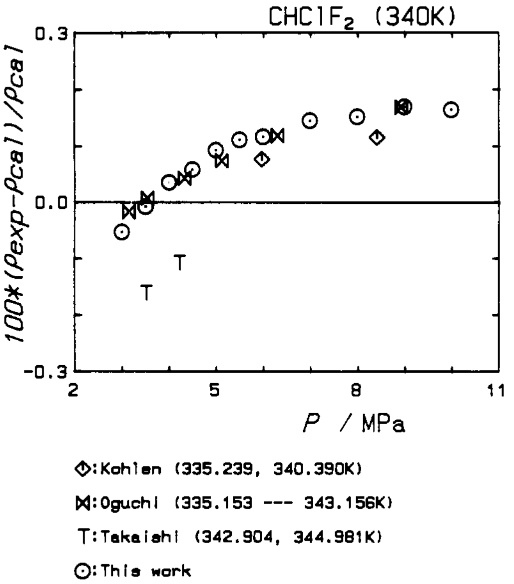

Figure 2. Deviation plots of the density data from the equation of state proposed by Kagawa et al. along the 340 K isotherm.

results agree well with the data by Michels (*9*) and those by Zander (*10*) within ±0.2% in pressure deviation.

We calculated the derivatives of density with respect to temperature at constant pressure and those of density with respect to pressure at constant temepratura from the data given in Table I by approximation as differences of these quantities. The values of the volume expansion coefficient and the isothermal compressibility thus obtained are given in Tables II and III, respectively.

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Literature Cited

(1) Hasegawa, N.; Uematsu, M.; Watanabe, K. *J. Chem. Eng. Data* **1985**, *30*, 32.
(2) Higashi, Y.; Uematsu, M.; Watanabe, K. *Int. J. Thermophys.* **1986**, *7*, 29.
(3) Kamimura, T.; Iso, A.; Higashi, Y.; Uematsu, M.; Watanabe, K. *Rev. Sci. Instrum.* **1989**, *60*, 3055.
(4) Kagawa, N.; Tanaka, H.; Uematsu, M.; Watanabe, K. *Nippon Kikai Gakkai Ronbunshu, B-hen* **1988**, *54*, 959.
(5) Oguchi, K.; Sagara, T.; Matsushita, Y.; Watanabe, K.; Tanishita, I. *Nippon Kikai Gakkai Ronbunshu, B-hen* **1979**, *45*, 1522.
(6) Takaishi, Y.; Kagawa, N.; Uematsu, M.; Watanabe, K. *Proc. 8th Symp. Thermophys. Prop.* **1982**, *2*, 387.
(7) Kohlen, R.; Kratzke, H.; Müller, S. *J. Chem. Thermodyn.* **1985**, *17*, 1141.
(8) Kumagai, A.; Iwasaki, H. *J. Chem. Eng. Data* **1978**, *23*, 193.
(9) Michels, A. *Ind. Eng. Chem.* **1967**, *59*, 34.
(10) Zander, M. *Proc. 4th Symp. Thermophys. Prop. Gases, Liq. Solids* 1968, 114.

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Solubility Products of the Trivalent Rare-Earth Phosphates

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The solubility and solubility products of 14 rare-earth phosphates in aqueous solution have been determined at 25 ± 1 °C. The most soluble compound is yttrium phosphate (p*K* = 24.76). The least soluble ones are lanthanum phosphate (p*K* = 26.15) and ytterbium phosphate (p*K* = 26.17). The rare-earth phosphates were prepared by precipitation from homogeneous solution. Saturated solutions were analyzed for pH, the concentrations of some rare-earth cations, and the total concentration of phosphate. Activity products were calculated from the experimental data. The solubilities of the rare-earth phosphates are so low that the solubility products and the activity products are essentially the same value. The rare-earth phosphates are more insoluble at higher temperatures. Lanthanum phosphate has a p*K* of 26.49 at 70 °C. Twelve values for the activity product of rare-earth phosphates at elevated temperatures were determined.

Introduction

Previous work by Jonasson, Bancroft, and Nesbitt (*1*) reported on the solubilities of only the lanthanum, praseodymium, neodymium, and erbium phosphates. Limited experimental information was presented. The study reported here involved the entire trivalent rare-earth series, excluding scandium and cerium. Solubilities at 25 °C and at higher temperatures are reported.

Experimental Section

Commercial rare-earth phosphates were unsatisfactory for use in this study. Colloidal suspensions formed that did not settle out of solution even after months of standing.

Satisfactory crystals of rare-earth phosphates were prepared by precipitation from homogeneous solution using the hydrolysis of urea.

Equimolar amounts (0.005 mol) of rare-earth cation and phosphoric acid were added to a 1-L beaker with 5 mL of 70% $HClO_4$ to prevent the rare-earth phosphate from precipitating. Deionized water was added to bring the volume to about 900 mL. A 3-5-g amount of urea was slowly added with constant stirring. The solution was heated to hydrolyze the urea, increase the pH, and bring about the precipitation of the rare-earth phosphate. The solution was heated for an additional hour after precipitation began. The resulting crystals were washed 10-15 times with deionized water. The last two washings were made with a 0.10 M perchloric acid solution to eliminate the possibility of rare-earth carbonate being present. No fizzing was ever observed. The washing removed any excess phosphate or rare-earth ions, as well as any colloidal material that might be present. All washings were discarded.

A second method of rare-earth phosphate preparation was also used. This took advantage of the decreased solubility of rare-earth phosphate with increasing temperature. To a 1-L beaker were added 2.5 mmol of rare-earth cation and 0.3 mL of 85% phosphoric acid, with 1.5 mL of 70% perchloric acid, in about 900 mL of deionized water. These quantities are just acidic enough to keep the rare-earth phosphates from precipitating at room temperature. The solution was then heated, with constant stirring, at about 100 °C, until precipitation took place. Heating was continued for 30 min after precipitation began. The solution was then cooled to room temperature. This precipitate, which appeared colloidal, was then used as seed crystals, following the same procedure. Denser crystals were produced in the second precipitation. These denser precipitates resembled the crystals obtained from urea hydrolysis.

Both types of crystals were used in this study, as well as a few commercial samples.

Saturated Solutions

The rare-earth phosphates are very insoluble in water. The pure saturated solutions of rare-earth phosphates would contain a rare-earth cation concentration that is on the order of 10^{-13} M. In order to bring enough rare-earth cations into solution for accurate analysis, dilute $HClO_4$ was used to partially dissolve the rare-earth phosphates.

An equilibrium exists between the rare-earth cation and the forms of phosphate present in solution: PO_4^{3-}, HPO_4^{2-}, $H_2PO_4^-$, and H_3PO_4. Two different concentrations of $HClO_4$ were used, 0.0697 and 0.0910 M. The rare-earth phosphate crystals were placed in perchloric acid, stoppered, and allowed to come to equilibrium with periodic shaking. About 80 days were required to reach equilibrium at 25 °C (*2*). The rare-earth phosphates were found to be more insoluble with increasing temperature, so heating the solutions did not bring about more rapid dissolution.

Most saturated solutions were in contact with the solid rare-earth phosphates for considerably longer than 3 months. Undoubtedly, the surfaces of the solid phase had achieved a thermodynamically stable hydrate form. The composition of this hydrated rare-earth phosphate was not determined.

Analysis

Analytical procedures, for the determination of some insoluble rare-earth compounds, have been reported by various workers (*3*). In this study, three different measurements were made on the saturated rare-earth phosphates solutions: determination of the pH, a spectrophotometric analysis of the molybdenum-blue phosphate complex, and a spectrophotometric analysis of four rare-earth cations, Pr, Nd, Ho, and Er.

The pH measurements were made with a Corning Model 4500 digital pH meter. Analytical results were reproducible to two figures.

The concentration of total phosphate in the saturated solution was determined with HACH Phos Ver III phosphate reagent powder pillows. The phosphate analysis used a 25-mL aliquot of a filtered, saturated rare-earth phosphate solution. This was usually diluted by 1:50 or 1:100. One Hack powder pillow was added and swirled for about 5 min. The colored solution was transferred to a 2-cm quartz cell. The cell containing the sample was placed in the Bausch & Lomb spectrophotometer 2000 and an absorbance reading taken 9 min from the initial addition of the powder pillow. The wavelength of maximum absorbance was 711 nm.

The rare-earth cation spectrophotometric analyses were made with Bausch & Lomb spectrophotometer 2000. A quartz cylindrical cell, 10 cm long, was used to hold the unknown sample. Before and after the unknown analysis a standard solution, containing the appropriate rare-earth perchlorate, was scanned by using the same control settings. The concentration of rare-earth cations in the unknown was determined by comparison with the standard at the appropriate wavelength (*4*). The analyses of the rare-earth concentration and the phosphate ion concentration are compared in Table I and show that the ratio is close to one. The analytical values determined for the saturated solutions at 25 °C are given in Table II. The analytical values determined for the saturated solutions at elevated temperatures are given in Table III.

Table I. Comparative Analysis of Phosphorous and Rare-Earth Ion Concentrations at 25 ± 1 °C

sample	[RE][a] × 10^4, M	C_T[b] × 10^4, M	[RE]/C_T ratio
Pr	3.84	4.04	0.95
	2.87	2.83	1.01
	4.65	4.60	1.01
Nd	4.95	5.09	0.97
	4.48	4.44	1.01
	4.39	5.09	0.86
Ho	3.14	3.32	0.95
	8.70	9.94	0.87
	6.16	6.64	0.93
Er	9.21	9.69	0.95
	5.10	5.33	0.96
	9.21	9.70	0.95

[a] Rare-earth ion concentration. [b] Total phosphate concentration.

Table II. Analytical Values Determined for Saturated Solutions at 25 ± 1 °C[a]

rare-earth sample	C_T × 10^4, M	pH[b]	rare-earth sample	C_T × 10^4, M	pH[b]
La	5.22	1.12	Tb	21.2	1.12
	5.84	1.12		21.4	(1.10)
	6.24	(1.10)		20.3	(1.11)
	8.60*	(1.10)	Dy	19.7	1.12
Pr	4.25	1.23		17.4	1.12
	3.17	1.23		20.6	1.12
	4.84	1.23	Ho	3.63	1.23
	7.76*	(1.10)		1.09	1.23
Nd	5.08	1.23		7.33	1.23
	4.48	1.23		20.0*	(1.10)
	5.23	1.23		9.59	(1.11)
	3.51	(1.10)	Er	10.5	1.23
	7.51*	(1.10)		5.80	1.23
	7.02	(1.10)		10.7	1.23
Sm	7.47	1.12		17.2	(1.10)
	7.11	1.12		5.87	(1.10)
	7.76	1.12		5.53	(1.11)
	6.83*	(1.10)		6.83	(1.10)
Eu	7.99	1.12	Tm	7.02	(1.10)
	8.00	1.12		6.26	(1.10)
	8.18	1.12		7.00	(1.11)
	16.2	(1.11)	Yb	5.88	(1.10)
	9.56	(1.10)		6.01	(1.09)
Gd	14.5	1.12		5.92	(1.11)
	14.1	1.12	Lu	14.5	(1.11)
	10.6	1.12		15.0	(1.12)
	19.9*	(1.10)		14.0	(1.10)

[a] Asterisks denote commercial samples. [b] A pH with parentheses is a measured value and without parentheses is a calculated value.

Table III. Analytical Values Determined for Saturated Solutions at Elevated Temperatures

rare-earth sample	C_T × 10^4, M	pH	rare-earth sample	C_T × 10^4, M	pH
La	4.09	1.04	Tb	7.61	1.04
Pr	2.65	1.15	Dy	1.07	1.04
Nd	2.56	1.15	Er	4.96	1.15
Sm	3.71	1.04	Tm	5.77	1.04
Eu	4.65	1.04	Yb	5.27	1.04
Gd	8.90	1.04	Lu	7.16	1.04

Table IV. pK_{AP} of the Rare-Earth Phosphates

rare-earth sample	pK_{AP}	rare-earth sample	pK_{AP}
Y	24.76 ± 0.14	Tb	25.07 ± 0.03
La	26.15 ± 0.52	Dy	25.15 ± 0.07
Pr	26.06 ± 0.18	Ho	25.57 ± 0.46
Nd	25.95 ± 0.06	Er	25.78 ± 0.45
Sm	25.99 ± 0.05	Tm	26.05 ± 0.06
Eu	25.75 ± 0.27	Yb	26.17 ± 0.01
Gd	25.39 ± 0.23	Lu	25.39 ± 0.03

Derivation of the Solubility Product Equation

The equilibrium between solid rare-earth phosphate and the dissolved ions is

$$LnPO_4(s) = Ln^{3+}(aq) + PO_4^{3-}(aq) \qquad (1)$$

(Ln = any rare-earth element). The solubility product expression for this equilibrium is

$$K_{sp} = [Ln^{3+}][PO_4^{3-}] \qquad (2)$$

In the saturated solution there is only one mathematically significant form of rare-earth ion and that is Ln^{3+}. Calculations indicate that other possible species such as $Ln(H_2PO_4)^{2+}$, $Ln(OH)_2^+$, and $Ln(HPO_4)^+$ are not present in significant quantities at the pH conditions found in the saturated solutions (*5*). H_3PO_4 is the only significant form of phosphate in the saturated solutions. In order to calculate the solubility product, it is essential to use the concentration of PO_4^{3-}. The concentration of PO_4^{3-} cannot be analytically determined, and therefore it cannot be used directly in the K_{sp} expression. The concentration of phosphate ion can be determined by using the weak acid dissociations of phosphoric acid.

The dissociation constants of phosphoric acid selected were a median of all the reported values at 25 °C with an ionic strength approaching zero (*6*).

$$K_1 = 7.11 \times 10^{-3}$$

$$K_2 = 6.34 \times 10^{-8}$$

$$K_3 = 4.17 \times 10^{-13}$$

The analytical concentration of total phosphate is given by

$$C_T = [H_3PO_4] + [H_2PO_4^-] + [HPO_4^{2-}] + [PO_4^{3-}] = [Ln^{3+}] \qquad (3)$$

$$\alpha_3 = \frac{[PO_4^{3-}]}{C_T} = \frac{K_1K_2K_3}{[H^+]^3 + [H^+]^2K_1 + [H^+]K_1K_2 + K_1K_2K_3} \qquad (4)$$

Suitable algebraic manipulations yield the solubility product:

$$K_{sp} = \frac{[Ln^{3+}]^2}{[H^+]^3/K_1K_2K_3 + [H^+]^2/K_2K_3 + [H^+]/K_3 + 1} \qquad (5)$$

The activity product form of eq 5 is

$$K_{AP} = \frac{[Ln^{3+}]^2 f_{Ln}^{\ 2}}{(a_{H^+})^3/K_1K_2K_3 + (a_{H^+})^2/K_2K_3 + a_{H^+}/K_3 + 1} \qquad (6)$$

From the solubility data given in Table II, the activity products were calculated. The ionic strength was determined by using the known perchlorate ion concentration, the hydrogen ion concentration from the pH, and measured rare-earth cation concentrations. The activity coefficient for each rare-earth cation was calculated from the extended Debye–Huckel expression (*7*). The activity products were then calculated. Twelve values for the activity products of the rare-earth phosphates at elevated temperatures were determined. These are given in Table V.

Table V. pK_{AP} of Rare-Earth Phosphates at Elevated Temperatures (72 ± 5 °C)[a]

rare-earth sample	pK_{AP}	T, °C	rare-earth sample	pK_{AP}	T, °C
La	26.49	70	Tb	25.95	71
Pr	26.48	72	Dy	25.65	76
Nd	25.51	69	Er	25.93	71
Sm	26.57	71	Tm	26.19	72
Eu	26.38	69	Yb	26.27	67
Gd	25.81	71	Lu	26.00	75

[a] These represent single determinations.

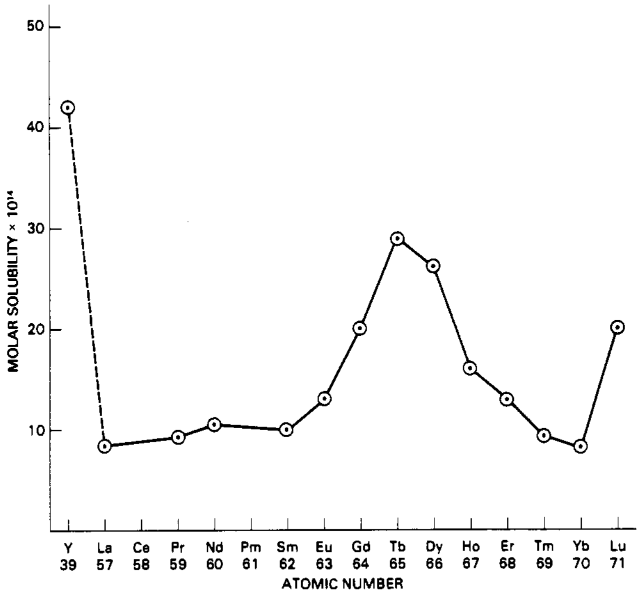

Figure 1. Solubilities of the rare-earth phosphates.

Discussion

The quantitative analysis of the total phosphate concentration and the hydrogen ion can best be represented in two figures. But the final results are given in one figure. The limiting factors that reduce the overall accuracy are due to several mathematical manipulations; i.e., the total phosphate concentration is equal to the rare-earth concentration which is squared, and the hydrogen ion concentration is cubed. Clearly, any small error in the experimental values would be magnified by the mathematical operation.

The saturated solution of lanthanide phosphate in pure water is approaching infinite dilution, about 10^{-13} M. This means that the activity product and solubility product are essentially the same. These values are given in Table IV. A graph of the molar solubility is given in Figure 1.

Literature Cited

(1) Jonasson, R. G.; Bancroft, G. M.; Nesbitt, H. W. *Geochim. Cosmochim. Acta* **1985**, *49*, 2133.
(2) Brune, S. N. Master's Thesis, Southern Illinois University at Edwardsville, IL, 1988.
(3) Firsching, F. H.; Mohammadzadei, J. *J. Chem. Eng. Data* **1986**, *31*, 40.
(4) Stewart, D. C.; Kato, D. *J. Anal. Chem.* **1958**, *30*, 164.
(5) Bingler, L. S.; Byrne, R. H. *Polyhedron* **1989**, *8*, 1315.
(6) Sillen, L. G.; Martell, A. E. *Stability Constants*; The Chemistry Society, Burlington House: London, 1964.
(7) Kolthoff, I. M.; Sandell, E. B.; Meehan, E. J.; Bruckenstein, S. Quantitative Chemical Analysis, 4th ed.; MacMillan: New York, 1969.

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