

flat. Five sprigs of Coastal Bermuda-grass were planted per flat on July 31, 1961, and the grass was allowed to spread for two months, during which time it was clipped four times and the clippings discarded. On October 4, the following materials and rates of nitrogen were applied uniformly on the soil surface (mg. of N per flat): ammonium nitrate—200, 400, 800, and 1600; urea—260 and 1050; urea pyrolyzate, cyanuric acid, ammeline and ammeline—200 and 800; urea formaldehyde and melamine—800. Four clippings were made as follows: October 25, November 22, January 23, and April 9.

Total yields of dry matter in the four clippings are given in Table IV and uptakes of nitrogen are given in Figure 2. As the 800-mg. rate of nitrogen was included for all sources, uptakes in the clippings at this rate were used to estimate the apparent recovery of applied nitrogen. Apparent recoveries per 100 mg. of applied nitrogen (total uptake less uptake with no N, divided by 8) were as follows: NH_4NO_3 and urea, 58; cyanuric acid, 41; ammeline, 29; urea pyrolyzate, 12; ammeline, 11; urea formaldehyde, 9; melamine, 3. Cyanuric acid applied at the 800-mg. rate of nitrogen was apparently toxic for the first clipping of grass. Relative values based on yields of dry matter showed the same order of relative availabilities.

As compared with results from soluble nitrogen applied for corn, cyanuric acid was relatively more available for Bermudagrass. Ammelide, ammeline, and melamine showed the same order of availability for both crops. Urea pyrolyzate was similar to ammeline in availability. This preparation was relatively more available, as compared with urea, than that applied for corn in Experiment 1. Actually, relative availabilities can

be changed rather widely by minor changes in pyrolysis conditions.

Field Experiments

Procedure. The various materials were compared as sources of nitrogen for fall-sown wheat on three Coastal Plain soils in Alabama (Table V). Each experiment received a uniform treatment of 500 pounds of 0-6-12 (0-14-14) applied at time of planting. The nitrogen sources were applied with the seed. Planting dates were September 15, 1961, on Etowah silt loam at Alexandria; October 17, on Greenville sandy loam at Prattville; and October 15, on Kalmia sandy loam at Brewton. Each treatment was replicated four times. Wheat was clipped for dry forage yield determinations one or two times during February or early March 1962.

Response by Wheat Forage. Yield results in Table V indicate marked response of wheat forage to urea nitrogen. Yield increases from urea pyrolyzate and urea formaldehyde were 35 and 49% of that from the same amount of nitrogen applied as urea, respectively. Cyanuric acid was toxic in all three experiments, as evidenced by lower yields than from no applied nitrogen. Less toxicity may be noted on the silt loam at Alexandria than on the two sandy loam soils, especially at Prattville. Small, non-significant increases in yields were obtained from ammeline, ammeline, and melamine in these experiments, but mean yields were only slightly higher than yields from no applied nitrogen. These three sources were only about 10% as effective as urea.

Discussion

Availability of the nitrogen in the four triazine compounds—cyanuric acid, am-

melide, ammeline, and melamine—was found to be in the reverse order of the substitution of hydroxyl by amino groups (Figure 1). This results in a decrease in availability of the nitrogen with increasing nitrogen content of compounds in the series. Thus, urea pyrolyzates having the highest possible nitrogen contents may have limited use for grain and hay crops. Cyanuric acid, which is toxic if applied at time of planting, would be expected to be more suitable if applied two weeks or more in advance of planting. Calcium cyanamide, for which the same precautions must be used, has found considerable use as a nitrogen fertilizer.

Ammeline, ammeline, and urea pyrolysis products were equal or superior to fertilizer-grade urea formaldehyde as sources of nitrogen for Bermudagrass. The latter has found considerable use for lawns, where even growth through a season, rather than rapid growth at any one time, is desirable. Another possible use for the triazine compounds may be for tree and shrub fertilization. The less available compounds might supply adequate growth over a period of several years. This potential use should be investigated.

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LIQUID FERTILIZERS

Solubility Relationships in Liquid Fertilizer Systems Based on Superphosphoric Acid

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THE NUTRIENT CONTENT of liquid fertilizers is limited by the solubility of the nutrient salts used. A means of increasing concentration is needed to reduce costs of handling, storage, and application. The recent introduction of superphosphoric acid (3, 6) has made this possible; superphosphoric acid is shipped at a concentration of 76% P_2O_5 (33% P), for maximum fluidity, and about half of the P_2O_5 is in nonortho-

forms (polyphosphoric acids). Ammoniation of the acid yields ammonium polyphosphates, which are more soluble than the ortho forms of ammonium phosphate.

Effects of superphosphoric acid on solubility in fertilizer systems were discussed by Striplin *et al.* (6). The more extensive study outlined here facilitates estimation of solubilities for all ratios thought to be of practical interest. Solubilities were obtained for "base

solutions" (ammoniated acids) and for N-P-K liquid fertilizers made by adding supplemental nitrogen and potassium to the base solutions. The variables included degree of ammoniation, source of supplemental nitrogen, and ratio of nutrient. Most of the measurements were made at 32° F. Temperature-solubility correlations were derived to permit estimation of solubilities at other temperatures. Similar measurements for

Solubilities in liquid fertilizer systems based on superphosphoric acid [a mixture of orthophosphoric and polyphosphoric acids containing about 76% P_2O_5 (33% P)] were determined by a crystal seeding method. Isotherms for 32° F. were developed for acids ammoniated to N: P_2O_5 weight ratios of 0.28 to 0.34 (N:P ratio, 0.64 to 0.78). Highest solubility was obtained at a N: P_2O_5 ratio of about 0.300 (N:P, 0.69). The solubility increased with increase in proportion of the acid in the polyphosphoric form. Measurements at 32° F. with ammoniated superphosphoric acid systems containing supplemental nitrogen (urea, ammonium nitrate) and potassium chloride yielded diagrams from which solubilities at various nutrient ratios can be estimated. Relatively high solubilities were found in the areas where ammonium phosphate was the equilibrium solid phase. Constants were derived for a general equation that permits estimation of solubilities at temperatures other than 32° F.

solutions made from orthophosphoric acid have been reported (4).

Methods and Procedures

Superphosphoric acid [76% P_2O_5 (33% P)] was prepared by dissolving anhydrous P_2O_5 in orthophosphoric acid (reagent grade chemicals). The acid was ammoniated batchwise in a 5-gallon stainless steel reactor; acid and ammonia, proportioned to maintain the desired pH, were added simultaneously with continuous stirring. To minimize hydrolysis, the temperature was held below 180° F. by cooling coils, and portions of the ammoniated product not needed immediately were stored at 32° F. (3). Supplemental nitrogen was added as ammonium nitrate, urea, and urea-ammonium nitrate solution (urea: ammonium nitrate weight ratio of 0.8). Potassium was added as potassium chloride.

Solubilities at 32° F. were determined by finding the maximum total plant nutrient that could be held in a stable aqueous solution. A solubility test was made by adding seed crystals of the least

soluble or crystallizing phase, as determined earlier by petrographic methods. A series of solutions at each ratio (differing by small increments in water content) were cooled to 32° F., and each solution (about 50 ml.) was seeded with about 50 mg. of crystals. The mixtures were shaken mildly until dissolution or growth of crystals was evident (usually by simple inspection; sometimes by petrographic examination). From 2 weeks to 3 months was required. Solubility was determined within 0.1 percentage point of the total plant nutrient content. (Plant nutrient content is expressed as N, P_2O_5 , and K_2O .)

Temperature-solubility coefficients were determined by polythermal methods using the data obtained at 32° F. as a guide; the solutions were cooled to crystallization, then warmed slowly (2° F. per hour), with continuous stirring, until the crystals disappeared (taken as the equilibrium temperature).

The System Ammonia-Superphosphoric Acid

Fertilizer producers often purchase ammoniated phosphoric acid "base solution" and mix it with other materials to make solutions of various compositions. Or they may make the base solution in their own plants and transport it to subsidiary mixing stations. Work by TVA (4) and others (5) with the orthophosphoric acid system has shown the important effect on solubility of relatively small differences in degree of ammoniation.

The effect of degree of ammoniation of superphosphoric acid on solubility was studied by ammoniating the acid [76% P_2O_5 (33% P)] to three levels—pH 5.6 [N: P_2O_5 weight ratio, 0.284 (N:P weight ratio, 0.65)]; pH 5.8 [N: P_2O_5 , 0.300 (N:P, 0.69)]; and pH 6.6 [N: P_2O_5 , 0.332 (N:P, 0.76)]. Solutions at intermediate pH levels (5.7, 5.9, 6.0, 6.2, 6.3) were prepared by blending.

Analyses by a method similar to that used by Hill *et al.* (7) showed that 53.9% of the P_2O_5 was in the polyphosphate form before ammoniation of the acid—46% after ammoniation. This decrease,

through hydrolysis, was somewhat greater than usually occurs in large-scale continuous ammoniation (3). Solubilities reported here thus may be slightly less than could be obtained with acid of equal P_2O_5 content in large-scale operation.

The solutions were seeded with crystals of ammonium phosphates—the solutions of pH 5.8 and lower with monoammonium phosphate, and those above pH 5.8 with diammonium phosphate. The results are shown in Figure 1. Maximum plant nutrient content, about 47%, was reached between pH 5.8 and 5.9, which corresponds to an N: P_2O_5 weight ratio of 0.300 to 0.303 (N:P, 0.69 to 0.70). In another test with ammoniated superphosphoric acid in which only 33% of the P_2O_5 was in the polyphosphate form, the shape of the solubility curve and the N: P_2O_5 ratio for maximum solubility were almost identical to those shown in Figure 1; however, the total plant nutrient solubilities were 2 to 3 percentage points lower. A similar solubility curve has been reported for the system ammonia-orthophosphoric acid (5); the maximum solubility, however, was only 38.8% (also obtained at pH 5.8).

Multicomponent Liquid Mixtures

As the maximum plant nutrient content in the system ammonia-superphosphoric acid was found at the N: P_2O_5 ratio 0.300 (N:P, 0.69), this ratio was used in studies of multicomponent liquid mixtures. The effects of the additions of supplemental nitrogen and potash are shown in Figures 2, 3, and 4. The superphosphoric acid used in these studies contained 75.5% P_2O_5 (33% P); after ammoniation, 43% of the P_2O_5 was in the polyphosphate form. The data for the nitrogen-potash baselines are from a study by Kapusta (2).

Contours of constant plant nutrient content are shown as solid lines in the diagrams. The label 25 on a line, for example, indicates that all solutions along the line have a total nutrient solubility of 25% at 32° F.

The contours were constructed by

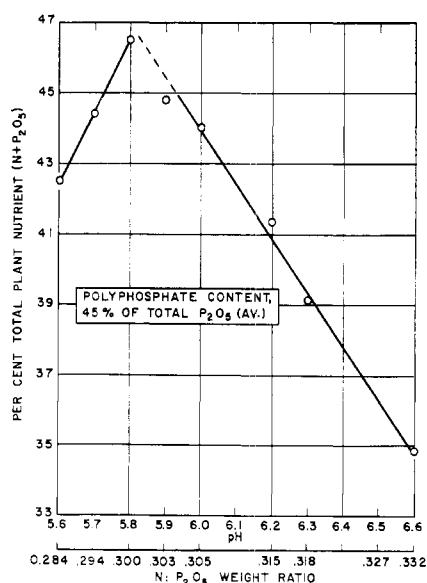


Figure 1. Solubility of ammoniated superphosphoric acid at 32° F. as a function of N: P_2O_5 weight ratio

Table I. Temperature-Solubility Coefficients for Liquid Fertilizers Made from Superphosphoric Acid

| Crystallizing Phase | Change in Total Plant Nutrient Solubility, Percentage Point per °F. (b in Eq. 1) |
|------------------------------------|--|
| $\text{NH}_4\text{H}_2\text{PO}_4$ | 0.115 ± 0.048 |
| $(\text{NH}_4)_2\text{HPO}_4$ | 0.045 ± 0.017 |
| $\text{CO}(\text{NH}_2)_2$ | 0.150 ± 0.021 |
| NH_4NO_3 | 0.143^a |
| NH_4Cl | 0.052^a |
| KCl | 0.084 ± 0.011 |
| KNO_3 | 0.215 ± 0.017 |

^a Too few points in this precipitating area to derive a standard deviation.

interpolation from smoothed graphs of total plant nutrient concentration versus nutrient ratio along various straight lines connecting the baselines to the opposite vertices. These connecting lines were selected to obtain the best possible coverage of the portions of the diagrams believed to be of the most practical use. Most of the ratios chosen for experimental work were at the intersection of two or three of the connecting lines. Various common ratios are shown on the charts. These ratios are, in general, those for which experimental data were obtained. The graphs used for interpolation were plots of total nutrient as a function of $\text{K}_2\text{O}:(\text{N} + \text{K}_2\text{O})$ and $\text{P}_2\text{O}_5:(\text{N} + \text{P}_2\text{O}_5)$ ratios.

The broken lines mark the areas wherein the specific salts named are the least soluble (the crystallizing phases) at 32° F. Comparison of these diagrams with those of the orthophosphoric acid system published previously (4) shows that ammonium phosphates occupy much smaller parts of the total diagrams in the superphosphoric acid systems, and potassium salts correspondingly larger parts. When urea was present, both monoammonium and diammonium phosphates appeared as stable solid phases. As the relative amount of urea was increased, the crystallizing phase at 32° F. changed from monoammonium phosphate to diammonium phosphate. When ammonium nitrate was the source of supplemental nitrogen, monoammonium phosphate was the only stable solid phosphate phase.

The greatest gain in total solubility occurred in areas near the point for the 1:3:0 N:P₂O₅:K₂O ratio (N:P:K, 1:1.3:0). A maximum difference of about 9 percentage points was found between corresponding points in Figure 2 and its counterpart in the orthophosphoric acid system (43% vs. 34% total nutrient). As indicated earlier, this difference was about 8 percentage points in the two-component systems. Although higher solubilities were noted to some degree over the entire area, the advantage decreased as the nitrogen and potash contents were increased.

Effects of Temperature on Solu-

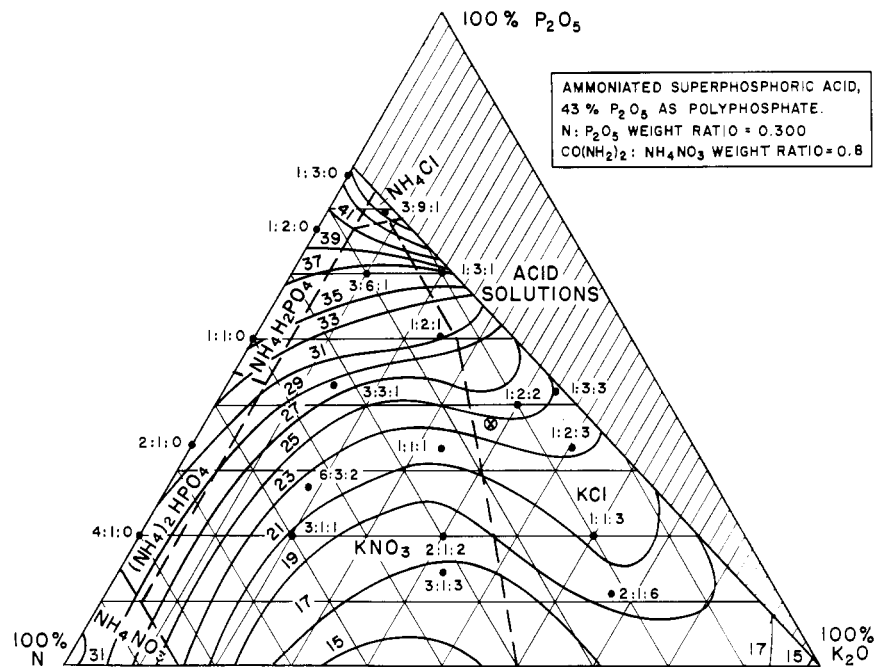


Figure 2. System: ammonia-superphosphoric acid-urea-ammonium nitrate-potassium chloride-water at 32° F.

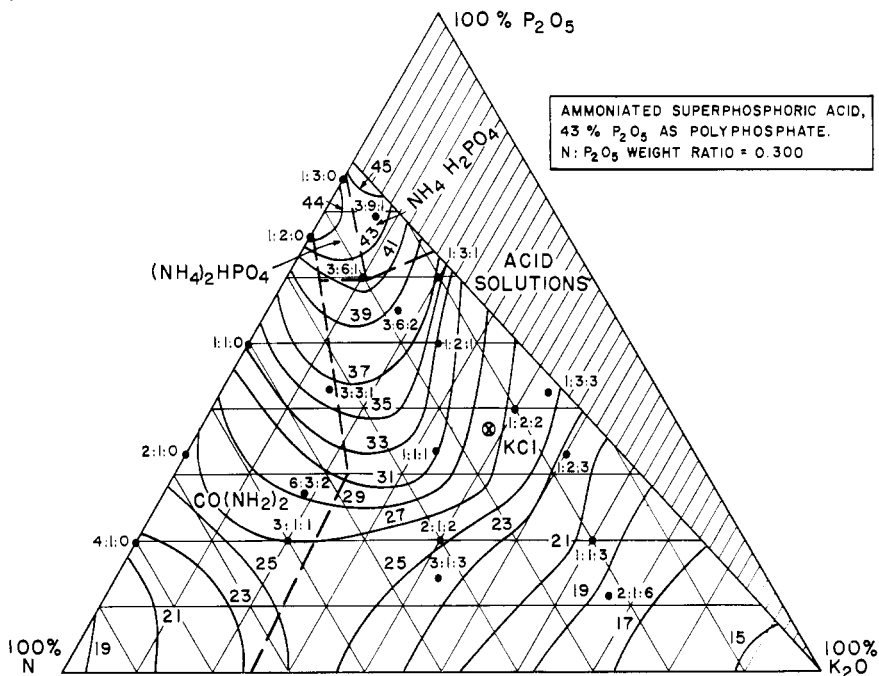


Figure 3. System: ammonia-superphosphoric acid-urea-potassium chloride-water at 32° F.

bility. The temperature-solubility coefficients in Table I enhance the value of the triangular diagrams. The accuracy of the coefficients depends on the linearity of the temperature-solubility relationship, which is shown by the two typical lines in Figure 5.

The general equation for utilizing the temperature-solubility coefficients is

$$y = a + b(t - 32^\circ \text{F.}) \quad (1)$$

where y = total plant nutrient content (%) for a saturated solution of given ratio and temperature,

a = total plant nutrient content for a saturated solution of

given ratio at 32° F.,
 b = temperature-solubility coefficient for the particular salt in equilibrium with saturated solution, and
 t = equilibrium temperature.

The equation can be used to calculate total soluble plant nutrient content at a given temperature or the equilibrium temperature for a given ratio and concentration.

Use of the Diagrams. The diagrams can be used to determine maximum concentrations (grades) at 32° F. for N:P₂O₅:K₂O ratios not plotted and to estimate the maximum grade that will

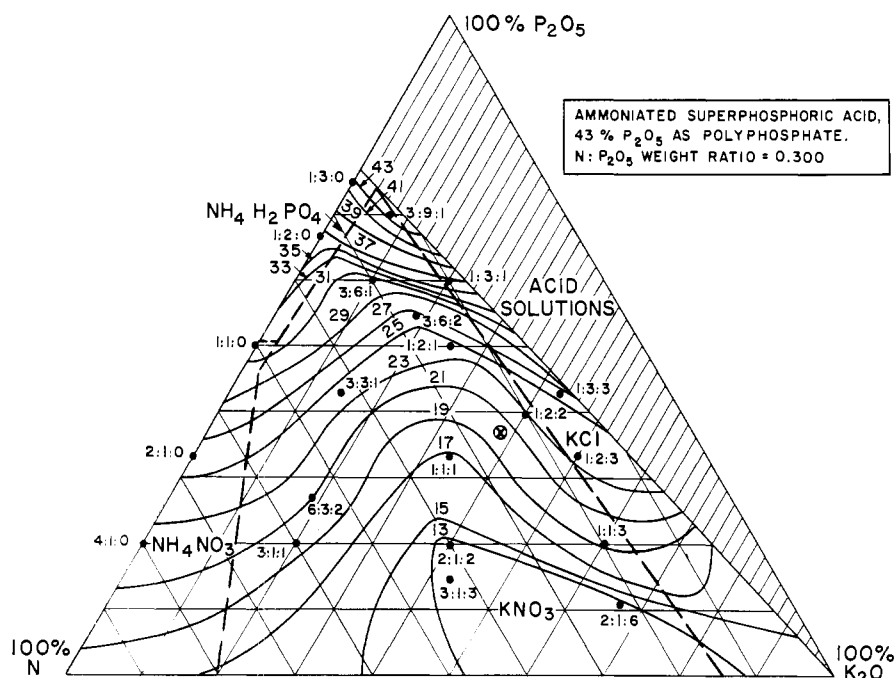


Figure 4. System: ammonia-superphosphoric acid-ammonium nitrate-potassium chloride-water at 32° F.

not crystallize at some other selected temperature. The maximum grade for a ratio not plotted is found by plotting the new ratio on the triangular diagram and then interpolating between the curved lines of constant nutrient content. The ratio point can be plotted easily when it is recognized that each vertex on the diagram represents a solution containing only the indicated plant nutrient; each baseline opposite the vertex for a given nutrient represents 0% of that nutrient and each guide line parallel to the base represents an increment of 10% of that nutrient; and any point on the diagram represents 100% of total plant nutrient. The point for the desired ratio then is located by plotting the individual percentages of the total for each plant nutrient. (Actually, the point is established by plotting only two of the nutrients; plotting the third serves as a check.)

For an example, determination of the position on the diagram corresponding to the ratio 2:3:3 (N:P:K, 1:0.7:1.2) is described. This ratio represents nitrogen, phosphorus pentoxide, and potassium oxide in the proportions 25.0%, 37.5%, 37.5%, respectively. First, interpolate between the 30 and 40% guide lines for phosphorus pentoxide to get a 37.5% line. Then interpolate to get a 37.5% line for potassium oxide. The juncture of these lines is the point desired (marked X on the charts). Note that this point reads 25% on the nitrogen guide lines. For the system in which urea-ammonium nitrate solution was used as supplemental nitrogen (Figure 2), the total plant nutrient content at point X is about 24%, for which the grade of a 2:3:3 (1:0.7:1.2) ratio is 6-9-9 (6-4-7).

Equation 1 is used in finding the maximum grade for temperatures other

than 32° F. For the 2:3:3 (1:0.7:1.2) ratio, the crystallizing phase (Figure 2) is potassium chloride; for this salt, b is 0.084 and a is 24. If the temperature in question is 70° F., the total plant nutrient content, y , is 27.3%, and the grade is 6.8-10.2-10.2.

The procedure for determining the equilibrium temperature for a specific grade of liquid fertilizer also is relatively simple. Assume a 12-24-4 (12-10-3) grade with urea-ammonium nitrate solution as the supplemental source of nitrogen. The ratio is 3:6:1 (1:0.9:0.3). The crystallizing phase (Figure 2) is potassium nitrate, for which b is 0.215 (Table I). The value for a is 36.5, and the value for y is 40. With these values in the equation, solution for t shows an equilibrium temperature of 48.3° F. The value determined experimentally was 50° F.

Discussion

The solubility data should be helpful in predicting the feasibility of liquid fertilizer formulations and concentrations [to judge from experience with the similar data (4) on solutions made from orthophosphoric acid]. In using the temperature coefficients, however, consideration must be given to phase changes that may occur with some ratios at temperatures other than 32° F. For example, the 1:2:0 (1:0.9:0) ratio in which urea alone is used (Figure 3) has diammonium phosphate as the stable solid phase for most of the range above 32° F., whereas urea is the solid phase at 32° F. and below. Fortunately, these phase changes usually occur in regions close to boundary lines between phases, and allowance can be made for possible error in these regions. Experience also

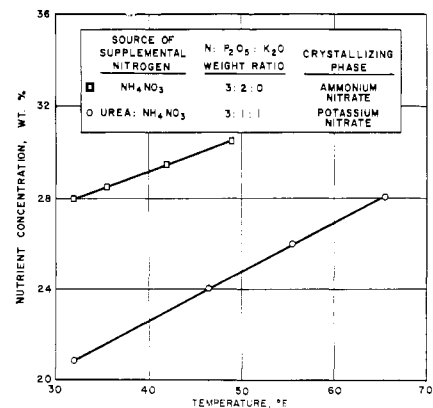


Figure 5. Variation of solubility with temperature

has shown that solutions in which diammonium phosphate is the crystallizing phase at 32° F. usually will have the dihydrate of diammonium phosphate as the crystallizing phase at lower temperatures—a situation in which extrapolation is undependable. Otherwise, approximations of solubilities through use of the diagrams and the temperature coefficients are expected to be quite useful to the liquid fertilizer industry.

The user should remember that ammoniated superphosphoric acid base solutions and liquid fertilizers made from them will hydrolyze to some extent during storage with consequent decrease in solubility. Limited tests (3) have shown that hydrolysis increases with rise of temperature and that hot weather storage for prolonged periods should be avoided. Further data are being obtained on the effects of time and temperature on hydrolysis and solubility. Also, base solutions with higher polyphosphate contents than those presented here are being produced, and solubility studies are being made with them.

Acknowledgment

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