the mother liquors were weakly acid and therefore during evaporation the acid interacted with the basic salt with liberation of water. The error from this cause, however, does not amount to more than 1% of the correction and may be ignored.

In Expt. 15, where the amount of sodium hydroxide was almost sufficient to transform the stannous sulfate into stannous oxide, the unwashed but dried precipitate contained 83.29% of tin and 3.56% of sulfate radical. With the correction as applied before, the analysis showed only 1.9% of sulfate. As 1.80 g. of sodium hydroxide was used and 1.86 g. is required, according to the ordinary equation for the complete transformation into stannous oxide, it is evident that this reaction takes place very nearly as the equation indicates.

The volumes of liquid in proportion to the weight of stannous sulfate were kept small in this work since preliminary experiments showed that when the volumes were large, the less basic precipitates could not be obtained. This is always true for salts of considerable solubility.

Summary

1. The precipitates formed at 100° by adding sodium hydroxide solution in various amounts to stannous sulfate have been analyzed.

2. Within two regions of alkali variation, the precipitates remain nearly constant in composition. The formula $SnSO_4.SnO$ probably represents a compound and $SnSO_4.2SnO$-unknown-H_2O may possibly do so.

3. A method is described for correcting the analyses of incompletely separated solid phases for the retained liquid phase.

HOUGHTON, MICHIGAN

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE FREE ENERGY OF HYDROGEN FLUORIDE

BY R. A. MORGEN AND J. H. HILDEBRAND

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Introduction

The determination of the free energy of fluorine compounds is a problem of extraordinary interest on account of the unique position of fluorine as the most electronegative of the elements. Attempts to determine the free energy of the fluorine electrode made in this Laboratory by Simons and Hildebrand[1] were unsuccessful. Electrodes of various noble metals and of graphite surrounded by fluorine did not give reproducible potentials either in liquid hydrogen fluoride or in fused potassium acid fluoride. These experiments seemed to indicate little prospect of success for the method and that the only hope would lie in measuring the dissociation

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[1] Simons and Hildebrand, THIS JOURNAL, **46**, 2223 (1924).

pressure of a fluoride. More recently, however, Dr. Ruhle, together with the senior author, in this Laboratory, has found it possible to get reproducible values for the decomposition potentials of fused lead chloride and bromide from polarized cells. This suggested a further attack upon the fluorine electrode by using electrolytically deposited fluorine instead of fluorine surrounding the electrode, where the small solubility of the gas in the electrolyte gives little opportunity for saturating the electrode.

Some attempts were made to find a suitable electrolyte other than fused potassium acid fluoride, in order to avoid the corrosive action of the hydrogen fluoride given off, for this gas and fluorine together yield a mixture of terrific corrosive power. Silver fluoride proved unsatisfactory because it gave sub-fluoride and apparently colloidal silver, so that no fluorine was deposited at the anode. Thallous fluoride was tried but gave thallic fluoride at the anode instead of fluorine. No other electrolyte offered better prospects so we finally returned to fused potassium acid fluoride. Using inert electrodes this gives, on electrolysis, hydrogen and fluorine at the cathode and anode, respectively, and if the electrodes are reversible the chemical reaction involved is: H_2 (1 atm.) + F_2 (1 atm.) = 2HF (p atm.) where p is the pressure of hydrogen fluoride in equilibrium with the fused bifluoride. The problem thus divides itself into two parts, the measurement first of the e.m.f. of the cell, and second, the dissociation pressure of the bifluoride.

Apparatus

The measurements had to be carried out above the melting point of potassium acid fluoride. An electric oven of large heat capacity was constructed of Transite asbestos board with a layer of magnesite packing followed by an outer layer of Silocel packing. The tightly fitting cover was similarly packed. A heavy iron box, within the oven, and two fans served effectively to keep the temperature uniform. The energy input was regulated by hand and a temperature as high as 500° could be maintained constant within 1°.

The temperature was measured by means of a single junction Chromel-Alumel thermocouple, carefully calibrated. The potentiometer serving to measure both the e.m.f. of the thermocouple and that of the cell was a Leeds and Northrup Type K instrument. Suitable precautions were taken in the set-up and manipulation to insure that any errors in measurement were far less than the variation in the cells used.

A 100cc. platinum crucible served as the cell for the fused bifluoride; this acted as the cathode and hydrogen electrode. The anode caused considerable difficulty; at first, graphite anodes were used, but the fluorine deposited upon them showed varying over-voltage which could not be very accurately determined by extrapolating backwards an e.m.f. time curve. The measurements herein recorded were obtained with a 90%

iridium plate about 1 sq. cm. in area. The electrode proved surprisingly resistant, and no over-voltage was apparent. A Transite cover for the crucible prevented undue loss of hydrogen fluoride.

The vapor pressures of the fused salt were obtained with the apparatus shown in Fig. 1.

A copper vessel, A, 5 cm. in diameter and 10 cm. high, was used to contain the salt. Tube B was used for filling the container with salt after a blank run had been made. It was sealed with pressure tubing closed with a screw cock, and covered with de Khotinsky cement. Tube C led to the glass manometer E. D was a mercury seal which prevented the hydrogen fluoride from getting to the glass, copper and glass being joined at I with pressure tubing and de Khotinsky cement. A constant amount of mercury was kept in the seal and the level always brought to a given mark so that the pressure on both sides was the same. K was a capillary which permitted control of the rate of flow of the air so as to obtain the proper pressure. G was a mercury well, attached to a length of pressure tubing, which could be raised or lowered to give final adjustment to the pressure. The 3-way stopcock H, connected the apparatus to the vacuum pump or to the air.

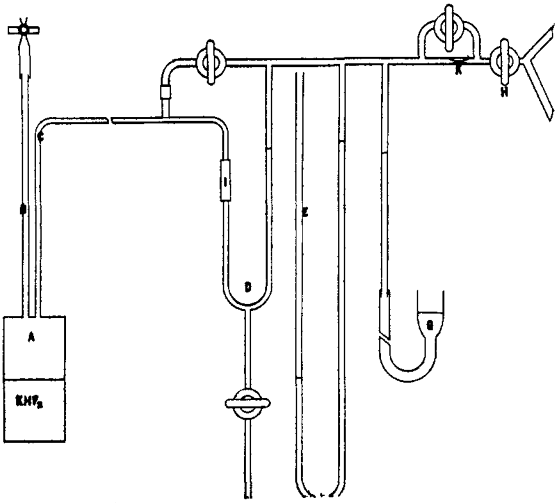

Fig. 1.—Vapor-pressure apparatus.

Purity of Materials.—The potassium acid fluoride was made by the procedure used by Simons,[2] from Baker's C. P. hydrofluoric acid and C. P. sticks of potassium hydroxide recrystallized from alcohol. However, when the salt was made in copper vessels small amounts of copper impurities plated out on the platinum crucible of the cell. In order to avoid this error, when the fused mass was almost free from water it was transferred from the copper vessel to one of platinum and the electrolysis continued until both the traces of water and copper salts were removed. In analyzing the substance after each run a small amount was placed in a weighed platinum crucible and heated to constant weight. The loss in weight represented hydrogen fluoride. The rest of the charge was saved for the vapor-pressure measurements.

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[2] Simons, This Journal, 46, 2175 (1924).

Experimental Procedure

Measurements with Iridium Electrode.—In the later electromotive-force measurements with the iridium electrode the maximum value of the voltage as suggested by Lorenz[3] is taken as the voltage of the cell. With this electrode the charging was done indiscriminately with the 110 d. c. supply or 2 Edison cells in series. No effect could be noticed by changing the source of supply. In every case the distance of the electrode from the bottom of the crucible was greater than the distance to the side so that practically no hydrogen bubbles came up through the bath to react with the fluorine on the electrode. When the charging was carried on at too high a rate, enough hydrogen was generated on the bottom so that minor explosions occurred in the apparatus.

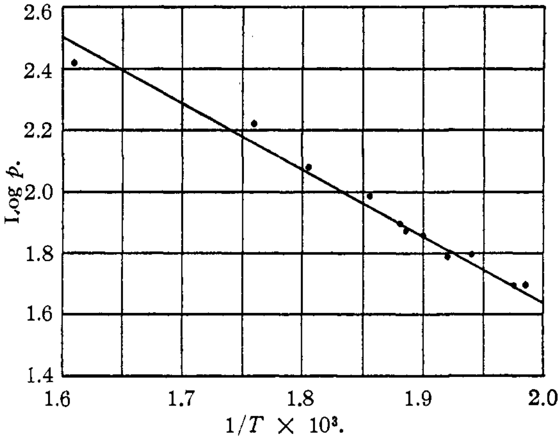

Fig. 2.

Vapor-Pressure Measurements.—The vapor-pressure measurements were made with the apparatus previously described. A blank run was made without the presence of the salt and a maximum variation of 4 mm. was noted. The salt was then placed in the copper vessel and the temperature of the furnace controlled by the rheostats. The entire apparatus was pumped to a vacuum of 1 mm., the mercury seal set at the designated mark and the stopcock to the mercury reservoir closed. The level of the mercury was maintained in the glass arm of the seal by admitting air. The apparatus was allowed to stand for 15 minutes to permit equilibrium to be reached and then the pressure was read on the open manometer. The temperature was then changed and the process repeated as often as desired. About five hours were necessary to obtain constant temperature.

Experimental Results

Vapor Pressure of Hydrogen Fluoride from the Fused Electrolyte.—

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[3] Lorenz and Czepinski, *Z. anorg. Chem.*, 19, 208 (1899).

Table I summarizes the values obtained for the pressure of hydrogen fluoride above the fused potassium acid fluoride. These values are plotted in Fig. 2. The equation for the line drawn through the observed values is $\log p = (-2150/T) + 5.94$.

The composition of the electrolyte was found to be constant because of the formation of two liquid phases, an upper, in which the electrodes dipped, consisting of potassium acid fluoride with a slight excess of potassium fluoride (compare Table II), and a lower, more viscous phase, containing material of approximately the composition $(KF)_2HF$. As hydrogen fluoride escaped from the electrolyte the lower phase increased at the expense of the upper but both remained constant in composition. Electrolysis with the electrodes in the lower layer was unsatisfactory due to its viscosity.

Table I

Vapor Pressure of Hydrogen Fluoride from Fused Potassium Bifluoride

Temp., °C.	230.5	233.0	242.0	248.0	253.5	257.0	258.5	266.0	281.0	294.0	347.5
Press., mm.	50.1	49.7	62.9	61.9	72.4	75.5	79.4	96.7	120.5	167.2	264.4

E.m.f. of the Cell.—Table II gives the values for the polarization potentials of the cells.

Table II

Polarization Potentials

Temp., ° C.	E.m.f.	Mol. frac., HF	Polarizing current			$-\Delta F$ corres. to 1 atm.
			Amp.	Volts	Time, min.	
223	1.505	...	0.05	2.1	5	31,800
224	1.479	0.470	.15	2.8	15	31,200
224	1.484	.478	.05	2.0	10	31,300
224	1.486	.478	.05	2.0	5	31,400
231	1.489	.480	.08	2.2	15	31,500
235	1.477	.480	.15	2.5	10	31,400
246	1.466	.479	.10	2.5	10	31,200
248	1.467	.479	.09	2.4	8	31,300
248	1.468	.479	.10	2.0	10	31,300
248	1.467	.478	.30	2.8	3	31,300
248	1.467	.479	.15	2.5	5	31,300
261	1.456	.482	.05	2.1	60	31,200
261	1.460	.482	.05	2.1	10	31,300
265	1.452	.476	.08	2.0	20	31,200
265	1.448	.476	.10	2.5	10	31,100
272	1.445	.478	.08	2.2	10	31,100
272	1.441	.478	.10	2.5	2	31,000

Calculation of Free Energy

The free energy of the reaction occurring in the cell is calculated from the e.m.f. by the equation[4] $\Delta F_1 = -\mathbf{NEF}$. The free energy for the re-

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[4] The notation of Lewis and Randall, "Thermodynamics," McGraw-Hill Book Company, **1923,** will be used in the following paragraphs.

action yielding hydrogen fluoride at 760 mm. instead of p mm. is $\Delta F_2 = \Delta F_1 - R\,T\,ln(p/760)$. The values so calculated are given in the last column of Table II and are plotted in Fig. 3 to give an idea of their concordance.

To calculate ΔF at the standard temperature, 298°K., we may use the slope of the line in Fig. 3 which gives $\Delta F_{298} = -32{,}500$. However, the temperature range of the measurements is so small compared with the interval of extrapolation that this value is subject to some uncertainty. A more reliable method for getting the temperature coefficient appears to be to use the relation $(\partial \Delta F/\partial T) = -\Delta S$, where ΔS is the change in entropy for the reaction, which may be calculated by the aid of some one of the equations that have been proposed for the purpose.[5] We have used the equation of Latimer,[6] which for diatomic gases at 298°K. is $S_{298} = {}^1/_2 R\; ln\; M^3\, A_1\, A_2 + 30.22$, where M is the molecular weight of the gas, A_1 and A_2 the respective atomic weights of the constituents. From this we calculate S for fluorine, 47.02; for hydrogen, 32.30; for hydrogen fluoride, 42.07. For the reaction, ${}^1/_2H_2 + {}^1/_2F_2 = HF$, ΔS then becomes 2.41. (Other entropy equations give almost identical results.)

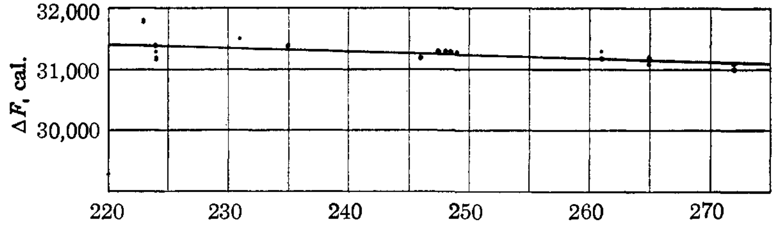

Fig. 3.

Using this value for S and taking the experimental value of ΔF at 520°K., from the middle values, which were most concordant, we calculate, $\Delta F_{298} = -31{,}300 - 222 \times 2.41 = -31{,}800$. This value we consider more reliable than the preceding.

We can get an independent check upon our experimental results by using the equation, $\Delta F = \Delta H - T\Delta S$, substituting therein the above value of ΔS and for ΔH the heat of reaction. Berthelot and Moissan[7] measured this by an indirect method, obtaining the value —38,500 cal. at 18°C. However, the gas under these conditions is not hydrogen fluoride but, as Simons and Hildebrand have shown, an equilibrium mixture of simple HF and $(HF)_6$ with a heat of association of —40,000 cal. per mole of $(HF)_6$. At the temperature at which the measurements of Berthelot and Moissan were made the apparent molecular weight is approximately 66, correspond-

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[5] Compare Tetrode, *Ann. Physik,* **38,** 434 (1912).

[6] Latimer, THIS JOURNAL, **43,** 824 (1921).

[7] Berthelot and Moissan, *Ann. chim. phys.,* [6] **23,** 572 (1891).

ing to the polymerization of 0.84 mole of HF per mole taken. The change in heat content when 0.84 mole of HF associates to $(HF)_6$ is, therefore, —0.84 × 6670 cal. or —5600 cal. The value of ΔH when monomolecular hydrogen fluoride is formed is, therefore, approximately —32,900 cal. Substituting in the above equation we then get $\Delta F = -32{,}900 + 298 \times 2.41 = -33{,}600$ cal., differing from the one above by an amount that may be regarded as within the limit of experimental errors, especially in view of the roundabout method used by Moissan.

It may be noted that the difference between ΔF and ΔH for the other hydrogen halides is small, the largest difference being 700 cal., for hydrogen chloride. The closeness of the values obtained for hydrogen fluoride is, therefore, evidence for their substantial accuracy.

Lewis and Randall have given a rough value for ΔF_{298} for hydrogen fluoride assuming that $\Delta S = 0$, and therefore placing $\Delta F = \Delta H$. They have neglected, however, to correct for the heat of polymerization of hydrogen fluoride, so that their value, —38,500, should be changed in the light of our correction to —32,900.

The value $\Delta F_{298} = -31{,}800$ cal. can be used in connection with the data of Simons and Hildebrand for the equilibrium between HF and $(HF)_6$ to calculate the free energy of the polymer. Substituting the value of the equilibrium constant, K, for the reaction, $HF = {}^1/_6(HF)_6$, in the equation $\Delta F = -R\,T\,ln\,K$, we get —3200 for the difference in free energy between the two forms of the acid, which gives $\Delta F_{298} = -35{,}000$ for the reaction ${}^1/_2H_2 + {}^1/_2F_2 = {}^1/_6(HF)_6$.

It is pointed out, in conclusion, that this work opens the way for the determination of the free energy of other fluorine compounds.

Summary

1. The e.m.f. of polarized electrodes in fused potassium acid fluoride has been measured between 223° and 272°C., corresponding to the reaction, ${}^1/_2H_2(1\text{ atm.}) + {}^1/_2F_2\,(1\text{ atm.}) = HF(p\text{ atm.})$.

2. The removal of hydrogen fluoride from fused potassium acid fluoride results in the formation of a second liquid phase, nearly immiscible with the first, consisting of a dipotassium acid fluoride, $HF(KF)_2$.

3. The vapor pressure of hydrogen fluoride from this two-liquid phase system has been measured between 226° and 348°C.

4. By the aid of the vapor-pressure measurements the free energy of the reaction forming hydrogen fluoride at one atmosphere has been calculated for temperatures between 223° and 272°. Extrapolation to 25° gives —32,500 cal.

5. Using the Latimer equation for the entropy of diatomic gases to extrapolate the value of ΔF to 25° gives for monomolecular hydrogen fluoride at 25°, —31,800 cal.

6. The value of ΔF at 25°, calculated from the heat of reaction and the entropy, is —33,600 cal.

7. The free energy of formation of $^1/_6(HF)_6$ is calculated to be —35,000 cal. at 25°, based upon the value —31,800 for monomolecular hydrogen fluoride.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE HAVEMEYER CHEMICAL LABORATORY, NEW YORK UNIVERSITY]

THE MUTUAL SOLUBILITY OF LIQUIDS. III. THE MUTUAL SOLUBILITY OF PHENOL AND WATER. IV. THE MUTUAL SOLUBILITY OF NORMAL BUTYL ALCOHOL AND WATER

BY ARTHUR E. HILL AND WILLIAM M. MALISOFF[1]

RECEIVED JANUARY 21, 1926 PUBLISHED APRIL 5, 1926

In an earlier publication[2] a new method was described for determining the mutual solubility of liquids by measuring the volumes of the two phases which result when the two components are put together in two different but known ratios by weight. If m represent the weight of one component taken for an experiment, a and b the volumes of the two phases resulting, x its concentration in g. per cc. in one phase and y its concentration in the second; and if the same symbols, written primed, be used for the second experiment, it follows that $ax + by = m$ and $a'x + b'y = m'$; from these simultaneous equations the concentrations x and y in g. per cc. can be calculated. If the weights of the second component, n and n', be now inserted in two similar equations, the concentration also of that component in each phase becomes known. By addition of the weights of the two components found in 1 cc. of each phase, the density of the phases also is found.

This method has recently been used by Kablukov and Malischeva[3] for measuring the mutual solubility of ether and water and of *iso*-amyl alcohol and water. The authors also include in their paper a general critique of the method, in which three principal points are raised; first, that the method does not require for accuracy such large volumes (100 to 400 cc.) as were used in our initial experiments;[2] second, that the apparent agreement between experimental results in a series of determinations depends upon the choice of the experiments taken for combination in the simultaneous equations; and third, that the inherent accuracy of the method is influenced largely by the relative weights (or volumes) of the com-

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[1] The material of this paper is part of a thesis presented by William M. Malisoff to the Graduate School of New York University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Hill, THIS JOURNAL, **45**, 1143 (1923).

[3] Kablukov and Malischeva, *ibid.*, **47**, 1553 (1925).