For molecules to have a significant number of bromine atoms the ratio of Br/Cl pressure must be large. The ratio in experiments 1–5 was approximately 6×10^4.

The decrease of moles of iron halide in the vapor with temperature is more pronounced than in the chloride system. The heats of reactions 4 and 5 are *ca.* 6.44 and 16.3 kcal., respectively; $-2.3R\cdot[\Delta \log n(\text{Fe})/n(\text{Br}_2)/(\Delta 1/T)]$ in the present system is 18.1 kcal. These values are not strictly comparable, however; the latter must be considered as a composite of a number of possible reactions and also does not allow for the difference in degree of dissociation of dimers to monomers at the two temperatures.

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The Fluoride Complexes of Zinc, Copper and Lead Ions in Aqueous Solution

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The equilibrium quotient for the reaction $\text{Zn}^{++} + \text{HF} = \text{ZnF}^{+} + \text{H}^{+}$ at 25° and an ionic strength of 0.50 has been determined to be $(6.6 \pm 1) \times 10^{-3}$. The corresponding value for cupric ion is $(6.2 \pm 1) \times 10^{-3}$. The reactions written as $\text{M}^{+2} + \text{F}^{-} = \text{MF}^{+}$ have equilibrium quotients of 5.4 ± 1 and 5.0 ± 1 for zinc and copper, respectively, under the same experimental conditions. Extrapolation of the latter values to zero ionic strength gives estimated values of 18 ± 4 and 17 ± 4, respectively, for the equilibrium constants. From measurements at 15 and 35° approximate values for ΔH and ΔS of the above reactions were obtained. The fluoride complex of Pb^{++} was too unstable to be detected unambiguously. An upper limit was set to its stability.

In recent years there has been interest in the stability of complexes formed between metal ions and fluoride ions in aqueous solution. In addition to the importance arising from the relatively high stability of many of these complexes, they should provide a simple series for the testing of any theory of ionic complexing.

The stability constants of the fluoride complexes of only three cations of charge +2 have previously been determined. Therefore it was desirable to extend the measurements to other cations and in particular to some of the elements of the first long series. Zinc, copper and lead were selected for study. Complexing constants previously had been measured for Be^{++},[1,2] Mg^{++}[3] and Sn^{++}.[4]

A potentiometric method[5] was used in which the concentration of the complexed fluoride was determined by measuring the change in fluoride complexing of ferric ion in the same solution. The latter was detected by the ferrous–ferric potential.

Experimental

The apparatus and procedure have been described in detail elsewhere.[3,6,7] Briefly, three half-cells A, B and C were prepared for each experiment with the same initial concentrations of $\text{Fe(ClO}_4)_3$, $\text{Fe(ClO}_4)_2$ and HClO_4. Half-cell A contained in addition a known concentration of zinc, copper or lead perchlorate. The ionic strengths of all were adjusted to 0.500 *M* with sodium perchlorate and the volumes were equal. To half-cells A and B were added measured volumes of 0.500 *M* sodium fluoride and the potentials of A–C and B–C were measured after each addition. Correction was made for the small initial potentials with no added fluoride which averaged 0.20 millivolt for the experiments.

Stock solutions of zinc perchlorate, cupric perchlorate and plumbous perchlorate were prepared by solution of the corresponding oxide in perchloric acid. The preparation of the other solutions has been given previously.[7] All concentrations are expressed in moles per liter, *M*, at room temperature.

The data for a typical experiment are shown in Table I. The potentials in the second and third columns are in millivolts, mv. In Table II are given the initial concentrations and highest stoichiometric fluoride concentrations, (ΣF^{-}), for all of the experiments. The complete data for the experiments may be found elsewhere.[8]

TABLE I

COMPLEXING OF ZINC ION BY FLUORIDE ION AT 25°

Initial concentrations: $\text{HClO}_4 = 0.005338$ *M*; $\text{Zn(ClO}_4)_2 = 0.08676$ *M*; $\text{Fe(ClO}_4)_2 = 0.0002221$ *M*; $\text{Fe(ClO}_4)_3 = 0.0006838$ *M*; $\text{NaClO}_4 = 0.2296$ *M*. Ionic strength = 0.5000 *M*; initial vol. = 110.06 ml.; NaF = 0.5000 *M*.

NaF added to cells A and B (ml.)	$E_{\text{B-C}}$ (mv.)	$E_{\text{A-C}}$ (mv.)	$\bar{n}$	$(\text{HF})/(\text{H}^{+})$
0.0489	8.65	8.26	0.00012	0.00272
.0978	19.51	18.91	.00014	.00888
.1467	32.43	31.57	.00017	.01532
.1956	46.32	45.15	.00021	.02740
.2445	59.07	58.02	.00022	.04312
.2934	71.97	70.23	.00030	.0628
.3423	83.42	81.05	.00056	.0849
.3912	93.98	90.70	.00082	.1088
.4648	108.12	105.41	.00109	.1545
.5384	120.84	116.46	.00118	.1974
.6120	132.14	127.71	.00154	.2500
.6856	142.13	136.12	.00250	.2961
.7592	151.28	142.19	.00370	.3333

Analysis of Results

The interpretation of the data follows that of references 3 and 7. The difference between the total fluoride concentrations in the sample half-cell A and the reference half-cell B at the same potential equals the concentration of fluoride com-

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(1) H. W. Dodgen and L. M. Yates, private communication.

(2) K. E. Kleiner, *J. Gen. Chem.* (*U.S.S.R.*), **21**, 19 (1951); Consultants Bureau Translation.

(3) R. E. Connick and Maak-Sang Tsao, THIS JOURNAL, **76**, 5311 (1954).

(4) W. B. Schaap, J. A. Davis and W. H. Nebergall, *ibid.*, **76**, 5226 (1954).

(5) C. Brosset and G. Orring, *Svensk. Kem. Tid.*, **55**, 101 (1943).

(6) H. W. Dodgen and G. K. Rollefson, *ibid.*, **71**, 2600 (1949).

(7) L. G. Hepler, J. W. Kury and Z. Z. Hugus, Jr., *J. Phys. Chem.*, **58**, 26 (1954).

(8) Armine D. Paul, Thesis, University of California, Berkeley, April, 1955; printed as unclassified University of California Radiation Laboratory Report UCRL-2926.

TABLE II

CONDITIONS FOR INDIVIDUAL EXPERIMENTS

Temp., °C.	$M(ClO_4)_2$,[a] $M \times 10^2$	$HClO_4$, $M \times 10^3$	$Fe(ClO_4)_3$,[b] $M \times 10^4$	$NaClO_4$, M	Highest (ΣF^-), $M \times 10^3$
			Zinc		
15, 25, 35	8.676	5.338	6.838	0.2296	3.4 to 4.0
15, 25, 35	2.779	5.699	7.299	.4058	3.7 to 4.3
15, 25, 35	2.779	21.64	7.299	.3899	7.5 to 7.7
			Copper		
15, 35	8.667	22.85	6.838	0.2127	7.8, 8.9
15, 35	4.543	12.83	7.161	.3396	6.4, 5.3
15, 35	4.543	22.60	7.161	.3361	7.2, 7.8
25	1.874	9.988	3.765	.4305	4.5
25	4.558	12.63	3.658	.3473	4.3
25	8.703	23.24	3.492	.2126	6.6
			Lead		
25	4.562	10.89	3.658	0.3490	3.2
25	1.876	3.471	3.765	.4366	3.7

[a] M = Zn, Cu or Pb. [b] The concentration of ferrous perchlorate was approximately one third that of ferric perchlorate in all experiments except those for lead and copper at 25° where the two iron concentrations were nearly equal.

plexed by the zinc, copper or lead. Division of this quantity by the total zinc, copper or lead concentration yields $\bar{n}$ (see column 4 of Table I).

It was assumed, and then confirmed by the fit of the data, that the only important equilibrium involving the +2 cation under investigation was the formation of the first fluoride complex where

$$M^{+2} + HF = MF^+ + H^+$$

$$Q_1 = \frac{(MF^+)(H^+)}{(M^{+2})(HF)}$$

parentheses represent concentrations in moles per liter and Q designates the equilibrium quotient expressed in concentrations. Rearrangement yields

$$\frac{1}{1 - \frac{(MF^+)}{(\Sigma M^{+2})}} = \frac{1}{1 - \bar{n}} = 1 + Q_1 \frac{(HF)}{(H^+)} \qquad (1)$$

where (ΣM^{+2}) indicates the total concentration of the +2 cation in half-cell A. The quantity $(HF)/(H^+)$ in half-cell A is essentially equal to that in half-cell B at the same potential and was calculated using the equilibrium quotients shown in Table III,[9] equation 22 of reference 7, and the relation

$$(\Sigma H^+) = (H^+) + (HF) + (FeOH^{+2})$$

TABLE III

EQUILIBRIUM QUOTIENTS USED IN CALCULATIONS[9]

	Q_1	Q_2	Q_3	$Q_H \times 10^3$	$Q_{HF} \times 10^3$
15°	192	11.5	1.0	1.18	1.42
25°	184	10.3	1.0	1.9	1.23
35°	178	10.0	1.0	3.2	1.01

The equilibrium quotients Q_1, Q_2 and Q_3 refer to the successive formation constants of ferric fluoride complexes containing the number of fluorides indicated by the subscript and with one HF consumed and one H^+ formed in each case. The hydrolysis constant of ferric ion to form $FeOH^{+2}$ is indicated by Q_H and the ionization constant of HF by Q_{HF}. All Q's are for an ionic strength of 0.50. Since the calculations were made, Milburn[10] has published new values for the ΔH of hydrolysis of ferric ion from which new values of Q_H can be calculated for 15 and 35°. It was found, however, that these values do not change the calculations significantly. The hydrolysis of ferrous ion[11] and the formation of HF_2^-[12] were negligible for all experiments.

Because of the weakness of the complexing and the resulting small, experimental effects, it is necessary to verify that the approximations made in the interpretation can be justified. The assumption of constant activity coefficients at essentially constant ionic strength has been discussed for a similar case.[3] The assumption of no fluoride complexing of ferrous ion,[6] if not strictly valid, would produce only a small change in the calculated $(HF)/(H^+)$. The neglect of the small volume difference between A and B at the same potential is justified. The dimerization of the hydrolyzed ferric species, $FeOH^{+2}$ was ignored in the calculations. Using results of Milburn[10] it is calculated that correction for this species would in the worst case raise the value of $(HF)/(H^+)$ by 2%, which change will affect the final result less than the experimental error.

According to equation 1 a plot of $1/(1 - \bar{n})$ *vs.* $(HF)/(H^+)$ should yield a straight line of intercept unity and slope equal to Q_1. Such plots of the data are shown for zinc and copper at 25° in Figs. 1 and 2. It is believed that the data fit a straight line within the experimental accuracy for the range of acidity, metal ion concentrations, and fluoride concentrations shown in Table II. The values of Q_1 deduced from these and similar plots are given in Table IV along with the equilibrium quotients for the complexing reactions written in terms of fluoride ion.

In Table V are given the thermodynamic quantities derived from the equilibrium quotients. The uncertainties listed for ΔH and ΔS were calculated using the highest values of K at 15° in Table IV in combination with the lowest values of K at 35°, and *vice versa*. An estimate was made of the equilibrium constant (*i.e.*, zero ionic strength value of Q) for the reaction $M^{+2} + F^- = MF^+$ at 25° using the empirical equation given by Näsänen[13] for $CuCl^+$. Values of 18 ± 4 and 17 ± 4 were obtained for zinc and copper, respectively.

For the first lead experiment of Table II the potentials of cells A–C and B–C were essentially the same up to a total fluoride concentration of 3.2×10^{-3} M. In the second experiment, where the acidity was decreased by a factor of 3, the potentials of the two cells were still the same up to a total fluoride concentration of 2×10^{-3} M, and it was only when the fluoride concentration was increased to 4×10^{-3} M that a difference of 0.25 millivolt, which may be significant, was obtained. Precipitation of lead fluoride prevented the attainment of higher fluoride concentrations.

If one assumes the maximum voltage difference between the two cells in the second experiment might have been 0.5 millivolt, then at $\mu = 0.50$

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[9] R. E. Connick, L. G. Hepler, Z. Z. Hugus, Jr., J. W. Kury, W. M. Latimer and Maak-Sang Tsao, THIS JOURNAL, **78**, 1827 (1956).

[10] R. M. Milburn, *ibid.*, **79**, 537 (1957).

[11] D. M. Leussing and I. M. Kolthoff, *ibid.*, **75**, 2476 (1952).

[12] W. M. Latimer, "Oxidation Potentials," Prentice-Hall Book Co., Inc., New York, N. Y., 1952.

[13] R. Näsänen, *Acta Chem. Scand.*, **4**, 140 (1950).

TABLE IV

VALUES OF EQUILIBRIUM QUOTIENTS FOR FLUORIDE COMPLEXING OF Zn^{++} AND Cu^{++} AT AN IONIC STRENGTH OF 0.50

Reaction	15°	25°	35°
$Zn^{++} + HF = ZnF^+ + H^+$	$(7.0 \pm 1) \times 10^{-3}$	$(6.6 \pm 1) \times 10^{-3}$	$(5.4 \pm 1) \times 10^{-3}$
$Zn^{++} + F^- = ZnF^+$	5.0 ± 1	5.4 ± 1	5.4 ± 1
$Cu^{++} + HF = CuF^+ + H^+$	$(7.4 \pm 1) \times 10^{-3}$	$(6.2 \pm 1) \times 10^{-3}$	$(5.6 \pm 1) \times 10^{-3}$
$Cu^{++} + F^- = CuF^+$	5.2 ± 1	5.0 ± 1	5.6 ± 1

TABLE V

THERMODYNAMIC FUNCTIONS FOR FLUORIDE COMPLEXING OF Zn^{++} AND Cu^{++} AT AN IONIC STRENGTH OF 0.50 AND 25°

Reaction	ΔF_{298}, kcal./mole	ΔH_{298}, kcal./mole	ΔS_{298}, e.u.
$Zn^{++} + HF = ZnF^+ + H^+$	2.9 ± 0.1	-2.3 ± 2.4	-17 ± 9
$Zn^{++} + F^- = ZnF^+$	$-1.0 \pm .1$	1.5 ± 2.4	8 ± 9
$Cu^{++} + HF = CuF^+ + H^+$	$3.0 \pm .1$	-2.6 ± 2.7	-19 ± 9
$Cu^{++} + F^- = CuF^+$	$-0.95 \pm .1$	0.9 ± 2.7	6 ± 9

and 25° an upper limit for Q_1 of 2×10^{-3} is obtained. For the complexing reaction written in terms of fluoride ion the upper limit is 2 at μ = 0.5 and estimated to be 6 at zero ionic strength.

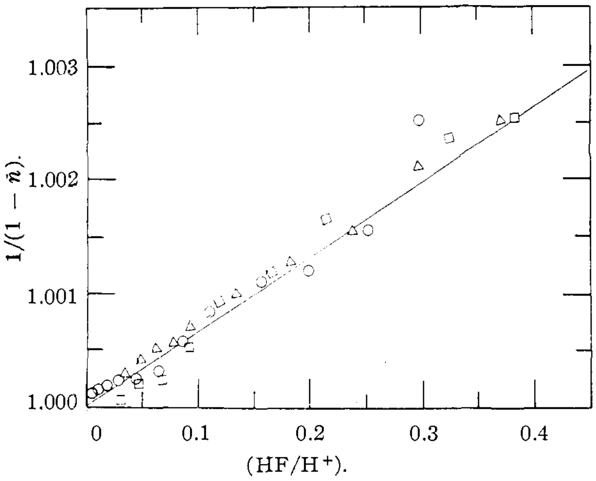

Fig. 1.—Fluoride complexing of zinc ion at 25° and ionic strength 0.50: ○, □ and △—first, second and third experiments of Table II, respectively.

From Table I and Figs. 1 and 2 it is apparent that only a small fraction of the added +2 ion was complexed. Consequently it was to be expected that small amounts of impurities in the +2 metal salt could invalidate the results, and such was found to be the case. For zinc, separate experiments were run at 25° using zinc perchlorate prepared from Mallinckrodt Analytical Reagent ZnO, Merck Reagent ZnO, and Baker's Analyzed ZnO. The values of Q_1 obtained were 6.6×10^{-3}, 5.7×10^{-3} and 1.2×10^{-2}, respectively. Impurities would be expected to give high values. The Mallinckrodt and Merck values agree within the experimental accuracy and constitute a check on the reliability of the data. Although the Merck value was slightly lower, the zero readings in those experiments were quite high, and therefore the Mallinckrodt values are reported in Table IV. Spectrographic analysis later showed the Baker sample to contain *ca.* 0.2% titanium.

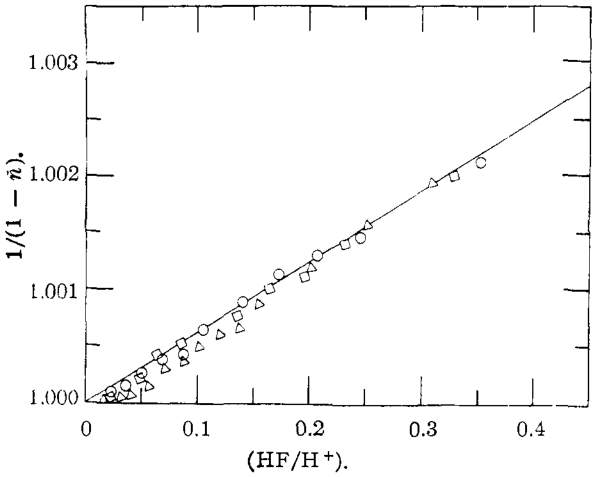

Fig. 2.—Fluoride complexing of cupric ion at 25° and ionic strength 0.50: □, ○ and △—first, second and third copper experiments at 25° of Table II, respectively.

Similarly separate experiments at 25° using cupric perchlorate prepared from Mallinckrodt, Baker, and Baker and Adamson CuO gave values of Q_1 of 6.2×10^{-3}, 6×10^{-2} and 7.4×10^{-3}. The Baker and Adamson and Mallinckrodt values agree within the experimental accuracy, and the latter material was used for the experiments of Table IV. The Baker sample was found by spectrographic analysis to contain 0.2 per cent. iron.

The comparison of the fluoride complexing constants of copper and zinc with those of other +2 ions will be reserved for a later paper.

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