The System $K_4P_2O_7$-$Na_4P_2O_7$-H_2O

Solubility, Temperature Dependence, and Composition of Solid Phases

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TETRAPOTASSIUM PYROPHOSPHATE is highly soluble in water, and its solubility shows little temperature dependence. The solubility of the corresponding tetrasodium pyrophosphate is much lower and shows marked temperature dependence. The solubility of a mixture of $K_4P_2O_7$ and $Na_4P_2O_7$ at 30° C. has been shown to increase along a smooth curve as $K_4P_2O_7$ content is enriched (*4*).

Solubility, temperature dependence, and composition of equilibrium solid phases present in the system $K_4P_2O_7$-$Na_4P_2O_7$-H_2O were determined. This work is related to that of Morey on the anhydrous system $NaPo_3$-$Na_4P_2O_7$-$K_4P_2O_7$-KPO_3 (*2*). The results reported here include solubility through a full range of compositions from $K_4P_2O_7$ to $Na_4P_2O_7$.

EXPERIMENTAL

The chemicals used were of the highest quality available. Assay of both $Na_4P_2O_7$ and $K_4P_2O_7$ exceeded 99%. The hygroscopic $K_4P_2O_7$ was stored in a desiccator over $CaSO_4$. Exposure during sample preparation was minimized to prevent moisture pickup. Moisture level in the $K_4P_2O_7$ was maintained below 0.5% H_2O. Distilled water was used for sample preparation.

Samples were equilibrated in sealed Erlenmeyer flasks at the desired temperature in a Research Specialties Co. temperature-controlled water bath shaker, Model 2156. This equipment was modified by adding an electric heater, cooling coil, and Lux variable thermoregulator. Temperature was controlled to ±0.2° C. at 25° and ±0.5° C. at 85°.

Table I. Isotherm Data at 25° C.

Initial Composition, Wt. %			Saturated Liquor, Wt. %		Wet Residue, Wt. %	Solid
$K_4P_2O_7$	$Na_4P_2O_7$	H_2O	H_2O	$Na_4P_2O_7$	H_2O	Phase[a]
69.00	0	31.00	34.43	...	...	[b]
72.00	0	28.00	34.38	...	...	[b]
66.00	0	34.00	34.31	...	...	[b]
67.98	1.04	30.98	34.21	0.45	15.04	I
66.91	2.02	31.08	34.30	0.31	18.72	I
65.28	3.91	30.81	34.32	0.43	16.35	I
60.56	6.66	32.78	39.22	2.03	18.24	I
58.77	8.34	32.89	40.65	3.32	17.67	I
54.84	9.31	35.85	42.16	6.40	18.20	I
53.02	11.15	35.84	41.90	8.20	18.53	I
49.80	10.89	39.31	41.99	9.09	18.67	I
47.18	12.97	39.85	41.88	11.38	18.24	I
44.95	14.75	40.30	41.88	13.30	16.94	I
43.85	17.42	38.17	41.60	13.17	21.12	I
41.81	19.47	38.72	41.62	12.85	22.80	I
39.79	20.24	39.97	41.51	12.85	24.85	I
34.33	18.96	46.71	47.51	...	...	II
24.44	23.13	52.43	56.28	...	...	II
20.53	19.98	59.50	63.23	...	...	II
15.48	15.32	69.19	71.74	...	...	II
9.48	17.42	72.75	78.04	...	...	II
6.48	14.18	79.34	83.62	...	...	II
...	...	...	95.24	4.76	...	II

[a] Determined by x-ray diffraction. I is a solid solution of composition $aK_4P_2O_7 \cdot bNa_4P_2O_7 \cdot 3(a + b)H_2O, 0 < a < 0.77, a + b = 1.00$. II = $Na_4P_2O_7 \cdot 10H_2O$. [b] $K_4P_2O_7 \cdot 3H_2O$.

Analysis on the equilibrated samples consisted of determination of ignition loss from a ZnO bed (*1*) and flame photometric sodium analysis using a Beckman DU spectrophotometer with hydrogen-oxygen flame attachment.

These analyses were done on the saturated liquor and on the wet residue (*3*) from which most of the liquor had been removed by filtration. The saturated liquor was obtained by decantation or, in samples where fine solids remained suspended, by centrifugation for 1 hour at 1200 G in a Servall angle centrifuge. Centrifugation was feasible for samples in the 25° C. isotherm only. Decantation was sufficient for liquor removal from samples in the 50° C. isotherm.

The solubility line at 10° and 85° C. was determined within limits of ±0.5 weight % solids by adding increments of water to solid-containing equilibrated samples until complete solubility was reached. A closed system of known composition was maintained by adding water via a hypodermic syringe through a rubber septum and weighing to ±0.0001 gram after the addition. Pressure build-up at 85° C. was avoided by releasing air expansion through a hyprodermic needle during temperature equilibration.

Composition of the equilibrium solid phases in the 25° and 50° C. isotherms was determined by construction of

Table II. Isotherm Data at 50° C.

(Tie line data in the two phase area and identification of the solid phase)

Initial Composition, Wt. %			Wet Residue, Wt. %			Solid
$K_4P_2O_7$	$Na_4P_2O_7$	H_2O	$K_4P_2O_7$	$Na_4P_2O_7$	H_2O	Phase[a]
69.46	1.94	28.60	80.09	4.80	15.11	I
66.81	4.42	28.76	72.19	11.11	16.70	I
60.91	9.17	29.92	66.12	16.12	17.76	I
55.50	13.37	31.13	60.71	22.50	16.79	I
52.22	12.03	35.76	49.98	23.57	26.45	II
50.31	17.23	32.46	49.73	22.37	27.90	II
49.56	14.49	35.95	44.37	28.06	27.57	II
46.16	19.48	34.35	47.69	22.46	29.85	II
36.64	26.48	36.87	38.54	29.87	31.59	II
20.10	25.10	54.80	...	59.59	40.41	III
10.05	22.00	67.95	...	57.89	42.11	III

(Determination of the solubility line between equilibrated compositions)[b]

Solids Present, Wt. %			Complete Dissolution, Wt. %		
$K_4P_2O_7$	$Na_4P_2O_7$	H_2O	$K_4P_2O_7$	$Na_4P_2O_7$	H_2O
66.46	0.64	32.90	65.74	0.63	33.62
58.12[c]	3.44	38.44	...	...	...
54.09	6.14	38.78	53.72	6.10	40.19
48.69[c]	8.79	42.53	...	...	...
42.60[c]	12.40	45.00	...	...	...
36.88	17.09	46.03	36.82	17.07	46.12
34.16	19.28	46.56	33.58	18.95	47.47
24.07	20.80	55.13	25.03	20.01	54.96
15.25	19.78	64.97	15.97	18.96	65.07
7.20	17.98	74.82	7.63	17.43	74.94

[a] I = $(K_4P_2O_7)^a \cdot (Na_4P_2O_7)_b \cdot 3(a + b)H_2O$, II = $(K_4P_2O_7)_a \cdot (Na_4P_2O_7)_b \cdot 6(a + b)H_2O, 0 < a < 0.61, a + b = 1.00$. III = $Na_4P_2O_7 \cdot 10H_2O$.

[b] 50° Solubility of pure salts: $K_4P_2O_7$, 66.60 g./100 g. of solution; $Na_4P_2O_7$, 14.06 g./100 g. of solution.

[c] Essentially on the solubility line. A few small crystals remain in this composition.

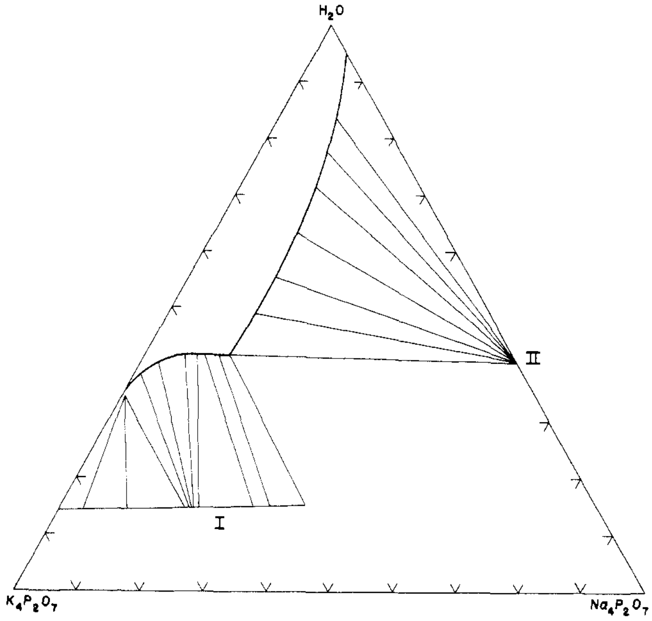

Figure 1. At 25° C., equilibrium solid phase I is solid solution of the composition $(K_4P_2O_7)_a \cdot (Na_4P_2O_7)_b \cdot 3(a\ \_\ b)H_2O$; phase II is $Na_4P_2O_7 \cdot 10H_2O$

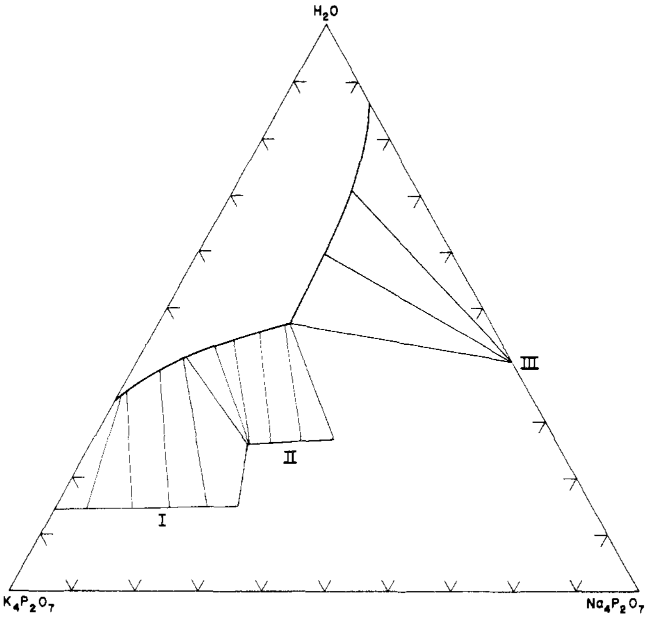

Figure 2. At 50° C., equilibrium solid phase I is solid solution of the composition $(K_4P_2O_7)_a \cdot (Na_4P_2O_7)_b \cdot 3(a + b)H_2O$; phase II is solid solution $(K_4P_2O_7)_a \cdot (Na_4P_2O_7)_b \cdot 6(a + b)H_2O$; phase III is $Na_4P_2O_7 \cdot 10H_2O$

tie lines from the point on the solubility curve and through the original composition point. Precision in the wet-residue analyses was less than for these two points. The wet-residue ignition loss indicated the degree of hydration in the equilibrium solid phase. The crystalline solid phase was confirmed by x-ray diffraction identification. X-ray measurements using copper $K\alpha$ radiation and a nickel filter were made by means of a North American Philips Co. x-ray diffractometer equipped with a scintillation detector.

The presence of a solid phase of varying composition, the solid solution, was confirmed by x-ray diffraction characterization of wet-residue samples.

RESULTS AND DISCUSSION

The 25° C. isotherm shown in Figure 1 is divided into two parts joined at an isothermally invariant composition:

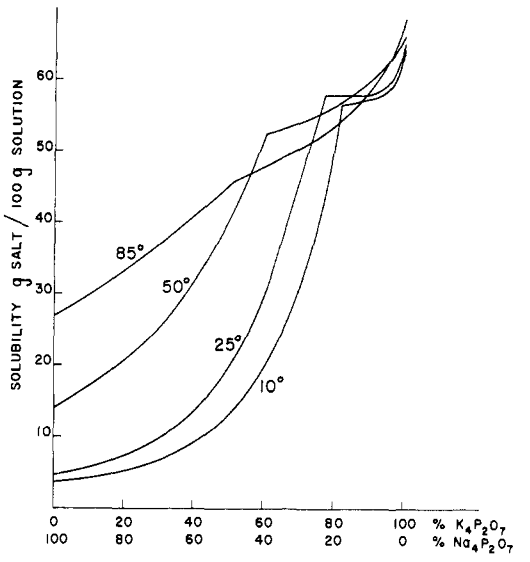

Figure 3. Solubility of the system $K_4P_2O_7$-$Na_4P_2O_7$-H_2O plotted as grams of salt per 100 grams of solution at 10°, 25°, 50°, and 85° C.

Table III. Isotherm Data[a] at 10° C.

Initial Composition, Wt. %			Saturated Liquor Wt. %	Solid Phase
$K_4P_2O_7$	$Na_4P_2O_7$	H_2O	H_2O	
44.78	12.00	43.22	43.38	$Na_4P_2O_7 \cdot 10H_2O$
37.97	12.03	50.00	50.45	$Na_4P_2O_7 \cdot 10H_2O$
28.07	11.98	59.95	60.82	$Na_4P_2O_7 \cdot 10H_2O$
19.30	10.72	69.98	70.91	$Na_4P_2O_7 \cdot 10H_2O$
11.34	8.65	80.01	80.65	$Na_4P_2O_7 \cdot 10H_2O$
4.05	6.02	89.93	90.42	$Na_4P_2O_7 \cdot 10H_2O$

(Determination of solubility line between equilibrated compositions.)

Solids Present, Wt. %			Complete Dissolution, Wt. %		
$K_4P_2O_7$	$Na_4P_2O_7$	H_2O	$K_4P_2O_7$	$Na_4P_2O_7$	H_2O
62.09[b]	0.56	37.36	...	...	...
58.46[b]	1.57	34.97	...	...	...
56.03[b]	2.79	41.18	...	...	...
54.34[b]	4.04	41.62	...	...	...
52.49	5.98	41.53	51.63	5.88	42.49
49.64	7.91	42.45	48.96	7.80	43.24
47.19[b]	9.77	43.03	...	...	...
39.57	10.63	49.80	40.56	9.57	49.87

[a] 10° C. Solubility of pure salts: $K_4P_2O_7$, 65.5 g./100 g. of solution; $Na_4P_2O_7$, 3.76 g./100 g. solution.

[b] Essentially on solubility line. A few small crystals remain in this composition.

Table IV. Isotherm Data[a] 85° C.

(Determination of solubility line between equilibrated compositions.)

Solids Present, Wt. %			Complete Dissolution, Wt. %		
$K_4P_2O_7$	$Na_4P_2O_7$	H_2O	$K_4P_2O_7$	$Na_4P_2O_7$	H_2O
63.01[b]	1.78	35.22	...	...	...
54.67[b]	5.11	40.22	...	...	...
46.96	9.01	44.03	45.34	8.70	45.96
39.12	14.10	46.78	37.49	13.62	48.89
24.72	22.57	52.70	24.07[c]	21.98	53.95
21.94[b]	23.03	55.03	...	...	...
...	...	...	14.11	24.90	60.99
10.20[b]	26.02	63.78	...	...	...
...	...	...	7.06	25.99	66.94

[a] 85° C. solubility of pure salts: $K_4P_2O_7$, 68.45 g./100 g. of solution; $Na_4P_2O_7$, 27.06 g./100 g. of solution, equilibrium solid phase anhydrous $Na_4P_2O_7$. At 79.5° C. $Na_4P_2O_7 \cdot 10H_2O = Na_4P_2O_7 + 10H_2O$.

[b] Essentially on solubility line. A few small solid particles remain in this composition.

[c] Very close to solubility line.

$Na_4P_2O_7$, 13.2; $K_4P_2O_7$, 45.0; and H_2O, 41.8 weight %. Data used in the development of this diagram and for the other three isotherms are given in tabular form.

The $K_4P_2O_7$-rich area shows a high solubility and an equilibrium solid phase which accepts $Na_4P_2O_7$ as an isomorphous adjunct. The convergence of experimentally determined tie lines is interpreted as a reflection of the curvature of the solubility line. These lines terminate in a hydrated solid solution rather than a crystalline double salt composition. The composition of the solid solution may be expressed as $(aK_4P_2O_7 \cdot bNa_4P_2O_7) \cdot 3(a + b)H_2O$, where $0 < a < 0.77$ and $a + b = 1.00$.

A series of x-ray diffraction patterns made from solids in this area was compared with the pattern for $K_4P_2O_7 \cdot 3H_2O$, the equilibrium solid phase from the $K_4P_2O_7$-H_2O system at 25° C., and the pattern for $Na_4P_2O_7 \cdot 10H_2O$, the equilibrium solid phase from the $Na_4P_2O_7$-H_2O system at 25° C. No new or different crystalline phase was indicated, although orientation effects caused some variation in line intensities.

The section of decreasing $K_4P_2O_7$ concentration moving from the invariant composition has an equilibrium crystalline solid phase of $Na_4P_2O_7 \cdot 10H_2O$, the only known hydrate of $Na_4P_2O_7$.

In figure 1, both solubility lines extrapolate from the invariant point into the two-phase areas so that the thermodynamic requirements for an isothermal junction are satisfied (*5*).

The shape of the solubility line in the $Na_4P_2O_7 \cdot 10H_2O$ area indicates that $K_4P_2O_7$ has a salting in effect when added to excess $Na_4P_2O_7$ in water.

The 50° C. isotherm shown in Figure 2 has the same form as the 25° C. isotherm, with $Na_4P_2O_7 \cdot 10H_2O$ and a hydrated solid solution as equilibrium solid phases. A hydrate transition was observed in the equilibrium solid phase between initial compositions containing 55.5% $K_4P_2O_7$ and 52.2% $K_4P_2O_7$ at a constant $Na_4P_2O_7$ concentration. This change in the solid phase is best interpreted as a transition from a trihydrate to a hexahydrate. This conclusion was based on composition analysis of wet-residue which was filtered at 50° C. to remove all but traces of the saturated liquor. No break was observed in the solubility line to correspond with this change in the solid phase.

The solubility lines for 10° and 85° are shown in Figure 3. The degree of hydration of the solid solution was not determined for these two temperatures.

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Solubilities of Some Heteropoly Salts in Aqueous Solutions

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IN A STUDY of some heteropoly compounds, it became necessary to determine the composition of several salts of these compounds as well as their solubilities. The electromotive force (e.m.f.) data of cells consisting of tungstophosphoric acids and mercury-mercurous tungstophosphate electrodes (*3*) could not be interpreted because of lack of knowledge of the composition of the solid phase of the mercurous tungstophosphate and of solubility data. These compounds were obtained by precipitation of 12-tungstophosphoric acid with mercurous nitrate by O.W. Gibbs as early as the second half of the last century and by H. Copaux at the beginning of this century (*10*). However, no quantitative data on composition or solubility were reported. In fact, the only quantitative data located were those of Rakovskii and Nikitina on tungstophosphoric acid, tungstomolybdic acid, and some of their sodium salts (*12*). Again, in studying the coagulation effects of 12-molybdoceric(IV) acid upon positive silver halide sols, the solubility of silver 12-molybdocerate(IV) had to be known (*9*). This slightly soluble salt was originally prepared by Barbieri (*1*), but its solubility had not been determined.

Vouk, Kratohvil, and Tezak (*16*) have shown that if the solid phase is known, the complex ionic species in equilibrium with solid silver halides can be determined by analysis of the general solubility curves (*7, 13*). Such curves are constructed from solubility data obtained in an excess of either component as well as in the presence of equivalent concentrations of each. In this work their method has been extended to the determination of the solid species.

The general solubility curves of silver 12-molybdocerate(IV), mercurous 12-tungstophosphate, and mercurous 9-tungstophosphate were determined, and from these solubility data conclusions as to the composition of the solid phase as well as the species of soluble complex ions could be drawn. In addition, the effect of pH upon solubility was studied for the two mercurous tungstophosphates.

EXPERIMENTAL

Method. Solubility was determined by a procedure described previously (*13, 16*). The sparingly soluble heteropoly salt was precipitated in the nascent state by mixing solutions of the two precipitating components—*viz.*, the heteropoly acid and a metal salt. The precipitation limit was determined by mixing 5 ml. of a solution of one precipitating component (usually the heteropoly acid) of constant concentration with 5 ml. of solutions containing the other component in various (gradually decreasing) concentrations. The concentrations of the variable component were always higher than the concentration of the constant component. All concentrations were calculated for the final volume of 10 ml. and expressed as molarities. Nitric acid was added to one of the components when it was required to adjust the pH. The limiting precipitation