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An Investigation of the Polythermal Diagram of the Ternary System H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$ between 0 and 25°C

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Isotherms at 0, 10, and 25°C of the H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$ ternary system have been established by conductivity measurements in the considered temperature range (0–25°C). Tracing the polythermal diagram has allowed to determine the existence domains of the solid phases: $(NH_4)_2HPO_4 \cdot 2H_2O$, $(NH_4)_2HPO_4$, and $(NH_4)_2SO_4$. © 2001 Academic Press

1. INTRODUCTION

Storage using latent melting heat is an attractive area for energy saving. The selection of the materials requires often polythermal diagram determinations. Phosphates and sulfates have been particularly investigated due to potential applications.

In such an approach we describe here the polythermal diagram of the H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$ ternary system. To our knowledge this system had not been previously studied.

Isotherms have been determined at 0, 10, and 25°C. The measurements have been carried out by conductivity whose principle and measurement device have been pointed out in previous papers (1–9). The isotherms have been represented using Janecke coordinates. They are defined as $X((NH_4)_2HPO_4) = m((NH_4)_2HPO_4)/M$, $Y((NH_4)_2SO_4) = m((NH_4)_2SO_4)/M$, and $Z(H_2O) = m(H_2O)/M$, with $M = m((NH_4)_2HPO_4) + m((NH_4)_2SO_4)$.

2. RESULTS

2.1. *Isotherm at 0°C*

The solubility values obtained at 0°C are reproduced in Table 1. The corresponding isotherm is showed in Fig. 1. At 0°C, two stoichiometric solid phases are in equilibrium with saturated solutions $(NH_4)_2HPO_4 \cdot 2H_2O$ (AP_2) and $(NH_4)_2SO_4$ (AS_0). A monovariant point (I) whose composition is obtained by extrapolation of the solubility curves has been determined.

2.2. *Isotherm at 10°C*

The solubility values at 10°C are given in Table 2 and Fig. 2. At this temperature three solid phases are in equilibrium with the solution: $(NH_4)_2HPO_4 \cdot 2H_2O$ (AP_2), $(NH_4)_2HPO_4$ (AP_0), and $(NH_4)_2SO_4$ (AS_0). The isotherm encloses two monovariant points, J and K.

2.3. *Isotherm at 25°C*

The solubility values are given in Table 3. Tracing of this isotherm (Fig. 3) gives evidence of one monovariant point, L.

TABLE 1
Solubility Values at 0°C in the Ternary System H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$

Janecke coordinates			Solid phases in equilibrium with saturated solutions
$X((NH_4)_2SPO_4)$	$Y((NH_4)_2SO_4)$	$Z(H_2O)$	
100.0	0.0	244.8	AP_2
97.5	2.5	244.5	AP_2
90.0	10.0	230.1	AP_2
80.0	20.0	218.5	AP_2
65.0	35.0	200.6	AP_2
50.0	50.0	176.3	AP_2
35.0	65.0	147.0	AP_2
32.5	67.5	141.0	AP_2
30.0	70.0	135.6	AP_2
32.5	67.5	112.6	$AP_2 + AS_0$
30.0	70.0	117.8	$AP_2 + AS_0$
22.5	77.5	111.3	$AP_2 + AS_0$
20.0	80.0	98.5	$AP_2 + AS_0$
22.5	77.5	124.7	AS_0
20.0	80.0	126.6	AS_0
15.0	85.0	131.6	AS_0
0.0	100.0	144.1	AS_0
Coordinates of the monovariant point I obtained by extrapolation			
25.0	75.0	122.8	$AP_2 + AS_0$

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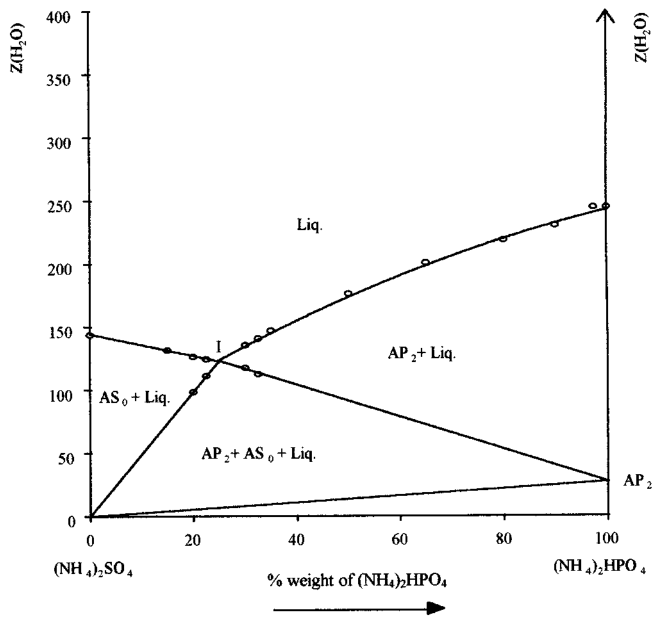

FIG. 1. Isotherm at 0°C of the ternary system H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$.

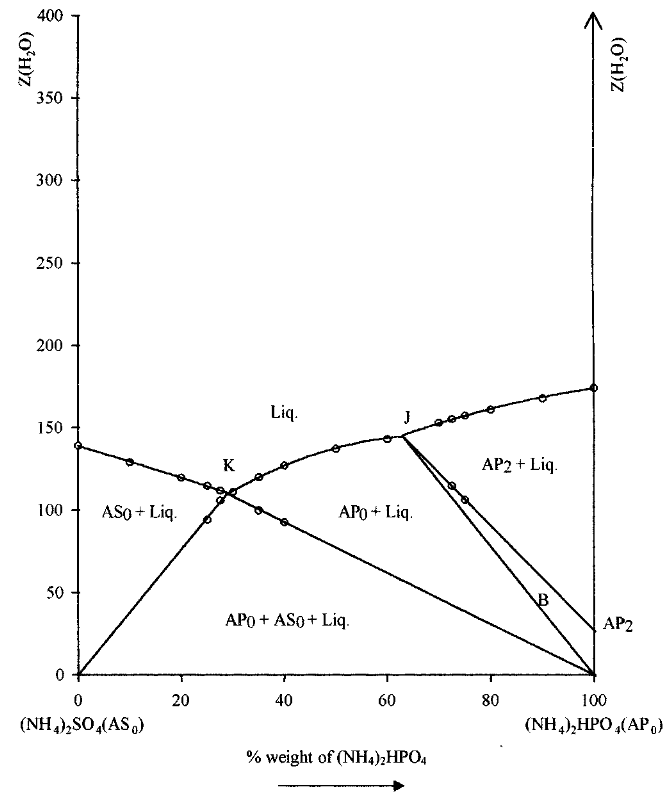

FIG. 2. Isotherm at 10°C of the ternary system H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$. B = AP_2 + AP_0 + liq.

TABLE 2
Solubility Values at 10°C in the Ternary System H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$

Janecke coordinates			Solid phases in equilibrium with saturated solutions
$X((NH_4)_2HPO_4)$	$Y((NH_4)_2SO_4)$	$Z(H_2O)$	
100.0	0.0	174.2	AP_2
90.0	10.0	168.0	AP_2
80.0	20.0	161.3	AP_2
75.0	25.0	157.5	AP_2
72.5	27.5	155.3	AP_2
70.0	30.0	153.2	AP_2
75.0	25.0	106.4	$AP_2 + AP_0$
72.5	27.5	114.9	$AP_2 + AP_0$
40.0	60.0	93.0	$AP_0 + AS_0$
35.0	65.0	100.2	$AP_0 + AS_0$
27.5	72.5	106.1	$AP_0 + AS_0$
25.0	75.0	94.5	$AP_0 + AS_0$
60.0	40.0	143.3	AP_0
50.0	50.0	137.5	AP_0
40.0	60.0	127.2	AP_0
35.0	65.0	120.1	AP_0
30.0	70.0	111.3	AP_0
27.5	72.5	112.0	AS_0
25.0	75.0	115.0	AS_0
20.0	80.0	120.1	AS_0
10.0	90.0	129.3	AS_0
0.0	100.0	139.2	AS_0
Coordinates of the monovariant points J and K obtained by extrapolation			
J 63.0	37.0	145.0	$AP_0 + AP_2$
K 29.1	70.9	110.1	$AP_0 + AS_0$

TABLE 3
Solubility Values at 25°C in the Ternary System H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$

Janecke coordinates			Solid phases in equilibrium with saturated solutions
$X((NH_4)_2HPO_4)$	$Y((NH_4)_2SO_4)$	$Z(H_2O)$	
100.0	0.0	146.2	AP_0
90.0	10.0	143.4	AP_0
80.0	20.0	139.1	AP_0
70.0	30.0	133.8	AP_0
60.0	40.0	128.7	AP_0
50.0	50.0	121.3	AP_0
41.9	58.1	112.5	AP_0
35.0	65.0	105.0	AP_0
40.0	60.0	89.8	$AP_0 + AS_0$
35.0	65.0	96.0	$AP_0 + AS_0$
27.5	72.5	89.5	$AP_0 + AS_0$
25.0	75.0	81.1	$AP_0 + AS_0$
30.0	70.0	103.5	AS_0
27.5	72.5	106.5	AS_0
25.0	75.0	107.3	AS_0
20.0	80.0	112.1	AS_0
10.0	90.0	121.3	AS_0
0.0	100.0	131.2	AS_0
Coordinates of the monovariant point L obtained by extrapolation			
31.8	68.2	101.8	$AP_0 + AS_0$

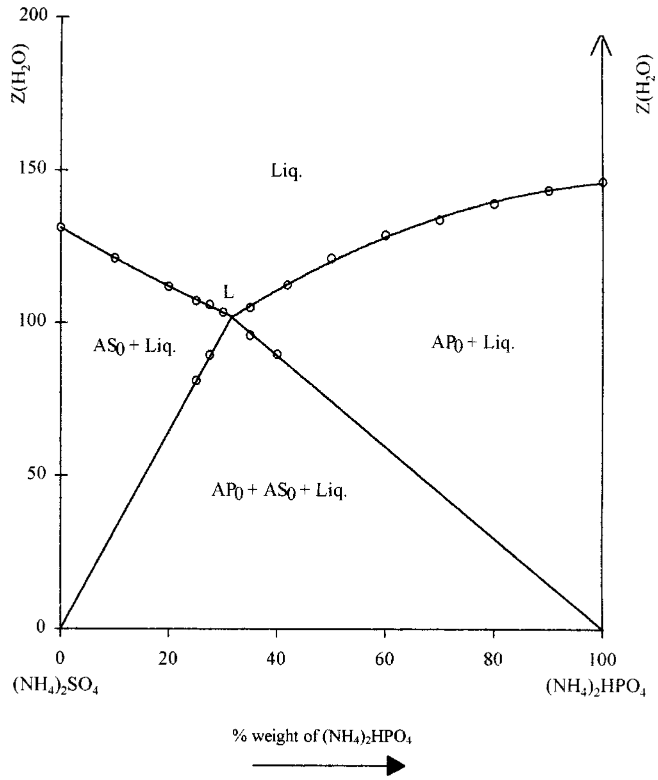

FIG. 3. Isotherm at 25°C of the ternary system H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$.

2.4. *Polythermal Diagram*

Drawing of the polythermal diagram for the ternary system by projection onto the composition plan has made it possible to delimit the existence domains of each solid phase present in the considered temperature range (0–25°C). The convergence of monovariant lines has led to the determination of an invariant transformation [T] (Fig. 4) between 0 and 10°C. The equilibrium reaction can be written

$$(NH_4)_2HPO_4 \cdot 2H_2O + (NH_4)_2SO_4 \leftrightarrows (NH_4)_2HPO_4 + \text{liq.} \qquad [T]$$

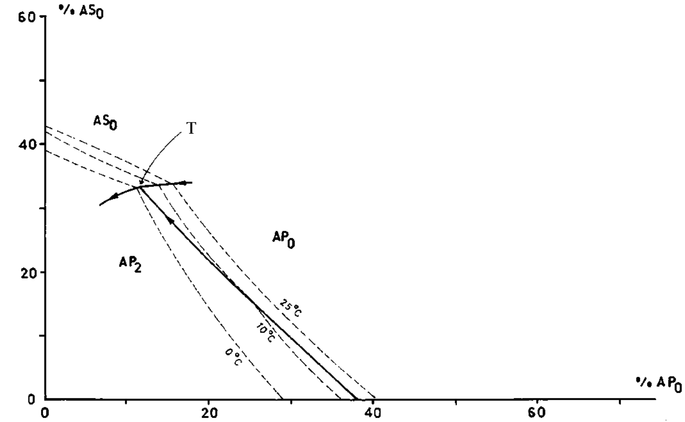

FIG. 4. Projection of the polythermal diagram of the H_2O-$(NH_4)_2HPO_4$-$(NH_4)_2SO_4$ system onto the composition plan.

3. CONCLUSION

The 0, 10, and 25°C isotherms of the H_2O–$(NH_4)_2HPO_4$–$(NH_4)_2SO_4$ ternary system have been established by conductivity measurements. On the basis of the isotherms, we have traced the part of the polythermal diagram relative to the temperature range situated between 0 and 25°C. The projection of the polythermal diagram onto the composition plan shows the existence of an invariant transformation between 0 and 10°C.

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