THE ALKALI ORTHOPHOSPHATES

PHASE EQUILIBRIA IN AQUEOUS SOLUTION

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I. INTRODUCTION

There are only a few solid phase–liquid phase systems that present so interesting a problem as the alkali metal orthophosphates. An unusually large number of phase changes, double salts, and singular points are presented over a wide range of concentration of the acid and bases. Much misinformation exists in both the chemical literature and patents. The systems of ammonia, potassium, and lithium have not been studied extensively, and discrepancies in existing data give sufficient reason for further work in this field. The object of the present paper is to review the available data on systems containing one alkali metal oxide, phosphorus pentoxide, and water. In general, a comparison will be made with the sodium oxide–phosphorus pentoxide–water system, which has been investigated thoroughly (18). Other systems have been investigated at only several temperatures and within limited concentration ranges.

The alkali metal orthophosphates are all-important industrial chemicals produced in tonnage quantities in continuous processes. Their uses center mainly in fertilizers, detergents, water conditioning, and food preparations, but they have scores of minor applications.

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II. THE SODIUM SYSTEM

A complete investigation of the system sodium oxide–phosphorus pentoxide–water was undertaken by Wendrow and Kobe (18) because of the lack of complete data on this system and the confusion existing regarding the solubility of trisodium phosphate and the composition of its crystalline forms. The phase diagram resulting from this work shows clearly the hydrates of trisodium phosphate, and demonstrates that this salt forms a complex with sodium hydroxide. It is this latter feature which has contributed to the errors in determining the solubility of trisodium phosphate.

The complete phase diagram of the system sodium oxide–phosphorus pentoxide–water from 25°C. to 100°C. is given in figure 1. The data for the system are given in table 1. The equilibrium diagram for this system consists of three main divisions or regions. The tertiary region is the one in which the solid phase consists of salts of the tertiary phosphate ion, PO_4^{---}; the secondary region has a solid phase consisting of the salts of the secondary phosphate ion, HPO_4^{--}; similarly, the primary region is associated with salts of the primary phosphate ion, $H_2PO_4^-$. There are also some regions containing double salts.

Van Wazer (17) has represented the 25°C. isotherm in a somewhat different manner (figure 2). Tie lines connect a portion of the solubility curve with the point representing the composition of the solid phase with which the solution is in equilibrium. In addition he has completed the diagram by including the phosphoric acid regions, H_3PO_4 and $H_3PO_4 \cdot \frac{1}{2}H_2O$. In the phase diagram the single-phase region (the vapor phase is disregarded) is the area beneath the solubility curve where a homogeneous solution exists, and the twelve points correspond to the twelve solid phases that can separate from the solution. There are formed twelve two-phase regions, which exist in the area between the solubility curve and the boundary tie lines to the equilibrium solid phase. The ten three-phase areas are numbered; they lie between tie lines to adjacent solid phases.

The system was first studied by D'Ans and Schreiner (4) at 25°C. over a fairly wide concentration range. In the tertiary region they list the solid phase as trisodium phosphate dodecahydrate. This report leads directly to the question of the composition of the true hydrates of trisodium phosphate.

Both commercial and reagent grades of trisodium phosphate dodecahydrate contain some free alkali, which is apparently held in the crystal lattice. Kobe and Leipper (7) found that a number of samples of reagent grade salt corresponded to the formula $Na_3PO_4 \cdot \frac{1}{7}NaOH \cdot 12H_2O$; other investigators have reported that the fraction of sodium hydroxide per mole of trisodium phosphate varies from $\frac{1}{11}$ to $\frac{2}{9}$ (13). Upon recrystallization of the reagent grade salt from hot water, Kobe and Leipper obtained a product with the formula $Na_3PO_4 \cdot \frac{1}{5}NaOH \cdot 12H_2O$. The use of three equivalents of sodium hydroxide with one of phosphoric acid gave the same product.

Bell (1) studied the hydrates of true trisodium phosphate and prepared several of the complex hydrates. He states that there are three hydrates of true trisodium phosphate—a hemihydrate, a hexahydrate, and an octahydrate. The hemihydrate was prepared by crystallizing it from a solution having the theo-

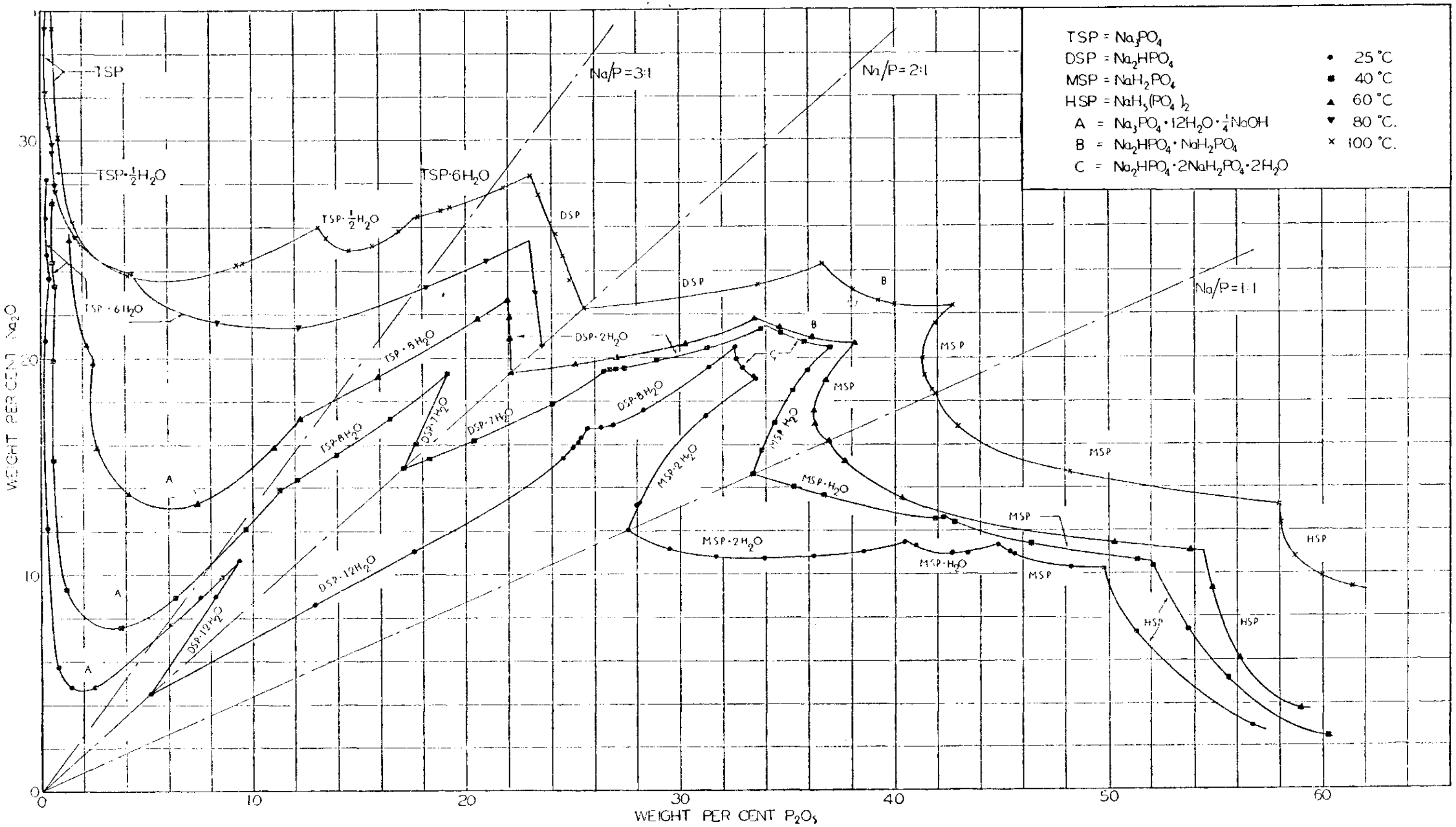

FIG. 1. The system Na_2O–P_2O_5–H_2O from 25°C. to 100°C.

TABLE 1

System Na_2O–P_2O_5–H_2O

Liquid Phase				Mole Ratio Na/P	Solid Phase*
Weight per cent		Mole per cent			
Na_2O	P_2O_5	Na_2O	P_2O_5		
Temperature = 0°C.					
per cent	*per cent*	*per cent*	*per cent*		
2.23	1.75	0.67	0.23	2.91	A
2.10	0.61	0.62	0.08	7.90	A
3.03	2.25	0.92	0.30	3.07	A
0.754	0.855	0.22	0.11	2.00	DSP·12H_2O
0.746	0.840	0.22	0.11	2.00	
9.28	21.26	3.58	3.58	1.00	
9.36	21.43	3.66	3.66	1.00	MSP·2H_2O
Temperature = 25°C.					
30.35	0.16	11.23	0.025	445	TSP·½H_2O
28.61	0.28	10.44	0.045	231	
28.30	0.31	10.21	0.050	208	TSP·½H_2O + TSP·6H_2O
26.48	0.28	9.49	0.042	225	TSP·6H_2O
24.77	0.30	8.75	0.046	190	
23.73	0.29	8.32	0.043	191	TSP·6H_2O + A
20.82	0.22	7.10	0.033	217	A
12.13	0.31	3.86	0.043	90.2	
5.75	0.75	1.75	0.099	17.6	
4.65	1.40	1.41	0.186	7.61	
4.61	2.50	1.41	0.335	4.22	
4.79	2.70	1.48	0.363	4.06	
7.76	6.12	2.53	0.87	2.91	
8.99	7.50	3.00	1.09	2.75	
9.91	8.53	3.36	1.26	2.66	
10.66	9.39	3.67	1.41	2.60	A + DSP·12H_2O
9.04	8.20	3.03	1.20	2.52	DSP·12H_2O
8.93	8.01	2.99	1.17	2.55	
4.52	5.23	1.42	0.72	1.99	
8.61	12.95	3.02	1.95	1.52	
11.02	17.59	4.17	2.90	1.43	
15.30	24.58	6.56	4.60	1.42	
15.82	25.05	6.88	4.75	1.45	
16.07	25.32	7.02	4.83	1.45	
16.24	25.37	7.12	4.85	1.46	
16.71	25.69	7.38	4.95	1.49	DSP·12H_2O + DSP·8H_2O
16.71	26.33	7.45	5.12	1.45	DSP·8H_2O
16.76	26.91	7.54	5.27	1.43	
17.58	28.26	8.12	5.70	1.42	
17.87	28.48	8.31	5.79	1.43	
19.48	31.39	9.61	6.75	1.42	
20.44	32.62	10.40	7.24	1.44	DSP·8H_2O + C
19.88	32.60	10.04	7.20	1.40	C
19.48	32.93	9.85	7.26	1.36	
19.08	33.49	9.70	7.44	1.30	
18.93	33.53	9.60	7.43	1.29	C + MSP·2H_2O
17.28	31.20	8.30	6.54	1.27	MSP·2H_2O
13.24	28.06	5.82	5.38	1.08	
13.22	27.84	5.79	5.33	1.08	
12.01	27.50	5.16	5.16	1.00	
11.15	29.50	4.88	5.63	0.87	
10.83	31.65	4.87	6.21	0.78	
10.71	33.94	4.82	6.66	0.72	
10.82	36.23	5.17	7.57	0.60	

TABLE 1—*Continued*

Liquid Phase				Mole Ratio Na/P	Solid Phase*
Weight per cent		Mole per cent			
Na_2O	P_2O_5	Na_2O	P_2O_5		
per cent	*per cent*	*per cent*	*per cent*		
10.98	38.60	5.45	8.37	0.65	
11.41	40.51	5.87	9.08	0.65	
11.33	40.95	5.85	9.26	0.63	MSP·H_2O
10.93	42.70	5.77	9.89	0.59	
10.88	43.37	5.80	10.13	0.57	
11.31	44.85	6.21	10.74	0.58	MSP·H_2O + MSP
11.16	45.39	6.18	11.00	0.56	MSP
11.08	45.65	6.23	11.18	0.56	
10.30	48.26	5.92	12.10	0.49	
10.19	49.80	6.00	12.82	0.47	MSP + HSP
7.25	51.33	4.20	12.99	0.32	HSP
2.88	56.77	1.73	14.88	0.12	
Temperature = 40°C.					
34.71	0.12	13.38	0.02	663	
29.19	0.31	10.75	0.052	217	TSP·½H_2O
28.79	0.38	10.52	0.061	173	
28.37	0.42	10.36	0.067	154	
27.78	0.48	10.11	0.076	133	TSP·6H_2O
27.54	0.47	10.00	0.074	134	
26.98	0.47	9.73	0.074	131	
25.43	0.53	9.06	0.082	110	
24.42	0.56	8.61	0.086	100	
23.80	0.61	8.36	0.093	90	
23.36	0.66	8.20	0.101	81	TSP·6H_2O + A
19.85	0.55	6.75	0.082	83	A
15.64	0.55	5.13	0.079	65	
15.32	0.59	5.02	0.084	60	
9.30	1.17	2.93	0.16	18.2	
8.59	1.54	2.70	0.21	12.8	
7.63	3.18	2.41	0.44	5.49	
7.54	3.73	2.40	0.52	4.63	
8.97	6.30	2.96	0.91	3.26	
12.21	9.60	4.28	1.47	2.91	
12.38	9.81	4.26	1.48	2.89	
13.88	11.31	5.02	1.79	2.81	A + TSP·8H_2O
14.16	11.76	5.16	1.87	2.76	TSP·8H_2O
14.33	12.13	5.26	1.94	2.71	
15.00	12.73	5.57	2.06	2.70	
15.59	13.94	5.90	2.30	2.56	
17.15	16.52	6.78	2.84	2.38	
17.72	17.31	7.10	3.03	2.34	
19.27	19.18	8.05	3.50	2.30	TSP·8H_2O + DSP·7H_2O
18.78	18.92	7.78	3.42	2.27	DSP·7H_2O
16.05	17.52	6.36	3.03	2.10	
15.10	17.33	5.92	2.96	2.00	
14.71	17.09	5.73	2.91	1.97	
15.34	18.32	6.10	3.18	1.92	
16.14	20.24	6.63	3.65	1.82	
17.87	24.05	7.83	4.60	1.70	
18.36	25.58	8.25	5.02	1.64	
19.18	26.43	8.80	5.30	1.66	DSP·7H_2O + DSP·2H_2O
19.39	26.72	8.96	5.39	1.66	DSP·2H_2O
19.33	26.99	8.96	5.46	1.64	
19.54	27.41	9.13	5.59	1.63	
19.55	27.82	9.19	5.71	1.61	

TABLE 1—*Continued*

Liquid Phase				Mole Ratio Na/P	Solid Phase*
Weight per cent		Mole per cent			
Na_2O	P_2O_5	Na_2O	P_2O_5		
per cent	*per cent*	*per cent*	*per cent*		
19.90	29.94	9.68	6.36	1.52	
20.44	31.23	10.20	6.80	1.50	
20.63	32.00	10.44	7.07	1.48	
20.74	32.34	10.56	7.19	1.47	
20.82	32.53	10.65	7.27	1.47	
21.34	33.79	11.20	7.75	1.45	
21.12	34.73	11.22	8.06	1.39	C
20.68	35.79	11.12	8.40	1.32	
20.32	36.26	10.98	8.53	1.28	
20.44	37.01	11.16	8.83	1.27	C + MSP·H_2O
19.46	35.90	10.31	8.31	1.24	MSP·H_2O
18.95	35.71	9.94	8.18	1.22	
18.76	35.52	9.79	8.10	1.21	
17.56	34.60	8.90	7.66	1.16	
17.09	34.50	8.60	7.58	1.13	
16.92	34.39	8.48	7.53	1.14	
15.77	33.78	7.73	7.23	1.07	
14.66	33.62	7.07	7.08	1.00	
13.96	35.31	6.84	7.56	0.91	
13.61	36.71	6.78	7.99	0.85	
13.07	38.05	6.61	8.40	0.77	
12.37	41.70	6.56	9.66	0.68	
12.53	42.27	6.72	9.90	0.68	
12.25	42.73	6.59	10.04	0.66	MSP
11.77	45.10	6.54	10.95	0.60	
11.44	46.38	6.60	11.68	0.56	
10.92	48.72	6.38	12.44	0.51	
10.66	51.35	6.51	13.69	0.48	
10.33	52.07	6.36	14.00	0.45	HSP
7.39	53.66	4.48	14.22	0.32	
5.10	55.39	3.09	14.64	0.21	
2.68	60.24	1.71	16.80	0.10	
Temperature = 60°C.					
34.39	0.094	13.22	0.016	840	TSP
30.14	0.136	11.16	0.022	506	
28.72	0.31	10.52	0.050	210	
28.29	0.52	10.34	0.082	127	TSP + TSP·½H_2O
26.25	0.90	9.46	0.14	67	TSP·½H_2O
25.68	1.19	9.24	0.19	49	
25.01	1.37	8.97	0.21	42	
23.76	1.54	8.44	0.24	35	
20.60	2.16	7.17	0.33	22	
19.72	2.47	6.84	0.37	18	A
18.71	2.55	6.43	0.38	16.8	
15.79	2.59	5.30	0.38	14	
14.71	3.05	4.92	0.45	11	
13.71	4.18	4.62	0.61	7.53	
13.28	7.41	4.58	1.11	4.11	
15.91	11.02	5.84	1.76	3.31	
17.15	12.24	6.46	2.01	3.21	A + TSP·8H_2O
17.29	12.71	6.65	2.13	3.12	TSP·8H_2O
17.79	13.01	6.80	2.17	3.14	
19.20	15.94	7.70	2.79	2.76	
21.73	20.63	9.10	3.95	2.30	
22.13	21.04	9.75	4.05	2.41	

TABLE 1—*Continued*

Liquid Phase				Mole Ratio Na/P	Solid Phase*
Weight per cent		Mole per cent			
Na_2O	P_2O_5	Na_2O	P_2O_5		
per cent	*per cent*	*per cent*	*per cent*		
22.48	21.65	10.05	4.21	2.38	
22.62	22.06	10.18	4.33	2.35	TSP·$8H_2O$ + DSP·$2H_2O$
22.12	21.85	9.90	4.25	2.33	DSP·$2H_2O$
20.86	21.82	9.56	4.16	2.30	
20.68	21.99	9.48	4.19	2.26	
19.26	22.11	8.34	4.17	2.00	
19.69	25.13	8.93	4.97	1.79	
19.95	27.09	9.31	5.52	1.69	
20.58	30.32	10.14	6.52	1.63	
21.38	32.29	10.96	7.23	1.52	
21.55	32.90	11.18	7.45	1.50	
21.81	33.43	11.44	7.66	1.49	DSP·$2H_2O$ + B
21.79	33.53	11.45	7.70	1.49	B
21.79	33.60	11.45	7.71	1.48	
21.66	33.69	11.39	7.74	1.47	
21.37	34.52	11.35	8.01	1.48	
21.30	34.67	11.31	8.05	1.47	
20.93	36.17	11.33	8.55	1.32	
21.02	36.78	11.53	8.81	1.31	
20.79	37.52	11.49	9.06	1.27	
20.74	38.20	11.61	9.32	1.24	B + MSP
18.92	36.76	10.07	8.55	1.18	MSP
17.50	36.21	9.09	8.20	1.11	
17.16	36.16	8.86	8.15	1.09	
16.83	36.13	8.65	8.09	1.07	
16.11	36.89	8.04	8.04	1.00	
15.08	37.72	7.77	8.49	0.92	
13.54	40.29	7.12	9.27	0.77	
12.41	43.02	6.72	10.18	0.66	
11.43	49.48	6.82	12.90	0.53	
11.39	50.32	6.89	13.29	0.52	
11.19	51.52	6.90	13.87	0.50	
10.89	54.09	7.02	15.23	0.46	
8.91	54.53	5.62	15.02	0.37	HSP
7.59	55.46	4.77	15.23	0.31	
6.01	56.11	3.73	15.22	0.25	
3.63	59.01	2.83	16.30	0.14	
Temperature = 80°C.					
36.39	0.140	14.30	0.024	597	TSP
32.11	0.210	12.10	0.034	352	
30.64	0.314	11.42	0.051	224	
30.28	0.373	11.26	0.061	186	
29.85	0.514	11.06	0.083	133	TSP·½H_2O
28.03	0.605	10.24	0.096	106	
27.72	0.617	10.07	0.098	103	
25.60	1.65	9.25	0.26	35.6	
25.24	1.79	9.12	0.28	32.3	
24.83	2.60	9.11	0.41	22.1	
23.87	4.29	8.75	0.69	12.8	TSP·½H_2O + TSP·$6H_2O$
21.61	8.35	8.11	1.37	5.93	TSP·$6H_2O$
21.35	12.15	8.35	2.08	4.03	
23.20	18.20	9.98	3.41	2.92	
24.51	20.96	11.07	4.13	2.68	
22.94	23.29	10.50	4.66	2.26	DSP·$2H_2O$
20.59	23.56	9.25	4.61	2.00	

TABLE 1—*Concluded*

Liquid Phase				Mole Ratio Na/P	Solid Phase*
Weight per cent		Mole per cent			
Na_2O	P_2O_5	Na_2O	P_2O_5		
Temperature = 100°C.					
per cent	*per cent*	*per cent*	*per cent*		
38.36	0.41	15.36	0.072	212	TSP
30.05	0.80	11.17	0.13	86	
26.19	1.33	9.48	0.21	45	
23.79	4.17	8.70	0.67	13	
24.37	9.26	9.46	1.57	6.03	
24.26	9.53	9.45	1.62	5.82	
25.98	13.18	10.76	2.38	4.51	
25.43	13.41	10.50	2.42	4.34	$TSP\cdot\frac{1}{2}H_2O$
24.97	14.60	10.42	2.66	3.92	
25.18	15.62	10.66	2.89	3.69	
25.76	16.93	11.18	3.20	3.49	
26.51	17.79	11.74	3.43	3.41	
26.75	18.87	12.03	3.70	3.24	$TSP\cdot 6H_2O$
26.90	19.29	11.86	3.71	3.19	
27.89	21.77	13.22	4.51	2.94	
28.31	23.01	13.69	4.86	2.81	
27.48	23.46	13.30	4.95	2.68	DSP
25.73	24.29	12.35	5.08	2.43	
24.69	24.59	11.73	5.10	2.30	
23.53	24.84	11.08	5.12	2.16	
22.13	25.56	10.35	5.22	2.00	
23.39	33.64	12.56	7.90	1.59	
24.34	36.61	13.93	9.15	1.52	DSP + B
23.07	38.09	13.31	9.57	1.39	B
22.54	39.21	13.14	10.00	1.31	
22.33	40.00	13.18	10.32	1.28	
22.40	42.73	13.31	11.64	1.14	B + MSP
21.48	41.91	13.00	11.04	1.17	MSP
19.87	41.25	11.55	10.50	1.10	
19.16	41.40	11.07	10.46	1.06	
18.36	41.72	10.51	10.46	1.01	
18.31	41.92	10.53	10.53	1.00	
16.71	42.90	9.57	10.74	0.89	
14.63	48.22	8.93	12.88	0.69	
13.14	58.04	9.95	18.33	0.54	
12.32	57.95	8.80	18.05	0.49	HSP
10.70	58.68	7.55	18.03	0.42	
9.86	60.08	7.06	18.74	0.38	
9.37	61.42	6.86	19.63	0.35	

* TSP = trisodium phosphate
DSP = disodium phosphate
MSP = monosodium phosphate
HSP = hemisodium phosphate
A = $4(Na_3PO_4\cdot 12H_2O)\cdot NaOH$
B = $Na_2HPO_4\cdot NaH_2PO_4$
C = $Na_2HPO_4\cdot 2NaH_2PO_4\cdot 2H_2O$
$TSP\cdot 6H_2O$ represents the hexahydrate of trisodium phosphate, and so on.
Na/P represents the ratio of moles of sodium oxide to moles of phosphorus pentoxide.

retical ratio of sodium oxide to phosphorus pentoxide, at the boiling temperature, and was found to be homogeneous under the microscope. The hexahydrate was prepared by crystallizing it above 86°C.; the composition of the liquor was not given. To prepare the octahydrate, a hot liquor of the proper composition

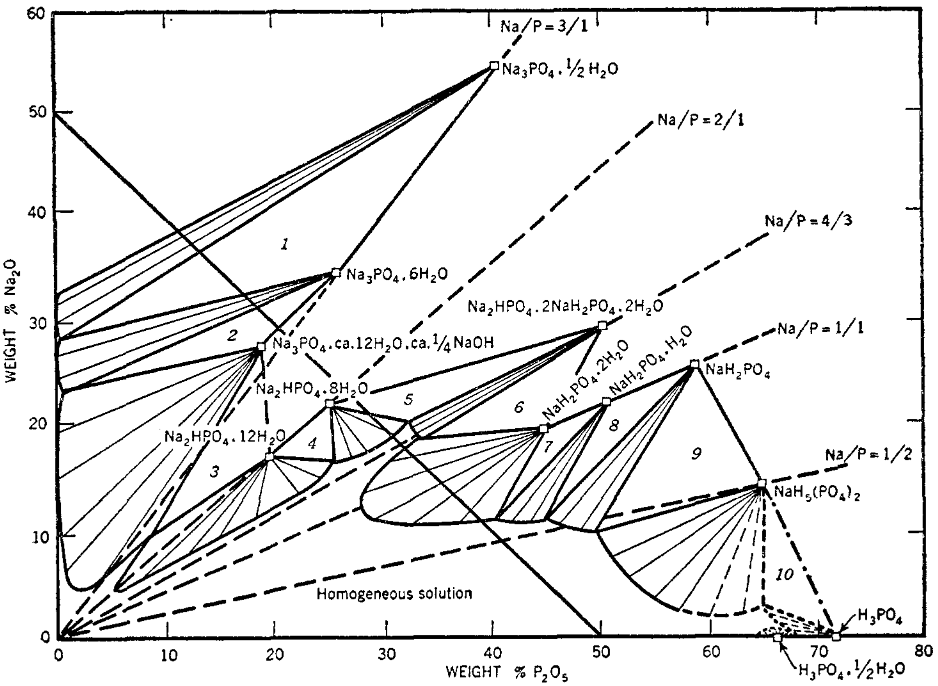

FIG. 2. The system Na_2O-P_2O_5-H_2O at 25°C. showing tie lines. Reprinted from the *Encyclopedia of Chemical Technology*, R. E. Kirk and D. F. Othmer, editors, Vol. X, p. 408, Interscience Publishers, Inc., New York and London (1953).

was agitated until complete crystallization had taken place. The crystals resemble those of the trisodium phosphate dodecahydrate–sodium hydroxide complex, but in polarized light they exhibit extinction angles up to 22°, while those of the complex exhibit only parallel extinction.

Bell states that any hydrate of trisodium phosphate higher than the octahydrate is actually a complex containing a monobasic anion. These higher hydrate complexes are divided into two groups; one is given by the formula $n\text{Na}_3\text{PO}_4\cdot\text{NaY}\cdot x\text{H}_2\text{O}$, where n is 1 or 2, Y is a monobasic anion, and x is 18 or 19; the second type is given by the formula $n(\text{Na}_3\text{PO}_4\cdot x\text{H}_2\text{O})\text{NaY}$, where n is 4–7, x is 11 or 12, and Y is a monobasic anion. The ordinary trisodium phosphate dodecahydrate of commerce is a complex belonging to the second type, and it is this one that Bell studied in detail. He varied the Na_2O/P_2O_5 mole ratio of the crystallizing solution from 2.82 to 3.75, and obtained complexes having Na_2O/P_2O_5 mole ratios of either 3.21 or 3.12. This shows that there are two hydroxide complexes having definite formulas, rather than a series of solid solutions in which the Na_2O/P_2O_5 mole ratio varies. It was also shown that the sodium hydroxide in the complex could be replaced with other sodium salts with univalent anions, such as sodium nitrate, sodium nitrite, sodium chloride, sodium hypochlorite, and sodium permanganate. The composition of these compounds is variable, ranging from $\frac{1}{4}$ to $\frac{1}{7}$ mole of salt per mole of trisodium phosphate. These compounds contain eleven molecules of water of crystallization. The compounds in this series are isomorphous.

D'Ans and Schreiner made no mention of the fact that the dodecahydrate of trisodium phosphate is actually a complex salt. In addition, their work did not carry the isotherm far enough into the highly alkaline region; thus the trisodium phosphate hexahydrate and trisodium phosphate hemihydrate were not isolated. In the secondary region they found the dodecahydrate and the heptahydrate as the solid phases. In the primary region the solid phase is given as the dihydrate. This dihydrate branch was carried to 45.4 per cent phosphorus pentoxide, where the isotherm was terminated. The region in which hemisodium phosphate, $NaH_5(PO_4)_2$, crystallizes was not investigated.

Kobe and Leipper (7) studied the system at 25°C. over a short range in the tertiary region, the phosphorus pentoxide concentration varying from 1.79 to 7.12 per cent. The solid phase was recognized to be the trisodium phosphate dodecahydrate complex. Their isotherm was quite different from that of D'Ans and Schreiner, thus indicating the need for a complete investigation.

A complete investigation of the tertiary region of the system sodium oxide–phosphorus pentoxide–water at 20°C. was made by Menzel and von Sahr (8). They found that as the Na_2O/P_2O_5 mole ratio of the solution was varied from 2.69 to 3.68, the Na_2O/P_2O_5 mole ratio of the equilibrium trisodium phosphate complex quickly increased from 3.11 to 3.22. Thereafter, as the Na_2O/P_2O_5 mole ratio of the solution was increased to 144.9, the same ratio in the complex increased slowly from 3.22 to 3.24. They concluded that the solid phase along this branch of the isotherm is a series of solid solutions, in which the mole ratio of Na_2O/P_2O_5 continually changes from a value of 3.11 to 3.24. The former value conforms to a formula having the composition $Na_3PO_4 \cdot \frac{1}{9}NaOH \cdot 12H_2O$, and the latter to the formula $Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$. X-ray patterns of four different members of the series did not reveal any differences among them. Menzel and von Sahr extended their isotherm in the highly alkaline region up to a concentration of 32.58 per cent sodium oxide. At 25.85 per cent, a transition from the trisodium phosphate complex to the hexahydrate of trisodium phosphate is found. The application of the wet-residue method was abandoned at concentrations of sodium oxide greater than 18 per cent, and the solid phases were identified by examination under the microscope and by x-ray patterns. At 31.07 per cent sodium oxide, the hemihydrate of trisodium phosphate first appeared. The solid phase was identified in the same manner as was the hexahydrate.

The most complete work performed to date on the system sodium oxide–phosphorus pentoxide–water is that of Wendrow and Kobe (18). Their work covers the temperature range from 25°C. to 100°C., a phosphorus pentoxide concentration range of from 0 to 62 weight per cent, and a sodium oxide concentration range of from 0 to 38.5 weight per cent. The results for this system are discussed in some detail so that the other alkali metal oxide systems can be compared directly with it.

A. The 25°C. isotherm

The solid phases found along the 25°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$Na_3PO_4 \cdot \frac{1}{2}H_2O$	0.16	0.31
$Na_3PO_4 \cdot 6H_2O$	0.31	0.29
$Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$	0.29	9.39
$Na_2HPO_4 \cdot 12H_2O$	9.39 (5.23)*	25.69
$Na_2HPO_4 \cdot 8H_2O$	25.69	32.62
$Na_2HPO_4 \cdot 2NaH_2PO_4 \cdot 2H_2O$	32.62	33.53
$NaH_2PO_4 \cdot 2H_2O$	33.53 (27.50)*	40.65
$NaH_2PO_4 \cdot H_2O$	40.65	44.85
NaH_2PO_4	44.85	49.80
$NaH_2PO_4 \cdot H_3PO_4$ [or $NaH_5(PO_4)_2$]	49.80	56.77

* Singular point.

The 25°C. isotherm was carried into the tertiary region to a point at which the concentration of sodium oxide in the solution was 30.3 weight per cent. At this concentration the equilibrium solid phase is $Na_3PO_4 \cdot \frac{1}{2}H_2O$. From figure 3 it is seen that this hydrate exists at this temperature only in equilibrium with highly alkaline solutions. The next phase encountered at 25°C. is the hexahydrate of trisodium phosphate.

The alkaline complex, $Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$, hereinafter called A, is found next in the tertiary region as the concentration of phosphoric acid is increased.

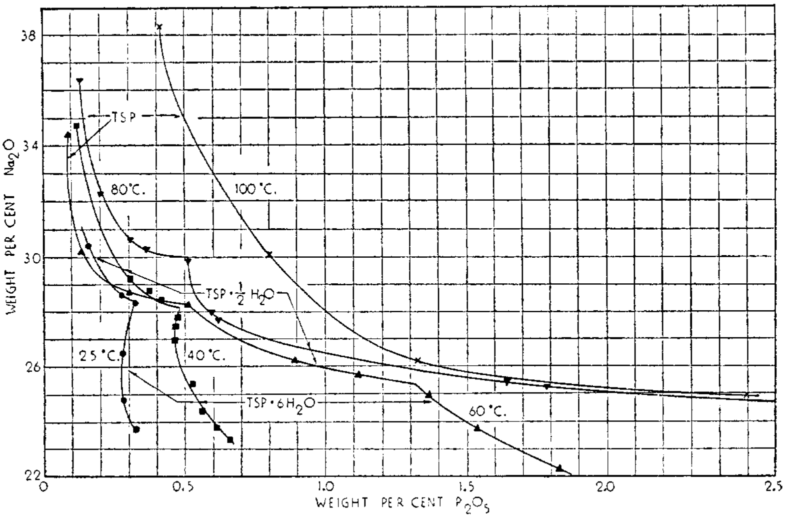

FIG. 3. The system Na_2O-P_2O_5-H_2O from 25°C. to 100°C. in the region of high alkalinity

At this temperature, two of the solid phases were found to have a Na_2O/P_2O_5 mole ratio of 3.14, representing $\frac{1}{7}$ mole of excess sodium hydroxide. The remainder of the solid phases had a mole ratio of 3.25, representing $\frac{1}{4}$ mole of excess sodium hydroxide. If the solid phase were pure trisodium phosphate, the Na_2O/P_2O_5 mole ratio would be exactly 3.00. It is concluded that there are two slightly different alkaline complexes of trisodium phosphate dodecahydrate, represented by the formulas $Na_3PO_4 \cdot \frac{1}{7}NaOH \cdot 12H_2O$ and $Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$. This is in accordance with the work of Bell mentioned earlier. The crystals of the alkaline complex A are long fine needles. They are the same in appearance as the octahydrate of trisodium phosphate but exhibit parallel extinction in polarized light. All of the solid phases along this branch of the isotherm were examined in polarized light and found to be the alkaline complex.

At the invariant point for the alkaline complex A and $Na_2HPO_4 \cdot 12H_2O$ the solubility of the latter decreases rapidly until the Na_2O/P_2O_5 mole ratio is 2.00, the point corresponding to the solubility of disodium hydrogen phosphate in water at 25°C. This point is also the minimum solubility in the secondary region; it is noted that in the tertiary region the minimum solubility lies to the left, or alkaline, side of the line denoting Na_2O/P_2O_5 mole ratios of 3.00.

Usually, a discontinuity or abrupt change in slope in an isotherm indicates a change in the composition of the solid phase. Although all of the alkali metal oxide–phosphorus pentoxide–water systems exhibit sharp changes in slope at solubility minima which are coincident with integral mole ratio "locus lines," in no instance is there a change in solid phase at this point. These solubility minima will be discussed later and will be referred to as "singular points."

The next branch of the isotherm represents the solubility of disodium phosphate octahydrate. From the data of the binary system disodium phosphate–water at 40°C. it might be expected that the solid phase would be the heptahydrate. To prove the existence of the octahydrate, solutions were made up from both the dihydrate and the heptahydrate. At equilibrium, analysis of the solid phases showed that the octahydrate is the stable phase in this region.

Upon increasing the concentration of phosphoric acid in the liquid phase, a double salt having the composition $Na_2HPO_4 \cdot 2NaH_2PO_4 \cdot 2H_2O$ appears as the solid phase. Examination of the double salt under the microscope revealed it to have a definite crystal form, establishing it as a chemical entity. No evidence of more than one crystal type was found.

In the primary region of the isotherm, the solid phases are first the dihydrate of monosodium phosphate, then the monohydrate, and finally the anhydrous salt. This region also has a singular point of minimum solubility at a Na_2O/P_2O_5 mole ratio of 1.00.

At very high concentrations of phosphoric acid, hemisodium phosphate, $NaH_5(PO_4)_2$, crystallizes as the solid phase. This salt sometimes appears as needles, sometimes as octahedra, depending upon the amount of free phosphoric acid in the solution. Hemisodium phosphate was first prepared in 1894 by Staudenmeier (16). Its solubility was determined by Parravano and Mieli (10).

B. The 40°C. isotherm

The solid phases found along the 40°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$Na_3PO_4 \cdot \frac{1}{2}H_2O$	0.12	0.48
$Na_2PO_4 \cdot 6H_2O$	0.48	0.66
$Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$	0.66	11.31
$Na_3PO_4 \cdot 8H_2O$	11.31	19.18
$Na_2HPO_4 \cdot 7H_2O$	19.18 (17.33)	26.43
$Na_2HPO_4 \cdot 2H_2O$	26.43	34.01
$Na_2HPO_4 \cdot 2NaH_2PO_4 \cdot 2H_2O$	34.01	37.01
$NaH_2PO_4 \cdot H_2O$	37.01 (33.62)	42.43
NaH_2PO_4	42.43	52.00
$NaH_5(PO_4)_2$	52.00	60.24

The 40°C. isotherm is quite similar to the one at 25°C. in the tertiary region, with several exceptions. The hemihydrate and hexahydrate of trisodium phosphate appear in that order, much as at 25°C. However, it will be remembered that at 25°C. the complex salt A had two forms, one with $\frac{1}{7}$ mole excess sodium hydroxide and the other with $\frac{1}{4}$ mole excess sodium hydroxide. At 40°C. only the form containing $\frac{1}{4}$ mole excess sodium hydroxide was found. A new phase, not found at 25°C., exists at the termination of the branch for alkaline complex A. This new phase is trisodium phosphate octahydrate, differentiated from the complex salt A by means of its extinction angle in polarized light.

The first solubility branch in the secondary region is disodium phosphate heptahydrate. Here again there is a singular minimum point having a Na_2O/P_2O_5 mole ratio of 2.00. With additional acid in the liquid phase, a transition to the dihydrate appears. The next branch of the isotherm has as the solid phase the same double salt (C) that appeared at 25°C.

Two forms of monosodium phosphate appear at 40°C., the monohydrate and the anhydrous salt. Although Imadsu (5) in 1911 reported that the dihydrate of monosodium phosphate exists up to 40.8°C., Wendrow and Kobe presented conclusive evidence that this is not the case. The latter investigators showed that crystals of the monohydrate found at 40°C. differed entirely from the crystals of the dihydrate found at 25°C.

The solubility branch of hemisodium phosphate at 40°C. is similar in shape to that found at 25°C. The crystals at 40°C. are large, well-formed octahedra.

C. The 60°C. isotherm

The solid phases found along the 60°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
Na_3PO_4	0.094	0.52
$Na_3PO_4 \cdot \frac{1}{2}H_2O$	0.52	1.32
$Na_3PO_4 \cdot 6H_2O$	1.32	2.50
$Na_3PO_4 \cdot \frac{1}{4}NaOH \cdot 12H_2O$	2.50	12.24
$Na_3PO_4 \cdot 8H_2O$	12.24	22.06
$Na_2HPO_4 \cdot 2H_2O$	22.06 (22.11)	33.43
$Na_2HPO_4 \cdot NaH_2PO_4$	33.43	38.20
NaH_2PO_4	38.20 (36.89)	54.50
$NaH_5(PO_4)_2$	54.50	59.01

At 60°C. the tertiary region of the isotherm is similar to that at 40°C., except that at highly alkaline concentrations a phase not found in either of the two previously discussed isotherms appears. This phase is anhydrous trisodium phosphate. Figure 2 shows that the solubility branch of the anhydrous trisodium phosphate crosses both the 25°C. and 40°C. isotherms; however, the solid phase in both of the latter isotherms at the points of crossing is $Na_3PO_4 \cdot \frac{1}{2}H_2O$. The solubility of the anhydrous salt is quite low, and the solutions are very concentrated with respect to sodium hydroxide.

The solubility branch of $Na_3PO_4 \cdot \frac{1}{2}H_2O$ is flatter at this temperature than at the lower temperatures and reaches a higher concentration of phosphoric acid before the solid phase changes to the hexahydrate.

The remainder of the tertiary region is similar to that at 40°C., the complex salt A having only one form, that containing ¼ mole of excess sodium hydroxide. The solubility branch of the octahydrate is longer than at 40°C. but has the same general shape.

Only one solid phase is present in the secondary region, disodium phosphate dihydrate, which normally exists in the system disodium phosphate–water at 60°C. The region is typical in that the minimum singular point at a Na_2O/P_2O_5 mole ratio of 2.00 exists, though it is apparent that the isotherms at the higher temperatures do not break as sharply to form these singular points.

A double salt, $Na_2HPO_4 \cdot NaH_2PO_4$, hereinafter called B, appears next as the solid phase. This compound is different from the double salt which appeared at 25°C. and 40°C., and was established as a definite compound through chemical and microscopic analysis.

In the primary region, only the anhydrous monosodium phosphate exists as the solid phase at 60°C. The region again has the singular minimum point of solubility, and again it is apparent that the isotherms are flattening out so that singular points are disappearing. The solubility branch of hemisodium phosphate is similar in shape to those at the lower temperatures. It should be noted that at 25°C. and above in the sodium system, the solid phase in equilibrium with solutions of hemisodium phosphate is the anhydrous salt.

D. The 80°C. isotherm

The solid phases found along the 80°C. isotherm in the tertiary region are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
Na_3PO_4	0.14	0.52
$Na_3PO_4 \cdot \frac{1}{2}H_2O$	0.52	4.29
$Na_3PO_4 \cdot 6H_2O$	4.29	23.00
$Na_2HPO_4 \cdot 2H_2O$	23.00 (23.56)	

The work at 80°C. was limited to the tertiary region. The first phase found is anhydrous trisodium phosphate, which is not much more soluble than at 60°C. The next branch of the isotherm represents the solubility of $Na_3PO_4 \cdot \frac{1}{2}H_2O$; this compound extends over a much greater range than at the lower temperatures.

The main portion of the 80°C. isotherm is the $Na_3PO_4 \cdot 6H_2O$ region, which is quite different from the isotherm at the lower temperatures, as it extends over a wide range of phosphoric acid concentrations. An important feature of this isotherm is that the alkaline complex A does not exist, but the next transition is to the secondary region. This is important, because the conditions have now been established at which it is possible to crystallize from solution an alkali-free trisodium phosphate, regardless of the concentrations of sodium hydroxide and phosphoric acid in the tertiary region.

E. The 100°C. isotherm

The solid phases found along the 100°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
Na_3PO_4	0.41	13.20
$Na_3PO_4 \cdot \frac{1}{2}H_2O$	13.20	17.60
$Na_3PO_4 \cdot 6H_2O$	17.60	23.02
Na_2HPO_4	23.02 (25.56)	36.61
$Na_2HPO_4 \cdot NaH_2PO_4$	36.61	42.73
NaH_2PO_4	42.73 (41.92)	58.08
$NaH_5(PO_4)_2$	58.08	61.42

The tertiary region of this isotherm differs markedly from that of any of the others. The solubility branch of the anhydrous trisodium phosphate extends over a concentration range four times as great as at 80°C., while the region of trisodium phosphate hemihydrate is limited to a small range. The last phase appearing in the tertiary region is that of the hexahydrate, and it is seen to be much shorter than at 80°C.

Only the anhydrous salts exist as solid phases in the secondary and primary regions at 100°C. Also, each region has its singular point, but these are less pronounced than at lower temperatures.

III. THE AMMONIA SYSTEM

The greatest amount of experimentation on the system ammonia–phosphoric acid–water has been carried out at a temperature of 25°C. The isotherm at 25°C. has been studied by D'Ans and Schreiner (4), Parker (11), Janecke (6), and Mouromtzev and Nazarova (9). The latter also investigated the system at 0°C. and 50°C., and Brosheer and Anderson (3) carried out some work at 60°C. and 75°C. The results of all the investigators are in good agreement, except those of Parker, whose data are quite different in the crystallization regions of the di- and tribasic phosphates. A discussion of the system follows. The complete data are shown in figure 4 and are listed in table 2.

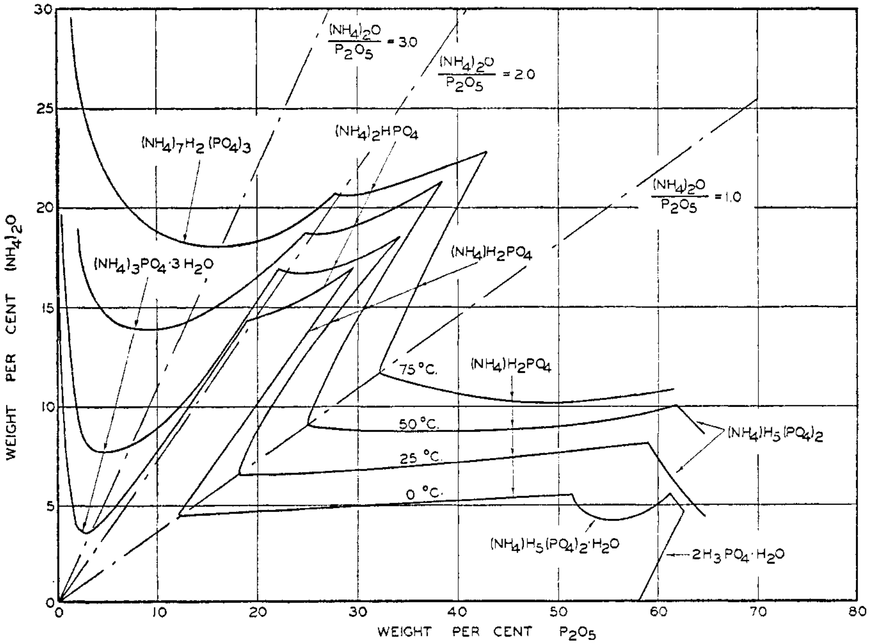

FIG. 4. The system $(NH_4)_2O$–P_2O_5–H_2O from 0°C. to 75°C.

TABLE 2

System NH_3–P_2O_5–H_2O

Liquid Phase				Solid Phase
Weight per cent		Mole per cent		
$(NH_4)_2O$	P_2O_5	$(NH_4)_2O$	P_2O_5	
Temperature = 0°C.				
per cent	*per cent*	*per cent*	*per cent*	
36.25	0.05	16.45	0.009	$(NH_4)_3PO_4 \cdot 3H_2O$
25.18	0.11	10.44	0.017	
21.21	0.17	8.53	0.025	
12.00	0.45	4.53	0.062	
4.92	1.36	1.78	0.180	
3.46	2.24	1.25	0.30	
3.68	3.79	1.35	0.51	
5.58	6.99	2.14	0.98	
10.90	14.42	4.70	2.28	
11.89	15.80	5.25	2.56	
12.50	16.60	5.59	2.72	
12.76	17.02	5.75	2.81	
14.28	19.22	6.68	3.30	$(NH_4)_3PO_4 \cdot 3H_2O + (NH_4)_2HPO_4$
15.23	23.43	7.57	4.27	$(NH_4)_2HPO_4$
15.49	24.07	7.78	4.43	
16.39	27.40	8.68	5.32	
17.04	29.75	9.37	6.00	$(NH_4)_2HPO_4 + NH_4H_2PO_4$
13.14	24.45	6.49	4.43	
9.67	19.59	4.36	3.24	
5.95	14.03	2.45	2.12	
5.38	13.02	2.19	1.94	
4.69	12.03	1.88	1.76	
4.35	13.52	1.76	2.01	
4.43	15.34	1.83	2.32	
4.59	17.57	1.94	2.73	
5.38	44.90	3.24	9.94	
5.35	50.27	3.52	12.10	$NH_4H_2PO_4 + NH_4H_5(PO_4)_2 \cdot H_2O$
5.41	51.50	3.64	12.69	$NH_4H_5(PO_4)_2 \cdot H_2O$
4.97	52.00	3.35	12.85	
4.13	54.00	2.85	13.62	
4.52	55.80	3.24	14.65	
4.31	57.35	3.17	15.44	
5.20	60.75	4.14	17.68	
5.38	61.25	4.33	18.06	$NH_4H_5(PO_4)_2$
4.46	62.50	3.63	18.65	$2H_3PO_4 \cdot H_2O$
2.61	60.06	1.97	16.59	
Temperature = 25°C.				
19.30	0.596	7.69	0.087	$(NH_4)_3PO_4 \cdot 3H_2O$
13.05	1.42	4.92	0.196	
7.67	3.27	2.87	0.45	
7.91	7.25	3.09	1.04	
8.63	9.38	3.47	1.38	
12.40	16.48	5.68	2.76	
16.85	22.45	8.41	4.10	$(NH_4)_3PO_4 \cdot 3H_2O + (NH_4)_2HPO_4$
16.74	22.9	8.40	4.20	$(NH_4)_2HPO_4$
16.80	26.55	8.82	5.11	
17.04	28.5	9.20	5.66	
17.65	30.8	10.44	6.68	
18.62	34.30	11.34	7.53	$(NH_4)_2HPO_4 + NH_4H_2PO_4$
17.48	32.2	9.97	6.73	$NH_4H_2PO_4$
14.62	27.5	7.64	5.25	
12.02	23.2	5.78	4.08	
7.07	18.40	3.08	2.94	

TABLE 2—*Continued*

Liquid Phase				Solid Phase
Weight per cent		Mole per cent		
$(NH_4)_2O$	P_2O_5	$(NH_4)_2O$	P_2O_5	
per cent	*per cent*	*per cent*	*per cent*	
6.51	18.05	2.81	2.86	
6.71	30.6	3.38	5.64	
7.28	44.25	4.46	9.95	
7.96	54.8	5.86	14.78	
8.06	56.00	6.07	15.44	
7.98	58.96	6.38	17.27	$NH_4H_2PO_4 + NH_4H_5(PO_4)_2$
5.00	63.33	4.17	19.40	$NH_4H_5(PO_4)_2$
4.43	64.41	3.74	20.11	
Temperature = 50°C.				
18.76	2.18	7.56	0.321	$(NH_4)_3PO_4 \cdot 3H_2O$
14.31	6.38	5.82	0.951	
13.72	10.21	5.78	1.58	
14.27	13.08	6.23	2.09	
17.11	21.02	8.40	3.79	
17.58	22.43	8.83	4.13	
18.67	24.70	9.75	4.73	$(NH_4)_3PO_4 \cdot 3H_2O + (NH_4)_2HPO_4$
18.41	25.14	9.65	4.83	$(NH_4)_2HPO_4$
18.36	25.22	9.61	4.85	
18.41	25.73	9.73	4.98	
18.47	26.13	9.82	5.09	
18.79	28.01	10.41	5.70	
19.34	30.68	11.05	6.43	
21.24	38.54	14.01	9.32	$(NH_4)_2HPO_4 + NH_4H_2PO_4$
13.00	29.28	6.81	5.63	$NH_4H_2PO_4$
10.22	25.81	4.99	4.63	
9.33	25.05	4.48	4.41	
8.94	25.72	4.31	4.55	
8.82	30.34	4.50	5.68	
8.68	39.68	5.03	8.43	
9.13	52.09	6.50	13.62	
9.91	60.14	8.36	18.60	
9.85	61.80	8.60	19.80	$NH_4H_2PO_4 + NH_4H_5(PO_4)_2$
8.99	63.78	8.09	21.07	$NH_4H_5(PO_4)_2$
Temperature = 60°C.				
19.48	29.87	10.65	6.22	$(NH_4)_2HPO_4$
18.90	27.49	9.93	5.50	
19.04	26.63	9.90	5.28	
19.17	26.00	9.90	5.12	
19.30	25.85	9.96	5.08	$(NH_4)_2HPO_4 + (NH_4)_7H_2(PO_4)_3$
19.33	25.79	9.97	5.07	$(NH_4)_2HPO_4 + (NH_4)_7H_2(PO_4)_3$
17.92	22.55	8.73	4.19	$(NH_4)_7H_2(PO_4)_3$
16.88	18.82	7.78	3.30	
Temperature = 75°C.				
36.28	0.79	16.09	0.13	$(NH_4)_7H_2(PO_4)_3$
31.30	1.39	13.38	0.23	
23.55	3.88	9.69	0.61	
20.60	6.42	8.51	1.01	
18.58	10.84	7.92	1.76	
18.26	15.11	8.15	2.57	

TABLE 2—*Concluded*

Liquid Phase				Solid Phase
Weight per cent		Mole per cent		
$(NH_4)_2O$	P_2O_5	$(NH_4)_2O$	P_2O_5	
Temperature = 75°C.—*Continued*				
per cent	*per cent*	*per cent*	*per cent*	
18.09	16.37	8.18	2.82	
18.32	18.64	8.53	3.31	
18.21	19.67	8.58	3.53	
18.47	21.42	8.92	3.94	
19.07	23.92	9.57	4.57	
19.69	25.79	10.20	5.09	
20.72	27.86	11.16	5.72	$(NH_4)_7H_2(PO_4)_3 + (NH_4)_2HPO_4$
20.46	28.02	11.01	5.75	$(NH_4)_2HPO_4$
20.52	28.34	11.10	5.84	
20.46	30.08	11.34	6.35	
20.76	31.62	11.82	6.87	
21.13	33.67	12.46	7.56	
21.77	36.16	13.46	8.52	
22.13	38.42	14.26	9.43	
22.48	41.18	15.26	10.65	
22.77	42.90	16.01	11.50	$(NH_4)_2HPO_4 + NH_4H_2PO_4$
22.34	42.41	15.48	11.20	$NH_4H_2PO_4$
22.00	42.31	15.15	11.10	
21.93	42.15	15.04	11.01	
21.56	41.78	14.61	10.79	
20.09	40.41	13.04	9.99	
19.94	39.87	12.80	9.75	
19.11	39.16	12.00	9.37	
18.46	38.57	11.38	9.06	
17.61	37.66	10.60	8.63	
17.36	37.38	10.37	8.51	
16.96	36.98	10.02	8.32	
16.12	36.02	9.29	7.91	
15.14	34.86	8.48	7.44	
14.86	34.80	8.29	7.40	
14.68	34.72	8.16	7.36	
14.17	34.17	7.78	7.14	
14.10	34.06	7.72	7.10	
13.04	32.82	6.94	6.65	
12.54	32.67	6.62	6.57	
12.40	32.53	6.52	6.52	
11.93	32.36	6.23	6.44	
11.94	32.26	6.23	6.41	
11.79	32.17	6.13	6.38	
11.44	32.77	5.98	6.52	
11.06	34.74	5.91	7.08	
11.09	36.06	6.04	7.99	
10.73	39.60	6.14	8.63	
10.67	39.70	6.11	8.65	
10.50	42.09	6.22	9.50	
10.32	46.25	6.52	11.13	
10.20	52.76	7.21	14.24	
10.24	53.28	7.32	14.50	
10.27	54.50	7.51	15.18	
10.47	58.20	8.27	17.50	
10.83	61.92	9.31	20.30	

A. The 0°C. isotherm

The solid phases found along the 0°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$(NH_4)_3PO_4 \cdot 3H_2O$	0.05	19.22
$(NH_4)_2HPO_4$	19.22	29.75
$NH_4H_2PO_4$	29.75 (12.03)	50.27
$NH_4H_5(PO_4)_2 \cdot H_2O$	50.27	61.00*
$NH_4H_5(PO_4)_2$	61.00	63.00*
$H_3PO_4 \cdot \frac{1}{2}H_2O$	63.00	58.00*

* Extrapolated.

The solubilities at 0°C. were determined by Janecke; for several reasons his data were criticized by Mouromtzev and Nazarova, who repeated the work. In the tertiary region a single branch is reported, along which the equilibrium solid phase is the trihydrate of triammonium phosphate. As in the sodium system, the minimum solubility in the tertiary region lies to the left of the line representing the locus of all points having an $(NH_4)_2O/P_2O_5$ mole ratio of 3.00.

As in the tertiary region, the secondary region has only one solid phase in equilibrium with solutions. This solid phase is anhydrous diammonium phosphate. From figure 4 it is seen that the solubility branch of this salt just crosses the line representing the locus of all $(NH_4)_2O/P_2O_5$ mole ratios equal to 2.00. According to Janecke's results, this branch of the isotherm does not cross the 2.00 mole ratio locus line; this would mean that diammonium hydrogen orthophosphate dissolves incongruently at 0°C. However, it is known that the salt does not dissolve incongruently, so it is concluded that the data of Janecke are incorrect in this region. It is also noticeable that the singular point of minimum solubility is absent from the secondary region.

The primary region of the isotherm consists of one branch, representing the solubility of anhydrous monoammonium phosphate. The branch has the shape of an acute angle, the apex of which lies on the 1.00 mole ratio locus line. This point at the apex is the singular point in the region.

As the phosphorus pentoxide concentration is increased to 12.10 mole per cent (50.27 weight per cent), the transition point is reached at which the solid phase changes from monoammonium phosphate to the monohydrate of hemiammonium phosphate, $NH_4H_5(PO_4)_2 \cdot H_2O$. Next there is a short branch along which the solid phase is the anhydrous hemiammonium phosphate. The 0°C. isotherm terminates with the solubility branch of a hydrated form of phosphoric acid, $2H_3PO_4 \cdot H_2O$. Note that all of the solubilities of the hemiammonium phosphates (or hemiacid phosphates) lie to the right of the line representing mole ratios of 0.5. This is in accord with the fact that the salts dissolve incongruently, forming monoammonium phosphate and phosphoric acid.

B. The 25°C. isotherm

The solid phases found along the 25°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$(NH_4)_3PO_4 \cdot 3H_2O$	0.596	22.45
$(NH_4)_2HPO_4$	22.45	34.30
$NH_4H_2PO_4$	34.30 (18.05)	58.96
$NH_4H_5(PO_4)_2$	58.96	64.41

With the exception of the solubility branch of the hemiammonium phosphate, the 25°C. isotherm is quite similar to the 0°C. isotherm with respect to shape, solid phases, and the singular point in the primary region.

The early work of D'Ans and Schreiner checks closely with that of Mouromtzev and Nazarova. The latter extended the existing data into higher concentrations of phosphoric acid and made a study of the singular point in the primary region. Mouromtzev and Nazarova found no hydrate of the hemiammonium phosphate at 25°C., and reported only the branch of the solubility of the anhydrous salt. The isotherm was terminated before the point at which solid phosphoric acid

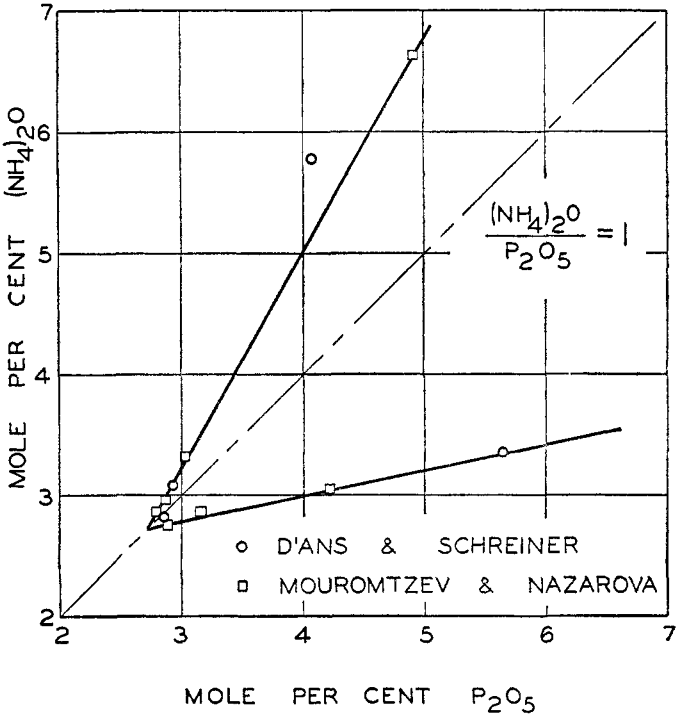

Fig. 5. Singular point on the $(NH_4)_2O$–P_2O_5–H_2O system at 25°C.

crystallizes. They also studied a few points close to the line representing the locus of $(NH_4)_2O/P_2O_5$ mole ratios of 1.00. Their objective was to determine if the singular point in the primary region is a sharp discontinuity or a rounded minimum. Although Mouromtzev and Nazarova claimed in their original paper that these data proved the existence of a discontinuity, figure 5 shows that the singular point could also be a rounded minimum.

C. The 50°C. isotherm

The solid phases found along the 50°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$(NH_4)_3PO_4 \cdot 3H_2O$	2.18	24.70
$(NH_4)_2HPO_4$	24.70	38.54
$NH_4H_2PO_4$	38.54 (25.05)	61.80
$NH_4H_5(PO_4)_2$	61.80	63.78

The 50°C. isotherm is quite similar to the one at 25°C. The trihydrate of triammonium phosphate remains as the only solid phase in the tertiary region. The curvature of this branch is considerably less than that of the corresponding branches at lower temperatures.

The following branch has the dibasic salt $(NH_4)_2HPO_4$ as the solid phase. This branch is almost straight, having a slight curvature only at the point of crossing the line representing all points of $(NH_4)_2O/P_2O_5$ mole ratios of 2.00.

The next branch is the solubility of the monophosphate $NH_4H_2PO_4$, differing from the same branch at 25°C. in that here, apparently, a singular point is absent. In place of the expected sharp discontinuity there is a curvature, that is, a rounded minimum.

Finally, in the region of high concentrations of phosphoric acid, there appears a small portion of the branch of the solubility of the acid salt $NH_4H_5(PO_4)_2$.

D. The 75°C. isotherm

The solid phases found along the 75°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$(NH_4)_7H_2(PO_4)_3$	0.79	27.85
$(NH_4)_2HPO_4$	27.85	42.88
$NH_4H_2PO_4$	42.88 (32.16)	53.28

Brosheer and Anderson (3) extended the data for the system ammonia–phosphoric acid–water to 75°C. They also determined a few points for the system at 60°C. The isotherm is similar to those found at the lower temperatures, except that the salt $NH_4H_5(PO_4)_2$ is apparently not found at 75°C. at phosphoric acid concentrations less than 86 per cent. The fields of stability of ammonium phosphate and diammonium phosphate at 75°C. are those that might be predicted from the data at the lower temperatures.

Previous investigators have stated that the solid phase in equilibrium with highly ammoniacal solutions, i.e., the tertiary region, is $(NH_4)_3PO_4 \cdot 3H_2O$. However, at 75°C. the equilibrium solid phase is $(NH_4)_7H_2(PO_4)_3$, which may be expressed as $(NH_4)_3PO_4 \cdot 2(NH_4)_2HPO_4$. The data at 60°C. indicate that this salt also exists as a stable solid phase. The compound $(NH_4)_7H_2(PO_4)_3$ has not been reported in the literature, although there is a reference (12) to a compound intermediate in composition to $(NH_4)_3PO_4$ and $(NH_4)_2HPO_4$, that is, $(NH_4)_5H(PO_4)_2$ or $(NH_4)_3PO_4 \cdot (NH_4)_2HPO_4$.

IV. THE POTASSIUM SYSTEM

The isotherms of the system potassium oxide–phosphorus pentoxide–water have been studied by Janecke (6), D'Ans and Schreiner (4), Parker (11), Berg (2), and Ravich (14). The work of Berg and of Ravich is the most recent, and because of better technique and methods used is believed to be the most accurate. Therefore, the following discussion will be based mainly on their results.

In general, the potassium system resembles the sodium system more closely than it does the ammonia system, as might be expected. The potassium system has a greater number of phases than the ammonia system, has singular points

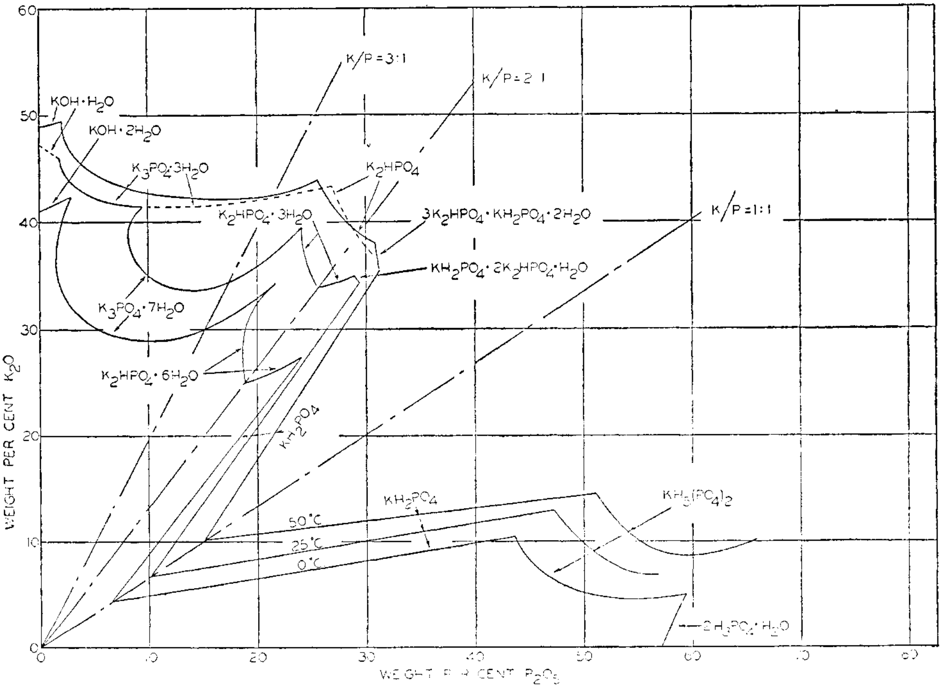

FIG. 6. The system K_2O–P_2O_5–H_2O from 0°C. to 75°C.

TABLE 3

System K_2O-P_2O_5-H_2O

Liquid Phase				Solid Phase
Weight per cent		Mole per cent		
K_2O	P_2O_5	K_2O	P_2O_5	
Temperature = 0°C.				
per cent	*per cent*	*per cent*	*per cent*	
	57.17		14.48	$2H_3PO_4 \cdot H_2O$
1.64	58.01	0.65	15.31	
3.78	58.84	1.58	16.37	
4.89	59.57	2.12	17.15	
5.06	59.50	2.20	17.16	$2H_3PO_4 \cdot H_2O + KH_5(PO_4)_2$
5.75	62.01	2.67	19.09	$KH_5(PO_4)_2$ (m)
5.51	61.60	2.52	18.70	(m)
5.27	61.11	2.37	18.23	(m)
4.93	58.92	2.12	16.76	
4.38	56.12	1.76	14.99	
4.33	55.87	1.73	14.85	
5.30	50.19	1.95	12.26	
6.05	47.93	2.17	11.41	
8.15	45.02	2.88	10.55	
10.37	43.6	3.70	10.33	$KH_5(PO_4)_2 + KH_2PO_4$
10.54	43.49	3.77	10.31	
10.92	45.04	4.02	11.01	KH_2PO_4 (m)
10.22	41.76	3.53	9.58	
8.93	35.92	2.78	7.42	
8.17	32.30	2.39	6.28	
6.85	22.48	1.75	3.81	
5.75	15.75	1.35	2.42	
4.89	9.75	1.07	1.41	
4.41	6.66	0.93	0.93	
6.35	8.05	1.38	1.16	
8.50	9.80	1.92	1.49	
15.18	15.10	3.89	2.57	
16.20	15.98	4.24	2.78	
21.18	19.86	6.20	3.84	
22.49	20.45	6.72	4.05	
27.10	24.00	9.06	5.33	
29.24	25.23	10.29	5.89	?
30.54	25.69	11.04	6.16	?
31.50	25.58	11.54	6.14	$K_2HPO_4 \cdot 3H_2O$ (m)
31.03	24.05	11.00	5.66	(m)
30.86	23.26	10.78	5.39	(m)
32.70	22.23	11.54	5.20	(m)
34.38	21.90	12.38	5.23	$K_2HPO_4 \cdot 3H_2O + K_3PO_4 \cdot 7H_2O$
34.49	22.06	12.47	5.29	
27.05	23.01	8.91	5.03	$K_2HPO_4 \cdot 6H_2O$
25.94	20.80	8.15	4.33	
24.91	18.82	7.48	3.76	
26.92	18.60	8.30	3.80	
29.35	18.72	9.36	3.96	
31.29	19.75	10.41	4.36	
32.83	19.80	11.17	4.47	$K_3PO_4 \cdot 7H_2O$
32.28	19.53	10.85	4.35	
31.26	17.55	10.07	3.6	
30.20	15.81	9.34	3.24	
29.46	14.80	8.89	2.96	
29.60	13.59	8.81	2.68	
29.20	7.25	7.97	1.32	
29.16	7.76	7.90	1.22	
33.19	2.12	8.89	0.38	
38.16	1.74	10.78	0.33	
40.16	2.11	11.68	0.41	
42.30	2.99	12.79	0.60	$KOH \cdot 2H_2O$
41.95	2.62	12.57	0.52	
41.80	2.17	12.42	0.43	
41.68	1.50	12.26	0.29	
41.01		11.73		

TABLE 3—*Continued*

Liquid Phase				Solid Phase
Weight per cent		Mole per cent		
K_2O	P_2O_5	K_2O	P_2O_5	
Temperature = 25°C.				
per cent	*per cent*	*per cent*	*per cent*	
47.25		14.62		$KOH \cdot 2H_2O$
46.18	1.73	14.44	0.36	$KOH \cdot H_2O$
45.92	1.78	14.32	0.37	
45.90	1.86	14.28	0.38	$KOH \cdot H_2O + K_3PO_4 \cdot 3H_2O$
45.75	1.85	14.25	0.38	$K_3PO_4 \cdot 3H_2O$
43.20	1.85	13.37	0.77	
41.69	3.75	13.65	1.97	
41.63	9.04	14.20	2.67	
41.55	11.78	14.55	3.14	(m)
41.50	13.51	14.78	3.36	(m)
41.56	15.45	15.03	3.70	(m)
41.87	16.54	15.49	4.06	(m)
42.12	17.69	15.95	4.45	(m)
42.44	20.78	17.08	5.54	(m)
43.44	26.75	19.93	8.16	$K_3PO_4 \cdot 3H_2O + K_2HPO_4$ (m)
41.53	9.52	13.67	2.08	$K_3PO_4 \cdot 3H_2O + K_3PO_4 \cdot 7H_2O$
37.18	8.15	11.32	1.65	$K_3PO_4 \cdot 7H_2O$
34.39	10.99	10.51	2.23	
34.06	16.70	11.25	3.66	
39.42	24.17	16.03	6.52	$K_3PO_4 \cdot 7H_2O + K_2HPO_4 \cdot 3H_2O$
41.48	25.62	17.99	7.37	$K_3PO_4 \cdot 7H_2O$
41.64	27.21	18.71	8.10	K_2HPO_4 (m)
41.07	27.46	8.35	8.14	(m)
40.22	27.79	17.80	8.16	(m)
37.59	30.03	16.57	8.78	(m)
37.20	30.72	16.51	9.04	(m)
36.96	30.65	16.31	8.96	(m)
41.90	24.89	18.06	7.11	$K_3HPO_4 \cdot 3H_2O$
40.33	24.62	16.81	6.80	
39.42	24.17	16.03	6.52	$K_2HPO_4 \cdot 3H_2O + K_3PO_4 \cdot 7H_2O$
36.69	24.37	14.22	6.28	$K_2HPO_4 \cdot 3H_2O$ (m)
34.15	25.48	13.03	6.45	(m)
34.05	25.52	12.98	6.45	(m)
34.97	29.04	14.42	7.95	$K_2HPO_4 \cdot 3H_2O + KH_2PO_4 \cdot 2KHPO_4 \cdot H_2O$ (m)
37.46	29.47	16.29	8.50	$KH_2PO_4 \cdot 2HPO_4 \cdot H_2O$ (m)
35.86	28.95	14.98	8.03	(m)
35.51	28.96	14.76	7.99	
35.16	29.01	14.54	7.96	
35.01	29.19	14.49	8.02	
34.48	29.39	14.19	8.02	$KH_2PO_4 \cdot 2K_2HPO_4 \cdot H_2O + KH_2PO_4$
33.32	28.30	13.18	7.42	
32.65	27.75	12.65	7.13	
31.30	27.12	11.98	6.72	
26.33	24.23	8.75	5.34	
20.12	19.67	5.78	3.75	
17.68	18.13	4.84	3.29	
14.20	15.89	3.64	2.70	
11.66	13.37	2.77	2.10	
7.77	10.73	1.76	1.61	
7.14	10.45	1.60	1.56	
6.87	10.17	1.53	1.51	
6.90	11.00	1.55	1.65	
7.06	11.44	1.60	1.72	
7.08	12.12	1.62	1.84	
8.49	20.35	2.15	3.43	
9.52	26.89	2.65	4.95	

TABLE 3—*Continued*

Liquid Phase				Solid Phase
Weight per cent		Mole per cent		
K_2O	P_2O_5	K_2O	P_2O_5	
Temperature = 25°C.—*Continued*				
per cent	*per cent*	*per cent*	*per cent*	
10.19	32.90	3.10	6.48	
11.69	42.42	4.18	10.05	(m)
12.50	46.38	4.84	11.91	(m)
12.68	47.40	5.01	12.43	(m)
12.91	49.90	5.38	13.49	$KH_2PO_4 \cdot 2K_2HPO_4 \cdot H_2O + KH_2PO_4$ (m)
13.67	50.76	5.86	14.43	(m)
14.29	53.94	6.49	16.26	(m)
12.77	47.16	5.04	12.33	$KH_2PO_4 + KH_5(PO_4)_2$
11.83	47.73			
10.27	48.66	3.99	12.54	$KH_5(PO_4)_2$
9.69	49.40	3.78	12.78	
8.36	51.58	3.32	13.57	
8.10	51.91	3.22	13.68	
6.99	55.23	2.90	15.19	
6.85	56.80	2.93	15.75	
Temperature = 50°C.				
48.83		15.42		$KOH \cdot H_2O$
49.44	2.13	16.60	0.47	$KOH \cdot H_2O + K_3PO_4 \cdot 3H_2O$
50.19	2.60	16.80	0.58	$K_3PO_4 \cdot 3H_2O$ (m)
46.60	2.64	14.85	0.56	
46.50	2.95	14.87	0.63	
44.88	4.70	14.40	1.00	
43.12	7.80	14.14	1.70	
42.35	12.36	14.74	2.85	
42.30	15.64	15.52	3.80	
42.25	21.07	17.03	5.63	
42.89	23.55	18.33	6.67	
43.80	25.64	19.85	7.71	$K_3PO_4 \cdot 3H_2O + K_2HPO_4$
42.39	26.14	18.90	7.73	K_2HPO_4
41.72	26.92	18.66	7.99	
41.39	26.87	18.38	7.92	
40.98	27.49	18.29	8.14	
40.84	27.59	18.26	8.18	
40.01	27.90	17.68	8.18	
39.68	28.48	17.63	8.39	
39.73	28.59	17.71	8.45	
39.52	28.59	17.55	8.42	
39.18	28.86	17.38	8.49	
38.98	29.29	17.38	8.66	
38.72	29.64	17.30	8.78	
38.70	30.00	17.41	8.95	(m)
38.12	31.13	17.36	9.41	$K_2HPO_4 + K_2HPO_4 + KH_2PO_4 \cdot 2H_2O$ (?)
37.96	31.24	17.27	9.43	
37.97	31.79	17.49	9.71	K_2HPO_4 (m)
38.50	29.60	17.12	8.73	
36.71	31.42	16.38	9.29	
38.93	30.57	17.80	9.27	$K_2HPO_4 \cdot KH_2PO_4 \cdot 2H_2O$ (?) (m)
38.83	30.74	17.78	9.34	(m)
38.06	30.78	17.19	9.22	$K_2HPO_4 + K_2HPO_4 \cdot KH_2PO_4 \cdot 2H_2O$ (?)
36.65	31.02	16.23	9.12	$K_2HPO_4 \cdot KH_2PO_4 \cdot 2H_2O$
36.61	31.38	16.28	9.26	
35.69	31.98	15.77	9.36	
35.77	31.10	15.94	9.19	KH_2PO_4

TABLE 3—*Concluded*

Liquid Phase				Solid Phase
Weight per cent		Mole per cent		
K_2O	P_2O_5	K_2O	P_2O_5	
Temperature = 50°C.—*Continued*				
per cent	*per cent*	*per cent*	*per cent*	
35.58	31.16	15.45	8.98	
35.54	31.30	15.47	9.04	
35.35	31.44	15.38	9.07	
34.00	30.30	14.12	8.35	
33.79	29.93	13.89	8.16	
33.70	30.25	13.91	8.28	
32.80	29.69	13.19	7.92	
31.80	29.08	12.44	7.54	
27.91	26.78	9.88	6.28	
25.60	25.20	8.54	5.58	
25.25	24.80	8.34	5.43	
21.78	22.71	6.66	4.61	
12.56	17.01	3.20	2.88	KH_2PC
10.63	15.31	2.60	2.49	
10.06	15.15	2.45	2.45	
10.15	15.30	2.47	2.45	
10.32	15.56	2.53	2.53	
10.48	17.87	2.64	2.99	
10.71	19.42	2.75	3.31	
11.11	25.51	3.09	4.71	
12.03	30.40	3.61	6.09	
12.24	31.94	3.77	6.51	
12.96	39.74	4.52	9.20	
13.22	40.85	4.71	9.66	
14.21	49.71	6.02	13.98	
14.30	49.87	6.09	14.09	
14.34	51.15	6.27	14.83	$KH_5(PO_4)_2$
9.65	55.84	4.25	16.30	
9.53	55.72	4.18	16.19	
8.84	57.92	3.59	17.45	
8.71	58.17	3.95	17.50	
8.68	60.24	3.50	16.13	
9.10	62.48	4.56	20.75	
10.05	65.93	5.60	24.38	

in the secondary region, and reveals also the existence of double salts (see figure 6 and table 3).

A. The 0°C. isotherm

The solid phases found along the 0°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$KOH \cdot 2H_2O$	0.0	2.99
$K_3PO_4 \cdot 7H_2O$	2.99	21.98
$K_2HPO_4 \cdot 6H_2O$	21.98 (18.82)	27.07
KH_2PO_4	27.07 (6.66)	43.54
$KH_5(PO_4)_2$	43.54	59.50
$H_3PO_4 \cdot \frac{1}{2}H_2O$	59.50	57.17

As seen in figure 6, the first branch of the isotherm, in the highly alkaline region, has as its equilibrium solid phase the dihydrate of potassium hydroxide. This salt exists only over a short range of concentration. It will be recalled that in the sodium system no solutions were found having sodium hydroxide or its hydrates as the solid phase.

A single branch exists in the tertiary region, along which the equilibrium solid phase is $K_3PO_4 \cdot 7H_2O$. As in the other systems, the minimum solubility lies to the left of the line representing the locus of K_2O/P_2O_5 mole ratios of 3.00. The octahydrate of tripotassium phosphate reported by Janecke was not found by Berg or by Ravich.

Two separate branches are found in the secondary region. One has as the equilibrium solid phase the hexahydrate of dipotassium phosphate. This branch is characterized by a minimum singular solubility point at a K_2O/P_2O_5 mole ratio of 2.00. The other branch in this region is similar in shape to that of the hexahydrate, but has the trihydrate as the solid phase. According to Ravich, the stable solid phase in the secondary region is the hexahydrate, while the trihydrate is considered to be metastable.

A single equilibrium solid phase exists in the primary region, the anhydrous monopotassium phosphate. The shape of the primary branch of the isotherm is that of an acute angle, much the same as in the ammonia system. The apex of the acute angle is the singular point, heaving a mole ratio of K_2O/P_2O_5 equal to 1.00.

The next branch of the isotherm corresponds to the solubility of the anhydrous form of hemipotassium phosphate, $KH_5(PO_4)_2$. This salt dissolves incongruently, inasmuch as its entire solubility branch lies on one side of the 0.5 mole ratio line. The isotherm is terminated with a short branch along which the equilibrium solid phase is $H_3PO_4 \cdot \frac{1}{2}H_2O$. It is also noted that this branch of the solubility curve of the hemipotassium phosphate can be continued into the metastable region.

B. The 25°C. isotherm

The solid phases found along the 25°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$KOH \cdot H_2O$	1.73	1.86
$K_3PO_4 \cdot 3H_2O$	1.86	9.52
$K_3PO_4 \cdot 7H_2O$	9.52	24.17
$K_2HPO_4 \cdot 3H_2O$	24.17 (25.52)	29.04
$KH_2PO_4 \cdot 2K_2HPO_4 \cdot H_2O$	29.04	29.39
KH_2PO_4	29.39 (10.17)	47.16
$KH_5(PO_4)_2$	47.16	56.80

The 25°C. isotherm is similar to that at 0°C., although there is some uncertainty regarding the stable solid phase in several ranges of concentration. For example, several phases exist simultaneously in both the tertiary and the secondary regions.

Two hydrates of potassium hydroxide, the mono- and dihydrates, are found in the highly alkaline region. However, the existence of the dihydrate is not completely defined, apparently because of some conflicting data (2). As to the monohydrate, Berg (2) believed its existence at this temperature has been proved.

The first phosphate salt appearing in the tertiary region at 25°C. is $K_3PO_4 \cdot 3H_2O$. Most of the solubility branch of this salt lies in the metastable range however, because at about 10 per cent phosphorus pentoxide by weight, the heptahydrate appears as the stable phase. Unlike the sodium system, there are no complex salts containing alkali found in the tertiary region.

The solubility branch of the trihydrate of tripotassium phosphate continues on as a metastable phase from about 10 per cent phosphorus pentoxide until about 27 per cent, at which point there is a transition to the solubility branch of anhydrous dipotassium phosphate. This latter salt also appears as a metastable phase at this temperature. This metastable branch crosses the K_2O/P_2O_5 mole ratio line of 2.00 without evidence of a singular point. At 24 per cent phosphorus pentoxide the stable phase $K_3PO_4 \cdot 7H_2O$ changes to the stable phase existing in the secondary region. The stable phase in the secondary region is the trihydrate of dipotassium phosphate. Its solubility branch contains a distinct discontinuity at a K_2O/P_2O_5 mole ratio of 2.00. At the termination of the dipotassium trihydrate branch, there is a transition to the double salt $KH_2PO_4 \cdot 2K_2HPO_4 \cdot H_2O$. This double salt exists only over a very short concentration range and can be followed into a metastable region. The appearance of this double salt is reminiscent of the sodium system.

The primary region of the 25°C. isotherm is almost identical with that at 0°C. The equilibrium solid phase is the same, the anhydrous monopotassium phosphate, and the shape of the solubility branch is the same. The singular point is also evident in the primary region. The isotherm terminates with a branch along which the solid phase is the anhydrous hemipotassium phosphate.

C. The 50°C. isotherm

The solid phases found along the 50°C. isotherm are as follows:

Solid Phase	P_2O_5 Range	
	Minimum	Maximum
	weight per cent	*weight per cent*
$KOH \cdot H_2O$	0	2.13
$K_3PO_4 \cdot 3H_2O$	2.13	25.64
K_2HPO_4	25.64	31.42
$3K_2HPO_4 \cdot KH_2PO_4 \cdot 2H_2O$	31.42	31.91
KH_2PO_4	31.91 (15.15)	51.10
$KH_5(PO_4)_2$	51.10	65.93

The 50°C. isotherm is similar to the other isotherms of the potassium system and is typical of this type of ternary system. The tertiary region contains a single phase, representing the solubility of $K_3PO_4 \cdot 3H_2O$. The presence of the trihydrate at 50°C. lends further weight to the fact that the heptahydrate is the stable phase at 25°C., because in general the degree of hydration decreases with increase in temperature.

The secondary region of the 50°C. isotherm differs from the isotherms at the lower temperatures in that there does not appear to be a singular point. The equilibrium solid phase found in this region is the anhydrous dipotassium phosphate.

Berg (2) found a number of double salts on the isotherm at 50°C. Only one of these double salts is shown in figure 5, because of lack of data for the others. The one considered to be the stable phase at 50°C. is $3K_2HPO_4 \cdot KH_2PO_4 \cdot 2H_2O$. A metastable double salt, also investigated by Berg, was found to be $K_2HPO_4 \cdot KH_2PO_4 \cdot 2H_2O$. The solubility of the double salts has proved to be a difficult study. Their regions of crystallization are small, and the solubility branches of the stable and metastable phases are so close together that the differences in the potassium and phosphorus contents of the salts approach the limits of the analytical methods. Schreinemakers' method of residues is of little use here, because of the possibility of the separation from solution of other solid phases, stable at the given temperature.

Berg states that the results obtained on the solubility of the double salts must be considered as only probable, but not definite. Two other double salts, $2K_2HPO_4 \cdot KH_2PO_4 \cdot H_2O$, and $5K_2HPO_4 \cdot KH_2PO_4 \cdot xH_2O$, were found by Berg, but he did not investigate their solubilities at 50°C. With regard to the degree of hydration of the double salts, chemical analysis points to a mono- and dihydrate, but crystallographic data show only one compound. It must be concluded that the water of hydration of the double salts as reported is not definite.

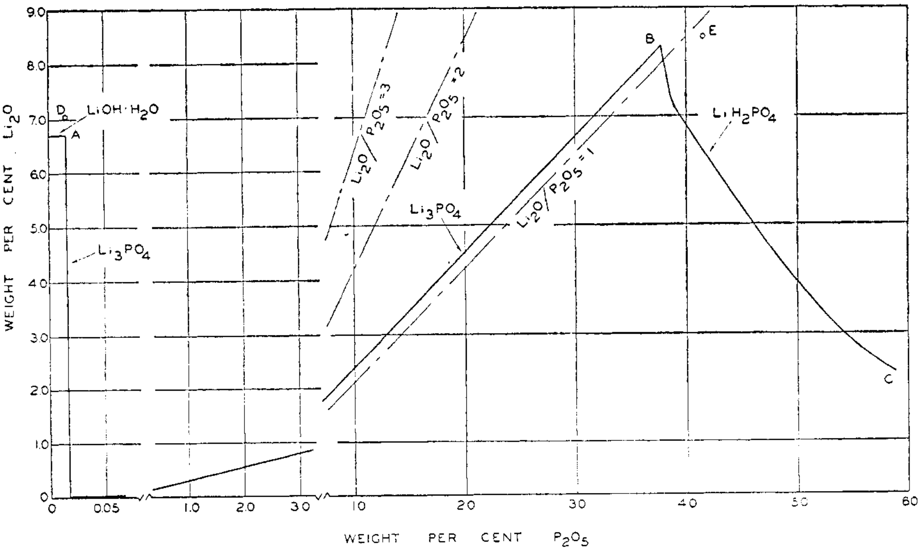

FIG. 7. The system Li_2O-P_2O_5-H_2O at 0°C. and 20°C. Note changes in abscissa scale.

The remainder of the isotherm, in the primary region, is analogous to the isotherms at 0°C. and 25°C.

V. THE LITHIUM SYSTEM

The system lithium oxide–phosphorus pentoxide–water has been studied at 0°C. and 20°C. only by Rollet and Lauffenburger (15). This system is drastically different from the other systems and is characterized by the insolubility of trilithium phosphate and the absence of dilithium phosphate from the phase diagram. None of the lithium phosphates is hydrated. The system is shown in

TABLE 4

The system Li_2O–P_2O_5–H_2O *at 0° and 20°C.*

Solid Phase	Liquid Phase, 0°C.				Liquid Phase, 20°C.			
	Li_2O	P_2O_5	Li_2O	P_2O_5	Li_2O	P_2O_5	Li_2O	P_2O_5
	weight per cent	*weight per cent*	*mole per cent*	*mole per cent*	*weight per cent*	*weight per cent*	*mole per cent*	*mole per cent*
$LiOH\cdot H_2O$	6.70	0.0	4.150	0.00				
$LiOH\cdot H_2O + Li_3PO_4$	(*A*) 6.72	0.015	4.163	0.00195	7.05	0.017	4.374	0.00222 (*D*)
	6.72	0.015	4.163	0.00195				
Li_3PO_4	5.58	0.02	3.441	0.00259	0.077	0.0165	0.04644	0.00209
	2.40	0.016	1.461	0.00205				
	0.49	0.02	0.2961	0.00254	0.0134	0.0210	0.00808	0.00269
	0.0088	0.0148	0.00530	0.00187	0.0165	0.0272	0.00995	0.00345
	0.0098	0.0163	0.00591	0.00206	0.0197	0.0345	0.01188	0.00437
	0.0185	0.0375	0.01115	0.00476	0.0203	0.0360	0.01224	0.00457
	0.025	0.058	0.01508	0.00736	0.050	0.116	0.03018	0.01473
	0.149	0.388	0.09019	0.04943	0.0965	0.242	0.05833	0.03078
	0.167	0.414	0.1011	0.05276	0.118	0.305	0.07137	0.03882
	0.174	0.452	0.1054	0.05762	0.150	0.409	0.09082	0.05212
	0.2285	0.635	0.1387	0.08111	0.205	0.620	0.1244	0.07917
	0.266	0.785	0.1617	0.1004	0.262	0.875	0.1594	0.1120
	0.270	0.80	0.1641	0.1024				
	0.330	0.96	0.2009	0.1230				
	0.403	1.355	0.2463	0.1743				
	0.520	1.88	0.3194	0.2431				
	0.74	2.74	0.4585	0.3573				
	2.55	11.03	1.721	1.567				
	3.90	17.2	2.818	2.616				
	4.58	20.26	3.431	3.194				
	4.97	22.16	3.809	3.574				
	5.42	24.30	4.264	4.024	5.73	27.5	4.687	4.234
	6.86	31.13	5.901	5.636	7.63	37.1	7.124	7.291
	7.55	34.43	6.800	6.527	7.95	38.8	7.613	7.820
$Li_3PO_4 + LiH_2PO_4$	(*B*) 8.29*	37.92*	7.859	7.567	8.45	41.6	8.446	8.752 (*E*)
LiH_2PO_4	8.19	37.95	7.763	7.571	7.73	41.7	7.701	8.744
	8.08	38.10	7.669	7.611	6.62	43.5	6.721	9.295
	7.68	38.20	7.281	7.623				
	7.54	38.45	7.167	7.692				
	7.18	38.85	6.847	7.798				
	4.62	47.5	4.919	10.64				
	3.21	53.05	3.693	12.85				
	2.74	55.65	3.283	14.03				
	(*C*) 2.22	58.8	2.801	15.62				

* Read from intersection of branch lines.

figure 7 at 0°C. with some of the 20°C. points indicated. Note that the abscissa scale changes twice and has been enlarged in the ranges 0–0.05 and 1.0 to 3.0 per cent phosphorus pentoxide to show more clearly the solubilities in these regions of low phosphate concentration. The data for this system are given in table 4.

The solid phases found along the isotherms are as follows:

Solid Phase	P_2O_5 Range in Weight Per Cent			
	0°C.		20°C.	
$LiOH \cdot H_2O$	0.0	0.015	0.0	0.017
Li_3PO_4	0.015	37.92*	0.017	41.6
LiH_2PO_4	37.92*	58.8	41.6	

* Read from intersection of curves.

Initially lithium hydroxide monohydrate is in equilibrium with the solution up to the invariant point *A*, where anhydrous trilithium phosphate also is in equilibrium. The solubility decreases rapidly to about 0.22 g. per liter at 0°C. The solubility remains low over a considerable range of phosphoric acid concentration and then increases to the invariant point *B*, at which Li_3PO_4 and LiH_2PO_4 are the solid equilibrium phases. Thus, no Li_2HPO_4 region exists and this salt is not known. The solubility of monolithium phosphate decreases with increasing acid concentration, but at 58 per cent phosphorus pentoxide (point *C*) there is no indication of the formation of a hemilithium phosphate. At 20°C. the invariant point for $LiOH \cdot H_2O$ and Li_3PO_4 is at *D*, while for Li_3PO_4 and LiH_2PO_4 it is at *E*. Point *E* is on the acid side of the $Li_2O/P_2O_5 = 1.00$ line, indicating that monolithium phosphate will dissolve incongruently to form trilithium phosphate and phosphoric acid until the composition of point *E* is achieved.

VI. COMPARISON OF THE SYSTEMS

Three systems discussed in this paper have been studied at one common temperature, 25°C. Figure 8 shows a comparison of the 25°C. isotherm of each system. It should be noted that the solubilities are now reported in mole percentage (rather than weight percentage as on previous figures), so that all systems are on a common basis.

In the tertiary region, the potassium salt is seen to be the most soluble, with the sodium salt least soluble. The potassium system has a short branch along which the solid phase is the monohydrate of potassium hydroxide. The hydroxide does not appear in the sodium system, at least in the ranges of concentration investigated therein. Only in the sodium system is there an alkaline complex in this region, the solid phases in the other two systems being hydrates of the pure salts. The general shape of the isotherms in this region is similar, although the sodium system exhibits more phases than the other two.

Both the sodium and the potassium systems are similar in the secondary region, in that each contains a singular minimum point of solubility, but this is

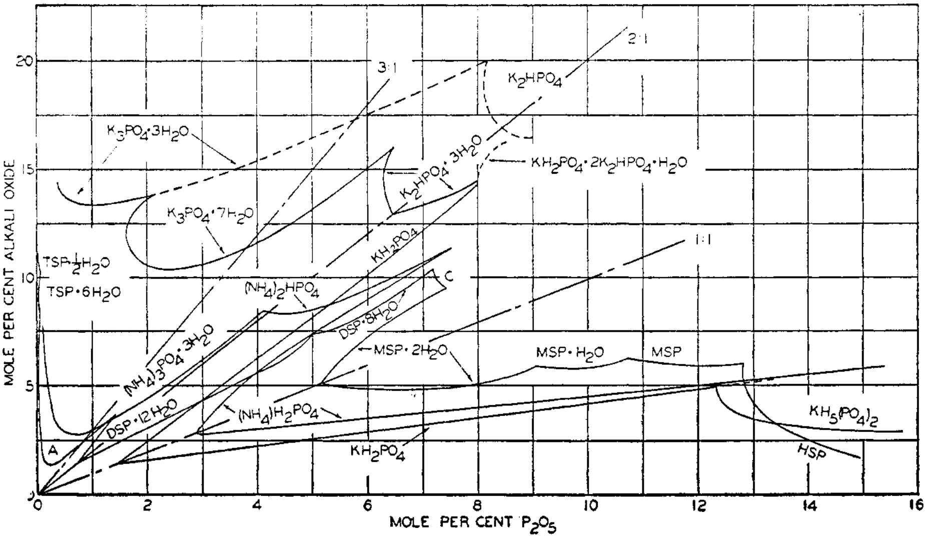

FIG. 8. Comparison of the sodium, potassium, and ammonium phosphate systems at 25°C.

not true of the ammonia system. Furthermore, the acid side of the secondary region in the sodium system extends over a much greater concentration range than the other systems, and in addition contains a transition to a lower hydrate. Even at this low temperature, the solid phase in the ammonia system is the anhydrous salt, while the dodecahydrate and the octahydrate exist in the sodium system, and the trihydrate exists in the potassium system.

The isotherms of the ammonia and potassium systems have approximately the same shape in the primary region, but the solubilities are now reversed from those in the tertiary region. The sodium salt has become the most soluble, and the potassium salt the least soluble. The sodium system has two transitions to lower hydrates in the acid side of the primary region, while the anhydrous salts exist throughout as the solid phases in the other two systems.

The existence of singular points is a characteristic common to the three systems. These are the points at which the isotherms cross the lines representing alkali/P_2O_5 ratios of 2.00 and 1.00. It will be noted that there are no singular points as the isotherms cross the lines representing mole ratios of 3.00. Each singular point represents the solubility of the pure salt in water at a particular temperature. Solutions above the lines representing mole ratios of 2.00 and 1.00 contain excess alkali, and those below the line contain excess acid. Therefore, the branch of the isotherm above the line represents the solubility of the salt in alkaline solutions. In studying the potassium system at 0°C., Ravich (14) stated that there are clearly evident singular points at mole ratios of 2.00 and 1.00, but did not check any points near the singular ones. Mouromtzev and Nazarova (9) made a study of some points very close to a singular point; their data show a discontinuity at the singular point (figure 5). On the other hand, the data of D'Ans and Schreiner (figure 5) show that the singular point occurs at a rounded minimum and that in some instances the curvature is too small to detect. This appears to be the case in the ammonia system at 50°C. Berg (2) simply states that there are sharp minima in the potassium system. There is apparently no consistent explanation of the existence of these singular points.

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