[CONTRIBUTION NO. 68 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

The Solubility of Ytterbium Oxalate and Complex Ion Formation in Oxalate Solutions*

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Introduction

The wide use of oxalate precipitation of rare earths both in large scale separation and recovery processes and in analytical procedures warrants a better understanding of the equilibria involved in such systems. The solubility of rare earth oxalates in excess oxalate has been noted previously by many workers in the field.[1] In general the ability of rare earth ions to form complexes increases with atomic number, and ytterbium as one of the heaviest members of the group might be expected to show a very marked increased in solubility in excess oxalate ion due to complex formation. A knowledge of the ytterbium–oxalate system was especially needed in studies of the ytterbium radioactivities induced by neutron irradiation since chemical separations were carried out on small samples. For such operations it was desirable to perform the precipitations under optimum conditions because the recovery of activity from filtrates involved tedious and time consuming evaporation and reprecipitation procedures. However the radioactivity greatly facilitated these studies since the necessary determination of very low concentrations could be conveniently performed with adequate accuracy by radioassays. For such work an isotope with a conveniently long half life and which can be prepared with a sufficiently high specific activity is required. Yb^{169} (K capture, 33 d half life) was found to be satisfactory for these studies. Electrons from two moderately converted and intense gamma transitions of 0.177 and 0.198 Mev.[2] together with the Tm K X-rays provided the greatest counting contribution with thin window G-M counters.

Accordingly, the data from radiochemical studies have indicated the formation of oxalate complexes and have served to permit estimates of equilibrium constants for possible reactions which adequately describe the solubilities in the regions considered. Interesting correlations may be possible when these procedures are applied to other members of the rare earth groups.

We wish to express our appreciation for the assistance and encouragement offered by Dr. F. H. Spedding and the Messrs. P. E. Porter and J. M. Wright who performed the separation of ytterbium from rare earth mixtures and provided the very pure sample which was needed for this work and other studies of the radioactive isotopes of ytterbium prepared by the mentioned irradiation. Also, their many suggestions regarding the properties and treatment of rare earth materials have proven most helpful.

Experimental

Materials.—Reagent grade chemicals and doubly distilled water were used throughout this work. A primary standard of Sörensen sodium oxalate was used to standardize the permanganate solutions. Oxalic acid–sodium oxalate buffers were used to adjust the *p*H of all solutions except the most acid to which standard hydrochloric acid was added. In all cases solutions of ytterbium chloride with a small known excess of hydrochloric acid to prevent hydrolysis were used in preparing the equilibrium precipitates.

The 1-g. sample of ytterbium oxide which was supplied by Dr. Spedding and his co-workers had been separated from other rare earths by them in the following manner: The cerium fraction including the elements samarium and europium had been removed by separations in ion exchange columns using Amberlite IR-100 ion exchange resin.[3] The ytterbium had then been separated from the other heavy rare earths by repeated sodium-amalgam reduction and extractions. Conditions for effecting the amalgam extraction have been described extensively by Moeller and Kremers.[4] The sample had finally been precipitated as the oxalate and ignited to oxide. Following this, it was irradiated for thirty days in the Argonne National Laboratory pile to produce Yb^{175} with a 100 hour half life and Yb^{169} with a 33 day half life. About 99% of the activity was carried in three extractions with sodium amalgam. Absorption curves for the radiation of the residue from these extractions indicated that any activity of significantly different character was probably less than 0.1% of the original. In particular, no evidence for the 105 day half life Tm^{170} activity was noted.

The ytterbium oxide returned from the neutron irradiation was precipitated as fluoride, dissolved by fuming with sulfuric acid, reprecipitated with oxalate, and finally ignited to ytterbium oxide again.

Procedures.—A Beckman Model "G" *p*H meter was used throughout this work; it was standardized with buffer solutions of *p*H 4, 7 and 10 supplied by the National Technical Laboratories of South Pasadena, California, which had been calibrated against a decinormal calomel electrode to yield *p*H on an activity scale. Radioactive samples were counted by means of Geiger-Mueller counters with an end mica window of 2.5 mg./sq. cm., model *VG*, manufactured by the Victoreen Instrument Co. The use of the thin window permitted counting of soft gamma ray conversion electrons present in moderately high intensity with the Yb^{169} undergoing K capture. The counter tube was operated with a conventional scale of 64 circuit. Counting was standardized by use of a commercial plastic counter mount with five shelves for supporting samples. Assay samples were prepared by the evaporation of known volumes of solution in aluminum dishes. Counting rates were maintained less than 5,000 c./m. so coincidence losses could be neglected.

To determine the specific activity, five samples of 50 to 75 mg. of the active ytterbium oxide were weighed on an analytical balance. Each sample was dissolved in hydrochloric acid and evaporated to dryness. The ytterbium

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* This article is based on work performed in the Ames Laboratory, Atomic Energy Commission.

[1] 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. 59.

[2] E. N. Jensen, private communication.

[3] F. H. Spedding, E. I. Fulmer, T. A. Butler, E. M. Gladrow, M. Gobush, P. E. Porter and J. M. Wright, THIS JOURNAL, **69**, 2812 (1947).

[4] T. Moeller and H. E. Kremers, *Ind. Eng. Chem., Anal. Ed.*, **17**, 798 (1945).

chloride crystals were dissolved in different solutions containing enough hydrochloric acid to give a *p*H of 5 and varied amounts of sodium chloride to give solutions whose ionic strengths covered the range of 10^{-3} to 10^{-1} molar. Each solution was diluted in a volumetric flask. Samples for counting were prepared by evaporating 10-100 μl aliquots, measured in micropipets, on the aluminum sample counting dishes. The specific activity obtained on the second shelf was originally of the order of 7.0×10^4 cts./mg. Yb min. and the variation was 5% over the range of ionic strengths prepared.

Equilibrium solutions were prepared in two ways: (1) Radioactive ytterbium chloride was added to buffered oxalate solutions. (2) Wet washed radioactive ytterbium oxalate was added to the oxalate solutions. In each case the solutions were shaken periodically by hand and allowed to come to equilibrium in a thermostat at 25.0°.

Each solution was analyzed once each day until results remained constant for several days. Precipitates appeared crystalline a few hours after formation and showed no evidence of colloid formation.

Analysis of a solution consisted of a *p*H measurement to give the hydrogen ion activity, a permanganate titration for total oxalate, and a counting determination of the Yb activity in an aliquot of solution. The aliquots used for counting were 10-100 μl portions evaporated in the aluminum dishes under infrared lamps to very thin deposits. For a few of the most acid solutions the aliquots were first neutralized with very dilute sodium hydroxide. At least 10,000 counts were obtained for each sample. The counting rate above background of each sample was then compared with that of a standard prepared simultaneously by the evaporation of a similar aliquot of the standard solution which most nearly matched the ionic strength of the equilibrium solution. From the ratio of the counting rates and the known ytterbium content of the standard, a value for the concentration of total ytterbium in the solution could be calculated for which errors due to decay, self absorption, and scattering were minimized. Radioassays of the same solution agreed in general to within ±2% and did not vary if the aliquots were withdrawn from near the surface or from the center of the solution.

Discussion of Results

Results of the analyses of equilibrium solutions are contained in Table I. From the data collected an estimate of the state of the oxalate–hydrogen ion equilibrium could be accomplished by means of the equations

$$M = m_{H_2C_2O_4} + m_{HC_2O_4^-} + m_{C_2O_4^{=}} \qquad (1)$$

and the first and second dissociation constants

$$\frac{(\gamma_1)(m_{HC_2O_4^-})(a_{H^+})}{(m_{H_2C_2O_4})} = K_1 = 5.38 \times 10^{-2(5)} \qquad (2)$$

$$\frac{(\gamma_2)(m_{C_2O_4^{=}})(a_{H^+})}{(\gamma_1)(m_{HC_2O_4^-})} = K_2 = 5.42 \times 10^{-5(6)} \qquad (3)$$

where

a's	represent activities
m's	represent molar concentrations
γ_1	represents the activity coefficient of the singly charged ion, $HC_2O_4^-$
γ_2	represents the activity coefficient of the doubly charged ion, $C_2O_4^{=}$ (the activity coefficient of $H_2C_2O_4$ was taken as 1.00)
M	represents the total molar oxalate concentration as determined from the permanganate titration.

TABLE I

DATA FROM SOLUBILITY EXPERIMENTS AT 25.0°

$\sqrt{\mu}$	*p*H	$-\log$ M*	$-\log$ $a_{C_2O_4^{=}}$	$-\log$ [Yb]** obs.	$-\log$ [Yb]** calcd.
0.223	4.47	1.11	1.57	3.41	3.27
.548	3.45	0.71	1.81	3.36	3.34
.429	3.98	1.12	1.88	3.30	3.39
.354	4.12	1.34	2.00	3.49	3.46
.309	4.00	1.49	2.19	3.53	3.56
.224	4.00	1.56	2.20	3.60	3.59
.224	3.78	1.48	2.25	3.70	3.61
.324	3.53	1.31	2.30	3.54	3.59
.448	4.22	1.14	2.40	3.60	3.64
.342	3.70	1.70	2.62	3.87	3.76
.334	3.35	1.74	2.87	4.09	3.89
.141	3.40	1.89	2.90	4.00	3.95
.308	2.30	0.95	3.08	4.20	3.99
.303	2.70	1.52	3.22	4.10	4.06
.320	3.76	2.86	3.68	4.10	4.25
.115	3.27	2.74	3.85	4.30	4.37
.366	1.47	0.92	4.01	4.20	4.36
.310	3.00	2.64	4.05	4.29	4.38
.245	1.27	0.92	4.26	4.20	4.44
.032	3.37	3.31	4.28	4.63	4.53
.255	1.19	0.89	4.35	4.36	4.45
.308	1.03	0.68	4.39	4.24	4.45
.141	1.90	1.77	4.44	4.48	4.49
.100	2.15	2.31	4.52	4.53	4.51
.302	3.30	3.54	4.71	4.31	4.46
.216	1.40	1.97	5.12	4.46	4.40
.291	1.25	1.76	5.14	4.54	4.37
.187	1.47	2.13	5.19	4.38	4.38
.333	0.96	1.67	5.52	4.25	4.22
.235	1.28	2.33	5.67	4.19	4.20
.540	0.55	1.52	6.06	3.78	3.80
.447	0.73	2.24	6.46	3.38	3.51
.707	0.34	1.90	6.82	2.81	2.83

* M = total oxalate, moles/liter

** [Yb] = total ytterbium, moles/liter

The assumption that only a negligible fraction of the oxalate was associated in ytterbium complexes, as is implied in equation 1, was justified in later portions of the calculations. The simultaneous solution of equations 1–3 yields the following expression for the oxalate ion activity. Within the accuracy of the data differences between molal and molar concentrations could be considered negligible for the concentrations employed.

$$a_{C_2O_4^{=}} = \frac{K_1 K_2 M}{a^2_{H^+} + \frac{a_{H^+} K_1}{\gamma_1} + \frac{K_1 K_2}{\gamma_2}} \qquad (4)$$

γ_1, was taken equal to $\gamma_\pm$ for hydrochloric acid in potassium chloride solutions of the same ionic strengths.[7] Values of the quantity $\gamma_{C_2O_4^{=}}/\gamma_{HC_2O_4^-}\gamma_{Cl^-}$ which were indicated in the potentiometric determination of K_2 for oxalic acid[6] were plotted as a function of ionic strength. γ_2 for each equilibrium solution was computed from this graph by multiplying values taken from this curve by γ_1^2 which had been estimated as described above. The calculation of the oxalate ion activity was accomplished for each solution by means of suc-

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(5) L. S. Darken, THIS JOURNAL, **63**, 1007 (1941).

(6) G. D. Pinching and R. G. Bates, *J. Research Nat. Bur. Standards*, **40**, 405 (1948).

(7) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **55**, 2179 (1933).

cessive approximations in which the ionic strength and hence the activity coefficients from each preceding computation were employed.

The total ytterbium content of the equilibrium solutions was found to depend primarily upon the oxalate ion activity. Variations of the *p*H were only effective in controlling the oxalate activity according to equation (4). Various attempts to include the binoxalate activity in the explanation of the experimental values failed to reveal any primary effect in controlling the solubility of ytterbium oxalate within the ranges tested, ($10^{-4} < a_{HC_2O_4^-} < 0.1$ molar). Experimental solubilities have therefore been shown in Fig. 1 as a function of oxalate ion activity.

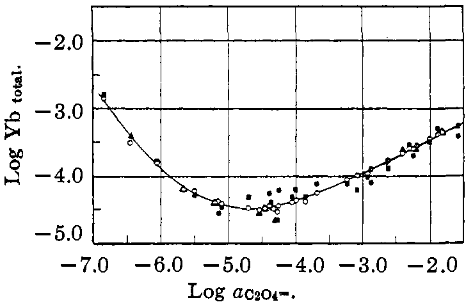

Fig. 1.—Yb (total) concentration in buffered oxalate solutions: ▲, experimental concentrations after dissolving wet washed crystals; ○, concentrations calculated by means of equation 9; ■, experimental concentrations after precipitation.

It should be noted that for precipitations carried out with the oxalate activity less than 10^{-4} molar changes in the analyses became very small after a few days. When equilibrium was approached from the opposite direction, however, much lower ytterbium concentrations were obtained. Subsequently, it was found that the precipitation process at 25° required thirty days or longer for the establishment of equilibrium in this region. The results from these long experiments were then in agreement with the equilibria attained fairly rapidly by dissolving the precipitates. At oxalate activities greater than 10^{-4} molar equilibrium was essentially attained from both directions after only a few days.

A striking feature of the system indicated by Fig. 1 is the slight variation of total ytterbium concentration (<100) over oxalate ion activities varying by more than 10^5. Also, the points clustered around a fairly definite smooth curve. These features together with the increasing solubility at high oxalate activity indicated that complex ions had formed. The possibility of ions of the type $Yb(C_2O_4)_n^{+3-2n}$ was considered. The slope of the curve representative of the data in the region of high oxalate ion activity should indicate the complex species present in this region since to a first approximation the formation of $Yb(C_2O_4)_3^{\equiv}$ would lead to a slope of +3/2, $Yb(C_2O_4)_2^-$ to a slope of +1/2 and $Yb(C_2O_4)^+$ to a slope of −1/2. The slope was almost exactly +1/2 for the curve which was nearly straight in the region for log $a_{C_2O_4^{=}} > -3.5$. Hence the presence of $Yb(C_2O_4)_2^-$ but not $Yb(C_2O_4)_3^{\equiv}$ was indicated. The experimental data could be adequately explained by postulating the two equilibria

$$\text{I} \qquad Yb(C_2O_4)_2^- \rightleftarrows Yb(C_2O_4)^+ + C_2O_4^{=}$$

$$\text{II} \qquad Yb(C_2O_4)^+ \rightleftarrows Yb^{+++} + C_2O_4^{=}$$

The formation of $Yb(C_2O_4)^+$ was found necessary to explain the flat minimum in Fig. 1, and it apparently offers an important contribution in the intermediate region of concentrations. Three equilibrium constants were therefore considered

$$m_{Yb(C_2O_4)^+}\, a_{C_2O_4^{=}}/m_{Yb(C_2O_4)_2^-} = K_I \qquad (5)$$

$$\gamma_3 m_{Yb^{+++}}\, a_{C_2O_4^{=}}/\gamma_1 m_{Yb(C_2O_4)^+} = K_{II} \qquad (6)$$

$$\gamma_1^2 m_{Yb(C_2O_4)^+}\, m_{Yb(C_2O_4)_2^-} = K_{SP} \qquad (7)$$

If the total Yb concentration $[Yb_{total}]$ were given by

$$[Yb_{total}] = m_{Yb^{+++}} + m_{Yb(C_2O_4)^+} + m_{Yb(C_2O_4)_2^-} \qquad (8)$$

the following equation is obtained from 5, 6 and 7

$$[Yb_{total}] = \sqrt{\frac{K_1 K_{SP}}{\gamma_1}\left[\frac{K_{II}\gamma_1}{\gamma_3} a_{C_2O_4^{=}}^{-3/2} + a_{C_2O_4^{=}}^{-1/2} + \frac{a_{C_2O_4^{=}}^{-1/2}}{K_I}\right]} \qquad (9)$$

Values of γ_1 (with the assumption that activity coefficients of the univalent ions were equal) were calculated as indicated above for $HC_2O_4^-$, and γ_3 was calculated from the values of γ_1 and the mean ionic activity coefficient of various rare earth chlorides reported as functions of ionic strength.[8] In solving equation (9) successive approximations were again required to obtain values of the activity coefficients and the ionic strength consistent with the answer.

The function represented in equation (9) appeared satisfactory with the choice of the following equilibrium constants

$K_I = 2.6 \times 10^{-5}$; $K_{II} = 5.0 = 10^{-8}$; and $K_{sp} = 1.9 \times 10^{-10}$

The circles in Fig. 1 were calculated by means of equation (9) from the oxalate ion activity for the equilibrium mixtures, and the curve actually drawn was fitted to these points. It should be noted that the circles did not fall exactly on the smooth curve because of the dependence of γ's on the individual ionic strengths which were employed. However, since in any one region of oxalate ion activity extremely great differences in ionic strength were not encountered, the calculated points did cluster around the smooth curve.

The precision of the experimental results was tested by the quantity, $\sqrt{\Sigma(1/N)\delta_i^2}$, where $\delta_i = \log[Yb_{obs}] - \log[Yb_{calcd.}]$. For the 33 points included in Fig. 1 this quantity amounted to 0.110. Contributions to this quantity were partly from the errors inherent in the micropipetting of solu-

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[8] H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, 1943, Table 13-7-1A.

tions and the subsequent radioassays by counting techniques. The major effect, however, is believed to be the difficulty in establishing true equilibrium during the precipitation of ytterbium oxalate at oxalate ion concentrations of less than 10^{-4} molar.

Additional Evidence for the Formation of a Negative Complex.—Rimbach and Schubert[9] reported that the specific conductance of not highly purified ytterbium oxalate in pure water was 4.85×10^{-6} ohms^{-1} cm.$^{-1}$ at 25°.

With the assumption that only the ions, Yb^{+++} and $C_2O_4^{=}$ were formed a value of 4.4×10^{-25} was computed for the solubility product from this value.[10] A value of the specific conductance for such a solution has been estimated on the basis of the equilibria proposed in this work by means of the relations

$$m[\mathrm{Yb_{total}}] = 2/3M$$

or

$$m_{\mathrm{Yb(+++)}} + m_{\mathrm{Yb(C_2O_4)^+}} + m_{\mathrm{Yb(C_2O_4)_2^-}} = 2/3\,[m_{\mathrm{C_2O_4^=}} + m_{\mathrm{Yb(C_2O_4)^+}} + 2m_{\mathrm{(YbC_2O_4)_2^-}}] \quad (11)$$

It can be shown that at the concentrations involved the equilibria yielding the formation of $HC_2O_4^-$, $H_2C_2O_4^-$ and H^+ may be neglected with little error. From equations (5), (6), (7), and (11) with the assumption that all γ's in this very dilute solution were equal to 1.0 the ionic concentrations in a saturated solution were calculated and have been included in Table II. With values of the equivalent conductance for the two complex ions estimated to be 50 ohms^{-1} equivalents^{-1} cm.^{2} a specific conductance of 2.8×10^{-6} ohms^{-1} cm.$^{-1}$ for a saturated solution was estimated. Thus the equilibria postulated accounted for a specific conductance of the proper order of magnitude.

TABLE II

CONDUCTIVITY OF SATURATED SOLUTION OF $Yb_2(C_2O_4)_3$ IN PURE H_2O AT 25.0°

Ion	Concentration, mole/l.	Equivalent conductance λ_0	$\frac{Ni^c \lambda_0}{1000} \times 10^6$ ohm^{-1} cm.$^{-1}$
Yb^{+++}	1.41×10^{-7}	72[a]	0.031
$Yb(C_2O_4)^+$	2.40×10^{-5}	50[b]	1.20
$Yb(C_2O_4)_2^-$	7.88×10^{-6}	50[b]	0.39
$C_2O_4^=$	8.50×10^{-6}	71	1.21
		Total specific conductance Σ =	2.83

[a] Calculated from data of Rimbach and Schubert using the methods of Onsager.[11] [b] Estimated. [c] Ni, ionic normality.

To demonstrate qualitatively the existence of a negative ion containing ytterbium the following ion migration experiment was performed. Three electrolysis cells with anode and cathode chambers separated by a fine sintered glass disk were equipped with Ag–AgCl electrodes. In one chamber was placed a solution of *p*H 3.38 and a total oxalate concentration of 4.43×10^{-2} molar containing radioactive ytterbium. Virtually 100% of the ytterbium in such a solution was predicted to be in the form of $Yb(C_2O_4)_2^-$. In the other chamber of the cell was placed an identical oxalate solution with no ytterbium. Three such cells were prepared. Cell 1 contained the ytterbium in the chamber with the negative electrode, cell 2 contained the ytterbium in the chamber with the positive electrode, and cell 3 was maintained as a diffusion control with no applied voltage. A current of 1.0 ma. was passed through the cells 1 and 2 for 10 hours and radioassay performed to determine the activity present in the cell which originally had contained no ytterbium. It was found that in cell 1 the rate of migration of ytterbium activity was twice as great as in cell 3. However, no detectable quantity of ytterbium activity had passed through the sintered glass barrier of cell 2 verifying the original assumption that most of the ytterbium was present as a negative ion. When the voltage was reversed on cell 2, the rate of migration was in this case again twice as great as in the diffusion control.

Still more evidence was obtained by batch experiments with ion exchange resins. The cation exchange resin "Amberlite IR 100" failed to adsorb a detectable amount of ytterbium activity in a *p*H range of 2.5–3.5 with sufficiently high oxalate concentrations that the major portion of the ytterbium was predicted to be in the form of $Yb(C_2O_4)_2^-$. However from these same solutions an anion exchanger resin, "Duolite A-2," adsorbed 75% of the activity. It would appear, therefore, that nearly all of the ytterbium in solutions of high oxalate activity must exist in the form of a negative ion. However the variation of solubility in the region of high oxalate activity indicated that trioxalate ion, $Yb(C_2O_4)_3^{\equiv}$, was not formed in significant quantities. The evidence for the existence of $Yb(C_2O_4)^+$ rests in the agreement between the solubility values calculated from equation 9 and the experimental points. Without the $a^{-1/2}$ term in equation 9 which represents the contribution of $Yb(C_2O_4)^+$, the calculated points would lie closely along a curve with a sharp minimum at a very much lower value. Although an attempt was made to fit an equation without this term to the experimental data, no satisfactory agreement could be made. It should be noted that with the equilibria postulated the major contribution to the conductivity of solutions in pure H_2O of $Yb_2(C_2O_4)_3$ was by the $Yb(C_2O_4)^+$ and the $C_2O_4^=$ ions.

Summary

Radiochemical assays have permitted the measurement of ytterbium concentrations in buffered oxalate solutions at 25°. The data have been interpreted on the basis of the formation of the ionic species Yb^{+++}, $Yb(C_2O_4)^+$ and $Yb(C_2O_4)_2^-$. The ion $Yb(C_2O_4)_3^{\equiv}$ was apparently not formed in appreciable concentrations. Instability con-

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[9] E. Rimbach and A. Schubert, *Z. physik. Chem.*, **67**, 198 (1909).

[10] W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Inc., New York, N. Y., 1938, pp. 268.

[11] L. Onsager, *Physik. Z.*, **28**, 277 (1927).

stants for the complex ions and a solubility product were computed. These equilibria yielded reasonable values for the specific conductance of saturated solutions of $Yb_2(C_2O_4)_3$ in pure H_2O. The existence of a negative complex ion was verified by ionic migration and ion exchange resin experiments.

Ames, Iowa Received June 24, 1949

[Contribution from the Radiation Laboratory and Department of Chemistry, University of California]

An X-Ray Study of the Rare-earth Oxide Systems: Ce^{IV}–Nd^{III}, Cr^{IV}–Pr^{III}, Ce^{IV}–Pr^{IV} and Pr^{IV}–Nd^{III}[1]

By J. D. McCullough[2]

This study was undertaken with the object of learning more about the behavior of the oxides of praseodymium, in particular the unusual properties of Pr_6O_{11} and the relationships of this oxide to Pr_2O_3 and to PrO_2. It has also been of interest to observe the effects of trivalent Nd^{III} and tetravalent Ce^{IV} on the tendency of Pr^{III} to be oxidized to Pr^{IV} (or beyond) in the oxide systems.

Materials.—The starting materials employed in most of the present study were commercial preparations of CeO_2, Pr_6O_{11} and Nd_2O_3 obtained from the Rohm and Haas Company, Philadelphia; the Research Chemicals Company, Burbank, California and from the Maywood Chemical Works, Maywood, New Jersey, respectively. Spectrographic analysis showed these oxides to be 99.5, 99.5 and 98.5% pure from the standpoint of the metal content. The more critical samples, including most of those higher than 80% in praseodymium, were prepared by use of column purified praseodymium. Spectrographic analysis of this material indicated no detectable amounts of other rare earths or of the metals lanthanum, scandium, yttrium, iron, aluminum and calcium. Certain of the cerium-rich samples were prepared from cerium oxalate obtained from Prof. F. H. Spedding. The only impurities detected in a spectrographic analysis of this material were 0.017% each of neodymium and lanthanum.

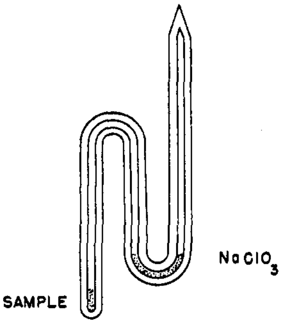

Fig. 1.—Quartz tube for oxidation of praseodymium samples.

In order to convert the starting materials to substances of definite composition in weighable form, they were strongly ignited in air. Since there was some doubt regarding the exact composition of the oxide of praseodymium resulting from air ignition, it was finally heated to approximately 1400° for two hours in high vacuum. This procedure yielded a pale green powder which was shown by means of its X-ray diffraction pattern to be the A (hexagonal) form of Pr_2O_3.

Procedure.—Stock solutions of the three rare-earths were prepared by dissolving weighed samples of the oxides in nitric acid. The dissolution of CeO_2 was hastened by the addition of hydrogen peroxide. Mixtures of the three pairs of rare-earths having the compositions shown in the tables were prepared by measuring appropriate volumes of the stock solutions. Each mixed solution was added quickly with stirring to an excess of freshly prepared aqueous ammonia. The resulting precipitates were collected on sintered glass, oven-dried, then ignited in air in platinum crucibles for two hours at 800°. Each sample was then ground in an agate mortar and heated in high vacuum for three hours at 1400°. This treatment was found to convert praseodymium to Pr^{III} and cerium to Ce^{IV} while neodymium remained in the trivalent state. X-Ray powder patterns were prepared of all samples in this state with the exception of some of the Pr–Nd and Ce–Pr mixtures. The Ce–Pr and Pr–Nd mixtures were then reheated in small open crucibles in a furnace at 600° for sixteen hours, after which X-ray powder patterns were again prepared. Finally, most of the praseodymium-containing samples were heated in sealed quartz tubes (Fig. 1) under an oxygen pressure of approximately 50 atmospheres. The oxygen was generated by decomposing a weighed sample of dry sodium chlorate in the tube after sealing, the approximate pressure being estimated from the volume of the tube and the weight of sodium chlorate taken. After decomposition of the sodium chlorate by local application of heat, the tubes were placed in a furnace for forty-eight hours at 300°. This treatment has been found to convert Pr_6O_{11} to PrO_2 and presumably con-

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(1) Based on work done for the United States Atomic Energy Commission under Contract W-7405-Eng.-48 with the Radiation Laboratory, University of California, Berkeley 4, California.

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