The System Ammonia–Pyrophosphoric Acid–Water at 0° and 25° C.

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Phase relationships in the system NH_3–$H_4P_2O_7$–H_2O over the pH range 4 to 8 were determined at 0° and 25° C. At 0° C., the saturating phases are $(NH_4)_2H_2P_2O_7$, $(NH_4)_3HP_2O_7 \cdot H_2O$, and $(NH_4)_4P_2O_7 \cdot H_2O$. These three compounds and $(NH_4)_4P_2O_7$ are the saturating phases at 25° C.

AMMONIUM polyphosphate fertilizers, which are mixtures of salts of ortho-, pyro-, and more highly condensed phosphoric acids, are prepared by ammoniation of superphosphoric acid (*6*, *7*), and they are finding increasing acceptance. As a part of a study of these materials, measurements were made at 0° and 25° C. of solubility in the system NH_3–$H_4P_2O_7$–H_2O over the pH range 4 to 8.

The ammonium pyrophosphates and their solutions were prepared by ammoniation and vacuum evaporation of 0.3*N* pyrophosphoric acid, that was prepared by ion exchange from solutions of recrystallized tetrasodium pyrophosphate. To minimize hydrolysis of the pyrophosphate, all operations were carried out at temperatures below 10° C.

Table I. The System NH_3–$H_4P_2O_7$–H_2O

Liquid Phase			
Composition, %			
N	P_2O_5	pH	Solid Phase
			Results at 0° C.
4.83	22.59	. . .	$(NH_4)_2H_2P_2O_7$
7.66	30.74	4.80	$(NH_4)_2H_2P_2O_7$
8.23	32.24	4.97	$(NH_4)_2H_2P_2O_7$
8.96	34.18	5.09	$(NH_4)_3HP_2O_7 \cdot H_2O + (NH_4)_2H_2P_2O_7$
9.05	31.02	5.81	$(NH_4)_3HP_2O_7 \cdot H_2O$
9.24	30.88	. . .	$(NH_4)_3HP_2O_7 \cdot H_2O$
10.04	31.42	. . .	$(NH_4)_3HP_2O_7 \cdot H_2O$
10.33	32.03	6.50	$(NH_4)_4P_2O_7 \cdot H_2O + (NH_4)_3HP_2O_7 \cdot H_2O$
9.26	27.36	6.88	$(NH_4)_4P_2O_7 \cdot H_2O$
7.75	20.65	7.80	$(NH_4)_4P_2O_7 \cdot H_2O$
			Results at 25° C.
6.11	28.85	3.51	$(NH_4)_2H_2P_2O_7$
8.33	35.34	4.40	$(NH_4)_2H_2P_2O_7$
9.52	38.89	4.66	$(NH_4)_2H_2P_2O_7$
11.05	42.39	4.84	$(NH_4)_3HP_2O_7 \cdot H_2O$
10.69	40.27	5.05	$(NH_4)_3HP_2O_7 \cdot H_2O$
10.49	38.52	5.30	$(NH_4)_3HP_2O_7 \cdot H_2O$
10.42	37.21	5.75	$(NH_4)_3HP_2O_7 \cdot H_2O$
10.61	36.22	5.91	$(NH_4)_3HP_2O_7 \cdot H_2O$
10.61	35.81	6.05	$(NH_4)_3HP_2O_7 \cdot H_2O$
11.29	35.99	. . .	$(NH_4)_3HP_2O_7 \cdot H_2O$
11.55	36.60	6.26	$(NH_4)_3HP_2O_7 \cdot H_2O + (NH_4)_4P_2O_7$
11.14	34.93	6.40	$(NH_4)_4P_2O_7$
11.13	35.10	6.43	$(NH_4)_4P_2O_7$
11.12	35.12	6.42	$(NH_4)_4P_2O_7$
11.05	34.62	6.42	$(NH_4)_4P_2O_7$
10.86	33.45	. . .	$(NH_4)_4P_2O_7 \cdot H_2O + (NH_4)_4P_2O_7$
10.52	31.82	6.79	$(NH_4)_4P_2O_7 \cdot H_2O$
9.79	28.63	7.02	$(NH_4)_4P_2O_7 \cdot H_2O$
9.00	24.86	7.35	$(NH_4)_4P_2O_7 \cdot H_2O$
8.53	22.67	7.95	$(NH_4)_4P_2O_7 \cdot H_2O$
8.26	21.27	8.20	$(NH_4)_4P_2O_7 \cdot H_2O$

In preparations of the salts, $(NH_4)_2H_2P_2O_7$ was obtained as orthorhombic plates by evaporation to dryness of a dilute pyrophosphate solution initially at pH 4. Compound $(NH_4)_3HP_2O_7 \cdot H_2O$ was obtained as relatively large triclinic plates by removing about 90% of the water by evaporation of a dilute solution initially at pH 7.5, raising the pH of the concentrated solution from 5.5 to 6.2 with ammonium hydroxide, and removing the rest of the water slowly with Drierite in a desiccator. Compounds $(NH_4)_4P_2O_7$ (monoclinic tablets) and $(NH_4)_4P_2O_7 \cdot H_2O$ (monoclinic rods) were prepared by ammoniating similarly concentrated solutions to pH 9, and then allowing the solutions to evaporate slowly at 30° or 15° C., respectively, in an atmosphere of ammonia.

In the solubility study, the complexes, in capped glass tubes, were equilibrated with occasional manual agitation in a cold room at 0° ± 0.5° C. or in a water bath at 25° ± 0.02° C. The approach to equilibrium was followed by periodic petrographic and x-ray examinations of the solid phases, and by determinations of composition and pH of the liquid phases.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*5*), and nitrogen was determined by distillation of ammonia with sodium hydroxide; pH was measured with a glass electrode in a commercial meter. Examination by one-dimensional paper chromatography (*3*) showed no significant hydrolysis of the pyrophosphate in the equilibrations.

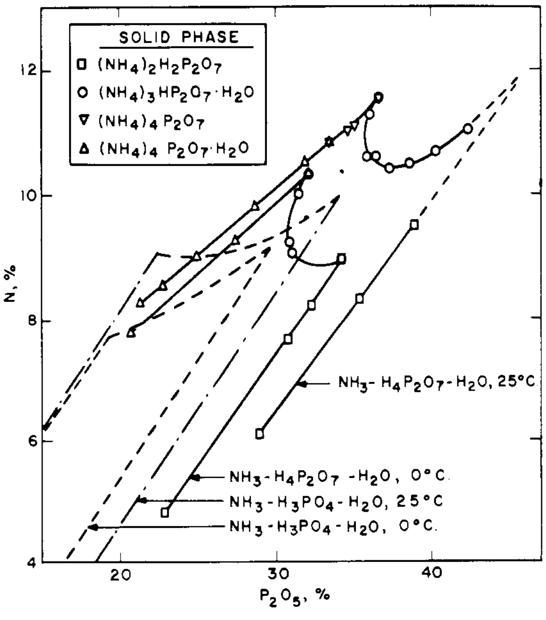

Figure 1. The system NH_3–$H_4P_2O_7$–H_2O

Equilibrium was obtained in 14 to 84 days. The results are listed in Table I and plotted, together with data for the system NH_3–H_3PO_4–H_2O (*1, 2, 4*), in Figure 1. Over the pH range 4 to 8, the saturating phases at 0° C. are $(NH_4)_2 \cdot H_2P_2O_7$, $(NH_4)_3HP_2O_7 \cdot H_2O$, and $(NH_4)_4P_2O_7 \cdot H_2O$. These three compounds and $(NH_4)_4P_2O_7$ are the saturating phases at 25° C. Both invariant points at 0° C. were determined. Two of the three invariant points at 25° C. were determined; the third, representing the solution saturated with $(NH_4)_2 \cdot H_2P_2O_7$ and $(NH_4)_3HP_2O_7 \cdot H_2O$, was estimated to contain 11.5% N and 44% P_2O_5 and to have a pH of 4.7.

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Thermodynamic Properties of Molten Solutions of $MgCl_2$–KCl, $MgCl_2$–NaCl, and $MgCl_2$–KCl–NaCl

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Thermodynamic properties of molten magnesium chloride–alkali metal chloride solutions have been evaluated from e.m.f. data obtained with galvanic cells of the type

$$MgBi(l) \mid MgCl_2(N_1)MCl(N_2)(l) \mid \text{graphite}, Cl_2(g)$$

where MCl represents the alkali metal chloride. Excess functions have been calculated for $MgCl_2$–KCl and $MgCl_2$–KCl–NaCl systems at 800° C. and for the $MgCl_2$–NaCl system at 825° C. The experimental values obtained for the excess partial molar free energy of $MgCl_2$ in these solutions have been compared with values calculated on the basis of the Temkin theory of molten salts. For the calculation, a model involving the existence of the complex ion $MgCl_4^{-2}$ was assumed. The agreement between experimental and calculated values is taken as evidence that the model can be used to interpret the systems studied.

THE thermodynamic properties of molten salt solutions are often indicative of strong deviations from ideality which are generally attributed to chemical interaction of the components to form relatively stable complex ions. The investigation reported in this paper consists of an evaluation and an interpretation of the thermodynamic properties of melts containing magnesium chloride and alkali metal chlorides.

Various experimental methods have been used by other workers to study the properties of chloride melts containing $MgCl_2$. These include measurement of density (*5. 16*), electrical conductivity (*2, 4, 16, 18, 26*), viscosity (*3*), surface tension (*8*), transference number (*1*), electromotive force (*22, 23*), and vapor pressure (*24*).

Many of the studies have provided evidence of the existence of mixed compounds and complex ions of magnesium. For example, the phase diagram of the $MgCl_2$–KCl system has been interpreted in terms of the formation of the solid compounds $MgCl_2$–KCl and $MgCl_2$–2KCl (*17, 19*), and the phase diagram of the $MgCl_2$–NaCl system has been similarly interpreted in terms of the compounds $MgCl_2$–NaCl and $MgCl_2$–2NaCl (*20*). Flood and coworkers (*11-13*) interpreted the shape of the liquidus curve in the phase diagram of the $MgCl_2$–KCl system as indicating the presence of the $MgCl_4^{-2}$ ion in the liquid phase. Flood and Urnes (*14*) propose that the compound $KMgCl_3$ undergoes the following dissociation on melting:

$$2KMgCl_3 \rightleftarrows 2K^+ + Mg^{+2} + MgCl_4^{-2} + 2Cl^-.$$

Other reported work relative to the solution thermodynamics of melts containing $MgCl_2$ includes a study (*29*) of the equilibrium:

$$MgCl_2(I) + \tfrac{1}{2}\,O_2(g) \rightleftarrows MgO(s) + \tfrac{1}{2}\,Cl_2(g).$$

In the investigation reported in this paper, electrochemical cells of the type

$$MgBi(l) \mid MgCl_2(N_1)MCl(N_2)(l) \mid \text{graphite}, Cl_2(g)$$

were employed. For comparison, the cells used by Markov (*22, 23*) were of two types, namely,

$$Mg \mid MgCl_2\text{–}KCl \text{ eut.} \mid \text{porcelain powder membrane} \mid MgCl_2(N_1)KCl(N_2 \mid Mg$$

and

$$Mg(l) \mid MgCl_2\text{–}KCl(l) \mid \text{graphite}, Cl_2(g).$$

The results obtained by Markov from the two cells were not in good agreement.

The use of galvanic cells for the study of high temperature molten chloride solutions is often limited by the solubility of metals in their molten chlorides. Metal-metal halide solubility has been investigated rather extensively by

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