[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA]

Heats and Entropies of Successive Steps in the Formation of AlF_6^{---}

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The heats of the six successive reactions of F^- with Al^{+++} to form AlF_6^{---} have been measured. These values with the equilibrium constants permit a calculation of the entropy change in each step. These values are $\Delta S_1^\circ = 32$, $\Delta S_2^\circ = 26$, $\Delta S_3^\circ = 18$, $\Delta S_4^\circ = 13$, $\Delta S_5^\circ = 5$ and $\Delta S_6^\circ = -3$ cal./deg. mole. The magnitude of these values is discussed with respect to two fundamental factors and compared with the entropy of formation of other complex ions.

The six constants for the formation of AlF_6^{---} have been determined by Brosset and Orring.[1] Hence measurement of the heats of these reactions permits a calculation of the successive entropy changes. There are not many reliable data in the literature for the entropies of formation of complex ions, and the values which we have obtained for the aluminum fluoride complexes add considerably to an understanding of the various factors involved.

Experimental Procedures

The calorimeter used in this investigation has been described elsewhere.[2,3] For the runs involving high concentrations of fluoride, the glass surfaces were coated with a thin layer of "Dri-Film" (dimethyldichlorosilane). Samples were contained in small glass bulbs and were introduced into the calorimetric solution by breaking the bulbs with a glass rod. All heats were measured at 25 ± 1° and are reported in terms of the defined calorie (1 cal. = 4.1833 int. joule). The uncertainty in the heats measured is ± 0.1 calorie.

The aluminum solutions were made up from reagent grade aluminum nitrate and measured amounts of standard nitric acid. The solutions were analyzed for aluminum by precipitating and igniting aluminum hydroxide.

C.P. sodium fluoride was dried for 1.5 hours at 130°. A stock solution of sodium fluoride was prepared by dissolving a weighed amount of the solid and diluting to a known volume.

A standard solution of ammonium fluoride was prepared by neutralizing reagent hydrofluoric acid with standard ammonium hydroxide. The ammonium fluoride solution used in run 19 was prepared by dissolving a weighed amount of reagent grade ammonium fluoride.

The Heat of Solution of Sodium Fluoride in Water and in Aluminum Solutions

Two measurements of the heat of solution of sodium fluoride in water were made. The details of the two runs are given in Table I.

TABLE I

THE DISSOLUTION OF NaF IN WATER

We take $\Delta H^\circ = 294 \pm 5$ cal./mole for $NaF(s) = Na^+(aq) + F^-(aq)$.

Run	NaF, g.	Water, g.	ΔH, cal./mole
1	1.063	1064	291
8	1.759	1042	297

Several measurements of the heat of solution of sodium fluoride in 1047 ml. of a solution 0.00973 M in $Al(NO_3)_3$ and 0.0011 M in HNO_3 were made. The reactions were endothermic when less than 1.9 g. of sodium fluoride were dissolved, but exothermic for larger amounts of sodium fluoride. (A fine precipitate, presumably some complex of AlF_3 and NaF, formed in the exothermic reaction. Since the composition and heat of precipitation of this precipitate are unknown, the results of the exothermic reactions are not reported.) Details for the endothermic runs are given in Table II. Brosset and Orring[1] and Kleiner[4] have observed that at low fluoride concentrations, the system Al^{+++}–F^- is very slow in attaining equilibrium. However, in the runs described in Table II, there were no unusual lags in the absorption of heat. The reactions were calorimetrically complete in about four minutes.

TABLE II

THE DISSOLUTION OF NaF IN Al^{+++} SOLUTION

Run	NaF, g.	Calories absorbed
2	0.0970	3.09
3	.8225	23.78
4	.3160	9.98
7	1.262	30.97

The Heat of Mixing $Al^{+++}(aq)$ and $F^-(aq)$

A series of calorimetric measurements were made in which 4.983 ml. of a solution 0.983 M in $Al(NO_3)_3$ and 0.0098 M in HNO_3 were mixed with 1047 ml. of aqueous fluoride solution of varying concentrations. The details are given in Table III.

TABLE III

HEAT OF MIXING Al^{+++} AND F^-

Run	Total fluoride, mole	Calories absorbed
10	0.00620 NaF	2.16
11	.0155 NaF	5.42
12	.0310 NaF	5.74
13	.0975 NH_4F	3.63
14	.01951 NH_4F	5.35
19	.1919 NH_4F	1.28
21	.1951 NH_4F	0.95

In order to correct the heats for the heat of dilution of 0.983 M $Al(NO_3)_3$, it was necessary to measure the heat of mixing of 4.983 ml. of the solution 0.983 M in $Al(NO_3)_3$ and 0.0098 M in HNO_3 with 1047 ml. of dilute aqueous HNO_3. The details are given in Table IV.

TABLE IV

HEAT OF DILUTION OF $Al(NO_3)_3$

Run	Final molarity of HNO_3	Calories evolved
9	0.00464	4.84
15	.00446	5.10
	Average	4.97 ± 0.15

Calorimetric experiments showed that the mixing of 4.983 ml. of 0.0098 M HNO_3 with 1047 ml. of aqueous fluoride involved a negligible amount of heat.

Calculations

The data presented in Tables I–IV may be used to calculate the heats for eleven reactions of the type

$$Al^{+3} + xF^- = x_0Al^{+3} + x_1AlF^{+2} + x_2AlF_2^{+1} \ldots + x_6AlF_6^{-3} + (x - x_1 - 2x_2 \ldots -6x_6)F^-$$

For each reaction, the coefficient x may be obtained from the experimental data. The coefficients x_n,

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(1) C. Brosset and J. Orring, *Svensk kem. Tid.*, **55**, 101 (1943).

(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) K. K. Kleiner, *J. Gen. Chem. U.S.S.R.*, **20**, 1809 (1950), Consultants Bureau Translation.

which add up to 1, may be calculated from the complexing constants at 25° reported by Brosset and Orring.[1] We shall report our heats using a function $\bar{n}$, which is the number of complexed fluorine atoms per aluminum atom, or the total concentration of complexed fluoride divided by the total concentration of aluminum. In Table V and Fig. 1 we have tabulated and plotted the heat absorbed per mole of aluminum as a function of $\bar{n}$ (for the general reaction discussed above).

TABLE V

Run	n	Cal. absorbed per mole Al	Run	n	Cal. absorbed per mole Al
2	0.227	240	12	4.17	2190
3	1.919	1770	13	4.91	1750
4	0.739	760	14	3.55	2110
7	2.908	2170	19	5.20	1275
10	1.265	1460	21	5.20	1210
11	3.045	2120			

The smooth curve through the points in Fig. 1 has been calculated using the heats of reaction summarized in Table VI. Our estimated accuracies are ±50 cal. for reaction (1), ±100 cal. for reactions (2), (3), (4) and (5) and ±200 cal. for reaction (6).

TABLE VI

THERMODYNAMIC FUNCTIONS FOR ALUMINUM–FLUORIDE COMPLEXES[a]

	ΔH^0	ΔF^0	ΔS^0	Charge effect
(1) $Al^{+++} + F^- = AlF^{++}$	1150	−8370	32	18
(2) $AlF^{++} + F^- = AlF_2^+$	780	−6850	26	12
(3) $AlF_2^+ + F^- = AlF_3(aq)$	190	−5250	18	3
(4) $AlF_3(aq) + F^- = AlF_4^-$	280	−3740	13	−3
(5) $AlF_4^- + F^- = AlF_5^{--}$	−750	−2220	5	−11
(6) $AlF_5^{--} + F^- = AlF_6^{---}$	−1550	−640	−3	−19
$Al^{+++} + 6F^- = AlF_6^{---}$	100	−27070	91	0

[a] The ΔF° values were measured at an ionic strength of 0.50, whereas the ΔH° values were measured at ionic strengths from 0.06 to 0.2.

Discussion of Results

There are two general factors which determine the entropy change in complex ion formation: (1) the entropy change involved in replacing a water molecule bound to the aqueous ion by the complexing ion or molecule; (2) the effect upon the surrounding water of changing the charge on the ion. For the first factor, we have in the case of complex fluorides

$$H_2O(\text{bound}) + F^-(aq) = H_2O(l) + F^-(\text{bound})$$
$$\Delta S^0 = 15.6 \text{ cal./deg. mole}$$

This ΔS^0 has been calculated using the values (in cal./deg. mole) of 9.4 for bound water, −2.3 for F^- (aq), 16.7 for $H_2O(l)$ and 6 for F^- bound to the aluminum. These values, previously given by Latimer,[5] are only approximate since the entropy of the bound water and fluoride will vary somewhat with the charge on the ion and with the coördination number, but they do give the magnitude of the entropy change associated with this process.

As an example of the reliability of such calculations we may cite the entropy changes in the formation of $Ag(NH_3)_2^+$ and $Cu(NH_3)_4^{++}$. For the reaction $H_2O(\text{bound}) + NH_3(aq) = H_2O(l) + NH_3(\text{bound})$, $\Delta S^0 = -5.5$ cal./deg. mole. In order to evaluate this ΔS^0 we have used the data of Hart and Partington[6] on the entropy of dissociation of 32 solid ammines to obtain the value 13.5 cal./deg. mole for the entropy of ammonia bound to a positive ion. The other values, H_2O(bound), 9.4, NH_3(aq), 26.3 and $H_2O(l)$, 16.7, are those given by Latimer.[5] Using $\Delta S^0 = -5.5$ units per ammonia, we may make the following comparison with the experimental values:

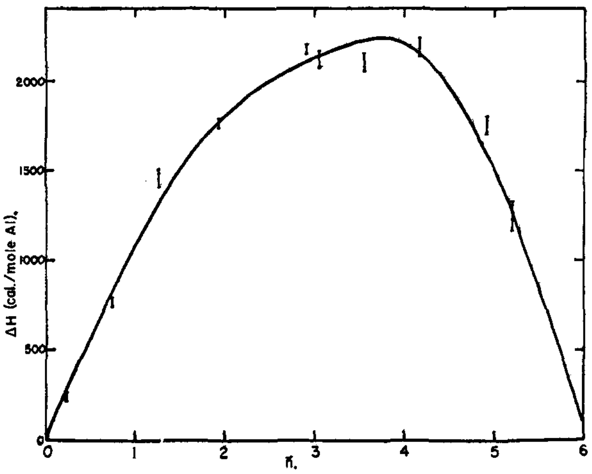

Fig. 1.

	ΔS^0 Exptl.	Calcd.
$Ag^+ + 2NH_3 = Ag(NH_3)_2^+$	−11.9 ± 0.5[7]	−11
$Cu^{++} + 4NH_3 = Cu(NH_3)_4^{++}$	−18 ± 3[8]	−22

In view of the approximate nature of the entropies of the bound molecules, the agreement is sufficient to indicate that this is the principal factor in the entropy of formation of these ions.

The second factor in the entropy of formation of complex ions is the effect of a change in total charge on the ion by the addition of a charged ion. In the case of the ammonia complex ions discussed above, this effect is zero since the ammonia molecule is neutral. However, in the formation of aluminum fluoride complexes, the charge changes from +3 in Al^{+++} to −3 in AlF_6^{---}. Powell and Latimer[9] have shown that for monatomic ions the partial molal entropies may be represented by an equation which contains the term $-270Z/(r + x)^2$, where Z is the charge, r the crystal radius in Å. units and x is 2 for positive ions and 1 for negative ions. This term represents the decrease in partial molal entropy due to the tying up of water by the interaction of the charge on the ion with water dipoles.

The agreement for the monatomic ions is excellent, but the quantitative application to complex ions fails because in general the total charge on the ion does not represent the effective charge for the solvent molecules in contact with the ion. How-

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[5] W. M. Latimer, "Oxidation Potentials," 2nd edition, Prentice-Hall, Inc., New York, N. Y., 1952, pp. 37, 52, 363.

[6] A. B. Hart and J. R. Partington, *J. Chem. Soc.*, 1943, 104.

[7] W. V. Smith, O. L. I. Brown and K. S. Pitzer, THIS JOURNAL, **59**, 1213 (1937).

[8] Calculated from the thermal data of Bouzat, *Ann. chim. phys.*, [7] **29**, 305 (1903), and the equilibrium constants given by J. Bjerrum, *Chem. Revs.*, **46**, 384 (1950).

[9] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951).

ever it is of interest to use our data for the aluminum fluoride complex ions to evaluate the charge effect for this series of reactions. For the over-all reaction $Al(H_2O)_6^{+++} + 6F^- = AlF_6^{---} + 6H_2O$, $\Delta S^0 = 91$. In our discussion above, we calculated 15.6 entropy units for the replacement of a water molecule by fluoride. For six fluorides this would be 93.6. The agreement with the experimental value of 91 is, of course, accidental but the calculation does show that in this case the charge effect is small. From the Powell and Latimer equation, one would predict about −15 for the effect since in general the solvation of negative ions is greater than positive ions because of the smaller value of x and the radii of $Al(H_2O)_6^{+++}$ and AlF_6^{---} are about equal. It is not surprising that the hydration of AlF_6^{---} is less than that predicted by the equation, as the effective charge on the surface of the ion is doubtless less than −3.

In the last column of Table VI the charge effect has been calculated for each step by subtracting the replacement entropy from the experimental entropy. It will be noted that the charge effect is symmetrical about the neutral molecule, again indicating that the effect is the same for the positive and negative ions. At present we have no method of estimating the hydration entropy for ions such as AlF^{++} or AlF_2^+, but the values calculated in Table VI form a basis for future comparisons.

The recent work of Jonte and Martin[10] on AgCl and $AgCl_2^-$ may be employed for such a comparison. These authors give

$$Ag^+ + Cl^- = AgCl(aq) \qquad \Delta S^0 = 6$$
$$AgCl(aq) + Cl^- = AgCl_2^- \qquad \Delta S^0 = 5$$

Using 10 for the entropy of bound Cl^- in AgCl and 11 for the value in $AgCl_2^-$, we calculate the replacement entropy as 4 for the first reaction and 6 for the second. The charge effect thus is 2 for the first and −1 for the second. These values are to be compared with 3 and −3 for the corresponding reaction of AlF_2^+ and AlF_3 with F^-. One would not expect that the charge effect would be exactly the same for ions of different size, such as $AgCl_2^-$ and AlF_4^-, but the agreement appears to confirm our interpretation that the contribution from the charge effect is small for reactions of this general type.

[10] J. H. Jonte and D. S. Martin, THIS JOURNAL, **74**, 2052 (1952).

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The Acid Strength of Halogens

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A consideration of the free energy of trihalide ions shows that the halogens can be classed as Lewis acids (electron acceptors) with decreasing acid strength as: ICl >> BrCl > IBr >> $I_2 > Br_2$ >> Cl_2, a classification which agrees with measurements on halogen complexes with aromatic hydrocarbons as well. A calculation of the free energy of isomerization of trihalide ions illuminates the fact that only those trihalide ions which have the heaviest atom in the middle position are known.

The molecular complexes between aromatic hydrocarbons and halogens which have been the subject of much interest in the last few years[1-6] are generally accepted to be examples of Lewis acid–base interactions in which the benzene, etc., acts as an electron donor ("base") and the halogen as an electron acceptor ("acid").

Of the three halogens whose complexes with benzene and other aromatic "bases" have been studied, ICl is the strongest "acid," followed by I_2 and then Br_2. This general rule is illustrated in Table I, which gives equilibrium constants[4,6] for the reaction

$$Ar + X_2 = Ar{\cdot}X_2$$

TABLE I

EQUILIBRIUM CONSTANTS FOR COMPLEX FORMATION

K_c in liters/mole CCl_4 solution at 25°

Base → Acid	Benzene	*p*-Xylene	Hexamethylbenzene	Naphthalene
ICl	0.54	1.51	22.7	1.39
I_2	.15	0.31	1.35	0.25
Br_2	.11	.23		

The formation of trihalide ions can also be regarded as a similar complexing reaction between a halide ion (base) and a halogen molecule (acid). Superficially, however, no regularity is found; for example, I_3^- is the stablest trihalide ion, although we might expect I_2Cl^- to be more stable since ICl is a stronger acid than I^-. As a result, the stability of the trihalides is usually discussed in terms of a number of empirical rules.[7]

This difficulty is resolved when we recognize that an unsymmetrical trihalide ion can be formed (and conversely, decompose) in two different ways

$$X\text{-}Y + Z^- \overset{K_1}{\rightleftarrows} [X\text{-}Y\text{-}Z]^-; \quad X^- + Y\text{-}Z \overset{K_2}{\rightleftarrows} [X\text{-}Y\text{-}Z]^-$$

The equilibrium constant K_1 measures the acid strength of XY and the base strength of Z^-; K_2, on the other hand, measures the acid strength of YZ and the base strength of X^-. The experimentally reported values are invariably for the reaction with smaller K; the other one can however be calculated by standard thermodynamic methods if the free energies of

[1] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **70**, 2832 (1948); **71**, 2703 (1949).

[2] R. S. Mulliken, *ibid.*, **72**, 600 (1950); **74**, 811 (1952).

[3] T. M. Cromwell and R. L. Scott, *ibid.*, **72**, 3825 (1950).

[4] R. M. Keefer and L. J. Andrews, *ibid.*, **72**, 4677, 5170 (1950).

[5] N. W. Blake, H. Winston and J. A. Patterson, *ibid.*, **73**, 4337 (1951).

[6] L. J. Andrews and R. M. Keefer, *ibid.*, **74**, 4500 (1952).

[7] See, for example, N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, pp. 1190–1197.