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THE COMPLEXING OF CERIUM (III), LANTHANUM (III) AND GADOLINIUM (III) BY FLUORIDE IONS IN AQUEOUS SOLUTION

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J. W. Kury, Z. Z. Hugus, Jr., and W. M. Latimer

January 31, 1957

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THE COMPLEXING OF CERIUM (III), LANTHANUM (III) AND GADOLINIUM (III) BY FLUORIDE IONS IN AQUEOUS SOLUTION[1]

By J. W. Kury, Z. Z. Hugus, Jr.,[2] and W. M. Latimer[3]

Contribution from the University of California Radiation Laboratory, and the Department of Chemistry and Chemical Engineering, University of California, Berkeley, California

January 31, 1957

ABSTRACT

The equilibrium quotients for the formation of CeF^{+2}, LaF^{+2} and GdF^{+2} in aqueous solution have been determined at an ionic strength of 0.50 and a temperature of 25° by means of the "ferri" method.

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(1) This work was performed under the auspices of the U. S. Atomic Energy Commission.

(2) School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota.

(3) Deceased.

THE COMPLEXING OF CERIUM (III), LANTHANUM (III) AND GADOLINIUM (III) BY FLUORIDE IONS IN AQUEOUS SOLUTION

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During the course of experiments in this Laboratory on the solubilities of rare-earth fluorides, it became necessary to measure the extent of complexing of cerium (III), lanthanum (III) and gadolinium (III) by fluoride ions. The experimental technique employed is based upon the competition between the rare-earth ion and iron (III) for fluoride ions in a ferrous-ferric concentration cell ("ferri" method).[4,5]

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

(5) H. W. Dodgen and G. K. Rollefson, J. Am. Chem. Soc., 71 2600 (1949).

Experimental

Cells.--The two concentration cells, A-C and B-C, and the potentiometer circuit have been previously described.[6,7]

(6) L. G. Hepler, J. W. Kury and Z Z. Hugus, Jr., This Journal, 58, 26 (1954).

(7) J. W. Kury, University of California Radiation Laboratory Report UCRL-2271, July, 1953.

Solutions.--The preparation of stock solutions of sodium fluoride, sodium perchlorate, perchloric acid and ferrous perchlorate-

ferric perchlorate-perchloric acid has also been previously described.[6,7] A stock solution of cerous perchlorate in perchloric acid was prepared in the following manner. Analytical reagent "ammonium hexanitrato cerate" was dissolved in distilled water. This solution was added with vigorous stirring to 2 M ammonium hydroxide. The light yellow precipitate was filtered and washed with distilled water. This hydrous ceric hydroxide was dissolved in perchloric acid and reduced with analytical grade 35% hydrogen peroxide. The resulting solution was boiled and, after several days, was filtered through sintered glass. The cerium (III) concentration was determined in a manner similar to that described by Smith.[8]

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(8) G. F. Smith, "Cerate Oxidimetry," G. F. Smith Chemical Co., Columbus, Ohio, 1942, p. 49.

After adding an excess of sodium fluoride to precipitate all the cerium, the perchloric acid concentration was determined by titrating with carbonate-free sodium hydroxide to a phenolphthalein end point. A stock solution of lanthanum perchlorate in perchloric acid was prepared by dissolving a known weight of lanthanum oxide in standard perchloric acid. Spectrographic analysis showed that the lanthanum oxide contained no other rare earths and less than 0.01% of Al, Ca, Fe or Si. The gadolinium perchlorate-perchloric acid stock solution was prepared by dissolving a known weight of gadolinium oxide (Research Chemicals, Inc. -- 0.8% Sm and 0.1% Dy) in standard perchloric acid.

Experimental Procedure.--All experiments were carried out at 25.00 ± 0.01°C and at an ionic strength of 0.50. Before each run the assembled cells and the stock solutions were brought to the temperature of the experiment.

One-hundred ml. aliquots of stock solution containing the desired concentrations of ferrous perchlorate, ferric perchlorate, perchloric acid and sodium perchlorate were pipetted into half-cells A, B, and C. A known volume of standard rare-earth perchlorate-perchloric acid solution was added to half-cell A. An equal volume of sodium perchlorate-perchloric acid solution, equivalent to the rare-earth

solution in total ionic strength and in acid concentration, was added to half-cells B and C.

Stirrers were activated and the potentials of half-cells A and B were measured with respect to reference half-cell C. After the small initial potentials (usually less than 0.3 mv.) had become constant, aliquots of standard sodium fluoride solution were added to half-cells A and B. The potentials of the cells were read after each addition. The stirrers were left on both while adding sodium fluoride and while reading the potential. The potential E_{B-C} became constant to a few hundredths of a millivolt within a minute after each addition. This was also true for E_{A-C} at low total fluoride concentrations in half-cell A. At high total fluoride concentrations though, E_{A-C} began to drift downward due to slow precipitation of the rare-earth fluoride. The noticeable onset of this downward drift in E_{A-C} approximately coincided with the appearance of a Tyndall beam in half-cell A.

Experimental Results.[9]--In all, four runs were made for both lanthanum and cerium, and one run was made for gadolinium.

(9) The data for all the runs are presented in Reference (7).

Table I

Experimental Conditions and Results for Cerium Run IV

$(\Sigma Ce_i^{+3})_A = 0.00829$ M

$(\Sigma H_i^+)_A = 0.05614$ M

$(V_i)_A = 109.9$ ml.

T = 25.00 ± 0.01°

$\mu = 0.50$

$(\Sigma F^-)_A$ x 10^4 (moles/l)	E_{A-C} (mv.)	V_A (ml.)	$(\Sigma F^-)_B$ x 10^4 (moles/l)	E_{B-C} (mv.)	V_B (ml.)
3.13	8.69	110.0	3.13	10.28	110.0
6.26	17.80	110.1	6.26	20.18	110.1
9.39	25.70	110.2	9.39	28.89	110.2
12.51	32.30	110.2	12.51	36.47	110.2
15.62	37.94	110.3	15.62	43.05	110.3
18.74	42.71	110.4			

Table I presents the data for cerium run IV. $(\Sigma Ce_i^{+3})_A$, $(\Sigma H_i^+)A$ and $(V_i)_A$ are, respectively, the initial total cerium (III) concentration, initial total hydrogen ion concentration, and initial volume in half-cell A. $(\Sigma F^-)_A$ and $(\Sigma F^-)_B$ refer to the total fluoride concentrations in half-cells A and B. The total initial iron (III) and iron (II) concentrations, (ΣFe_i^{+3}) and (ΣFe_i^{+2}) respectively, were approximately 5×10^{-4} M in all the half-cells.

The initial conditions for all the runs are given in Table II. In each run anywhere from 5 to 11 e.m.f. determinations were made at different fluoride concentrations.

Table II

Initial Conditions for Individual Experiments

$\mu = 0.50$

$T = 25.00^{\circ}$

$(\Sigma Fe_i^{+3}) \sim 5 \times 10^{-4}$ M

$(\Sigma Fe_i^{+2}) \sim 5 \times 10^{-4}$ M

Metal	Run	(ΣH_i^+) M	$(\Sigma M_i^{+3}) \times 10^3$ M
Cerium	I	0.0566	4.21
	II	0.0987	4.34
	III	0.0507	1.79
	IV	0.0561	8.29
Lanthanum	I	0.0545	8.88
	II	0.0996	8.88
	III	0.0562	1.28
	IV	0.0527	4.65
Gadolinium	I	0.0498	2.77

Analysis of Results

In Fig. 1, E_{B-C} and E_{A-C} (up to the point of precipitation) are plotted as a function of the total fluoride concentration for cerium run IV. The fact that the two curves are not identical, and also that one does not observe a Tyndall effect in half-cell A over this range, indicates the presence of complex fluorides of cerium (III).

It is possible to interpret satisfactorily the experimental results by assuming the presence of only the simplest complexed species, MF^{+2} (M = cerium, lanthanum or gadolinium). The equilibria in question are:

$$Fe^{+3} + HF = FeF^{+2} + H^+ \qquad K_1 \qquad (1)$$

$$FeF^{+2} + HF = FeF_2^{\ +} + H^+ \qquad K_2 \qquad (2)$$

$$Fe^{+3} + H_2O = FeOH^{+2} + H^+ \qquad K_H \qquad (3)$$

$$HF = H^+ + F^- \qquad K_{HF} \qquad (4)$$

$$M^{+3} + HF = MF^{+2} + H^+ \qquad K_3 \qquad (5)$$

where the K's are equilibrium quotients, for example:

$$K_3 = \frac{(MF^{+2})_A\ (H^+)_A}{(M^{+3})_A\ (HF)_A}\ . \qquad (6)$$

Concentration in moles/l in half-cell A is represented by $(\ )_A$. The values of K_1, K_2, K_H and K_{HF} at 25° used in these calculations are given in Table III.[10]

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(10) R. E. Connick et.al., J. Am. Chem. Soc., 78, 1827 (1956).

Table III

Values of Equilibrium Quotients Used in Calculations

$\mu = 0.50$	$T = 25.0^{\circ}$
$K_1 = 184$	$K_H = 1.9 \times 10^{-3}$
$K_2 = 10.3$	$K_{HF} = 1.23 \times 10^{-3}$

We shall now define $\Delta(\Sigma F^-)$ as:

$$\Delta(\Sigma F^-) = (\Sigma F^-)_A - (\Sigma F^-)_B \tag{7}$$

at $E_{A-C} = E_{B-C}$. Since half-cells A and B have the same (ΣH_i^+), (ΣFe_i^{+3}) and (ΣFe_i^{+2}), and since $V_A = V_B$ to within a few tenths of a percent, $\Delta(\Sigma F^-)$ is a measure of the fluoride ions complexing M^{+3}. Stoichiometric considerations give:

$$(\Sigma M^{+3})_A = (M^{+3})_A + (MF^{+2})_A \tag{8}$$

$$\Delta(\Sigma F^-) = (MF^{+2})_A. \tag{9}$$

Combination of equations (6), (8) and (9) yields:

$$\frac{\Delta(\Sigma F^-)}{(\Sigma M^{+3})A - \Delta(\Sigma F^-)} = K_3(HF/H^+)_A \tag{10}$$

If we plot $(HF/H^+)_A$ vs. $\dfrac{\Delta(\Sigma F^-)}{(\Sigma M^{+3})_A - \Delta(\Sigma F^-)}$, we should obtain a

straight line of slope K_3 and intercept zero (Fig. 2).[11]

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(11) The deviation of the experimental point from the straight line in Fig. 2 at the larger fluoride ion concentrations indicates the presence of a small amount of a higher complex, such as CeF_2^+.

$\Delta(\Sigma F^-)$ and $(\Sigma M^{+3})_A$ are calculated directly from the experimental data. Since $(HF/H^+)_A = (HF/H^+)_B$ when $E_{A-C} = E_{B-C}$, $(HF/H^+)_A$ can be calculated from equations (11) and (12).[12]

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(12) These equations have been derived in references (6) and (10).

$$\left\{1 + \frac{K_H}{(H^+)_B}\right\}\left\{e^{\mp E/RT} - 1\right\} = K_1\left(\frac{HF}{H^+}\right)_B + K_1K_2\left(\frac{HF}{H^+}\right)_B^2 . \quad (11)$$

$$(\Sigma H^+)_B \cong (H^+)_B + (HF)_B . \quad (12)$$

The values obtained for K_3 are presented in Table III.

Table III

Equilibrium Quotients for the Fluoride Complexing of Cerium (III), Lanthanum (III) and Gadolinium (III)

$T = 25^{\circ}$ $\mu = 0.50$

Reaction	Run	K_3
$Ce^{+3} + HF = CeF^{+2} + H^{+}$	I	1.5
	II	1.7
	III	1.4
	IV	1.7
	average	1.6
$La^{+3} + HF = LaF^{+2} + H^{+}$	I	0.62
	II	0.60
	III	0.55
	IV	0.57
	average	0.59
$Gd^{+3} + HF = GdF^{+2} + H^{+}$	I	2.9

The following assumptions were made in the above calculations. The hydrolysis of the rare-earth ion and ferrous ion is negligible at the acidities used. There is no fluoride complexing of ferrous ion and the amount of bifluoride present in any of the solutions is negligible. There is no change in activity coefficients when rare-earth perchlorate is replaced by sodium perchlorate at constant total ionic strength. The perchlorate complexing of the rare-earth ions has been neglected. Any such complexing would however be absorbed in K_3.[13]

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(13) Recently Heidt and Berestecki[14] have given a value for the

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(14) L. J. Heidt and J. Berestecki, J. Am. Chem. Soc., 77, 2049 (1955).

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equilibrium quotient, K_c, at $\mu = 0.50$ and $T = 25.0$:

$$K_c = \frac{\left[Ce(ClO_4)^{+2}\right]}{(Ce^{+3})(ClO_4^-)} = 5.0 \ . \qquad (13)$$

Using this value of K_c, one obtains a K_3° of 5.4 for the following reaction at $T = 25.0^{\circ}C$ and $\mu = 0.50$:

$$Ce^{+3} + HF = CeF^{+2} + H^+ \qquad K_3^{\circ} . \qquad (14)$$

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