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Solubility in the System Urea–Potassium Phosphates–Water at 0 and 25 °C

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The solubility isotherms of the quarternary system $CO(NH_2)_2$–K_2O–H_3PO_4–H_2O and (N quinary system $CO(NH_2)_2$–K_2O–H_3PO_4–$H_4P_2O_7$–H_2O were determined at 0 and 25 °C and in the pH range 4–10. The solubility is expressed as the total plant food (N + P_2O_5 + K_2O) being a function of K_2O/P_2O_5. Various invariant solutions were identified, as were the precipitation fields of various potassium phosphate and pyrophosphate salts.

With the increased use of urea as a source of plant food, a study was made of its solubility in potassium pyro- and/or orthophosphate solutions that are typical of liquid fertilizers. In this study the phase relationships in the system urea–potassium oxide–orthophosphoric acid–pyrophosphoric acid–water were determined where the solid phases of urea and potassium phosphates were in equilibrium over the pH range 4.0–9.8.

The di- and tripotassium pyrophosphates were prepared according to Frazier et al. (*1*), and the urea and mono- and dipotassium orthophosphates were reagent grade. From previous data (*1–3*) the precipitating potassium salts were selected for the desired pH. Stock solutions of the potassium orthophosphates were prepared by saturating distilled water at 35 °C with the respective salt and cooling to room temperature. Portions of the stock solution of the salt found at the desired pH were saturated with the stable potassium pyrophosphate found at that particular pH. These solutions then were saturated with urea. The solution pH was adjusted with 85% H_3PO_4 or a 20% KOH solution.

Table I. System $CO(NH_2)_2$-K_2O-H_3PO_4-H_2O at 0 and 25 °C

	liquid composition, %						
pH	N	P_2O_5	K_2O	urea	KH_2PO_4	K_2HPO_4	solid phase[a]
			0 °C				
9.28	4.03	18.89	24.4	8.64	1.93	43.88	B, C
9.04	3.68	19.64	24.6	7.89	4.23	42.78	B, C
9.00	3.63	20.67	25.5	7.78	5.58	43.58	B, C
8.78	1.71	25.12	30.7	3.67	7.62	51.89	A, B, C
8.58	5.80	17.66	20.6	12.43	8.20	32.85	A, C
7.51	9.00	13.39	15.0	19.29	8.00	22.61	A, C
6.89	15.50	5.88	5.7	33.23	6.08	6.65	A, C
6.00	17.30	3.95	3.0	37.09	6.48	1.40	A, C
5.80	17.50	3.86	2.8	37.51	6.71	0.88	A, C
5.18	17.70	3.77	2.6	37.94	6.94	0.36	A, C
4.56	17.70	3.76	2.5	37.94	7.19	0.02	A, C
4.05	17.70	3.88	2.5	37.94	7.23	0.15[b]	A, C
			25 °C				
9.65	3.03	24.72	32.0	6.50	2.33	57.68	B, C
9.58	2.96	25.12	31.8	6.35	4.44	55.96	B, C
9.46	294	25.42	32.2	6.30	4.44	56.70	B, C
9.23	2.79	26.18	32.5	5.98	6.49	55.95	B, C
8.92	2.57	27.40	33.6	5.51	7.99	57.02	A, B, C
8.29	4.87	22.93	26.4	10.44	11.65	41.36	A, C
7.79	11.40	15.17	16.7	24.44	9.92	24.53	A, C
7.68	14.30	12.32	13.4	30.65	8.52	19.32	A, C
7.22	18.10	8.42	8.8	38.80	6.86	11.88	A, C
7.09	20.70	5.98	5.5	44.37	7.04	5.67	A, C
6.75	21.80	4.85	4.1	46.73	6.75	3.26	A, C
6.47	22.80	4.39	3.2	48.88	7.59	1.06	A, C
6.14	23.20	4.10	2.8	49.73	7.63	0.29	A, C
6.10	23.10	4.20	2.8	49.52	8.02	0.05	A, C
5.68	23.20	3.90	2.6	49.73	7.44	0.04	A, C
5.59	23.20	3.90	2.6	49.73	7.44	0.04	A, C
5.18	22.90	3.99	2.7	49.09	7.50	0.19	A, C
4.21	23.30	4.02	2.4	49.95	6.93	0.55[b]	A, C

[a] Identified by microscopic examination: A = KH_2PO_4, B = $K_2HPO_4 \cdot 3H_2O$, C = $CO(NH_2)_2$. [b] Reported as % H_3PO_4.

One group of complexes was equilibrated at 0.0 ± 0.5 °C in a cold room with periodic agitation, and the other group was equilibrated at 25.0 ± 0.5 °C in a water bath with continuous agitation at 4 rpm. The approach to equilibrium was followed by petrographic examination of the solid phase. When any of the salts were missing, a few grams of the salt was added and equilibration continued. When it was observed microscopically that there was no change in the nature or abundance of the solid phases, equilibrium was assumed to have been attained. Duplicate samplings at 1-week intervals were made to assure that equilibrium had been attained.

Nitrogen was determined by distillation of ammonia with sodium hydroxide after decomposing with sulfuric acid and Devarda's alloy (*4*); the potassium was determined volumetrically by using STPB (*4*); the phosphorus was determined gravimetrically as quinolinium molybdophosphate (*4*); and the distribution of phosphate species was determined by one-dimentional paper chromatography (*5*, *6*). The pH measurements were made with a commercial meter and a glass electrode.

Results

Subsystem $CO(NH_2)_2$–KOH–H_3PO_4–H_2O. Equilibrium was

Table II. System $CO(NH_2)_2$-K_2O-H_3PO_4-$H_4P_2O_7$-H_2O at 0 and 25 °C

	liquid phase					
	composition, %			distribution, % of P_2O_5		
pH	N	P_2O_5	K_2O	ortho	pyro	solid phase[a]
			0 °C			
4.06	13.3	12.80	8.5	21.4	78.6	A, B, D
5.26	11.0	15.64	11.6	18.9	81.1	A, B, D
6.00	6.1	22.97	19.2	15.3	84.7	A, B, D
6.45	3.4	28.00	24.7	12.7	87.3	A, B, D, E
7.02	3.8	24.72	24.0	23.6	76.4	A, B, E
7.70	3.2	24.30	25.8	42.9	57.1	A, B, E
8.08	2.6	24.91	27.7	56.3	43.7	A, B, E
8.92	1.4	28.00	33.2	77.5	22.5	A, B, C, E
8.99	1.6	27.14	32.4	77.5	22.5	A, C, E
9.42	1.5	26.80	32.7	75.0	25.0	A, C, E
9.77	1.2	27.00	34.4	65.3	34.7	A, C, E
9.80	1.4	27.06	34.3	62.0	38.0	A, C, E
			25 °C			
4.02	19.0	11.67	7.3	28.6	71.4	A, B, D
4.60	18.6	11.93	7.8	31.3	68.7	A, B, D
5.43	16.3	14.09	10.3	31.3	68.7	A, B, D
6.47	4.2	29.74	26.3	20.0	80.0	A, B, D, E
7.18	5.0	26.56	25.5	40.0	60.0	A, B, E
7.66	4.4	26.25	26.9	39.8	60.2	A, B, E
8.12	3.5	27.06	29.3	52.8	47.2	A, B, E
8.87	2.4	29.28	33.5	72.4	27.6	A, B, E
9.31	2.2	29.41	34.7	70.0	30.0	A, B, C, E
9.48	2.3	28.70	34.8	64.3	35.7	A, C, E
9.60	2.3	28.52	35.3	59.1	40.9	A, C, E

[a] Identified by microscopic examination: A = $CO(NH_2)_2$, B = KH_2PO_4, C = $K_2HPO_4 \cdot 3H_2O$, D = $K_2H_2P_2O_7 \cdot 0.5H_2O$, E = $K_3HP_2O_7 \cdot 3H_2O$.

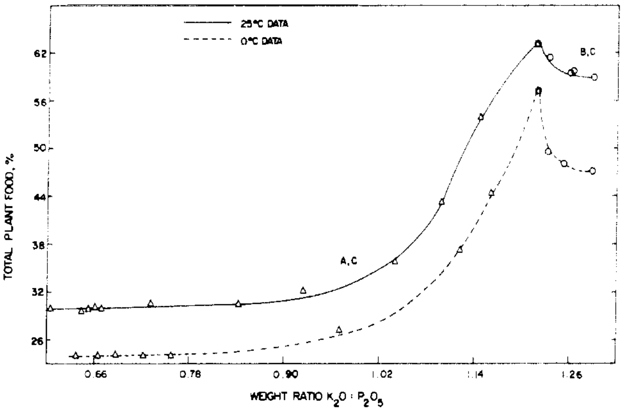

Figure 1. Solubility in the system $CO(NH_2)_2$–K_2O–H_3PO_4–H_2O at 0 and 25 °C (saturating solids: A = KH_2PO_4, B = $K_2HPO_4 \cdot 3H_2O$, C = $CO(NH_2)_2$).

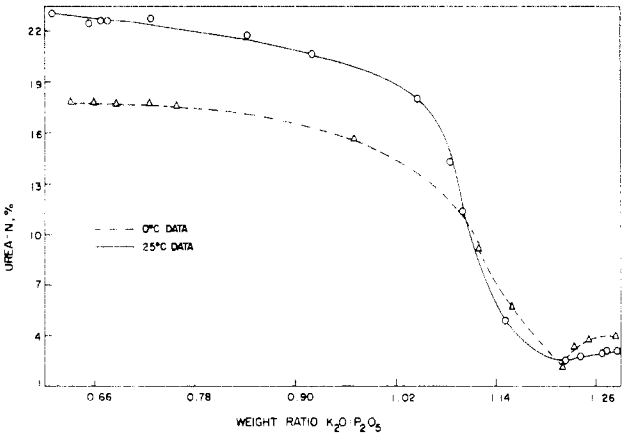

Figure 2. Solubility of urea N in potassium phosphate solutions at 0 and 25 °C.

attained in 9–27 days, and the results are summarized in Table I and plotted in Figures 1 and 2. The coordinates in Figure 1 were chosen to facilitate the comparison of the total plant food (N + P_2O_5 + K_2O) of the saturated solutions at two temperatures. There were two branches of the isotherms over the pH range studied. The solid phases urea and monopotassium orthophosphate were the saturating salts over most of the pH range, with urea and dipotassium orthophosphate being the stable phases in the more alkaline solutions.

The invariant solution had a weight ratio K_2O/P_2O_5 of 1.22 at 0 °C and 1.23 at 25 °C. Both values approximate that described by Ravich (*3*). The maximum total plant food in solution is at the invariant points which increased from 57.5 to 63.6% at 0 and 25 °C, respectively.

Figure 2, which shows the urea nitrogen in solution, is the inverse of Figure 1; i.e., the urea nitrogen is a minimum when the plant food is a maximum and vice versa. In solutions at the higher pH range the solubility of urea is slightly greater at 0 °C than at 25 °C; the deleterious effect of the increasing solubility of potassium phosphates on the solubility of urea is greater than the temperature effect in this pH range.

System $CO(NH_2)_2$–K_2O–H_3PO_4–$H_4P_2O_7$–H_2O. Equilibrium in this system was established in 4–28 days. The results are summarized in Table II and Figures 3 and 4. The coordinates of Figure 3 are the same as in Figure 1 for comparison of the two systems. There were three branches of each isotherm with the saturating phases of the branches being $CO(NH_2)_2$, KH_2PO_4, and $K_2H_2P_2O_7 \cdot 0.5H_2O$; $CO(NH_2)_2$, KH_2PO_4, and $K_3HP_2O_7 \cdot 3H_2O$; and $CO(NH_2)_2$, K_2HPO_4, and $K_3HP_2O_7 \cdot 3H_2O$. One of the invariant solutions had two orthophosphate salts as well as urea and a pyrophosphate salt in equilibrium, while the other was equilibrated with two pyrophosphate salts, urea, and an orthophosphate salt at each temperature. When the temperature was increased to 25 °C, the plant food in solution at constant K_2O/P_2O_5 was increased 4–6% over the entire range.

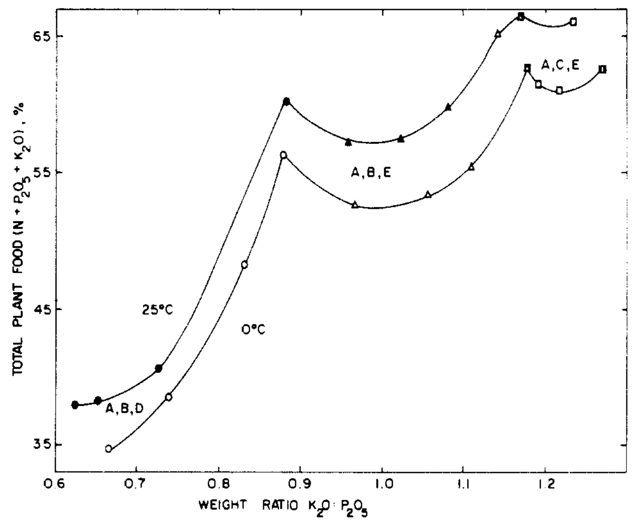

Figure 3. Solubility in the system $CO(NH_2)_2$–K_2O–H_3PO_4–$H_4P_2O_7$–H_2O (saturating solids: A = $CO(NH_2)_2$, B = KH_2PO_4, C = $K_2HPO_4 \cdot 3H_2O$, D = $K_2H_2P_2O_7 \cdot 0.5H_2O$, E = $K_3HP_2O_7 \cdot 3H_2O$).

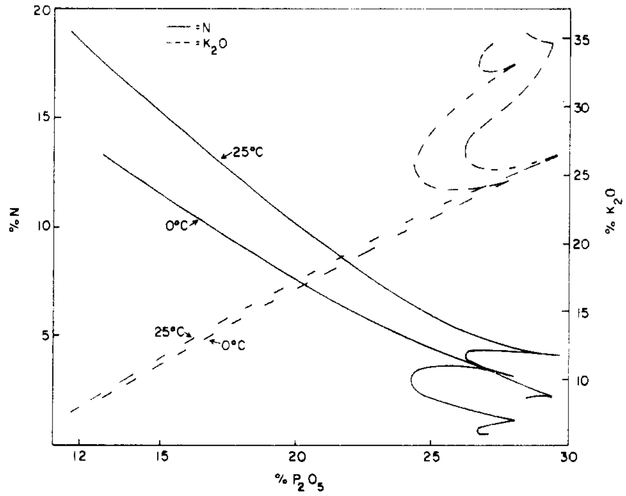

Figure 4. Solubility of urea N and K_2O in solutions containing ortho- and pyrophosphates.

Figure 4 shows the relationship of N and K_2O contents to the P_2O_5 content of the saturated solutions. As the P_2O_5 increases, the nitrogen in solution decreases and the potassium increases. At 25 °C and in the pH range in which most liquid plant foods are produced (pH 5–7), the nitrogen content varies from 4 to 17% and the grades of these solutions vary from 4–30–26 to 17–13–9. The most concentrated solution in this pH range is the invariant solution containing di- and tripotassium pyrophosphate and has 55 and 60% plant food at 0 and 25 °C, respectively. The mutual salting-out effect between urea and potassium phosphate salts is very evident from Figure 4.

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