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.

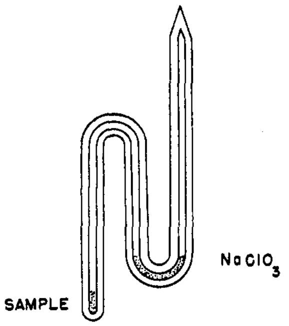

Fig. 1.—Quartz tube for oxidation of praseodymium samples.

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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verts all praseodymium in the mixtures to Pr^{IV}. This assumption is substantiated by the nature of the solid–solution diagrams shown in Figs. 2, 3 and 4. X-Ray powder patterns were prepared for all of the oxygen-treated samples.

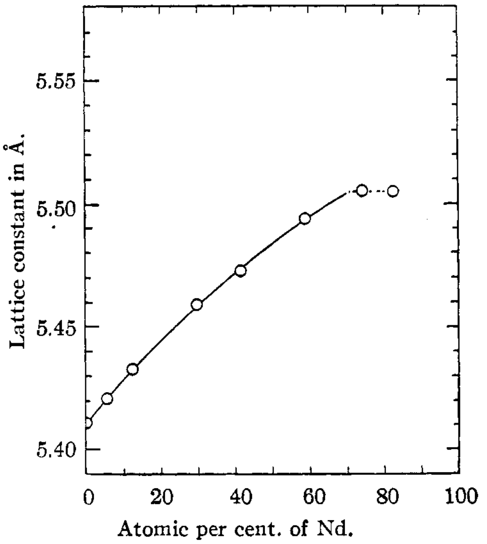

Fig. 2.—Lattice constants for solid solutions in the ceric oxide–neodymium oxide system with fluorite-type structure.

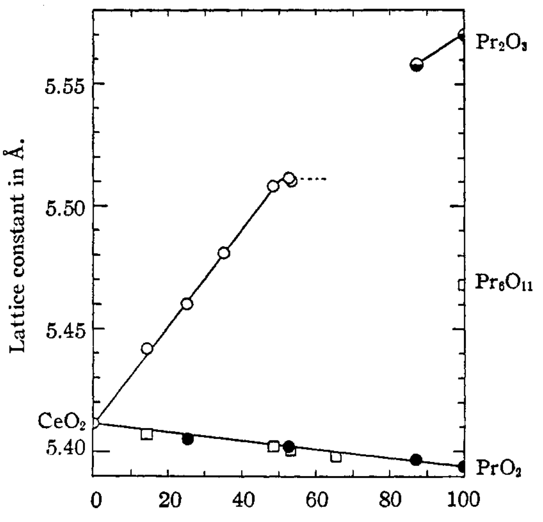

Fig. 3.—Lattice constants for solid solutions in the ceric oxide–praseodymium oxide systems: O, heated in vacuum, fluorite-type phase; ●, heated in oxygen, fluorite-type phase; ⊖, heated in vacuum, C-type phase; □, heated in air, fluorite-type phase.

X-Ray Diffraction.—Powder diffraction photographs were prepared by use of copper radiation filtered through nickel foil. The camera was of the cylindrical back-reflection type with an effective diameter of 9.013 cm. Calibration of the camera was based on powder photographs of reagent grade sodium chloride prepared by use of unfiltered copper radiation. The lattice constant of sodium chloride was taken as 5.639 Å. This and all other lattice constants reported in this paper are in Ångström units based on the X-ray wave lengths: CuKα = 1.5418 Å., CuKα_1 = 1.5405 Å. and CuKα_2 = 1.5443 Å.

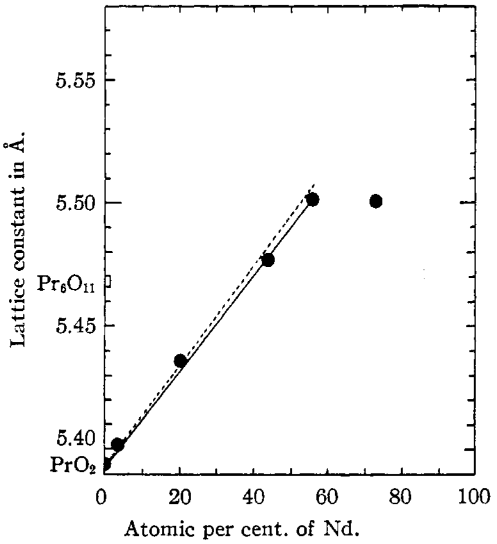

Fig. 4.—Lattice constants for solid solutions in the praseodymium oxide–neodymium oxide system: ●, heated in oxygen, fluorite-type phase; □, heated in air, fluorite-type phase.

Results and Discussion.—The experimental data are given in Tables I, II and III, and are shown graphically in Figs. 2, 3 and 4. It is seen that in the single-phase regions, the oxide systems Ce^{IV}–Nd^{III}, Ce^{IV}–Pr^{IV}, Ce^{IV}–Pr^{III} and Pr^{IV}–Nd^{III} show a nearly linear relationship between the lattice constant, a_0, and the composition in terms of the atomic per cent. of the total rare-earth metal present in the trivalent form. In Fig. 5, the oxide systems Ce^{IV}–La^{III},[3] Ce^{IV}–Pr^{III}, Ce^{IV}–Nd^{III} and Pr^{IV}–Nd^{III} are shown together for comparison purposes. The relative slopes of the lines are in keeping with the relative radii of the cations involved. Exact computa-

TABLE I

LATTICE CONSTANTS FOR SOLID SOLUTIONS OF CERIC AND NEODYMIUM OXIDES

Sample	Atomic % Nd	Lattice constant, Å. Fluorite structure
1	0	5.411 ± 0.001
2	5.7	5.421 ± 0.001
3	12.5	5.433 ± 0.002
4	30.0	5.459 ± 0.003
5	41.7	5.473 ± 0.003
6	58.8	5.494 ± 0.004
7	74.1	5.505 ± 0.004
8	82.8	5.505 ± 0.006

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(3) E. Zintl and U. Croatto, *Z. anorg. allgem. Chem.*, **242**, 79 (1939).

Table II

Lattice Constants for Solid Solutions of Praseodymium and Cerium Oxides

Sample	Atomic % Pr	Lattice constants, Å. Fluorite structure Heated in vacuum	Heated in air	Heated in oxygen
1	0.0	5.411 ± 0.001	5.411 ± 0.001	5.411 ± 0.001
2	14.5	5.442 ± 0.002	5.407 ± 0.001	
3	25.3	5.460 ± 0.002	5.405 ± 0.001	5.406 ± 0.001
4	35.6	5.481 ± 0.003		
5	48.5	5.508 ± 0.003	5.402 ± 0.002	
6	52.5	5.511 ± 0.002[a]		5.402 ± 0.001
7	53.1	5.510 ± 0.002[a]	5.400 ± 0.002	
8	65.3	5.52 ± 0.01[a]	5.398 ± 0.002	
9	77.5		5.398 ± 0.005 5.465 ± 0.005 5.40 ± 0.01	
10	87.2	5.558 ± 0.002[b]	5.465 ± 0.003	5.397 ± 0.003
11	91.9		5.468 ± 0.003	
12	94.4		5.468 ± 0.002	
13	97.0		5.468 ± 0.002	
14	100.0	5.570 ± 0.002[b]	5.468 ± 0.001	5.394 ± 0.002

[a] Two phases, fluorite type plus "C" type Pr_2O_3. [b] One phase, "C" type (cubic) Pr_2O_3. Cell constant given is one-half of true value. Pure Pr_2O_3 also crystallizes as "A" (hexagonal) type.

Table III

Lattice Constants for Solid Solutions of Praseodymium and Neodymium Oxides

Sample	Atomic % Pr	Lattice constants, Å. Fluorite structure Heated in air	Heated in oxygen
1	28.2	5.49 ± 0.01[a]	5.50 ± 0.01[a]
2	44.0	5.490 ± 0.004[a]	5.502 ± 0.005
3	55.9	5.490 ± 0.004	5.477 ± 0.003
4	79.7	5.468 ± 0.003	5.436 ± 0.006
5	96.6	5.468 ± 0.002	5.402 ± 0.004
6	100.0	5.468 ± 0.001	5.394 ± 0.002

[a] Shows two phases, the non-fluorite phase being unidentified but probably rich in Nd_2O_3.

tion of these slopes from the ionic radii is complicated by the variable coördination number of the cation (8 in CeO_2 and 6 in the cubic M_2O_3 structure) and by the lattice defects caused by unoccupied anion sites.

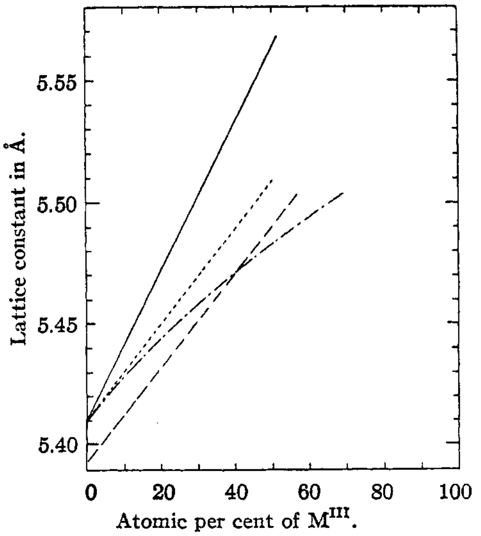

Fig. 5.—Comparison of solid solutions in rare earth oxide systems: ——, CeO_2–La_2O_3; ---------, CeO_2–Pr_2O_3; —·—·—, CeO_2–Nd_2O_3; — — — —, PrO_2–Nd_2O_3.

As indicated in the tables, a number of the samples show two (or possibly more) phases, but in all such cases at least one phase is of the fluorite type. In the Ce^{IV}–Nd^{III} oxide system, a second phase, presumably rich in Nd_2O_3, is indicated at a composition corresponding to 70 atomic per cent. of neodymium from the standpoint of the metal content. This second phase is definitely not of the A or C type of Nd_2O_3, and has not as yet been characterized. In the Ce^{IV}–Pr^{III} and the Pr^{IV}–Nd^{III} oxide systems, saturation of the fluorite structure is indicated at 50 atomic per cent. and 56 atomic per cent. of the trivalent metal, respectively. On this same basis, saturation is reached in the Ce^{IV}–La^{III} system at 60 atomic per cent. of La^{III}.

In the Ce^{IV}–Pr^{III} oxide system the second phase produced above 50 atomic per cent. of Pr^{III} is the C-type cubic M_2O_3 structure. Above approximately 85 atomic per cent. of Pr^{III}, the C-type phase is the only one present. The lattice constants in Table II for the C phase are given as one-half of the true values in order to be on a basis comparable to the fluorite phase. Pure Pr_2O_3 also crystallizes in the hexagonal A form of rare-earth sesquioxide.

The behavior of Pr_6O_{11} is of particular interest. This oxide results when any other oxide of praseodymium or salts such as the nitrate or oxalate are strongly heated in air. The lattice constant of Pr_6O_{11} is quite reproducible under widely different methods of preparation with a value of 5.468 ± 0.001 Å. This figure is at variance with the literature values of 5.499 and 5.536 kX,[4,5] but is the result of the measurement of diffraction photographs of over twenty samples prepared in this Laboratory, including column purified material. The solubility of Pr_2O_3 and PrO_2 in the Pr_6O_{11} phase is apparently too small to alter the lattice constant appreciably and the composition Pr_6O_{11} appears to be an isolated point in the praseodymium–oxygen system.

The individuality of the Pr_6O_{11} phase is also indicated by the praseodymium-rich, air-ignited samples in the Ce–Pr and the Pr–Nd oxide systems. In the Ce–Pr oxide system (Table II), the Pr_6O_{11} phase with unaltered lattice constant persists until the praseodymium content has dropped below 77.5%. As the cerium content increases, a new fluorite type phase appears which is probably a solid solution of CeO_2 in PrO_2. Samples No. 9 and No. 10 both show an unaltered Pr_6O_{11} phase plus the solid solution phase. As one proceeds from sample 14 to sample 9, the intensities of the lines due to the Pr_6O_{11} phase diminish in relative intensity and the lines become broader and more diffuse while the opposite

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(4) V. M. Goldschmidt, F. Ulrich and T. Barth, "Struktürbericht," Vol. I, p. 198.

(5) V. M. Goldschmidt, *ibid.*, p. 198.

effects are noted for the solid solution. By the time the praseodymium content has dropped to 65%, only the solid solution phase remains. Judging by the lattice constant of the solid solution which is presumably in equilibrium with Pr_6O_{11}, its composition is approximately 75% PrO_2 and 25% CeO_2. That the solid solution is in equilibrium with Pr_6O_{11} is indicated by the fixed value of its lattice constant while the Pr_6O_{11} phase is still present. After the Pr_6O_{11} phase disappears, the lattice constant of the solid solution varies as indicated by the air-ignited values for samples 1–8 in Table II. The failure of the lines of the solid solution to appear on the photographs of samples 11–13 is believed to be due to an extremely small particle size. This is indicated by the broadening of the lines on the pattern for sample 10 and to a lesser degree on that for sample 9.

The behavior of Pr_6O_{11} is similar in the air-ignited samples of the Pr–Nd oxide system. Neodymium in amounts up to 20% does not alter the lattice constant of the Pr_6O_{11} phase. In this case a second phase does not appear on the films but there is considerable diffuse scattering in evidence. When the praseodymium content is reduced below 65%, the behavior on air-ignition is not reproducible unless the conditions are carefully controlled. All of the samples reported in Table III were ignited in a furnace simultaneously.

Pure PrO_2 is readily prepared by heating any lower oxide in oxygen gas at a pressure of approximately 50 atmospheres and a temperature of approximately 300°. The range of temperature and oxygen pressure over which the change may be accomplished was not determined in this study but is under investigation by others in this Laboratory. The lattice constant of PrO_2 was found in the present study to have the reproducible value of 5.394 ± 0.002 Å. and is also at variance with the literature values of 5.373 and 5.40 kX.[5,6] Several attempts to prepare a single phase with a composition between Pr_6O_{11} and PrO_2 were made by heating intimate mixtures of the two oxides in sealed quartz tubes. No such phase appears to exist, the usual result of the attempts being the two starting materials with unaltered lattice constants. Incomplete oxidation of Pr_6O_{11} with oxygen gas was also found to yield the two phases Pr_6O_{11} and PrO_2, each with its characteristic lattice constant.

There has been some speculation regarding an oxidation state of +5 for praseodymium. Prandtl and Rieder[7] have reported that praseodymium is oxidized beyond the +4 state when in the presence of a trivalent rare-earth. Yttrium was the trivalent element actually used in their work in order to eliminate the possibility of any oxidation other than that of praseodymium. Marsh,[8] in attempting to repeat the work of Prandtl and Rieder, was able to oxidize praseodymium only to the +4 state in the presence of Y_2O_3. The present work offers good evidence indicating that praseodymium is oxidized to, but not beyond, the +4 state. The dotted line on Fig. 4 represents a prediction of the lattice constants for the Pr^{IV}–Nd^{III} oxide system as a function of composition. The slope of this line was taken equal to that for the Ce^{IV}–Pr^{III} oxide system (Fig. 3) because of the similarities in relationships involved in the two systems. It is significant that the experimental points for the oxidized samples in the Pr–Nd oxide system are close to this predicted line. This indicates that the praseodymium in the samples is oxidized completely to the +4 state, but not beyond, even in the presence of trivalent neodymium and at oxygen pressures of approximately 50 atmospheres.

It is also interesting to note that in the portion of the Ce–Pr oxide system below 65% praseodymium, that element is easily oxidized to the +4 state on being heated in air. Evidently the presence of Ce^{IV} makes the oxidation of praseodymium to the +4 state easier than when alone or when trivalent neodymium is present. This may be due to the identity of the crystal structure of PrO_2 to that of CeO_2.

The Structure of Pr_6O_{11}.—Clearly, a substance with the stoichiometric formula Pr_6O_{11} cannot have the ideal fluorite structure assumed by CeO_2 and PrO_2. However, powder photographs of Pr_6O_{11} are indistinguishable from those of PrO_2 except for differences in dimensions caused solely by the differences in lattice constants. Annealing Pr_6O_{11} for two weeks at 400° sharpened the lines slightly but caused no change in pattern. Higher annealing temperatures were avoided because of the unknown dissociation pressure of Pr_6O_{11} to a lower oxide.

Pr_6O_{11} can adjust itself to a fluorite type of structure in either of two ways: Case I. By addition of extra cations at random in the vacant interstitial positions in the simple cubic lattice formed by the anions. Case II. By the random omission of one-twelfth of the anions from the structure.

A choice between the two possibilities may be made either by comparing the observed density with the densities computed for the two cases by use of the lattice constant or by comparing the observed relative intensities of the diffraction lines with those computed for each of the two possible structure variations. Because of the experimental difficulties involved in the accurate measurement of the density of a small sample of a fine, fluffy powder, the latter procedure involving relative intensities was employed. The neighboring lines (331) and (420) which have the same multiplicity factor, 24, and only slightly different

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(6) Scherer and Polacios, "Strukturbericht," Vol. II, p. 259

(7) W. Prandtl and G. Rieder, *Z. anorg. allgem. Chem.*, **238**, 225 (1938).

(8) J. K. Marsh, *J. Chem. Soc.*, 5 (1946).

values of the Bragg angle, Θ, are well suited to the purpose. The relative intensities of these lines are nearly proportional to the squares of their structure factors, $|F_{331}|^2$ and $|F_{420}|^2$, which have for Case I the values

$$|F_{331}|^2 = [40/11 f_{\mathrm{Pr}}]^2 = 16{,}400$$
$$|F_{420}|^2 = [48/11 f_{\mathrm{Pr}} - 8 f_0]^2 = 16{,}900$$

and for Case II the values

$$|F_{331}|^2 = [4 f_{\mathrm{Pr}}]^2 = 20{,}000$$
$$|F_{420}|^2 = [4 f_{\mathrm{Pr}} - 44/6 f_0]^2 = 14{,}400$$

We thus see that the computed ratios of I_{331}/I_{420} are 0.97 for Case I (extra cations) and 1.39 for Case II (missing anions). The intensities observed on a Norelco X-Ray Spectrometer for Pr_6O_{11} powder are in the ratio I_{331}/I_{420} of 1.4, which is in good agreement with the computed intensity ratio for the structure involving randomly missing anions. Spectrometer recordings for two preparations of Pr_6O_{11} are reproduced in Fig. 6. These are typical of six such recordings made.

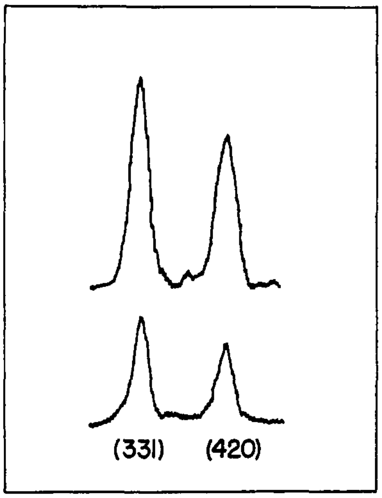

Fig. 6.—Spectrometer intensities for 331 and 420 lines of Pr_6O_{11}.

Acknowledgment.—The author is indebted to Mrs. Lee Jackson and Mrs. Carol Dauben for preparing and measuring some of the powder photographs, to Mr. J. Conway for the spectrographic analyses, to Mr. R. C. Lilly and Mr. D. C. Stewart for the column purification of praseodymium and to Dr. B. B. Cunningham for many helpful discussions.

Summary

An X-ray study of the oxide systems Ce^{IV}–Nd^{III}, Ce^{IV}–Pr^{III}, Ce^{IV}–Pr^{IV} and Pr^{IV}–Nd^{III} has been carried out with the following results:

1. Solid solutions with the fluorite structure are formed in all cases and lattice constants have been determined as a function of composition. For the oxide systems M^{IV}–M^{III} there is an upper solubility limit varying from 50 to 67 atomic per cent. of the trivalent metal.
2. Praseodymium is readily oxidized to Pr^{IV} in the presence of Ce^{IV}, but more difficultly in the presence of Nd^{III}.
3. In no case is there evidence for the oxidation of Pr beyond the +4 state, even under oxygen pressures as high as 50 atmospheres.
4. Evidence is given in support of the existence of Pr_6O_{11} as a separate and distinct phase in the praseodymium–oxygen system.

BERKELEY 4, CALIFORNIA RECEIVED AUGUST 9, 1949

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

Calcium Nitrate. V. Partial Molal Volumes of Water and Calcium Nitrate in Concentrated Solutions

BY WARREN W. EWING AND RICHARD J. MIKOVSKY

This article is a continuation of a series of studies on the properties of calcium nitrate solutions. Previous studies[1] have been made on T–X and P–T–X relations and on heats of solution, dilution and hydration. Data are now presented on the partial molal volumes of water and calcium nitrate over the concentration range one to twenty molal at temperatures from 25 to 60°. Pearce and Blackman[2] have determined partial molal volumes at 25° up to 8.36 molal. Scott and Bridger[3] have presented data at 35° on the apparent molal volumes.

This system is well adapted to studies of very concentrated solutions of electrolytes because of the high solubility of the calcium nitrate, which amounts to about 78% (20 *m*) for the saturated solution of the anhydride. Up to this concentration the highest m. p. of the system is 52°. However, supersaturation below the m. p.'s can be easily obtained by maintaining the solutions at 60° overnight with subsequent cooling. The slightly supersaturated solutions show some tendency to crystallize but it is difficult to crystallize the more concentrated solutions without seeding. Samples of these supersaturated solutions, sealed in glass

[1] Ewing, Krey, Law and Lang, THIS JOURNAL, 49, 1958 (1927); Ewing, *ibid.*, 49, 1963 (1927); Ewing, Rogers, Miller and McGovern, *ibid.*, 54, 1339 (1932); Ewing and Rogers, *ibid.*, 55, 3603 (1933).

[2] Pearce and Blackman, *ibid.*, 57, 24 (1935).

[3] Scott and Bridger, *J. Phys. Chem.*, 40, 461 (1936).