However, the amount of premelting is small at 1750°K. (*i.e.*, at 98% of the absolute melting point), which is confirmation of the high purity of the substance. Because of the temperature limitation of the equipment, only two measurements were obtained in the liquid range, at 1792.8 and 1809.2° K. These two measurements indicate a normal magnitude for the heat capacity of the liquid, 57.9 cal./deg. mole or 8.27 cal./deg./mean gram atom.

TABLE II

HEAT CONTENTS (CAL./MOLE) AND ENTROPIES (CAL./DEG. MOLE) ABOVE 298.16 °K.

| | $Ta_2O_5$ | | $Nb_2O_5$ | |
|---|---|---|---|---|
| $T$, °K. | $H_T - H_{298.16}$ | $S_T - S_{298.16}$ | $H_T - H_{298.16}$ | $S_T - S_{298.16}$ |
| 400 | 3,430 | 9.87 | 3,410 | 9.82 |
| 500 | 7,070 | 17.98 | 6,970 | 17.75 |
| 600 | 10,950 | 25.05 | 10,730 | 24.60 |
| 700 | 14,990 | 31.28 | 14,630 | 30.62 |
| 800 | 19,130 | 36.81 | 18,630 | 35.95 |
| 900 | 23,340 | 41.76 | 22,710 | 40.76 |
| 1000 | 27,630 | 46.29 | 26,860 | 45.13 |
| 1100 | 31,990 | 50.44 | 31,050 | 49.13 |
| 1200 | 36,410 | 54.29 | 35,280 | 52.80 |
| 1300 | 40,880 | 57.86 | 39,550 | 56.22 |
| 1400 | 45,390 | 61.20 | 43,860 | 59.42 |
| 1500 | 49,970 | 64.36 | 48,230 | 62.43 |
| 1600 | 54,630 | 67.37 | 52,670 | 65.30 |
| 1700 | 59,380 | 70.25 | 57,190 | 68.04 |
| 1785 | .... | ... | 61,090(c) | 70.28 |
| 1785 | .... | ... | 85,680(1) | 84.05 |
| 1800 | 64,220 | 73.01 | 86,550 | 84.53 |

Table II contains smooth values of the heat contents to 1800°K. and the corresponding entropy increments, computed to match the heat contents by the method of Kelley.[6]

The following relationships, which represent the heat content values to within the average limits shown in parentheses, were derived for use by those who make thermodynamic calculations by means of equations.

$Ta_2O_5$(c)

$$H_T - H_{298.16} = 37.00T + 3.28 \times 10^{-3}T^2 + 5.92 \times 10^5 T^{-1} - 13{,}309;\ (0.4\%,\ 298\text{–}1800°\text{K.})$$

$Nb_2O_5$(c)

$$H_T - H_{298.16} = 36.23T + 2.77 \times 10^{-3}T^{-2} + 4.88 \times 10^5 T^{-1} - 12{,}685;\ (0.5\%,\ 298\text{–}1785°\text{K.})$$

$Nb_2O_5$(1)

$$H_T - H_{298.16} = 57.90T - 17{,}672;\ (0.1\%;\ 1785\text{–}1810°\text{K.})$$

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[6] K. K. Kelley, U. S. Bur. Mines Bulletin 476 (1949).

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# The Heat and Entropy of Ionization of Hydrofluoric Acid. The Entropy of Bifluoride Ion

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The heats of solution of sodium fluoride in water and in aqueous perchloric acid have been measured. These values are used to calculate the heat of ionization of hydrofluoric acid. By combining this heat with the free energy of ionization, we have calculated the entropy of ionization. We found $\Delta H^0 = -3180$ cal./mole and $\Delta S^0 = -25.2$ e.u. This value is used in calculating the entropy of bifluoride ion which is found to be 26 e.u.

Because of the unusual structure of bifluoride ion, $FHF^-$, a value for its entropy in aqueous solution is of considerable interest. This work was undertaken to obtain this value and also to clear up uncertainties in the heat and entropy of ionization of aqueous HF.

The equilibrium constants for the dissociation of hydrofluoric acid and for the formation of $HF_2^-$ have been determined by Broene and DeVries.[1] Hence measurement of the heat of solution of sodium fluoride in water and in acid enables one to calculate the heat and entropy of ionization of aqueous hydrofluoric acid and the $HF_2^-$ entropy.

## Experimental Procedures

The calorimeter used in this investigation has been described in detail elsewhere.[2,3] For the runs involving acid solutions, the glass surfaces of the calorimeter were coated with a thin layer of Tygon Paint (Series K, White, U. S. Stoneware). Samples of sodium fluoride were contained in small thin glass bulbs and were introduced into the calorimetric solution by breaking the bulbs against the bottom of the dewar. The sample bulbs were coated with paraffin wax for the runs using acid solutions. All heats were measured at 25 ± 1° and are reported in terms of the defined calorie.

C.P. sodium fluoride was dried for two hours at 150° and then stored in a desiccator until used.

Double vacuum-distilled 72% perchloric acid was diluted with distilled water to make a stock solution which was standardized against mercuric oxide. Concentration expressed in moles of acid/liter was converted to molality by using the relation due to Stonehill.[4]

**The Heat of Solution of Sodium Fluoride in Water.**—One measurement of the heat of solution of sodium fluoride in water was made. The result of this experiment is in agreement with the values obtained by Latimer and Jolly.[5] The details are given in Table I, where the most recent determination is designated as Run 3.

TABLE I

| Run | NaF, g. | $H_2O$, g. | $\Delta H$, cal./mole |
|---|---|---|---|
| 1[5] | 1.063 | 1064 | 291 |
| 2[5] | 1.759 | 1042 | 297 |
| 3 | 1.598 | 1060 | 290 |

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

[2] B. J. Fontana, "National Nuclear Energy Series IV-19B," McGraw-Hill Book Co., Inc., New York, N. Y., 1950, p. 321.

[3] H. W. Zimmermann and W. M. Latimer, THIS JOURNAL, **61**, 1550 (1939).

[4] H. Stonehill, *Trans. Faraday Soc.*, **36**, 76 (1943).

[5] W. M. Latimer and W. L. Jolly, THIS JOURNAL, **75**, 1548 (1953).

Data from the Bureau of Standards[6] compilation have been employed to correct these heats to infinite dilution. We obtain $\Delta H^\circ = 213 \pm 10$ cal./mole.

**The Heat of Solution of Sodium Fluoride in Perchloric Acid Solution.**—Three measurements of the heat of solution of sodium fluoride in perchloric acid were made. In each experiment the initial perchloric acid concentration was such as to ensure the presence of an excess of acid after the addition of the sodium fluoride. The results of these experiments are presented in Table II.

TABLE II

| Run | NaF, g. | $H_2O$, g. | $HClO_4$ mole | $Q_{(1)}$, cal. |
|---|---|---|---|---|
| 4 | 2.4098 | 1027 | 0.08255 | −185.50 |
| 5 | 2.3122 | 1025 | .08255 | −182.86 |
| 6 | 2.5477 | 1024 | .08255 | −200.58 |

## Calculations

The calorimetric reaction is considered to be

$$(a + b + c)\text{NaF(s)} + (a + c/2)\text{H}^+ = (a + b + c)\text{Na}^+ + a\text{HF} + b\text{F}^- + c/2\text{HF}_2^- \quad (1)$$

where $a$ represents the moles of HF, $b$ the moles of $F^-$, and $c/2$ the moles of $HF_2^-$ formed in the reaction. The coefficients $a$, $b$ and $c$ may be calculated using the equilibrium constants of Broene and DeVries,[1] since the initial acid concentration and the total fluoride added are known quantities. To reaction (1) we will add reactions (2) and (3), thus obtaining (4).

$$b\text{F}^- + b\text{H}^+ = b\text{HF} \quad (2)$$

$$c/2\text{HF}_2^- + c/2\text{H}^+ = c\text{HF} \quad (3)$$

$$(a + b + c)\text{NaF(s)} + (a + b + c)\text{H}^+ = (a + b + c)\text{Na}^+ + (a + b + c)\text{HF} \quad (4)$$

It is seen that $Q_{(1)} + Q_{(2)} + Q_{(3)} = Q_{(4)}$. As a first approximation, we take $Q_{(2)} = -3003b$ calories and $Q_{(3)} = -1050c$ calories.[7] Finally, the heat for the reaction

$$\text{NaF(s)} + \text{H}^+ = \text{Na}^+ + \text{HF} \quad (5)$$

was calculated from $\Delta H_{(5)} = -Q_{(4)}/(a + b + c)$ cal./mole. This value for the heat was then used for another, final, approximation. An exact knowledge of $Q_{(2)}$ and $Q_{(3)}$ is not critical for the calculation of $Q_{(4)}$ as the correction introduced by $Q_{(2)}$ is of the order of 1–2% of $Q_{(1)}$ while the correction introduced by $Q_{(3)}$ is of the order of 0.1% of $Q_{(1)}$.

The heats of dilution of sodium perchlorate and perchloric acid for the solutions in runs 4, 5 and 6 may be estimated from Bureau of Standards data.[6] The heats of dilution are found to be of the same magnitude but of opposite sign. Hence we take $\Delta H_{(5)}$ as the heat of this reaction at infinite dilution.

The heat of ionization may now be computed as the difference between $\Delta H_{(5)}$ and the heat of solution of sodium fluoride in water. The heats calculated are recorded in Table III.

TABLE III

THE HEAT OF IONIZATION OF HYDROFLUORIC ACID

| Run | $\Delta H$, cal./mole |
|---|---|
| 4 | −3110 ± 60 |
| 5 | −3187 ± 15 |
| 6 | −3189 ± 20 |

The uncertainties in $\Delta H$ recorded in Table III have been estimated from our calorimetric temperature drift uncertainties. We shall take −3180 ± 15 cal./mole as the best value for the heat of ionization of hydrofluoric acid. We combine this value with the free energy of ionization to calculate $\Delta S^0 = -25.2$ e.u. If the partial molal entropy of fluoride ion is taken as −2.3, the entropy of $HF_{aq}$ is seen to be 22.9 e.u. The above value for the entropy of HF may be combined with the value for the entropy change for the reaction $HF + F^- = HF_2^-$, calculated from the data of Broene and DeVries[1] to give the partial molal entropy of $HF_2^-$ ion as 26 e.u.

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[6] National Bureau of Standards, Circular 500 (Feb., 1952), "Selected Values of Chemical Thermodynamic Properties."

[7] These heats have been calculated from the temperature coefficients of the equilibrium constants, given in reference (1).