COMPONENTS:

(1) Trisodium Phosphate; Na_3PO_4; [7601-54-9]
(2) Phosphoric acid; H_3PO_4; [7664-38-2]
(3) Sodium hydroxide; NaOH; [1310-73-2]
(4) Water; H_2O; [7732-18-5]

EVALUATOR:

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July, 1986

CRITICAL EVALUATION:

Solubility data for the Na_2O-P_2O_5-H_2O system have been reported in 13 different publications (1-13). Some of these (1-7) report the solubility in systems in which there is a range of Na/P ratios. Others (8-13) are limited to one Na/P ratio, i.e., the solubility of a given sodium phosphate in water is reported.

Many solid phases have been reported or suggested as being in equilibrium with saturated solutions in the Na_2O-P_2O_5-H_2O system. These are:

NaOH; [1310-73-2]
$Na_3PO_4 \cdot 1/4NaOH \cdot 12H_2O$; [12362-10-6]
$Na_3PO_4 \cdot 1/7NaOH \cdot 12H_2O$; [101056-44-4]
$Na_3PO_4 \cdot 12H_2O$; [10101-89-0]
$Na_3PO_4 \cdot 10H_2O$; [10361-89-4]
$Na_3PO_4 \cdot 8H_2O$; [60593-59-1]
$Na_3PO_4 \cdot 6H_2O$; [15819-50-8]
$Na_3PO_4 \cdot 0.5H_2O$; [60593-58-0]
Na_3PO_4; [7601-54-9]
$Na_2HPO_4 \cdot 12H_2O$; [10039-32-4]
$Na_2HPO_4 \cdot 8H_2O$; [67417-37-2]
$Na_2HPO_4 \cdot 7H_2O$; [7782-85-6]
$Na_2HPO_4 \cdot 2H_2O$; [10028-24-7]
Na_2HPO_4; [7558-79-4]
$Na_2HPO_4 \cdot NaH_2PO_4$; [65185-91-3]
$Na_2HPO_4 \cdot 2NaH_2PO_4 \cdot 2H_2O$; [66905-89-3]
$NaH_2PO_4 \cdot 4H_2O$; [101056-45-5]
$NaH_2PO_4 \cdot 2H_2O$; [13472-35-0]
$NaH_2PO_4 \cdot H_2O$; [10049-21-5]
NaH_2PO_4; [7558-80-7]
$Na_3H_3(PO_4)_2 \cdot 7.5H_2O$; [101056-46-6]
$Na_3H_3(PO_4)_2 \cdot 1.5H_2O$; [101917-67-3]
$NaH_2PO_4 \cdot H_3PO_4$; [14887-48-0]
$H_3PO_4 \cdot 0.5H_2O$; [16271-20-8]

The conditions under which these phosphates exist is discussed in the Critical Evaluation of the respective binary systems.

Na_3PO_4-NaOH-H_2O system. Menzel and von Sahr (1) studied this system at 298 K. They found that as the mole ratio Na_2O/P_2O_5 in the saturated solutions varied from 2.69 to 3.68, the same ratio in the solid phase increased from 3.11 to 3.22. Thereafter as the Na/P ratio in the solution increased to about 145, the same ratio in the solid phase changed only from 3.22 to 3.24. They concluded that the equilibrium solid phases were solid solutions although X-ray diffraction diagrams of four such solid phases showed little difference among them.

Kobe and Leipper (2) suggested that the commercial trisodium phosphate has the formula $Na_3PO_4 \cdot 1/7NaOH \cdot 12H_2O$. Later Kobe returned to this problem and studied systems of high Na_2O/P_2O_5 ratios (3). He and his co-worker found the system to be a complex one. The anyhdrous form of Na_3PO_4 as well as the hemihydrate, the hexahydrate and the octahydrate were identified as equilibrium solid phases. An alkaline complex salt was also observed. The complex was studied further and, in agreement with Bell (14), they suggested that at 273-333 K two different complexes are present: $Na_3PO_4 \cdot 1/7NaOH \cdot 12H_2O$ and $Na_3PO_4 \cdot 1/4NaOH \cdot 12H_2O$ but they included only the latter in their Tables. At 353-373 K they found only the hydrates of Na_3PO_4 in the highly alkaline solutions. This agrees with the opinion of others (4) who mention no complex formation in this system at 423, 523 and 623 K.

The transition of the different hydrates and the identification of these hydrates at increasing NaOH concentrations cannot be evaluated because of lack of corroborating work by others. However, Ravich and Shcherbakova (23) did present X-ray evidence for the formation of solid solutions m $Na_3PO_4 \cdot$n Na_2HPO_4. These solid solutions are reported to coexist with saturated solutions having Na/P ratios even greater than 3 at 523, 573 and 638 K. This is in agreement with the observations of Broadbent, et al. (18) who found equilibrium solid phases in which the Na/P ratio varied from 2.64 to 2.82 at 524 and 573 K.

As noted above, this system has been studied at temperatures of 293 K (1), 298 K (2, 3, 5) and at elevated temperatures 423, 523 and 623 K (4) and 523, 573 and 638 K (23). The lower temperature results are shown on Figure 1. The data agree fairly well with each other except for one data point (5) which is obviously incorrect. Except for this one data point these results can be accepted tentatively. A similar comparison cannot

(continued next page)

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

EVALUATOR:

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July, 1986

CRITICAL EVALUATION:

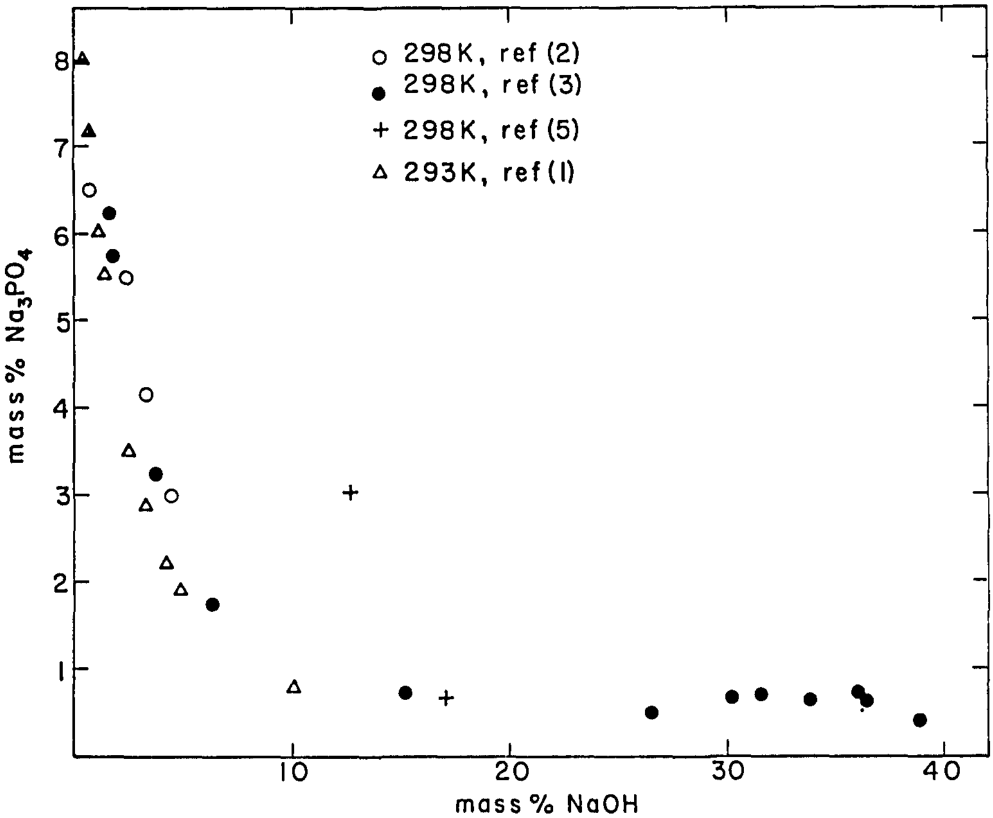

Figure 1. Solubility of Na_3PO_4 in aqueous NaOH.

COMPONENTS:	EVALUATOR:
(1) Trisodium phosphate; Na_3PO_4; [7601-54-9] (2) Phosphoric acid; H_3PO_4; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia July, 1986

CRITICAL EVALUATION:

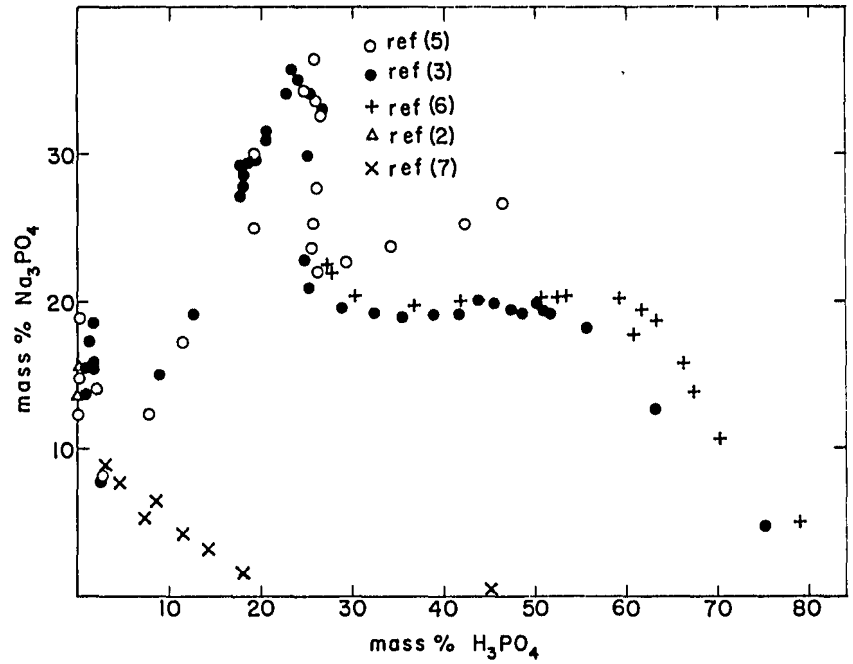

Figure 2. Solubility of Na_3PO_4 in aqueous H_3PO_4 at 298 K.

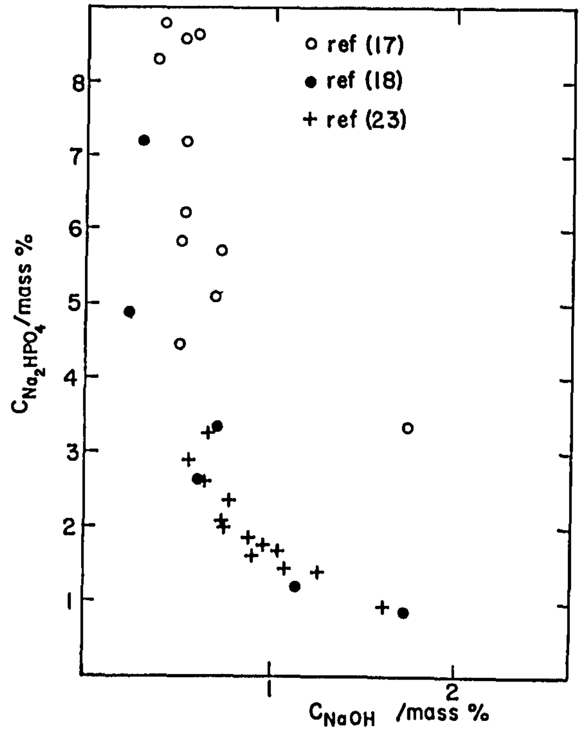

Figure 3. Solubility of Na_2HPO_4 in aqueous NaOH at 573 K.

COMPONENTS:	EVALUATOR:
(1) Trisodium Phosphate; Na_3PO_4; [7601-54-9] (2) Phosphoric acid; H_3PO_4; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia July, 1986

CRITICAL EVALUATION: (cont'd)

be made for the results obtained at elevated temperatures. The data points of Ravich and Shcherbakova (23) are concentrated in a narrow range of Na/P ratios and can be compared with only one data point of Broadbent, et al. (18) and of Panson, et al. (17).

Na_3PO_4-H_3PO_4-H_2O system. Solubility studies have been made at 298 K in systems which have a wide range of Na/P ratios (3, 5). Studies at 298 K in a more limited range have also been made: the Na_3PO_4-Na_2HPO_4-H_2O system (2); the NaH_2PO_4-H_3PO_4-H_2O system (6); and the Na_2HPO_4-H_3PO_4-H_2O system (7). The Na_3PO_4-Na_2HPO_4-H_2O system has also been studied at 293 K (1).

Figure 2 shows the solubility results obtained at 298 K. It is apparent that the work of Beremzhanov, et al. (7) ignores the existence of NaH_2PO_4 and the results are clearly incorrect. The data in the region where P/Na>1 (5) probably are for supersaturated solutions. For this region the results of Wendrow and Kobe (3) and Lilich, et al. (6) are tentatively accepted. Between Na_2HPO_4 and NaH_2PO_4 the solubility data of Wendrow and Kobe (3) and D'Ans and Schreiner (5) are very close to each other and are tentatively accepted as describing the solubility in this region. With respect to the identity of the solid phases in equilibrium with these saturated solutions, more work is needed before a decision can be made.

Phosphates in which the Na/P ratio is other than 3, 2 or 1, e.g., $Na_2HPO_4 \cdot NaH_2PO_4$ and $Na_2HPO_4 \cdot 2NaH_2PO_4 \cdot 2H_2O$, have been reported as existing in a very narrow concentration range (3). Their existence has not been confirmed by others, and more work is needed before a judgment about the existence of such phosphates can be made.

The hydrates $Na_3H_3(PO_4)_2 \cdot 7.5H_2O$ and $Na_3H_3(PO_4)_2 \cdot 1.5H_2O$ have been reported to exist in equilibrium with very concentrated solutions having a pH = 7 (15). There is no other report on the existence of these phosphates. They probably are metastable (5).

The existence of $NaH_2PO_4 \cdot H_3PO_4$ in strongly acid solutions has been reported by several investigators (3,6,8). The solubility of this substance has been measured over a range of temperatures. As a result of such a study Paravano and Mieli (8) state that the system is glass-forming in the temperature range 235 to 307 K. By extrapolating their values it appears that the composition of the system at 323 K is 45 mass% NaH_2PO_4 and 37.4 mass% H_3PO_4. This is in good agreement with the value reported by Lilich, et al. (6), especially if their value of 28.7 mass% H_3PO_4 at 323 K is a typographical error and the correct value should be 38.7 mass%. Their reported value for NaH_2PO_4 is 46 mass%. Paravano and Mieli (8) state that at temperatures below about 373 K, $NaH_2PO_4 \cdot H_3PO_4$ has an incongruent solubility. This is consistent with work reported by others (3,6). However, there are significant differences in the 298 K solubility isotherms reported for this substance (3,6) and further work is necessary before this matter can be resolved.

Solubility measurements have also been made at elevated temperatures (17-19, 23). Some of the data are shown on Figure 3. At 573 K the solubility results of Ravich, et al. (23) and of Panson, et al. (17) agree fairly well with each other while the values reported by Broadbent, et al. (18) have a significant amount of scatter and generally report a larger NaOH content. Therefore, the data of Braodbent, et al. (18) should probably be rejected because of an apparent systematic error. There is another report of solubility data under these conditions (20) but the data are presented only in graphical form. The author states that tetrasodium diphosphate and sodium triphosphate are equilibrium solid phases, but this seems unlikely in view of the conditions for the preparation of pyro- and tri-phosphates (21). In still another report (22), $Na_4P_2O_7$ was the only solid phase found at 573 K and its existence was estimated to be limited to the 563-573 K temperature interval.

Marshall (19) reviewed all this work and considered that the reported compositions of the saturated solutions were in fairly good agreement.

Liquid-liquid immiscibility is the phenomenon that characterizes this system at high temperatures.

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(1) Trisodium Phosphate; Na_3PO_4; [7601-54-9] (2) Phosphoric acid; H_3PO_4; [7664-38-2] (3) Sodium hydroxide; NaOH; [1310-73-2] (4) Water; H_2O; [7732-18-5]	J. Eysseltová Charles University Prague, Czechoslovakia July, 1986

CRITICAL EVALUATION: (cont'd)

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