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An investigation of the ternary system: magnesium sulfate - urea - water

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AN INVESTIGATION OF THE TERNARY SYSTEM:

MAGNESIUM SULFATE - UREA - WATER

by

David Brian Holland

UC 1964

Senior Thesis Submitted
in Partial Fulfillment
of the Requirements of Graduation

DEPARTMENT OF CHEMISTRY

UNION COLLEGE

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INTRODUCTION

Magnesium sulfate hydrate and urea are common constituents of many commercial fertilizers. A common reaction between these constituents is:



The result of the above reaction is the formation of the ternary compound and excess water which combine to form a sticky mass. This sticky mass is very difficult to handle and sometimes causes damage to materials with which it comes into contact.

Several studies have been made in attempts to find stable ternary compounds which avoid this problem. Difficulties have arisen, however, because compounds discovered in each study have not been even hinted at in other studies. There are a number of possible explanations for this fact.

It is the purpose of this investigation into the ternary system: magnesium sulfate - urea - water to try to resolve these discrepancies and also to further investigate the ternary system.

HISTORICAL

Whittaker, Lundstorm, and Shimp(13) reported the establishment of the isotherm of the ternary system: magnesium sulfate - urea - water at 30° C. This isotherm was found to consist of three branches corresponding to the solid phases:

- 1. $MgSO_4 \cdot 7H_2O$
- 2. $CO(NH_2)_2$
- 3. $MgSO_4 \cdot CO(NH_2)_2 \cdot 3H_2O$

The method employed was simple. They mixed solutions containing sufficient amounts of material so as to obtain mixtures situated on the desired portion of the solubility curve. They mention no evidence of any solid phases other than those on their curve. A photocopy of their curve, obtained from Graham(6) is shown on page 27.

Yee et. al.(15) prepared mixtures of magnesium sulfate hydrate and urea in methanol at 25° C. They reported the identification, by both chemical and crystallographic methods, of two new ternary compounds:

- 1. $MgSO_4 \cdot 5CO(NH_2)_2 \cdot 2H_2O$
- 2. $MgSO_4 \cdot 6CO(NH_2)_2 \cdot 2H_2O$

forming crystalline solids.

Graham(6) studied this problem for a short time and confirmed the existence of the two ternary compounds of Yee, but did not pursue his studies into any relationship between the two previous studies. He also reported the probable existence of another compound:



not previously discovered.

A photocopy of x-ray powder pictures of the two compounds of Yee, taken by Graham, are shown on page 28.

MATERIALS

Chemically pure reagents were obtained for all work and experimental materials were prepared from them.

Urea was obtained in crystalline form and dried, according to Duval(2) for 4 days at 110° C. to remove any adsorbed water. The resulting crystals were then powdered for ease of handling and stored over calcium chloride.

Magnesium sulfate was obtained in the form of the hydrate, $MgSO_4 \cdot 7H_2O$. For accurate and meaningful work, it was necessary to determine the amount of molecularly bound water in this compound. Again according to Duval(2) the material was heated for 4 days at 450° C. to remove all the water of crystallization. The number of moles of water on each $MgSO_4$ molecule was calculated as follows:

sample number	1	2	3	4
hydrate weight	4.1295 gm	4.3848 gm	3.5474 gm	4.1926 gm
anhydrous weight	2.0419 gm	2.1642 gm	1.7506 gm	2.0703 gm
ratio of anhydrous to hydrate	0.4944	0.4935	0.4934	0.4937
molecular weight of hydrate	243.51	243.95	243.99	243.85
molecular weight of water in hydrate	123.12	123.56	123.62	123.46
moles of water	6.83	6.86	6.86	6.85

The average of these values is $6.85H_2O$. Letting $y = \% MgSO_4 \cdot 7H_2O$:

$$7(y) + 1(1-y) = 6.85$$

$$7y + 1 - y = 6.85$$

$$y = 0.975 = 97.5 \% MgSO_4 \cdot 7H_2O$$

$$2.5 \% MgSO_4 \cdot H_2O$$

SAMPLE PREPARATION

The mixtures corresponding to the phase diagram of Whittaker, Lundstern, and Shimp(13) were prepared by mixing amounts of magnesium sulfate hydrate, urea, and water in such amounts as to fall within the boundary curve. These samples were numbered from 1M to 24M. The amounts of the various compounds were calculated as follows, using sample 1M as an example:

total sample weight	weight of $MgSO_4 \cdot 6.85H_2O$	weight of $CO(NH_2)_2$
3.9272 gm	2.8076 gm	0.0397 gm

The ratio of the molecular weights of $MgSO_4$ and $MgSO_4 \cdot 6.85H_2O$ is found:

$$\frac{MgSO_4}{MgSO_4 \cdot 6.85H_2O} = \frac{120.37}{243.78} = 0.49376$$

and the weight of $MgSO_4 = 0.49376 \times$ weight of $MgSO_4 \cdot 6.85H_2O$ so that:

total sample weight	weight of $MgSO_4$	weight of $CO(NH_2)_2$
3.9272 gm	1.3863 gm	0.0397 gm

The Percentage composition by weight is found:

$$100(1.3863/3.9272) = 35.30 \% MgSO_4$$

$$100(0.0397/3.9272) = 1.01 \% CO(NH_2)_2$$

$$100.00 - 35.30 - 1.01 = 63.69 \% H_2O$$

This calculation was adapted to a digital computer by means of the program shown on page 19 for accuracy and speed of calculation.

All samples were maintained in a constant-temperature water bath at 30° C. for several days and allowed to come to equilibrium.

The compounds of Yee et. al.(15) were prepared according to the method used by them, as follows:

For the preparation of $\text{MgSO}_4 \cdot 5\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$:

Put 1 gram of powdered $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ into a 9 cm. crystallizing dish or a 50 ml. round-bottomed flask and add 20 ml of methanol. Then add 2.5 grams of powdered urea and stir gently to dissolve the components. Place in a water bath at 30°C . until crystals form. These samples were numbered 5H-1 to 5H-4.

For the preparation of $\text{MgSO}_4 \cdot 6\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$:

Put 2 grams of powdered $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ into a 9 cm. crystallization dish or a 50 ml. round-bottomed flask and add 25 ml. of methanol. Then add 4 grams of powdered urea and stir gently as before. Place in a water bath at 25°C . until crystals form. Actually, these samples were placed in a 30°C . water bath for convenience and consistency. These samples were numbered 6H-1 to 6H-4.

Amounts of magnesium sulfate hydrate added were adjusted for the differences in water of hydration. Composition was determined by the same technique used in the determination of the composition of samples 1M to 24M.

Other samples were prepared in methanol using compositions different from those recommended by Yee et. al. These samples were numbered 1A to 6A. Their composition was determined in the same fashion as for the other samples. All temperatures were maintained at 30°C .

Compositions of the samples are shown in the tables on the following pages.

COMPOSITION OF ORIGINAL MIXTURES

sample number	total sample weight in grams	weight of $MgSO_4 \cdot 6.85H_2O$ in grams and % $MgSO_4$	weight of $CO(NH_2)_2$ in grams and % $CO(NH_2)_2$	% H_2O
5H-1	3.4883	0.9985 13.99%	2.4998 71.66%	14.35%
5H-2				
5H-3				
5H-4				
(4 identical samples)				
6H-1	5.9837	1.9971 16.31%	4.0066 66.96%	16.73%
6H-2				
6H-3				
6H-4				
(4 identical samples)				

sample number	total sample weight in grams	weight of $\text{MgSO}_4 \cdot 6.85\text{H}_2\text{O}$ in grams and % MgSO_4	weight of $\text{CO}(\text{NH}_2)_2$ in grams and % $\text{CO}(\text{NH}_2)_2$	% H_2O
1M	3.9272	2.8076 35.30%	0.0397 1.01%	63.69%
2M	2.0178	1.3527 33.10%	0.0565 2.80%	64.10%
3M	3.1138	2.0180 32.00%	0.1554 4.99%	63.01%
4M	5.5401	3.8373 34.20%	0.3767 6.80%	59.00%
5M	3.5080	2.5861 36.40%	0.2494 7.11%	56.49%
6M	2.4989	1.8928 37.40%	0.3648 14.60%	48.00%
7M	2.4921	1.7160 34.00%	0.4473 17.95%	48.05%
8M	2.2774	1.6143 35.00%	0.4247 18.65%	46.35%
9M	2.2994	1.6299 35.00%	0.4944 21.50%	43.50%
10M	3.1250	1.9999 31.60%	0.7813 25.00%	43.40%
11M	2.6982	1.8033 33.00%	0.7555 28.00%	39.00%
12M	2.7749	1.9669 35.00%	0.8019 28.90%	36.10%
13M	2.4159	1.4116 28.85%	0.8093 33.50%	37.65%
14M	2.4834	1.3983 27.80%	0.9015 36.30%	35.90%
15M	3.0128	1.5254 25.00%	1.2292 40.80%	34.20%

sample number	total sample weight in grams	weight of $\text{MgSO}_4 \cdot 6.85\text{H}_2\text{O}$ in grams and % MgSO_4	weight of $\text{CO}(\text{NH}_2)_2$ in grams and % $\text{CO}(\text{NH}_2)_2$	% H_2O
16M	3.1140	1.6334 25.90%	1.3732 44.10%	30.00%
17M	3.1273	1.6563 26.15%	1.5480 49.50%	24.35%
18M	3.8806	1.8234 23.20%	2.1188 54.60%	22.20%
19M	6.3703	1.9998 15.50%	3.8317 60.15%	24.35%
20M	7.1969	1.8948 12.99%	4.0015 55.60%	31.40%
21M	8.1694	1.8365 11.10%	4.4196 54.10%	34.80%
22M	11.8918	1.7581 7.30%	7.2064 60.59%	32.10%
23M	17.8771	1.7379 4.80%	11.0659 61.90%	33.30%
24M	4.5515	0.1899 2.06%	2.8538 62.70%	35.24%

sample number	total sample weight in grams	weight of $\text{MgSO}_4 \cdot 6.85\text{H}_2\text{O}$ in grams and % MgSO_4	weight of $\text{CO}(\text{NH}_2)_2$ in grams and % $\text{CO}(\text{NH}_2)_2$	% H_2O
1A	2.7889	0.9885 17.50%	1.8004 64.55%	17.94%
2A	3.0892	0.9885 15.80%	2.1007 68.00%	16.20%
3A	2.4629	0.9885 20.02%	1.4644 59.46%	20.52%
4A	3.8059	0.9885 12.95%	2.8074 73.75%	13.28%
5A	2.1907	1.0001 22.54%	1.1906 54.35%	23.11%
6A	2.7270	0.9915 17.95%	1.7355 63.64%	18.41%

SAMPLING TECHNIQUES

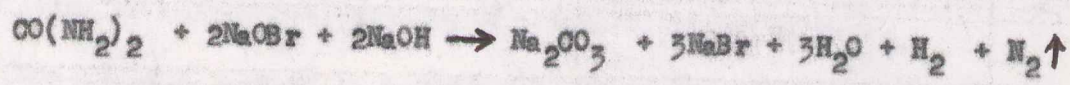
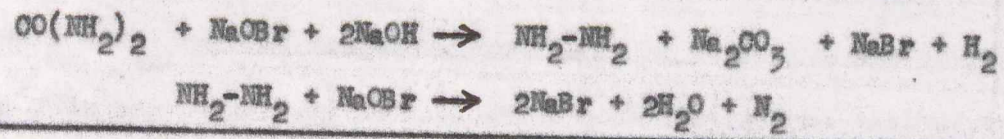
The liquid phases were removed carefully from the equilibrium mixtures by pipetting out as much liquid as possible. A bunch of glass-fiber material was held to the end of the pipet by rubber bands and served to filter out the solid material. The liquid samples were transferred directly to previously-weighed flasks and the flasks were then again weighed to determine the weight of the sample removed.

The solid phases were removed with a monel spatula into a wide-mouthed flask which had been previously weighed. This flask was then weighed again to determine the weight of the sample removed.

In many cases it was difficult to separate the phases. Centrifuging and filtration through glass-fiber material was helpful in most cases. The usual weight of sample was between 0.25 grams and 1.50 grams, although both larger and smaller samples were taken.

ANALYTICAL METHODS FOR UREA

I attempted first to analyze the urea in the ternary compounds by the hypobromite method. This method is based on the reaction, found in the text by Noller(11):



Measurement of the nitrogen gas evolved will allow calculation of the amount of urea.

I attempted to measure the amount of nitrogen gas at constant pressure and temperature by means of gravimetric determination of displaced water, since nitrogen gas is negligibly soluble in water. I found this method rather unsatisfactory because the reaction between the hypobromite and the urea tended to go very slowly at normal temperatures. Raising the temperature would have resulted in a vastly larger volume of displaced water and also inaccurate measurements. After a long period of time, the reaction would seem to stop, but at this point a yield of only from 76% to 89% of the theoretical value resulted, and this fraction of expected yield was not constant.

I also found, in the course of studying the reaction, that when I attempted to introduce the urea sample into the hypobromite solution in gelatine capsules, an odd event occurred. The idea of the gelatine capsules was to prevent the reaction from occurring until the apparatus was sealed. The gelatine capsules dissolved in the hypobromite solution, did not themselves produce any gas, but seemed in some fashion to inhibit the reaction between the urea and the hypobromite solution.

Another disadvantage of the hypobromite method was that fresh supplies of sodium hypobromite had to be prepared daily from concentrated sodium hydroxide (approximately 50%) and pure liquid bromine:



since the hypobromite was very unstable and decomposed rapidly. Liquid bromine is very unpleasant and dangerous. It is corrosive and irritating to the eyes and lungs even in very small quantities. I determined to try another method of analysis for the determination of urea.

The Kjeldahl method is a standard method for the determination of the amount of nitrogen in compounds. The compound, in this case urea, is hydrolyzed by concentrated sulfuric acid to ammonium bisulfate:



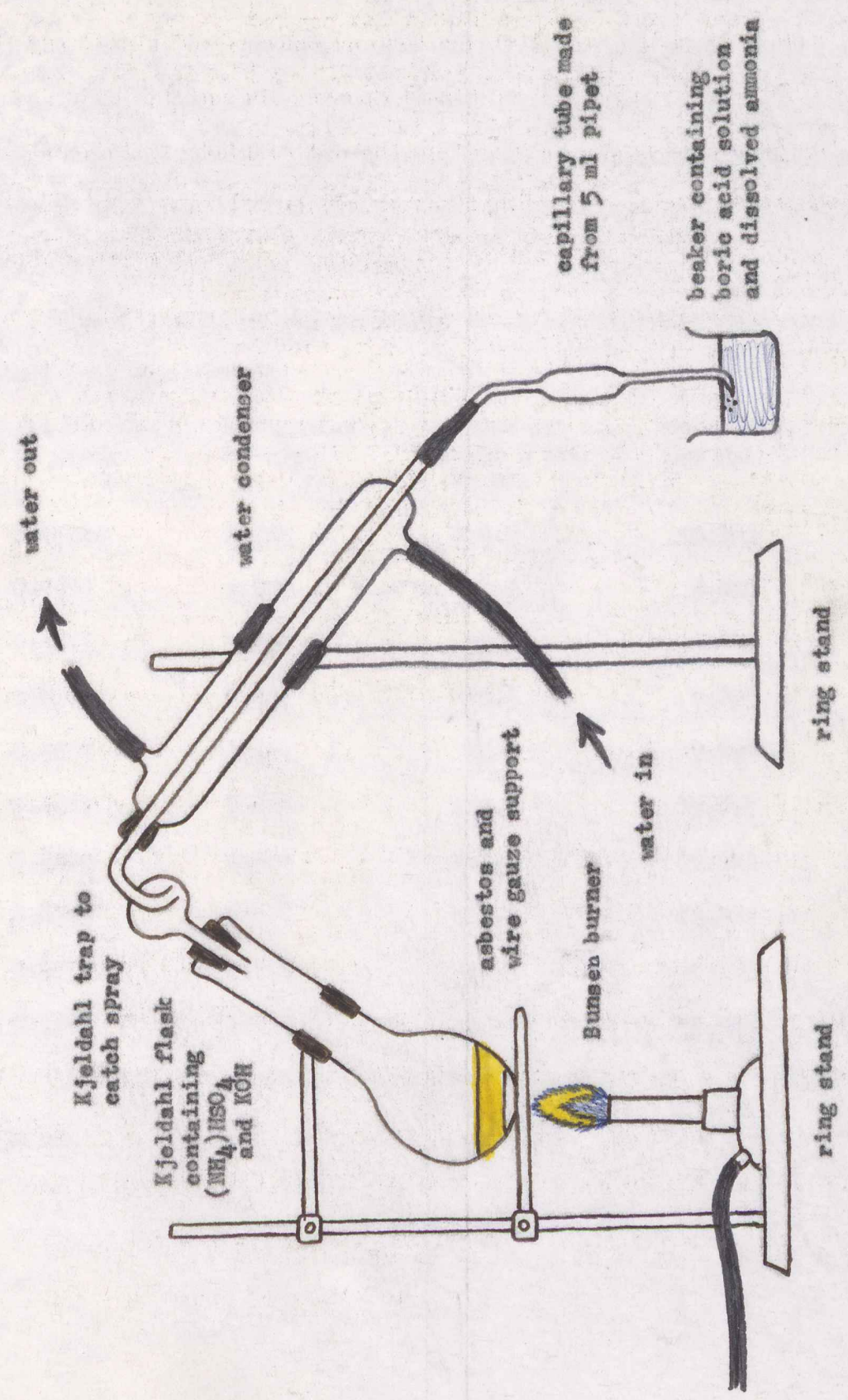
The ammonium bisulfate thus produced is then treated with 45%-50% KOH or NaOH solution in a special Kjeldahl flask. The reaction occurs:



In the modified Kjeldahl method used by Graham(6), Kolthoff(8), Mullen(10), and others, the ammonia is collected in a boric acid solution. Since the acidity of the boric acid solution is negligible, the solution containing the ammonium hydroxide may be titrated with standardized hydrochloric acid. The boric acid solution will absorb more than 99% of the ammonia produced. In this investigation, bromphenol blue was used as an indicator because it has a sharp end-point when changing from basic (blue) to acid (light yellow).

A diagram of the Kjeldahl apparatus is shown on the next page.

Kjeldahl Nitrogen Determining Apparatus:



The urea sample is placed in a flask and the sulfuric acid is added. The flask is then heated very strongly until sulfur trioxide begins to form. If this is not done, the urea will not be completely digested. Then the Kjeldahl flask and the concentrated alkali solution to be added are cooled so that the reaction will not proceed until the apparatus is sealed. The burner is then applied and the Kjeldahl flask heated until no more bubbles appear in the boric acid solution.

An accuracy check was performed using hydrochloric acid standardized against sodium carbonate:

weight of urea in grams	millimoles of urea	volume of 0.1164 N HCl in ml.	millimoles of HCl	efficiency
0.4724	7.865	134.9	15.702	99.8%
0.1757	2.925	50.0	5.820	99.4%
0.1163	1.936	33.0	3.841	99.2%
0.0581	0.967	16.3	1.897	98.1%
0.3264	5.435	85.9	9.999	92.0%
0.4611	7.677	129.7	15.097	98.3%
0.5892	9.810	167.6	19.509	99.4%
0.4033	6.715	112.4	13.081	97.6%
0.4272	7.113	118.3	13.771	96.8%
0.3986	6.637	115.2	13.407	101.0%

average and standard deviation

98.2% \pm 2.5%

Keeping the pH over 10, as recommended by Flaschka(4) will prevent the formation of any species other than the EDTA^{-4} ion. With the pH over 10, therefore, the reaction between the EDTA ion and the Mg ion becomes stoichiometric and can be a reliable method of analysis for magnesium.

Following the standardization procedures recommended by Flaschka(4) but substituting a prepared standard solution of MgCl_2 for the ZnCl_2 solution, the EDTA was standardized a short time after preparation.

An accuracy check was performed using the EDTA and the results are shown in the table below:

weight of $\text{MgSO}_4 \cdot 6.85\text{H}_2\text{O}$ in grams	millimoles of Mg^{++}	volume of 0.0997 M EDTA in ml.	millimoles of EDTA	efficiency
2.4959	10.238	102.3	10.197	99.6%
3.2151	13.189	131.6	13.120	99.4%
1.9873	8.152	81.9	8.168	100.2%
2.3048	9.454	93.6	9.331	99.7%
2.5072	10.285	98.8	9.853	95.8%
2.7419	11.247	108.6	10.831	96.3%
2.1153	8.678	86.0	8.574	98.8%
1.9760	8.106	80.8	8.051	99.2%
2.0649	8.470	85.9	8.563	101.1%
2.2367	9.175	90.9	9.065	98.8%

average and standard deviation

98.8% \pm 1.6%

The sample containing the Mg^{++} ion was placed in a flask, dissolved in water, and heated. Then 10 ml. of buffer solution was added and a few grains of Eric-T indicator. The solution was then titrated with the EDTA until the color just changed from maroon to dark blue. That was the end-point.

Preparation of buffer solution, indicator, and other advice on EDTA titrations may be found in the text by Flaschka(4). Care must be taken not to contaminate the EDTA solutions, since EDTA will complex with the ions in the walls of glass containers. For this reason, all EDTA solutions were stored in polyethylene containers, actually old Clorox bottles. Contact with metal surfaces, especially copper, must be avoided at all times.

Another advantage of the EDTA method is that it may be used on the sample upon which a urea determination has already been made. It can not be performed before the urea determination because this would add amine groups to the solution which would react along with the urea. Such extra amine groups would completely invalidate the results of the urea determination.

Neither sodium nor potassium ions interfere with the determination of magnesium ion because the formation constant of the magnesium ion is much different.

CALCULATIONS

Magnesium sulfate: The volume of EDTA is multiplied by the concentration to give the number of milliequivalents:

$$\text{sample 1M solid: } (31.6 \text{ ml EDTA})(0.0997 \text{ M EDTA}) = 3.15 \text{ m. eqs.}$$

and this number is then multiplied by the milliequivalent weight of MgSO_4 , which is 0.12037, to obtain the weight of MgSO_4 :

$$(3.15 \text{ m. eqs.})(0.12037) = 0.3969 \text{ grams}$$

This weight is then set over the total sample weight, 0.9870 grams:

$$0.3969/0.9870 = 0.3842 = 38.42\% \text{ MgSO}_4$$

Urea: The volume of hydrochloric acid is multiplied by the concentration to give the number of milliequivalents:

$$\text{sample 1M solid: } (2.9 \text{ ml HCl})(0.1164 \text{ N HCl}) = 0.338 \text{ m. eqs.}$$

and this number, the number of milliequivalents of NH_4^+ ion, must be divided by 2 to give the number of milliequivalents of urea since each urea molecule produces 2 ammonium ions. Then this figure is multiplied by the milliequivalent weight of urea, which is 0.06006, to obtain the weight of $\text{CO}(\text{NH}_2)_2$:

$$(0.338 \text{ m. eqs.})(0.06006)\left(\frac{1}{2}\right) = 0.0099 \text{ grams}$$

This weight is then set over the total sample weight, 0.9870 grams:

$$0.0099/0.9870 = 0.0103 = 1.03\% \text{ urea}$$

Water: The percentage of water was found by the difference between the total, 100%, and the percentages of magnesium sulfate and urea:

$$\text{sample 1M solid: } 100.00\% - 38.42\% - 1.03\% = 60.55\% \text{ water}$$

Computer program: These calculations were made into a computer program which is shown on the next page, the comments at the top and the source Program at the bottom, for speed and accuracy of calculation.

DAVID B. HOLLAND
 UNION COLLEGE 1964
 CHEMISTRY 56 RESEARCH PROJECT

AN INVESTIGATION OF THE TERNARY SYSTEM
 MAGNESIUM-SULFATE / UREA / WATER

THIS PROGRAM WAS COMPILED IN FORTRAN 0.
 IT CAN BE USED ON THE IBM 1620 OR THE IBM 1710 COMPUTER.
 THIS PROGRAM CALCULATES COMPOSITION FOR THE TERNARY SYSTEM.
 PLACE PROGRAM SWITCH 1 ON
 TYPE IN MOLAR CONCENTRATION OF EDTA AND HYDROCHLORIC ACID
 PLACE PROGRAM SWITCH 1 OFF TO RETAIN THESE VALUES.
 DATA IS ENTERED ON CARDS FOR EASE AND SPEED OF OPERATION
 WEIGHTS ARE IN GRAMS , VOLUMES ARE IN MILLILITERS.

PLACE PROGRAM SWITCH 2 ON TO HANDLE FINAL COMPOUNDS
 PUNCH IN VOLUME OF EDTA, VOLUME OF HCL, AND SAMPLE WEIGHT.
 MACHINE WILL THEN PRINT OUT ON TYPEWRITER
 VOLUME OF EDTA, VOLUME OF HCL, SAMPLE WEIGHT
 WEIGHT OF MAGNESIUM-SULFATE, WEIGHT OF UREA
 PERCENTAGES OF MAGNESIUM-SULFATE, UREA, WATER.

PLACE PROGRAM SWITCH 2 OFF TO HANDLE INITIAL MIXTURES
 PUNCH IN WEIGHTS OF HYDRATE, UREA, AND TOTAL.
 MACHINE WILL THEN PRINT OUT ON THE TYPEWRITER
 WEIGHTS OF HYDRATE, MAGNESIUM-SULFATE, UREA, TOTAL
 PERCENTAGES OF MAGNESIUM-SULFATE, UREA, WATER.

```

IF(SENSE SWITCH 1)2,3
2 ACCEPT,CEDTA,CHCL
  FEDTA=0.12037*CEDTA
  FHCL=0.03003*CHCL
  PAUSE
3 CONTINUE
  IF(SENSE SWITCH 2)4,5
4 READ,VEDTA,VHCL,WTSUM
  WTMG=FEDTA*VEDTA
  WTUR=FHCL*VHCL
  PRINT,VEDTA,VHCL,WTSUM
  PRINT,WTMG,WTUR
  GO TO 6
5 READ,WTHYD,WTUR,WTSUM
  WTMG=0.49376*WTHYD
  PRINT,WTHYD,WTMG,WTUR,WTSUM
6 PMG=(WTMG/WTSUM)*100.
  PUR=(WTUR/WTSUM)*100.
  PWO=100.-PMG-PUR
  PRINT,PMG,PUR,PWO
  GO TO 3
END
  
```


EXPERIMENTAL DATA TABLES

Composition of wet solids

sample number	total sample weight in grams	volume of 0.0997 M EDTA in ml. and % $MgSO_4$	volume of 0.1164 N HCl in ml. and % $CO(NH_2)_2$	% H_2O
5H-1	1.2390	27.5 26.44%	233.6 65.90%	7.65%
5H-2	0.9806	21.1 25.82%	181.8 64.81%	9.37%
5H-3	1.1004	24.8 27.05%	204.9 65.09%	7.87%
5H-4	1.4222	30.9 26.07%	264.1 64.91%	9.02%
6H-1	1.0348	20.1 23.31%	217.3 73.40%	3.29%
6H-2	0.6792	13.6 24.03%	132.1 67.99%	7.98%
6H-3	0.7925	15.1 22.87%	151.5 66.82%	10.31%
6H-4	0.5445	10.5 23.14%	103.9 66.70%	10.16%

Composition of wet solids

sample number	total sample weight in grams	volume of 0.0997 N EDTA in ml. and % $MgSO_4$	volume of 0.1164 N HCl in ml. and % $CO(NH_2)_2$	% H_2O
1M	0.9870	31.6 38.42%	2.9 1.03%	60.55%
2M	0.6452	20.0 37.20%	3.7 2.00%	60.79%
3M	1.1303	35.1 37.27%	12.4 3.33%	58.90%
4M	2.6394	86.4 39.30%	30.3 4.01%	56.68%
5M	0.9743	34.2 42.13%	13.9 4.99%	52.89%
6M	0.5259	20.5 46.78%	18.1 12.03%	41.19%
7M	0.6602	24.2 43.99%	28.3 14.98%	41.02%
8M	0.6530	23.9 43.92%	28.0 14.99%	41.09%
9M	0.6896	25.1 43.68%	37.7 19.11%	37.21%
10M	0.8145	26.3 38.75%	58.3 25.02%	36.23%
11M	0.7831	26.9 41.22%	65.5 29.24%	29.54%
12M	0.7260	24.9 41.16%	56.1 27.01%	31.83%
13M	0.7831	25.5 39.08%	65.8 29.37%	31.55%
14M	0.7421	26.5 42.85%	62.2 29.30%	27.85%
15M	0.8892	26.7 36.04%	89.0 34.99%	28.98%

Composition of wet solids

sample number	total sample weight in grams	volume of 0.1096 M EDTA in ml. and % $MgSO_4$	volume of 0.0985 N HCl in ml. and % $CO(NH_2)_2$	% H_2O
16M	0.8418	21.8 34.16%	109.6 38.51%	27.32%
17M	0.9693	23.7 32.26%	160.4 48.95%	18.80%
18M	1.0531	20.9 26.18%	205.1 57.61%	16.21%
19M	0.2211	2.2 13.12%	50.8 67.96%	18.91%
20M	0.2774	2.3 10.94%	61.0 65.04%	24.01%
21M	0.3343	2.5 9.87%	73.0 64.59%	25.54%
22M	0.3683	3.2 11.46%	82.3 66.09%	22.44%
23M	0.8363	2.4 3.79%	189.9 67.17%	29.05%
24M	1.0187	1.2 1.55%	238.8 69.34%	29.11%

Composition of wet solids

sample number	total sample weight in grams	volume of 0.0997 M EDTA in ml. and % MgSO_4	volume of 0.1164 N HCl in ml. and % $\text{CO}(\text{NH}_2)_2$	% H_2O
1A	0.1352	2.4 21.30%	24.1 62.33%	16.38%
2A	0.0675	2.2 39.11%	10.5 54.37%	6.52%
3A	0.4022	10.4 31.03%	28.0 24.33%	44.65%
4A	0.2465	4.7 22.88%	47.0 66.65%	10.47%
5A	0.0430	1.7 47.50%	4.8 39.07%	13.43%
6A	0.1063	3.3 34.03%	17.3 56.84%	9.13%

Composition of saturated solutions

sample number	total sample weight in grams	volume of 0.0997 M EDTA in ml. and % $MgSO_4$	volume of 0.1164 N HCl in ml. and % $CO(NH_2)_2$	% H_2O
1M	1.0036	23.3 27.86%	4.5 1.57%	70.57%
2M	1.0169	24.1 28.44%	8.7 2.99%	68.57%
3M	0.9742	23.3 28.70%	18.6 6.67%	64.62%
4M	1.2603	31.5 30.00%	33.5 9.29%	60.71%
5M	1.4120	33.3 28.30%	50.9 12.60%	59.10%
6M	1.5399	36.1 28.13%	74.9 17.00%	54.86%
7M	1.1348	26.4 27.92%	63.8 19.65%	52.43%
8M	1.3699	31.2 27.33%	86.6 22.10%	50.57%
9M	1.1800	26.6 27.05%	79.7 23.61%	49.34%
10M	1.3090	29.2 26.77%	92.7 24.75%	48.48%
11M	0.8882	18.1 24.46%	73.2 28.81%	46.74%
12M	1.7306	33.5 23.23%	159.9 32.30%	44.47%
13M	0.9167	17.4 22.78%	94.1 35.88%	41.34%
14M	1.0061	17.9 21.35%	114.0 39.61%	39.04%
15M	1.4980	25.6 20.51%	184.9 43.15%	36.35%

Composition of saturated solutions

sample number	total sample weight in grams	volume of 0.1096 M EDTA in ml. and % MgSO_4	volume of 0.0985 N HCl in ml. and % $\text{CO}(\text{NH}_2)_2$	% H_2O
16M	1.6375	23.8 19.17%	266.3 48.10%	32.72%
17M	1.9328	28.6 19.52%	328.3 50.24%	30.24%
18M	1.8005	28.1 20.59%	317.7 52.19%	27.22%
19M	1.6536	22.7 18.11%	290.1 51.89%	30.00%
20M	1.0027	11.4 15.00%	178.3 52.60%	32.40%
21M	0.2571	2.4 12.32%	46.1 53.04%	34.65%
22M	1.1760	8.3 9.31%	210.7 53.00%	37.69%
23M	0.6666	2.9 5.74%	121.7 54.00%	40.26%
24M	1.5275	2.8 2.42%	285.5 55.29%	42.30%

PHASE DIAGRAM

CO(NH₂)₂

Samples 1M - 2M in BLUE

Samples 1A - 6A in GREEN

Samples 5H-1 - 5H-4
and 6H-1 - 6H-4 in RED

*4 = MgSO₄ · 4CO(NH₂)₂ · 2H₂O

*5 = MgSO₄ · 5CO(NH₂)₂ · 2H₂O

*6 = MgSO₄ · 6CO(NH₂)₂ · 2H₂O

MgSO₄ · 7H₂O

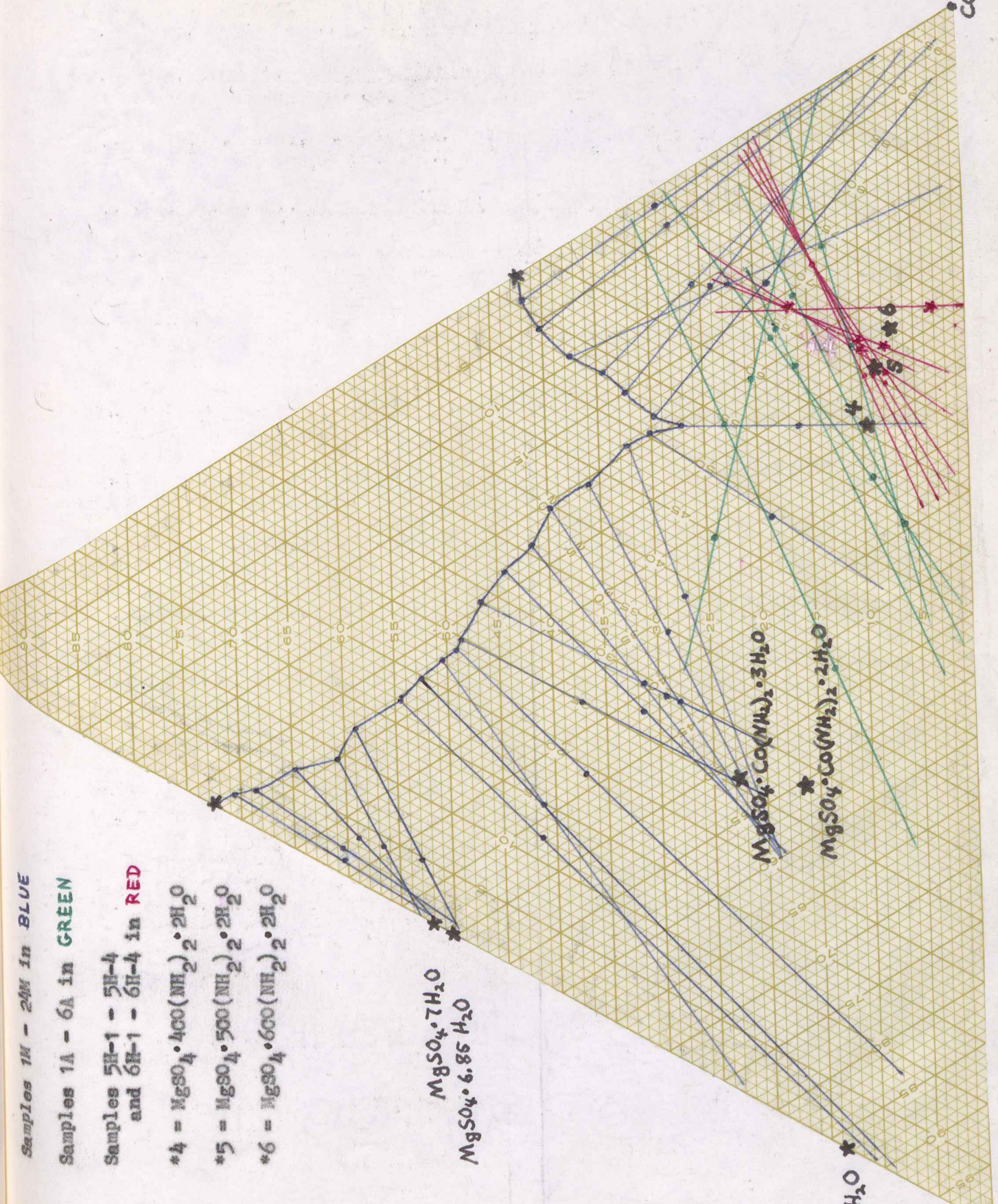
MgSO₄ · 6.85 H₂O

MgSO₄ · CO(NH₂)₂ · 3H₂O

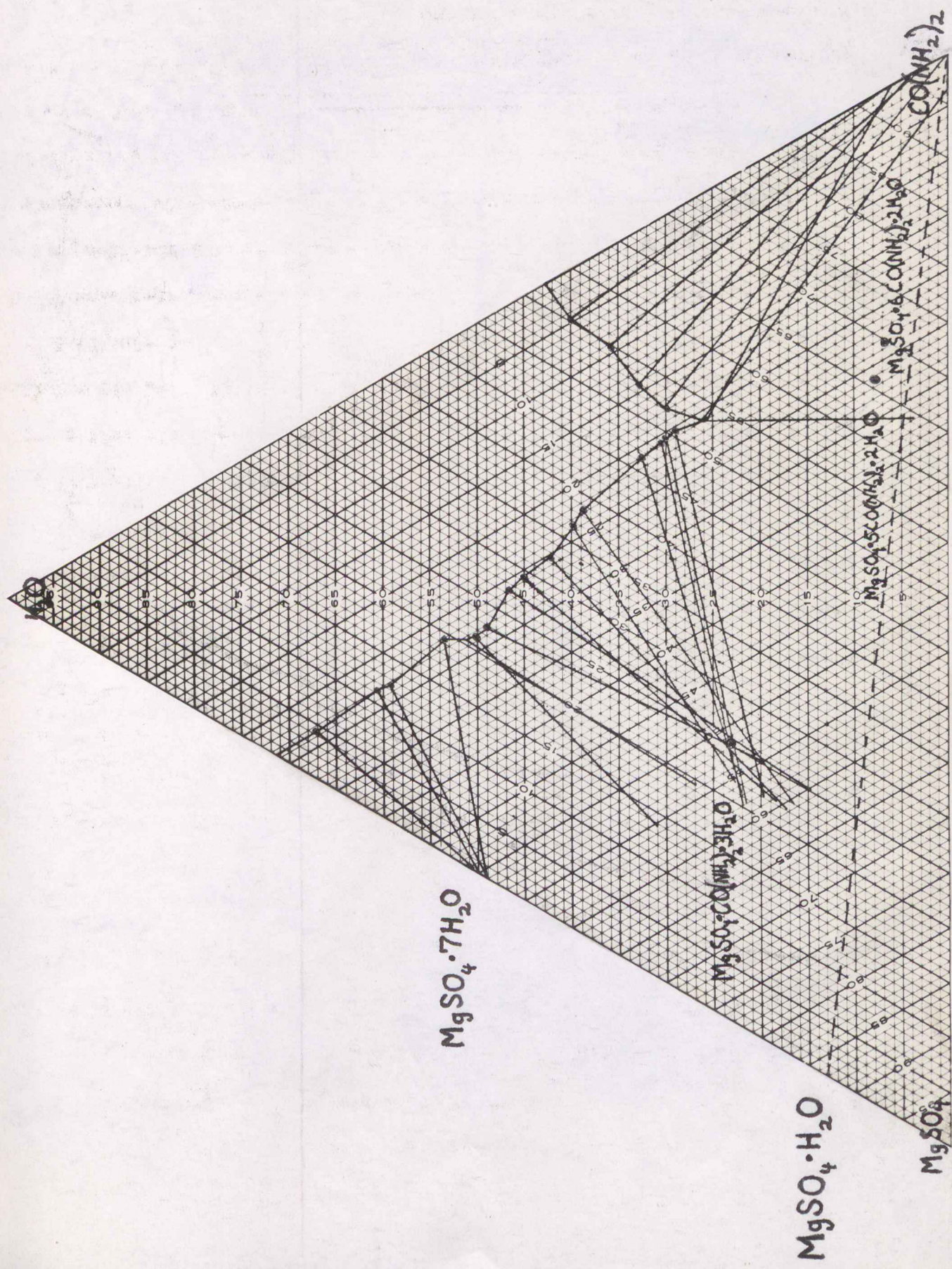
MgSO₄ · CO(NH₂)₂ · 2H₂O

MgSO₄ · H₂O *

MgSO₄

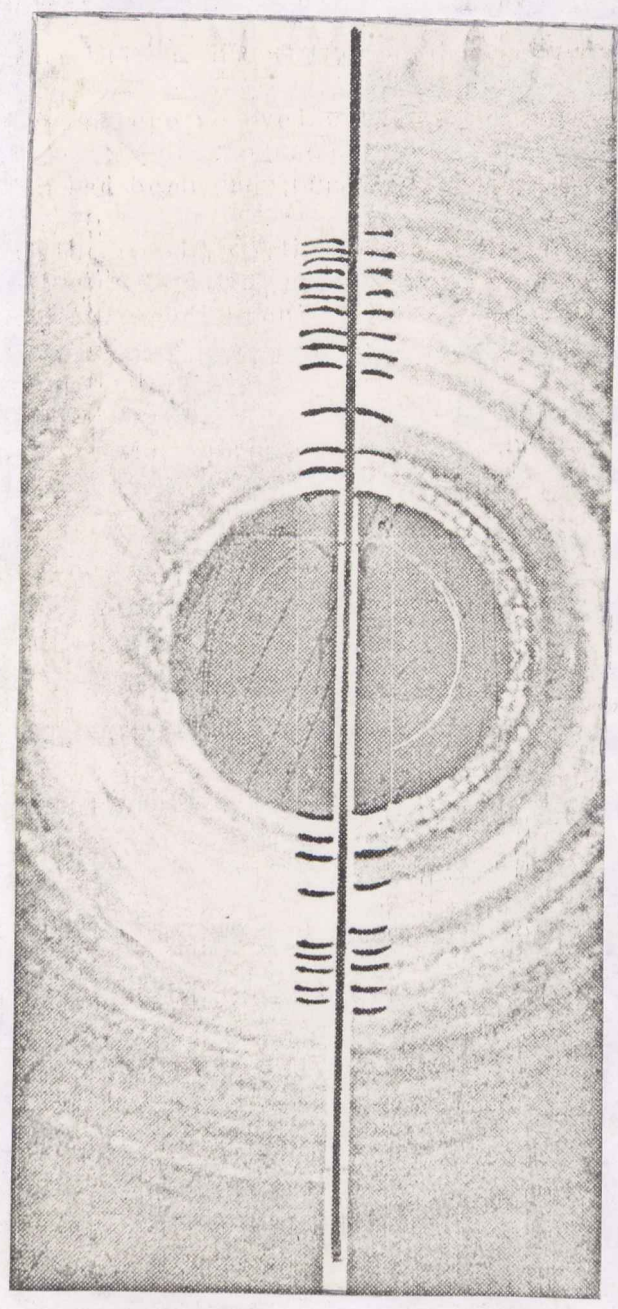
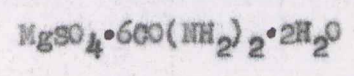
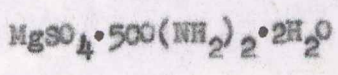


PHOTOCOPY OF WHITTAKER PHASE DIAGRAM



PHOTOCOPY OF X-RAY POWDER PICTURES BY GRAHAM

X-RAY POWDER DIFFRACTION OF CRYSTALS FORMED FROM
THE COMPOUND SYNTHESIZED BY YEE



SUMMARY AND CONCLUSIONS

After plotting the results of the calculations on the phase diagram on page 26 of this thesis, I concluded the following:

1. There seems to be evidence for the existence of another compound, $\text{MgSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$, formed in methanol, which has not been reported previously.
2. The two ternary compounds of Yee et. al.(15) exist as stable forms.
3. The monohydrate of magnesium sulfate, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ may probably exist as a solid phase along a portion of the boundary curve in the ternary system. Whittaker et. al.(15) did not apparently study this region of the curve thoroughly.
4. The compound reported by Graham(6), $\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$, does not seem to exist. His deduction for its existence is probably due to inaccurate analytical technique, especially with regard to urea.
5. The methanol seems to remove the water of crystallization from the magnesium sulfate hydrate by some solvent effect. If the solubility in methanol of water and urea were different, this effect would be expected. This removal of water causes more combination between the urea and the anhydrous magnesium sulfate. Methanol completely changes the solubility properties of the ternary system.

REFERENCE TABLESPercentage Composition

compound	% MgSO_4	% $\text{CO}(\text{NH}_2)_2$	% H_2O
$\text{MgSO}_4 \cdot \text{H}_2\text{O}$	86.98	0	13.02
$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$	48.83	0	51.17
$\text{MgSO}_4 \cdot 6.85\text{H}_2\text{O}$	49.38	0	50.62
$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O}$	60.66	30.26	9.08
$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$	55.61	27.74	16.65
$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O}$	51.33	25.61	23.06
$\text{MgSO}_4 \cdot 5\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$	26.35	65.75	7.90
$\text{MgSO}_4 \cdot 6\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$	23.29	69.73	6.98
$\text{MgSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O}$	30.35	60.57	9.09
$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2$	66.71	33.29	0

Molecular weights

$$\text{Mg} = 24.31$$

$$\text{KOH} = 56.11$$

$$\text{NaOH} = 40.11$$

$$\text{MgSO}_4 = 120.37$$

$$\text{MgSO}_4 \cdot \text{H}_2\text{O} = 138.39$$

$$\text{MgSO}_4 \cdot 6.85\text{H}_2\text{O} = 243.78$$

$$\text{MgSO}_4 \cdot 7\text{H}_2\text{O} = 246.51$$

$$\text{H}_2\text{O} = 18.02$$

$$2\text{H}_2\text{O} = 36.04$$

$$3\text{H}_2\text{O} = 54.06$$

$$7\text{H}_2\text{O} = 126.41$$

$$6.85\text{H}_2\text{O} = 123.41$$

$$\text{CO}(\text{NH}_2)_2 = 60.06$$

$$5\text{CO}(\text{NH}_2)_2 = 300.30$$

$$6\text{CO}(\text{NH}_2)_2 = 360.36$$

$$\text{NH}_4\text{Cl} = 53.49$$

$$\text{H}_2\text{Na}_2\text{-EDTA} \cdot 2\text{H}_2\text{O} = 372.25$$

$$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot \text{H}_2\text{O} = 198.45$$

$$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O} = 216.47$$

$$\text{MgSO}_4 \cdot \text{CO}(\text{NH}_2)_2 \cdot 3\text{H}_2\text{O} = 234.49$$

$$\text{MgSO}_4 \cdot 5\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O} = 456.71$$

$$\text{MgSO}_4 \cdot 6\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O} = 516.77$$

$$\text{MgSO}_4 \cdot 4\text{CO}(\text{NH}_2)_2 \cdot 2\text{H}_2\text{O} = 396.65$$

$$\text{Ratio: MgSO}_4 / \text{MgSO}_4 \cdot 6.85\text{H}_2\text{O} = 0.49376$$

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