COMPONENTS:

(1) Cesium dihydrogenphosphate; CsH_2PO_4; [18649-05-3]

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

EVALUATOR:

J. Eysseltová
Charles University
Prague, Czechoslovakia

December, 1983

CRITICAL EVALUATION:

Three cesium orthophosphates are reported in the literature (1, 2): tricesium phosphate, pentahydrate, $Cs_3PO_4 \cdot 5H_2O$, [101056-43-3]; dicesium hydrogenphosphate, monohydrate, $Cs_2HPO_4 \cdot H_2O$, [50292-03-0]; and cesium dihydrogenphosphate, CsH_2PO_4, [18649-05-3]. No quantitative solubility data are available for the tricesium phosphate or the dicesium hydrogenphosphate. The solubility of the cesium dihydrogenphosphate was studied because its crystals had certain desirable electrical characteristics.

Bykova, et al. (3) report the solubility of cesium dihydrogenphosphate in the binary system while all the other reports of solubility data (3-6) are for ternary systems. A direct analytical solubility method was used in all the solubility studies. However, there is some disagreement about the validity of the experimental methods. In one study a potentiometric titration with aqueous KOH was used (4) and the results are reported to have an accuracy of ± 0.2 mass%. Gravimetric procedures were used in the other studies, phosphorus being weighed as $Mg_2P_2O_7$. In two of the studies (5, 6) phosphorus was precipitated as $(NH_4)_3PMo_{12}O_{40}$ and then reprecipitated and transformed to $NH_4MgPO_4 \cdot 6H_2O$. Nothing is said about the accuracy or the precision of the results. In the other study (3), phosphorus was precipitated directly as $NH_4MgPO_4 \cdot 6H_2O$ under precisely defined and carefully controlled conditions. A thorough discussion of this analytical procedure is given. Literature data are presented for the co-precipitation of cesium phosphomolybdate (7, 8) and/or cesium magnesium phosphate (1, 9). The solubility of the cesium phosphomolybdate is reported to be 4.2×10^{-6} mol dm^{-3} in 0.1 mol dm^{-3} HNO_3 at 293 K. Because of this, Bykova, et al. (3) recommend that NH_4MgPO_4 be precipitated from solutions containing less than 0.3 g $H_2PO_4^-$ per 100 cm^3, and that the amount of $Mg_2P_2O_7$ produced be no greater than 0.06 g. They criticized the analytical procedures used by the other investigators (4-6). As a matter of fact, the results of Bykova, et al. (3) do agree with those obtained by potentiometric titration (4), but they are significantly lower than those reported by others (5, 6).

THE BINARY SYSTEM

Bykova, et al. (3) measured solubilities in the 273-353 K temperature range, and the temperature coefficient of molal solubility in the 273-333 K range was also determined. A recalculation of the results by the Evaluator, using linear regression, gives equation [1].

$$c_{CsH_2PO_4} = a \cdot (T-273) + b \qquad [1]$$

When c is expressed as mass%, the coefficients are:
a = 0.25 ± 0.01 and b = 52.2 ± 0.6 with R = 0.9916. When c is expressed as mol/kg the coefficients are: a = 0.0681 ± 0.0007 and b = 4.64 ± 0.03 with R = 0.9991.

MULTICOMPONENT SYSTEMS

Cesium dihydrogenphosphate was chosen as a component in four ternary systems. These systems are discussed individually.

1. The CsH_2PO_4-$CsCl$-H_2O system. Solubilities in this system have been measured at 298 K (3). The system is reported to be of the eutonic type and a saturated solution in equilibrium with both CsH_2PO_4 and CsCl has the composition 0.58 mol/kg CsH_2PO_4 and 10.5 mol/kg CsCl.

2. The CsH_2PO_4-MH_2PO_4-H_2O system where M is K^+ or NH_4^+. Solubility in the CsH_2PO_4-$NH_4H_2PO_4$-H_2O system was measured at 298 K (5) and solubility in the CsH_2PO_4-KH_2PO_4-H_2O system was also measured at 298 K (6). In both studies the analysis of phosphorus was made by precipitating it as $(NH_4)_3PMo_{12}O_{40}$ and this is the method that has been criticized (3). Therefore, the solubilities reported in these studies may be incorrect. This is especially true in the system containing $NH_4H_2PO_4$ where the solubility of pure CsH_2PO_4 was reported to be significantly larger than other reported results. Besides this, there is a discrepancy between tabular and graphical data in the article (5). The tabular data have been replotted, Figure 1, and there are intersections of some tie lines that make no physical sense. Therefore, these results (5) are not reliable and must be rejected.

(continued next page)

COMPONENTS:

(1) Cesium dihydrogenphosphate; CsH_2PO_4; [18649-05-3]

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

EVALUATOR:

J. Eysseltová
Charles University
Prague, Czechoslovakia

December, 1983

CRITICAL EVALUATION:

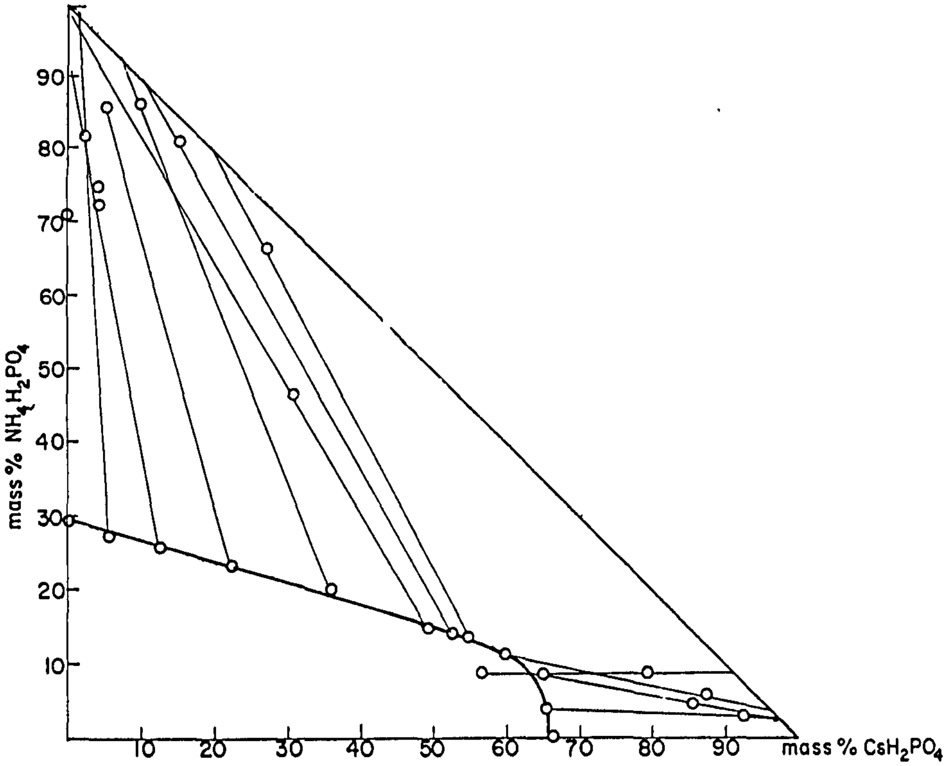

Figure 1. Phase diagram for the CsH_2PO_4-$NH_4H_2PO_4$-H_2O system at 298 K, ref. (5).

COMPONENTS:

(1) Cesium dihydrogenphosphate; CsH_2PO_4; [18649-05-3]

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

EVALUATOR:

J. Eysseltová
Charles University
Prague, Czechoslovakia

December, 1983

CRITICAL EVALUATION: (continued)

Although there is a question about the solubilities reported for these systems, the formation of solid solutions in these systems has been established. In the system containing KH_2PO_4 there are 3 crystallization fields. Solid KH_2PO_4 exists in equilibrium with solutions containing 1.32 to 1.55 mol/kg KH_2PO_4 and 0 to 0.71 mol/kg CsH_2PO_4. Solid CsH_2PO_4 exists in equilibrium with solutions containing 0 to 1.98 mol/kg KH_2PO_4 and 4.86 to 6.37 mol/kg CsH_2PO_4. Solid solutions are the equilibrium solid phases between these 2 crystallization fields. The data are given on Figure 2. It is impossible to place this system into one of Roozeboom's categories (10) because of the limited solid solubility.

For the system containing $NH_4H_2PO_4$ there is, in addition to the uncertainty discussed earlier, an uncertainty about the composition of the invariant solution. The data of Zvorykin, et al. (5) are plotted on Figure 3 and, again, because of the limited amount of data, this system cannot definitely be placed in one of Roozeboom's classifications (10).

3. The Cs_2O-P_2O_5-H_2O system. Rashkovich, et al. (4) measured solubilities in solutions in equilibrium with solid CsH_2PO_4 and $CsH_5(PO_4)_2$ at 298 and 323 K along with a few solutions at 306.2, 312 and 317.7 K. They expressed their data in terms of Cs_2O and P_2O_5. The compiler converted their data to that of the quaternary system CsH_2PO_4-Cs_2O-H_3PO_4-H_2O. These values are given on Figure 4. In the CsH_2PO_4-Cs_2O-H_2O part of the system, the solubility of cesium dihydrogenphosphate is affected only slightly by changes in solution composition. However, on the CsH_2PO_4-H_3PO_4-H_2O side of the diagram, the solubility of cesium dihydrogenphosphate increases with increasing phosphoric acid content until the invariant point is reached. Beyond this, the solid phase may be $CsH_5(PO_4)_2$ but this has not been confirmed experimentally. In the 323 K isotherm the data points in the phosphoric acid region do not lie on a smooth line as do those on the 298 K isotherm. Therefore, it is possible that a new crystallization field comes into existence here. A similar situation exists with ammonium phosphates where the formation of $3NH_4H_2PO_4 \cdot H_3PO_4$ has been suggested (11).

The evaluator has used a linear regression method to treat the experimental data in ref. (4). The results for the 298 K isotherm, Figure 4, can be expressed by equation [2].

$$c_{CsH_2PO_4} = a \cdot c_{H_3PO_4} + b \qquad [2]$$

When c is expressed as mass%, a = 0.56 ± 0.02, b = 58.3 ± 0.2 and R = 0.9923. When c is expressed as mol/kg, a = 1.17 ± 0.02, b = 6.11 ± 0.06 and R = 0.9990. The authors (4) also linearized their results but they gave no details about the method that was used. Later (12) they linearized the results in the region where $P/Cs < 1$. However, the compiler's method of linear regression gave negative correlation coefficients for these results.

CONCLUSIONS

The reliability of the solubility data for cesium dihydrogenphosphate depends on the analytical method that was used. This matter was discussed by Bykova, et al. (3) and they were careful in their experimental work. Their data agree fairly well with those obtained by extrapolation of solubility isotherms measured by others (4). Therefore, the data of Bykova, et al, (3) as well as their equation for the temperature dependence of the solubility of cesium dihydrogenphosphate are recommended values. The solubility data published by others (5, 6) are rejected because of analytical uncertainties. The only information that can be considered to be proved is the occurrence of solid solutions in the CsH_2PO_4-$NH_4H_2PO_4$-H_2O and CsH_2PO_4-KH_2PO_4-H_2O systems at 298 K.

References

1. von Berg, E. *Ber.* 1901, *34*, 4182.
2. Lauffenburger, R. Thesis, Strasbourg 1932.
3. Bykova, I.N.; Kuznetsova, G.P.; Kolotilova, V.Ya.; Stepin, B.D. *Zh. Neorg. Khim.* 1968, *13*, 540.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Cesium dihydrogenphosphate; CsH_2PO_4; [18649-05-3] (2) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia December, 1983

CRITICAL EVALUATION:

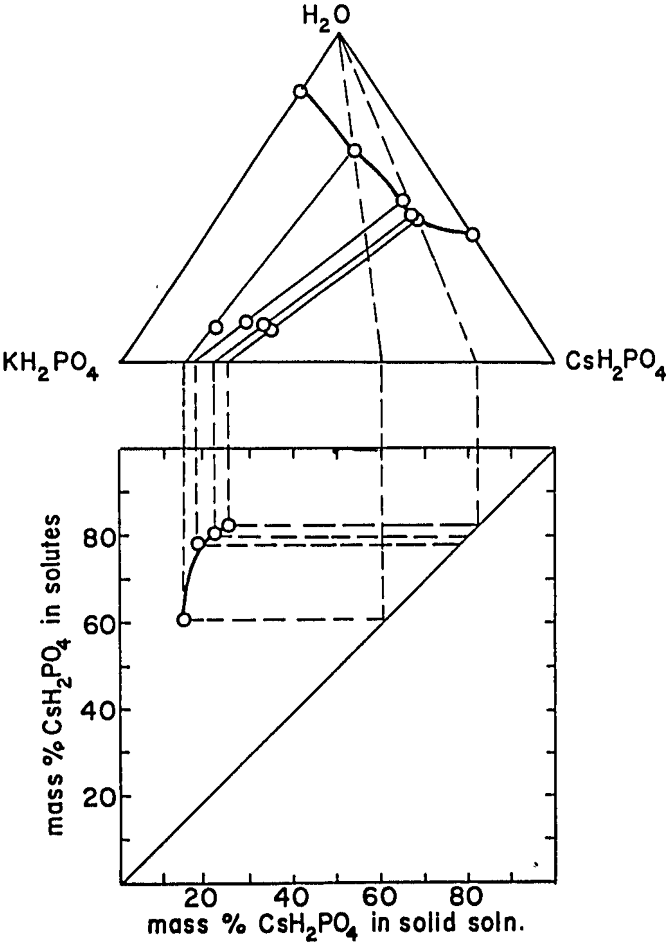

Figure 2. Phase diagram and distribution curve for the CsH_2PO_4-KH_2PO_4-H_2O system at 298 K. The data are from ref. (6).

COMPONENTS:	EVALUATOR:
(1) Cesium dihydrogenphosphate; CsH_2PO_4; [18649-05-3] (2) Water; H_2O; [7732-18-5	J. Eysseltová Charles University Prague, Czechoslovakia December, 1983

CRITICAL EVALUATION:

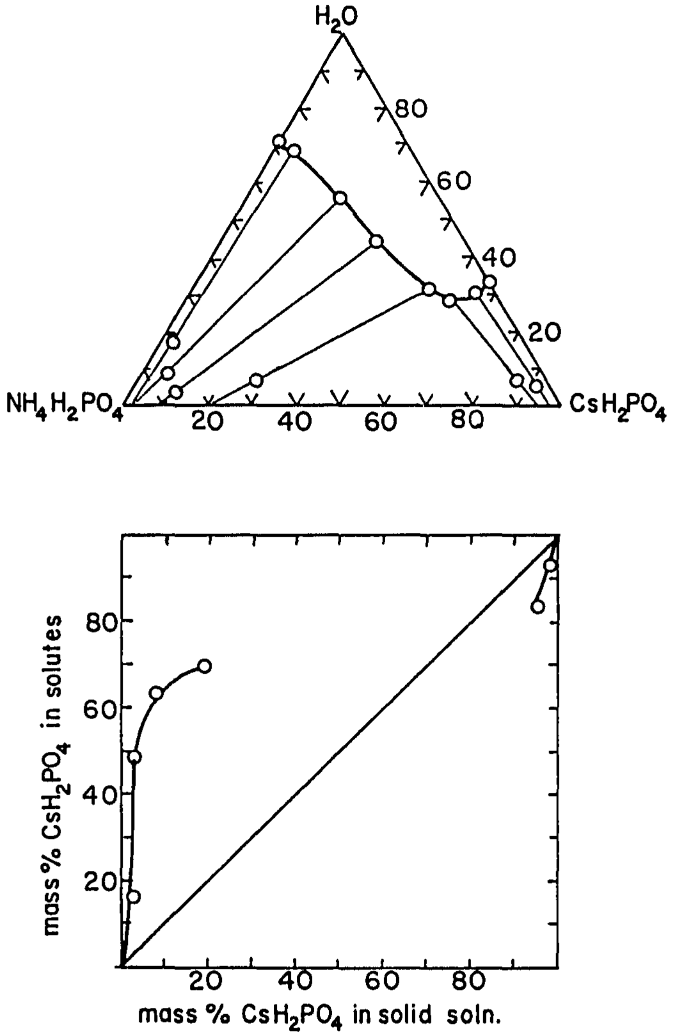

Figure 3. Phase diagram and distribution curve for the CsH_2PO_4-$NH_4H_2PO_4$-H_2O system at 298 K, ref. (5).

COMPONENTS:	EVALUATOR:
(1) Cesium dihydrogenphosphate; CsH_2PO_4; [18649-05-3] (2) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia December, 1983

CRITICAL EVALUATION:

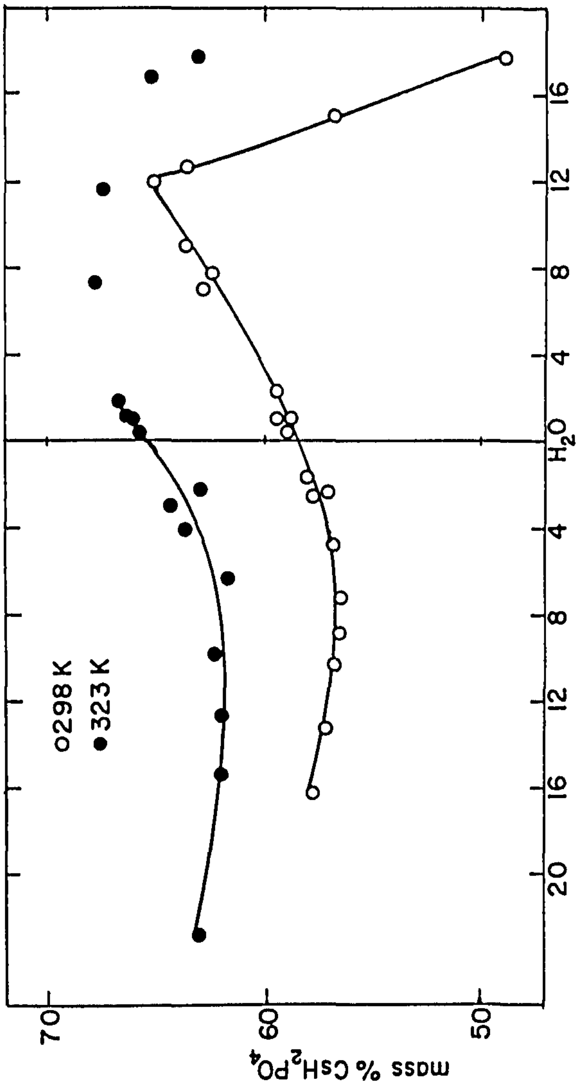

Figure 4. Solubility in the $Cs_2O-P_2O_5-H_2O$ system. The data have been calculated from ref. (4) by the compiler.

COMPONENTS:	EVALUATOR:
(1) Cesium dihydrogenphosphate; CsH_2PO_4; [18649-05-3] (2) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia December, 1983

CRITICAL EVALUATION: (continued)

4. Rashkovich, L.N.; Meteva, K.B.; Shevchik, J.E. *Zh. Neorg. Khim.* 1977, *22*, 1982.
5. Zvorykin, A.Ya.; Ratnikova, V.D. *Zh. Neorg. Khim.* 1963, *8*, 1018.
6. Sayamyan, E.A.; Bashugyan, D.P.; Karapetyan, T.I.; Grigoryan, K.G.; Kohachikyan, A.V. *Zh. Neorg. Khim.* 1977, *22*, 1119.
7. Broadbank, R.W.C.; Dhabanandana, S.; Harding, R.D. *J. Inorg. Nucl. Chem.* 1961, *23*, 311.
8. Nikitina, E.A.; Sokolova, O.N. *Zh. Obshch. Chim.* 1954, *24*, 1123.
9. Erdmann, H.; Kothner, P. *Ann Chem.* 1897, *274*, 72.
10. Roozeboom, B. *Z. Physik. Chem.* 1891, *8*, 521.
11. Flatt, R.; Brunisholz, G.; Chapuis-Goitreux, S. *Helv. Chim. Acta* 1951, *34*, 884.
12. Rashkovich, L.N.; Momtaz, R.Sh. *Zh. Neorg. Khim.* 1978, *23*, 1349.