Some of the tie lines between each liquid phase point on the line of saturation and its respective wet solid phase point, x, have been omitted for clarity. However, boundary tie lines are given to separate isothermally invariant three phase regions from the two phase regions.

A new double compound, having an equimolecular composition of NaCN and NaOH, was found at 35 and 55° (see D in Figs. 2 and 3). As a consequence, there are two isothermally invariant points on each isotherm, e (9.0% NaCN, 59.0% NaOH) and h (17.0% NaCN, 47.0% NaOH) at 55°, and f (10.5% NaCN, 51.5% NaOH) and g (15.0% NaCN, 47.5% NaOH) at 35°. The range of existence of the compound is much wider at 55° than at 35°, and it vanishes somewhere between 35 and 25°. The double compound, NaCN·NaOH, has a retrograde effect on the solubility of $\mathrm{NaOH \cdot H_2O}$ at 55° but not at 35°. Since the compound is incongruently saturating, it will decompose with the deposition of a single salt when added to water, and can never give a saturated solution lying within areas S + D. Solubility curves fg and eh of Figs. 2 and 3 were more difficult to obtain than the others because of the high viscosity of the caustic solutions and the nature of the solid phase. The solid phase, NaCN·NaOH, deposited as fine crystals which made the separation from the mother liquor very difficult; consequently, a greater scattering of tie lines around D prevailed. The dihydrate,[3] $\mathrm{NaCN \cdot 2H_2O}$, is the stable solid below 34.7°; however, the anhydrous salt appears as a solid phase at 25° in NaOH concentrations above 10%. Thus, a caustic concentration greater than 10% prevents the formation of the dihydrate at 25°. The invariant points for the 25° isotherm are j (14.0% NaCN, 56.0% NaOH) and k (34.2% NaCN, 9.8% NaOH).

(3) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," Vol. 1, D. Van Nostrand Co., Inc., New York, N. Y., 1940, p. 1190.

TEXAS CITY, TEXAS

[CONTRIBUTION FROM THE GEOPHYSICAL LABORATORY, CARNEGIE INSTITUTION OF WASHINGTON]

The Binary Systems $\mathrm{NaPO_3–KPO_3}$ and $\mathrm{K_4P_2O_7–KPO_3}$

BY GEORGE W. MOREY

RECEIVED APRIL 16, 1954

The phase equilibrium curves in the binary systems $\mathrm{NaPO_3–KPO_3}$ and $\mathrm{K_4P_2O_7–KPO_3}$ have been determined. In the system $\mathrm{NaPO_3–KPO_3}$ a compound, $\mathrm{3NaPO_3 \cdot KPO_3}$, is formed which melts incongruently at 552° to form crystalline $\mathrm{NaPO_3}$ and a liquid containing 0.31 weight fraction $\mathrm{KPO_3}$. $\mathrm{3NaPO_3 \cdot KPO_3}$ is the stable crystalline phase from its incongruent melting point to its eutectic with $\mathrm{KPO_3}$, at 547°, 0.505 weight fraction $\mathrm{KPO_3}$. In the system $\mathrm{K_4P_2O_7–KPO_3}$ a compound, $\mathrm{K_5P_3O_{10}}$, is formed which melts incongruently at 641.5° to form crystalline $\mathrm{K_4P_2O_7}$ and a liquid containing 0.54 weight fraction $\mathrm{KPO_3}$. $\mathrm{K_5P_3O_{10}}$ is the stable crystalline phase from its incongruent melting point to its eutectic with $\mathrm{KPO_3}$, at 613°, 0.59 weight fraction $\mathrm{KPO_3}$.

The two systems described in this paper are parts of a larger system, $\mathrm{Na_4P_2O_7–NaPO_3–KPO_3–K_4P_2O_7}$, work on which has not yet been completed. The binary system $\mathrm{NaPO_3–Na_4P_2O_7}$ was described by Partridge, Hicks and Smith[1] and by Morey and Ingerson,[2] and the binary system $\mathrm{H_2O–NaPO_3}$ by Morey.[3]

These studies offered no difficulty. The components in the system $\mathrm{NaPO_3–KPO_3}$ were easily made by heating recrystallized $\mathrm{NaH_2PO_4 \cdot H_2O}$ or $\mathrm{KH_2PO_4}$ until all the water was driven off. They were usually heated to above the melting point, then crystallized by heat treatment. Intermediate compositions were made by mixing weighed portions of the two end members, melting, powdering and remelting. The mixtures were all easily crystallized and all measurements in this system could be made by the quenching method,[4] often described from this Laboratory. All mixtures are easily quenched to glass, but pure $\mathrm{KPO_3}$ requires rapid cooling. $\mathrm{K_4P_2O_7}$ and mixtures rich in it cannot be quenched to a glass, and hence the heating curve method was used for it and for the mixture containing 0.18 weight fraction $\mathrm{KPO_3}$ in the binary system $\mathrm{K_4P_2O_7–KPO_3}$; the quenching method was used for the mixtures richer in $\mathrm{KPO_3}$. Temperatures were measured by a platinum–platinum 10% rhodium thermocouple and a White potentiometer. The couples were standardized at the melting point of gold, 1092.6°; of NaCl, 800.4°[3]; of zinc, 419.4°; and were frequently checked at the incongruent melting point[2] of $\mathrm{Na_5P_3O_{10}}$, 622°.

The phase equilibrium diagram for the binary system $\mathrm{NaPO_3–KPO_3}$ shown in Fig. 1, is based on the quenching results of Table III. The optical properties of the compounds are given in Table I. Table II gives the X-ray spacings in ångström units as determined by my colleague J. L. England by the Debye–Scherrer powder method with a North American Philips high-angle Geiger counter goniometer, using copper Kα radiation and a nickel fil-

TABLE I

COMPOUNDS AND INVARIANT POINTS IN THE SYSTEM $\mathrm{NaPO_3}$-$\mathrm{KPO_3}$

$\mathrm{3NaPO_3 \cdot KPO_3 \rightleftarrows NaPO_3} + L$; $t = 552°$; $L = 0.31$ wt. fraction $\mathrm{KPO_3}$. $\mathrm{3NaPO_3 \cdot KPO_3 + KPO_3} \rightleftarrows L$; $t = 547$; $L = 0.505$ wt. fraction $\mathrm{KPO_3}$

Compound	Sign	2V	α	ω	β	ϵ	γ	M.p., °C.
$\mathrm{NaPO_3}$	−	80°	1.474		1.478		1.480	627.6
$\mathrm{3NaPO_3 \cdot KPO_3}$	−	40°	1.493		1.500		1.514	552.0
$\mathrm{KPO_3}$	+			1.465		1.483		

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(1) E. P. Partridge, V. Hicks and G. W. Smith, THIS JOURNAL, **63**, 454 (1941).

(2) G. W. Morey and E. Ingerson, *Am. J. Sci.*, **242**, 1 (1944).

(3) G. W. Morey, THIS JOURNAL, **75**, 5794 (1953).

(4) E. S. Shepherd and G. A. Rankin, *Am. J. Sci.*, **28**, 293 (1909); G. W. Morey, *J. Wash. Acad. Sci.*, **13**, 326 (1923); G. W. Morey and N. L. Bowen, *J. Phys. Chem.*, **28**, 1167 (1924).

ter. The scanning was at 1/2° per minute and the recording at 2° per inch. The relative intensities, *I*, are based on a scale of ten.

TABLE II

X-RAY SPACINGS[a]

KPO_3 d(Å.)	KPO_3 I^b	$3NaPO_3 \cdot KPO_3$ d(Å.)	$3NaPO_3 \cdot KPO_3$ I^b
6.3	10	8.9	5
5.2	2	6.8	4
5.1	3	6.2	4
4.51	3	5.4	3
3.75	2	5.13	4
3.45	5	5.04	3
3.38	3	4.42	4
3.29	3	4.06	4
3.16	6	4.87	3
3.09	2	3.43	4
2.83	2	3.29	4
2.75	2	3.10	6
2.68	4	3.00	4
2.59	2	2.97	10
2.39	1	2.86	4
2.34	1	2.79	3
2.26	4	2.69	5
2.22	2	2.63	4
2.09	1	2.57	3
2.05	1	2.43	3
2.02	1	2.18	3
1.89	1	2.09	3
1.87	1	1.86	3
		1.84	1
		1.80	1
		1.74	1
		1.69	1
		1.67	1
		1.64	1
		1.61	1
		1.51	1

[a] Debye–Scherer powder method. North American Phillips high-angle goniometer (copper Kα radiation, nickel filter). [b] Relative intensities on a scale of 10.

TABLE III

THE MELTING POINTS IN THE SYSTEM $NaPO_3$–KPO_3

Wt. fraction KPO_3	Mole fraction K_2O	Liquidus temp., °C.	Primary phase
0	0	627.6	$NaPO_3$
.10	.0438	606	$NaPO_3$
.20	.0888	582	$NaPO_3$
.2785[a]	.125	563	$NaPO_3$
.30	.1351	555	$NaPO_3$
.34	.154	551	$3NaPO_3 \cdot KPO_3$
.3666	.1667	550	$3NaPO_3 \cdot KPO_3$
.40	.1827	548.4	$3NaPO_3 \cdot KPO_3$
.45	.2071	547.9	$3NaPO_3 \cdot KPO_3$
.50	.2318	547.1	$3NaPO_3 \cdot KPO_3$
.55	.2568	583.1	KPO_3
.70	.3342	676	KPO_3
.80	.3878	721.5	KPO_3
1.0	.50	813	KPO_3

[a] The compound $3NaPO_3 \cdot KPO_3$.

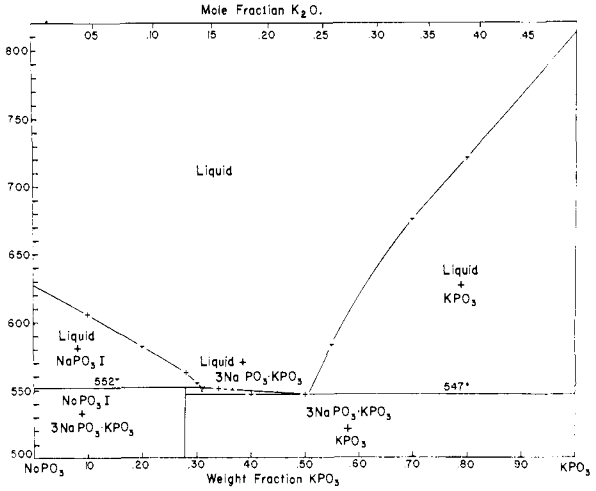

Fig. 1.—Phase equilibrium diagram of the binary system $NaPO_3$–KPO_3.

The melting point of $NaPO_3$, 627.6°, was determined by Partridge, Hicks and Smith[1] and by Morey and Ingerson.[2] All of the melting region in which $NaPO_3$ is primary phase is in the stability range of $NaPO_3$I, often called sodium trimetaphosphate, which has optical properties given in Table I. A compound is formed between the two components, of composition $3NaPO_3 \cdot KPO_3$, which melts incongruently at 552° to form crystalline $NaPO_3$I and a liquid containing 0.31 weight fraction KPO_3; the composition of the liquid in oxide mole fractions is $Na_2O:K_2O:P_2O_5$ (0.36, 0.14, 0.50), On further heating $NaPO_3$I remains the crystalline phase to the liquidus at 563°. Accordingly, the field of $NaPO_3$ extends from zero to 0.31 weight fraction KPO_3.

The field of $3NaPO_3 \cdot KPO_3$ extends from the above invariant point

$$3NaPO_3 \cdot KPO_3 \rightleftarrows KPO_3 + L$$

to the eutectic with KPO_3 at 547°. Here the reaction is

$$3NaPO_3 \cdot KPO_3 + KPO_3 \rightleftarrows L$$

and the liquid composition is 0.505 weight fraction KPO_3; the composition of the liquid in oxide mole fractions is $Na_2O:K_2O:P_2O_5$ (0.266, 0.234, 0.500). The melting point curve then rises to the melting point of KPO_3. This was found by van Klooster[5] to be 810°, by Parravano and Calcagni[6] to be 825°. The value obtained in this study, both by the quenching method and by the heating curve method, was 813°.

The phase equilibrium diagram for the system $K_4P_2O_7$–KPO_3 is shown in Fig. 2, based on the melting points shown in Table IV; the properties of the compounds are given in Table V. The melting point of $K_4P_2O_7$ was given by Parravano and Calcagni[6] as 1092°; the value found in this study, by the heating curve method, was 1104°. $K_4P_2O_7$ is the stable crystalline phase in contact with liquid from zero to 0.54 weight fraction KPO_3.

A binary compound, $K_5P_3O_{10}$, analogous to sodium tripolyphosphate, $Na_5P_3O_{10}$, is formed between the end members, $K_4P_2O_7$ and KPO_3. $K_5P_3O_{10}$ resembles $Na_5P_3O_{10}$ in melting incongruently

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(5) H. S. van Klooster, *Z. anorg. Chem.*, **69**, 122 (1911).

(6) N. Parravano and G. Calcagni, *ibid.*, **65**, 1 (1910).

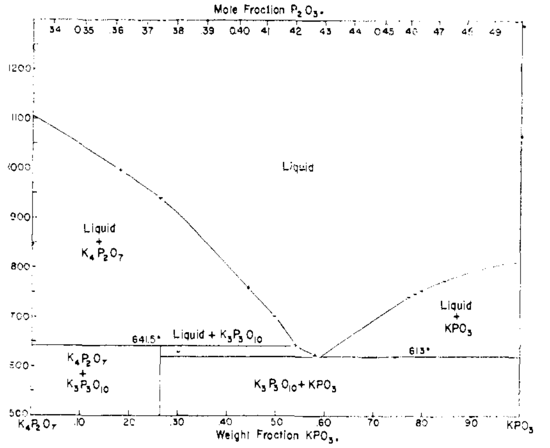

Fig. 2.—Phase equilibrium diagram of the binary system $K_4P_2O_7$–KPO_3.

with formation of pyrophosphate and liquid. The reaction

$$K_5P_3O_{10} \rightleftarrows K_4P_2O_7 + L$$

takes place at 641.5°, and the liquid contains 0.54 weight fraction KPO_3, or, expressed in mole fraction K_2O and P_2O_5, 0.58 and 0.42. $K_5P_3O_{10}$ is the stable crystalline phase in contact with liquid from this invariant point to the eutectic with KPO_3 at 613°. At this invariant point the reaction

$$K_5P_3O_{10} + KPO_3 \rightleftarrows L$$

takes place, and the liquid contains 0.59 weight fraction KPO_3, or expressed in mole fractions K_2O and P_2O_5, 0.571 and 0.429. From this eutectic the melting point curve rises to the melting point of KPO_3, 813°, with KPO_3 as the stable crystalline phase.

TABLE IV

MELTING POINTS IN THE SYSTEM $K_4P_2O_7$–KPO_3

Wt. fraction KPO_3	Mole fraction P_2O_5	Liquidus temp., °C.	Primary phase
0	0.3333	1109	$K_4P_2O_7$
.1800	.3616	995	$K_4P_2O_7$
.2634	.3759	940	$K_4P_2O_7$
.4977	.4134	702	$K_4P_2O_7$
.5400	.4204	644	$K_4P_2O_7$
.5802	.4271	625	$K_5P_3P_{10}$
		613	Eutectic
.7986	.4645	754	KPO_3
1.0	.5	813	KPO_3

TABLE V

COMPOUNDS AND INVARIANT POINTS IN THE SYSTEM $K_4P_2O_7$–KPO_3

$K_5P_3O_{10} \rightleftarrows K_4P_2O_7 + L$; $t = 641.5°$; $L = 0.54$ wt. fraction KPO_3

$K_5P_3O_{10} + KPO_3 \rightleftarrows L$; $t = 613°$; $L = 0.59$ wt. fraction KPO_3

Compound	Sign	ω	ϵ	M.p., °C.
$K_4P_2O_7$	+	1.495	1.502	1105
$K_5P_3O_{10}$	−	1.520	1.516	
KPO_3	+	1.465	1.483	813

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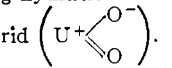
Polymerization of Uranyl–Citrate, –Malate, –Tartrate and –Lactate Complexes[1]

BY ISAAC FELDMAN, JEAN R. HAVILL AND W. F. NEUMAN

RECEIVED FEBRUARY 19, 1954

Titrimetric and spectrophotometric studies suggest the following conclusions: (1) When equimolar mixtures of uranyl nitrate and citric, tartaric, and malic acids are raised to *p*H 3.5, practically all the uranium reacts with the organic groups by tridentate chelation to form polynuclear complexes having a 1:1 molar ratio and held together by oxygen bridges or by hydroxyl bridges between uranium atoms. On the basis of previous polarographic evidence, the polymers are believed to be dimers. (2) At slightly alkaline *p*H these dimers react completely to form trinuclear complexes. There exist two trimers, having (uranium/organic group) ratios of *3:3* and *3:2*. The stability of the *3:3* trimer relative to the *3:2* trimer decreases in the order —UMal > UTar > UCit—probably due to electrostatic effects. It is believed that steric hindrance to linearity of the (O═U═O) group is produced by the tridentate chelation with either (a) an accompanying hydration of one of the originally double-bonded oxygens of the uranyl group or (b) formation of the bent resonance hybrid  $\left(U^{+}\!\langle{}^{O^-}_{O}\right)$. Possible structures for the polymers are presented and discussed. Titration results also suggest dimerization and trimerization of the uranyl–lactate complex in an equimolar mixture.

The titrimetric and spectrophotometric studies reported here were carried out as part of a program of investigation of the reactions of uranyl ions with organic acids.[2] These studies have furnished information regarding the polymerization of complex ions formed by the reaction of uranyl ions with citrate, malate, tartrate and lactate ions.

Experimental

Materials.—The malonic, tricarballylic and l-malic acids were all Eastman White Label grade. Mallinckrodt U.S.P. sodium barbital was used. All other chemicals were C.P. grade. C.P. β-hydroxybutyric acid was obtained from Matheson Co. Distilled water was used for each solution. To avoid photochemical effects all solutions were prepared in semi-darkness and stored in the dark.

Methods.—Potentiometric titrations were carried out in a semi-dark room at room temperature with the aid of a Beckman Model G *p*H meter using external electrodes. Spectrophotometric measurements were made with a Beckman DU

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[1] This paper is based on work performed under contract with the United States Atomic Energy Commission at the University of Rochester, Atomic Energy Project, Rochester, New York. Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society at Kansas City, Missouri, April, 1954.

[2] Previous papers in this series are: (a) I. Feldman and W. F. Neuman, THIS JOURNAL, **73**, 2312 (1951); (b) W. F. Neuman, J. R. Havill and I. Feldman, *ibid.*, **73**, 3593 (1951); (c) I. Feldman and J. R. Havill, *ibid.*, **76**, 2114 (1954).