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UREA: A VERSATILE SOURCE OF NITROGEN

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by

Donald L. Kachelman, Chemical Engineer
and
Carl A. Cole, Jr., Chemical Engineer
Field Engineering Staff
Division of Technology Development
National Fertilizer Development Center

TENNESSEE VALLEY AUTHORITY
Muscle Shoals, Alabama

Urea: A Versatile Source of Nitrogen

Last year, reduced urea prices caused fertilizer manufacturers to consider using more urea to meet their nitrogen requirements. Due to the recent popularity of urea and the many questions on its use, the Tennessee Valley Authority has written a book on various ways to use urea. This paper will serve as an overview of ways to use urea in combination with ammonium nitrate, ammonium sulfate, ammonia, monoammonium phosphate (MAP), phosphoric acid, potassium chloride, and sulfuric acid to produce solutions and suspensions. Methods using urea and phosphoric acid to produce fluid fertilizers containing low polyphosphate contents to improve storability are discussed. Production schemes on using solid urea as a feedstock to produce granular urea-ammonium phosphate and granular urea-ammonium sulfate are described.

Using Urea in Solutions

Urea solutions usually contain 18 to 20% nitrogen and have salt-out temperatures between 28 and 40°F. However, concentrations as high as 23% nitrogen with a salt-out temperature of 61°F are used in some areas. Figure 1 shows the salt-out temperatures and specific gravities for urea solutions of various concentrations at different temperatures (1).

Urea has a negative heat of solution (95 Btu's/lb), which means that it absorbs heat as it dissolves (2). This cools the solution so that the urea dissolves very slowly. If it cools the mixture enough to approach the salt-out temperature of the solution in the tank, the dissolution rate becomes extremely slow. The urea does not stop dissolving completely because some heat will flow in from the atmosphere unless the air temperature is lower than the temperature of the mixture.

To produce urea solutions containing 18 to 20% nitrogen from solid urea, warm water between 80 to 90°F is needed for a satisfactory production rate. If the water is 50 to 60°F, only a 15 to 16% nitrogen solution can be produced with a satisfactory production rate. If 15% nitrogen is too low, it can be pumped to storage and allowed to warm up (1 or 2 days) and then pumped back to the mixer to produce an 18 to 20% nitrogen solution.

Adding 50 to 150 pounds of ammonia, which has a positive heat of solution, per ton of mixture will provide heat to help dissolve urea in strong nitrogen solutions. But this must be done with care. Most of the ammonia will remain in the solution and will probably show up as nitrogen if an analysis is made. If such a mixture is broadcast, most of the nitrogen from the anhydrous ammonia will probably be lost. If the mixture is injected and covered up, the ammonia nitrogen will probably be recovered. Water heaters, which give satisfactory production rates (20 tons/hr plus), cost from $15,000 to $25,000 and require burning fossil fuel to provide heat. Although a hot water boiler has a high initial capital cost, heating water in a hot water boiler using natural gas is about 28 times cheaper for the same amount of heat supplied by ammonia. The cost for 10,000 Btu's from ammonia is about $1.43, while the cost for 10,000 Btu's from natural gas is about $0.05.

Urea-ammonium nitrate (UAN) solutions usually contain 28 to 32% nitrogen and the ratios of urea to ammonium nitrate calculate to give the lowest salt-out temperature possible. The lowest salt-out temperatures for 28, 30, and 32% nitrogen UAN solutions are -1°F, 14°F, and 28°F, respectively. Figure 2 shows the solubility system for urea, ammonium nitrate, and water (3).

A 28% nitrogen UAN solution absorbs 80.6 Btu's per pound of solid; 30% absorbs 77.7 Btu's per pound of solid; and 32% absorbs 65.1 Btu's per pound of solid (4). These mixtures absorb enough heat so that production of UAN solution, particularly 32%, is agonizingly slow unless some outside heat source is supplied or one of the techniques discussed for urea is used. Experience shows that water at 130°F will make a batch of 28% nitrogen UAN solution from solid urea and solid ammonium nitrate in about 17 minutes. Water at 180°F will make 30% nitrogen UAN solution from solid urea and solid ammonium nitrate in about 26 minutes and water at 200°F will make 32% nitrogen UAN solution from solid urea and solid ammonium nitrate in about 34 minutes.

UAN solution can be made from solid urea and ammonium nitrate solution at a satisfactory production rate if the ammonium nitrate solution temperature is above its salt-out temperature. To make a 28% nitrogen solution from solid urea, an ammonium nitrate solution containing 21% nitrogen with a salt-out temperature of 48°F is needed and to make a 30% nitrogen solution, an ammonium nitrate solution containing 23% nitrogen with a salt-out temperature of 70°F is needed. To make a 32% nitrogen solution, an ammonium nitrate solution containing 25% nitrogen with a salt-out temperature of 95°F is needed.

UAN solutions can be made from solid ammonium nitrate and urea solution at a satisfactory production rate if the urea solution temperature is above its salt-out temperature. To make a 28% nitrogen solution from solid ammonium nitrate, a urea solution containing 24% nitrogen with a salt-out temperature of 68°F is needed. To make a 30% nitrogen solution, a urea solution containing 27% nitrogen with a salt-out temperature of 93°F is needed and to make a 32% nitrogen solution, a urea solution containing 31% nitrogen with a salt-out temperature of 122°F is needed.

UAN solution needs a corrosion inhibitor if it is to be stored in mild steel tanks because the corrosion rates are considerably higher than for urea solution. Frequently, about 0.2% P_2O_5, supplied by ammonium polyphosphate solution (10-34-0), is used. Some manufacturers merely add enough anhydrous ammonia to bring the pH of the solution up to 7.4.

Urea-ammonium sulfate (UAS) solutions can be produced to make useful sulfur-containing solutions. Common UAS solution grades are 21-0-0-3S with a salt-out temperature of 41°F and 20-0-0-5S with a salt-out temperature of 32°F. Figure 3 shows the solubility system for urea, ammonium sulfate, and water. Usually UAS solutions with a salt-out temperature of 32°F made from solid urea and solid ammonium sulfate need water of at least 90°F for a satisfactory production rate. If only 50 to 60°F water is available, only urea-ammonium sulfate solutions with salt-out temperatures below 20°F can be produced at a satisfactory rate.

Urea-ammonium nitrate-ammonium sulfate (UANAS) solutions can be produced to make useful sulfur-containing solutions. UANAS solutions can have a wide range of compositions because three salts exist instead of the two salt solutions made before. Data only exists for adding ammonium sulfate to commercial UAN solution containing 32% nitrogen. Figure 4 shows the solubility system for UAN solution (32% nitrogen), ammonium sulfate, and water (5). Commercial UAN solutions (28 to 32% nitrogen) contain about 50% of the nitrogen from urea and about 50% of the nitrogen from ammonium nitrate. Although little data exist, it has been noted that slightly higher analysis grades may be possible for some N to S ratios when 75 to 90% of the nitrogen other than the nitrogen from ammonium sulfate is supplied by urea.

Common UANAS solution grades with salt-out temperatures of 32°F are 25-0-0-3S and 20-0-0-5S. Usually, to produce UANAS solutions with salt-out temperatures of 32°F from commercial UAN solutions (28 to 32% nitrogen) and solid ammonium sulfate, it is best to dissolve the ammonium sulfate in water before adding the UAN solution.

Usually a water temperature of 50 to 60°F will dissolve the ammonium sulfate at a satisfactory rate if UAN solution is used to supply the remainder of the nitrogen. To prevent problems, be sure the percent ammonium sulfate in water is less than 41.5% ammonium sulfate since the solubility of ammonium sulfate changes drastically above 41.5% ammonium sulfate. Hot water (180°F or higher) is needed to make high nitrogen to sulfur ratio UANAS solutions such as 27-0-0-2S from solids. To produce lower nitrogen to sulfur ratio grades, such as 20-0-0-5S, from solids, warm water at 130°F is usually sufficient for a satisfactory production rate. To produce lower nitrogen sulfur grades such as 13-0-0-7.5S from solid materials, warm water at 80°F is usually sufficient to give a satisfactory production rate. If only cool water, 50 to 60°F, is available to produce solutions from solids, lower salt-out temperature solutions (0°F or less) should be produced to obtain a satisfactory production rate.

Ammonia-urea solutions can be produced which contain 29 to 32% nitrogen with no vapor pressure at 90°F and salt-out temperatures between 14 and 41°F. Figure 5 shows the solubility system for ammonia, urea, and water at various temperatures (6). These solutions have to be handled and applied like aqua ammonia but have the advantage of being higher in analysis than aqua ammonia. Too, the heat supplied by the ammonia is enough to dissolve the urea so that hot water is not needed and a cooler is not needed to cool the solution as is the case with straight aqua ammonia.

Solubility data for NP, NK, and NPK solutions produced from ammonia, urea, ammonium nitrate, orthophosphoric acid, polyphosphoric acid, and potassium chloride are usually divided into one of four categories.

Supplemental Nitrogen Source	Phosphate Source	Potassium Source
(1) Urea (100% urea N)	Ortho	Potassium chloride
(2) Urea (100% urea N)	Poly	Potassium chloride
(3) UAN (50% urea N and 50% ammonium nitrate N)	Ortho	Potassium chloride
(4) UAN (50% urea N and 50% ammonium nitrate N)	Poly	Potassium chloride

For these solutions ammonia has been used to neutralize the phosphate source to an N to P_2O_5 ratio of 0.3 (10-34-0) or 0.333 (8-24-0). The solubility system for urea, ammonium polyphosphate, potassium chloride, and water at 32°F is shown in figure 6 (7). The salt-out temperature for any NP, NK, or NPK grade can be estimated with the use of this chart.

If a solution contains additional nitrogen so that the N to P_2O_5 ratio is higher than 0.3 or 0.333, this additional nitrogen comes from some source other than ammonia and is called supplemental nitrogen.

Supplemental nitrogen is usually UAN solution which contains about 50% of its nitrogen from urea and 50% from ammonium nitrate. For solutions with a high N to P_2O_5 ratio which do not contain potassium chloride, the solubility is better when 50% of the supplemental nitrogen is from urea and 50% is from ammonium nitrate (UAN solutions). For solutions that contain potassium chloride, the solubility is usually better when more of the supplemental nitrogen is from urea. This is shown in figure 7 (8). The ammonium nitrate in UAN reacts with potash in NPK solutions to form potassium nitrate. Potassium nitrate has a solubility much lower than urea or ammonium nitrate at ordinary temperatures, and therefore raises the salt-out temperature of grades containing it.

Urea in Suspensions

Figure 8 shows the calculated percent solids by weight at different temperatures for various concentrations of urea suspensions. Urea suspensions have the disadvantage of having drastic changes in percent solids by weight as the temperature changes. This causes the crystals to fuse together and causes crystal growth. It is best for urea suspensions to be periodically agitated (recirculated with a pump) during storage as the temperature of the suspension changes. Small-scale tests have shown that a 28 or 29% nitrogen suspension with 1.5% clay is satisfactory. A 30% nitrogen suspension has been satisfactory above 50°F. These satisfactory suspensions correspond to about 30% solids by weight.

The ideal way to produce urea suspensions is to rapidly cool the hot urea solution from a urea plant below its salt-out temperature. This rapid cooling will produce many tiny crystals which will produce a satisfactory suspension. To produce these suspensions from solid urea, hot water and steam would be required to dissolve all of the urea. It may be possible that warm water at 130 to 150°F would be satisfactory in reducing the particle size of the urea to produce satisfactory suspensions. One fertilizer dealer claims that he has produced a 28% nitrogen solution from urea and water at 55°F. He claims that after mixing for 20 to 30 minutes the particle size has been reduced so that it can be suspended with clay. He reports that he stores this material for short periods of time (less than 2 days). Other dealers report that they have produced suspensions from microprilled urea (16 to 28 mesh).

For several years TVA has demonstrated a UAN suspension containing 36% nitrogen with 72.2% of the nitrogen from urea and 27.8% of the nitrogen from ammonium nitrate (9). Figure 9 shows the calculated percent solids by weight at different temperatures for this UAN suspension. The change in percent solids by weight as the temperature changes for this suspension is not as drastic as a urea suspension.

The ideal way to produce this suspension is to rapidly cool the hot UAN solution from a UAN plant below its salt-out temperature. This rapid cooling will produce many tiny crystals which will produce a satisfactory suspension. To produce these suspensions from solid urea and solid ammonium nitrate, hot water and steam would be required to dissolve all of the solids.

Another method to produce this suspension is to add solid ammonium nitrate to a hot solution (>79% urea concentration). Adding the solid ammonium nitrate to the hot urea solution will cool the solution below its saturation temperature producing many tiny urea crystals, and all of the ammonium nitrate will go into solution.

This 36% nitrogen suspension with this concentration is not the only UAN suspension that can be produced. There are many different combinations of urea and ammonium nitrate that will make satisfactory suspensions. One dealer reports that he adds solid urea to UAN solution (28% N) and fluid clay to produce a 33% nitrogen suspension. All of the urea does not go into solution but it is reduced in size so that he can use it for direct application. He reports that he does not store this material. However, if UAN suspensions are planned to be stored, it is recommended that they be periodically agitated.

For several years TVA has demonstrated a urea-ammonium sulfate suspension with a grade of 29-0-0-5S (9). Figure 10 shows the calculated percent solids by weight at different temperatures for this urea-ammonium sulfate suspension and for several other suspensions with different N to S ratios. The 30-0-0-3S suspension has about the same change in percent solids by weight as the temperature changes in a urea suspension. As the amount of sulfur increases, the change in percent solids by weight as the temperature changes becomes less. This occurs because ammonium sulfate is the crystal that is present instead of urea. The change in percent solids by weight as the temperature changes for ammonium sulfate is very low.

TVA produces the 29-0-0-5S grade from hot urea solution from the urea plant, sulfuric acid, and ammonia. This solution is rapidly cooled below its salt-out temperature to produce many tiny urea crystals. Urea-ammonium sulfate suspensions can be produced from solid urea, sulfuric acid, and ammonia, or solid urea, solid ammonium sulfate, sulfuric acid, and ammonia. The amount of sulfuric acid and ammonia can be determined to provide enough heat to dissolve the urea and the remainder of the sulfur can be supplied from solid ammonium sulfate. Hot water and steam would be required to produce these suspensions from solid urea and solid ammonium sulfate. It is recommended that urea-ammonium sulfate suspensions be periodically agitated.

Suspension grades that can be produced from urea and ammonium sulfate (30-0-0-3S, 29-0-0-5S, 26-0-0-9S, 23-0-0-12S, 20-0-0-15S) can also be produced from urea, ammonium nitrate, and ammonium sulfate. The urea to ammonium nitrate ratio for these suspensions is the same as it is for commercial UAN solutions (28 to 32% N). These suspensions have the advantage over urea-ammonium sulfate suspensions in that they contain less solids by weight for the same grade. This system is complicated by the formation of two ammonium nitrate-ammonium sulfate double salts. Therefore, these suspensions can have up to six different types of crystals present.

The best way to produce these suspensions is to add solid fluid grade ammonium sulfate to UAN solution. For some grades the quality of the suspension is improved if the urea to ammonium nitrate ratio is increased. Therefore, it might be advantageous to add solid urea to UAN solution and solid fluid grade ammonium sulfate to produce these suspensions.

If urea is used as the supplemental nitrogen source or if additional urea is used in combination with UAN solution to produce NPK suspensions, the suspensions should be less viscous due to better solubility.

The maximum N to P_2O_5 ratio that can be produced by dissolving urea using the heat of reaction between phosphoric acid and ammonia is 2.7 to 1 corresponding to a 27-10-0 grade. The maximum N to S ratio that can be produced by dissolving urea using the heat of reaction between sulfuric acid and ammonia is 10 to 1 corresponding to a 30-0-0-3S grade. The maximum N to P_2O_5 ratio that can be produced by dissolving urea using the heat of reaction between MAP and ammonia is 1 to 1 corresponding to a 18-18-0 grade.

To produce grades from phosphoric acid, ammonia, and urea it is best to add the urea to the water followed by phosphoric acid addition and ammoniation.

To produce grades from sulfuric acid, ammonia, and urea it is best to add the urea to the water followed by sulfuric acid addition and ammoniation. For grades with a sulfur content above 5%, it is probably best to use solid ammonium sulfate along with sulfuric acid and ammonia. Only enough sulfuric acid to provide enough heat to dissolve the urea is required. If all of the sulfur is to be obtained from sulfuric acid, it is best that the ammonia and sulfuric acid are added simultaneously to keep the pH between 5 and 7 to minimize corrosion. Also quite a bit of water will be evaporated due to the high heat of reaction between sulfuric acid and ammonia.

To produce grades from MAP, ammonia, and urea it is best to add the MAP to water and ammoniate to produce a 10-30-0 or 11-33-0 grade. This is desired so that the temperature of the mixture will be sufficient to dissolve the MAP. Urea is added after the MAP has dissolved. Tests have shown that a 1 to 1 ratio corresponding to a 18-18-0 grade will completely dissolve the urea. It may be possible to produce grades with a higher N to P_2O_5 ratio although not all of the urea will dissolve. An 18-9-9 grade was produced from water at 70°F and the urea that did not dissolve in the hot 10-30-0 mix was reduced in size such that it could be easily applied with size 40 flood nozzles. It is recommended that dealers start off producing grades with the 1 to 1 ratio and gradually increase this ratio until the urea is not satisfactorily reduced in size.

Acid Fertilizers

Figure 11 shows the solubility system for urea, phosphoric acid, and water (10). Common solution grades with salt-out temperatures between 28 and 38°F are 6-18-0, 14-14-0, and 18-6-0. Although the reaction between urea and phosphoric acid is slightly exothermic, the final mix temperature should not exceed 140°F. These solutions have a pH of about 1.5 and are highly corrosive to mild steel.

Figure 12 shows the solubility system for UAN (32% N), phosphoric acid, and water. Common solution grades with salt-out temperatures of 32°F are 4-12-0, 8-8-0, and 13.5-4.5-0. The solubility for this system, 50% of the nitrogen from urea and 50% of the nitrogen from ammonium nitrate, is not as high as when 100% of the nitrogen is from urea.

Figure 13 shows that the lowest salt-out temperature for a 3-1-0 ratio grade is when 80% of the nitrogen is from urea and 20% of the nitrogen is from ammonium nitrate.

Figure 14 shows the solubility system for urea, sulfuric acid, and water (11). Common solution grades with salt-out temperatures below 50°F are 9-0-0-25S, 18-0-0-17S, and 29-0-0-9S. The reaction between urea and sulfuric acid is extremely exothermic with final mix temperatures reported as high as 280°F. These solutions are highly corrosive to mild steel and can be damaging to stainless steel.

Satisfactory NPK acid solutions can be produced from urea, phosphoric acid, and potassium chloride. Several reported solution grades with salt-out temperatures of 32°F are 11-8-8, 6-30-6, and 16-11-5. From tests conducted thus far, when potash is needed in the grade, the desired source of nitrogen is from urea. Tests show that when ammonium nitrate is added to grades containing potash the solubility decreases, probably due to the formation of potassium nitrate.

<u>Urea-Ammonium Polyphosphate Solutions</u>

Typical ammonium orthophosphate solutions (8-24-0) produced from merchant-grade wet-process phosphoric acid (Florida phosphate rock) can develop 10 to 20% by volume of sludge during storage. One way to reduce this amount of sludge is to add urea to the phosphoric acid prior to ammoniation so that polyphosphates will be produced during ammoniation. Ammoniation of a mixture of urea and phosphoric acid produces polyphosphates by the following reaction at temperatures above 250°F.

$$2\{CO(NH_2)_2 \cdot H_3PO_4\} \xrightarrow{\Delta} (NH_4)_2H_2P_2O_7 + CO(NH_2)_2 + CO_2\uparrow$$

Tests have shown that a 12-25-0 solution containing 10 to 15% polyphosphate can reduce the amount of sludge significantly.

Urea: Solid Feedstock in Granulation Plants

For some granular fertilizer producers it is advantageous to produce a granular urea-ammonium phosphate or granular urea-ammonium sulfate product suitable for direct application or bulk blending. For regional granulation plants, the usual size of urea is too large to add directly to the granulator to produce a high nitrogen homogeneous product that does not have a bulk blended appearance. One method is to crush the urea in a roll mill before it is added to the granulator. Another method is to add the urea directly to a preneutralizer with an ammonium phosphate slurry ($NH_3:H_3PO_4$ mole ratio = 0.5) or an ammonium bisulfate slurry ($NH_3:H_2SO_4$ mole ratio = 1.0) while keeping the temperature of the slurry below 200°F to prevent the urea from decomposing.

The slurry along with the rest of the formulated ammonia is added to the granulator. Tests have shown that a granular urea-ammonium phosphate of grade 28-28-0 can be produced by this method using merchant-grade wet-process phosphoric acid. The product does have to be dried since the slurry from the preneutralizer contains 9 to 10% moisture. Tests have also shown that a granular urea-ammonium sulfate of grade 37-0-0-8S can be produced by this method using 93% sulfuric acid. Due to the small amount of moisture present in this formulation very little drying is required.

Conclusion

Urea is a cheap and versatile source of nitrogen. Urea can easily be used in combination with ammonium nitrate, ammonium sulfate, ammonia, MAP, phosphoric acid, potassium chloride, and sulfuric acid. Urea has many advantages for production of solution, suspension, and granular fertilizer products.

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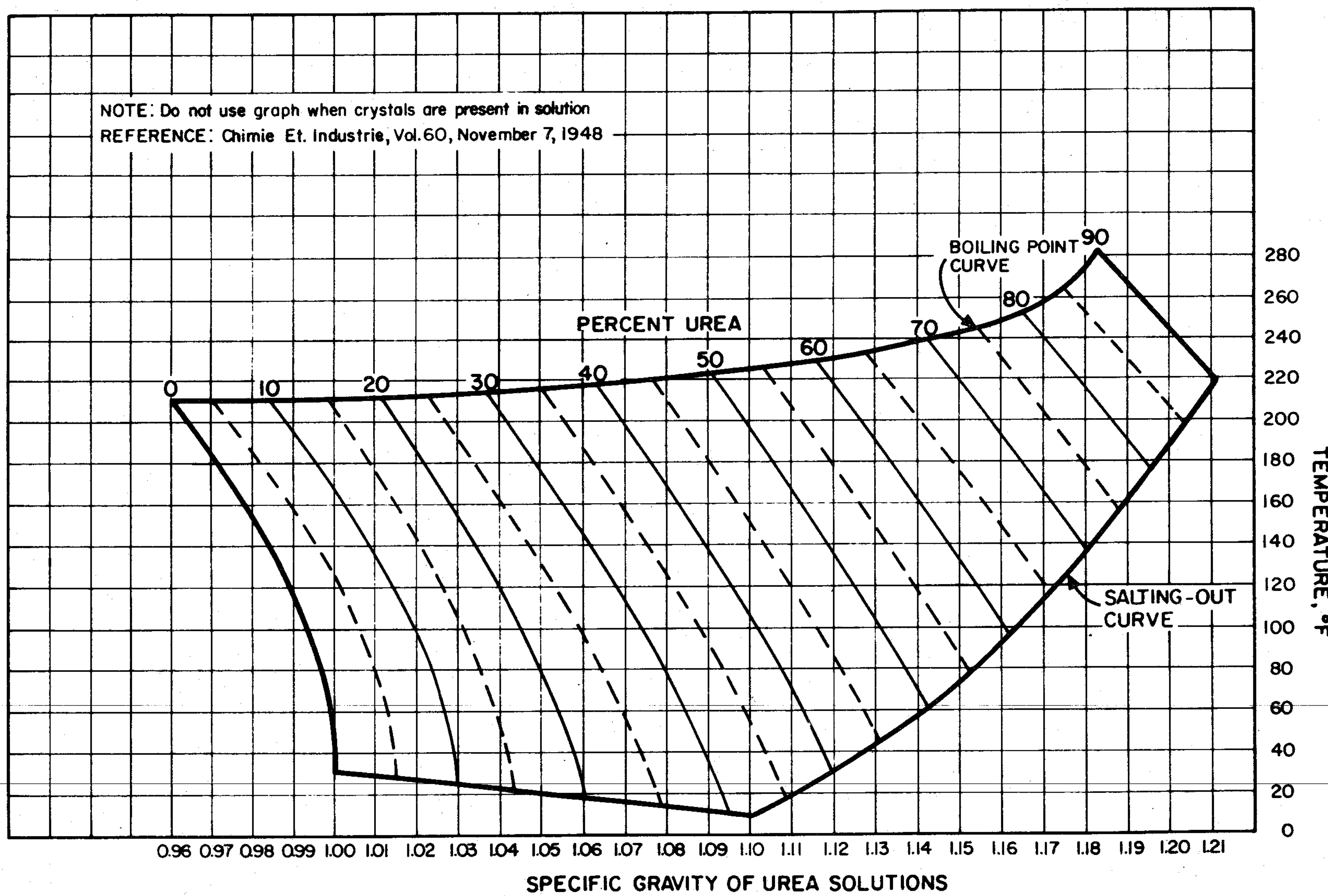


FIGURE 1

PHYSICAL PROPERTIES OF UREA SOLUTIONS

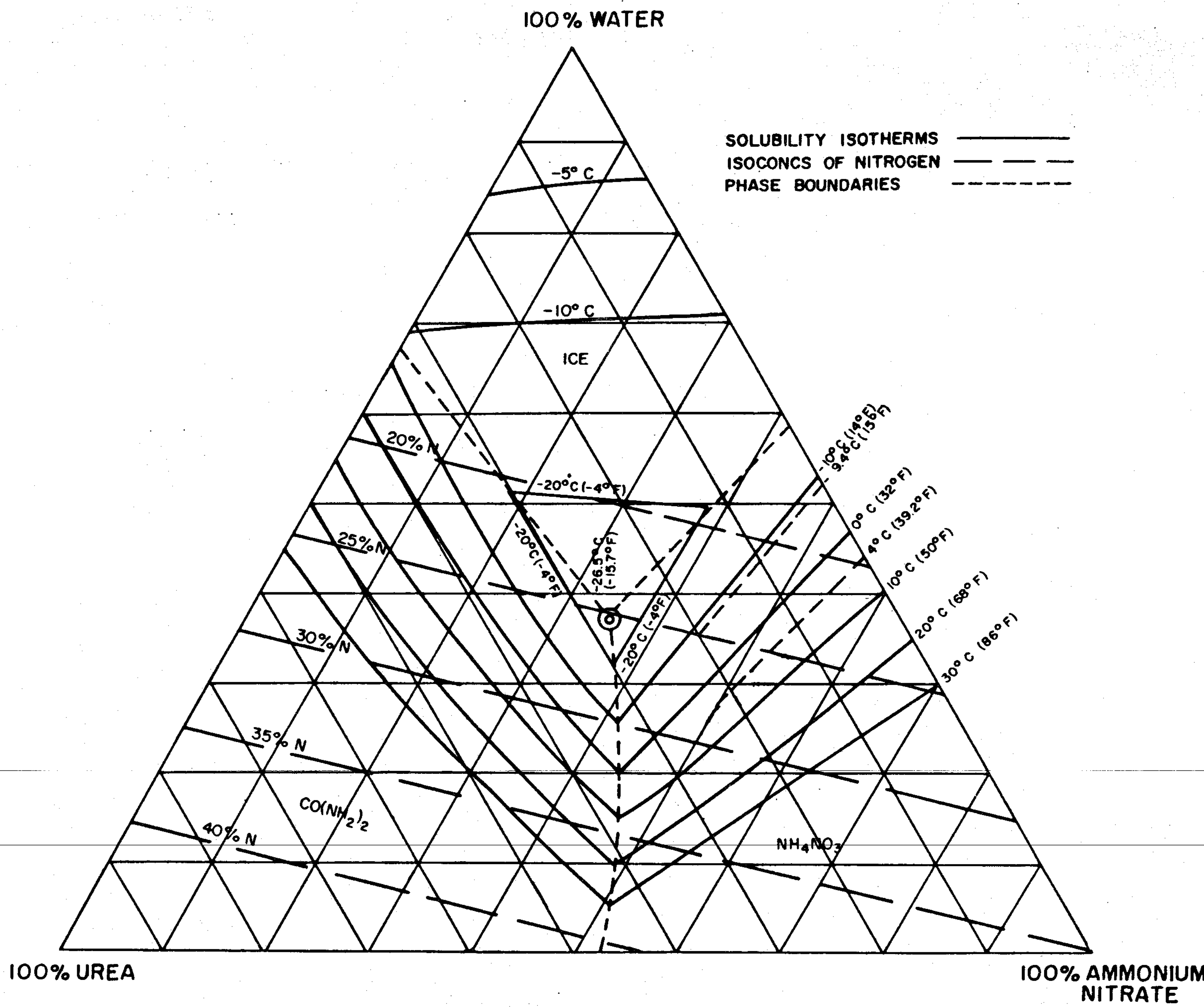


FIGURE 2
SOLUBILITY SYSTEM OF AMMONIUM NITRATE-UREA-WATER

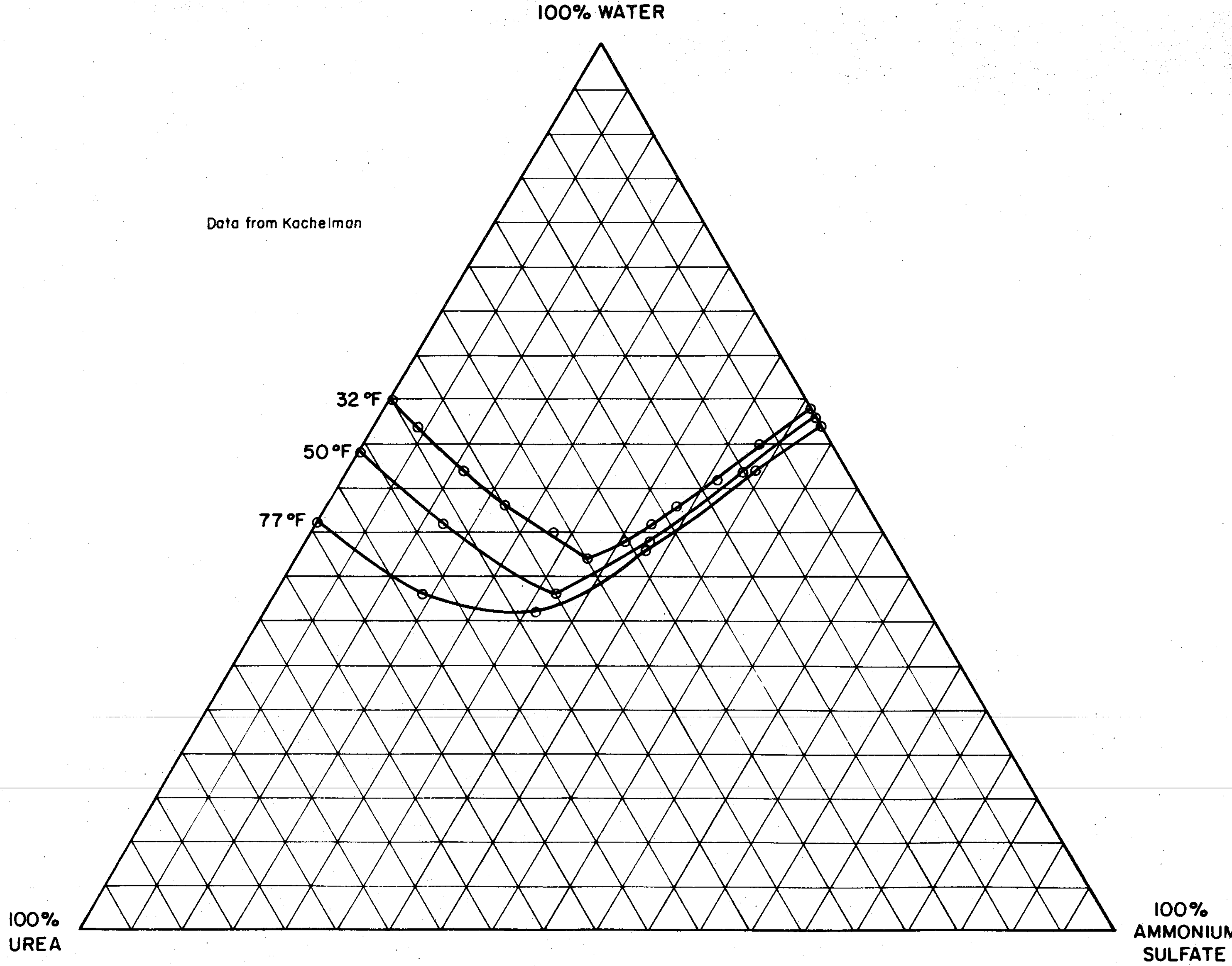


FIGURE 3

SOLUBILITY SYSTEM FOR UREA-AMMONIUM SULFATE-WATER

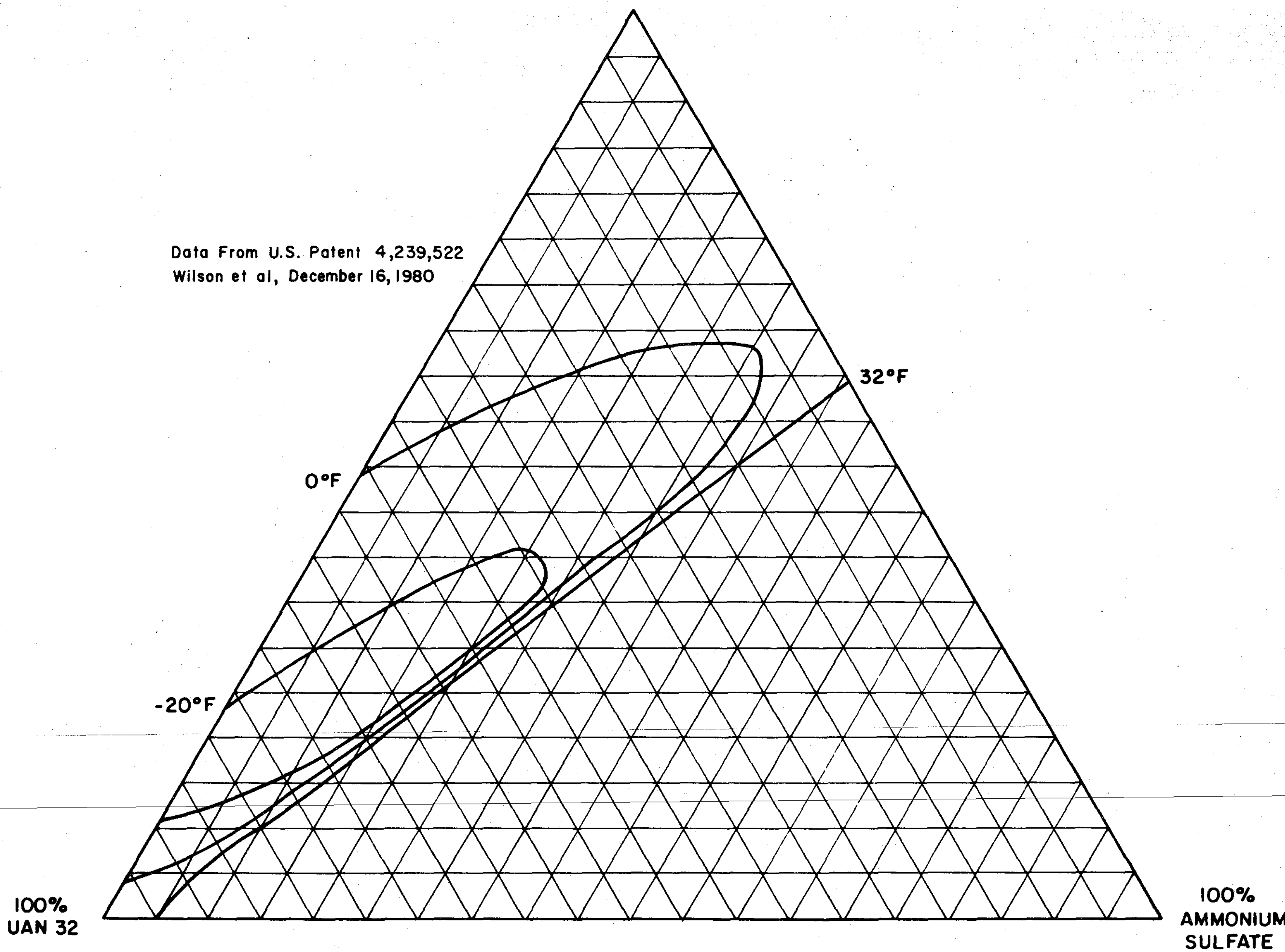


FIGURE 4

SOLUBILITY SYSTEM FOR UAN 32 - AMMONIUM SULFATE-WATER

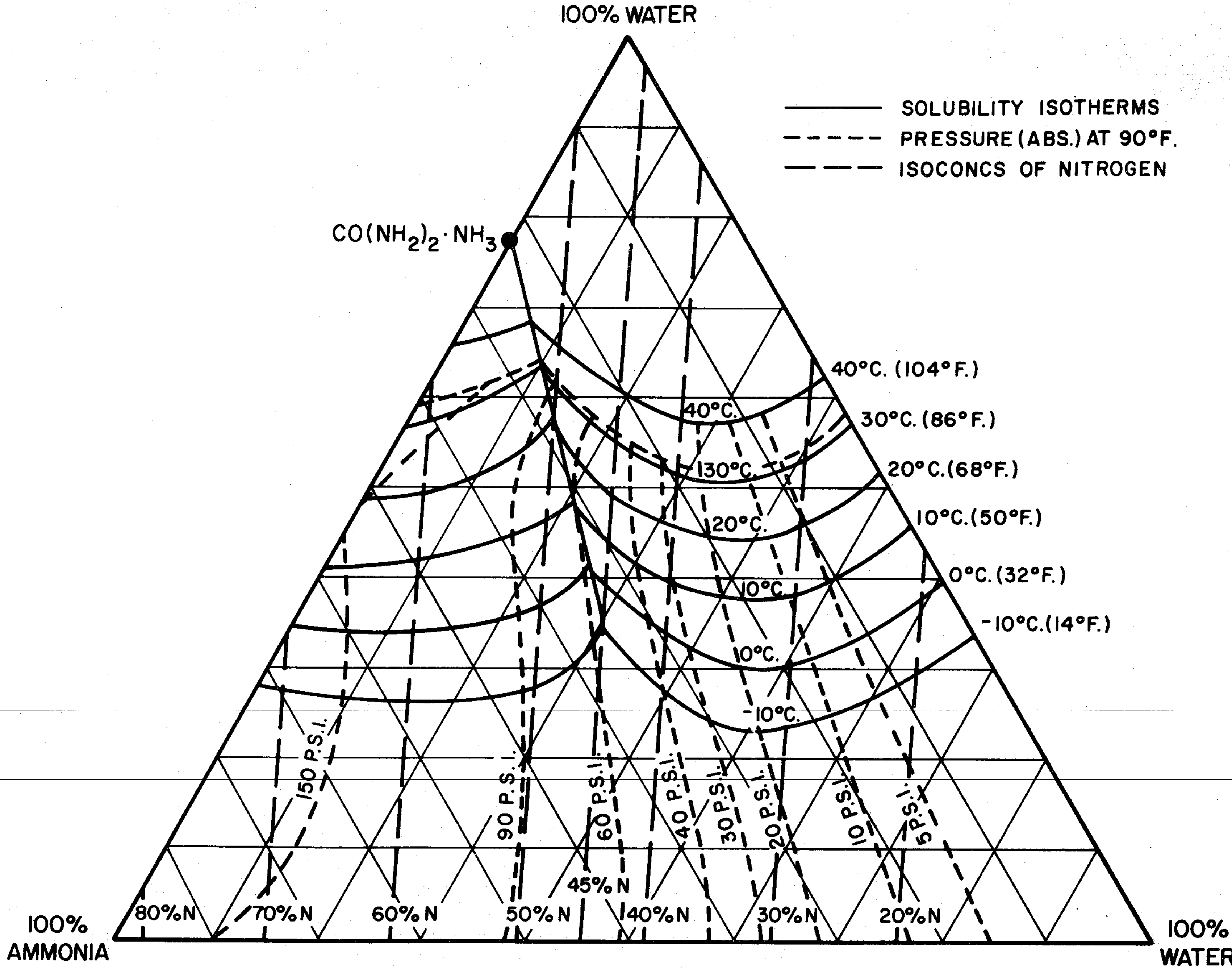


FIGURE 5

SOLUBILITY SYSTEM FOR AMMONIA-UREA-WATER

Supplemental Nitrogen Source	Urea
Phosphate Source	45% poly
N:P_2O_5 Ratio	1:3.4 or .3

b coefficients, °F

Urea	$(CO(NH_2)_2)$	.15
Monoammonium Phosphate	$(NH_4H_2PO_4)$	.12
Potassium Chloride	(KCl)	.08
Diammonium Phosphate	$((NH_4)_2HPO_4)$	.06

10-34-0 FROM PIPE REACTOR PROCESS
NUMBERS ON LINE INDICATE % TOTAL PLANT NUTRIENT SOLUBLE $(N + P_2O_5 + K_2O)$

Data from Slack, Potts, Shaffer

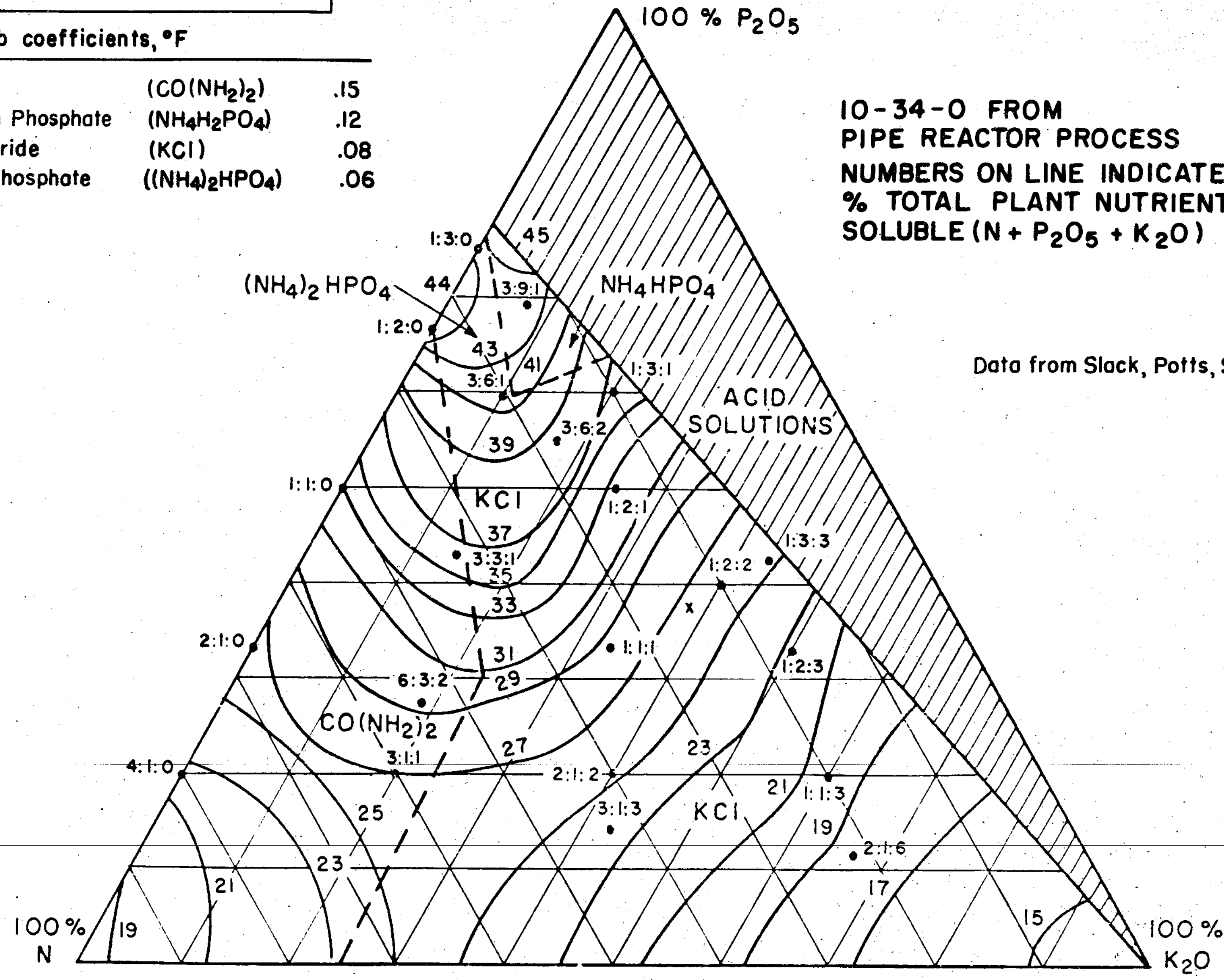
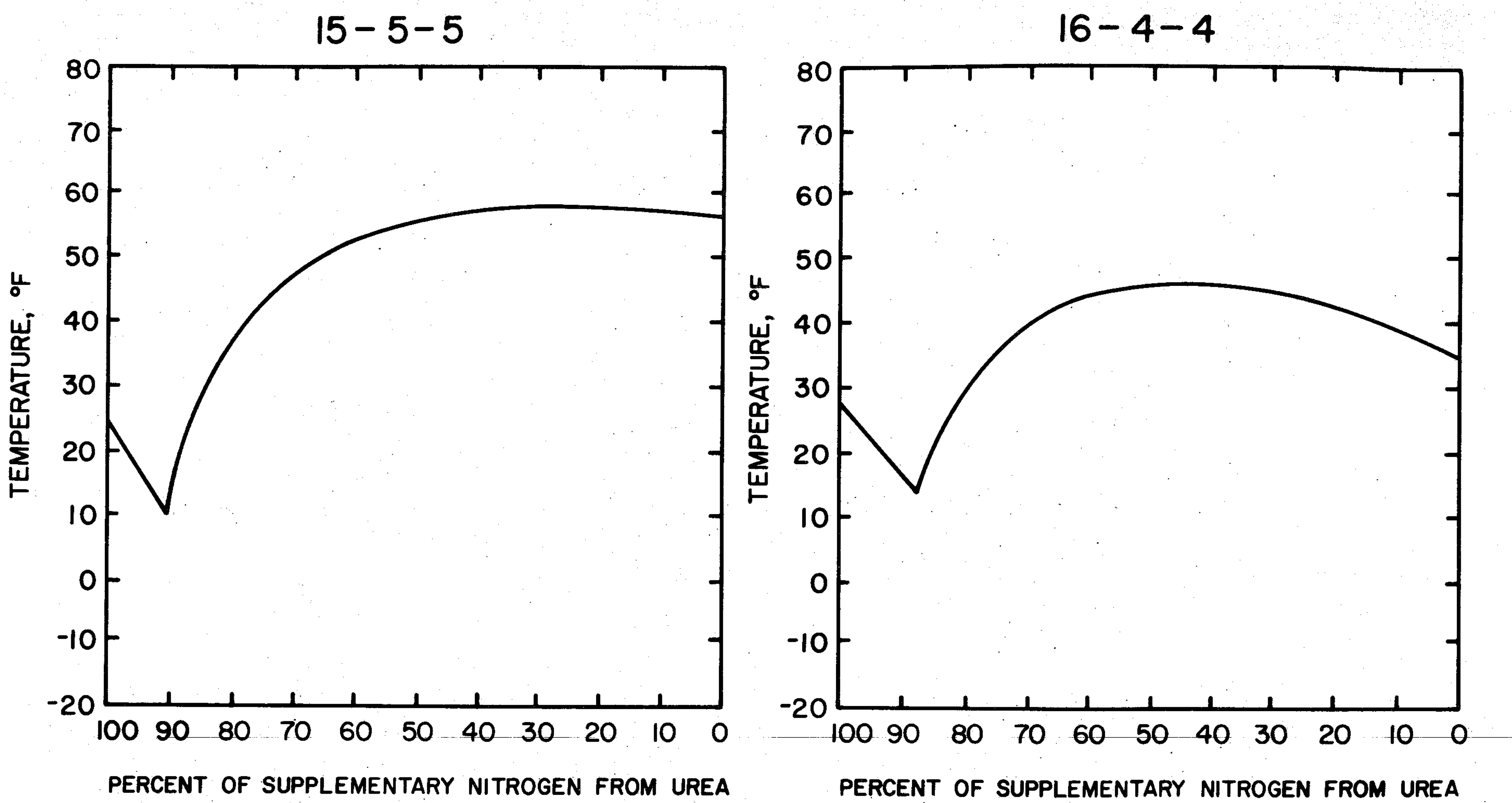


FIGURE 6
SYSTEM 10-34-0, UREA, POTASSIUM CHLORIDE, WATER AT 32°F.

FIGURE 7



7.1 ← PRODUCT pH RANGE → 6.0

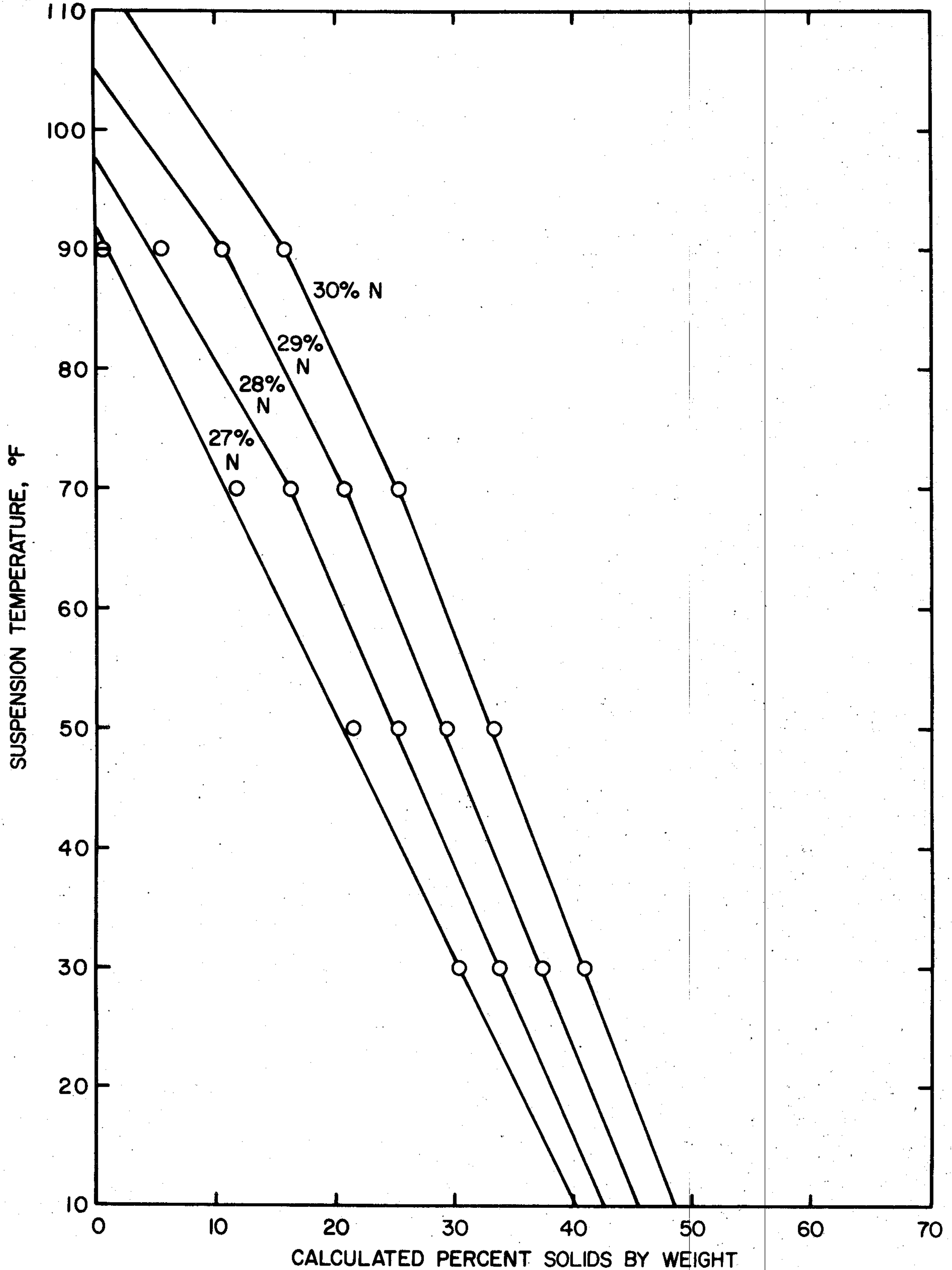
10.1 ← PRODUCT DENSITY RANGE → 10.8
(LBS. PER GAL. AT 60°F)

7.0 ← PRODUCT pH RANGE → 5.9

9.7 ← PRODUCT DENSITY RANGE → 10.6
(LBS. PER GAL. AT 60°F)

FIGURE 8

CALCULATED PERCENT SOLIDS BY WEIGHT VERSUS SUSPENSION TEMPERATURE FOR VARIOUS CONCENTRATIONS OF UREA SUSPENSIONS



CALCULATED PERCENT SOLIDS BY WEIGHT VERSUS SUSPENSION TEMPERATURE FOR A UREA-AMMONIUM NITRATE SUSPENSION CONTAING 36% N WITH 72.2% OF THE NITROGEN FROM UREA AND 27.8% OF THE NITROGEN FROM AMMONIUM NITRATE

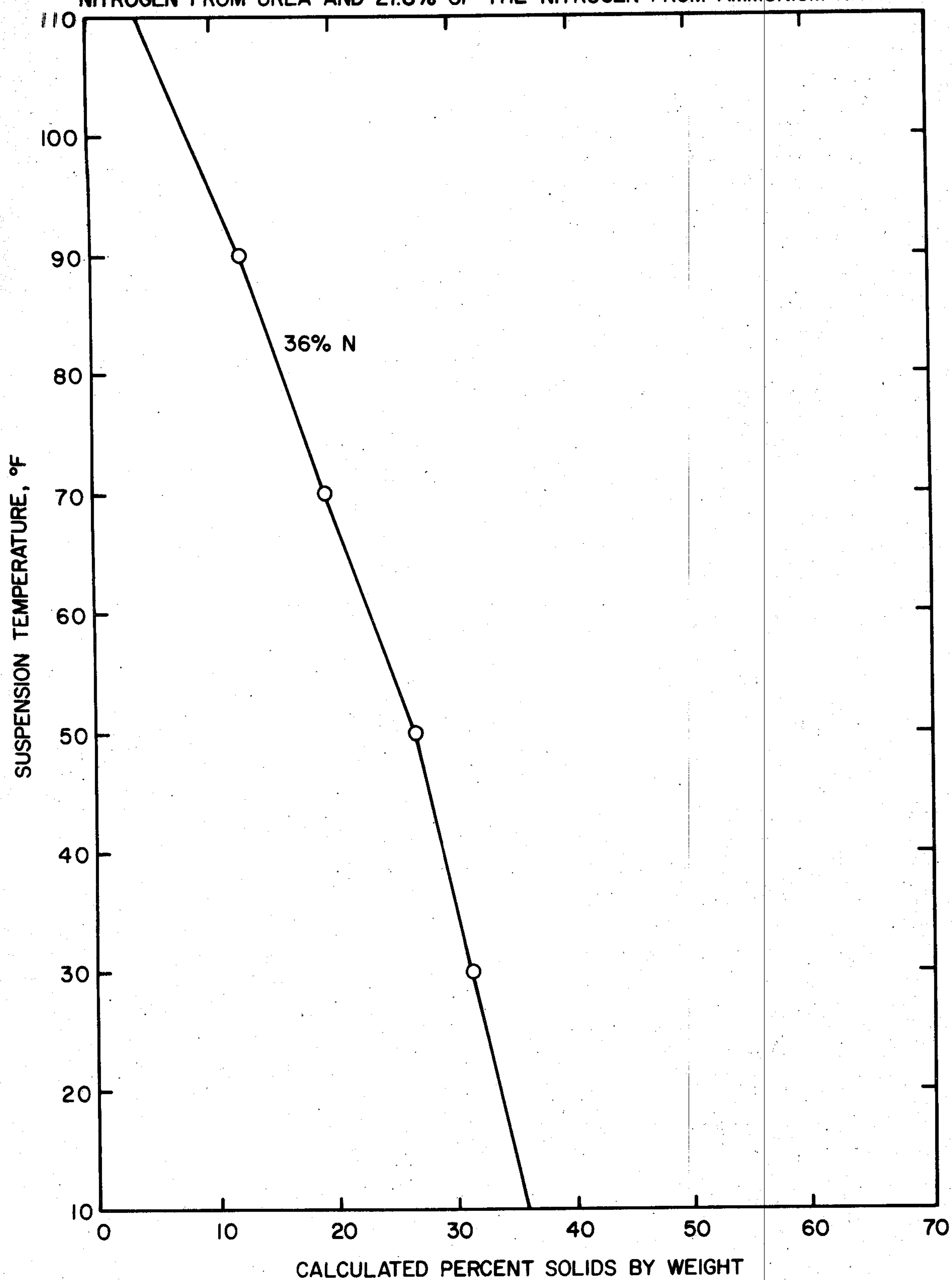
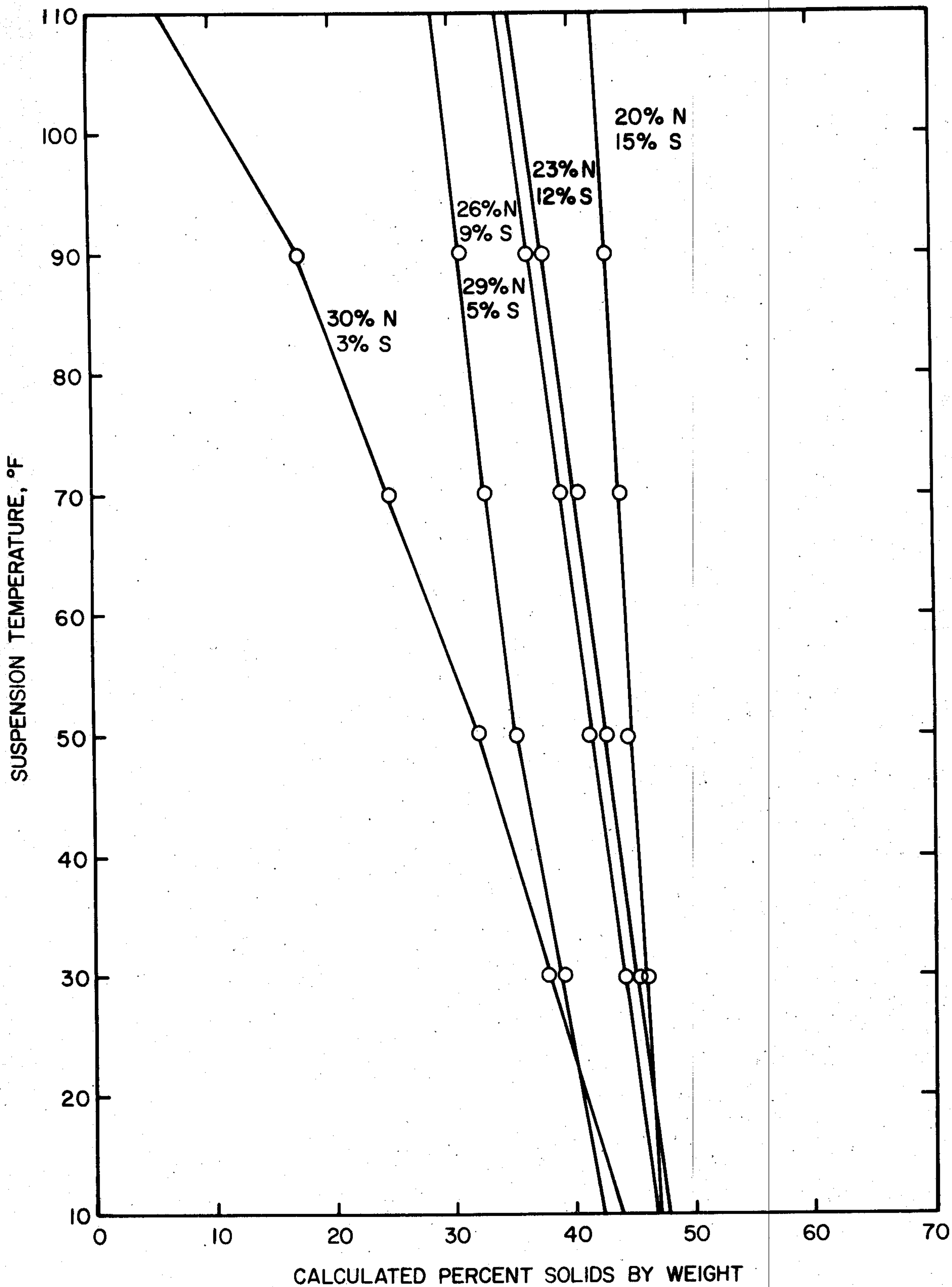


FIGURE 9

FIGURE 10

CALCULATED PERCENT SOLIDS BY WEIGHT VERSUS SUSPENSION TEMPERATURE FOR VARIOUS CONCENTRATIONS OF UREA-AMMONIUM SULFATE SUSPENSIONS



Data From Nurakhmetov, Beremzhanov, and Khanapin

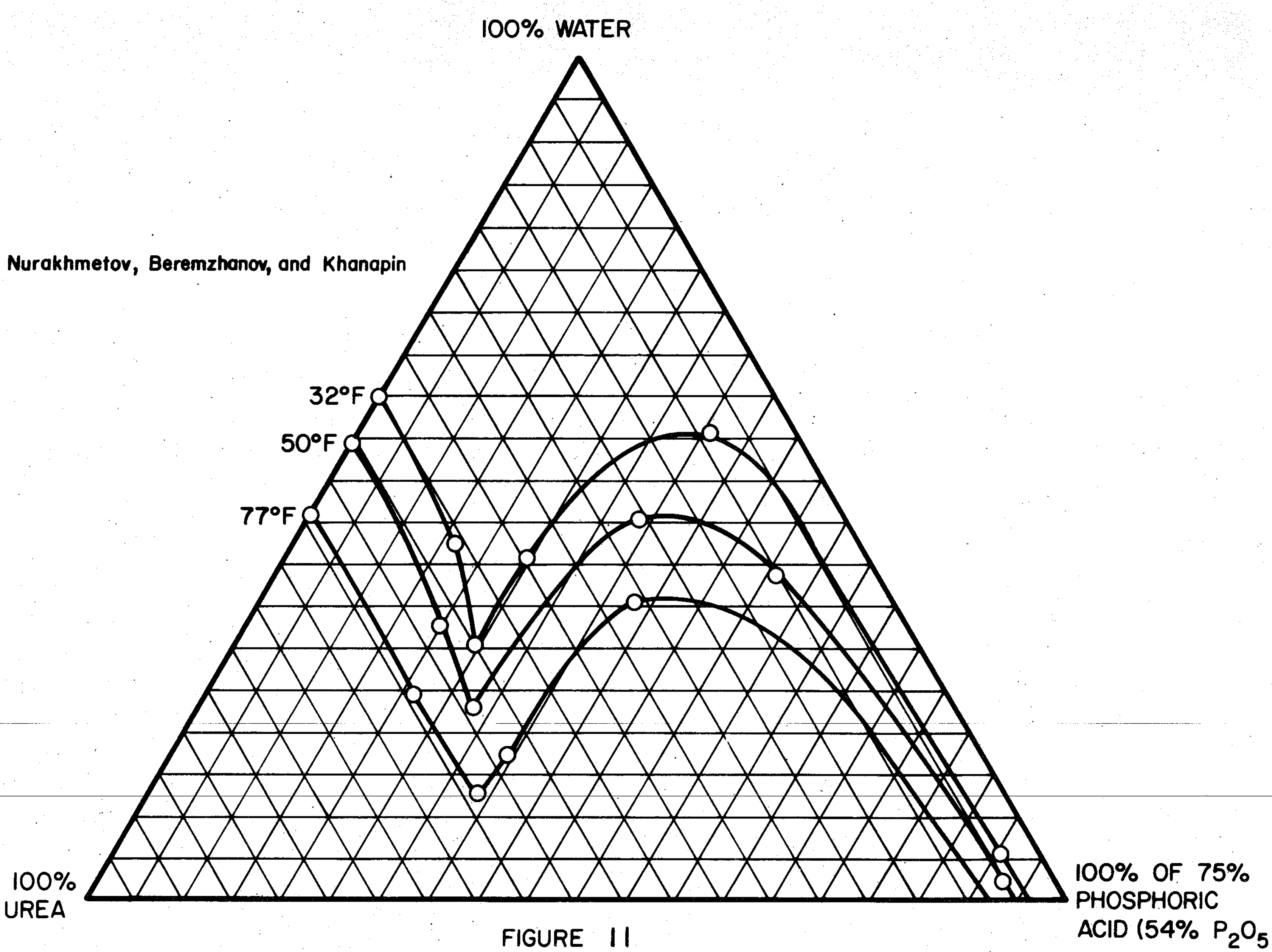


FIGURE 11

SOLUBILITY SYSTEM FOR UREA - PHOSPHORIC ACID - WATER

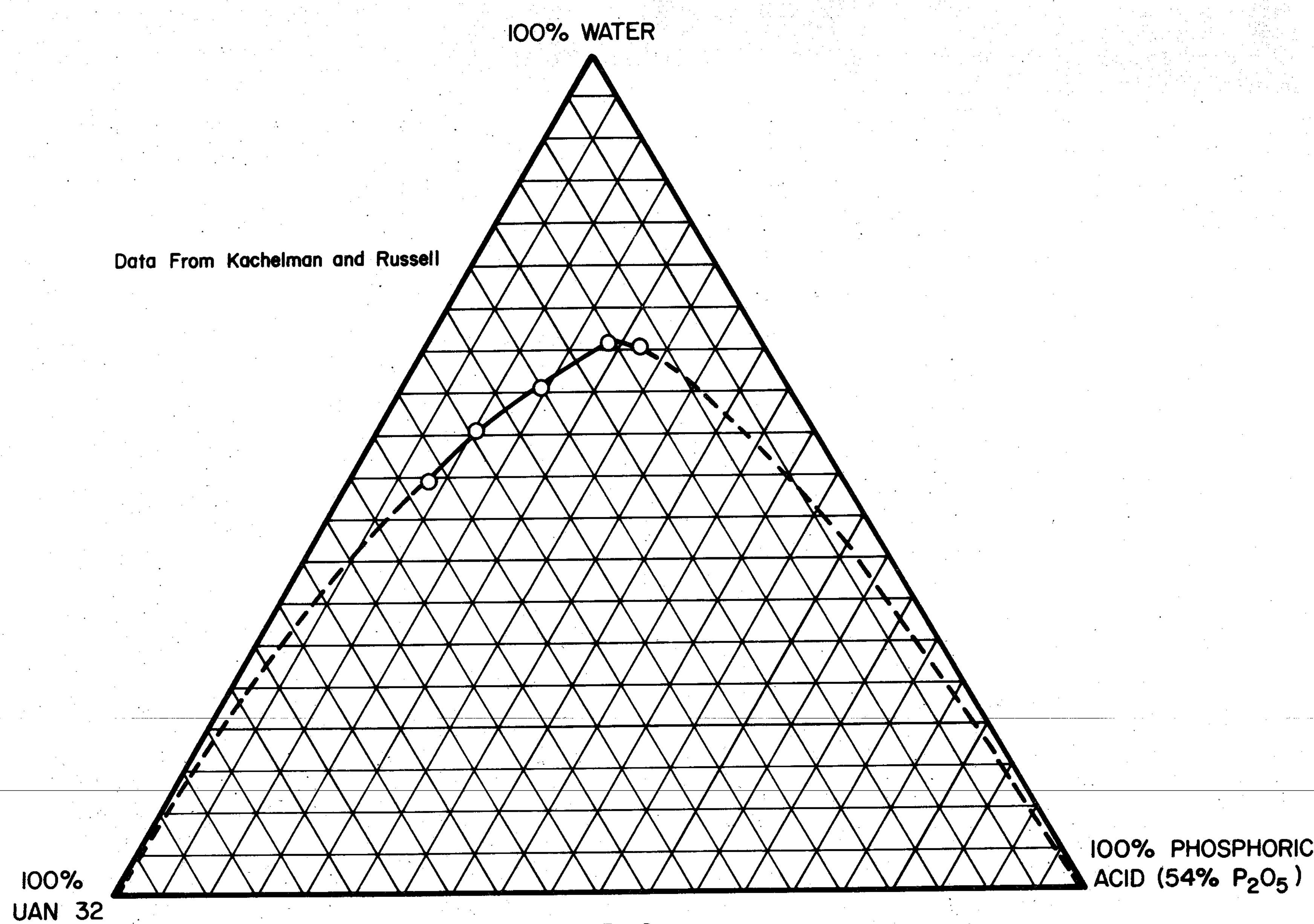


FIGURE 12

SOLUBILITY SYSTEM FOR UAN 32 - PHOSPHORIC ACID-WATER AT 32°F

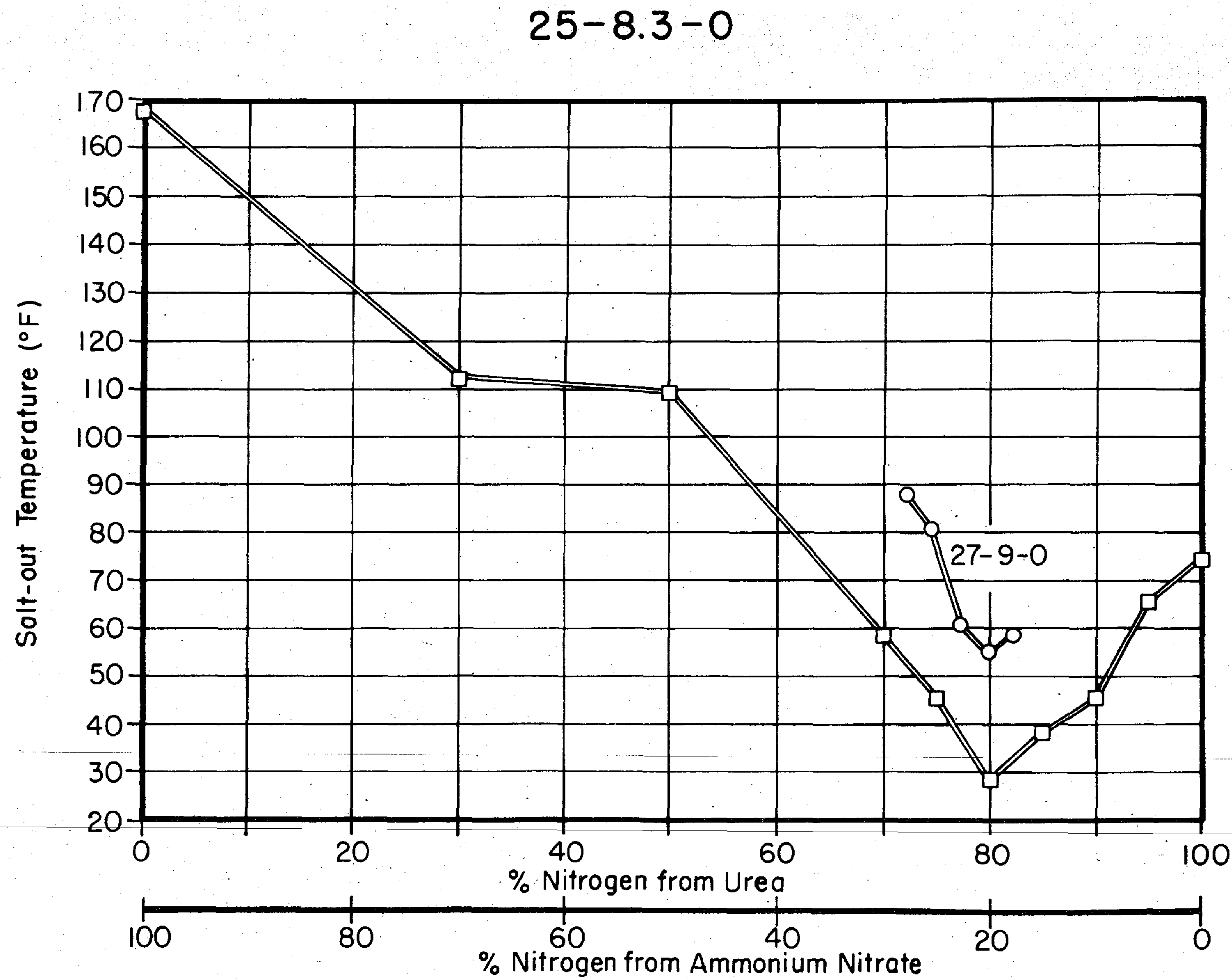


FIGURE 13

Acid solutions of Ratio 3-1-0 from Urea, Ammonium Nitrate and Phosphoric Acid.
(Data from Kachelman and Bogan)

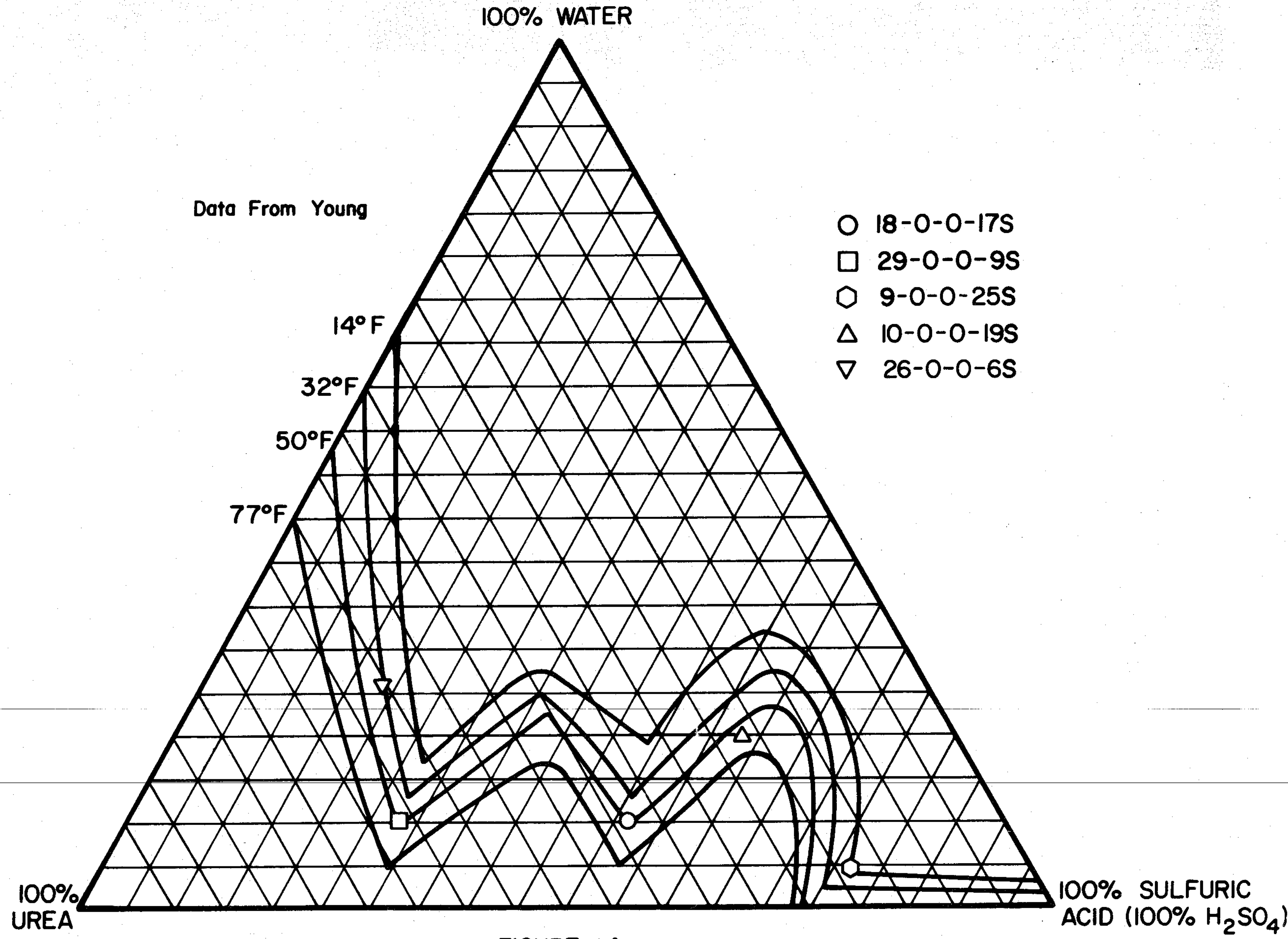


FIGURE 14

SOLUBILITY SYSTEM FOR UREA-SULFURIC ACID-WATER