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

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

and for Case II the values

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

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.

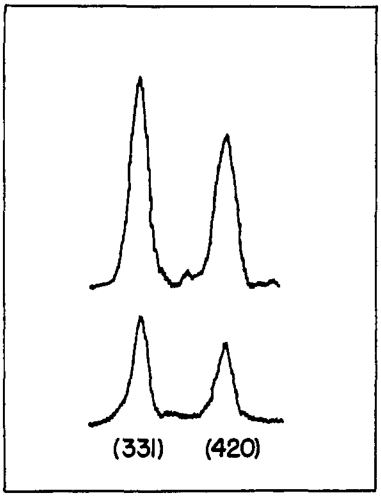

Fig. 6.—Spectrometer intensities for 331 and 420 lines of Pr_6O_{11}.

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

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[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).

bulbs, have now withstood the vicissitudes of ordinary laboratory conditions for twenty years without crystallizing. At one time one of them even was plunged into a Dry Ice-bath without starting crystal formation.

The experimental procedure consisted of measuring the densities of the various solutions at 25, 30, 40, 50 and 60°. Conventional pycnometers were not satisfactory for use with these supersaturated solutions because of the difficulty in removing entrapped air bubbles. Difficulty was also encountered in filling the viscous solutions through a narrow capillary tube. Finally, with pycnometers having a ground glass, capillary tube for a stopper, the chances of crystallization on seating the stopper were increased. Consequently, a method for determining the densities of solutions was devised based on Archimedes' principle. The solution was weighed first in air and then immersed in a *n*-heptane-bath at the various temperatures. Any heptane remaining over the solution was then removed by evaporation, and the concentration of the solution was determined. Heptane was chosen as the bath liquid because of the very small mutual solubilities of the water–heptane system. Also, its volatility was high enough so that traces could be evaporated quickly and completely in the analysis, and sufficiently low so that there was little loss from the bath by evaporation at the highest temperature at which the densities were measured.

Experimental

Apparatus and Procedure.—The apparatus is shown in Fig. 1. The half-pint Dewar flask was supported on a metal stand above the pan of an analytical balance. A thermometer, a ring stirrer, a heater and a platinum wire for supporting the solution all passed through holes in a cork stopper. The lower end of the platinum wire held a wire spring, A, which, when hooked under the neck of the weighing bottle which contained the solution, allowed a free swinging support. The nichrome wire heater, 20 watts at 16 volts d. c., was in direct contact with the heptane. It raised the temperature of the system approximately one degree per minute. The heater was supported by a metal strip, B, which was bound to the outside of the Dewar. The platinum wire was suspended from the pan support at the end of the balance beam. The top of the balance case contained an opening through which the thermometer, the heater and the stirrer projected. The weighing bottles had standard taper ground glass stoppers which prevented evaporation of the solution when exposed to air. The heater was controlled manually and the temperature of the bath was maintained constant to ±0.05° for one-half hour while being stirred constantly to ensure temperature equilibrium in the solutions. A change of 0.1° in temperature gave a noticeable change in weight.

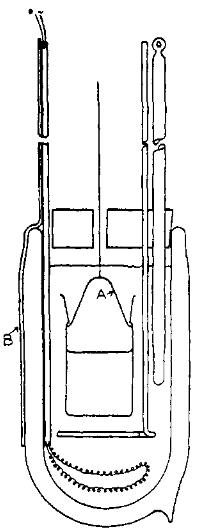

Fig. 1.—Apparatus for density determination.

The sensitivity of the balance, when the solution was immersed in the heptane was 1.5 mg. per scale division. The volume of the solution was about 10 ml.

The density of the *n*-heptane was found at the various temperatures by using a quartz bob of a predetermined volume of about 5 ml. The density was checked repeatedly and did not vary although the heptane was used over and over again. The average density of five Pyrex weighing bottles was found to be 2.2273 ± 0.001 g./ml. The deviations were found to be randomly distributed over the twenty-five determinations, five temperatures for five bottles, so the value 2.2273 was used in making calculations.

It was necessary to remove air, dissolved and entrapped in the calcium nitrate solutions, by boiling briefly in a vacuum immediately before immersion of the solution in the heptane. In order to check the accuracy of the method the density of water was determined. The averages of three runs gave deviations from the accepted values for water of −0.0001 at 25°, −0.0003 at 30°, −0.0003 at 40°, −0.0003 at 50° and −0.0001 at 60°. The maximum deviation in the fifteen data was −0.0004.

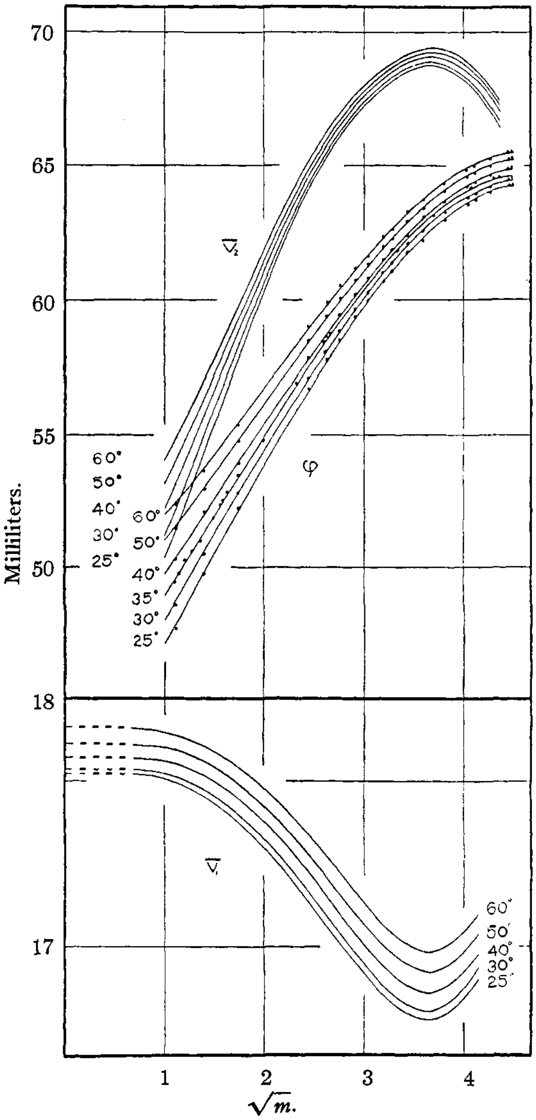

Fig. 2.—The partial molal volume of $Ca(NO_3)_2$ and H_2O, ($\bar{v}_2$ and $\bar{v}_1$), and the apparent molal volume of $Ca(NO_3)_2$, (φ). The 35° curve is from the data of Scott and Bridger.

TABLE I

DENSITIES OF SOLUTIONS AND APPARENT MOLAL VOLUMES OF CALCIUM NITRATE

% $Ca(NO_3)_2$	m	Densities 25°	30°	40°	50°	60°	Empirical apparent molal volumes[a] $\varphi_{25°}$	Δ	$\varphi_{30°}$	Δ	$\varphi_{40°}$	Δ	$\varphi_{50°}$	Δ	$\varphi_{60°}$	Δ
00.000	00.0000	0.9970	0.9956	0.9921	0.9880	0.9832	(40.164)		(42.415)		(44.454)		(46.580)		(48.001)	
17.255	1.2708	1.1364	1.1334	1.1280	1.1218	1.1154	47.62	+0.21	48.73	+0.13	50.00	+0.13	51.31	+0.03	52.27	+0.02
24.476	1.9750	1.2024	1.1992	1.1928	1.1862	1.1792	49.75	+ .03	50.52	+ .10	51.75	− .01	52.73	+ .07	53.56	+ .08
34.052	3.1466	1.2984	1.2949	1.2881	1.2806	1.2728	52.41	− .08	52.97	− .01	53.82	+ .10	54.66	+ .13	55.40	+ .11
50.358	6.1819	1.4850	1.4808	1.4728	1.4645	1.4561	57.19	− .26	57.59	− .26	58.22	− .22	58.78	− .17	59.26	− .13
53.108	6.9018	1.5206	1.5161	1.5076	1.4990	1.4905	57.88	− .12	58.28	− .16	58.93	− .17	59.48	− .15	59.94	− .12
56.201	7.8196	1.5608	1.5565	1.5481	1.5392	1.5304	58.81	− .10	59.14	− .10	59.72	− .08	60.26	− .10	60.72	− .10
57.952	8.3989	1.5845	1.5799	1.5713	1.5624	1.5531	59.29	− .04	59.64	− .07	60.21	− .07	60.73	− .08	61.22	− .14
60.263	9.2418	1.6158	1.6114	1.6030	1.5938	1.5857	60.00	− .02	60.31	− .03	60.82	− .01	61.34	− .04	61.67	+ .02
62.765	10.272	1.6505	1.6459	1.6374	1.6285	1.6195	60.77	.00	61.07	− .02	61.56	− .01	62.02	− .02	62.43	+ .04
64.320	10.986	1.6726	1.6683	1.6596	1.6505	1.6420	61.23	+ .02	61.50	+ .04	61.98	+ .02	62.44	.00	62.79	+ .02
66.122	11.894	1.6981	1.6934	1.6847	1.6759	1.6671	61.82	− .01	62.11	− .03	62.57	− .04	62.99	− .04	63.35	− .06
68.124	13.024	1.7299	1.7259	1.7168	1.7080	1.6991	62.24	+ .18	62.45	+ .23	62.92	+ .18	63.32	+ .18	63.67	+ .16
70.469	14.542	1.7654	1.7607	1.7520	1.7428	1.7351	62.93	+ .15	63.19	+ .14	63.61	+ .12	64.02	+ .08	64.26	+ .16
72.503	16.068	1.7989	1.7941	1.7854	1.7770	1.7677	63.40	+ .20	63.65	+ .19	64.05	+ .17	64.38	+ .20	64.74	+ .14
73.396	16.812	1.8132	1.8096	1.8010	1.7921	1.7831	63.65	+ .15	63.81	+ .22	64.19	+ .20	64.56	+ .21	64.89	+ .17
75.145	18.424	1.8431	1.8384	1.8302	1.8207	1.8124	64.05	+ .08	64.27	+ .07	64.62	+ .09	65.01	+ .05	65.28	+ .07
76.711	20.073	1.8689	1.8642	1.8555	1.8467	1.8387	64.49	− .19	64.71	− .19	65.08	− .20	65.41	− .19	65.67	− .15
76.815	20.190	1.8704	1.8653	1.8578	1.8491	1.8402	64.54	− .22	64.78	− .25	65.07	− .19	65.40	− .18	65.71	− .18

[a] The parentheses indicate values calculated from the least-squared equations.

The following data were necessary for the calculations of the densities: density of the heptane, density of the glass, weight of the weighing bottle, weight of the solution in air, weight of the solution immersed in *n*-heptane and the correction for immersed wire support.

Reagents and Solutions.—Freshly boiled, laboratory grade distilled water was used throughout.

The *n*-heptane was at least 99 mole per cent. pure. Any impurities were probably the various isomers.

The calcium nitrate was a C. P. grade recrystallized four times from water as the tetrahydrate. It was dried over concentrated sulfuric acid and finally stored over phosphorus pentoxide, thus dehydrating it to approximately the anhydride.

The solutions were made up in weighing bottles from weighed amounts of the dried salt and water. The bottles were then capped and placed in a 60° oven overnight to ensure supersaturation on cooling. Only once during these runs did a supersaturated solution made by this procedure crystallize during the experimental manipulation.

The analyses of the solutions were carried out by the procedure as suggested by Ewing[1] and modified by Scott and Bridger.[3] After a run, the solution whose weight had been determined, was placed in an oven and the temperature was gradually raised from 115 to 170° over a period of three days. Overnight at 170° was sufficient to ensure complete dehydration. The anhydride was then cooled over phosphorus pentoxide and finally capped and weighed. Check weighings were made after storing the anhydride over phosphorus pentoxide for one week.

Results

The concentration and the densities of the various solutions are tabulated in Table I. Apparent molal volumes of the calcium nitrate, ϕ, were calculated from each individual density by the definition that

$$\phi = \frac{1}{d}\left[M_2 - \frac{1000}{m}\frac{(d - d_1)}{d_1}\right] \qquad (1)$$

where d is the density of the solution, M_2 is the molecular weight of the calcium nitrate, m is the molality, and d_1 is the density of water at the temperature in question. These individual ϕ values are plotted *vs.* $\sqrt{m}$ as points in Fig. 2.[4] The shape of the curves indicated that a third degree polynomial equation in $\sqrt{m}$ would fit these data. By applying the method of least squares to all the values of ϕ using a weighting factor of unity, the constants in the following six analytical expression were obtained

$$\phi_{25°} = 40.164 + 6.3098m^{1/2} + 0.6472m - 0.1903m^{3/2}$$
$$\phi_{30°} = 42.415 + 4.8587m^{1/2} + 1.0061m - 0.22081m^{3/2}$$
$$\phi_{35°} = 43.200 + 4.9135m^{1/2} + 0.8987m - 0.20738m^{3/2}$$
$$\phi_{40°} = 44.454 + 4.0641m^{1/2} + 1.1143m - 0.22415m^{3/2}$$
$$\phi_{50°} = 46.580 + 3.0556m^{1/2} + 1.3055m - 0.23637m^{3/2}$$
$$\phi_{60°} = 48.001 + 2.5945m^{1/2} + 1.3363m - 0.23274m^{3/2}$$

These empirical equations are plotted as lines in Fig. 2 in order to compare them with the values calculated from the experimental density data. These equations hold for a range of molality between 1 and 20 *m*. The deviations of values calculated from the polynomials from the experimental points are shown in the columns headed Δ in Table I. The average deviation is approximately 0.1 cc. These deviations are to be compared in the curves of Fig. 2, with a precision on the other axis, *viz.*, molality, of at least 0.1%. Scott and Wilson[5] have pointed out that the deviation to be expected in computations of ϕ may reach slightly above 0.1 cc. because of the subtraction which is necessary. The $\phi_{35°}$ expression fits the data of Scott and Bridger a little better than their equation using molarity. It should be noted that the maximum Δ listed in Table I corresponds to a density increment approximately the size of the experimental precision.

When the apparent molal volume obeys the relation as obtained above

$$\phi = \phi^\circ + am^{1/2} + bm + cm^{3/2} \qquad (2)$$

the partial molal volume of the calcium nitrate may be calculated from the equation

$$\bar{V}_2 = \phi^\circ + 3/2\ am^{1/2} + 2bm + 5/2\ cm^{3/2} \qquad (3)$$

The plots for these curves are also given in Fig. 2.

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(4) All 35° values in this article are calculated from the data of Scott and Bridger.

(5) Scott and Wilson, *J. Phys. Chem.*, **38**, 951 (1934).

The total volume of solution containing 1000 g. of water may be obtained by integrating $\bar{V}_2$ with respect to m. The result is

$$V = \left(\frac{1000}{d_1}\right) + \phi^\circ m + am^{3/2} + bm^2 + cm^{5/2} \quad (4)$$

If the integration constant, which represents the volume of 1000 g. of pure water at the given temperature, is obtained by inserting experimental values into equation 4, values are obtained which are practically coincidental with the experimental volumes of pure water at the same temperatures.

Finally, the partial molal volume of the water may be obtained as a function of the molality by utilizing the expression

$$\bar{V}_1 = \left(\frac{18.016}{d_1}\right) - 0.018016\,[1/2\,am^{3/2} + bm + 3/2\,cm^{5/2}] \quad (5)$$

The intercepts represent the molal volume of pure water at the given temperatures. The partial molal volumes of water are also plotted in Fig. 2.

The maxima and minima in the curves of $\bar{V}_2$ and $\bar{V}_1$ in Fig. 2 occur at approximately $m = 13.2$. This concentration corresponds to 4.2 moles of water per mole of calcium nitrate. This ratio is of doubtful significance because there does not appear to be any sharp break in the curve. These stationary points may indicate, however, a change in the status of hydration of the solute or of molecular association of the solvent or solute.

Summary

The densities of aqueous solutions of calcium nitrate have been determined over the concentration range one to twenty molal, and the temperature range 25 to 60°. The solutions were supersaturated in a part of these ranges.

Analytical expressions for the partial molal volumes of both the solute and solvent, the apparent molal volume of the solute, and the total volume of solution, as a function of $\sqrt{m}$, have been determined.

A maximum in the partial molal volume of calcium nitrate and a minimum in the partial molal volume of water have been observed.

BETHLEHEM, PENNSYLVANIA RECEIVED JULY 27, 1949

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

Dissociation Constant of Aqueous Ammonia at 0 to 50° from E. m. f. Studies of the Ammonium Salt of a Weak Acid

BY ROGER G. BATES AND GLADYS D. PINCHING

The acidic dissociation constant of ammonium ion has been determined recently from measurements of the electromotive force of cells with hydrogen electrodes and silver–silver chloride electrodes in buffer–chloride solutions[1] by the method that has proved successful in studies of the ionization of many weak acids and ampholytes.[2] However, this procedure is not ideally suited to investigations of basic dissociation. For highest accuracy, corrections for the solubility of silver chloride in the cell solutions and for volatility of the free base may be necessary. It is nonetheless desirable that the dissociation constants of bases should relate to the hydrogen–silver chloride cell. If the ratio of the concentration of base to that of salt is small, the corrections may be insignificant, but the exact buffer ratio is still difficult to establish. Hence, in some instances the constant can be obtained to better advantage from electromotive force measurements of the hydrolysis of a salt of the weak base with a weak acid of known dissociation constant.[3] If the constant, K_a, of the acid selected is appreciably greater than K_w/K_b (the ratio of the ionization constant of water to the dissociation constant of the base), the concentration of free base formed by hydrolysis may be small. In contrast with the conventional method, the buffer ratio need not be known precisely. Furthermore, the combined buffer action of the two systems assures an adequate buffer capacity, even though the degree of hydrolysis be rather small.

When the base is uncharged and the acid is a singly charged anion, the extrapolation to zero ionic strength is made with somewhat more certainty than in the usual method. However, the precision in K_b obtainable is only one-half that of the conventional procedure, for, in addition to ionic concentrations, the electromotive force is dependent upon the geometric mean of K_a and K_w/K_b rather than upon K_w/K_b alone. This method can be employed successfully only when log K_a and log (K_w/K_b) differ by less than 2 units. Thus ammonium acetate and secondary ammonium phosphate (or microcosmic salt, $NaNH_4HPO_4 \cdot 4H_2O$) are insufficiently hydrolyzed to yield accurate results. The dissociation constant of ammonia at 0 to 50° has now been calculated from electromotive force studies of the extent of hydrolysis in mixtures of ammonia and potassium *p*-phenolsulfonate. The results are in good agreement with the earlier determination.[1]

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[1] R. G. Bates and G. D. Pinching, *J. Research Natl. Bur. Standards*, **42**, 419 (1949).

[2] (a) H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932); (b) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Chapter 15, Reinhold Publishing Corp., New York, N. Y., 1943.

[3] R. G. Bates and G. D. Pinching, *J. Research Natl. Bur. Standards*, **43**, 519 (1949).