[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, LOS ALAMOS SCIENTIFIC LABORATORY]

A Spectrophotometric Study of the Complex Formed between Cerous and Sulfate Ions[1]

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Dissociation equilibrium quotients for $CeSO_4^+$ have been determined as a function of ionic strength in sodium perchlorate solutions at 25°. Between ionic strengths of 0.2 and 2.0 *M* this function was found to be: $\log K = -3.371 + 6.108\,\mu^{1/2}/(1 + 1.885\,\mu^{1/2})$. The equilibrium quotients were also studied as a function of temperature in solutions of unit ionic strength; from these data the following thermodynamic quantities were calculated for the dissociation of $CeSO_4^+$ in sodium perchlorate solutions of unit ionic strength: $\Delta F = 1.68 \pm 0.02$ kcal., $\Delta H = -3.64 \pm 0.30$ kcal., $\Delta S = -17.8 \pm 1$ e.u.

Introduction

The sulfate complex of cerous ion was studied since it is probably typical of the sulfate complexes of the other tripositive rare earth and actinide ions. Connick and Mayer[2] obtained a value for the association quotient of $CeSO_4^+$ at 25° in 0.5 *M* sodium perchlorate by studying the effect of sulfate ion on an ion exchange equilibrium involving cerous ion. In the research described here, a spectrophotometric method has been used to redetermine this value and to extend the work to other ionic strengths and temperatures. In addition, solubility data from the literature have been used to calculate values of the dissociation quotients of $CeSO_4^+$ in solutions with low ionic strengths.

The spectrum of Ce(III) in solution consists of four bands in the ultraviolet.[3] In the present work it was found that the height, but not the wave length, of the weak band at 296 mμ depends on the sulfate ion concentration but that the other three bands are nearly unchanged by sulfate ion. It was also found that at constant ionic strength the 296 mμ band is independent of hydrogen ion concentration between 0.01 and 1.0 *M*. The change in the Ce(III) absorption at 296 mμ upon the addition of sulfate was used in this study to measure the extent of complexing.

Experimental

Apparatus.—All the spectrophotometric measurements were made with a Cary Recording Quartz Spectrophotometer (Model 11). In order to control the temperature, water from a thermostat was circulated through the double walls of the cell compartment. The absorption cells were brought to temperature in the thermostat before being placed in the cell compartment.

Reagents.—The sodium sulfate stock solution was made by dissolving analytical reagent material in distilled water. It was analyzed by drying to constant weight at 140°. The perchloric acid stock solution was made by diluting 71% acid with distilled water. It was analyzed by titration with sodium hydroxide which had been standardized against potassium acid phthalate. The sodium perchlorate was prepared by neutralizing sodium carbonate with perchloric acid. A slight excess of acid was used, the carbon dioxide was boiled out, and the solution filtered. The excess acid was determined by titration, and the salt concentration was determined by drying to constant weight at 140°.[4] The cerous perchlorate stock solution was prepared from G. F. Smith Chemical Company ceric perchlorate. After precipitation of most of the perchlorate with an excess of potassium nitrate, the cerium was purified twice by precipitation as $(NH_4)_2Ce(NO_3)_6$.[5] This material was dissolved and reduced to the cerous state with hydrogen peroxide. The excess peroxide was destroyed with sodium bromide; the resulting bromine was removed by boiling. The cerous ion was precipitated with sodium carbonate, filtered and redissolved in hydrochloric acid. This was repeated several times. The final precipitate was washed free of chloride and dissolved in a slight excess of perchloric acid. The excess acid was determined by titration after removal of the Ce(III) as the oxalate. The concentration of cerous ion in this solution was evaluated spectrophotometrically using the absorption coefficients given by Stewart.[3]

Procedure.—Sets of solutions were made with constant ionic strength, constant total cerous concentration, essentially constant hydrogen ion concentration, and varying concentrations of sulfate ion. These experimental solutions were made from the stock solutions described above using calibrated pipets for the cerous perchlorate and sodium sulfate solutions and burets for the sodium perchlorate and perchloric acid solutions. After being mixed, the solutions were filtered through a Pyrex "fine" sintered filter, brought to temperature in the thermostat, and measured in the spectrophotometer. The method of treating these data will be discussed below.

Test of Beer's Law.[6]—In the calculation of equilibrium quotients from the spectrophotometric data, it is assumed that Beer's law is valid. This assumption was proved at 2965 A. for cerous perchlorate in solutions of constant hydrogen ion concentration and essentially constant perchlorate concentration. Values of the molar absorption coefficient were calculated using the data from 10 different solutions with cerous concentrations ranging from 0.002 to 0.010 *M*. Twice the standard deviation of the average[7] of these determinations was 0.26%. Similar determinations were made on 10 solutions in which the sulfate concentration was 0.33 *M;* again Beer's law was obeyed within the experimental error. In this series, twice the standard deviation of the average was 0.21%. These experiments not only give an estimate of the precision of the spectrophotometric measurements, but also make it appear likely that monomeric species involving cerous ion are the only important ones in the solutions studied.

Results and Discussion

The equilibrium quotients were calculated from the experimental data by the use of a modification of the method given by Lewis.[8] It is assumed that the chemical changes occurring in the system can be represented by the single equilibrium

$$Ce(SO_4)_n^{+3-2n} \rightleftharpoons Ce^{+3} + nSO_4^{=} \qquad (1)$$

where *n* is a positive integer. If the total cerous

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[1] Work done under the auspices of the AEC and presented in part before the Physical and Inorganic Division of the American Chemical Society, Buffalo, N. Y., March 23–27, 1952.

[2] R. E. Connick and S. W. Mayer, THIS JOURNAL, **73**, 1176 (1951).

[3] See, for example, D. C. Stewart, Atomic Energy Commission Declassified Document AECD-2389 (1948), Technical Information Branch, Oak Ridge, Tenn.

[4] The reagents used for these solutions were analytical reagent grade manufactured by the Mallinckrodt Chemical Works.

[5] D. M. Yost, H. Russell and C. S. Garner, "The Rare-Earth Elements and Their Compounds," John Wiley and Sons, Inc., New York, N. Y., 1947, p. 60.

[6] This law is used in the form: $D = \epsilon cd$, where *D* is the optical density, $\log_{10} (I/I_0)$, ϵ is the molar absorption coefficient, *c* is the concentration of the absorbing species in moles/liter, and *d* is the path length in cm.

[7] Calculated according to H. Margenau and G. M. Murphy, "The Mathematics of Physics and Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1943, p. 497.

[8] W. B. Lewis, Thesis, University of California at Los Angeles, 1942.

concentration and the optical path are held constant and, in addition, it is assumed that Beer's law is obeyed, it can be shown that

$$D = (-K)[(D - D_0)/(SO_4^{=})^n] + D_1 \qquad (2)$$

where K is the equilibrium quotient, D is the observed optical density, D_0 is the density of a solution containing no sulfate, and D_1 is the density the solution would have if all the Ce(III) were in the form of the complex. Thus, a plot of D *versus* $[(D - D_0)/(SO_4^{=})^n]$ should give a straight line with a slope of $-K$ and an intercept of D_1.

Preliminary experiments established the fact that n in equation (1) is unity; plots of equation (2) using $n = 2$ or 3 resulted in lines with much more curvature than those using $n = 1$. It was also shown that equation (2) is valid only at low sulfate concentrations.

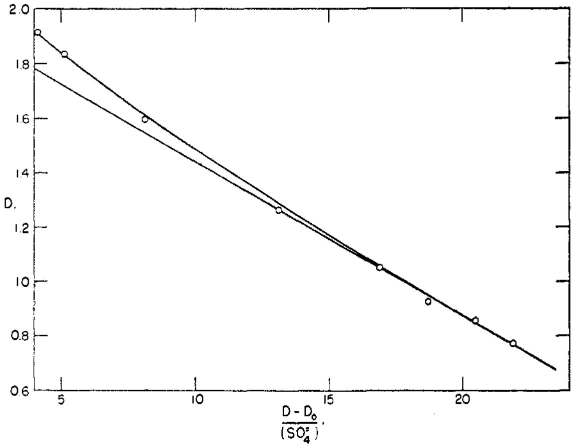

Fig. 1.—The plot from which K is determined.

Figure 1 shows a plot of equation (2) with $n = 1$, covering the rather wide range of sulfate concentrations from 0.00442 to 0.299 M. It is seen that the lower five points, with sulfate concentrations from 0.00442 to 0.0451 M fit a straight line satisfactorily, but that the points with higher sulfate concentrations lie above it. This curvature might be due to changing activity coefficients at constant ionic strength as the sodium sulfate concentration is increased. For example, if it is assumed that only one complex is formed in the whole sulfate concentration range, values of K may be determined at each experimental point. This was accomplished as follows: The linear portion of the plot was extrapolated to determine D_1; this, together with D_0 and the observed densities, was used to calculate the concentrations of cerous ion and the complex. From these quantities values of K were calculated; the results of these calculations are given in Table I.

It is seen that the values of K are nearly constant until the sodium perchlorate concentration has decreased to 0.828 M (86.5% of its highest value). The diminishing of K at the lower sodium perchlorate concentrations may easily be due to changes in the relevant activity coefficients as the medium is changed from one which is predominantly sodium perchlorate to one which is predominantly sodium sulfate.

Another explanation for the curvature is that a second complex is important in the high sulfate range. Under the assumption that the activity coefficients involved are unchanged in the concentration range studied, it was found that the following values of equilibrium quotients and limiting optical densities fit the data satisfactorily: $K = 0.057$, $D_1 = 2.02$, $K' = 5$, and $D_2 = 4.1$; here K' and D_2 apply to the complex, $Ce(SO_4)_2^-$. The curved line shown in Fig. 1 was calculated using these four constants.

TABLE I

VALUES OF THE EQUILIBRIUM QUOTIENT AT 25° AND UNIT IONIC STRENGTH ASSUMING $CeSO_4^+$ IS THE ONLY COMPLEX

Na_2SO_4 concn., M	$NaClO_4$ concn., M	Equilibrium quotient, M
0.00516	0.954	0.0569
.0103	.941	.0564
.0155	.927	.0582
.0258	.899	.0571
.0517	.828	.0573
.129	.608	.0518
.258	.236	.0354
.336	.001	.0245

Since the true situation probably lies somewhere between these two explanations, no reliable information can be obtained spectrophotometrically concerning the second complex. The value of K for the first complex is probably reliable, however, since it is essentially constant over a tenfold change in sulfate concentration.

In order to obtain the actual sulfate concentrations required by equation (2), it is necessary to subtract from the total sulfate concentration the small concentrations of bisulfate ion and complex ion. The concentration of bisulfate ion need not be known with high precision since in 0.01 M acid solutions its concentration is relatively low. The results of Bray and Liebhafsky[9] were extrapolated to an ionic strength of two to provide approximate values for the acid dissociation quotients for the bisulfate ion. The values of these quotients chosen for the calculation of bisulfate ion concentrations are listed in column 7 of Table III. The correction for the sulfate in the complex was made by a series of approximations. First, equation (2) was plotted using sulfate concentrations which were uncorrected for the amount of sulfate in the complex. An approximate value of the dissociation quotient was thus obtained; this was used to calculate the concentrations of the complex and to provide improved values for the sulfate concentrations. The data were then replotted using these improved values to obtain a better value of K and the whole process repeated. Usually three approximations were necessary. In the final plots the slopes were determined by the method of averages.

The additional determinations at 25° and unit ionic strength as well as those at other ionic strengths and temperatures were made in such a way that the concentration of sodium perchlorate was never less than 85% of its largest value at the ionic strength concerned. The discussion of Fig. 1 shows that this precaution is necessary if it is to be assumed that the activity coefficients of the reactants and products remain nearly constant or only one complex is important as the sulfate concentration

[9] W. C. Bray and H. Liebhafsky, THIS JOURNAL, **57**, 51 (1935).

is varied or both. Thus, the equilibrium quotients determined in this work apply to dilute solutions of cerous perchlorate and sodium sulfate in fairly concentrated solutions of sodium perchlorate.

Some determinations were made at unit ionic strength and 25° in which the total cerous ion concentration, the hydrogen ion concentration, and the wave length were varied. The results of these determinations are given in Table II.

TABLE II

EFFECT OF WAVE LENGTH AND THE CONCENTRATIONS OF TOTAL CEROUS AND HYDROGEN ION ON THE EQUILIBRIUM QUOTIENT

Wave length, Å.	Total cerous ion, *M*	Hydrogen ion, *M*	Equilibrium quotient, *M*	No. detns.
2965	0.00185	0.010	0.0589	2
2965	.0037	.010	.0588	6
2965	.0074	.010	.0621	3
2965	.0111	.010	.0580	2
2965	.0037	.001	.0571	2
2848	.0037	.010	.0595	2

It is seen that these changes do not affect the apparent values of the equilibrium quotient significantly. The fact that a sixfold variation in the total cerous concentration and a tenfold change in the hydrogen ion concentration did not change the value of the apparent *K* indicates that the complex involves only one cerous ion and that it is sulfate and not bisulfate which forms the complex.

Most of the determinations of *K* were made with the hydrogen ion concentration[10] held constant at 0.01 *M* and the total cerous concentration held at 0.0037 *M*. The wave length used was 2965 Å. The results of these determinations are given in Table III.

TABLE III

SUMMARY OF EXPERIMENTAL DATA AND CALCULATED QUANTITIES

Temp., °C.	Ionic strength, *M*	No. of detns.	Equilibrium quotient: Average exptl. value, *M*	Equilibrium quotient: Twice std. dev. of av., %	Equilibrium quotient: Calcd. from eq. (4), *M*	Acid dissociation quotient used, *M*	Absorption coefficient for Ce^{+++}, M.$^{-1}$ cm.$^{-1}$	Absorption coefficient for $CeSO_4^+$, M.$^{-1}$ cm.$^{-1}$
25.0 ± 0.2	0.20	4	0.0131	3.6	0.0129	0.048	19.5	49.2
25.0 ± .2	.35	4	.0212	3.4	.0218	.063	19.1	50.0
25.0 ± .2	.50	4	.0296	3.2	.0302	.075	18.6	51.1
25.0 ± .2	1.00	6	.0588	3.1	.0557	.090	18.2	53.8
25.0 ± .2	2.00	3	.0950	7.3	.0966	.100	16.8	56.8
15.0 ± .5	1.00	5	.0722	2.1	....	.110	15.8	48.6
15.0 ± .5	0.20	6	.0148	7.3	....	.065	..	..
35.3 ± .2	1.00	6	.0471	1.6	....	.073	20.8	59.5
44.7 ± .2	1.00	6	.0402	5.6	....	.060	23.0	68.4

Columns 8 and 9 of Table III show that the molar absorption coefficients of both the uncomplexed cerous ion and of the complex are functions of the temperature and the ionic strength. It was found that it is the ionic strength and not the perchlorate concentration which influences the absorption coefficients by determining them for cerous ion in solutions of magnesium and barium perchlorate.

The equilibrium quotients at unit ionic strength were used to estimate ΔH for the dissociation of the complex in sodium perchlorate solutions. When log *K* was plotted against $1/T$, a straight line resulted (see Fig. 2). The method of least squares was used to determine the best straight line through all the data. The uncertainty in the slope and hence in ΔH was estimated using the formulas given by Margenau and Murphy.[11]

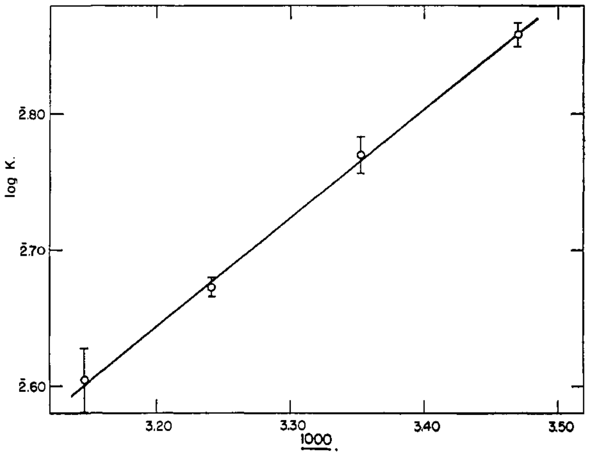

Fig. 2.—The effect of temperature on *K* at unit ionic strength.

It was found that $\Delta H = -3.64 \pm 0.30$ kcal. In the same solution $\Delta F = -RT \ln K$ at 25° was found to be 1.68 ± 0.02 kcal. and ΔS was calculated to be -17.8 ± 1.0 e.u. It should be emphasized that these values apply only to solutions of sodium perchlorate at unit ionic strength and 25°; in solutions of other ionic strengths ΔF is known by experiment to be different, and since ΔH is probably slightly different, one should expect ΔS to be significantly different. For example, if $\mathring{a}$ in equation (4) (see below) is independent of temperature in the neighborhood of 25°, at zero ionic strength ΔH would be -4.69 kcal. and ΔS would be -31.2 e.u.

It is of interest to compare these thermodynamic quantities with the analogous ones reported by Mattern[12] for the dissociation of $LaSO_4^+$ at 25° in solutions of sodium perchlorate at unit ionic strength. He found $\Delta F = 1.9$ kcal., $\Delta H = -2.5 \pm 0.7$ kcal. and $\Delta S = -15 \pm 3$ e.u. The values for ΔS agree within the experimental error, though perhaps the one for the lanthanum reaction is a little less negative. This is what might be expected

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(10) This was calculated from the total acid present and the appropriate value of the acid dissociation quotient of HSO_4^-.

(11) Reference 7, p. 502.

(12) K. L. Mattern, Thesis, University of California, Berkeley, 1951, or University of California Radiation Laboratory Unclassified Document No. 1407.

since the formula given by Powell and Latimer[13] indicates that the entropy of La^{+++} is about 1 e.u. higher than that of Ce^{+++}. Thus, if the entropies of the two complex ions are about the same, the ΔS for the dissociation of the lanthanum complex should be about 1 e.u. less negative than that for the cerous complex.

Calculation of Equilibrium Quotients from Solubility Data.—The solubility of cerous iodate has been measured carefully by Chloupek, Daneš and Danešova[14] at 25° in solutions of potassium nitrate and in solutions of potassium sulfate. If two reasonable assumptions are made, these data may be used to calculate equilibrium quotients for the dissociation of $CeSO_4^+$. The two assumptions are (1) that the activity coefficients of the ions involved in the dissociation equilibrium are the same in a solution of potassium nitrate as in a solution of potassium sulfate at the same low ionic strength, and (2) that nitrate and iodate do not complex cerous ion significantly in the solutions considered. First it was found that the solubility data in potassium nitrate from 0 to 0.5 M could be represented by

$$\log K_s = \log K_s^0 + 0.509\Delta z^2 \mu^{1/2}/(1 + 0.329\, \mathring{a}\, \mu^{1/2}) \quad (3)$$

In this expression, which has the Debye–Hückel form, there are two adjustable parameters, K^0, the solubility product at zero ionic strength, and $\mathring{a}$, which is related to the distance of closest approach of the ions. The numerical constants apply to water at 25°, μ is the ionic strength, Δz^2 is the change, in the equation for the reaction of the square of the charges on the ions (12 in this case), and K_s is the observed solubility product. With K^0_s taken as 3.166×10^{-10} and $\mathring{a}$ as 5.0 Å. the expression above reproduces the experimental solubilities with a mean deviation of 1.5% and a maximum deviation of 2.6%.

The value of K, the dissociation equilibrium quotient of $CeSO_4^+$, is calculated as follows: Let K_s be the solubility product of $Ce(IO_3)_3$, let $x = (CeSO_4^+)$, and let S be the observed solubility of $Ce(IO_3)_3$. Then $3S = (IO_3^-)$ and $S - x = (Ce^{+++})$. Let C equal the concentration of K_2SO_4; then $C - x = (SO_4^=)$. Now, $K = (S - x)(C - x)/x$, $K_s = (S - x)(3S)^3$, $\log K_s = -9.5 + 5.108\mu^{1/2}/(1 + 1.645\mu^{1/2})$, and $\mu = 6S - 6x + 3C$. These four equations have four unknowns: K, K_s, x and μ. They are solved simultaneously by a series of approximations to give a value of K for each of the solubility determinations. The results of these calculations are given in Table IV. The data in the first two columns are from Chloupek, Daneš and Danešova.[14]

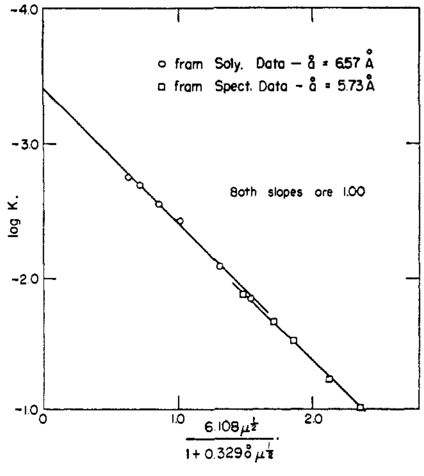

Fig. 3.—The effect of ionic strength on K at 25°. The solid lines are from the Debye–Hückel equation using the parameters indicated.

TABLE IV

CALCULATION OF EQUILIBRIUM QUOTIENTS FROM THE SOLUBILITY DATA

C, concn. of K_2SO_4, M	S, soly. of $Ce(IO_3)_3$, $M \times 10^3$	Ionic strength, M	X, concn. of $CeSO_4^+$, $M \times 10^3$	Equilibrium quotients From soly. data, $M \times 10^3$	From eq. (4), $M \times 10^3$
0.002	3.0271	0.01786	1.050	1.789	1.714
.005	3.5635	.02375	2.104	2.008	2.028
.010	4.2392	.03725	3.031	2.777	2.711
.020	5.2785	.06607	4.266	3.732	4.074
.050	6.8114	.15647	5.732	8.333	8.017
.100	8.512	.30671	7.393	14.02	13.84

The ionic strength dependence of the equilibrium quotients at 25° from both the solubility and the spectrophotometric data can be expressed by an equation with the Debye–Hückel form.[15]

$$\log K = \log K^0 + 0.509\Delta z^2\mu^{1/2}/(1 + 0.329\mathring{a}\mu^{1/2}) \quad (4)$$

In this case, K is the equilibrium quotient and K^0 is the equilibrium quotient at zero ionic strength. The other symbols and constants have the same significance as in equation (3); again Δz^2 is 12.

It can be seen that if equation (4) is satisfactory and if $\mathring{a}$ is chosen correctly, a plot of log K *vs.* $0.509\Delta z^2\mu^{1/2}/(1 + 0.329\mathring{a}\mu^{1/2})$ will give a straight line with a slope of unity and an intercept of log K^0. In Fig. 3 such plots are shown for the equilibrium quotients from the spectrophotometric data as well as the solubility data. Both sets of data are fit satisfactorily by equation (4) but with different values of K^0 and $\mathring{a}$. With $K^0 = 4.26 \times 10^{-4}$ and $\mathring{a} = 5.73$ Å., equation (4) reproduces the spectrophotometric equilibrium quotients with a mean deviation of 2.8% and a maximum deviation of 5.4%. The same equation also reproduces the equilibrium quotients from the solubility data with a mean deviation of 3.3% and a maximum deviation of 9.1% if $K^0 = 3.99 \times 10^{-4}$ and $\mathring{a} = 6.57$ Å. The two values of K^0 agree within 6.3%, which is quite good considering the long extrapolation to zero ionic strength in the case of the spectrophotometric data. It is not surprising that the values of $\mathring{a}$ are quite different since they apply to different solutions. The equilibrium quotients from the solubility data apply to potassium sulfate solutions, whereas those from the spectrophotometric data apply to

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[13] R. E. Powell and W. M. Latimer, *J. Chem. Phys.*, **19**, 1139 (1951). In using this formula, the contribution to the entropy of the multiplicity of the ground state has been neglected. This was done since it will contribute equally to entropies of the aqueous ions and the complex ions.

[14] J. B. Chloupek, V. S. Daneš and B. A. Danešova, *Coll. Czech. Chem. Comm.*, **4**, 473 (1932).

[15] K. A. Kraus and F. Nelson have shown that an expression of this form can be used to represent the ionic strength dependence of both the disproportionation of uranium(V) and the hydrolysis of uranium(IV). See THIS JOURNAL, **72**, 3901 (1950), and **73**, 2157 (1951).

sodium perchlorate solutions. This difference in $\mathring{a}$ values is in good agreement with that found by Näsänen[16] in his study of the dissociation of $CuSO_4$ He found that in potassium sulfate $\mathring{a}$ is 15.4% higher than in sodium perchlorate solutions; this is to be compared with 14.7% for the corresponding difference in the dissociation of $CeSO_4^+$.

It should be pointed out that at zero as well as unit ionic strength $LaSO_4^+$ is more stable than $CeSO_4^+$. Thus, for the dissociation of $LaSO_4^+$ at zero ionic strength, Davies[17] reported 2.2×10^{-4} on the basis of solubility measurements and Jenkins and Monk[18] reported 2.4×10^{-4} on the basis of conductivity measurements. At zero ionic strength the dissociation constant for $LaSO_4^+$ is 44% smaller than the dissociation constant for $CeSO_4^+$. At unit ionic strength Mattern[12] reported 25 for the association quotient or 0.040 for the dissociation quotient of $LaSO_4^+$. This result was obtained by an indirect spectrophotometric method. At this ionic strength the dissociation quotient for $LaSO_4^+$ is 32% smaller than the dissociation quotient of $CeSO_4^+$. As might be expected, the ionic strength dependences of these two equilibria are approximately the same.

Connick and Mayer[2] reported 60 for the association quotient or 0.017 for the dissociation quotient for $CeSO_4^+$ at an ionic strength of 0.5. This value is significantly smaller than 0.0296, which we have found spectrophotometrically; the reason for this discrepancy is not known.

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(16) R. Näsänen, *Acta Chem. Scand.*, **3**, 959 (1949).

(17) C. W. Davies, *J. Chem. Soc.*, 2421 (1930).

(18) I. L. Jenkins and C. B. Monk, THIS JOURNAL, **72**, 2695 (1950).

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

The Crystal Structures of YF_3 and Related Compounds

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The crystal structure of YF_3 has been determined from single crystal X-ray diffraction data. It is orthorhombic, space group Pnma, with $a = 6.353$, $b = 6.850$, $c = 4.393$, $Z = 4$, and $D_x = 5.069$. The atomic parameters are similar to those in cementite, Fe_3C, but the coördination numbers are different. The unit cells have been determined for the compounds SmF_3, EuF_3, GdF_3, TbF_3, DyF_3, HoF_3, ErF_3, TmF_3, YbF_3 and LuF_3 which are isostructural with YF_3. SmF_3, EuF_3, HoF_3 and TmF_3 were also observed with hexagonal structures like that of LaF_3. Three cubic phases are tentatively identified as $NH_4Ho_3F_{10}$, $NH_4Er_3F_{10}$ and $NH_4Tm_3F_{10}$, and a structure is proposed for these and for the cubic "YF_3" of Nowacki. HoOF is cubic with a disordered CaF_2 type structure.

Introduction

In the course of a routine examination of certain rare earth fluorides by the X-ray powder diffraction method, it was found that they had a structure like that of YF_3 prepared in this Laboratory, rather than that of LaF_3. This paper reports the determination of the YF_3 structure from single crystal diffraction data and a study of rare earth fluorides by the powder method. A cubic structure was reported by Nowacki[1] for a sample thought to be YF_3, but we believe it to have been another compound for reasons which are discussed below.

Experimental

Dry Method of Synthesis.—Several milligrams of the appropriate sesquioxide contained in a platinum crucible were placed in a platinum vacuum apparatus. After evacuation, a dry mixture of hydrogen and hydrogen fluoride was passed through the system. The temperature was raised and maintained at 700° for two hours. After cooling, the apparatus was again evacuated and then opened for removal of the fluoride product.

Wet Method of Synthesis.—From 5 to 15 mg. of the appropriate oxide was dissolved in 4 ml. of 6 *M* hydrochloric acid. The solution was neutralized with 6 *M* ammonium hydroxide until the gelatinous hydroxide appeared, and a few drops of hydrochloric acid were added until the solution was again clear. The solution, in a plastic, hydrofluoric acid resistant, test-tube was heated in a boiling water-bath. One to two milliliters of concentrated hydrofluoric acid was added. After one hour of heating, the precipitate was centrifuged, washed with water and dried in air between 100 and 150°. The dried material was heated in an electric furnace in vacuum (10^{-5} to 10^{-6} mm.) to a temperature between 1000 and 1400° for one hour. In all cases the trifluorides were gray in color after heating to the high temperature, while the unheated samples were white. This observation has been made previously by others, but we know of no explanation.

Yttrium Trifluoride.—YF_3 was prepared by the dry method. To obtain single crystals, a few milligrams of the product in a platinum crucible was heated to 1400° in a vacuum (10^{-5} to 10^{-6} mm.). The temperature was lowered about 2°/min. to 1000°, then rapidly to room temperature. When the crucible was cut open, several irregular anhedral single crystal fragments were found adhering to the sides. Spectrographic and spectrophotometric analysis showed the presence of a few per cent. of rare earth impurities, chiefly dysprosium, erbium and ytterbium, in this material which was used for the single crystal work. Another sample of YF_3, prepared by the wet method from yttrium oxide containing less than 0.1% total metallic impurities, was found to have unit cell dimensions equal within experimental error to those found for the impure YF_3. Therefore it is believed that the impurities have a negligible effect on the atomic parameters.

Samarium Trifluoride.—SmF_3 prepared by the dry method one time had the orthorhombic (YF_3 type) structure, one time the hexagonal (LaF_3 type) structure, and in other cases consisted of mixtures of the two. SmF_3 prepared by the wet method after drying was hexagonal; after the high temperature heat treatment it was a mixture of both forms. The samarium used was spectrographically pure of other rare earths.

Europium Trifluoride.—EuF_3 prepared by the dry method was orthorhombic. When made by the wet method, modified in this case by omitting the ammonium hydroxide and

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(1) W. Nowacki, *Z. Krist.*, **100**, 242 (1938).