COMPONENTS:

(1) Lithium phosphate; Li_3PO_4; [10377-52-3]
(2) Ammonia; NH_3; [7664-41-7]
(3) Lithium hydroxide; LiOH; [1310-65-2]
(4) Phosphoric acid; H_3PO_4; [7664-38-2]
(5) Water; H_2O; [7732-18-5]

EVALUATOR:
J. Eysseltová
Charles University
Prague, Czechoslovakia
and
M. Salomon
U.S. Army Research Laboratories
Ft. Monmouth, NJ 07703
U.S.A.
December 1981

CRITICAL EVALUATION:

There have been relatively few solubility studies on Li_3PO_4-aqueous systems (1-5). Four of the studies (1-4) report solubilities based on direct analysis of the binary system, and three studies (2, 3, 5) report the solubility of Li_3PO_4 in ternary systems.

THE BINARY SYSTEM

1. Solubilities at 273 K to 298 K. The direct determination of the solubility of Li_3PO_4 in pure water has proved difficult due to the formation of a fine colloid which cannot be removed by filtration (1,4). Thus Rammelsberg's value (1) of 0.0104 mol kg^{-1} at 288 K is undoubtedly much too high, and this work has therefore not been compiled. Although Mayer's average value of 0.00340 mol kg^{-1} (0.394 g kg^{-1}) appears slightly high, he certainly was aware of this problem (2,3): in a footnote on page 201 of reference (2), Mayer states that turbidity in saturated solutions does not occur if the solution is heated. Although not stated, the evaluators assume that Mayer prepared his saturated solutions by first heating the solutions (i.e. from supersaturation). Since Mayer's value is slightly high, the evaluators were considering rejecting these data but decided against this as his data constitute one of two direct measurements on the binary system [the other being from ref (4)], and his results are the most widely quoted ones in various important handbooks (e.g. see references 6-8). Mayer's value of 0.0394 g per 100 g H_2O is usually quoted for 291 K when his solutions were equilibrated over the temperature range of 288 - 291 K.

Rollet and Lauffenburger (5) obtained solubility values for the binary system at 273 K and 293 K by extrapolation of the isotherms in the Li_2O-P_2O_5-H_2O ternary systems. Their results for the solubility of Li_3PO_4 in pure water are: m_{satd} = 0.0019 mol kg^{-1} at 273 K, and m_{satd} = 0.0026 mol kg^{-1} at 293 K. These data suggest that the solubility of Li_3PO_4 in pure water increases with temperature and therefore casts some doubt on the accuracy of Mayer's value of 0.00340 mol kg^{-1} at 288-291 K. Adding to the uncertainty in the solubility of this salt is the value of 0.00227 mol dm^{-3} at 298 K calculated by the evaluators (see below) using the conductivity data of Rosenheim and Reglin (4). If we assume the solubility follows a log m_{satd} vs 1/(T/K) relation, then using Rollet and Laufenburger's extrapolated solubility values for 273 K and 293 K, the evaluators calculate m_{satd} = 0.0028 ± 0.0002 mol kg^{-1} at 298 K (this corresponds to c_{satd} = 0.00279 mol dm^{-3} (evaluators)).

Rosenheim and Reglin (4) measured the electrolytic conductivity of saturated Li_3PO_4 slns. Their calculation of κ_{salt} (corrected for the electrolytic conductivity of water) is in error, and the correct average determined by the compilers is 9.30×10^{-4} S cm^{-1}. In computing the solubility from κ_{salt}, one cannot neglect, as did Rosenheim and Reglin, the hydrolysis of the phosphate ion according to

$$PO_4^{3-} + H_2O = HPO_4^{2-} + OH^- \qquad [1]$$

The thermodynamic equilibrium constant for this hydrolysis reaction is obtained from

$$K^\circ_h = K^\circ_w / K^\circ_{a3} \qquad [2]$$

(continued next page)

COMPONENTS:

(1) Lithium phosphate; Li_3PO_4; [10377-52-3]
(2) Ammonia; NH_3; [7664-41-7]
(3) Lithium hydroxide; LiOH; [1310-65-2]
(4) Phosphoric acid; H_3PO_4 [7664-38-2]
(5) Water; H_2O; [7732-18-5]

EVALUATOR:

J. Eysseltová
Charles University
Prague, Czechoslovakia
and
M. Salomon
U.S. Army Research Laboratories
Ft. Monmouth, NJ 07703
U.S.A.
December 1981

CRITICAL EVALUATION:

In eq [2] $K_w^\circ = 1.005 \times 10^{-14}$ (9), and the third acid dissociation constant of H_3PO_4 is $K_{a3}^\circ = 4.217 \times 10^{-13}$ (10): thus $K_h^\circ = 0.02383$ at 298 K, and the major ions in solution are Li^+, HPO_4^{2-}, OH^- and a small but significant amount of PO_4^{3-}. It is reasonable to assume that further hydrolysis to $H_2PO_4^-$ is negligible (11), that ion association of Li^+ and OH^- is negligible (12-14), and that ion association of Li^+ and HPO_4^{2-} is negligible (15). For saturated solutions, we have

$$K_h^\circ\{y_\pm(PO_4^{3-})/[y_\pm(OH^-)y_\pm(HPO_4^{2-})]\} = [OH^-][HPO_4^{2-}]/[PO_4^{3-}] = \alpha^2 c_{satd}/(1 - \alpha) \qquad [3]$$

where α is the degree of hydrolysis and $y_\pm$ is the mean molar activity coefficient of the indicated species. The solubility of Li_3PO_4 in pure water can be calculated from Rosenheim and Reglin's average κ_{salt} value from

$$10^3\kappa_{salt}/c_{satd} = 2\alpha\Lambda(Li_2HPO_4) + \alpha\Lambda(LiOH) + 3(1 - \alpha)\Lambda(Li_3PO_4) \qquad [4]$$

where the molar conductivities, Λ, can be calculated for a given concentration, c_i, of the various species using Robinson and Stokes' equation (9)

$$\Lambda = \Lambda^\infty - \{0.77816|z_1z_2|q\Lambda^\infty/(1 + q^2) + 30.16(|z_1| + |z_2|)\}c_i \qquad [5]$$

The reader is referred to reference (9) for definition of q and the origins of the numerical terms. Limiting molar conductivities are separated into individual ionic contributions, e.g. for Li_2HPO_4, we have $\Lambda^\infty = \lambda^\infty(Li^+) + \lambda^\infty(\tfrac{1}{2}HPO_4^{2-})$ and $c_i = \alpha c_{satd}$. We first assume a value for c_{satd} and compute α iteratively from eq [3]. In solving for α from eq [3], the Davies eq

$$\log y_\pm = -0.5115z^2\{I^{1/2}/(1 + I^{1/2}) - 0.3I\} \qquad [6]$$

was used (16). The ionic strength I was calculated from

$$I = 2c_{satd}(3 - \alpha) \qquad [7]$$

For the assumed c_{satd} and the corresponding α, eq [4] is solved for κ_{salt} and the calcs repeated until the experimental value $\kappa_{salt} = 9.30 \times 10^{-4}$ S cm^{-1} is obtained. Although the solution of eq [4] employing eqs [3], [5]-[7] is fairly straight forward, there is at least a 5% uncertainty in the refined c_{satd} due to the uncertainties in the molar conductivities at infinite dilution for HPO_4^{2-} and PO_4^{3-}. $\lambda^\infty(\tfrac{1}{2}HPO_4^{2-})$ values of 53.4 S cm^2 mol^{-1} (17) and 57 S cm^2 mol^{-1} (18) have been reported, and the uncertainty is probably higher than indicated by the closeness of these two values. For the present calculations, the evaluators have taken $\lambda^\infty(\tfrac{1}{2}HPO_4^{2-}) = 53.4$ S cm^2 mol^{-1}. Greater uncertainty is associated with the value for $\lambda^\infty(1/3PO_4^{3-})$ as reported values range from 69.0 S cm^2 mol^{-1} (17) to 82.3 S cm^2 mol^{-1} (19) and 92.8 S cm^2 mol^{-1} (20). Milazzo's value (20) appears much too high, and for consistency in the calculations, we have used Prideaux's value (17) of $\lambda^\infty(1/3PO_4^{3-})$ and 67 S cm^2 mol^{-1}. For the remaining molar conductivities, we have used $\lambda^\infty(Li^+) = 38.71$ S cm^2 mol^{-1} (13) and $\lambda^\infty(OH^-) = 199.18$ S cm^2 mol^{-1} (21). Our final results are: $c_{satd} = 0.00227$ mol dm^{-3} and $\alpha = 0.8875$. Thus the extent of hydrolysis of PO_4^{3-} in the saturated solution is about 89%, and the fact that Rosenheim and Reglin obtain a c_{satd} close to 0.00227 mol dm^{-3} neglecting hydrolysis is attributed to their use of inaccurate λ^∞ values.

(continued next page)

COMPONENTS:
(1) Lithium phosphate; Li_3PO_4; [10377-52-3]
(2) Ammonia; NH_3; [7664-41-7]
(3) Lithium hydroxide; LiOH; [1310-65-2]
(4) Phosphoric acid; H_3PO_4; [7664-38-2]
(5) Water; H_2O; [7732-18-5]

EVALUATOR: J. Eysseltová
Charles University
Prague, Czechoslovakia
and
M. Salomon
U.S. Army Research Laboratories
Ft. Monmouth, NJ 07703
U.S.A.
December 1981

CRITICAL EVALUATION:

We now review the status of the solubility of Li_3PO_4 in pure water. Mayer's oft quoted value of 0.0034 mol kg^{-1} at 288-293 K is probably too high by at least 15%. Using the conductivity data of Rosenheim and Reglin, the evaluators have calculated a solubility value of 0.0023 ± 0.0001 mol dm^{-3} at 298 K. This value is not in very good agreement with the extrapolated value of 0.0028 ± 0.0002 mol kg^{-1} estimated by the evaluators from Rollet and Lauffenburger's extrapolated values of 0.0019 mol kg^{-1} at 273 K and 0.0026 mol kg^{-1} at 293K.

2. The Solubility Product Constant. For the reaction

$$3Li^+ + PO_4^{3-} = Li_3PO_4(s) \qquad [8]$$

the thermodynamic solubility product constant is defined by

$$K^\circ_{s0} = \{Li^+\}^3\{PO_4^{3-}\} = 27(1 - \alpha)c^4_{satd}y^3_\pm(Li^+)y_\pm(PO_4^{3-}) \qquad [9]$$

Based on the solubility of 0.00227 mol dm^{-3} calculated by the evaluators from the conductivity data, it is found that $K^\circ_{s0} = 2.370 \times 10^{-11}$ mol^2 dm^{-6}, or $pK^\circ_{s0} = 10.625$. In the latest revision of Lange's *Handbook*, Dean (8) reports $pK_{s0} = 8.5$. It is not stated whether this is a pK or a pK° value, what the temperature is, and the origin of this value. It appears (see below) that this pK_{s0} was incorrectly calculated from Mayer's m_{satd}, and since earlier versions of Lange's *Handbook* (e.g. see ref. 7) do not report a K_{s0} for Li_3PO_4, the value $pK_{s0} = 8.5$ is probably one of Dean's contributions to the revised *Handbook*. If we incorrectly neglect hydrolysis and activity coefficients, K_{s0} would be given by

$$K_{s0} = [Li^+]^3[PO_4^{3-}] = 27\ c^4_{satd} \qquad [10]$$

Using Mayer's value of m_{satd} = 0.00340 mol kg^{-1} at 288-291 K, eq [10] give $K_{s0} = 3.61 \times 10^{-9}$ mol^2 kg^{-2}, or $pK_{s0} = 8.44$ which is practically identical to Dean's value of 8.5.

Two additional sources (22,23) quote a value of $pK_{s0} = 12.5$ but fail to state whether this is a pK or pK° value, and fail to cite the original publication. The evaluators could not find the source of this pK_{s0} in spite of an exhaustive literature search. Fitting eq [3] to this pK_{s0} requires c_{satd} = 0.000875 mol dm^{-3}, and we therefore conclude that the pK_{s0} value of 12.5 is in serious error and must be rejected.

MULTICOMPONENT SYSTEMS

Of the few solubility studies on multicomponent systems (1-3, 5, 24) only ternary systems have been investigated and only references 2,3 and 5 report quantitative data. Qualitative studies state that Li_3PO_4 is soluble in strong acids (1-3, 24), is difficult to dissolve in acetic acid (2,3) and that addition of NH_4Cl tends to increase the solubility (2,3). The quantitative studies are discussed below.

1. The Li_3PO_4-NH_3-H_2O system. Mayer (2,3) reported only one data point for this system at 288-291 K. In approximately 1.6 mol kg^{-1} NH_3 solution, the average value of the soly as calculated by the compilers is 0.0015 mol kg^{-1} ($\sigma = 0.0001$).

2. The Li_2O-P_2O_5-H_2O System. This is the most complete phase study available for Li_3PO_4 systems. Rollet and Laueffenburger (5) reported the compositions of saturated solutions at 273 K and 293 K in mass% of Li_2O and P_2O_5. The compiler separated appropriate data

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Lithium phosphate; Li_3PO_4; [10377-52-3] (2) Ammonia; NH_3; [7664-41-7] (3) Lithium hydroxide; LiOH; [1310-65-2] (4) Phosphoric acid; H_3PO_4; [7664-38-2] (5) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia and M. Salomon U.S. Army Research Laboratories Ft. Monmouth, NJ 07703 U.S.A. December 1981

CRITICAL EVALUATION:

into two compilations corresponding to the ternary systems Li_3PO_4-LiOH-H_2O and Li_3PO_4 - H_3PO_4-H_2O. The original phase diagrams are reproduced in Figures 1 and 2. Note that Figure 2 is an expanded detail of the initial portion of Figure 1. Numerical data corresponding to the points A-E are given in the compilations as well as the compiler's conversions from mass% to mol% and mol kg^{-1}. At 273 K, $LiOH \cdot H_2O$ is the initial solid phase up to invariant point A where Li_3PO_4 is also in equilibrium with the solution. The solubility then decreases rapidly and then increases slowly to invariant point B at which point both Li_3PO_4 and LiH_2PO_4 solid phases are in equilibrium with the solution. Between B and C, LiH_2PO_4 precipitates. The 293 K isotherm is similar to the 273 K isotherm. The invariant points are D and E. Note that point E is on the acid side of the line for $P_2O_5/Li_2O = 1.00$ which means that LiH_2PO_4 will dissolve incongruently to form Li_3PO_4 and H_3PO_4 until the composition of point E is reached.

SOLID PHASES

A number of solid phases have been reported or suggested to be in equilibrium with saturated Li_3PO_4 solutions. They are

lithium hydroxide hydrate; $LiOH \cdot H_2O$; [1310-66-3]
lithium phosphate; Li_3PO_4; [10377-52-3]
lithium phosphate dihydrate; $Li_3PO_4 \cdot 2H_2O$; [74893-09-7]
lithium phosphate hemihydrate; $Li_3PO_4 \cdot \frac{1}{2}H_2O$; [10102-26-8]
lithium dihydrogen phosphate; LiH_2PO_4; [13453-80-0]

Rollet and Lauffenburger's detailed phase study (5) reports the absence of any phosphate hydrates as well as the absense of Li_2HPO_4 for their experimental conditions. On the other hand, Rosenheim and Reglin (4) state that their solid phase is the dihydrate which forms by precipitation from aqueous H_3PO_3 with excess LiOH. These conflicting results are difficult to assess since neither study describes sufficient details of the analyses of the solid phases. Presumably Rollet and Lauffenburger used a wet residue method such as Schreinemakers' method, and Rosenheim and Reglin simply air dried their solid at 289 K so that it is quite possible that the water they found in the solid was not water of hydration. Upon drying at 333 K for several days, Rosenheim and Reglin state that they obtain the hemihydrate. It may indeed be possible that the hemihydrate is stable under the conditions reported by Rosenheim and Reglin since Sanfourche (25) reported that the neutralization method of preparation of Li_3PO_4 actually yields the hemihydrate, and that the water of hydration can be removed only at red heat. These results combined with Rollet and Lauffenburger's findings that no hydrate is formed at ambient temperatures casts some doubt on the nature of the solid phases present in all of the reported solubility studies. Because of this situation, and of the uncertainties in the reported solubility data, the evaluators feel that new studies are required before recommended data can be specified.

(continued next page)

COMPONENTS:

(1) Lithium phosphate; Li_3PO_4; [10377-52-3]

(2) Ammonia; NH_3; [7664-41-7]

(3) Lithium hydroxide; LiOH; [1310-65-2]

(4) Phosphoric acid; H_3PO_4; [7664-38-2]

(5) Water; H_2O, [7732-18-5]

EVALUATOR:

J. Eysseltová
Charles University
Prague, Czechoslovakia
and
M. Salomon
U.S. Army Research Laboratories
Ft. Monmouth, NJ 07703
U.S.A.
December 1981

CRITICAL EVALUATION:

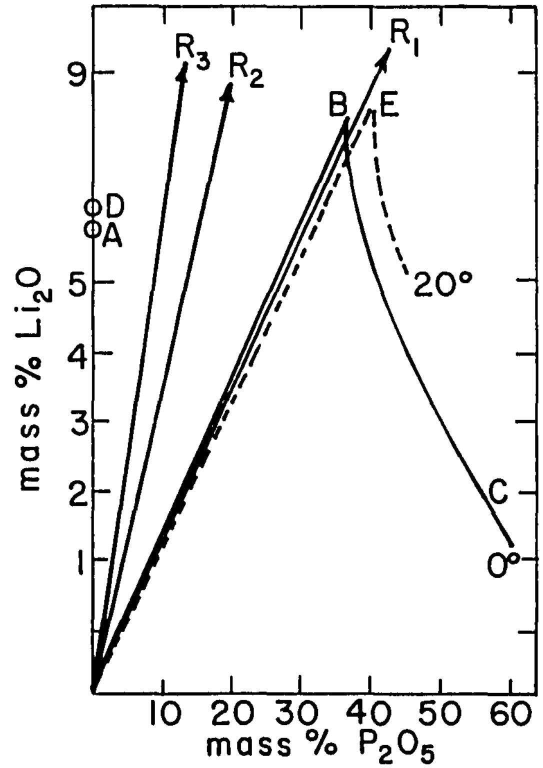

Figure 1. Isotherms for the Li_2O-P_2O_5-H_2O system.

$R_1 = Li_2O/P_2O_5 = 1$

$R_2 = Li_2O/P_2O_5 = 2$

$R_3 = Li_2O/P_2O_5 = 3$

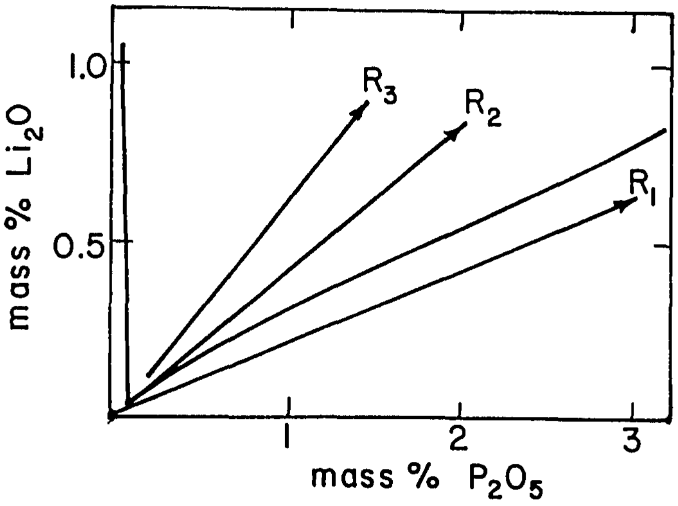

Figure 2. Detail of the 0° isotherm on Figure 1.

(continued next page)

COMPONENTS:

(1) Lithium phosphate; Li_3PO_4; [10377-52-3]

(2) Ammonia; NH_3; [7664-41-7]

(3) Lithium hydroxide; LiOH; [1310-65-2]

(4) Phosphoric acid; H_3PO_4; [7664-38-2]

(5) Water; H_2O; [7732-18-5]

EVALUATOR: J. Eysseltová
Charles University
Prague, Czechoslovakia
and
M. Salomon
U.S. Army Research Laboratories
Ft. Monmouth, NJ 07703
U.S.A.
December 1981

CRITICAL EVALUATION:

REFERENCES

1. Rammelsberg, F.C. *Wied. Ann.* 1882, *16*, 707.
2. Mayer, W. *Ann. Chem. u. Pharm.* 1856, *98*, 193.
3. Mayer, W. *Ann. Chim.* 1856, *47*, 288.
4. Rosenheim, A.; Reglin, W. *Z. Anorg. Chem.* 1921, *120*, 103.
5. Rollet, A.P.; Lauffenburger, R. *Bull. Soc. Chim. France* 1934, 146.
6. Latimer, W.M.; Hildebrand, J.H. *Reference Book of Inorganic Chemistry.* 3rd Edit. Macmillan, N.Y. 1951.
7. Lange, N.A.; Forker, G.M. *Handbook of Chemistry.* 10th Edit. McGraw-Hill. N.Y. 1961.
8. Dean, J.A. *Lange's Handbook of Chemistry.* 11th Edit. McGraw-Hill. N.Y. 1973.
9. Robinson, R.A.; Stokes, R.H. *Electrolyte Solutions.* Butterworths. London. 1955.
10. Vanderzee, C.E.; Quist, A.S. *J. Phys. Chem.* 1961, *65*, 118.
11. Butler, J.N. *Ionic Equilibrium: A Mathematical Approach.* Addison Wesley. Reading, Mass. 1964.
12. Gimblett, F.G.R.; Monk, C.B. *Trans. Faraday Soc.* 1954, *50*, 965.
13. Corti, H.; Crovetto, R.; Fernandez-Prini, R. *J. Solution Chem.* 1979, *8*, 897.
14. Note that for the LiOH association constant, ref. 12 gives $K_A = 1.504$ and ref. 13 gives $K_A = 0.97$ mol^{-1} dm^3 at 298 K.
15. Smith, R.M.; Alberty, R.A. *J. Phys. Chem.* 1956, *60*, 150. These authors report $K_A(LiHPO_4^-) = 5.2$ mol^{-1} dm^3 at 298 K.
16. Davies, C.W. *Ion Association.* Butterworths. London. 1962.
17. Prideaux, E.B.R. *J. Chem. Soc.* 1944, 606.
18. Landolt-Bornstein. *Zahlenwerte und Funktionen.* 3rd Erg. Band III. 1936.
19. Bottger, W. *Z. Phys. Chem.* 1903, *46*, 596.
20. Milazzo, C. *Electrochemistry.* Elsevier. Amsterdam. 1963.
21. Marsh, K.N.; Stokes, R.H. *Austr. J. Chem.* 1964, *17*, 740.
22. Moeller, T. *Qualitative Analysis.* McGraw-Hill, N.Y. 1958.
23. Jaulmes, P.; Brun, S. *Trav. Soc. Pharm. Montpellier* 1965, *25*, 98.
24. de Schulten, M.A. *Bull. Soc. Chim.* 1889, *1*, 479.
25. Sanfourche, A.A. *Bull. Soc. Chim.* 1938, *5*, 1669.