Thermodynamics of System H_2O-Na_2HPO_4-$(NH_4)_2HPO_4$ at 25°C

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Solubility measurements and vapor-pressure measurements are reported for the ternary system H_2O–Na_2HPO_4–$(NH_4)_2HPO_4$. From these, the phase diagram for the system is constructed; the double salt $NaNH_4HPO_4 \cdot 4H_2O$ is congruently soluble at 25°C. The excess free energies of mixing of the constituent salts are small and negative.

Stercorite ($NaNH_4HPO_4 \cdot 4H_2O$) is a water-soluble mineral found in guano deposited on islands off the coasts of South-West Africa and Peru (*5*). In view of its importance as a component in fertilizers, a study was made of this compound and of its two constituent salts, Na_2HPO_4 and $(NH_4)_2HPO_4$. The water solubility of each salt has been reported (*4*), but the only other thermodynamic data are the osmotic and activity coefficients for the sodium salt reported by Scatchard and Breckenridge (*7*). The purpose of the present study is to complete the solubility and free energy data for the system at 25°C.

Experimental

Reagents. The AR grade phosphates were recrystallized once from water. The Na_2HPO_4 was dried at 105°C, and the $(NH_4)_2HPO_4$ was dried in vacuum over H_2SO_4 at room temperature. Any attempt to dry the ammonium salt at temperatures much above room temperature resulted in a loss of ammonia, as determined by analysis for the ammonium ion. The isopiestic reference salt was dried NaCl.

Method. The solubilities for the ternary system were determined by conventional measurements on aliquots of saturated solutions. The ammonium salt was determined gravimetrically as ammoniumtetraphenylboron (*8*), and the total salt content was determined by evaporation in vacuum over H_2SO_4 to constant weight. The sodium salt was then estimated by difference. The system contains two congruent points of mutual saturation with two salts (eutonics). The composition of these eutonics and of the solid phases in equilibrium with them were checked by an isopiestic method (*6*).

The procedure consists of equilibrating unsaturated aqueous mixtures of the two salts through the vapor phase with a control solution having the composition of the eutonic and containing a large excess of the solid salts in equilibrium with it. Water distills from the unsaturated mixtures until one of the equilibrium solid phases precipitates out and continues to distill until the solution becomes just saturated with the second solid phase, at which point the overlying solution will have the same composition (and the same vapor pressure) as that of the eutonic, and the distillation will stop.

The apparent compositions of these solutions, which can be determined by weighing, must lie on straight lines joining the eutonic composition and the compositions of the solid phases in equilibrium with it. The intersection of the pair of lines associated with each eutonic can be used to fix the composition of that eutonic.

The free energies of mixing unsaturated solutions of the phosphates were also determined isopiestically, by a previously described procedure (*1*, *2*). Mixed solutions were equilibrated through the vapor phase with a reference solution of NaCl, whose water activity, a_w, is known as a function of composition. A knowledge of how the water activity over a solution depends on solution composition is sufficient to permit calculation of the free energy change on mixing the solutions.

Results and Discussion

The solubilities for the system are given in Table I, and the smoothed ternary solubility diagram is shown in Figure 1. The single salt solubilities were 10.4 and 41.5 wt % for the sodium and ammonium salts, respectively. The corresponding literature values (*4*) ranged from 10.3 to 10.8 wt % and from 41.0 to 42.3 wt %. The system is characterized by two eutonic points whose existence was verified by use of the isopiestic technique described earlier (*6*). The solid phases in equilibrium with the eutonic solutions were not examined, but their compositions were deduced from the isopiestic tie lines given in Figure 1 (*4*, *6*).

The osmotic and activity coefficients of the single salt solutions and the excess free energies of mixing of the two-salt solutions were calculated from isopiestic measurements on unsaturated, and, where this was possible, on supersaturated solutions (*2*). The isopiestic compositions for these solutions are shown in Table II. The first column in each set gives the molality of the sodium chloride solution in equilibrium with the other solutions, the next two columns give the molalities of the two phosphate salts, and the fourth column gives the osmotic coefficient, ϕ, of the phosphate salt or mixture on that line. The last column gives a deviation function (see Nomenclature)

$$(\phi - y_A \phi_A{}^\circ - y_B \phi_B{}^\circ)/y_A y_B I$$

which is used to calculate the excess free energy of mixing as described later.

The osmotic coefficients for the two single phosphate solutions were smoothed by use of the curve fitting equa-

Table I. Solubilities in Stercorite System at 25°C

Na_2-HPO_4, wt %	$(NH_4)_2$-HPO_4, wt %	Solid phase
10.4	0.0	$Na_2HPO_4 \cdot 12H_2O$
12.3	2.0	
16.0	3.3 (E_1)	$Na_2HPO_4 \cdot 12H_2O + NaNH_4HPO_4 \cdot 4H_2O$
15.6	4.6	$NaNH_4HPO_4 \cdot 4H_2O$
13.6	5.9	
11.3	7.0	
10.5	8.9	
9.7	12.8	
9.1	14.4	
8.2	18.0	
8.4	20.4	
8.0	25.5	
7.8	31.2	
8.5	40.1 (E_2)	$NaNH_4HPO_4 \cdot 4H_2O + (NH_4)_2HPO_4$
7.1	41.3	$(NH_4)_2HPO_4$
4.8	40.8	
1.8	41.3	
0.0	41.5	

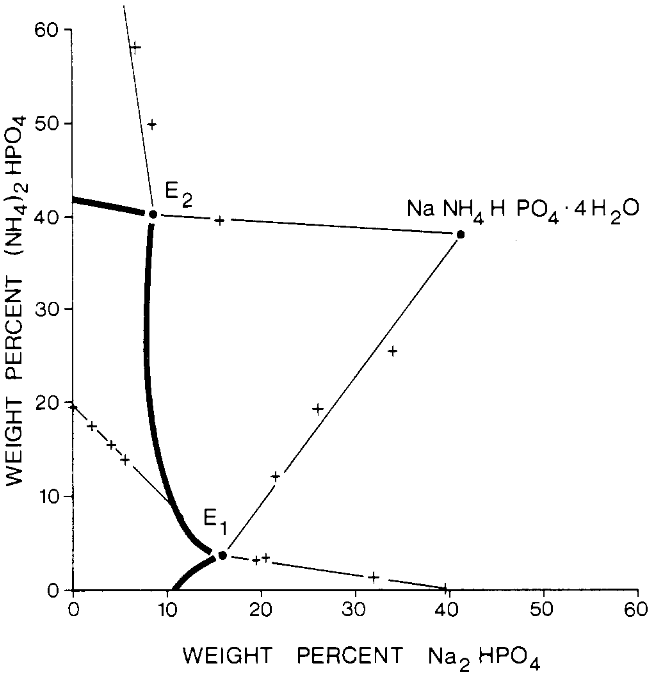

Figure 1. Solubility diagram for stercorite system at 25°C
▬ Solubility curve
— Tie line
+ Isopiestic tie points

Table II. Isopiestic Compositions of Phosphates at 25°C

m_{NaCl}	$m_{Na_2HPO_4}$	$m_{(NH_4)_2HPO_4}$	ϕ	$\Delta/y_A y_B I$
0.1134	...	0.1058	0.6652	...
0.1661	...	0.1572	0.6524	...
0.2020	...	0.1951	0.6381	...
0.2908	0.2349	...	0.7606	...
	0.1660	0.1042	0.6612	−0.077
	0.1266	0.1551	0.6342	−0.079
	...	0.3044	0.5868	...
0.4818	0.4265	...	0.6933	...
	0.2903	0.1822	0.6258	−0.010
	0.2203	0.2699	0.6033	−0.002
	...	0.5305	0.5574	...
0.6798	0.6518	...	0.6434	...
	0.4767	0.2406	0.5847	−0.018
	0.2487	0.5318	0.5373	−0.010
	...	0.8344	0.5026	...
0.7584	0.7480	...	0.6269	...
	0.4413	0.3889	0.5648	+0.006
	0.4223	0.4128	9.5615	+0.006
	...	0.9285	0.5050	...
0.8455	0.8565	...	0.6122	...
	0.5187	0.4571	0.5373	−0.011
	0.4875	0.4853	0.5390	−0.010
	...	1.1074	0.4735	...
0.9720	...	...	...	...
	0.7450	0.3630	0.5464	−0.003
	0.3881	0.8299	0.4973	−0.004
	...	1.3122	0.4616	...
1.084	1.1729	...	0.5784	...
	0.7286	0.6419	0.4950	−0.017
	0.6976	0.6819	0.4918	−0.017
	...	1.5716	0.4317	...
1.194	1.3290	...	0.5643	...
	0.9836	0.4964	0.5066	−0.013
	0.5183	1.1084	0.4610	−0.016
	...	1.7005	0.4410	...
1.273	1.441	...	0.5571	...
	1.145	0.561	0.4706	−0.035
	0.515	1.226	0.4613	−0.008
1.476	1.734	...	0.5420	...
1.533	...	2.345	0.4175	...
1.748	2.121	...	0.5328	...
	...	2.792	0.4047	...
1.886	...	3.107	0.3954	...
2.183	2.605	0.530	0.4613	−0.049
	2.235	1.094	0.4345	−0.032
	1.021	2.433	0.4186	−0.013
	0.618	2.867	0.4150	−0.008

tion of Lietzke and Stoughton (*3*), and the mean activity coefficients were calculated from the coefficients of the equation. Because many of the solutions were supersaturated with Na_2HPO_4, the concentration range over which we now have data for this salt has been extended from the maximum of 1*m* reported by Scatchard and Breckenridge (*7*) to more than 3*m*. In the concentration range below 1*m*, my osmotic coefficients agreed with theirs to within 0.005, and the standard deviation in the combined results for Na_2HPO_4 was ±0.002 in ϕ.

The osmotic coefficients for the $(NH_4)_2HPO_4$ and for the mixtures showed much larger scatter than this, presumably because of the difficulty of drying this salt without driving off some constituent ammonia. The procedure of drying over H_2SO_4 at a temperature of between 20° and 35° usually gave material containing the theoretical amount of ammonia, but even so, the standard deviation of the fitted osmotic coefficients was ±0.015 for the $(NH_4)_2HPO_4$. The osmotic and activity coefficients for both single salt solutions are listed in Table III; the values for the sodium salt are uncertain by about ±0.5%, and for the ammonium salt they may be uncertain by as much as ±5%. The values are given to three decimal places to reduce rounding errors in interpolation.

The ternary system was treated by a method described previously (*2*). The osmotic coefficients of these mixtures can be expressed by the simple equation

$$\phi = \phi_A^\circ y_A + \phi_B^\circ y_B + y_A y_B \{b_{01} I + b_{02} I^2\} \qquad (1)$$

in which case, the excess free energies of mixing equal amounts of the two single salt solutions at constant ionic strength can be shown to be given by the expression

$$G^E = \tfrac{1}{4} RTI \{b_{01} I + \tfrac{1}{2} b_{02} I^2\} \qquad (2)$$

The coefficients in Equation 1, evaluated graphically, were $b_{01} = -0.005$ and $b_{02} = -0.002$. The set of points at $m \simeq 0.3$ was ignored; the reliability of these measurements becomes poor at low concentrations. These coefficients used in Equation 2 give the free energies of mixing of equal quantities of solutions of equal molalities, and these are given in Table IV.

The solubility and activity data provide enough information to check on the internal consistency of the results. The activity product of the sodium salt at composition E_1 must be the same as that in the binary system. Converting the weight concentrations in Table I to molalities and interpolating activity coefficients from Table III, we have the activity product for $Na_2HPO_4 \cdot 12H_2O$ given by

$$K_A = 4\, m_A{}^3 \gamma_A{}^3 a_w{}^{12} = 4 \times 0.83^3 \times 0.213^3 \times 0.973^{12} = 0.016$$

Using the measured value of $a_w = 0.956$ at E_1 and calculating $\gamma_A = 0.140$ for the mixed salt solution as previously described (*2*) gives

$$K_A = 2.78^2 \times 1.69 \times 0.140^3 \times 0.956^{12} = 0.020$$

Table III. Osmotic and Activity Coefficients for Phosphates at 25°C

	Na_2HPO_4		$(NH_4)_2HPO_4$	
m	$\phi_A°$	$\gamma_A°$	$\phi_B°$	$\gamma_B°$
0.1	0.802	0.467	0.707	0.368
0.3	0.720	0.331	0.596	0.225
0.5	0.670	0.269	0.544	0.171
0.7	0.634	0.232	0.513	0.142
0.9	0.608	0.205	0.490	0.122
1.0	0.596	0.195	0.481	0.115
1.5	0.555	0.158	0.449	0.0895
2.0	0.538	0.137	0.429	0.0746
2.5	0.538	0.124	0.415	0.0647
3.0	0.549	0.115	0.405	0.0575
3.5	0.563	0.105	0.397	0.0520

Table IV. Excess Free Energies of Mixing Na_2HPO_4 and $(NH_4)_2HPO_4$ at Constant Ionic Strength in J kg^{-1}

I	1	2	3	4	5	6
G^E	−4	−17	−45	−90	−155	−245

The agreement between the two values leaves something to be desired, but in view of the difficulty of working with the volatile ammonium salt, it is probably about all that can be expected. In fact, an error of about 1 wt % in the solubilities would account for most of the discrepancy.

It is not possible to extend the same kind of calculation to the eutonic at E_2 because of lack of data for the high ionic strength of the mixture (about 21).

Nomenclature

ϕ = molal osmotic coefficient of ternary mixture = $-55.51 \ln a_w/3\,(m_A + m_B)$ where a_w is the water activity over the solution, and m_A and m_B are the molalities of the two phosphates
$\phi_A°, \phi_B°$ = osmotic coefficients of single salt solutions of Na_2HPO_4 and $(NH_4)_2HPO_4$, respectively, at the same molality as the mixture
y_A, y_B = molality fraction of each salt in the mixture
I = ionic strength of a solution assuming each salt to be a 1-2 electrolyte
γ_A, γ_B = mean activity coefficients of Na_2HPO_4 and $(NH_4)_2HPO_4$ in ternary mixture
$\gamma_A°, \gamma_B°$ = mean activity coefficients of salts in their binary solutions

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Correction

In the article, "Binary Diffusion Coefficients of *n*-Pentane in Gases," by Minoru Nagasaka [*J. Chem. Eng. Data*, **18** (4), 388 (1973)], two lines were omitted in the abstract and two lines were printed twice. The abstract should read as follows:

The Stefan method was used to measure the binary gaseous diffusion coefficients of *n*-pentane (*n*Pe) in hydrogen, helium, nitrogen, air, and argon at 1 atm pressure and a temperature from −15° to 25°C at intervals of 5°C. The diffusion coefficient of each system at 25°C was as follows: *n*Pe–H_2, 0.3404 ± 0.0009 cm^2/sec; *n*Pe–He, 0.3044 ± 0.0003 cm^2/sec; *n*Pe–N_2, 0.0885 ± 0.0001 cm^2/sec; *n*Pe–air, 0.0877 ± 0.0002 cm^2/sec; and *n*Pe–Ar, 0.0792 ± 0.0007 cm^2/sec. The temperature exponent for each system lay between 1.778 and 1.971, in good agreement with the predicted values based upon the Lennard-Jones force constants in the Chapman-Enskog approximate kinetic theory.