

also makes contacts with three Cl atoms at 3.54–3.61 Å and with two I atoms at 3.97 Å. Although these contacts are about 0.2 Å short of the sums of the usual van der Waals radii, they cannot be considered to be bonds. Thus selenium forms three strong bonds and there is no indication of secondary bonding of the type found in $C_4H_8OSeI_2$ ¹⁰ and in $C_4H_8SeI_2$.¹¹ The Se–I bond of 2.630 Å is the shortest reported thus far, and, presumably, as a result, the I–Cl bond is lengthened from its uncomplexed value of 2.32 to 2.73 Å. This situation

(11) H. Hope and J. D. McCullough, *Acta Cryst.*, **17**, 712 (1964).

and the fact that the chlorine forms no other bonds than the weak one to iodine suggest that there is considerable ionic character in the I–Cl bond. This is a step in the direction of the formation of a selenonium salt, $[C_4H_8OSeI]^+Cl^-$.

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Ceric Ion Equilibrium in Aqueous Acetic Acid¹

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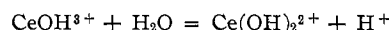
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The equilibria among cerium(IV) species in aqueous acetic acid have been studied spectrophotometrically. In contrast to earlier studies, the principal equilibrium was found to involve monomeric and trimeric cerium(IV) species with the dimer being relatively unimportant. This equilibrium responds to the inverse cube of the acid concentration.

Introduction

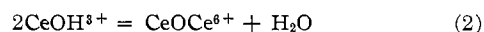
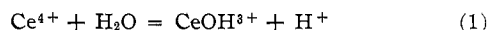
The oxidation of aldehydes, ketones, and similar compounds having an α -hydrogen using a variety of oxidizing agents usually leads to attack at the α position. In fact, many oxidants such as copper(II), iron(III), and thallium(III) do not react with benzaldehyde or pivalaldehyde under ordinary conditions. Ceric ion is interesting in that it is capable of effecting oxidation at the carbonyl function and readily oxidizes benzaldehyde to benzoic acid. In order to interpret the data obtained in studying the latter reaction, it was necessary to study the nature of the cerium(IV) species present in solution. Since most interesting organic substrates are at best sparingly soluble in water, aqueous acetic acid was chosen as the solvent. This solvent is relatively inert to oxidants and has frequently been used in the study of oxidation reactions.

A number of studies have been made on the equilibria between various forms of cerium(IV) in aqueous solution. Smith and Goetz³ found the oxidation potential of the Ce(III)–Ce(IV) couple to increase with increasing perchloric acid concentration. Sherrill, King, and Spooner⁴ showed the increase in potential to be independent of the perchlorate ion concentration and concluded that neither Ce(III) nor Ce(IV) reacts with perchlorate and that Ce(IV) is hydrolyzed even in strongly acidic solution. They estimated an equilibrium constant for the second hydrolysis reaction



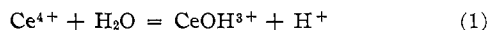
However, their constant did not include a correction for the presence of polymeric Ce(IV) species which were observed in later investigations.

Heidt and Smith, in studying the photooxidation of water by ceric perchlorate, concluded that cerium(IV) dimers must have been present.⁵ King and Pandow⁶ observed deviations from Beer's law in the spectral range 440–530 $m\mu$ for 4×10^{-4} to 0.1 M cerium(IV) solutions in aqueous perchloric acid. Hardwick and Robinson observed similar deviations from Beer's law from 395 to 430 $m\mu$.⁷ Their quantitative study for solutions in 0.2–2.0 M perchloric acid appeared consistent with the model



Here, $K_1 = 5.2$ and $K_2 = 16.2$ at 25°. Migration experiments confirmed the presence of only positively charged ceric species in solution.

More recently, Baker, Newton, and Kahn determined equilibrium constants for the hydrolysis of cerium(IV) in perchloric acid solution in connection with a kinetic study of the U(IV)–Ce(IV) reaction.⁸ The constants obtained for the equilibria



were $K_1 > 15$ and $K_3 = 0.15$ at 25°. They concluded that $CeOH^{3+}$ is the predominant species at 2.0 M

(5) L. J. Heidt and M. E. Smith, *ibid.*, **70**, 2476 (1948).

(6) E. L. King and M. L. Pandow, *ibid.*, **74**, 1966 (1952).

(7) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 818 (1951).

(8) F. B. Baker, T. W. Newton, and M. Kahn, *J. Phys. Chem.*, **64**, 109 (1960).

(1) This investigation was supported by the National Science Foundation. Taken from part of the Ph.D. thesis of P. C. Ford, 1967.

(2) NIH predoctoral fellow, 1963–1966.

(3) G. F. Smith and C. A. Goetz, *Ind. Eng. Chem., Anal. Ed.*, **10**, 191 (1938).

(4) M. S. Sherrill, C. B. King, and R. C. Spooner, *J. Am. Chem. Soc.*, **65**, 170 (1943).

perchloric acid. Equilibrium constants more consistent with those of Hardwick and Robertson were obtained by Stead from his investigation of the cerium(IV)–mercury(I) and cerium(IV)–thallium(I) reactions.⁹ His values were $K_1 = 4.8$ – 7.2 and $K_3 = 0.2$ – 0.09 at 20° . Other studies of these equilibria have been reported by Kraus, Homberg, and Nelson¹⁰ and by Blaustein and Gryder.¹¹

In contrast to solutions containing perchlorate as the anion, cerium(IV) is found complexed with the anion when nitrate^{11,12} or sulfate^{13,14} is present. It seems safe to conclude that cerium(IV) will form a complex with any nucleophilic ion present in the reaction medium.

Results

The equilibria among the various cerium(IV) species were studied spectrophotometrically using ranges of 10^{-4} to 4×10^{-2} *M* cerium(IV), 0.05 – 1.0 *M* perchloric acid, and 5 – 90 wt % acetic acid as the solvent with a constant ionic strength. Absorbance measurements were made between 360 and 450 $m\mu$ at 10 - $m\mu$ intervals.

A major difficulty with the spectrophotometric studies in aqueous solution results from the relatively small change in apparent absorbancy index with changing cerium(IV) or acid concentrations. The aqueous acetic acid solutions were strikingly different. When a low perchloric acid concentration was used, the addition of acetic acid to cerium(IV) in water resulted in a decrease in absorbance. On the other hand, when a relatively high perchloric acid concentration was used, the same experiment led to a large increase in absorbance. Apparently, acetic acid considerably increases the difference in absorbancy index between some of the various cerium(IV) species.

When the cerium(IV) concentration was increased, keeping the ionic strength, temperature, acid concentration, and solvent composition constant, the apparent absorbancy index (absorbance divided by total cerium(IV) concentration) decreased. This result implies the presence of at least two cerium(IV) species, at least one of which is a dimer or higher polymer.

The following approach was used to determine the nature of the principal polymeric species. If the apparent absorbancy index is plotted against the log of the total cerium(IV) concentration, a curve is obtained (Figure 1) whose shape is independent of the equilibrium constant¹⁵ but whose slope at the midpoint is a function of the nature of the polymeric form in a monomer–polymer equilibrium. A comparison of the experimental points with theoretical curves demonstrates that the reaction involves primarily a monomer–trimer equilibrium. The curves drawn through the experi-

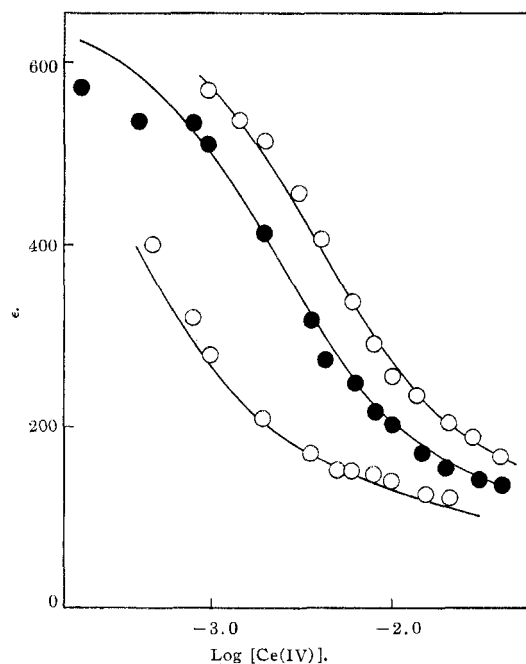


Figure 1.—Experimental data and calculated curves for the change in apparent absorbancy indexes with cerium(IV) concentration in 50% acetic acid. The lower curve is for 0.1 *M* acid, the middle curve is for 0.3 *M* acid, and the upper curve is for 0.5 *M* acid.

mental points of Figure 1 are theoretical curves for the monomer–trimer model. Except for the lowest cerium(IV) concentrations where the experimental error is largest, the fit is quite good.

This approach also gives information concerning the actual values of equilibrium constants. A relationship between the equilibrium constant and the total concentration at the point where the monomer and polymer concentrations are equal may be derived as follows. Here C_m is the concentration of monomer, C_p is the concentration of polymer, C_t is the total cerium(IV) concentration, and n is the order of polymerization

$$C_m = C_p$$

$$C_t = C_m + nC_p = C_m(n + 1)$$

$$C_m = C_t/(n + 1)$$

$$K = C_p/C_m^n = 1/C_m^{n-1}$$

$$K = (n + 1)^{n-1}C_t^{1-n}$$

or

$$\log K = (n - 1) \log (n + 1) - (n - 1) \log C_t$$

The value of K is the composite of all of the equilibria between monomeric species and trimeric species, since relationships between species of the same order do not change with ceric concentration. It can also be seen in Figure 1 that a change in acid concentration does not appear to affect the maximum apparent absorbancy index nor the minimum. This result implies that the equilibria between the various monomeric species and between the various trimeric species are not acid dependent.

(9) Stead, Thesis, Manchester, 1959. This is referred to by M. G. Anderson, F. S. Dainton, and P. Glentworth, *Trans. Faraday Soc.*, **61**, 689 (1965).

(10) Kraus, Homberg, and Nelson, USAEC Report, May 1962. This is referred to by Anderson, *et al.*, ref 9.

(11) B. D. Blaustein and J. W. Gryder, *J. Am. Chem. Soc.*, **79**, 540 (1957).

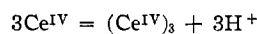
(12) L. O. Tuazon, Ph.D. Thesis, Iowa State University, 1959.

(13) R. L. Moore and R. C. Anderson, *J. Am. Chem. Soc.*, **67**, 167 (1945).

(14) T. J. Hardwick and E. Robertson, *Can. J. Chem.*, **29**, 828 (1951).

(15) The equilibrium constant simply shifts the whole curve along the concentration axis.

Estimates of K were made for each set of data obtained at a constant acid concentration. A plot of the logarithms of the values of K against $\log [H^+]$ gives a straight line with a slope of -3.1 (Figure 2). Thus, the monomer-trimer equilibrium must be described by



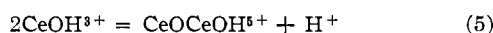
where the ligands about the cerium species are not specified.

In constructing a model for the several possible equilibria, it was apparent that the monomeric cerium(IV) should be represented by at least one species containing acetic acid or acetate ion as a ligand. This was required by the effect of acetic acid on the absorbance of the solution. Similarly, the principal trimer probably contains acetic acid or acetate ion as a ligand. Observations concerning the combined effect of acetic acid and perchloric acid on the absorbance for solutions having low concentrations of cerium(IV) suggested the equilibrium between monomeric cerium(IV) to be

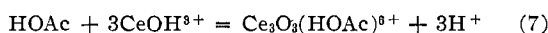


where the remaining coordination sites are occupied by water.

In accord with the model of Hardwick and Robertson, monomer-dimer equilibria were included



Finally the following monomer-trimer equilibrium was employed



The equilibrium constants would be

$$K_4 = \frac{[CeOH(HOAc)^{3+}]}{[HOAc][CeOH^{3+}]}$$

$$K_5 = \frac{[CeOCeOH^{5+}][H^+]}{[CeOH^{3+}]^2}$$

$$K_6 = \frac{[CeOCeOAc^{5+}][H_2O][H^+]}{[HOAc][CeOH^{3+}]^2}$$

$$K_7 = \frac{[Ce_3O_3(HOAc)^{6+}][H^+]^3}{[HOAc][CeOH^{3+}]^3}$$

All of the data obtained at 400 $m\mu$ (110 experimental points) which covered a range of 5–90% acetic acid were fit to the above model using an iterative computer program which employs the method of steepest descent.¹⁶ The rms fractional deviation¹⁷ dropped to 0.1, which is quite good considering the wide range of solvent composition used. The calculated equilibrium constants and absorbancy indices were: $K_4 = 0.390$; $K_5 = 16.3$; $K_6 = 0.0375$; $K_7 = 1.62 \times 10^5$; $CeOH^{3+}$, ϵ 163; $CeOH(HOAc)^{3+}$, ϵ 902; $CeOCeOH^{5+}$, ϵ 210; $CeOCeOAc^{5+}$, ϵ 230; trimer, ϵ 278.

An examination of the magnitude of the equilibrium constants indicates that the concentrations of dimers are small compared to monomer or trimer. It was pos-

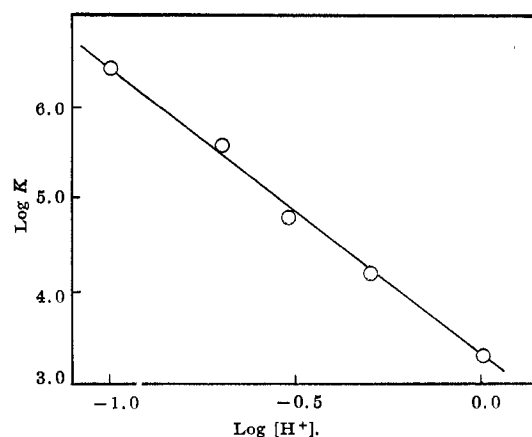


Figure 2.—Effect of acid concentration on the monomer-trimer equilibrium constants in 50% acetic acid.

sible that the equilibrium constants calculated for the monomer-dimer equilibrium resulted solely from the error minimization procedure. The equilibrium constants were recalculated using only equilibria 4 and 7 above. A recalculation using this simplified model resulted in a negligible increase in the rms error. Thus, there is no experimental evidence for the presence of dimers.

The data obtained at 380, 390, 410, and 420 $m\mu$ were treated in the same fashion. All converged on approximately the same values of K_4 and K_7 . Average values for the constants were taken, and the error was minimized with respect to the absorbancy indices for the cerium(IV) species. The resulting parameters are summarized in Table I. A plot of the absorbancy indices against wavelength gives a smooth curve.

TABLE I
PARAMETERS FOR THE CERIUM(IV)
MONOMER-TRIMER EQUILIBRIUM^a AT 25°.

Wave-length, $m\mu$	ϵ_A	ϵ_B	ϵ_C	K_4	K_7	Rms dev ^b
380	267	1492	1124	0.420	1.51×10^5	0.093
390	215	1140	568	0.420	1.51×10^5	0.101
400	163	842	274	0.420	1.51×10^5	0.103
410	125	585	124.4	0.420	1.51×10^5	0.121
420	85	397	52.7	0.420	1.51×10^5	0.133

^a A is $CeOH^{3+}$, B is $CeOH(HOAc)^{3+}$, and C is the trimer.

^b The root-mean-squared value of the deviation where the latter is defined as (calculated absorbance - absorbance)/absorbance.

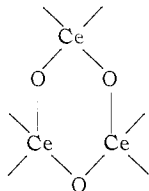
The data clearly demonstrate that the trimer is the principal polymeric species in 5–90% acetic acid solutions and the value of the equilibrium constant is probably well defined. It would be naive to pretend that the nature of the monomeric and trimeric species is equally well defined. A very simple model has been used for a wide range of solvent composition; the absorbancy indices have been assumed to be independent of solvent; and the change in the effective acidity of perchloric acid as the proportion of water in the solvent is decreased has been ignored. However, although undoubtedly oversimplified, the present model has the virtue of satisfactorily correlating a large num-

(16) The program as well as the output for the data at 400 $m\mu$ are given in the thesis of P. C. F. This will be available through University Microfilms.

(17) Defined as (calculated absorbance - absorbance)/absorbance.

ber of measurements dealing with a wide variety of conditions.

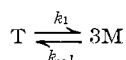
The observation that the trimer rather than the dimer is the first important polymeric Ce(IV) species suggests that it may have a special structural feature. The more obvious possibility is that it exists in a cyclic form



The formation of such a species has many analogies. Thus, alcohols generally form trimers rather than dimers, and the trimer probably involves a six-membered ring held together by hydrogen bonds.¹⁸

Although equilibrium between trimer and monomer is achieved fairly rapidly, it was possible to observe the rate of the transformation. A plot of absorbance *vs.* time for an experiment in which the cerium(IV) was rapidly diluted by a factor of 5, keeping solvent composition and acidity constant, is shown in Figure 3.

For the sake of simplicity, the kinetics of trimer dissociation will be treated as the reversible process



The rate of change in absorbance is then given by

$$\frac{d(\text{abs})}{dt} = \frac{d[T]}{dt} \epsilon_T + \frac{d[M]}{dt} \epsilon_M = (\epsilon_T - 3\epsilon_M) \frac{d[T]}{dt}$$

where

$$\frac{d[T]}{dt} = -k_1[T] + k_{-1}[M]^3$$

The ratio of k_1/k_{-1} or K may be determined from the equilibrium data given previously. Thus we may write

$$\begin{aligned} \frac{d(\text{abs})}{dt} &= (\epsilon_T - 3\epsilon_M)(-k_1[T] + Kk_1[M]^3) \\ &= C([T] - K[M]^3) \end{aligned}$$

where

$$C = (3\epsilon_M - \epsilon_T)k_1$$

and both C and K are functions of the acid concentration. Table II gives the data used in the calculation of k_1 as a function of acid concentration. A plot of k_1 against the perchloric acid concentration is linear with a nonzero intercept (Figure 4) suggesting the rate law

$$v = k_s[T] + k_a[H^+][T]$$

where k_s (0.22 sec^{-1}) is the rate constant for the solvent-assisted dissociation of the trimer and k_a ($3.30 \text{ mole}^{-1} \text{ sec}^{-1}$) is the constant for the acid-catalyzed dissociation.

Finally, the effect of nitrate ion on the monomer-trimer equilibrium may be noted. Data for two concentrations of nitrate ion are summarized in Figure 5.

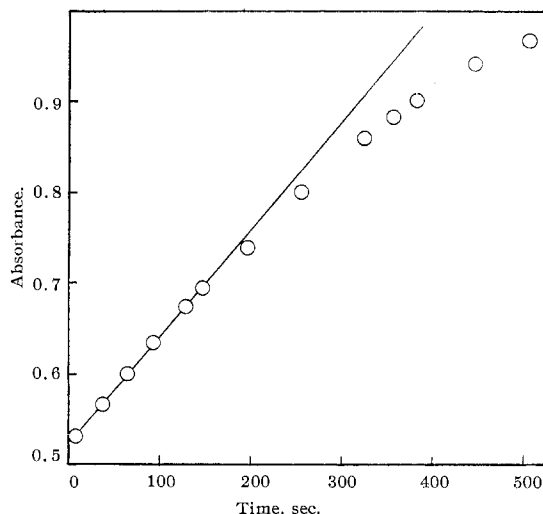


Figure 3.—Equilibration of cerium(IV) (0.02 *M*) after a fivefold dilution.

TABLE II
RATE CONSTANTS FOR TRIMER DISSOCIATION

[H ⁺], <i>M</i>	10 ² <i>v</i> ₁ ^a	10 ⁻⁶ <i>K</i> ^b	([T] - <i>K</i> [M] ³) _i	<i>C</i> ^c	10 ² <i>k</i> ₁ ^d sec ⁻¹
0.10	0.84	7.69	0.000594	14.2	0.64
0.20	1.04	1.09	0.000516	20.1	0.91
0.30	1.31	0.383	0.000487	26.9	1.21

^a Initial rate in units of absorbance/sec; 85% HOAc, 25°, $\mu = 0.6$. ^b $K = [T]_e/[M]_e^3$. ^c $C = v_i/([T] - K[M]^3)$. ^d $k_1 = C/(3\epsilon_M - \epsilon_T)$; ϵ_T 280 and ϵ_M 835.

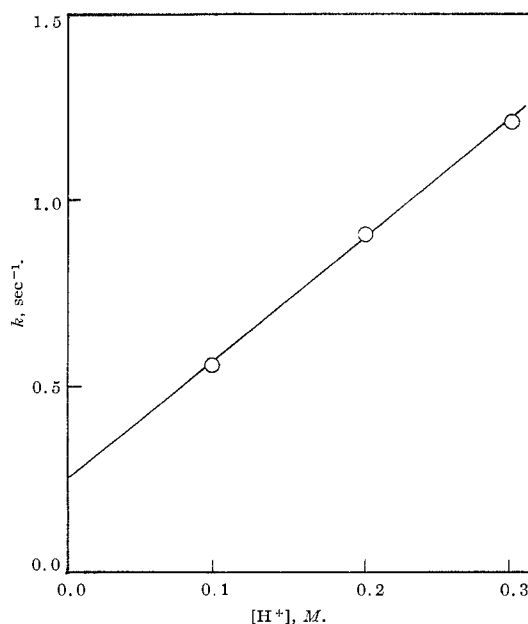


Figure 4.—Acid dependence of trimer dissociation rate constant.

With a relatively high nitrate concentration, the solutions obeyed Beer's law over a wide range of cerium(IV) concentration and only monomeric cerium(IV) species were present. However, a lower concentration of nitrate, although still in considerable excess over that of cerium(IV), had only a small effect on the monomer-trimer equilibrium.

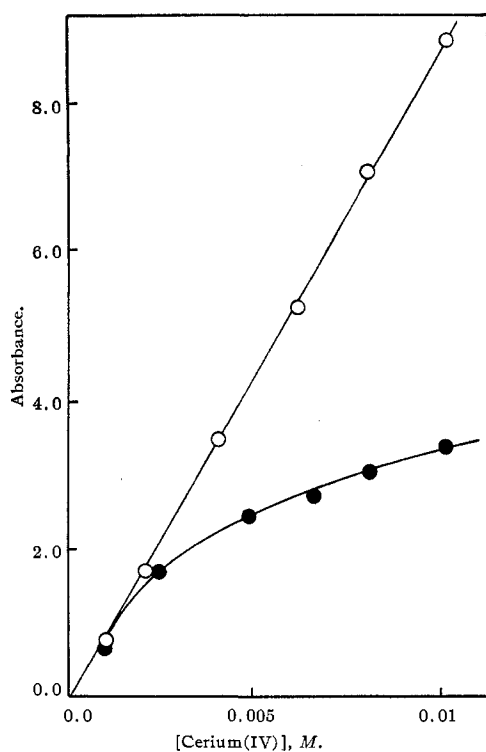


Figure 5.—Effect of nitrate ion on the absorbance of cerium(IV) solutions in 85% acetic acid. The linear relationship is obtained with 0.9 *M* nitrate and the curve corresponds to 0.05 *M* nitrate.

Experimental Section

Materials.—Ceric perchlorate was obtained from the G. F. Smith Chemical Co. as an approximately 0.5 *M* solution in 3 *M* perchloric acid. The cerium(IV) content was determined iodometrically. The acid content was determined by diluting with acetic acid, adding an excess of acetic anhydride to remove water, and titrating potentiometrically with standard sodium acetate in glacial acetic acid. Perchloric acid was obtained from Mallinckrodt as a 70% solution and nitric acid was obtained from Fisher as a 70% solution.

Acetic acid was purified as described previously.¹⁹ The water content was determined spectrophotometrically using acetic anhydride.²⁰ Water was purified by distillation from chromic acid.

Spectrophotometric Measurements.—The spectra were determined using a Beckman DU quartz spectrometer with 10-mm and shorter cells, or with a Perkin-Elmer Model 350 recording spectrometer using long cells. The Beckman spectrometer was equipped with a thermostated water bath in the light path and made it possible to maintain the temperature at 25.00 ± 0.01°. The temperature in the cell compartment of the Perkin-Elmer spectrometer varied from 23 to 26°. No significant difference was noted in the data obtained using the two spectrometers. The ionic strength was maintained at either 0.6 or 1.0 *M* by the addition of sodium perchlorate. No significant change in absorbance was noted for a change in ionic strength within this range. Cerous ion, in the concentration which might be present as an impurity in the ceric ion solutions, was found to have no significant effect on the observed absorbance values.

(19) K. B. Wiberg and T. Mill, *J. Am. Chem. Soc.*, **80**, 3022 (1958).

(20) S. Bruckenstein, Ph.D. Thesis, University of Minnesota, 1951.

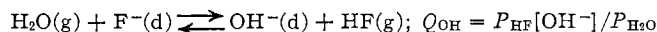
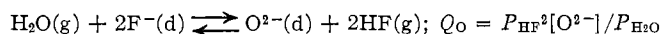
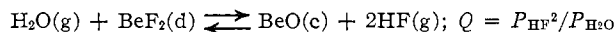
CONTRIBUTION FROM THE REACTOR CHEMISTRY DIVISION,
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Oxide Chemistry and Thermodynamics of Molten LiF-BeF₂ Solutions^{1,2}

BY A. L. MATHEWS AND C. F. BAES, JR.

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A transpiration method was used to equilibrate dilute gaseous mixtures of HF and H₂O in hydrogen with molten LiF-BeF₂ solutions, both saturated and unsaturated with crystalline BeO. The observed effluent partial pressures of HF and H₂O were interpreted in terms of equilibrium quotients for the reactions



Values of Q , Q_{O} , and Q_{OH} were determined as functions of melt composition ($X_{\text{BeF}_2} = 0.3-0.8$) and temperature (500–700°). The ratio Q_{O}/Q gave the solubility of BeO which was in the range 0.005–0.1 mole of O²⁻/kg of salt. Since Q should be proportional to the activity of BeF₂ in the solutions, activity coefficients were derived for BeF₂ (and LiF). Positive deviations from ideal behavior were found at $X_{\text{BeF}_2} > 0.5$ and negative deviations at $X_{\text{BeF}_2} < 0.5$. Comparison of the observed Q values with the LiF-BeF₂ phase diagram suggests that the heat of fusion of BeF₂ is ~5.8 kcal/mole. Improved values of the heat and free energy of formation of BeF₂(c) were also calculated from these results. If at low LiF concentrations random mixing of bridging and nonbridging fluorides is assumed, it would appear that nonbridging F⁻ ions occur in groups of four or more.

Introduction

Molten fluoride mixtures in which the principal constituents are LiF and BeF₂ have been the subject of

(1) Based upon a Ph.D. Dissertation by A. L. Mathews, submitted to the University of Mississippi, 1965. Also issued as ORNL-TM-1129, May 7, 1965. This research was performed at ORNL under the Oak Ridge Graduate Fellowship Program of The Oak Ridge Associated Universities.

(2) Research sponsored by the USAEC under contract with Union Carbide Corp.

extensive investigations at this laboratory for a number of years in connection with the development of a molten salt fueled nuclear reactor (MSRE).³ In the course of this work the oxide chemistry of these fluoride

(3) C. F. Baes, Jr., "The Chemistry and Thermodynamics of Molten Salt Reactor Fluoride Solutions," in "Thermodynamics," Vol. 1, IAEA, Vienna, 1966, p 409.