Hansen et al. (*3*) summarized data for the thermal conductivity of plasticized polymers. The thermal conductivity was proportional to the weight fraction of polymer. This conclusion for a solid solution is in agreement with the present work.

Hansen et al. (*3*) also found the thermal conductivity of low-molecular-weight polystyrene to increase as much as twofold with increasing molecular weight. In the present work a change in concentration of polystyrene in toluene can be thought of as increasing the average molecular weight of the solution.

Ueberreiter and Nens (*8*) studied the thermal conductivity of distyrene and polystyrene melts. They postulated that the influence of structure was not as important in a melt as in a solid because the polymer chains were free to experience a twisting type of vibration. The same postulate would explain why polystyrene has no more effect on the thermal conductivity when in solution in toluene than has been observed in this work.

Conclusions

Although the effect of structure on thermal conductivity can be important in solids (e.g., the method of production of polymers and the allotropic forms of carbon), the effect of structure in liquids can only be detected by precise methods. However, the thermal conductivity of polystyrene in toluene solutions does increase with polystyrene concentration. The dependence of thermal conductivity on concentration at 30°C can be expressed as a linear function.

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Nomenclature

c = concentration, grams of polystyrene per liter of solution
λ = thermal conductivity of solution, W/m/°C
λ_t = thermal conductivity of toluene, W/m/°C

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Solubility in System NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O at 25°C

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Measurements were made of the composition of solution in the system NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O at 25°C in which solid phases of all three phosphate species are in equilibrium over the pH range 4.6–7.1. Solubility expressesd as percent ($N + P_2O_5$) ranged from 1.5 to 4.7% higher at 25° than at 0°C where the isotherms overlap. The most concentrated solution contained 12.1% N and 46.6% P_2O_5 and had a pH of 5.0.

Previous studies of the properties of ammonium polyphosphates (*1–6*) have been concerned mainly with their saturated solutions at 0°C. In this study the phase relationships in the system ammonia–orthophosphoric acid–pyrophosphoric acid–tripolyphosphoric acid–water at 25°C were determined in regions where solid phases of all three phosphate species are in equilibrium over the pH range 4.6–7.1.

Experimental

The equilibration mixtures were prepared from reagent grade mono- and diammonium orthophosphates and from di-, tri-, and tetraammonium pyrophosphates, and tetra- and pentaammonium tripolyphosphates that were crystallized from liquid fertilizers produced by ammoniation of 80% P_2O_5 electric-furnace polyphosphoric acid (*11*). Stock solutions of the ammonium orthophosphates were prepared by saturating distilled water at 40°C with the respective salts and cooling to room temperature. A portion of the ammonium orthophosphate solution at the desired pH was saturated with the ammonium pyrophosphate salt that is stable at that pH. These orthophosphate–pyrophosphate solutions were readjusted to the desired pH with reagent grade 85% orthophosphoric acid or with gaseous ammonia. The solutions then were saturated with the ammonium tripolyphosphate salt that is stable at the pH of the respective solutions. The different ammoniated salts of ortho-, pyro-, and tripolyphosphoric acid were selected from the ternary systems at 25°C (*1, 2, 9*).

The solutions in plastic bottles were rotated four times per minute in a water bath at 25° ± 0.05°C. The approach to equilibrium was followed by periodic petrographic examinations of the solid phases (*8*) and by determinations of the composition and pH of the liquid phases. When examination of the wet solids indicated the absence of any of the three phosphate species, a few grams of the missing species were added, and equilibration was continued.

Phosphorus was determined gravimetrically as quinolinium molybdophosphate (*10*), and nitrogen was determined by distillation of ammonia with sodium hydroxide; pH measurements on the supernatant liquid phases were made with a commercial meter and a glass electrode. The phosphate distribution was determined by one-dimensional paper chromatography (*7*).

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Table I. System NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O at 25°C

	Composition, %		Distribution, % of total P_2O_5			
pH	N	P_2O_5	Ortho	Pyro	Tri-poly	Solid[a] phase
7.08	11.70	33.84	34	35	31	B, E, G
6.55	12.10	36.95	33	44	23	B, E, G
6.11	12.60	40.84	33	51	16	B, D, E, G
6.03	12.51	41.37	35	49	16	B, D, G
5.85	12.49	42.44	38	45	17	B, D, G
5.72	12.47	42.77	40	42	18	A, B, D, G
5.65	12.35	43.09	37	43	20	A, D, G
5.33	12.09	44.00	29	45	26	A, D, G
5.20	12.04	44.52	24	43	33	A, D, G
5.22	12.12	45.14	27	42	31	A, D, G
5.10	12.13	45.72	21	43	36	A, D, G
4.98	12.04	45.89	20	45	35	A, D, G
4.99	12.09	46.59	21	43	36	A, D, F, G
4.80	11.94	46.37	19	43	38	A, C, F
4.74	11.75	46.11	18	40	42	A, C, F
4.60	11.36	45.59	18	35	47	A, C, F

[a] Identified by microscopic examination: A = $(NH_4)H_2PO_4$, B = $(NH_4)_2HPO_4$, C = $(NH_4)_2H_2P_2O_7$, D = $(NH_4)_3HP_2O_7{\cdot}H_2O$, E = $(NH_4)_4P_2O_7$, F = $(NH_4)_4HP_3O_{10}$, G = $(NH_4)_5P_3O_{10}{\cdot}H_2O$.

Results

Equilibrium was established in 14–40 days. The results of 16 saturated solutions are summarized in Table I and plotted in Figure 1, which includes the 0°C isotherm of the same system (*3*). The coordinates of Figure 1 were selected to facilitate comparison of the total plant-nutrient contents, N + P_2O_5, of the saturated solutions at 0° and 25°C.

The isotherm at 25°C of the quinary system over the experimental range of pH comprises four branches representing solutions saturated, respectively, with $(NH_4)_2HPO_4$, $(NH_4)_4P_2O_7$, and $(NH_4)_5P_3O_{10}{\cdot}H_2O$; $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7{\cdot}H_2O$, and $(NH_4)_5P_3O_{10}{\cdot}H_2O$; $NH_4H_2PO_4$, $(NH_4)_3HP_2O_7{\cdot}H_2O$, and $(NH_4)_5P_3O_{10}{\cdot}H_2O$; and $NH_4H_2PO_4$, $(NH_4)_2H_2P_2O_7$, and $(NH_4)_4HP_3O_{10}$. Three invariant solutions were noted, and the properties of these solutions are shown in Table I. A fourth invariant point representing a solution saturated with $NH_4H_2PO_4$, $(NH_4)_2H_2P_2O_7$, $(NH_4)_3HP_2O_7{\cdot}H_2O$, and $(NH_4)_4HP_3O_{10}$ was estimated from plots of pH vs. N or P_2O_5 contents to contain 12.0% N and 46.5% P_2O_5 and to have a pH of 4.9.

The solution saturated with $NH_4H_2PO_4$, $(NH_4)_2HPO_4$, $(NH_4)_3HP_2O_7{\cdot}H_2O$, and $(NH_4)_5P_3O_{10}{\cdot}H_2O$ at 0°C had a weight ratio N:P_2O_5 of 0.293, whereas at 25°C the weight ratio N:P_2O_5 was 0.292; the pH of this invariant solution was 5.75 at 0°C and 5.72 at 25°C. The total plant nutrients (N + P_2O_5) in this solution increased from 53.00 to 55.25% when the temperature was raised from 0° to 25°C. Higher total plant-nutrient contents were obtained at lower values of pH.

The 0° and 25°C isotherms overlap in the weight ratio N:P_2O_5 range of 0.27 to 0.35. Figure 2 shows this region with the ratio of the solubility of total nutrients at 25°C to that at 0°C on the left ordinate scale and the difference in percent total nutrient content at 25°C from that at 0°C on the right ordinate scale. From this figure the percentage of plant nutrients that would crystallize from a liquid in lowering the temperature 25°C can be determined. Also, the amount of plant nutrients that is removed from solution can be determined when there is a 25°C temperature differential. When a small temperature variation is expected between time of production and use, the liquid could be formulated at the high points on the curves; and with a large temperature differential between the time of production and use, it would be advantageous to formulate at the lower points.

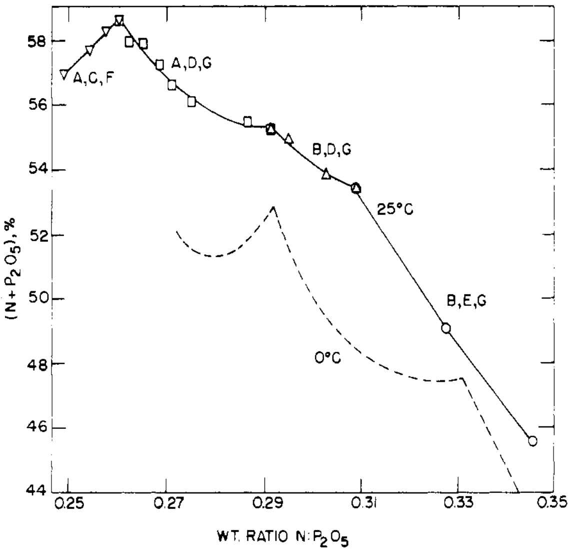

Figure 1. Solubility in system NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O at 25°C

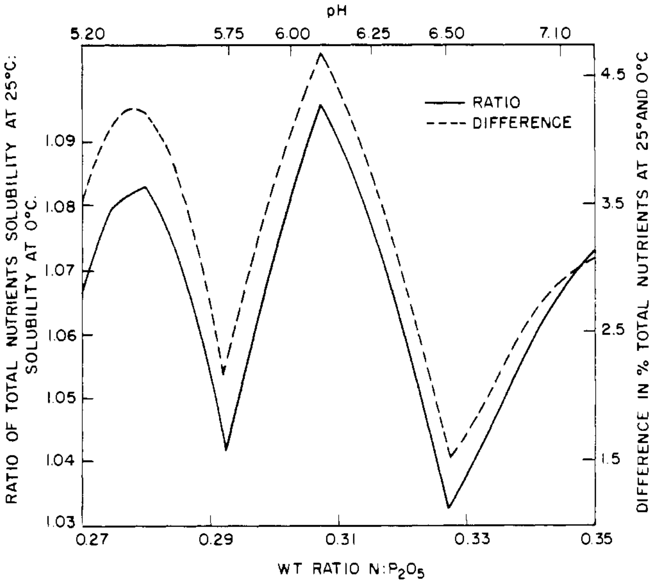

Figure 2. Relationship of total nutrient content (N + P_2O_5) to wt ratio N:P_2O_5 in system NH_3–H_3PO_4–$H_4P_2O_7$–$H_5P_3O_{10}$–H_2O at 25° and 0°C

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