β-carbon instead of the α-carbon of the adsorption complex agree well with the average value, 13%, deduced from the degradation experiments on propane and propylene.

In conclusion it should be emphasized that the observations reported in the present paper were all made on the products from synthesis runs over a single iron catalyst at one atmosphere pressure for a 1:1 carbon monoxide–hydrogen gas at space velocities in the range 100 to 240 and at temperatures ranging from 210 to 243°. Care must therefore be exercised in extrapolating these data to the higher temperatures and pressures used in commercial or pilot plant operation, though we see no reason to doubt the applicability of this same mechanism to the synthesis at higher pressure, temperature and space velocity.

PITTSBURGH, PA. RECEIVED JUNE 30, 1950

[CONTRIBUTION NO. 108 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Solubility of the Rare Earth Oxalates and Complex Ion Formation in Oxalate Solution. II. Neodymium and Cerium(III)[1]

BY CARL E. CROUTHAMEL[2] AND D. S. MARTIN, JR.

The solubilities of cerium(III) and neodymium in buffered oxalate solutions have been determined by means of radiochemical assays. The data have permitted the calculation of equilibrium constants which satisfactorily describe the systems. These constants have been compared with those from earlier work with ytterbium. The results have indicated that neodymium formed the complex ions $Nd(C_2O_4)^+$ and $Nd(C_2O_4)_2^-$ with very nearly the same stability constants as ytterbium, but that it had a minimum solubility of about 1.5 × 10^{-6} mole/liter compared to 3 × 10^{-5} mole/liter for ytterbium. Evidence was found for the formation of $Ce(C_2O_4)^+$, $Ce(C_2O_4)_2^-$ and $Ce(C_2O_4)_3^{\equiv}$; and cerium had a minimum solubility of about 1.7 × 10^{-6} mole/liter.

Introduction

Previous studies with ytterbium in oxalate solutions[3] have demonstrated that the determination of concentrations by radioassay would permit the evaluation of equilibrium constants for the system. The present paper describes results of similar experiments with neodymium and cerium. Since the lighter rare earths have greater ionic radii,[4] it was expected that the degree of complexing would be less and a lower solubility in oxalate would result. The data presented in this paper for neodymium and cerium confirmed the lower solubility but indicated that the complexes were not substantially weaker. The behavior of cerium was markedly different from that of ytterbium and neodymium in that definite evidence was found for the formation of a trioxalate complex.

We wish to express our appreciation to Dr. F. H. Spedding, and Messrs. T. Butler and J. Powell, who prepared the very pure sample of neodymium oxide, for their assistance, interest and encouragement of this work.

Experimental

Materials.—As source material for cerium, a sample of cerium(IV) ammonium nitrate standard of reference supplied by the G. Frederick Smith Co. was used. This material was analyzed spectroscopically in this Laboratory, and other rare earths were not detected. A sample of cerium(IV) oxide was prepared from this sample and irradiated in the Argonne National Laboratory pile for three months to prepare the Ce^{141} isotope. Ce^{141} has been reported to decay with a half-life of 28–32 days by emission of β^- with a maximum energy of 0.53 mev. and with a partially converted 0.146 mev. gamma ray accompanying 70% of the disintegrations.[5,6,7]. Ce^{139} with a 140 day half life would not have been formed in sufficient quantities to be significant.[8] However, the formation of the 33 hour Ce^{143} which decays to a β-emitting daughter Pr^{143} with a half-life of 13.8 days would be expected to introduce a significant radioactive impurity into the sample.[9] To eliminate the praesodymium fraction, the irradiated sample was reduced to the Ce^{III} state and then incompletely oxidized to Ce^{IV} with sodium bromate. A precipitation of the cerium(IV) iodate according to the procedure of Boldridge and Hume[10] was then effected. Finally, the cerium(IV) iodate was reduced by hydrogen peroxide in sulfuric acid solution and the oxalate precipitated and washed until no barium sulfate test was obtained on the wash solution.

Standard solutions were prepared from samples of 50–100 mg. of CeO_2 weighed on an analytical balance. Aliquots of these solutions withdrawn by means of micro pipets and mounted for counting in the normal procedure yielded specific activities for second shelf geometry of 3 × 10^6 ct./(min.)(mg. Ce).

Absorption and decay curves indicated no appreciable radioactive impurities.

A sample of the Lindsay Light Co. neodymium carbonate was the neodymium source material. The product was supplied to us after two separations in ion exchange columns[11] and was reported as "spectroscopically pure." It is believed that the upper limit of any rare earth impurity was less than 0.1%.

The neodymium oxide was irradiated with slow neutrons for one month in the Argonne National Laboratory pile to form Nd^{147} which decays by the emission of a 0.9 mev., β^- or a β^- and 0.58 mev. γ with a half-life of 11.0 d.[12,13] The daughter isotope Pm^{147} is also radioactive, decaying by the emission of a 0.2 mev. β^- with a half-life of 3.7 years.

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[1] Work performed in the Ames Laboratory of the Atomic Energy Commission.

[2] Argonne National Laboratory, Chicago, Illinois.

[3] C. E. Crouthamel and D. S. Martin, Jr., THIS JOURNAL **72**, 1382 (1950).

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[5] W. H. Burgus, "Plutonium Project Report" CC-680, p. 13 (May, 1943).

[6] L. R. Shepard, *Research*, **1**, 671 (1948).

[7] (a) M. Ter-Pogassion, C. S. Cook, C. H. Goddard and J. E. Robinson, *Phys. Rev.*, **76**, 909 (1949); (b) D. Walker, *Proc. Phys. Soc.*, **62A**, 799 (1949).

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[10] W. F. Boldridge and D. N. Hume, AECD 2531-C.

[11] F. H. Spedding, E. I. Fulmer, J. E. Powell and T. A. Butler, THIS JOURNAL, **72**, 2354 (1950).

[12] G. J. Seaborg and I. Perlman, *Rev. Mod. Phys.*, **20**, 585 (1948).

[13] J. A. Marinsky, L. E. Glendenin and C. D. Coryell, THIS JOURNAL, **69**, 2781 (1947).

The mass of this element formed would be of only a "tracer" magnitude and would not be expected to influence the equilibrium. However, the activity, defined as disintegrations per unit time would be appreciable; the ratio of Pm/Nd disintegration rates was computed to be 0.007 at the end of the 30-day irradiation and 0.07 30 days later. Consequently, in the counting measurements performed a month after the end of irradiation a 30 mg./cm.[2] Al absorber was employed which was estimated to reduce the Pm/Nd counting ratio by a further factor of at least $^1/_{20}$–$^1/_{40}$. Any effect of this daughter was believed to have been effectively removed from the measurements.

The lead absorption curve of the radiation gave a half thickness of 5.4 g./sq. cm. (corresponding to 0.57 mev.) and the estimated end-point for the range of the electrons in Al was 400 mg./sq. cm.[2] (corresponding to about 1.0 mev.). The half-life estimated from a decay curve in this laboratory was 11.6 days. No evidence to indicate any other short lived activity was discovered; it was therefore concluded that the sample of neodymium oxide had been exceptionally pure. The specific activity at the time of the first assay was 2×10^6 cts./(min.)(mg. Nd). The standard solutions used for preparing equilibrium mixtures were prepared by dissolving weighed quantities of the radioactive Nd_2O_3 in perchloric acid. A large portion of the excess acid was evaporated off. Perchlorate ion concentrations needed for the subsequent calculation of ionic strength were estimated by means of a careful measurement of *p*H and a radioassay. Since for these solutions

$$m_{ClO_4^-} = m_{H^+} + 3m_{Nd^{+++}} \qquad (1)$$

(m's represent molar concentrations, mole/liter), the concentration of ClO_4^- was computed from these data by the use of a unicharged ion activity coefficient which was consistent with the finally calculated ionic strength for converting H^+ activity to concentration.

Procedure.—For the most part the experimental details have been described in the previous paper.[3] Some significant changes were required to attain equilibrium quickly because of the fairly short half-life of the neodymium and the fact that the solubility of the oxalate was so low (about a factor of 10 less than for the ytterbium salt). A Burrell shaker was used to aid the establishment of the equilibrium. Each solution was shaken in a constant temperature bath at 25.0° for 12 hours before measuring the *p*H or withdrawing samples for radioassay and the oxalate titration.

The neodymium concentration of all solutions as indicated by the radioassays remained constant after the fifteenth day and all solutions were checked 30 days after preparation. Equilibrium was approached by direct precipitation from neodymium perchlorate with the addition of oxalate buffers in both hot and cold solutions. Also wet washed neodymium oxalate crystals were brought into equilibrium with oxalate buffers. All the methods gave essentially the same equilibrium values and the difficulties in establishing equilibrium which were encountered with the ytterbium experiments did not appear.

With cerium, equilibrium was attained by adding the wet washed cerium(III) oxalate crystals to the oxalate buffer solutions. In some instances the crystals were dissolved at 60° in which case concentrations approximately ten times greater than equilibrium values at 25° were established. These solutions were then brought to equilibrium by mechanical shaking in a thermostat at 25.0°. In these cases the equilibrium was attained in about 1 day; however, the majority of the solutions were checked over a period of 90 days.

The methods for calculating oxalate ion activity and the necessary activity coefficients have been described in the previous paper.[3]

Since the preparation of that paper, however, the new edition of Harned and Owen[14] has pointed out that the original calculations for the activity coefficients of $LaCl_3$ were in error. However, in the ytterbium work activity coefficients of rare earth chloride were extrapolated to approach the limiting law for low concentrations. Consequently, the values of γ_3, the activity coefficient for a trivalent ion used, gave a $\gamma_\pm$ for the chloride which were not greatly different from the corrected values of $LaCl_3$. In the present work γ_3's have been computed from the new $LaCl_3$ values and accordingly the standard free energy changes for the ytterbium which are included in Table IV have been recalculated from the old data with these new coefficients. To facilitate the use of the data presented in this paper tabulations of γ_1, γ_2, γ_3 employed have been given in Table I. In most equilibrium solutions the square root of ionic strength was below a value of 0.3 so that a treatment considering activity coefficients as a function of only charge and ionic strength would be satisfactory. In the few solutions at very low oxalate activity which were attained by a low *p*H in the buffered solutions, the square root of ionic strength was about 0.5–0.7. For these solutions the activity coefficients must be somewhat in question. However, it should be emphasized that errors have been minimized by using experimentally determined activity coefficient products and ratios for very similar ionic species to those involved in this work.

Discussion of Results

Experimental results obtained with 21 cerium equilibrium solutions have been collected in Table II. As was the case with ytterbium wide variations in binoxalate ion activities appeared to have

TABLE I

IONIC ACTIVITY COEFFICIENTS EMPLOYED IN THE RARE EARTH OXALATE EQUILIBRIA

$\sqrt{\mu}$	γ_1		γ_3
0.050	0.945	0.795	0.700
.100	.905	.660	.473
.150	.870	.561	.333
.200	.835	.488	.231
.250	.810	.426	.170
.300	.790	.384	.134
.350	.775	.349	.111
.400	.760	.318	.092
.450	.750	.301	.080
.500	.735	.278	.070
.550	.730	.264	.063
.600	.720	.249	.056
.650	.710	.234	.052
.700	.705	.224	...
.750	.700	.216	...

TABLE II

DATA FROM SOLUBILITY EXPERIMENTS OF $Ce_2(C_2O_4)_3 \cdot 9H_2O$ AT 25.0°

$\sqrt{\mu}$	*p*H	$-\log M$[a]	$-\log a_{C_2O_4^=}$	$-\log Ce$[b] Obsd.	Calcd.
0.558	4.20	0.73	1.48	4.20	4.16
.607	5.85	0.90	1.53	4.16	4.18
.425	4.25	1.07	1.59	4.40	4.39
.230	7.60	1.75	2.09	4.81	4.98
.182	5.22	1.93	2.25	5.02	5.09
.157	7.20	2.09	2.36	5.06	5.18
.107	7.76	2.42	2.61	5.35	5.33
.094	6.90	2.53	2.70	5.34	5.40
.079	7.34	2.69	2.82	5.47	5.47
.074	5.03	2.70	2.88	5.52	5.50
.076	4.11	2.51	2.98	5.56	5.54
.074	3.60	2.37	3.17	5.66	5.62
.062	3.09	2.47	3.71	5.82	5.76
.100	2.03	1.94	4.20	5.66	5.72
.072	2.30	2.25	4.29	5.75	5.75
.200	1.45	1.81	4.90	5.43	5.49
.245	1.25	1.58	4.95	5.37	5.46
.490	0.62	1.47	5.88	4.43	4.52
.437	0.72	1.91	6.15	4.18	4.21
.570	0.61	1.86	6.27	4.00	3.93
.570	0.62	2.56	6.97	2.94	2.92

[a] M is the total oxalate concentration, moles/liter.
[b] Ce is the total rare earth solubility, moles/liter.

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[14] H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publishing Corp., New York, N. Y., 1950, p. 427.

no primary effect in controlling the solubility, so within the ranges tested the solubility could be represented satisfactorily as a function of just the oxalate ion activity. Therefore, the experimentally determined values of log $m_{\text{Ce-total}}$ have been plotted against log $a_{C_2O_4}$ in Fig. 1. The points clustered around a smooth curve. The similar curve obtained with ytterbium has also been shown in this figure. Differences between cerium and ytterbium were quite significant. The ytterbium curve approached accurately a limiting slope of one-half in the region of high oxalate ion activity indicating the formation of $Yb(C_2O_4)_2^-$ but no appreciable $Yb(C_2O_4)_3^=$. In this region the slope of the cerium curve was significantly greater than 0.5 although somewhat less than 1.5. Accordingly, in a treatment similar to that in the previous work with the consideration of complexes of the form, $RE(C_2O_4)_n^{3-2n}$ (RE = rare earth), values of n equal to 1, 2 and 3 were required for cerium. The formation of a trioxalate complex should lead, as a first approximation, to a limiting slope of 3/2. Thus, the system is characterized by the four equilibria

$$RE(C_2O_4)_3^= \rightleftharpoons RE(C_2O_4)_2^- + C_2O_4^= \qquad (I)$$

$$RE(C_2O_4)_2^- \rightleftharpoons RE(C_2O_4)^+ + C_2O_4^= \qquad (II)$$

$$RE(C_2O_4)^+ \rightleftharpoons RE^{+++} + C_2O_4^= \qquad (III)$$

$$RE_2(C_2O_4)_3\ (s) \rightleftharpoons 2RE^{+++} + 3C_2O_4^= \qquad (IV)$$

The solid phase should of course be the appropriate hydrate. The four equilibrium constants were defined in this manner.

$$K_I = \gamma_1 m_{RE(C_2O_4)_2}\, a_{C_2O_4^=} / \gamma_3 m_{RE(C_2O_4)_3^=} \qquad (2)$$

$$K_{II} = m_{RE(C_2O_4)^+}\, a_{C_2O_4^=} / m_{RE(C_2O_4)_2^-} \qquad (3)$$

$$K_{III} = \gamma_3 m_{RE^{+++}} a_{C_2O_4^=} / \gamma_1 m_{(REC_2O_4)^=} \qquad (4)$$

$$K_{sp1} = \gamma_3^2\, m^2{}_{RE^{+++}}\, a_{C_2O_4^=} \qquad (5)$$

For convenience in the computations another solubility product was also used for the reaction

$$RE_2(C_2O_4)_3(s) \rightleftharpoons RE(C_2O_4)^+ + RE(C_2O_4)_2- \qquad (V)$$

This solubility product, K_{sp2}, is related to the other equilibrium constants by the relation

$$K_{sp_1} = K_{sp_2} K_{II}\, K^2{}_{III} \qquad (6)$$

From this set of equilibrium constants the molar concentrations of each species were expressed in terms of the oxalate ion activities. By summing these terms an expression for the total rare earth concentration would result

$$m_{\text{RE-total}} = m_{RE^{+++}} + m_{RE(C_2O_4)^+} + m_{RE(C_2O_4)_2^-} + m_{RE(C_2O_4)_3^=} \qquad (7)$$

Substituting expressions for the individual species in this equation yielded

$$m_{\text{RE-total}} = \left(\frac{\sqrt{K_{sp_2} K_{II}}\, K_{III}}{\gamma_3}\, a^{3/2}_{C_2O_4^-}\right) + \left(\frac{\sqrt{K\, K_{sp_2 II}}}{\gamma_1}\, a^{-1/2}_{C_2O_4^-}\right) + \left(\frac{\sqrt{K_{sp2} K_{II}}}{\gamma_1 K_{II}}\, a^{1/2}_{C_2O_4^-}\right) + \left(\frac{\sqrt{K_{sp_2} K_{II}}}{\gamma_3 K_I K_{II}}\, a^{3/2}_{C_2O_4^-}\right) \qquad (8)$$

This equation was rewritten

$$m_{\text{RE-total}} = \left(\frac{A}{\gamma_3}\, a^{-3/2}_{C_2O_4^=}\right) + \left(\frac{B}{\gamma_1}\, a^{-1/2}_{C_2O_4^=}\right) + \left(\frac{C}{\gamma_1}\, a^{-1/2}_{C_2O_4^=}\right) + \left(\frac{D}{\gamma_3}\, a^{-3/2}_{C_2O_4^=}\right)$$

The coefficients, A, B, C and D, were computed to fit the experimental data. Although this may appear to be a large number of empirical constants, it must be noted that variations of the oxalate ion activity parameter amounted to 10^6. Therefore, each of the coefficients was defined fairly unambiguously. It was found that if any one of the coefficients was varied by ±5% and the other coefficients adjusted to give the best fit, very serious deviations of the calculated solubilities from the experimental points would occur. The constants obtained described the system very satisfactorily as can be seen by a comparison of the calculated and experimental solubilities given in Table II or by examination of Fig. 1. As a test of the precision of the data, the quantity $\sqrt{1/N\Sigma\delta_i^2}$ for the 21 points was found to be 0.065 where N is the number of points and δ_i = log $m_{\text{Ce-total}}$ (calculated) − log $m_{\text{Ce-total}}$ (observed) for the ith point.

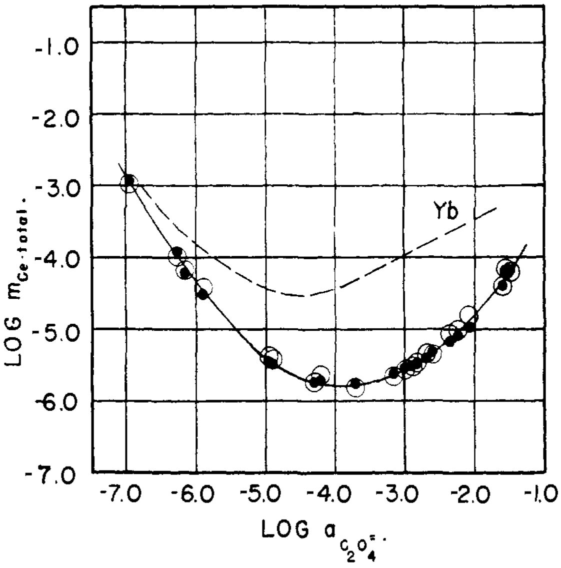

Fig. 1.—Ce (total) concentration in buffered oxalate solutions: ○, experimental concentrations from radioassays; ●, concentrations calculated by means of equation 8 and the equilibrium constants in Table IV.

The experimental results for 27 neodymium solutions have been included in Table III and also shown on Fig. 2. For this element results similar to ytterbium were obtained in that the limiting slope at high oxalate ion activity was +1/2, hence there was no evidence for the formation of a trioxalate complex. The constants K_{II}, K_{III}, K_{sp1} and K_{sp2} were evaluated in the same manner as for cerium. A lower limit for K_I was estimated by the following arguments. A typical solubility of neodymium in a solution with $a_{C_2O_4^=} = 3.16 \times 10^{-2}$ and $\gamma_3 = 0.2$ would be 1.78×10^{-5} mole/liter. If the total solubility were approximately 0.5×10^{-5} mole/liter higher, it would have been considered an appreciable deviation from the +1/2 slope observed. The additional solubility would have been due mainly to the term $m_{RE(C_2O_4)_3^=}$. By the use of this value and the expression

$$K_I = \frac{K_{sp_2}}{K_{II}\gamma_3 m_{RE(C_2O_4)_3^=}} \qquad (10)$$

Table III

Data from Solubility Experiments of $Nd_2(C_2O_4)_3 \cdot 10H_2O$ at 25.0°

$\sqrt{\mu}$	pH	−log M[a]	−log $a_{C_2O_4^=}$	−log Nd[b] Obsd.	−log Nd[b] Calcd.
0.252	3.29	1.41	1.11	4.70	4.51
.258	4.00	1.41	2.07	5.08	4.96
.185	4.46	1.83	2.26	5.05	5.10
.196	4.70	1.91	2.30	5.33	5.12
.154	3.58	1.92	2.79	5.34	5.36
.179	3.15	1.55	2.79	5.54	5.36
.083	5.62	2.73	2.79	5.28	5.39
.092	3.90	2.30	2.90	5.19	5.44
.140	3.12	1.94	3.20	5.77	5.56
.079	2.75	1.92	3.50	5.82	5.70
.054	3.40	2.73	3.59	5.82	5.73
.084	3.37	2.68	3.68	5.81	5.76
.075	2.43	1.91	3.81	5.82	5.80
.135	2.20	1.90	4.07	5.96	5.83
.136	2.13	1.88	4.14	5.66	5.83
.053	2.69	2.55	4.18	5.71	5.86
.135	2.03	1.87	4.23	5.83	5.83
.117	1.90	1.77	4.28	5.75	5.84
.070	2.25	2.28	4.37	5.83	5.86
.055	2.63	2.66	4.37	5.91	5.87
.136	1.75	1.82	4.50	5.72	5.83
.026	3.00	3.20	4.51	5.56	5.84
.057	2.48	2.79	4.64	5.61	5.83
.088	1.73	2.68	5.37	5.46	5.58
.188	1.50	3.16	6.17	5.00	5.09
.500	0.60	2.68	7.12	3.36	3.67
.543	0.52	2.73	7.32	3.38	3.33

[a] M is the total oxalate concentration, moles/liter.
[b] Nd is the total rare earth solubility, moles/liter.

a limiting value of 90 was obtained. This value should be compared with 0.15 obtained for cerium. For the neodymium data the test of the precision, $\sqrt{1/N\Sigma\delta_i^2}$, was equal to 0.150 for the 27 points.

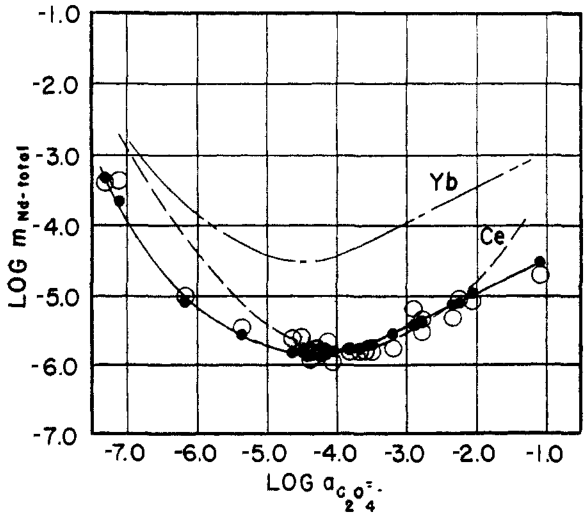

Fig. 2.—Nd (total) concentration in buffered oxalate solutions: ○, experimental concentrations from radioassays; ●, concentrations calculated by means of equation 8 and the equilibrium constants in Table IV.

For purposes of comparison the corresponding equilibrium constants of ytterbium taken from the earlier paper[3] have been included in Table IV.

Table IV

Solubility Products and Instability Constants of Cerium, Neodymium and Ytterbium Oxalates

Equilibrium constants	Ce	Nd	Yb
K_{sp_2}	6.0×10^{-13}	4.0×10^{-13}	1.9×10^{-10}
K_{sp_1}	5.9×10^{-30}	7.7×10^{-32}	1.24×10^{-29}
K_I	0.15	>90	>90
K_{II}	1.1×10^{-4}	5.0×10^{-5}	2.6×10^{-5}
K_{III}	3.0×10^{-7}	6.2×10^{-8}	5.0×10^{-8}

On the basis of these equilibria the solubility of cerium(III) oxalate and neodymium oxalate in pure water have been calculated and the specific conductance of these solutions estimated. As shown in the previous paper a solution must satisfy to a good approximation the relation

$$m_{\text{RE-total}} = {}^2/_3 m_{\text{oxalate-total}} \tag{11}$$

and activity coefficients would be nearly unity. Maintaining the terms of equation 9, the following equation must be solved by trial and error for the solution

$$\left(3Am_{C_2O_4^=}^{-3/2}\right) + \left(Bm_{C_2O_4^=}^{-1/2}\right) - \left(Cm_{C_2O_4^=}^{1/2}\right) - \left(3Dm_{C_2O_4^=}^{3/2}\right) - \left(2m_{C_2O_4^=}\right) = 0 \tag{12}$$

The concentrations and specific conductances calculated from the experimentally determined cofficients, A, B, C and D have been collected in Table V for cerium and Table VI for neodymium.

Table V

Calculated Specific Conductance and Molar Concentrations of $Nd_2(C_2O_4)_3 \cdot 10H_2O$ in Conductivity Water at 25°

Ion	Concn. × 10^6, m./l.	Equivalent conductance. λ_0	$N_i\lambda_0/1000 \times 10^6$ ohm^{-1} cm.$^{-1}$
Nd^{+++}	0.11	72[b]	0.204
$Nd(C_2O_4)^+$	3.35	70[a]	.235
$Nd(C_2O_4)_2^-$	0.12	70[a]	.008
$C_2O_4^=$	1.80	71	.256

$m_{\text{Nd-total}} = 3.58 \times 10^{-6}$ m./l. Total sp. cond. = 0.523×10^{-6} ohm^{-1} cm.$^{-1}$

5.36×10^{-6} m./l.[e] 0.75×10^{-6}[c]

3.7×10^{-6}[d]

[a] Estimated. [b] Anfrect, Inaugural Dissertation, Berlin, 1904. [c] Specific conductance values of Rimbach and Schubert.[15] [d] Specific conductances calculated from data of Sarver and Brinton.[16] [e] Gravimetric values of Sarver and Brinton.[16]

Table VI

Calculated Specific Conductance and Molar Concentrations of $Ce_2(C_2O_4) \cdot 9H_2O$ in Conductivity Water at 25°

Ion	Concn., m./l.	Equivalent conductance, λ_0	$N_i\lambda_0/1000 \times 10^6$ ohm^{-1} cm.$^{-1}$
Ce^{+++}	0.471×10^{-6}	72[b]	0.102
$Ce(C_2O_4)^+$	4.67×10^{-6}	70[a]	.327
$Ce(C_2O_4)_2^-$	0.13×10^{-6}	70[a]	.009
$Ce(C_2O_4)_3^=$	2.6×10^{-12}	. . .	. . .
$C_2O_4^=$	2.95×10^{-6}	71	.418

$m_{\text{Ce-total}} = 5.27 \times 10^{-6}$ m./l. Total sp. cond. = 0.856×10^{-6} ohm^{-1} cm.$^{-1}$

1.51×10^{-6} m./l.[e] 0.651×10^{-6}[c]

1.24×10^{-6}[d]

Agreement with values obtained by a gravimetric method by Sarver and Brinton[15] can be seen to be only fair. The estimated specific conductances have also been compared with the values of Rimback and Schubert[16] and those of Sarver and Brinton.

Standard free energy changes for the reactions of interest have been given in Table VII for the three elements. Structures of rare-earth oxalates have not been determined; however, it has been reported that both lanthanum and cerium form a 9-hydrate whereas the heavier rare earths precipitate as a 10-hydrate. The decrease in hydration of cerium and lanthanum may be the result of a higher coördination of oxalates about these ions. The absence of evidence of trivalent oxalate complex in the case of the heavier neodymium and ytterbium ions with smaller ionic radii may well be caused by steric factors.

TABLE VII

STANDARD FREE ENERGY CHANGES OF THE REACTION INVOLVING CERIUM, NEODYMIUM AND YTTERBIUM AT 25°

	Ce, kcal.	Nd, kcal.	Yb, kcal.
$\Delta F°_{\text{I}}$	+ 1.12	<-2.67	<-2.67
$\Delta F°_{\text{II}}$	+ 4.40	+ 5.87	+ 6.26
$\Delta F°_{\text{III}}$	+ 8.90	+ 9.83	+ 9.96
$\Delta F°_{\text{sp}_1}$	+39.87	+42.43	+39.35
$\Delta F°_{\text{sp}_2}$	+16.67	+16.91	+13.26

The stability of the monoxalate and dioxalate complexes seemed surprisingly independent of ionic radius as indicated by the similarity in values of $\Delta F°_{\text{II}}$ and $\Delta F°_{\text{III}}$. This was particularly apparent with the pair, neodymium and ytterbium. Although $\Delta F°_{\text{II}}$ and $\Delta F°_{\text{III}}$ were slightly larger for neodymium than for ytterbium as had been expected, the difference must be considered negligible in view of the fairly large difference of ionic radius which must be nearly 0.2 Å. It may be noted that if the two elements have nearly equal values for K_{II} and for K_{III}, the solubility curves differ only by a vertical displacement. This feature of the neodymium–ytterbium systems is apparent in Fig. 2. The fairly large difference in the solubilities of the oxalates of these two elements must then have resulted largely from differences in the crystal energies.

Another feature of these systems was the stability of the dioxalate complexes relative to the monoxalate. Thus the values of $\Delta F°_{\text{II}}$ seemed particularly large when compared with the corresponding values of $\Delta F°_{\text{III}}$ which would contain contributions from the separation of a greater charge and the low entropy of a trivalent RE ion. It would appear therefore that the presence of one oxalate expedites the addition of a second ion.

AMES, IOWA RECEIVED JULY 31, 1950

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[15] L. A. Sarver and H. M. P. Brinton, THIS JOURNAL, **49**, 943 (1927).

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

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Thermodynamic Properties of Naphthalene

BY GORDON M. BARROW[1] AND A. L. MCCLELLAN[2]

The heat of vaporization of naphthalene has been measured and found to be 11,086 ± 30 cal./mole at 209 mm. pressure and 440.9°K. From vapor heat capacity determinations at 451.0 and 522.7°K. the heat capacity in the ideal gas state at these temperatures has been obtained. Values of the entropy and heat capacity of solid and liquid naphthalene were taken from the literature and used with the heat of vaporization determined here to calculate 95.9 ± 0.4 cal./deg. mole for the entropy of naphthalene in the ideal gas state at 440.9°K. Thermodynamic functions have been calculated from spectroscopic data for the range 298.16 to 1500°K. Comparison shows agreement between calculated and experimentally determined properties.

Naphthalene, one of the simplest polycyclic compounds, is the logical starting point for an extension of the calculated thermodynamic properties of hydrocarbons as compiled by the American Petroleum Institute, Research Project 44. A reliable vibrational assignment obtained in this Laboratory provides a basis for the necessary statistical calculations, and experimental vapor heat capacity and entropy determinations verify the calculated values.

Experimental

Materials and Apparatus.—The material used in the heat of vaporization and heat capacity determinations was Baker and Adamson resublimed naphthalene, repeatedly crystallized from ether and suction dried. The measurements were made in a flow calorimeter similar in design to those described by Pitzer[3] and by Waddington, Todd and Huffman.[4] A more complete description of this apparatus will be given in a later paper. Although the calorimeter was primarily intended for determining the vapor heat capacities and heats of vaporization of compounds liquid at room temperature and boiling below 180°, only slight modifications were necessary for the measurements on naphthalene.

A suitable boiling point of naphthalene, was obtained by controlling the pressure of the system at 209 mm. during all the measurements. At this pressure the boiling point was 167.7°. Solidification of the naphthalene was prevented by passing steam through the reflux condenser and enclosing the exposed tubing in hot air jackets.

With these additions the heat capacities and heats of vaporization were determined in the usual way as discussed, for example, by Pitzer.[3]

Heat of Vaporization.—Four separate determinations of the heat of vaporization at 209 mm. and 440.9°K. were made at various flow rates. The results, after the usual corrections[2] for heat lost in the vaporizer heater leads and the change in liquid volume, are

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[3] K. S. Pitzer, THIS JOURNAL, **63**, 2413 (1941); K. S. Pitzer and W. D. Gwinn, *ibid.*, **63**, 3313 (1941); R. Spitzer and K. S. Pitzer, *ibid.*, **68**, 2537 (1946).

[4] G. Waddington, S. S. Todd and H. M. Huffman, *ibid.*, **69**, 22 (1947).