raised as to whether this reaction affords a good test of the radiation hypothesis.

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[Contribution from the Chemical Laboratory of the University of California]

THE POTENTIAL OF THE FLUORINE ELECTRODE FROM THERMAL DATA

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The recent determinations of v. Wartenberg[1] of the heats of two reactions involving fluorine, together with the values of Latimer and Buffington[2] for the ionic entropies, permit the calculations of a new value of the potential of the fluorine electrode, long a quantity of much uncertainty. The reactions studied and their heats are

$$\tfrac{1}{2}H_2 + \tfrac{1}{2}F_2 = HF_{sol};\ \Delta H = -75.6 \text{ kg. cal.} \qquad (1)$$

$$Cl^- + \tfrac{1}{2}F_2 = F^- + \tfrac{1}{2}Cl_2;\ \Delta H = -39.9 \text{ kg. cal.} \qquad (2)$$

The calculations in this article will show that these heats lead to concordant values for the fluorine electrode almost a volt higher than the value estimated from the heat of formation of hydrogen fluoride by Berthelot and Moissan.[3]

The concentration of hydrogen fluoride in Reaction 1 was one mole in 400 moles of water. Even at this dilution, hydrogen fluoride is far from complete ionization, as is shown by the fact that its heat of neutralization is about 3000 cal. more than that of typical strong acids. Since we have insufficient data to calculate the entropy and free energy of dissociation of hydrogen fluoride in solution we shall not attempt to use Equation 1 directly, but shall use the values for the heat of formation of the metal fluorides derived from it by combination with data for the heat of formation of the metal oxides and their heats of neutralization by hydrogen fluoride. These values have been calculated by v. Wartenberg[4] and are given in the first column of Table I. The entropy of the reactions for the formation of the metal fluorides in solution may be calculated from the values for the entropies of the metals, their ions, fluorine gas and fluoride ions. These values, tabulated in Table I, have been taken from papers by Lewis, Gibson and Latimer,[5] and by Buffington and Latimer,[6] with the exception of the value for fluorine, which has been taken in agreement with the Tetrode equation[7] in the modified form given by Latimer.[8]

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[1] v. Wartenberg, *Z. anorg. allgem. Chem.*, **151**, 313 (1926).

[2] Latimer and Buffington, This Journal, **48**, 2297 (1926).

[3] Berthelot and Moissan, *Ann. phys. chim.*, [6] **23**, 570 (1891).

[4] Ref. 1, p. 326.

[5] Lewis. Gibson and Latimer, This Journal, **44**, 1008 (1922).

[6] Buffington and Latimer, *ibid.*. **48**, 2305 (1926).

[7] Tetrode, *Ann. Physik*, **33**, 434 (1912).

[8] Latimer, This Journal, **43**, 818 (1921).

The free energies of formation of the ions in hypothetical 1 *M* solution have been calculated from the equation, $\Delta F = \Delta H - T\Delta S$. These values, combined with those for the free energies of formation of the metal ions[9] referred to $H = 0$, then give the free energy of formation of F^-.

TABLE I

FREE ENERGY OF FORMATION OF FLUORIDE ION FROM HEATS AND ENTROPIES OF FORMATION OF METAL FLUORIDES IN SOLUTION

	ΔH of formation from elements	S_{metal}	$S_{\text{metal ion}}$	ΔS using $S_{F^-} = -5$ $S_{F_2} = 47.0$	ΔF°	$F^\circ_{\text{metal ion}}$	$F^\circ_{F^-}$
$Li^+ + F^-$	−143.7	7.6	+ 1	−30.6	−134.6	−68.3	−66.3
$Na^+ + F^-$	−136.0	12.3	15	−25.8	−128.3	−62.6	−65.7
$K^+ + F^-$	−138.1	16.6	22	−23.1	−131.2	−67.4	−63.8
$Tl^+ + F^-$	− 80.5	14.6	26.5	−16.6	− 75.5	− 7.8	−67.7
$Ag^+ + F^-$	− 53.5	10.3	16	−22.8	− 46.7	+18.5	−65.2
$Cd^{++} + 2F^-$	−173.7	11.8	−14	−82.7	−149.0	−18.4	−65.3
$Fe^{++} + 2F^-$	−177.2	7.7	−22	−86.8	−151.3	−20.4	−65.5
$Pb^{++} + 2F^-$	−153.8	15.5	2	−70.4	−132.8	− 5.6	−63.6
$Fe^{+++} + 3F^-$	−253.1	7.7	−67	−160.1	−205.3	− 3.1	−67.4
						Av.	−65.6

The agreement of the values for $F^\circ_{F^-}$ in the final column is excellent considering the large errors involved in the calorimetric determination of the reaction heats and gives added proof of the reliability of the values of the ionic entropies. In many of the reactions, errors of several tenths of a kg. cal. exist due to the fact that corrections should be applied to change the heat of the reaction to that at infinite dilution of the ions. The average value —65.6 ± 1.0 kg. cal. gives for the potential of the fluorine electrode 2.85 ± 0.04 volts.

With Reaction 2 we may proceed directly to the calculation of the free-energy change. For ΔS°_{298} we find —18.5, using for the entropies of the substances involved: Cl^-, 15.5; F_2, 47.0; Cl_2, 51; and F^-, —5; and for ΔF°_{298}, 34.3 ± 1.0 kg. cal. This makes the fluorine electrode 1.49 ± 0.04 volts more positive than the chlorine electrode, and a normal potential referred to hydrogen of +2.85 ± 0.04 volts.

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Summary

It has been shown that the heat of formation of hydrogen fluoride from hydrogen and fluorine, and the heat of replacement of chlorine in chloride by fluorine both lead to the value, +2.85 ± 0.04 volts, for the potential of the normal fluorine electrode.

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[9] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, 1923.