

Solubility Relationships in Liquid Mixed Fertilizer Systems

A. V. SLACK, J. D. HATFIELD,
H. B. SHAFFER, and J. C. DRISKELL
Tennessee Valley Authority,
Wilson Dam, Ala.

The solubility of combinations of fertilizer salts is important in the liquid mixed fertilizer industry. Few data are available on solubility relationships in the complex systems involved. Three systems were studied: $\text{CO}(\text{NH}_2)_2\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$, $\text{NH}_4\text{NO}_3\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$, and $[\text{CO}(\text{NH}_2)_2\text{-NH}_4\text{NO}_3\text{ (fixed ratio)}]\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$. Fixed $\text{NH}_3\text{-H}_3\text{PO}_4$ mole ratios of 1.5, 1.6, and 1.7 were used. In the first system, studied in the range 0° to 25° C., the plant nutrient content of the saturated solution was found to be a linear function of the temperature when nutrient ratio and $\text{NH}_3\text{-H}_3\text{PO}_4$ ratio were fixed. The last two systems were studied only at 0° C. Solubilities were measured only for selected nutrient ratios. However, graphic presentation of the data permits estimation of the solubility of other ratios at 0° C. and in the range of $\text{NH}_3\text{-H}_3\text{PO}_4$ mole ratios studied. Isotherms at other temperatures may be constructed in the system containing urea. A general solubility equation was also developed by which crystallization temperatures can be approximated over a wide range of conditions.

THE PRODUCTION OF MIXED FERTILIZERS in liquid form has grown rapidly in recent years (20, 27). One of the major problems of the new industry is the limited solubility of plant nutrients. The major raw materials are ammonia, phosphoric acid, urea, ammonium nitrate, and potassium chloride. The ammonia and acid are the principal materials and the others are added when the particular grade requires it. Thus, the phase systems involved may have as many as six components.

The major practice of limiting liquid mixes to neutral solutions makes $\text{NH}_3\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ the basic phase system. Practical compositions in this system are those in equilibrium with monoammonium phosphate or diammonium phosphate, or both, at the saturation temperature. Brosheer and Anderson (9) assembled and compared various data for the 0° and 25° C. isotherms in this system; the maximum solubility was found to occur at the transition point between monoammonium phosphate and diammonium phosphate, for which the $\text{NH}_3\text{-H}_3\text{PO}_4$ mole ratio is 1.56 at 0° C. and 1.53 at 25° C.

Other pertinent phase studies include the systems:

$\text{NH}_4\text{NO}_3\text{-NH}_3\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$ (10), $\text{NH}_4\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$ (2, 17, 19), $\text{NH}_4\text{H}_2\text{PO}_4\text{-CO}(\text{NH}_2)_2\text{-H}_2\text{O}$ (6, 18), $\text{NH}_4\text{H}_2\text{PO}_4\text{-NH}_4\text{NO}_3\text{-H}_2\text{O}$ (4, 5, 7), $(\text{NH}_4)_2\text{HPO}_4\text{-NH}_4\text{NO}_3\text{-H}_2\text{O}$ (74), $\text{CO}(\text{NH}_2)_2\text{-KCl-H}_2\text{O}$ (8, 16), $\text{NH}_4\text{NO}_3\text{-KCl-H}_2\text{O}$ (7, 3, 12), and $\text{CO}(\text{NH}_2)_2\text{-NH}_4\text{NO}_3\text{-H}_2\text{O}$ (11, 22).

The study reported in this paper includes portions of the systems $\text{CO}(\text{NH}_2)_2\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$, $\text{NH}_4\text{NO}_3\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$, and $[\text{CO}(\text{NH}_2)_2\text{-NH}_4\text{NO}_3\text{ (fixed ratio)}]\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$.

$\text{H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$. The fixed ratio of urea to ammonium nitrate in the last system corresponds to that in commercial urea-ammonium nitrate solutions [1.065 $\text{CO}(\text{NH}_2)_2\text{-NH}_4\text{NO}_3$ mole ratio]. Limited investigations of these systems have been reported (15); the present work extends the data to a wider range of composition.

The main problem in studying solubility of liquid mixed fertilizers is the great number of determinations required to cover fully the complicated phase systems involved. Some limitation must be imposed to keep any unit study within reasonable bounds. In this study, only the most used levels of variables such as nutrient ratio, temperature, urea- $\text{NH}_4\text{-NO}_3$ ratio, and $\text{NH}_3\text{-H}_3\text{PO}_4$ ratio were studied. However, a further objective of the study was to develop means for estimating or approximating solubility for other levels and combination of variables.

Methods and Procedures

The total content of plant nutrients ($\%N + \%P_2O_5 + \%K_2O$) in the saturated solution was employed as a convenient means of expressing solubility in the systems. The experiments were designed to cover the range of the more commonly used fertilizer ratios. The composition variables and their levels were (1) weight ratio $P_2O_5\text{-N}$ of 0.5, 1, 2, 3; (2) weight ratio $K_2O\text{-N}$ of 0, 1, 3; and (3) mole ratio $\text{NH}_3\text{-H}_3\text{PO}_4$ of 1.5, 1.6, 1.7.

A complete factorial experiment in these three variables were performed for each system at $-1.5^\circ \pm 0.7^\circ$ C. This particular temperature was used because

the large cold room employed in the tests was difficult to adjust closely to a specified temperature. The 0° C. isotherm was easily obtained from the -1.5° C. data by interpolation. The tests were made by seeding solutions with a small amount of crystals of the crystallizing phase. A series of solutions of each ratio, differing by small increments in water content, were cooled to -1.5° C., and each solution (about 50 ml.) was seeded with about 50 mg. of crystals. The solutions and crystals were agitated mildly in a shaking apparatus for about 3 days. The disappearance or growth of crystals in the different samples in this period permitted determination of the solubility within 0.1 to 0.2% of the plant nutrient.

The solubility in the temperature range 0° to 25° C. for the system $\text{CO}(\text{NH}_2)_2\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$ was determined by a polythermal method. The solutions were cooled until crystallization occurred and then warmed very slowly, with continuous stirring, until the last crystals disappeared. The heating rate was 2° C. per hour. Measurements were made in triplicate when urea or ammonium phosphate crystallized and in duplicate when other salts crystallized. The crystalline phases were identified petrographically.

The polythermal technique was adopted to speed up the work. The isotherm method, while accurate, is very time-consuming. Tests of the polythermal method at -1.5° C. gave good agreement with the isotherm measurements, provided that the rate of heating was not faster than 2° C. per hour. Methods involving appearance of crystals were found to be undependable, even

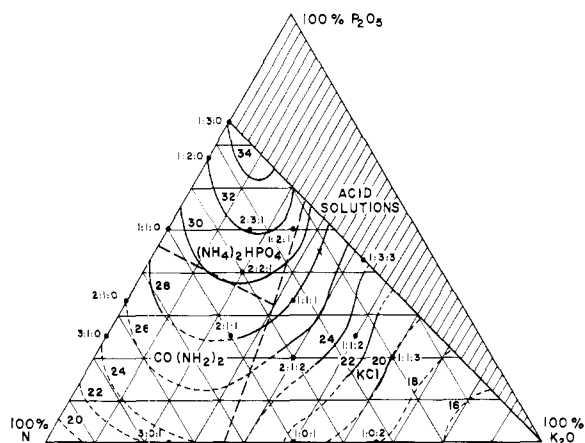


Figure 1. System urea-ammonia-phosphoric acid-potassium chloride-water at 0° C.

Moles ammonia per mole phosphoric acid = 1.7

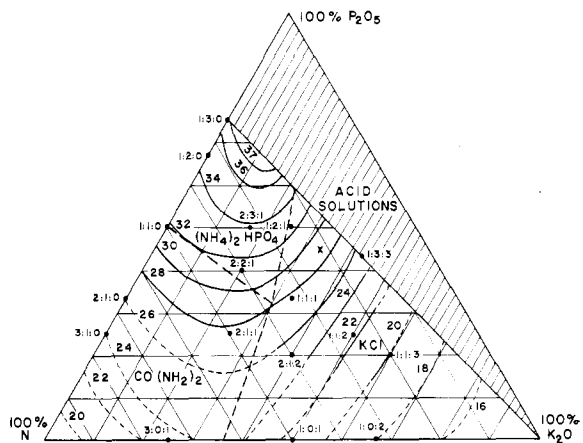


Figure 2. System urea-ammonia-phosphoric acid-potassium chloride-water at 0° C.

Moles ammonia per mole phosphoric acid = 1.6

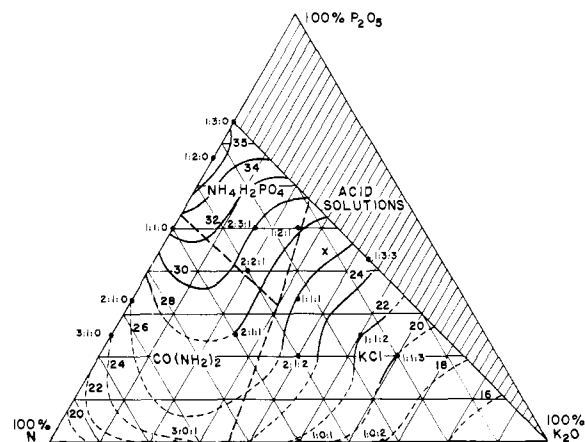


Figure 3. System urea-ammonia-phosphoric acid-potassium chloride-water at 0° C.

Moles ammonia per mole phosphoric acid = 1.5

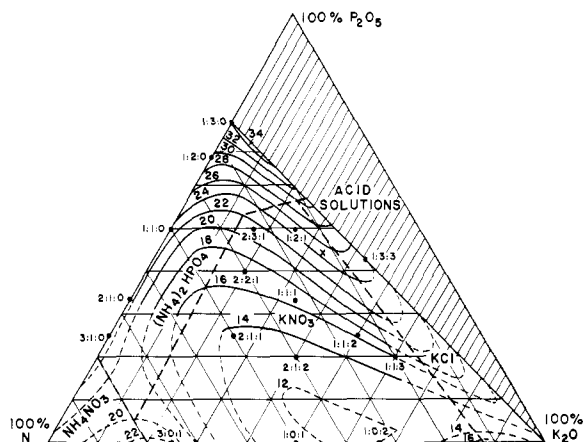


Figure 4. System ammonium nitrate-ammonia-phosphoric acid-potassium chloride-water at 0° C.

Moles ammonia per mole phosphoric acid = 1.7

though mechanical shock or a chilled wire was used to minimize supercooling. The usual method of equilibrating with excess solid could not be used, because the composition of the saturated solution was fixed.

The materials used to prepare the solutions were urea, ammonium nitrate, monoammonium phosphate, diammonium phosphate, and potassium chloride—all of reagent grade—and deionized water. The two ammonium phosphate salts were carefully analyzed for nitrogen and phosphate content and were mixed together to obtain the desired $\text{NH}_3\text{-H}_3\text{PO}_4$ ratio. Aqueous stock solutions of these salt mixtures were prepared, and supplementary nitrogen and potassium chloride were added to aliquots of the stock solutions to obtain the various nutrient ratios. The supplementary nitrogen was added from concentrated aqueous stock solutions which were analyzed for nitrogen content. It was convenient and considerably more accurate than handling the hygroscopic salts. Potassium chloride was added as the salt. Deionized water was added as required to give the desired concentration. The stock solutions and water

were metered from automatic burets which had been calibrated for weight delivery of the liquids at 25° C.

Results and Discussion

The data obtained by the isothermal and polythermal techniques for the system containing urea were expressed by

$$y = a + bt \quad (1)$$

where y is the per cent total plant nutrient in the saturated solution at temperature t (° C.), and a and b are constants for each combination of nutrient ratio and ammoniation level. a and b were determined by the least squares method. a represents solubility at 0° C. and b the incremental change in plant nutrient content per degree. Equation 1 satisfactorily represented the data for each composition as long as the crystallizing phase did not change in the temperature range studied. Where this occurred, separate values for the constants were derived for each crystallizing compound. The standard deviation of Equation 1 from the measured values was 0.12% in plant nutrient. This corresponds to 1° C. or less over the region studied.

Table I gives the data for the system $\text{CO(NH}_2)_2\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$ in terms of the parameters a and b of Equation 1. Figures 1, 2, and 3 show the 0° C. isotherm in this system at fixed values of $\text{NH}_3\text{-H}_3\text{PO}_4$ mole ratio.

Table II contains the data at -1.5° C. for various nutrient ratios and degrees of ammoniation in the systems containing ammonium nitrate and the urea-ammonium nitrate mixture. Figures 4 and 5 show the 0° C. isotherms for these systems at 1.7 $\text{NH}_3\text{-H}_3\text{PO}_4$ mole ratio. The slight adjustment necessary to convert from -1.5° to 0° C. was estimated from the temperature gradients already established for potassium chloride and for ammonium phosphates as the crystallizing solid phase and from additional tests to determine the temperature gradient for potassium nitrate.

In Figures 1 to 5 contours of constant plant nutrient content in the saturated solution are shown with the nutrient ratios as the variables. These contours were constructed from smooth graphs of plant nutrient content along various tie lines from the P_2O_5 and K_2O vertices to the corresponding opposite sides. The data were extended to the $\text{N-K}_2\text{O}$

line for the systems containing urea (Figures 1, 2, and 3) by use of the data of Polosin and Ozolin (16). Similarly, the data of Janecke (12) on the system $\text{NH}_4\text{NO}_3\text{-KCl-H}_2\text{O}$ at 0°C . permitted extension of the contours to the $\text{N-K}_2\text{O}$ line in Figure 4. Recent data (13) of the system $\text{CO(NH}_2)_2\text{-NH}_4\text{NO}_3\text{-KCl-H}_2\text{O}$ were used to complete Figure 5. The region of the present study is shown by solid contour lines in the figures. Dotted contours indicate interpolation between the regions of the present study and those of the other workers. Broken lines indicate the regions of existence of the various crystallizing phases. These were identified from data gathered in this study and from results reported by Langguth *et al.* (15).

Graphs similar to those of Figures 1 to 3 may be constructed at any temperature in the range 0° to 25°C . by using the data in Table I. Likewise the 0°C . isotherms at 1.5 and 1.6 $\text{NH}_3\text{-H}_3\text{PO}_4$ mole ratio for systems containing ammonium nitrate or urea-ammonium nitrate may be constructed from the data in Table II.

Effect of Variables

Nutrient Ratio. The greatest solubility at 0°C . occurred in each system in the region involving small additions of the supplementary materials, nitrogen or potassium chloride, to the basic system $\text{NH}_3\text{-H}_3\text{PO}_4\text{-H}_2\text{O}$. When diammonium phosphate crystallized from the basic system (Figures 1, 2, 4, and 5) the maximum solubility occurred at about 2:6:1 nutrient ratio. When monoammonium phosphate crystallized (Figure 3), maximum solubility occurred at about the 1:2:0 nutrient ratio.

Source of Supplemental Nitrogen. Urea as a rule gave greater solubility than ammonium nitrate. The combination of the two in the fixed commercial ratio usually gave an intermediate solubility, particularly at high levels of supplemental nitrogen. The effect of the source of supplemental nitrogen was most pronounced for ratios which involved considerable addition of both supplemental nitrogen and potassium chloride.

The solubility contours at 0°C . in the system containing urea (Figures 1, 2, and 3) show that the first additions of potassium chloride cause little solubility change, but further additions give a rapid decrease. In the ammonium nitrate system (Figure 4) the reverse is true; the first increments of potassium chloride gave a rapid decrease in solubility but further additions had little effect. In the system containing both urea and ammonium nitrate (Figure 5), the effect of potassium chloride resembled that in the ammonium nitrate system at high nitrogen ratios and that

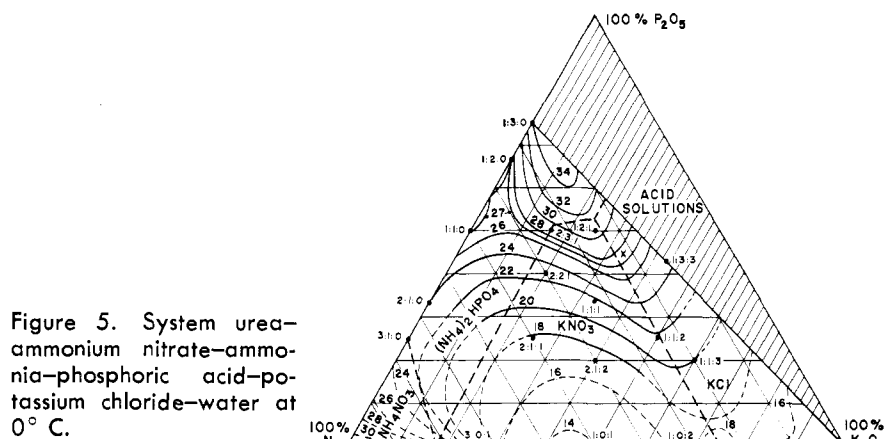


Figure 5. System urea-ammonium nitrate-ammonia-phosphoric acid-potassium chloride-water at 0°C .

Table I. Constants Relating Solubility to Temperature in System

Nutrient Ratio	$\text{CO(NH}_2)_2\text{-NH}_3\text{-H}_3\text{PO}_4\text{-KCl-H}_2\text{O}$					
	Mole Ratio $\text{NH}_3\text{-H}_3\text{PO}_4$					
	1.5	1.6	1.7	1.5	1.6	1.7
	Constant a^a			Constant b^c		
1-3-0	34.6 ^b	36.9 ^c	34.1 ^c	0.342	0.141	0.119
1-2-0	35.8 ^b	34.7 ^c	32.1 ^c	0.244	0.123	0.119
1-1-0	32.7 ^d	31.8 ^e	29.1 ^e	0.241	0.082	0.119
	34.6 ^f			0.065		
2-1-0	26.2 ^g	26.1 ^h	26.1 ⁱ	0.283	0.281	0.262
		30.3 ^j	28.6 ^k		0.071	0.070
1-3-1	31.2 ^b	34.9 ^c	32.1 ^c	0.233	0.133	0.115
1-2-1	28.2 ^b	32.5 ^l	31.3 ^c	0.245	0.130	0.117
1-1-1 ^l	25.9	27.6	27.9	0.156	0.155	0.131
2-1-2 ^l	25.2	25.2	25.2	0.118	0.121	0.118
1-3-3 ^l	24.7	24.8	24.5	0.138	0.135	0.139
1-2-3 ^l	22.7	22.6	22.6	0.124	0.134	0.129
1-1-3 ^l	20.0	19.9	20.0	0.121	0.125	0.121
2-1-6 ^l	18.3	18.5	18.5	0.121	0.117	0.117

^a See Equation 1 text. Crystallizing phases: ^b Monoammonium phosphate, ^c Diammonium phosphate, ^d Urea ($t < 10.8^\circ\text{C}$.), ^e Diammonium phosphate ($t > -1.5^\circ\text{C}$.); urea crystallizes below -1.5°C . ^f Diammonium phosphate ($t > 10.8^\circ\text{C}$.), ^g Urea, ^h Urea ($t < 20.0^\circ\text{C}$.), ⁱ Urea ($t < 12.9^\circ\text{C}$.), ^j Diammonium phosphate ($t > 20.0^\circ\text{C}$.), ^k Diammonium phosphate ($t > 12.9^\circ\text{C}$.), ^l Potassium chloride.

Table II. Solubility^a in Systems Containing Ammonium Nitrate at -1.5°C .

Grade Ratio	Source of Supplemental Nitrogen					
	Ammonium Nitrate			Ammonium Nitrate-Urea ^b		
	Mole Ratio $\text{NH}_3\text{-H}_3\text{PO}_4$			Mole Ratio $\text{NH}_3\text{-H}_3\text{PO}_4$		
	1.5	1.6	1.7	1.5	1.6	1.7
1-3-0	31.9 ^c	35.9 ^d	33.9 ^d	33.7 ^c	32.9 ^d	33.9 ^d
1-2-0	27.6 ^c	30.5 ^d	29.3 ^d	31.3 ^c	30.5 ^d	26.9 ^d
1-1-0	24.1 ^c	27.2 ^d	23.5 ^d	28.0 ^c	27.5 ^d	26.9 ^d
2-1-0	21.5 ^c	24.9 ^d	22.9 ^d	26.9 ^c	25.7 ^d	23.7 ^d
1-3-1	30.5 ^c	34.3 ^d	31.9 ^d	32.1 ^c	34.1 ^d	31.9 ^d
1-2-1 ^e	23.1	23.7	24.5	29.1	29.5	30.1
1-1-1 ^e	16.1	15.7	16.1	20.5	20.7	21.3
2-1-2 ^e	12.7	12.7	12.7	16.7	16.5	16.5
1-3-3 ^f	24.9	24.3	24.3	24.5	24.6	24.3
1-2-3 ^f	22.1	23.3	22.9	22.7	22.3	22.3
1-1-3	15.1 ^e	15.3 ^e	15.5 ^e	19.9 ^f	19.7 ^f	19.9 ^f
2-1-6	12.5 ^e	13.1 ^e	12.9 ^e	18.1 ^f	18.3 ^f	18.3 ^f

^a % $\text{N} + \text{P}_2\text{O}_5 + \text{K}_2\text{O}$. ^b Mole ratio $\text{CO(NH}_2)_2\text{-NH}_4\text{NO}_3 = 1.065$. Crystallizing phases: ^c Monoammonium phosphate, ^d Diammonium phosphate, ^e Potassium nitrate, ^f Potassium chloride.

in the urea system at low nitrogen ratios.

Ammoniation Ratio. The effect of the mole ratio $\text{NH}_3\text{-H}_3\text{PO}_4$ was significant in solutions from which ammonium phosphate or urea crystallized but was usually minor in solutions from which potassium chloride or potassium nitrate crystallized. The effect, when

noticeable, showed a maximum solubility between the 1.5 and 1.6 ratios.

Temperature. The plant nutrient content for a given fertilizer ratio was a linear function of temperature, provided the crystallizing phase did not change in the temperature interval. The temperature coefficient varied with the nutrient ratio and the nature of the crystallizing

phase; the latter had the greater effect. The effect of nutrient ratio was greatest in regions near the existence of two crystallizing phases.

Estimation of Solubility. Figures 1 to 5 can be used to estimate the solubility at 0° C. for nutrient ratios other than the ones studied. The ratio is located on the diagram and the corresponding solubility estimated by interpolation.

If it is desired to find the solubility of a 2:4:3 fertilizer ratio at 0° C., the ratio, which corresponds to 22.2% of nitrogen, 44.4% of phosphorus pentoxide, and 33.3% of potassium oxide, is shown by an *x* in Figures 1 to 5. The plant food content for each system at 0° C. is as follows:

Figure	Supplementary Nitrogen	Total Plant Nutrient in Saturated	
		Mole Ratio NH ₃ -H ₃ PO ₄	Ratio Soln. at 0° C., %
1	Urea	1.7	28.0
2	Urea	1.6	29.0
3	Urea	1.5	26.5
4	NH ₄ NO ₃	1.7	24.6
5	Urea + NH ₄ NO ₃	1.7	27.5

From this it is concluded that a 6:12:9 (27% nutrient content) would not salt out at 0° C. in the urea systems at 1.6 and 1.7 neutralization ratios and in the urea-ammonium nitrate system at the 1.7 ratio (Figures 1, 2, and 5). However, the highest whole grade soluble at 0° C. in the systems of Figures 3 and 4 would be 4:8:6 (18% nutrient content).

Extrapolation of Data to Lower Temperature. The parameters of Equation 1 listed in Table I permit extrapolation of the solubility data—for the system CO(NH₂)₂-NH₃-H₃PO₄-KCl-H₂O—outside the temperature range studied. A few of these extrapolated values were checked experimentally by the polythermal technique at temperatures below 0° C. (Figure 6). The agreement between the measured and extrapolated results was satisfactory, although the data indicate the extrapolated values may be slightly high. The slight difference may be due either to curvature in the temperature relationship or to an experimental error, because of the slower rate of dissolution of the crystallized phase at the low temperature.

Extrapolation to lower temperatures is considered acceptable, if there is not a phase change in the extrapolated region. The results in Figure 6 for the solid phases urea, monoammonium phosphate, and potassium chloride did not involve phase changes. However, for solutions from which diammonium phosphate crystallizes, a phase change occurred in the region below 0° C. The new phase was identified by chemical analysis as diammonium phosphate dihydrate, (NH₄)₂HPO₄·2H₂O. X-ray and petro-

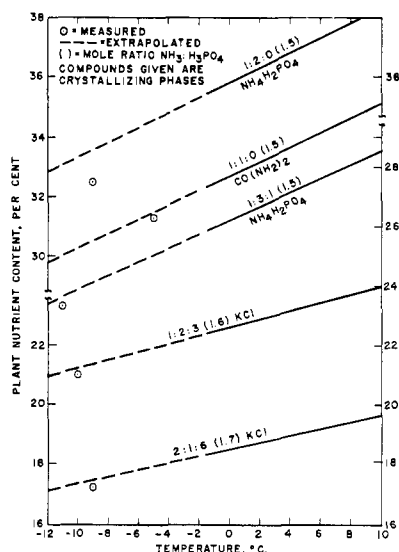


Figure 6. Measured and extrapolated solubilities in the subzero range of the system urea-ammonia-phosphoric acid-potassium chloride-water

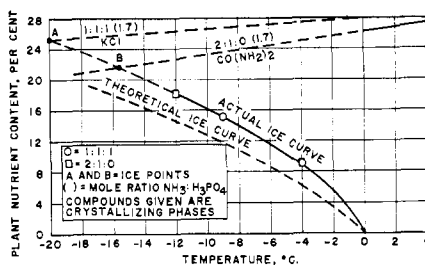


Figure 7. Solubility at low temperatures in the system urea-ammonia-phosphoric acid-potassium chloride-water

graphic data on the new phase were not obtained, because it was unstable at room conditions, converting rapidly to the anhydrous salt.

In Figure 7 full solubility curves, including the ice section, are shown for two solutions. The theoretical ice curve was calculated on the assumption that urea does not ionize, but that monoammonium phosphate, diammonium phosphate, and potassium chloride ionize completely. The actual ice curve indicates incomplete ionization; it was drawn through experimental points for the two solutions and extrapolated to intersect the solubility curves at *A* and *B*, respectively, for the 1:1:1 and 2:1:0 ratio liquids. The transition points, at which both ice and a salt are at equilibrium, thus will vary from one liquid mix to another. For most liquids the transition point probably is between -12° and -20° C. Ice was formed in this temperature range in many of the solutions tested. From the practical viewpoint this means that there is a limit to the degree to which the salting out temperature can be lowered by decreasing the nutrient content of the solution. When the ice point is reached further decrease raises the crystallization temperature instead of lowering it.

By coincidence, the two solutions in Figure 7 have the same ice curves, both theoretical and experimental. Solutions with other nutrient ratios would not necessarily have the same curve.

General Equation for Solubility. The foregoing methods allow estimation of solubility for several combinations of variables not studied. However, wider applicability and easier application of the estimating method would be desirable. An effort was made, therefore, to develop a general equation for estimating solubility.

It was found that Equation 1 can be used as such a general equation by using for temperature coefficient *b* an average value, based on the nature of the crystallizing phase. Although parameter *b* varies with both the crystallizing phase and the nutrient ratio, the independent effect of the latter is relatively minor. Values obtained by averaging data from tests grouped on the basis of the crystallizing phase are as follows.

Crystallizing Phase	Temperature Coefficient, <i>b</i>	Value	Std. dev.
NH ₄ H ₂ PO ₄	0.266	±0.051	
(NH ₄) ₂ HPO ₄	0.123	±0.009	
CO(NH ₂) ₂	0.267	±0.020	
KCl	0.129	±0.012	
KNO ₃	0.369	±0.042	

In using the equation, values for parameter *a* are obtained from isotherms in Figures 1 to 5, or similar 0° C. isotherms, depending upon the phase system. The crystallizing phase is also determined from these figures and the corresponding value for parameter *b* is obtained from the above table. Substitution may then be made in Equation 1 to obtain either the maximum solubility at a given temperature or the crystallization temperature for a given grade. In the latter case the equation is used in the form

$$t = \frac{y - a}{b} \quad (2)$$

The high temperature coefficient of potassium nitrate is especially notable. Because of this, systems from which potassium nitrate crystallizes show a relatively high gain in solubility with increase in temperature.

Use of the equation on a general basis—i.e., for any nutrient ratio and temperature in any of the systems studied—is subject to the following sources of error.

Variation of the real value of the temperature coefficient from the average value used. A 10% error in the coefficient corresponds at most to about 1° C. in the range -10° to +10° C. and about 2° C. in the range -20° to +20° C.

Nonlinearity of the relation between nutrient content and temperature in the range under consideration. The experimental data showed little variation from linearity between +25° and -10° C. in the system CO(NH₂)₂-NH₃-H₃PO₄-KCl-H₂O.

Any change in crystallizing phase in the temperature range from 0° C. to the estimated crystallization temperature. This is a serious source of error in the range below 0° C. for a solution from which diammonium phosphate crystallizes above 0° C. The equation should not be used in this case. Other phase changes are shown in Table I. Estimation of solubility in regions near a phase change is generally not as accurate as in regions remote from the boundary of two phases.

Although the equation gives only an approximation, it should be useful in practice as a rough guide for predicting salting out temperature.

Acknowledgment

The assistance of A. D. Jones, Owen W. Livingston, James E. Tackett, and Gail Barclay Colley in various aspects of the laboratory work is gratefully acknowledged.

Literature Cited

(1) Aronova, S. I., Lunskaia, Z. N., *Kalii (U.S.S.R.)* 1933, No. 2, 24-8.

- (2) Askenasy, Paul, Nessler, F., *Z. anorg. u. allgem. Chem.* **189**, 305-28 (1930).
 (3) Bergman, A. G., *Bull. acad. sci. (U.R.S.S.) Classe Sci. math. nat., Sér. chim.* **1938**, No. 1, 203-16.
 (4) Bergman, A. G., Bochkarev, P. F., *J. Applied Chem. (U.S.S.R.)* **10**, 1531-6 (1937).
 (5) Bergman, A. G., Bochkarev, P. F., *Bull. acad. sci. (U.R.S.S.) Classe math. nat., Sér. chim.* **1938**, No. 1, 237-65.
 (6) Blidin, V. P., *J. Gen. Chem. (U.S.S.R.)* **11**, 887-90 (1941).
 (7) Bochkarev, P. F., *Trudy Vostochno-Sibirskogo Gosudarst. Inst.* **1937**, No. 3, 3-22; *Khim. Referat. Zhur.* **1**, No. 8-9, 11-12 (1938).
 (8) Bokhovkin, I. M., Bokhovina, J. I., *J. Gen. Chem. U.S.S.R.* **17**, 621-4 (1947).
 (9) Brosheer, J. C., Anderson, J. F., *J. Am. Chem. Soc.* **68**, 902 (1946).
 (10) Flatt, R., Brunisholz, G., Blumer, O., *Helv. Chim. Acta* **38**, 3753-69 (1955).
 (11) Howells, W. J., *J. Chem. Soc.* **1929**, 910-15.
 (12) Janecke, E. Z., *Angew. Chem.* **41**, 916-24 (1928); **42**, 318 (1929).
 (13) Kapusta, E. C., *Com. Fertilizer and*

- Plant Food Ind.* **97**, 24-9 (1958).
 (14) Kuznetsov, D. I., Kozhukhovskii, A. A., Borovaya, F. E., *J. Appl. Chem. (U.S.S.R.)* **21**, 1278-81 (1948).
 (15) Langguth, R. P., Payne, J. H., Arvan, P. G., Sisler, C. C., Brautigam, G. F., *J. AGR. FOOD CHEM.* **3**, 656-62 (1955).
 (16) Polosin, V. A., Ozolin, R. F., *J. Gen. Chem. U.S.S.R.* **17**, 403-10 (1947).
 (17) Polosin, V. A., Shakhparonov, M. I., *J. Phys. Chem. (U.S.S.R.)* **21**, 119-23 (1947).
 (18) Polosin, V. A., Treshchov, A. G., *Izvest. Timiryazev. Sel'skokhoz. Akad. No. 2 (3)*, 203-20 (1953).
 (19) Ravich, M. I., Popova, Z. V., *Ann. secteur anal. physico-chim. Inst. chim. gen. (U.S.S.R.)* **14**, 373-86 (1941).
 (20) Slack, A. V., *Coml. Fertilizer and Plant Food Ind.* **95**, 28 (August 1957).
 (21) Slack, A. V., *J. AGR. FOOD CHEM.* **3**, 568 (1955).
 (22) Sokolov, V. A., *J. Gen. Chem. (U.S.S.R.)* **9**, 753-8 (1939).

Received for review December 12, 1958.
 Accepted March 2, 1959.

FERTILIZER RAW MATERIALS

Use of Wet Process By-Product Gypsum in Fertilizer Manufacture

M. A. LARSON and D. R. BOYLAN

Department of Chemical Engineering, Iowa State College, Ames, Iowa

By-product gypsum from the manufacture of wet process phosphoric acid was fused with phosphate rock. Products having phosphorus pentoxide contents greater than 90% were obtained from mixtures of three parts of dehydrated gypsum and one part of phosphate rock produced in a gas-fired laboratory fusion furnace. A 1-ton-per-day pilot plant fusion furnace produced products having from 10.1 to 13.6% total phosphorus pentoxide. Phosphorus pentoxide availability ranged from 88 to 93% based on solubility in 2% citric acid and 80 to 90% based on solubility in neutral ammonium citrate. This process provides a possible method for the utilization of wet process by-product gypsum in a granular, nonhygroscopic, nonacidic phosphate fertilizer.

PHOSPHATE ROCK can be fused with certain addition agents to produce available phosphorus pentoxide. The fused mass is generally quenched in a high velocity stream of water and the resulting products are usually granular, nonacidic, nonhygroscopic, and easily ground. No attention is given to the removal of fluorine and the phosphorus pentoxide is soluble in neutral ammonium citrate or 2% citric acid.

This type process has been studied using olivine as the addition agent in an electric furnace (5, 6, 9). Moulton (7) described a commercial plant using the olivine process and Davy (4) demonstrated its feasibility in a gas fired furnace. Bridger and Boylan (2) developed a process using langbeinite as

the addition agent and a gas-fired furnace. The authors (7) studied a process using mineral gypsum as an addition agent and produced an 0-10-0 fertilizer material in the laboratory. Stinson and Munna (8) produced a phosphate slag as a by-product of a process designed to recover sulfur dioxide from by-product gypsum obtained in the manufacture of phosphoric acid.

The present study was a direct attempt to produce a phosphate fertilizer from phosphate rock and by-product gypsum obtained from wet process phosphoric acid, without the addition of any other material. Such a process would have the advantage of a no-cost raw material at the site of supplies of the other raw material.

Raw Materials and Analysis

Phosphate rock (Davison Chemical Corp.) was used in these studies (Table I). Ground rock A was dried at 212° F. for 5 hours before using. The ground rock, as well as the unground, non-dried rock B, was used in the pilot plant.

The by-product gypsum (Davison Chemical Corp., Joplin, Mo.) was received wet and was dehydrated at 500° F. before use. A portion of the gypsum was reduced to the hemihydrate before agglomeration for use in the pilot plant. It was not ground in either case.

The mineral gypsum (U. S. Gypsum Corp., Fort Dodge, Iowa) was treated similarly as the by-product gypsum before use. The chemical and the Tyler Standard screen analyses of these raw materials are given in Table I.