COMPONENTS:	EVALUATOR:
(1) Tripotassium phosphate; K_3PO_4; [7778-53-2] (2) Phosphoric acid; H_3PO_4; [7664-38-2] (3) Potassium hydroxide; KOH; [1310-58-3] (4) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia July, 1986

CRITICAL EVALUATION:

The K_2O-P_2O_5-H_2O system

The K_2O-P_2O_5-H_2O system has been the subject of study in fifteen papers (1-15). Some of these (1-8) report the solubility over a wide range of K/P ratios; others (9-15) limit the study to a narrow range of K/P ratios. In the latter papers the study is often limited to the solubility of compounds such as KH_2PO_4 or $KH_5(PO_4)_2$.

Figures 1-3 illustrate the difficulties encountered in attempting to determine solubilities in this system. One of the characteristics of this system is its tendency to form supersaturated solutions. This fact has been stressed by those who have made the most comprehensive studies (3-7) and is especially characteristic at K/P ratios ≥ 2. In such solutions the reported solubilities vary widely.

Only two conclusions can be deduced from a camparison of solubility studies made on this system.

1. The determination of the solubility of all potassium phosphates except KH_2PO_4 and $KH_5(PO_4)_2$ is extremely difficult and considerable care must be given to the conditions under which the determinations are made.
2. Most of the results reported by Jänecke (2) have a systematic error and should be rejected.

Because of the complexity of the system, a large number of equilibrium solid phases have been reported. They are listed below.

$K_3PO_4\cdot 7H_2O$	[22763-02-6]	$3K_2HPO_4\cdot KH_2PO_4\cdot 2H_2O$	[101056-48-8]
$K_3PO_4\cdot 3H_2O$	[22763-03-7]	$K_5H_4(PO_4)_3\cdot H_2O$	[101056-49-9]
K_3PO_4	[7778-53-2]	$K_2HPO_4\cdot KH_2PO_4\cdot 3H_2O$	[101056-50-2]
$K_2HPO_4\cdot 6H_2O$	[101056-47-7]	$K_2HPO_4\cdot KH_2PO_4\cdot 2H_2O$	[66922-99-4]
$K_2HPO_4\cdot 3H_2O$	[16788-57-1]	KH_2PO_4	[7778-77-0]
K_2HPO_4	[7758-11-4]	$KH_5(PO_4)_2$	[14887-42-4]

The conditions under which these hydrates exist and their transition points are discussed in the Critical Evaluation of the binary systems.

The incongruently soluble $KH_5(PO_4)_2$ has been observed in all studies which investigated strongly acid solutions (1,3-7,9) and its existence may be taken as proved. A study of the temperature dependence of the solubility of this compound (13) has proved that it is incongruently soluble up to 373 K.

K/P ratios between 1 and 2. Some compound may also exist in the region between KH_2PO_4 and K_2HPO_4 but the solubility results that have been reported (1,3-9) differ substantially. Parker (1) did not observe K_2HPO_4 and his solid phase formulations in this region are probably incorrect. Berg (3,4) reports the presence of $K_2HPO_4\cdot KH_2PO_4\cdot 3H_2O$ at 298 K in a very limited concentration interval: 35.53 to 34.48% K_2O and 29.09 to 29.39% P_2O_5, i.e., 53.40 to 52.85% K_3PO_4 and 15.54 to 15.69% H_3PO_4. Flatt, et al. (9) reported the presence of $K_5H_4(PO_4)_3\cdot H_2O$ or $2K_2HPO_4\cdot KH_2PO_4\cdot H_2O$ at 298 K in the concentration range 51.5 to 52.4% K_3PO_4 and 16.3 to 15.7% H_3PO_4. This compound was also reported by Staudenmayer (16).

A careful study of the transition between KH_2PO_4 and K_2HPO_4 at 298 K has been made (8). The existence of the above reported complexes was not observed, nor was the presence of $K_2HPO_4\cdot 3H_2O$. These authors suggest that the crystallization of K_2HPO_4 and KH_2PO_4 occurs somewhere between 20.5 to 31.3% K_3PO_4 and 13.7 to 14.8% H_3PO_4, i.e., at a significantly lower K_3PO_4 content.

Ravich (6,7) studied the system at 273 K and reports no solid phase with a K/P ratio between 1 and 2. Berg (5) reported the presence of $K_2HPO_4\cdot KH_2PO_4\cdot 2H_2O$ and $3K_2HPO_4\cdot KH_2PO_4\cdot 2H_2O$ at 323 K. The latter compound was also observed by Staudenmayer (16). However, Berg (5) was not certain of the identity of these compounds.

In conclusion, the Evaluator believes that no decision about the existence of the solid phases in the K_2O-P_2O_5-H_2O system can be made until further studies are reported. In making such investigations the existence of very viscous solutions will be encountered. These solutions become supersaturated very readily. Meanwhile, the data of Berg (3-5) and Ravich (6,7) are to be considered as tentative values.

The solubility curves for KH_2PO_4 (1,3-14) agree satisfactorily. Punin's smoothing equation (15) may be useful for temperature extrapolation, but its use for the binary KH_2PO_4-H_2O system shows a systematic error of about +10% when compared with accepted experimental values.

(continued next page)

COMPONENTS:	EVALUATOR:
(1) Tripotassium phosphate; K_3PO_4; [7778-53-2] (2) Phosphoric acid; H_3PO_4; [7664-38-2] (3) Potassium hydroxide; KOH; [1310-58-3] (4) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia July, 1986

CRITICAL EVALUATION:

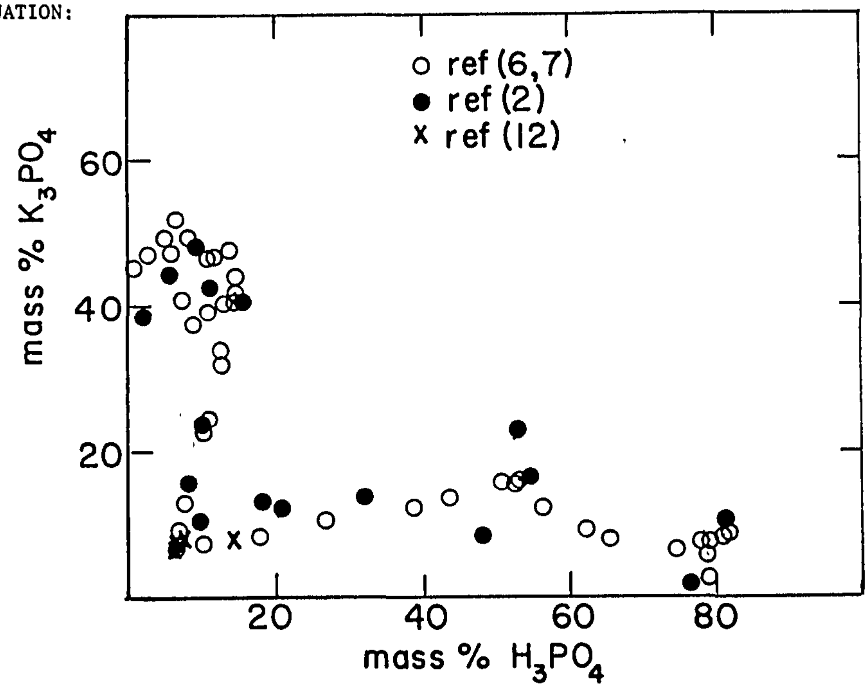

Figure 1. Solubility in the K_3PO_4-H_3PO_4-KOH-H_2O system at 273 K.

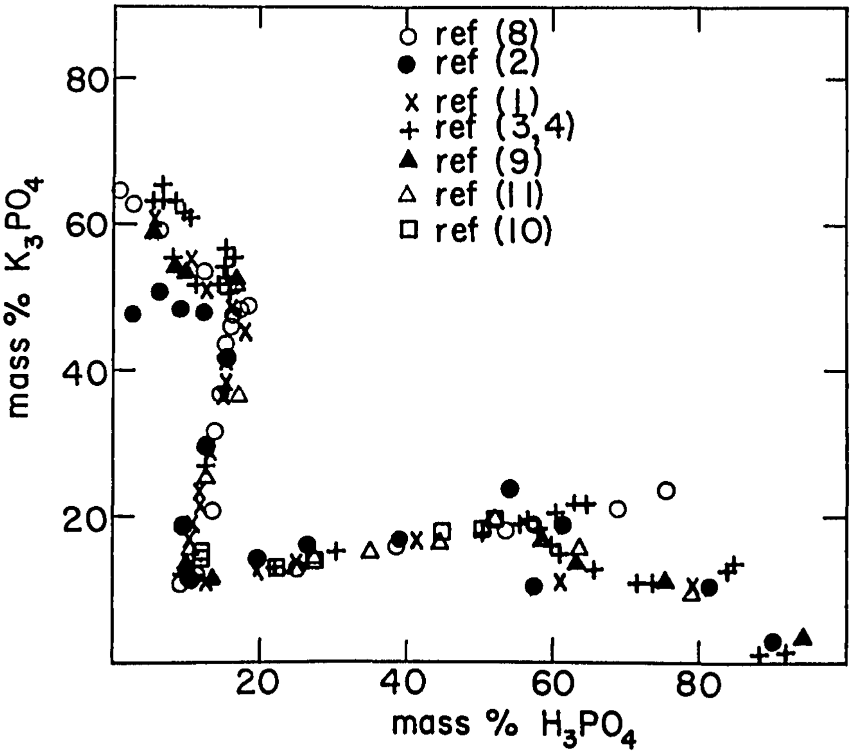

Figure 2. Solubility in the K_3PO_4-H_3PO_4-KOH-H_2O system at 298 K.

COMPONENTS:	EVALUATOR:
(1) Tripotassium phosphate; K_3PO_4; [7778-53-2] (2) Phosphoric acid; H_3PO_4; [7664-38-2] (3) Potassium hydroxide; KOH; [1310-58-3] (4) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia July, 1986

CRITICAL EVALUATION:

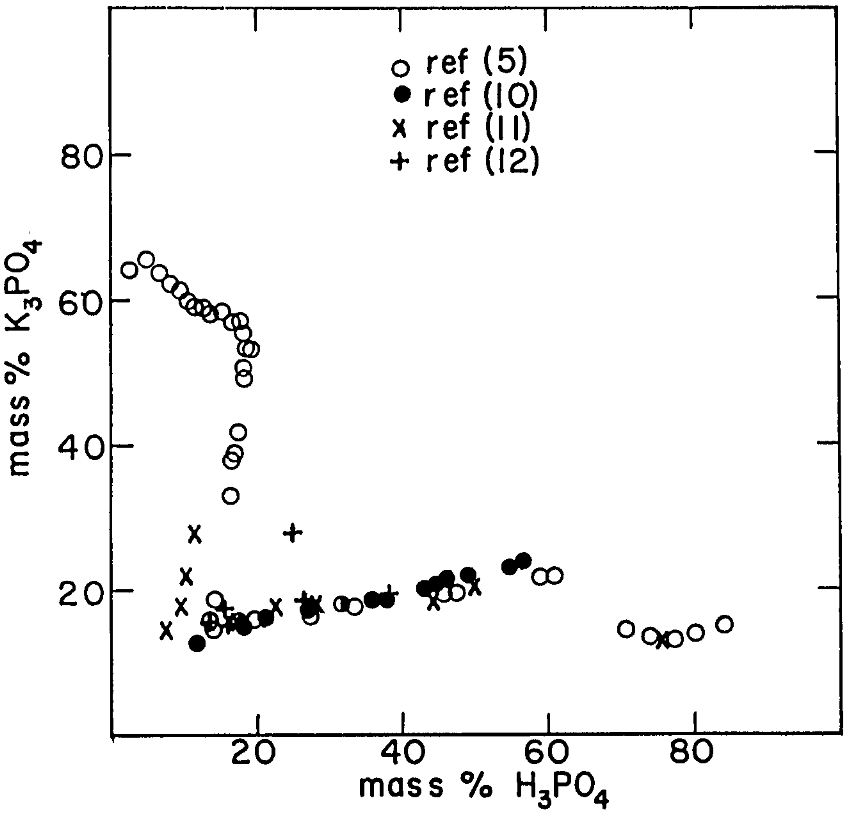

Figure 3. Solubility in the $K_3PO_4-H_3PO_4-KOH-H_2O$ system at 323 K.

COMPONENTS:	EVALUATOR:
(1) Tripotassium phosphate; K_3PO_4; [7778-53-2] (2) Phosphoric acid; H_3PO_4; [7664-38-2] (3) Potassium hydroxide; KOH; [1310-58-3] (4) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia July, 1986

CRITICAL EVALUATION: (cont'd)

Solubilities in some segments of this system have been determined at elevated temperatures (17,18). The system is similar to the $Na_2O-P_2O_5-H_2O$ system (see chap. 2, p. 11). The presence of liquid-liquid immiscibility is characteristic of this system at high temperatures.

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