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ACID FERTILIZER SOLUTION PRODUCTION

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by

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## Acid Fertilizer Solution Production

There is an increasing interest in the production and use of acid fertilizer solutions. Acid fertilizer solutions typically are produced batchwise from urea, urea-ammonium nitrate (UAN) solution, merchant-grade wet-process phosphoric acid, potassium chloride, and sulfuric acid. These solutions usually have a pH less than 2.5. Solubility diagrams and specific field grades are discussed. Methods and equipment used for the production, handling, storage, and application of these acid solutions are described.

### Solubility Systems

The most common acid solutions are produced from urea and phosphoric acid. Figure 1 shows the solubility system for urea, phosphoric acid, and water at 32°F, 50°F, and 77°F (1). Maximum solubility for this system at 32°F occurs with an N:P<sub>2</sub>O<sub>5</sub> ratio of 1.5 corresponding to a grade of 21-14-0. Lowest solubility occurs with an N:P<sub>2</sub>O<sub>5</sub> ratio of 0.4. This is the ratio of pure urea phosphate.

In Florida where ammonium nitrate is the preferred source of nitrogen, acid solutions containing ammonium nitrate and phosphoric acid are popular. Figure 2 shows the solubility system for ammonium nitrate, phosphoric acid, and water at 32°F. Solubility of this system increases as the P<sub>2</sub>O<sub>5</sub> to N ratio increases.

Figure 3 shows the solubility system for UAN solution (50% of the nitrogen from urea), phosphoric acid, and water at 32°F. Solubility for this system is quite low and can be greatly improved by varying the urea to ammonium nitrate ratio. Figures 4 through 8 show the effect on salt-out

temperature when the urea to ammonium nitrate ratio is varied. Table 1 compares the maximum grade with a 32°F salt-out temperature for the different solubility systems.

Adding ammonium sulfate to phosphoric acid is popular in southern Texas. Figure 9 shows the solubility system for ammonium sulfate, phosphoric acid, and water at 75°F. Grades produced from these raw materials are shown below.

1-50-0-1.1  
2-46-0-2.2  
3-39-0-3.4  
4-30-0-4.5  
5-24-0-5.7  
6-21-0-6.8  
7-15-0-8.0  
8-12-0-9.1

Figure 10 shows the solubility system for urea, sulfuric acid, and water (2). Typical grades produced from this system are 29-0-0-9S, 18-0-0-17S, and 9-0-0-25S. Adding urea to sulfuric acid results in a high heat of reaction which must be controlled.

Figure 11 shows the solubility system for phosphoric acid, potassium chloride, and water at 32°F. Grades of common ratios produced are shown below.

0-21-7  
0-18-9  
0-10-10  
0-6-12  
0-4-12

Figure 12 shows the solubility system for sulfuric acid and potassium chloride at 32°F. A significant amount of hydrochloric acid fumes form when potassium chloride is added to concentrated sulfuric acid. The sulfuric

acid should be diluted to a 50% concentration or lower and cooled before potassium chloride addition. Grades of common ratios produced are shown below.

0-0-9-3  
0-0-7.6-3.8  
0-0-5.7-5.7  
0-0-3.9-7.8  
0-0-2.9-8.7

Table 2 shows common P<sub>2</sub>O<sub>5</sub>:S ratios made from phosphoric acid and sulfuric acid. These two acids can be mixed in any ratio to produce satisfactory solutions. The salt-out temperatures of these solutions are below 32°F.

#### Complex Acid Solutions

Complex acid solutions contain 3 or 4 of the major plant nutrients--nitrogen, phosphorus, potassium, and sulfur. Table 3 shows complex acid solutions made from urea, phosphoric acid, and potassium chloride having salt-out temperatures of 32°F.

Tests show that when potash is needed, the best source of nitrogen is urea. Table 4 shows that when ammonium nitrate is added to grades containing potash, the solubility decreases, probably due to formation of potassium nitrate. Grades with 83% of their nitrogen from urea that have been stored successfully at 32°F are 8-8-8, 7-14-7, 3-9-9, 5-20-5, 10-10-5, 12-4-4, 9-3-6, and 12-6-3. Solubility of these grades should increase if all of their nitrogen comes from urea.

Table 5 shows complex acid solutions produced from urea, ammonium nitrate, phosphoric acid, potassium chloride, and sulfuric acid. Many of these grades have been produced and used successfully in commercial operations.

### Acid Suspensions

Acid fertilizer suspensions are attractive because suspensions allow higher analyses than solutions, especially for high potassium grades made from potassium chloride. These suspensions can be produced from urea, UAN solution, phosphoric acid, potassium chloride, sulfuric acid, ammonium sulfate and/or elemental sulfur. Cost effective O-X-X and O-X-X-S grades which cannot be produced from traditional neutral fluid fertilizers are possible.

To produce these suspensions, attapulgite or bentonite clay should first be gelled in water. Clays do not gel well in acids. More clay is needed in acid suspensions than in traditional suspensions. These suspensions are taken to the field and applied immediately because the clay gel will deteriorate quickly in the acid environment. Maximum storage time is less than 2 days.

### Corrosion

Acid solutions are more corrosive than neutral solutions. Table 6 shows results of corrosion tests using acid solutions. These grades severely attack carbon steel and will attack 304 stainless steel. Corrosion rates increase when potassium chloride is used in the solution. Corrosion on 316 stainless steel is negligible. However, at elevated temperatures and high fluid velocities, there is corrosion on 316 stainless steel.

### Typical Plant Design

One commercial plant uses a scale-mounted, heavy-duty, 1,650-gallon, cone-bottom polyethylene mixing tank. Agitation is provided by a recirculation pump (4" x 3", 3,600 rpm, 25 hp) made from 316 stainless steel. The

plumbing is schedule 40 PVC. Phosphoric acid, sulfuric acid, and UAN solution are stored in 6,500-gallon polyethylene storage tanks. These raw materials are added to the mix tank through separate lines and pumps. Urea and potash are added to the mix tank using separate augering systems. The cost for this small plant is about \$55,000 including storage costs.

#### Agronomic Tests

TVA has conducted agronomic tests with low pH fertilizers such as urea phosphate (UP). Results show that UP is equivalent to the more conventional higher analysis fertilizers as a phosphate source (3). The UP is equivalent to urea as a nitrogen source under most conditions and probably is better than urea where nitrogen volatilization losses can occur. Other agronomic advantages include enhanced micronutrient availability, increase in phosphorus availability, reclamation of sodic soils, less germination damage, and treating irrigation water (4, 5, 6, 7, 8).

#### Physical and Chemical Advantages and Disadvantages

Acid solutions definitely have some physical and chemical advantages as compared to neutral solutions (9). Some of these are:

1. Usually higher analysis solution grades can be produced as acid solutions as compared to those produced from neutral solutions. For example, a 25-8.3-0 acid solution can be produced and safely stored at 32°F. But, a neutral solution of 18-6-0 is the highest grade one can safely store at 32°F.
2. These solutions can be produced from merchant-grade phosphoric acid (54%), but neutral ammonium polyphosphate solutions must be produced

from superphosphoric acid (68 to 72%  $P_2O_5$ ). More energy is required to concentrate from 0-54-0 to superphosphoric acid (68 to 72%  $P_2O_5$ ); therefore, 0-54-0 acid can usually be bought at a lower price.

3. Usually larger quantities of micronutrients can be dissolved in acid solutions than in neutral solutions.
4. Acid solutions work well in irrigation systems which use hard water. With neutral solutions, a troublesome precipitate forms with hard water.
5. Less pure phosphoric acids can be used to produce acid solutions. Impurities from the phosphoric acid cause amorphous gels in neutral solutions which cause problems during storage and application. These gels do not form in acid solutions.

There are two main disadvantages for acid solutions:

1. The solutions are very corrosive to carbon steel and can corrode stainless steel.
2. These solutions are not as economical to produce as bulk blends produced from urea and diammonium phosphate (DAP) because DAP can usually be delivered at a lower price than merchant-grade phosphoric acid. However, there are some advantages to solution fertilizers which can be met by acid solutions.

Summary

Some commercial firms have reported agronomic advantages to banding acid solution fertilizers. Agronomic research with these solutions is continuing. Laboratory test data show that acid solutions have physical and chemical advantages not normally provided by other liquids. They may be more economical to produce and store than other phosphate solutions.

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Table 1

Summary of Maximum Grades for Acid Fertilizer Systems<sup>a</sup>

Ratio	Urea	Ammonium Nitrate	UAN Solution		Urea, Ammonium Nitrate	
	<u>Phosphoric Acid</u>	<u>Phosphoric Acid</u>	<u>Phosphoric Acid</u>	<u>% N from Urea</u>	<u>Phosphoric Acid</u>	<u>% N from Urea</u>
3-1-0	18-6-0	16.5-5.5-0	13.5-4.5-0	50	25-8.3-0	80
2-1-0	20-10-0	16-8-0	11-5.5-0	50	23-11.5-0	90
1-1-0	14-14-0	14-14-0	8-8-0	50	16-16-0	95
1-2-0	8-16-0	11.5-23-0	5-10-0	50	9-18-0	85
1-3-0	6-18-0	10-30-0	4-12-0	50	6-18-0	85

a. Grades have salt-out temperatures between 28°F and 38°F.

Table 2

Solutions Produced from Phosphoric Acid (54% P<sub>2</sub>O<sub>5</sub>)  
And Sulfuric Acid (93% H<sub>2</sub>SO<sub>4</sub>) with  
Salt-Out Temperatures Below 32°F

<u>Ratio</u>	<u>Grade</u>
0-3-0-1	0-33-0-11
0-2-0-1	0-28-0-14
0-1-0-1	0-19-0-19
0-1-0-2	0-11-0-22
0-1-0-3	0-8-0-24

Table 3

Complex Acid Solutions from Urea, Phosphoric Acid, and  
Potassium Chloride with Salt-Out Temperatures of 32°F

Grade

8-15-8  
11-8-8  
14-5-8  
16-11-5  
6-6-11  
3-3-12  
17-2-8  
4-14-10  
20-4-6  
17-18-2  
7-21-6  
6-30-6

Table 4

Effect of Nitrogen Source on Salt-Out Temperature for  
Complex Acid Fertilizer Solutions<sup>a</sup>

Ratio:	1-3-1	2-2-1	3-1-1
Grade:	6-18-6	12-12-6	18-6-6

<u>% N from Urea</u>	<u>% N from Ammonium Nitrate</u>	<u>Salt-Out Temperature (°F)</u>		
0	100	61	66	69
25	75	55	71	72
50	50	52	68	75
75	25	30	49	65
100	0	<4	42	55

a. Produced from urea, ammonium nitrate, phosphoric acid, and potassium chloride.

Table 5

Complex Acid Solutions from Urea, Ammonium Nitrate,  
Phosphoric Acid, Potassium Chloride, and Sulfuric Acid

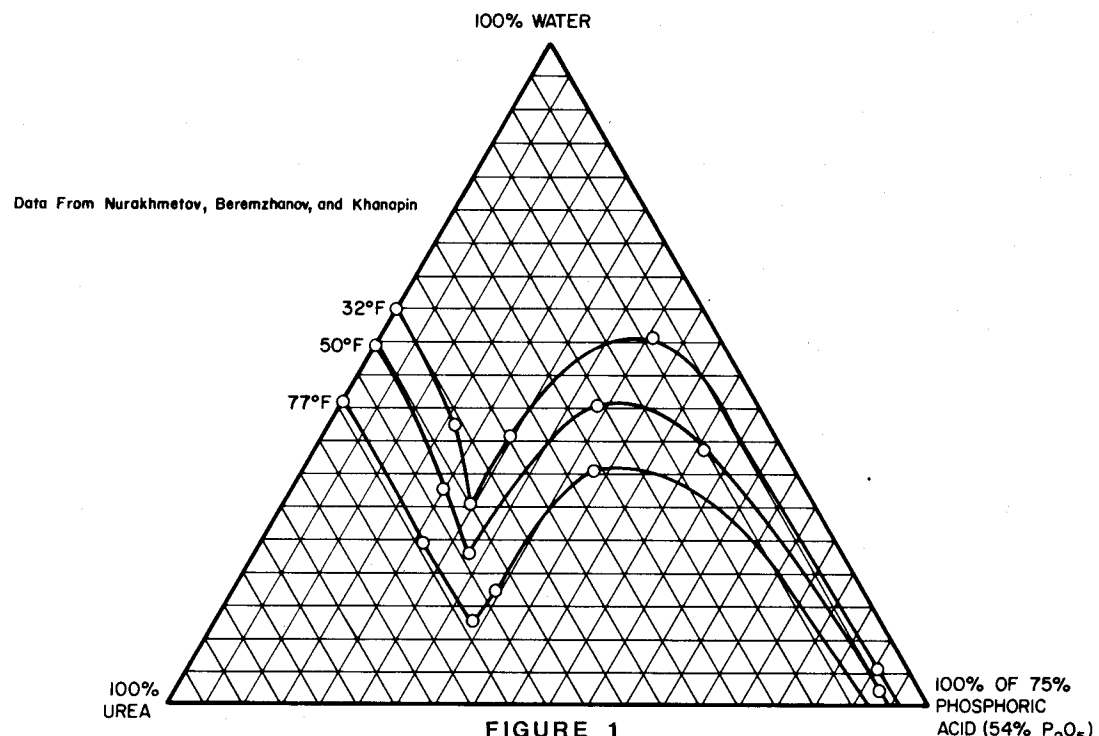
9-9-0-9S  
7-7-0-21S  
15-15-0-5S  
21-7-0-7S  
8-24-0-8S  
5-34-0-4S  
6-21-3-3S  
6-6-6-6S  
5-26-3-3S  
4-10-10-2S  
22-.05-2-2S  
14-0-4-2S

Table 6

Corrosion Tests on Acid Fertilizer Solutions<sup>a</sup>

<u>Grade</u>	<u>pH</u>	<u>Alloy Tested</u>	<u>Corrosion Rate Mils/year</u>
27-9-0	1.7	A283 carbon steel	200
27-9-0	1.7	304 stainless steel	<0.05
27-9-0	1.7	316 stainless steel	<0.05
8-8-8	1.0	A283 carbon steel	740
8-8-8	1.0	304 stainless steel	60
8-8-8	1.0	316 stainless steel	1
10-10-5	1.0	A283 carbon steel	855
10-10-5	1.0	304 stainless steel	18
10-10-5	1.0	316 stainless steel	<0.05
16-8-4	1.4	A283 carbon steel	640
16-8-4	1.4	304 stainless steel	<0.05
16-8-4	1.4	316 stainless steel	<0.05

a. Produced from urea, ammonium nitrate, phosphoric acid, and potassium chloride.



**FIGURE 1**

SOLUBILITY SYSTEM FOR UREA - PHOSPHORIC ACID - WATER

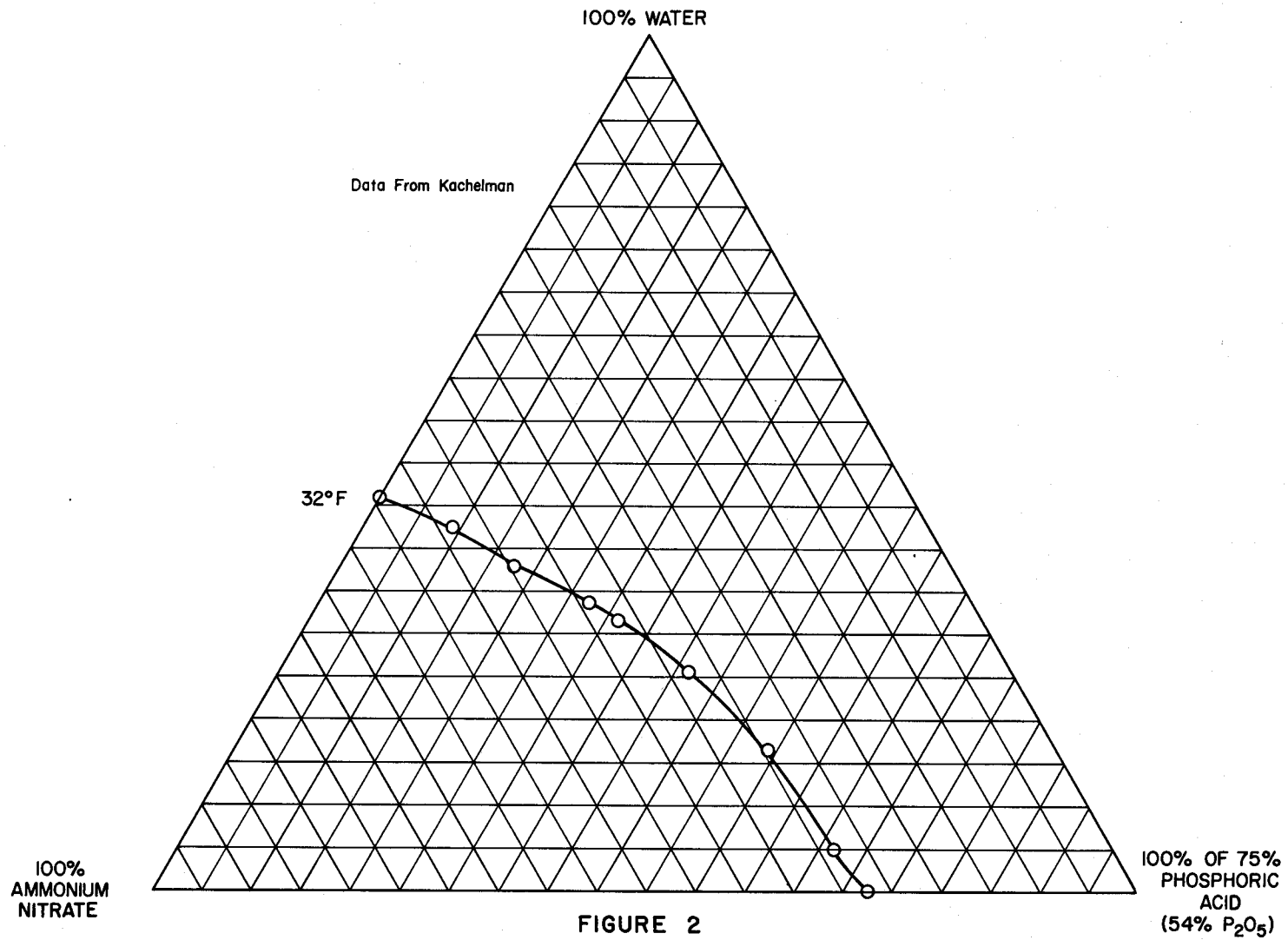
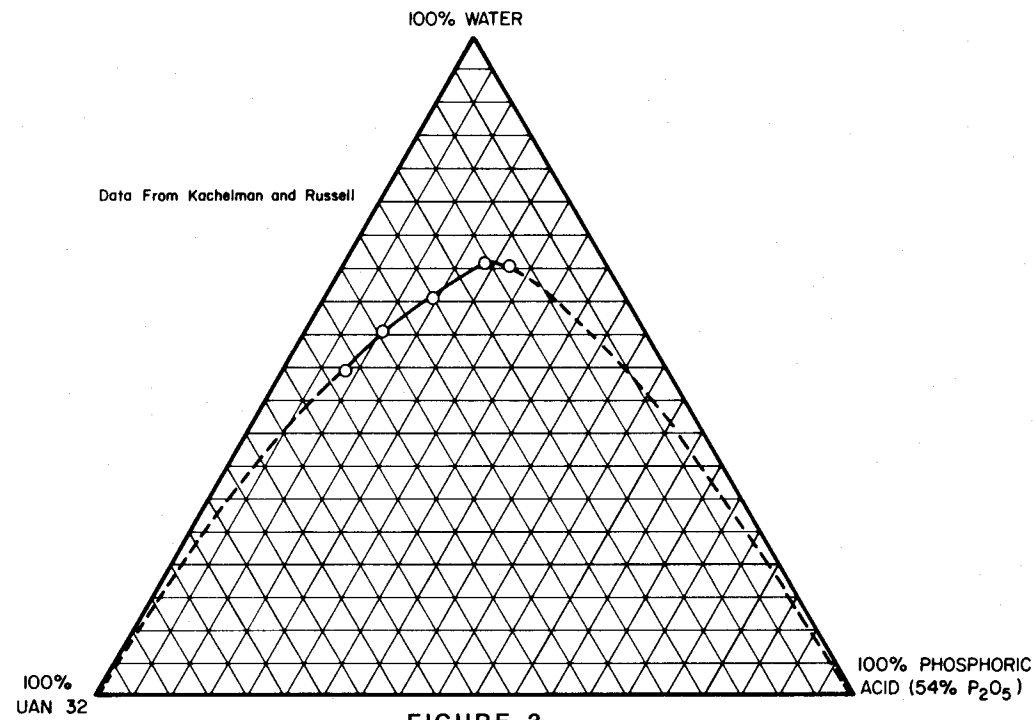


FIGURE 2  
 SOLUBILITY SYSTEM FOR AMMONIUM NITRATE-PHOSPHORIC ACID-WATER



**FIGURE 3**  
 SOLUBILITY SYSTEM FOR UAN 32-PHOSPHORIC ACID-WATER AT 32°F

25-8.3-0

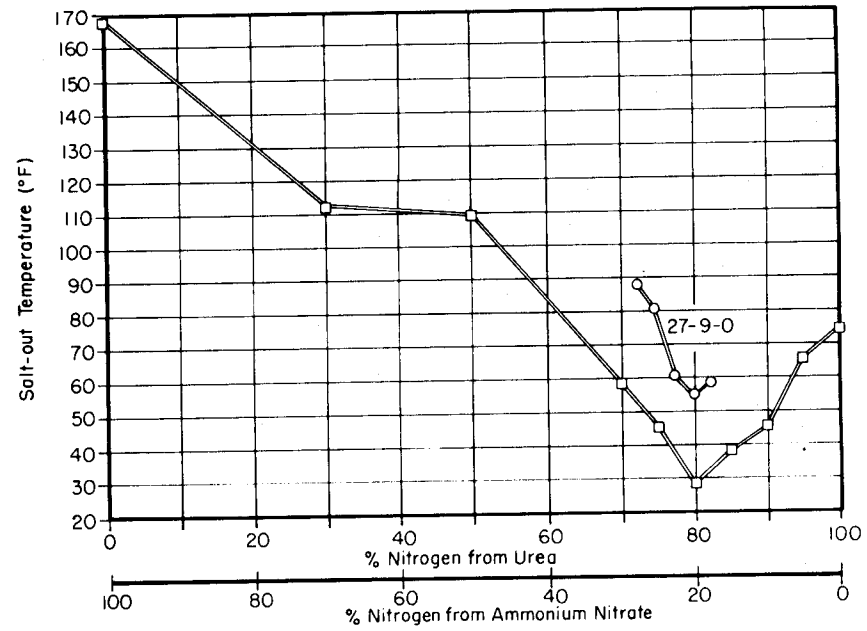


FIGURE 4

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

22-11-0

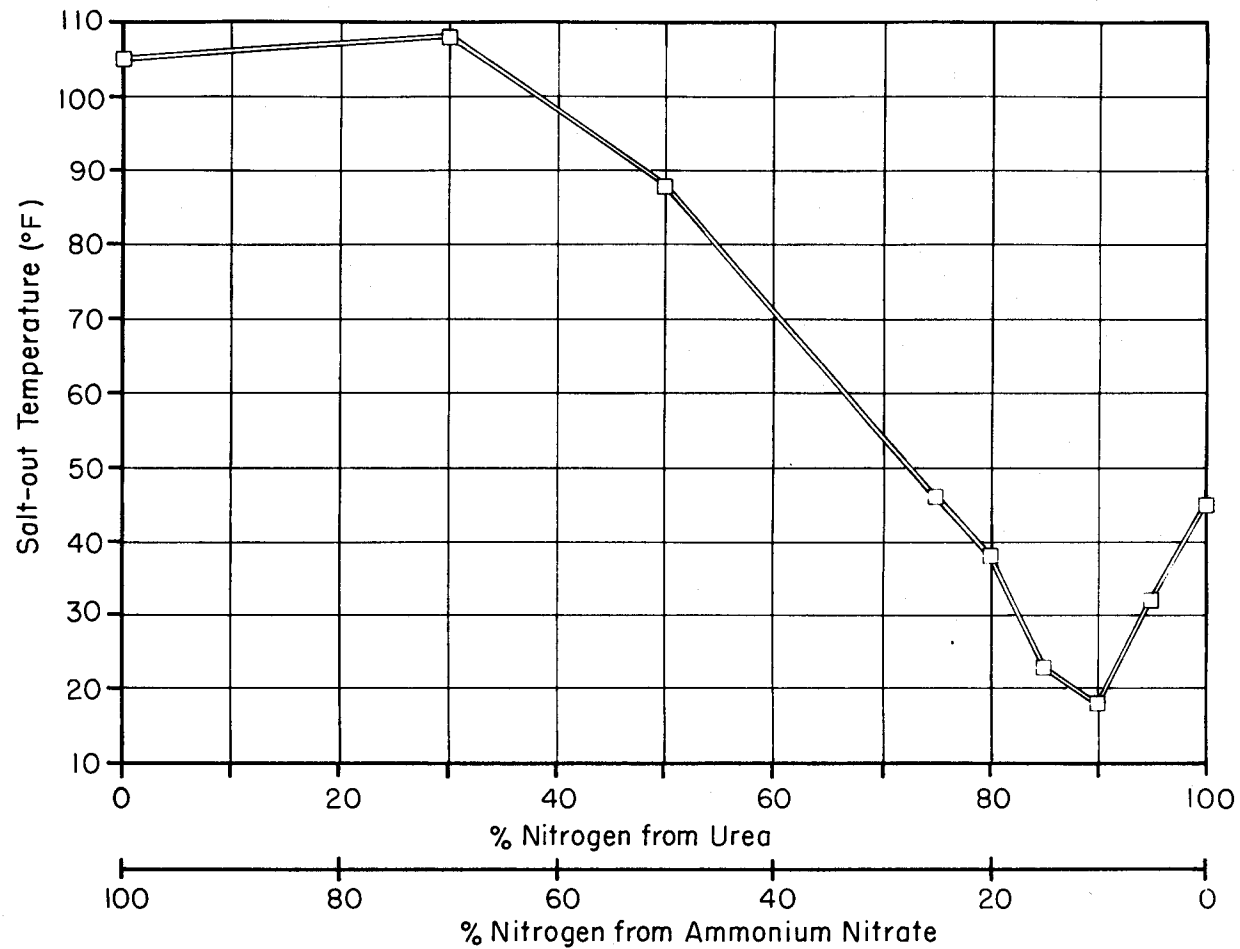


FIGURE 5

Acid solutions of 22-11-0 from Urea, Ammonium Nitrate and Phosphoric Acid.

(Data from Kachelman and Bogan)

16-16-0

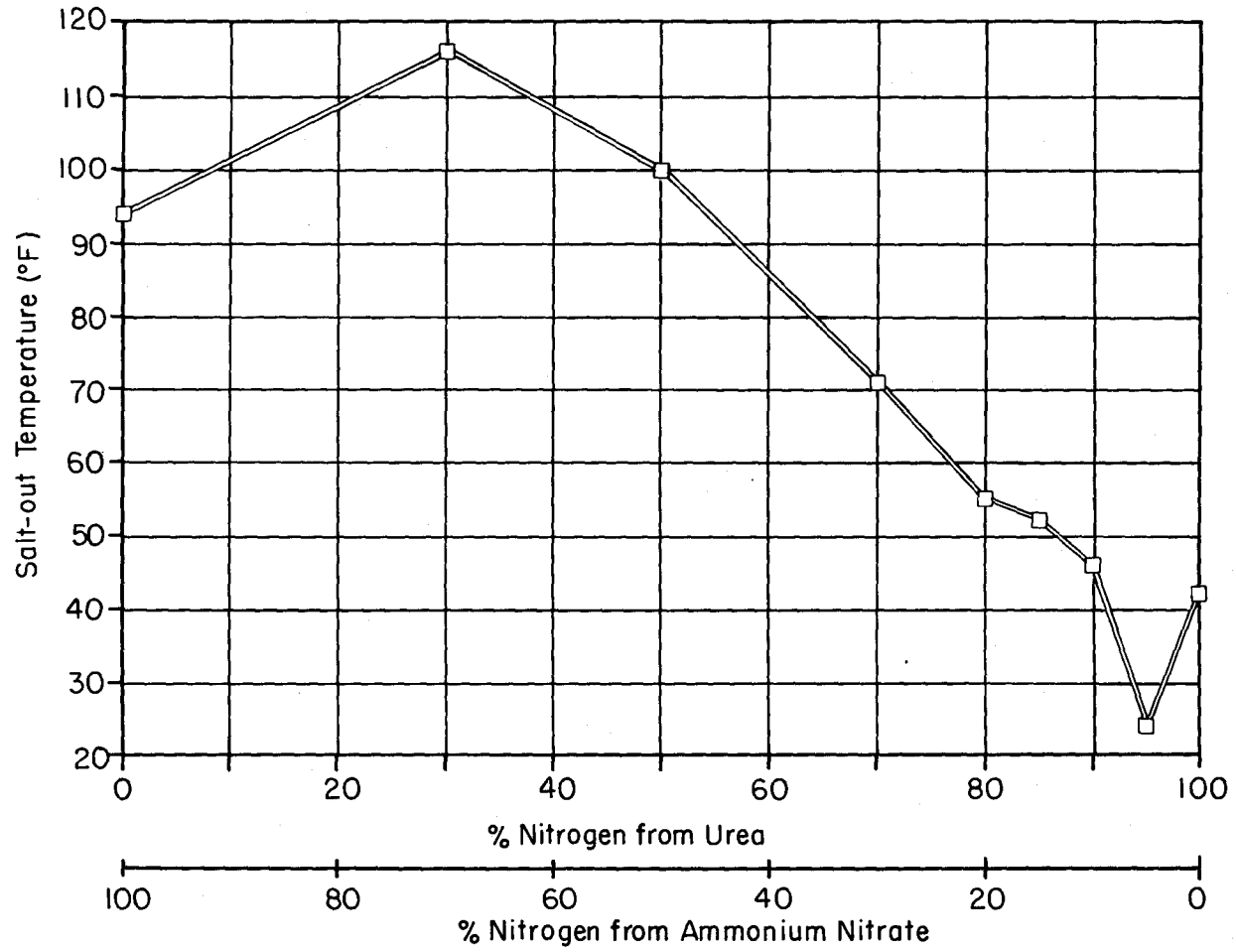


FIGURE 6

Acid solutions of 16-16-0 from Urea, Ammonium Nitrate and Phosphoric Acid.  
(Data from Kachelman and Bogan)

10-20-0

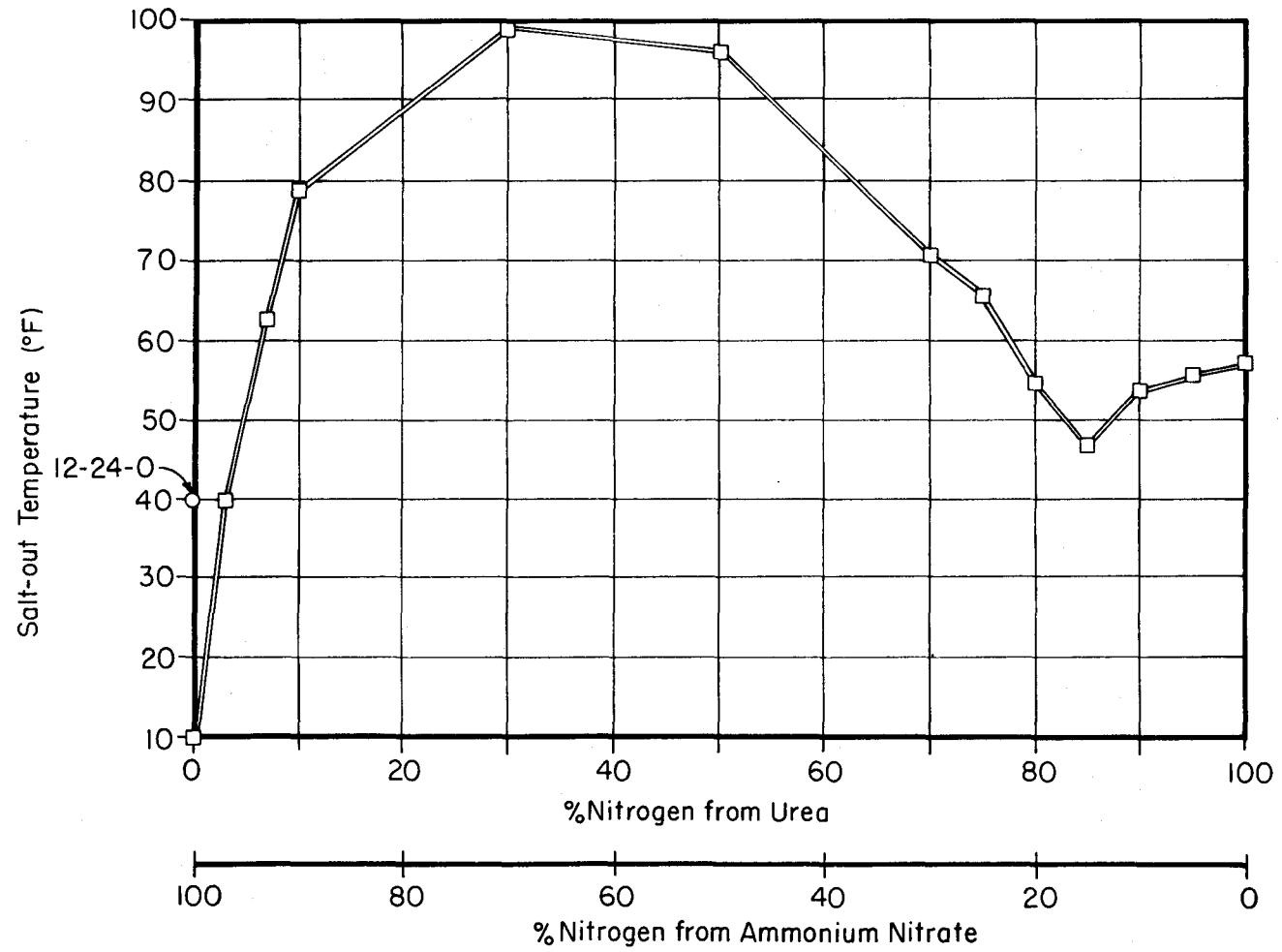


FIGURE 7

Acid solutions of 10-20-0 from Urea, Ammonium Nitrate and Phosphoric Acid.  
(Data from Kachelman and Bogan)

7-21-0

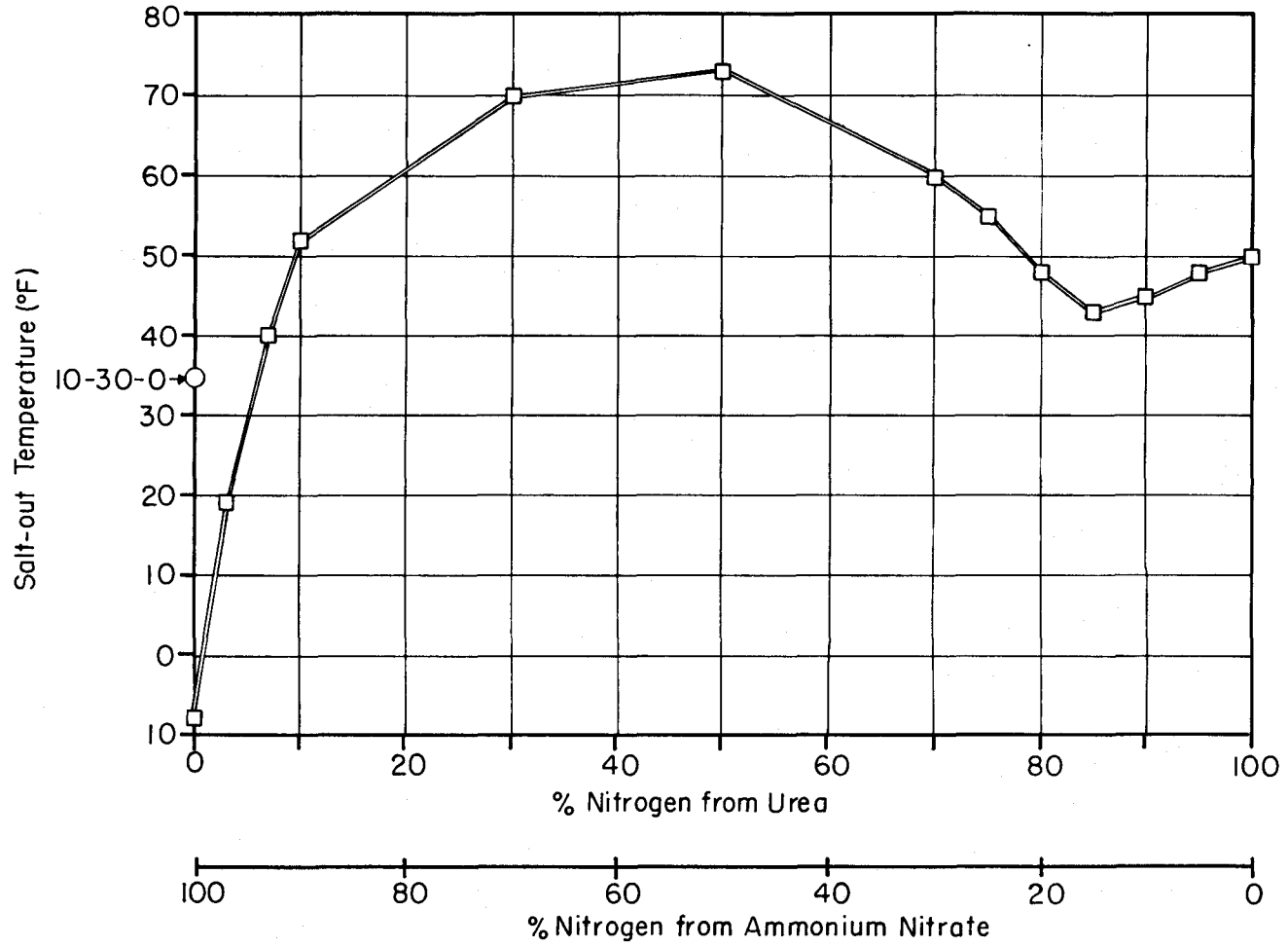
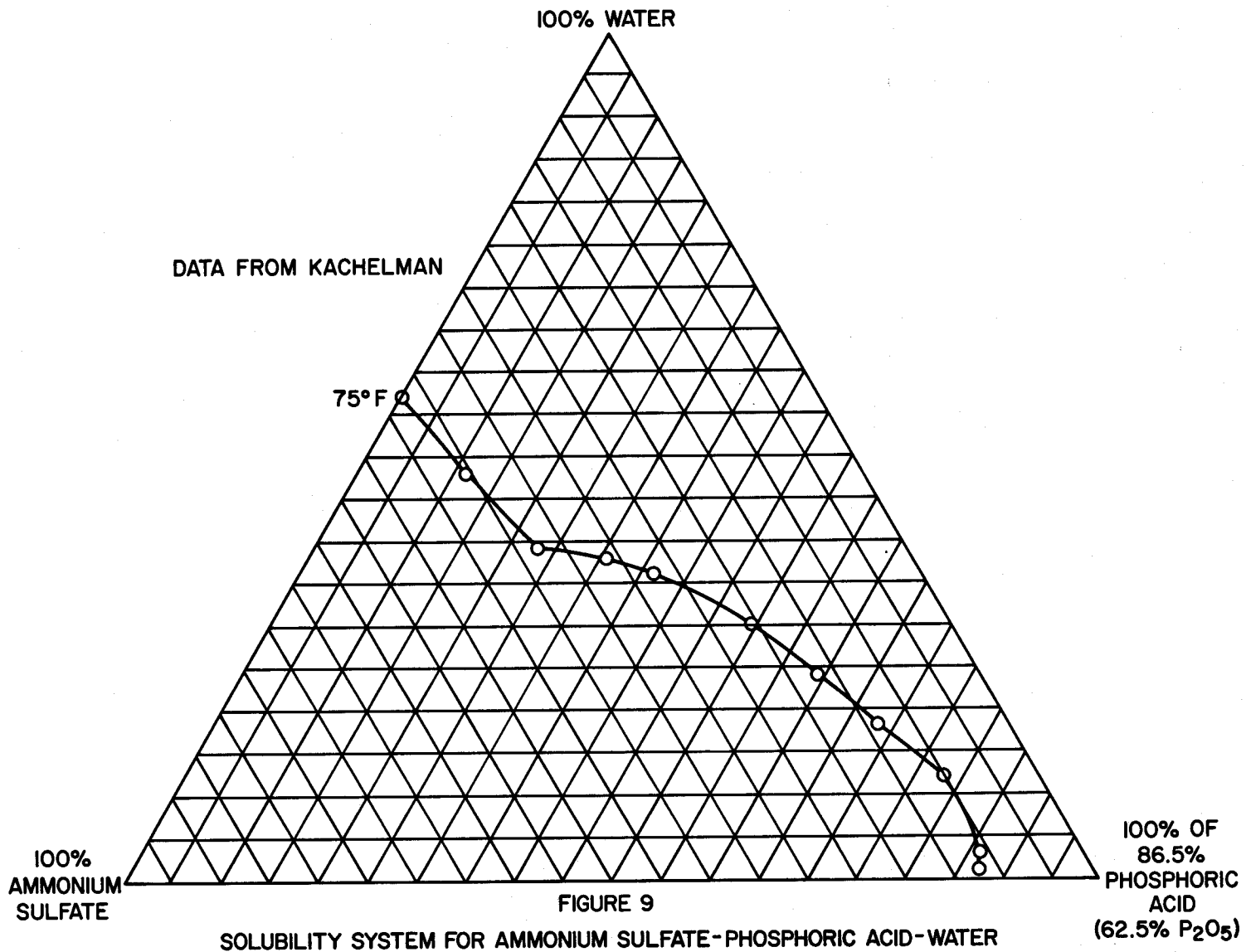


FIGURE 8

Acid solutions of 7-21-0 from Urea, Ammonium Nitrate and Phosphoric Acid.  
(Data from Kachelman and Bogan)



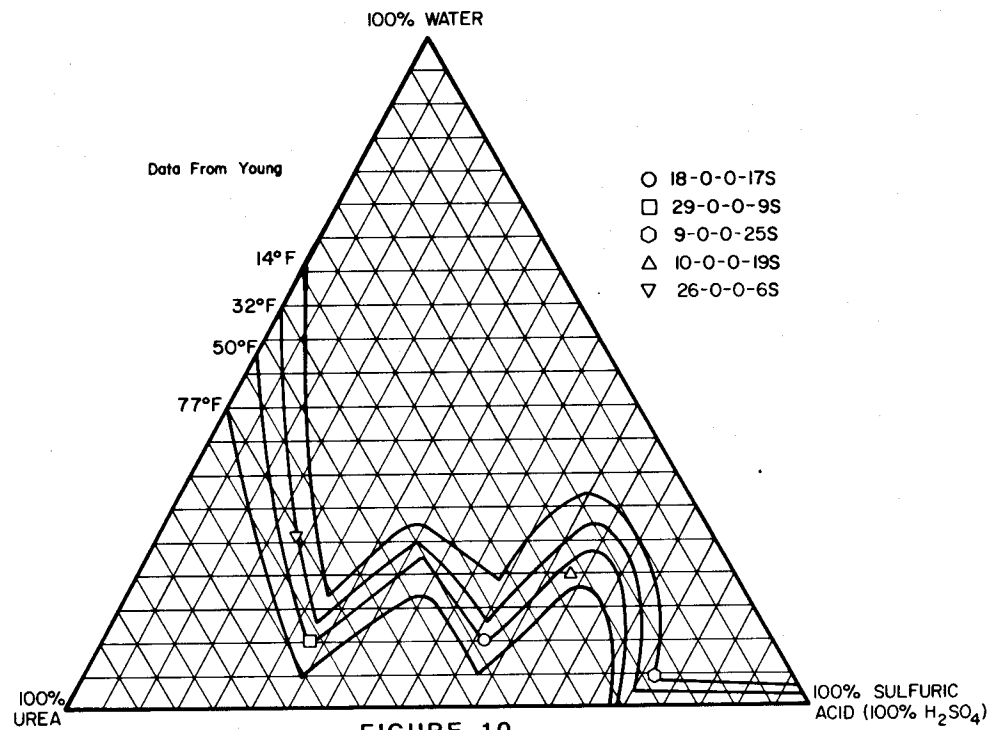


FIGURE 10

SOLUBILITY SYSTEM FOR UREA-SULFURIC ACID-WATER

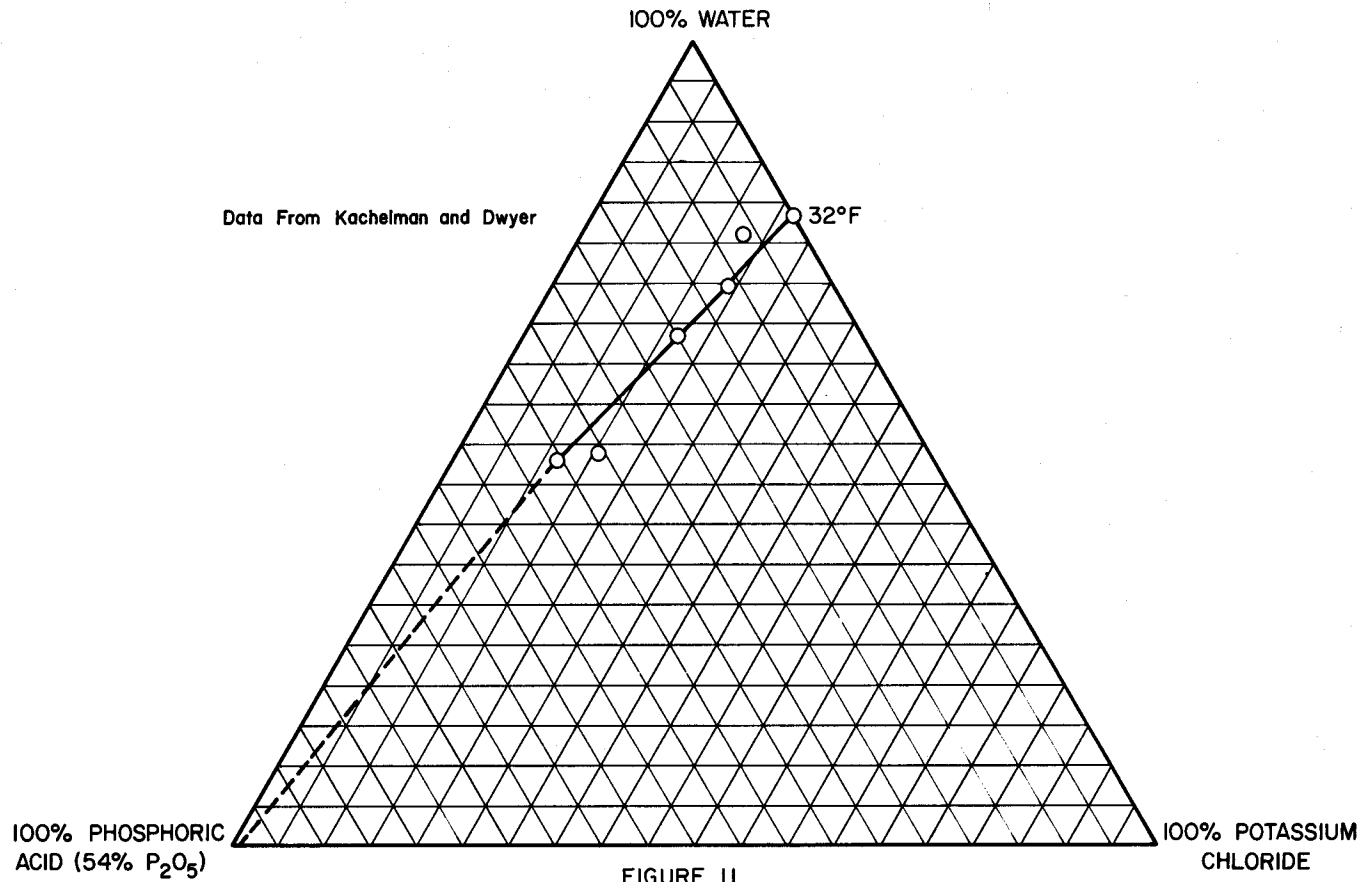


FIGURE II

SOLUBILITY SYSTEM FOR PHOSPHORIC ACID-POTASSIUM CHLORIDE-WATER AT 32°F

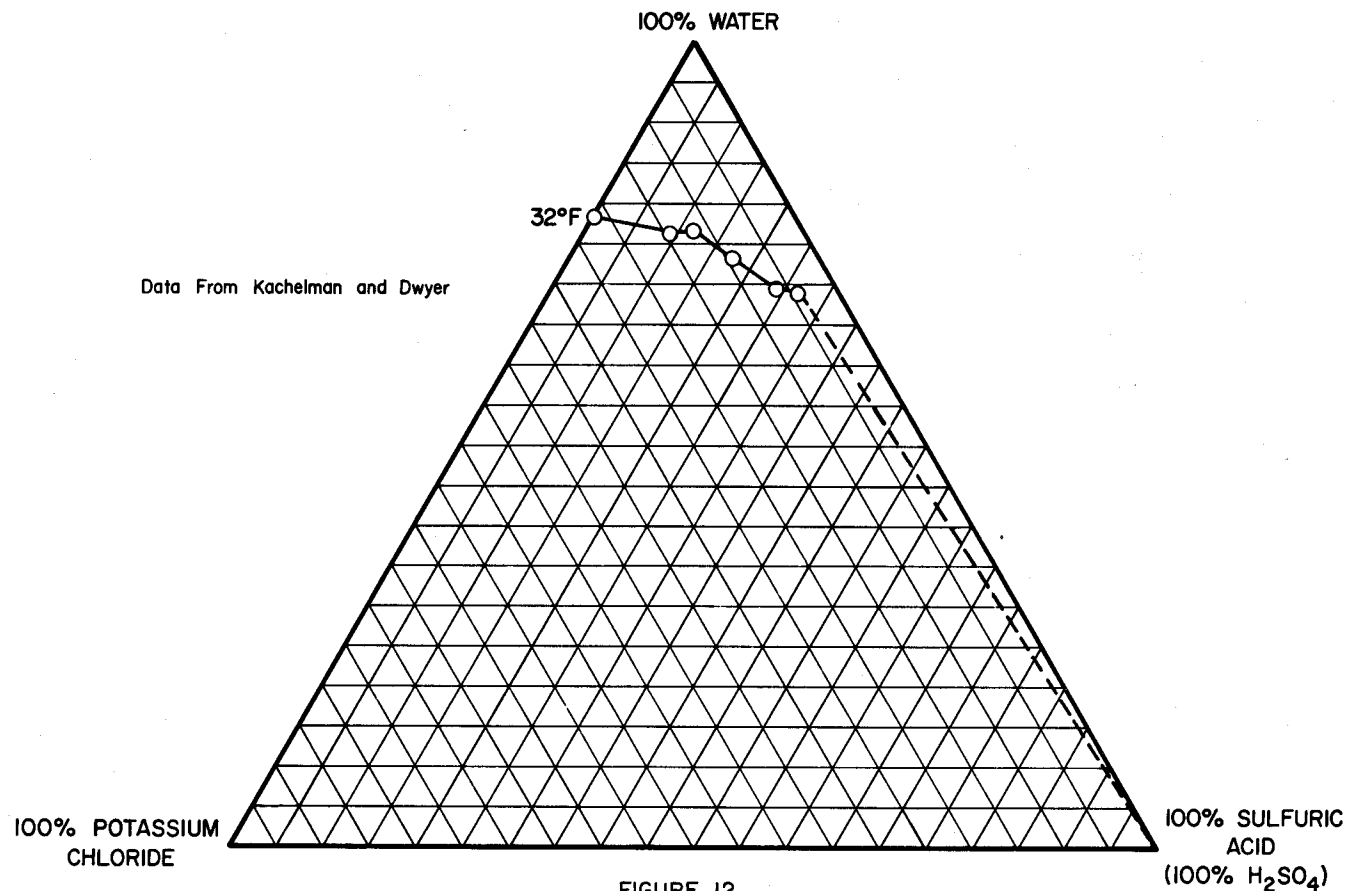


FIGURE 12

SOLUBILITY SYSTEM FOR POTASSIUM CHLORIDE-SULFURIC ACID-WATER AT 32°F