3] K. Fredenhagen, G. Cadenbach and W. Klatt, *Z. physik. Chem.*, **A164**, 176 (1933).

[4] J. H. Simons and J. H. Hildebrand, THIS JOURNAL, **46**, 2183 (1924).

[5] R. H. Gerke, *ibid.*, **44**, 1684 (1922).

Combination of these results yields

$Pb(s) + 2^1/_2HF(l) + Hg_2F_2(s) \longrightarrow PbF_2 \cdot 2^1/_2HF(s) + 2Hg(l);\ \Delta F_{273} = -49.09$ kcal. (1)

The Cell Cu(het. amal.),$CuF_2(s)/HF(NaF)/Hg_2F_2(s)$,Hg.—For this cell the reaction is

$Cu(\text{het. amal.}) + Hg_2F_2(s) \longrightarrow CuF_2(s) + 2Hg(l);$
$E_{283} = 0.283 \pm 0.002$ volt, $\Delta F_{283} = -13.1$ kcal.
$E_{273} = 0.274 \pm 0.005$ volt, $\Delta F_{273} = -12.6$ kcal.

The following values are obtained from Oku's[6] measurements of the cell $Cu/Cu^{++}/Cu$(het. amal.)

$Cu(s) \longrightarrow Cu(\text{het. amal.});\ \Delta F_{283} = -0.19$ kcal., $\Delta F_{273} = -0.15$ kcal.

Combination of these results yields

$Cu(s) + Hg_2F_2(s) \longrightarrow CuF_2(s) + 2Hg(l);\ \Delta F_{283} = -13.2$ kcal. (2); $\Delta F_{273} = -12.8$ kcal. (3)

The Cell Cd(het. amal.), $CdF_2(s)/HF(NaF)/Hg_2F_2(s)$,Hg.—The cell reaction is

$Cd(\text{het. amal.}) + Hg_2F_2(s) \longrightarrow CdF_2(s) + 2Hg(l);\ E_{283} = 1.0337 \pm 0.0009$ volt, $\Delta F_{283} = -44.70$ kcal.

Measurements of the cell $Cd/Cd^{++}/Cd$(het. amal.)[7] yields

$Cd(s) \longrightarrow Cd(\text{het. amal.});\ \Delta F_{283} = -2.45$ kcal.

Combining these results yields

$Cd(s) + Hg_2F_2(s) \longrightarrow CdF_2(s) + 2Hg(l);\ \Delta F_{283} = -50.51$ kcal. (4)

The Cell Pb(het. amal.), $PbF_2 \cdot 2^1/_2HF/HF$-(NaF)/$CdF_2(s)$,Cd(het. amal.).—For this cell the reaction is

$Pb(\text{het. amal.}) + CdF_2(s) + 2^1/_2HF(l) \longrightarrow PbF_2 \cdot 2^1/_2HF + Cd(\text{het. amal.});\ E_{273} = 0.0300 \pm 0.0012$ volt, $\Delta F_{273} = -1.38$ kcal.

Combination of this result with

$Cd \longrightarrow Cd(\text{het. amal.});\ \Delta F_{273} = -2.61$ kcal.[7]
$Pb \longrightarrow Pb(\text{het. amal.});\ \Delta F_{273} = -0.19$ kcal.[5]

gives

$Cd(s) + PbF_2 \cdot 2^1/_2HF(s) \longrightarrow CdF_2(s) + Pb + 2^1/_2HF;\ \Delta F_{273} = -1.04$ kcal. (5)

All of the above cells were measured over a range of mole fractions of sodium fluoride of 0.01 to 0.04. Cells containing the Pb(het. amal.), $PbF_2 \cdot 2^1/_2HF$ electrode would be expected to have potentials that would be dependent upon the activity of the hydrogen fluoride. If it be assumed that the activity of the hydrogen fluoride is equal to its mole fraction, the variation of potential with mole fraction can be calculated from the equation

$$E = E^0 + \frac{5 \times 0.0542}{4} \log X_{HF}.$$

The extreme variation of potential with concentration would be 0.0012 volt, which is so near to the standard deviation of the measurements that no definite change with concentration could be observed.

Jahn-Held and Jellinek[8] evaluated the standard free energy of formation for a number of metal fluorides at 15, 25 and 35°. The following results are obtained by extrapolation of the values they obtained for the standard free energy of formation of cadmium fluoride

$Cd(s) + F_2(g) \longrightarrow CdF_2(s);\ \Delta F^0_{283} = -154.5$ kcal., $\Delta F^0_{273} = -154.8$ kcal.

Equations (4) and (5) can be combined with the appropriate value of the standard free energy of formation of cadmium fluoride to give

$2Hg(l) + F_2(g) \longrightarrow Hg_2F_2(s);\ \Delta F_{283} = -104.5$ kcal. (6)
$Pb(s) + 2^1/_2HF(l) + F_2(g) \longrightarrow PbF_2 \cdot 2^1/_2HF;\ \Delta F_{273} = -153.8$ kcal. (7)

Equation (7) can be combined with the result from the measurement of the vapor pressure of the system lead fluoride–hydrogen fluoride

$PbF_2(s) + 2^1/_2HF(l) \longrightarrow PbF_2 \cdot 2^1/_2HF(s);\ \Delta F_{273} = -4.5$ kcal.

to give

$Pb(s) + F_2(g) \longrightarrow PbF_2(s);\ \Delta F^0_{273} = -149.3$ kcal. (8)

Combination of equations (1) and (7) gives

$2Hg(l) + F_2(g) \longrightarrow Hg_2F_2(s);\ \Delta F^0_{273} = -104.5$ kcal. (9)

Combination of equations (2) and (6) and (3) and (9) gives

$Cu(s) + F_2(g) \longrightarrow CuF_2(s);\ \Delta F_{273} = -117.3$ kcal., $\Delta F_{283} = -117.7$ kcal.

Extrapolation of Jahn-Held and Jellinek's[8] data for the standard free energy of formation of lead fluoride gives a value of −148.0 at 0° as compared with −149.1 kcal. from this research. About 0.2 kcal. of this discrepancy may be ascribed to an uncertainty in the value found for the vapor pressure of the system PbF_2–$PbF_2 \cdot 2^1/_2HF$.

An independent check can be made upon the value found for the standard free energy of formation of cupric fluoride in the following way. The entropies of copper and fluorine at 25° are 7.96 and 48.6 E.U.[9] and the entropy of cupric fluoride at 25° can be calculated by the method of Latimer[10] to be 25.7 E.U. From this the entropy change for the reaction $Cu(s) + F_2(g) \rightarrow CuF_2(s)$ is calculated to be −31.5 E.U. From reference (8) it is found that the enthalpy change for the reaction is −126.9 kcal. Combining these gives a value of −117.5 kcal. at 298°K. for the calculated standard free energy of formation of cupric fluoride. This compares well with the value found in this research.

There is not sufficient thermal data in the literature to make an independent check of the value found for mercurous fluoride.

The Cell Hg,$Hg_2F_2(s)$/NaF(in HF)//NaF,H_3OF, AgF(in HF)/Ag.—This cell was studied for the purpose of investigating the thermodynamics of solutions in hydrogen fluoride. The liquid junction potential was minimized by making the ionic strengths of the solutions on both sides of the junction equal and by having the mole fraction of silver fluoride low in comparison with the mole fraction of the sodium fluoride. The mole fraction of silver fluoride was equal to 2/13 of the total mole fraction of all the electrolytes in the solution in contact with the silver electrode. The potential of the cell was measured over a range of ionic strengths from 0.5005 to 2.503. The cell reaction

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(6) M. Oku, *Science Reports Tohoku Imp. Univ. Ser. 1*, **22**, 290 (1933).

(7) "International Critical Tables," Vol. VII, p. 256, 1930.

(8) W. Jahn-Held and K. Jellinek, *Z. Elektrochem.*, **42**, 401 (1936).

(9) National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," Table 34 (1949).

(10) W. M. Latimer, THIS JOURNAL, **43**, 818 (1921).

is $Hg + Ag^+ + F^- \rightarrow {}^1/_2Hg_2F_2(s) + Ag$, and the equation relating the potential of the cell to the concentration of the ions to which the electrodes are reversible is

$$E = E^0 + 0.542 \log X_{Ag^+} \times f_{Ag^+}X_{F^-} \times f_{F^-} \quad (10)$$

If the assumption is made that the individual ion activity coefficients of the silver and fluoride ions depend only upon the ionic strength, and not upon the ion species making up the ionic strength, the Debye–Hückel equation can be substituted into equation (10) to give

$$E = E^0 + 0.0542 \{\log X_{Ag^+} \times X_{F^-} - 2A\sqrt{\mu} + 2C\mu\} \quad (11)$$

Since the mole fraction of the silver ion is equal to $^2/_{13}$ of the mole fraction of the fluoride ion, this can be substituted into equation (11) and the result rewritten as

$$E^{0\prime} = E - 0.0542 \left\{\log \frac{2X_{F^-}^2}{13} - 2A\sqrt{\mu}\right\} = E^0 + 0.1084C\mu \quad (12)$$

The constant A has the value 0.529 for hydrogen fluoride at 0°. All of the quantities on the left-hand side of equation (12) are known or measured. The left-hand side of equation (12) is designated as $E^{0\prime}$. The various values of $E^{0\prime}$ found for different ionic strengths are given in Table II. Figure 3 shows a plot of $E^{0\prime}$ against the ionic strength. The intercept gives the E^0 of the cell, which is 0.3510 volt, and the slope of the line gives a value of 0.0793 for the parameter C. The data in Table II marked with an asterisk were obtained by a slightly different procedure. In these cases the concentration of sodium fluoride was constant throughout the cell and silver fluoride was added to the solution placed in contact with the silver electrode. In these cases it can be shown that

$$E - 0.0542 \{\log X_{NaF} \times X_{AgF} - A(\sqrt{\mu} + \sqrt{\mu'})\} = E^0 + 0.0542C(\mu + \mu')$$

The left-hand side of this equation serves as the definition of the $E^{0\prime}$ that appears in Table II for the data to which it is applicable.

TABLE II

VARIATION OF THE POTENTIAL OF THE CELL $Hg,Hg_2F_2(s)/NaF$(IN HF)//NaF,H_3OF,AgF(IN HF)/Ag WITH CONCENTRATION OF ELECTROLYTES AT 0°

Mole fraction NaF	Mole fraction AgF	Potential	Ionic strength μ	Ionic strength μ'	$E^{0\prime}$
0.05000	0.00769	0.0964	2.503	2.503	0.3721
.04000	.00615	.0915	2.002	2.002	.3682
.03600[a]	.0060	.0901	1.802	1.502	.3666
.03400[a]	.0040	.0763	1.702	1.502	.3613
.03200[a]	.0020	.0642	1.602	1.502	.3644
.02000	.00308	.0737	1.001	1.001	.3593
.01000	.00154	.0543	0.5005	0.5005	.3557

[a] A slightly different procedure was used for these data. $E^{0\prime}$ is given by the formula $E^{0\prime} = E - 0.0542\{\log X_{Ag} \times X_{F^-} - A(\sqrt{\mu} + \sqrt{\mu'})\}$.

Table III is a list of calculated activity coefficients for silver fluoride in hydrogen fluoride at 0°. These coefficients were calculated from the Debye–Hückel equation

$$\log f_{\pm} = \frac{-A\sqrt{\mu}}{1 + aB\mu}$$

in order to evaluate the quantity a which is supposed to represent the mean ionic diameter. This method of calculating a gives it the value 1.9×10^{-8} cm., which is comparable to similar values found for electrolytes in aqueous solutions.

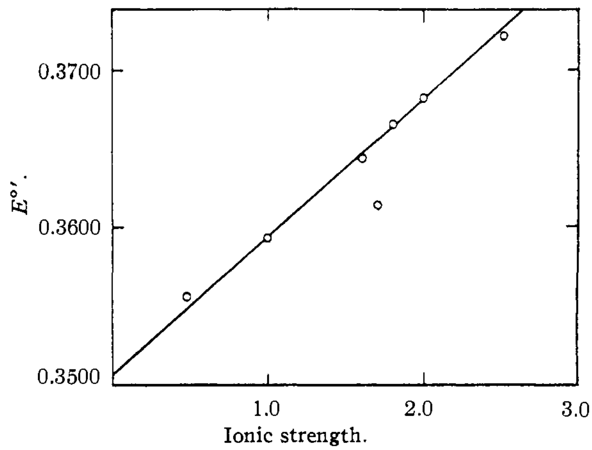

Fig. 3.—$E^{0\prime}$ vs. ionic strength at 0°.

TABLE III

CALCULATED ACTIVITY COEFFICIENTS OF SILVER FLUORIDE IN HYDROGEN FLUORIDE AT 0°

Mole fraction AgF	Activity coefficient
0.001	0.752
.01	.460
.02	.352
.03	.293
.04	.254
.05(satd.)	.229

The solubility of silver fluoride in hydrogen fluoride was found by Fredenhagen and co-workers[3] to be 33 g. per 100 g. of hydrogen fluoride at −15°. The compound AgF·HF is probably the solid phase in contact with the saturated solution at 0°.[11] If it be assumed that the solubility does not change greatly with temperature, the standard free energy of formation of AgF·HF can be calculated approximately from the results of this research. The mole fraction of silver fluoride in its saturated solution is 0.0494. The activity coefficient of silver fluoride at this concentration is 0.227. These values can be substituted into equation (10) to calculate the potential of the hypothetical cell $Hg,Hg_2F_2(s)/NaF\cdot(a = 0.227 \times 0.0494)//AgF$ (satd.)/Ag. This calculation gives a value of 0.1400 volt which corresponds to a free energy change of −3.23 kcal. for the reaction $Hg(l) + AgF$ (satd. soln.) $\rightarrow {}^1/_2Hg_2F_2(s) + Ag(s)$. This can be combined with the value of the standard free energy of formation of mercurous fluoride to give

$$Ag(s) + {}^1/_2F_2(g) + HF(l) \longrightarrow AgF\cdot HF(s); \quad \Delta F_{273} = -49.0 \text{ kcal.}$$

Acknowledgment.—The authors wish to express their gratitude to the Allied Chemical and Dye Corp. for providing the funds for the fellowship under which part of this work was done, and to Dr. A. L. Rocklin of the Dow Chemical Co., Pittsburg, Calif., who directed the research during its initial phases.

LAFAYETTE, INDIANA

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[11] J. H. Simons, Ed., "Fluorine Chemistry," Academic Publishing Co., Inc., New York, N. Y., 1949.