solubility measurements. Passage of HCl through such a melt for 1 hour did not completely remove the water.

Solubility Measurements.—The apparatus consisted of a globe of known volume, a water reservoir, a mercury manometer, and the absorption vessel holding the salt crucible. The absorption vessel consisted of two concentric Pyrex tubes, both closed at the top, with space between the upper ends for the crucible. The outer tube was connected through a stopcock to the globe. The open bottoms of the tubes were joined with a 45/50 ₮ joint that projected below the furnace. The volume of the vessel was kept as small as possible by using closely fitted tubing.

The total apparent volume of the system was determined for each run under operating conditions by a helium or nitrogen calibration. The globe was filled to about 30 mm. and then was opened to the absorption vessel. The apparent volume was calculated from the two pressures, these being measured to ±0.1 mm. with an Eberbach cathetometer.

Solubility measurements were made by following a similar sequence of operations with water vapor, the initial pressure in this case being that obtained immediately after H_2O vapor was admitted to the salt vessel. Solubility calculations were made using the ideal gas equation, which was adequate in the temperature and pressure ranges used. About 4 hours was required for equilibrium with a salt sample of 25 g. and a pressure drop of 4 mm. Six to 8 hours was required at final pressures above 18 mm. due to the slow hydrolysis reaction and diffusion of HCl to cooler parts of the apparatus. At least 4 measurements at successively higher pressures were made on each salt sample. Ambient temperatures of 34° were necessary to prevent condensation. The average deviations of solubility results in the low pressure region were 3%.

The furnace was controlled to ±1° by a Brown Electronik proportioning controller. After a run the actual salt temperature was also checked by dipping a thermocouple into the salt.

Distillation of the salt from the crucible was kept to a minimum by avoiding sharp temperature gradients near the salt. The method of stirring, which employed a glass-enclosed, magnetic stirring bar driven by a magnet revolving just below the crucible, introduced no troublesome temperature gradients. The adsorption of small amounts of water by any film of salt that did collect on the container walls was not reflected in the pressure drop used in the calculations since this process took place rapidly before the initial pressure reading was made.

Vacuum Hydrolysis.—A number of experiments relating to the water content and hydrolysis of untreated melts were performed. Nine grams of a 68% mixture prepared directly from bottled chemicals was melted under an argon atmosphere and then evacuated for 1 hour. The subsequent rate of hydrolysis was measured by collection of HCl in one of two parallel traps cooled with liquid N_2, followed by titration with a mixed brom thymol blue, phenol red indicator. Hydrolysis was enhanced by $PbCl_2$, $NaPO_3$, Pb, Zn and Bi, and eliminated by the addition of 1 mole% LiOH. In some cases the simultaneous loss of water and HCl was measured by weighing the collected sample prior to titration of the acid. Stirring increased the relative rate of water loss.

The results of quantitative measurement of total water content or reactivity toward a given metal of such preparations were found to be somewhat irreproducible and dependent on the history of the sample in an indeterminable manner.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

The Dissociation Pressure of Sodium Bifluoride—the Free Energy and Enthalpy Change for the Reaction $NaHF_2(s) \rightarrow NaF(s) + HF(g)$ from 157 to 269°[1]

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The dissociation pressure of sodium bifluoride has been determined from 157 to 269° in a nickel and Monel system. Equations for the free energy change and the average enthalpy change from 157 to 269° were obtained for the reaction $NaHF_2(s) \rightarrow NaF(s) + HF(g)$.

Sodium fluoride is often used as an absorbant for hydrogen fluoride and sodium bifluoride is used as a source of hydrogen fluoride. Sodium fluoride–zirconium fluoride mixtures are used, in their molten state, as media for the hydrofluorination of uranium in zirconium matrix fuel elements, in a process for the recovery of uranium from spent fuels. The dissociation pressure of sodium bifluoride and the thermodynamic information that can be derived from it are therefore very important.

Experimental

Materials.—Merck reagent grade sodium fluoride was used after volatile impurities were vacuum distilled from the salt. Hydrogen fluoride obtained from the Harshaw Chemical Company was purified by vacuum distillation. Hydrogen and other non-condensable gases were distilled from the solid hydrogen fluoride, contained in a nickel vessel cooled with liquid nitrogen. The hydrogen fluoride was then distilled from the vessel, cooled with "Dry Ice" and collected in a nickel storage vessel. This procedure was repeated several times and the vapor pressure of the hydrogen fluoride prepared in this manner agreed with the literature value at zero degree.[2] The vapor density of the product determined by the Regnault method at 100° and 657 mm. pressure was 20.3 g./GMV, which is in good agreement with the formula weight of 20.01. The deviation from ideal gas behavior is small and the effect of any impurity would be evident.

Apparatus.—The apparatus was constructed with nickel and Monel components, which were either welded together or joined by Teflon gasketed, flared connectors. The component parts were separated by Monel, Teflon seated, bellows valves. The pressure measurements were made in a Monel vessel 6 inches long made from 1 inch Monel tubing. A thermocouple well extended into the bottom of the tube. The pressure measuring vessel was welded to a 20 inch long, $^3/_8$ inch nickel tube, which was flared at the open end and connected to a Booth–Cromer pressure transmitter and self-balancing relay.[3] The transmitter served to isolate the system containing the reactants from the mercury manometer used to measure the pressure with a precision of ±0.2 mm. The pressure measuring vessel and transmitter were connected to a manifold, which was connected to a helium supply, hydrogen fluoride storage vessel, traps and vacuum system, that could be evacuated to one micron, as detected with a thermocouple gage. The hydrogen fluoride storage vessel was kept at room temperature. Manifold, gas measuring vessels, pressure transmitters and the line leading to the pressure measuring vessel were kept between 100 and 105° by containing them in an insulated, thermostated box in which air was circulated. The pressure measuring vessel

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) R. L. Jarry and W. Davis, Jr., "The Vapor Pressure, Association, and Heat of Vaporization of Hydrogen Fluoride," Carbide and Carbon Chemical Co., K-25 plant, Oak Ridge, Tenn., K-968, 10, 1952.

(3) S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," S.A.M. Laboratories, Columbia University, MDDC-803, 1947.

was placed midway in a 12 inch long, 1.5 inch wide heavy duty tube furnace. Temperatures were measured with a Chromel–Alumel thermocouple located in the thermocouple well in the bottom of the pressure measuring vessel. The temperature was controlled by a similar thermocouple in conjunction with a Powerstat in series with a Wheelco, Capacitrole electronic pyrometer. The temperature of the measuring thermocouple, which was calibrated with a standard resistance thermometer, was obtained with a Rubicon type B potentiometer. Temperatures were measured to ±0.1° with a maximum uncertainty of one degree as estimated from the standard deviation of the results.

Procedure.—In order to minimize the corrosion of the pressure measuring vessel it was hydrofluorinated at a hydrogen fluoride pressure of 500–600 mm. at 300° until there was no indication of any reaction of the gas with the vessel, as evidenced by a change in pressure. The vessel was then evacuated, filled with helium at atmospheric pressure and detached from the manifold.

Nine to fifteen grams of sodium fluoride was added to the vessel and it was attached to the pressure transmitter. In order to remove all volatile matter the system was degassed at 300° to a pressure less than 10 μ. An amount of hydrogen fluoride (shown in Table I), measured by the decrease in pressure in a second vessel, was admitted to the vessel containing the sodium fluoride at 25°. At this temperature the absorption of the last portion of hydrogen fluoride was very slow. Therefore, a small amount of gas was removed from the system by evacuating to less than one mm. The sample was then heated and held at constant temperature until a constant pressure reading was obtained.

TABLE I

DECOMPOSITION PRESSURE OF SODIUM BIFLUORIDE 157 TO 269°

	NaF (g.)	Compn. of complex HF (moles)	Mole % HF
A	9.72	0.103	31
B	14.9	.055	13
C	12.0	.056	16
D	12.0	.077	21

Temp., °C.	Obsd. pressure, mm.	% dev. Obsn. *vs.* calcn. eq. 1	Compn. of complex
156.9	19.3	+1.3	A
161.2	22.8	+3.1	A
173.0	37.0	+4.7	A
180.3	52.8	−3.3	C
182.6	56.2	0.0	C
193.5	82.9	+2.6	C
200.2	113	−3.7	A
200.5	108	+1.8	A
205.0	131	−0.8	A
213.0	163	+4.9	C
216.9	204	−3.9	B
228.4	291	−2.8	B
231.3	313	0.0	A
232.3	319	+1.5	B
238.6	391	+0.8	B
239.3	391	+2.3	C
245.3	500	−3.6	C
249.3	529	+3.0	B
254.7	622	−2.7	B
255.9	670	−1.3	A
257.3	687	+0.3	D
257.7	685	+1.6	B
263.8	829	+0.1	B
266.8	912	−1.3	D
268.5	965	−2.2	B
269.1	938	+2.2	A
	Av.	±2.1	

At several points equilibrium was approached from both higher and lower temperatures. At a few points a portion of the hydrogen fluoride was pumped from the system and second readings were obtained after the system returned to equilibrium. Four sets of data were obtained using different ratios of hydrogen fluoride to sodium fluoride as shown in Table I.

During the course of the experiments the salt samples were intermittently evacuated to less than one mm. at 25° to remove any hydrogen that may have formed due to corrosion of the vessel.

The pressure transmitter and the line connecting it to the pressure measuring vessel were maintained at a temperature above 100° in order that the molecular species in the gas phase would be the diatomic form of hydrogen fluoride.[2,4]

The solid phase was ascertained as being a mixture of sodium fluoride and sodium bifluoride from an isotherm of the system at 216°. The pressure remained constant throughout the stepwise addition of an equimolar amount of hydrogen fluoride to 0.5 g. of sodium fluoride.

Results and Discussion

The decomposition pressures of sodium bifluoride from 156 to 269° are shown in Table I. Results from four different mixtures of sodium fluoride and hydrogen fluoride are given. The data were plotted as the log of the pressure in mm. *vs.* the reciprocal of the absolute temperature, from which equation 1 was obtained graphically.

$$\log P \text{ (mm.)} = 9.475 - \frac{3.521}{T} \times 10^3 \qquad (1)$$

The per cent. deviation of each observed value of the pressure from the value calculated using equation 1 is shown in Table I. The average deviation is ±2.1%.

The reaction studied is that of equation 2, and

$$\text{NaHF}_2\text{(s)} = \text{NaF(s)} + \text{HF(g)} \qquad (2)$$

The equilibrium constant is expressed by equation 3.

$$K_p = P(\text{HF, atm.}) \qquad (3)$$

The standard free energy of the reaction as a function of the absolute temperature is given by equation 4.

$$\Delta F^0 = 16.11 \times 10^3 - 30.17T \qquad (4)$$

The linear variation of the log P *vs.* $1/T$ indicates that the enthalpy change for the reaction does not vary to any appreciable extent in the temperature studied. The average standard enthalpy change for the reaction from 160 to 269° was calculated from the van't Hoff equation to give a value of ΔH^0 of 16.1 kcal./mole. This value may be compared with a ΔH^0 of 18.4 kcal. at 500°K. obtained by Westrum for the reaction $\text{KHF}_2\text{(s)} = \text{KF(s)} + \text{HF(g)}$.[5] The sodium ion appears to weaken the hydrogen bond in the F–H–F$^-$ ion.

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LEMONT, ILL.

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[4] R. W. Long, J. H. Hildebrand and W. E. Morrell, THIS JOURNAL, **65**, 182 (1943).

[5] E. F. Westrum and K. S. Pitzer, *ibid.*, **71**, 1940 (1949).