PROPERTIES OF HYDRAZINE

I. QUANTITATIVE DETERMINATION OF HYDRAZINE

II. PREPARATION OF ANHYDROUS HYDRAZINE

III. PHASE EQUILIBRIA IN TERNARY SYSTEMS CONTAINING HYDRAZINE

BY

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A.B., Millikin University, 1941
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THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY
IN THE GRADUATE SCHOOL OF THE
UNIVERSITY OF ILLINOIS, 1947

URBANA, ILLINOIS

UNIVERSITY OF ILLINOIS

THE GRADUATE SCHOOL

August 23, 1947

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY SUPERVISION BY ROBERT ALLEN PEIFFER

ENTITLED I. PROPERTIES OF HYDRAZINE
II. QUANTITATIVE DETERMINATION OF HYDRAZINE
III. PREPARATION OF ANHYDROUS HYDRAZINE
IV. PHASE EQUILIBRIA IN TERNARY SYSTEMS CONTAINING HYDRAZINE

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000—7-47—35914

ACKNOWLEDGMENT

The author wishes to express his keen appreciation to Professor L. F. Audrieth for his valuable advice and the friendly, cooperative attitude which characterized his able direction of this research.

Gratitude is expressed to the National Research Council for the Fellowship which made it possible for the author to complete his graduate training.

Acknowledgment is also made to the Olin Industries Inc., for a grant of funds which was used to provide the services of a part-time analyst during a certain portion of this research.

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PART I. QUANTITATIVE DETERMINATION OF HYDRAZINE

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A. INTRODUCTION

Investigation of methods for preparing quantities of hydrazine of 95% concentration or greater necessitated a rapid, convenient analytical procedure. A search of the literature revealed no recent survey of analytical methods. Two summaries of work by individual investigators were published in 1924 (1,2) but no complete survey has appeared since that date. The importance of hydrazine as a rocket fuel has focused attention on methods of producing hydrazine in tonnage quantities, with consequent increased interest in and need for analytical or assay procedures. The instability of free hydrazine and the ease of catalytic decomposition make necessary frequent analyses.

Stolle (3) reported that hydrazine in bicarbonate solution decomposes slowly. Bray and Guy (2) obtained similar results for solutions containing a phosphate buffer at pH 7. They assumed that dissolved oxygen was responsible for the decomposition since, in a closed, unshaken flask, 0.9% of 0.1 M hydrazine disappeared in the first two hours and only 1.9% in the next twenty-two hours. From an open flask a loss of 8.1% in 48 hours was noted. They confirmed that oxygen was causing the decomposition of the hydrazine; by excluding oxygen, the decomposition of an alkaline hydrazine solution was negligible in 24 hours (4). Work by Brown (5) in this laboratory demonstrated that cupric and zinc ions,

as well as manganese dioxide, cause catalytic decomposition of hydrazine. The observations of Gilbert (6) were extended by Brown (5) to show that atmospheric oxidation of hydrazine in solutions up to 0.8 M is catalyzed by caustic soda; the catalytic effect reaches a maximum at 0.02-0.03 M NaOH. Concentrations of sodium hydroxide greater than 0.20-0.40 M effectively inhibit this oxidation.

Survey of analytical methods

Because of the need for an accurate quantitative method for hydrazine, this summary of analytical procedures was prepared from a careful survey of the literature. Several of these procedures were checked by the author on samples of differing hydrazine content. The available methods and reagents used for the quantitative determination of hydrazine are:

1. *Direct acid titration.
2. **Combination acidimetric and iodate.
3. *Direct iodate, using solvent.
4. *Direct iodate with internal indicator.
5. Indirect iodate.
6. *Direct iodine.
7. Indirect iodine.
8. *Direct permanganate.
9. *Indirect permanganate.
10. Bromate.
11. Ferricyanide-cerimetric.
12. Sodium-p-toluolsulfonchloramide.
13. Bromine and hypochlorous acid methods.

*Denotes methods checked in the present study.
**An original method proposed and evaluated by the author.

Special factors to be considered in the quantitative determination of hydrazine.

The usual requirements of accuracy and reproducibility are

extremely important in the analysis of hydrazine, since oxidation of hydrazine can result in a variety of products. Principal products which have been observed are hydrazoic acid, nitrogen, and ammonia (2,4,7). An oxidizing agent such as permanganate which is satisfactory in the presence of hydrochloric acid, gives a variety of side products if sulfuric acid is used (1). Potassium dichromate is useless if oxidation to nitrogen is desired (4,7).

Ammonia is a decomposition product of hydrazine as well as a raw material for its production. Thus a desirable analytical method must be specific for hydrazine in the presence of ammonia. In addition, the method must be applicable both to free hydrazine and to hydrazine salts. Since side reactions (2,4) can be influenced by various conditions, such as acid concentration, type of oxidizing agent, or presence of metallic ions, it is advisable to check any analytical method for reproducibility where unusual conditions are encountered. The rapidity and suitability of a method to routine analysis are, of course, other factors to be considered.

Since a direct titration is better in principle, and more convenient where analyses must be made frequently, the indirect iodate and iodine methods were not checked, even though excellent accuracy is claimed for them (1,2). The bromine and hypochlorous acid methods were not evaluated, the reagents being of an objectionable nature. Because of the similarity between the iodate and the bromate methods, the latter was not checked. The experience gained through several hundred analyses has shown that the

direct iodate and the combination acid-iodate procedures are the most suitable, especially when free hydrazine and/or hydrazine in basic solution is to be determined. For completeness, all the methods listed above are described in detail in the experimental section, even though several of these were not evaluated experimentally.

B. EXPERIMENTAL

Recommended techniques for handling solutions to be analyzed

a) Since solutions containing free hydrazine in appreciable concentration are subject to oxidation by atmospheric oxygen, fume badly, and pick up carbon dioxide, all sample weighing should be made using weight burets or pipets.

b) The hydrazine should be added to water containing a slight excess of acid followed by dilution in a volumetric flask to approximately 0.1 N (0.025 M). Where iodate oxidation is to follow, hydrochloric acid should be used. Hydrochloric acid is preferred to sulfuric acid since the hydrochloride is more soluble than the sulfate. Such acid solutions are stable for long periods.

c) In the acidimetric titration of free hydrazine, recently boiled (oxygen and carbon dioxide free) water should be used for dilution of the sample.

d) With sufficient care, the use of micro pipets has been shown to give results which are accurate to within 0.1%-0.2%, especially where very small amounts of concentrated hydrazine solutions were analyzed. Micro pipets, 115-580 microliters in volume, were constructed from capillary tubing by blowing two

tiny reservoirs and drawing the capillary down at both ends. Using a 1 ml. hypodermic syringe, the pipet was filled with the liquid to be analyzed. Since the openings of the capillary were extremely fine, the pipet could be wiped and weighed with no additional precaution against hydrazine loss. Furthermore, the results in Table 1 show that the reproducibility of filling and transfer of the contents is excellent. In effecting discharge of the pipet, the tip is placed beneath the surface of 50 ml. of boiled water and the contents are expelled by depressing the plunger of the syringe. The tip is moved to another section of the liquid, filled and emptied twice. Finally, the tip is washed with a few drops of distilled water and quantitative transfer is complete. Before re-use, the pipet is dried by connecting it to the laboratory vacuum line and drawing air through it.

Direct acid titration (3,8)

$$N_2H_4 + H^+ \longrightarrow N_2H_5^+$$

A rapid and convenient method for the analysis of free hydrazine involves titration with a strong acid. The titration was followed with a pH meter, and either methyl red or methyl orange were found to be satisfactory indicators. In the preliminary experiments, 0.1000 N sulfamic acid, a convenient, solid, primary standard was used. It was found that this acid concentration was too weak, giving an indicator error. As a result, 0.5000 N HCl was used, and was standardized against freshly prepared Na_2CO_3. Typical titration curves are depicted in Figure 1.

The two indicators are satisfactory if used correctly. The

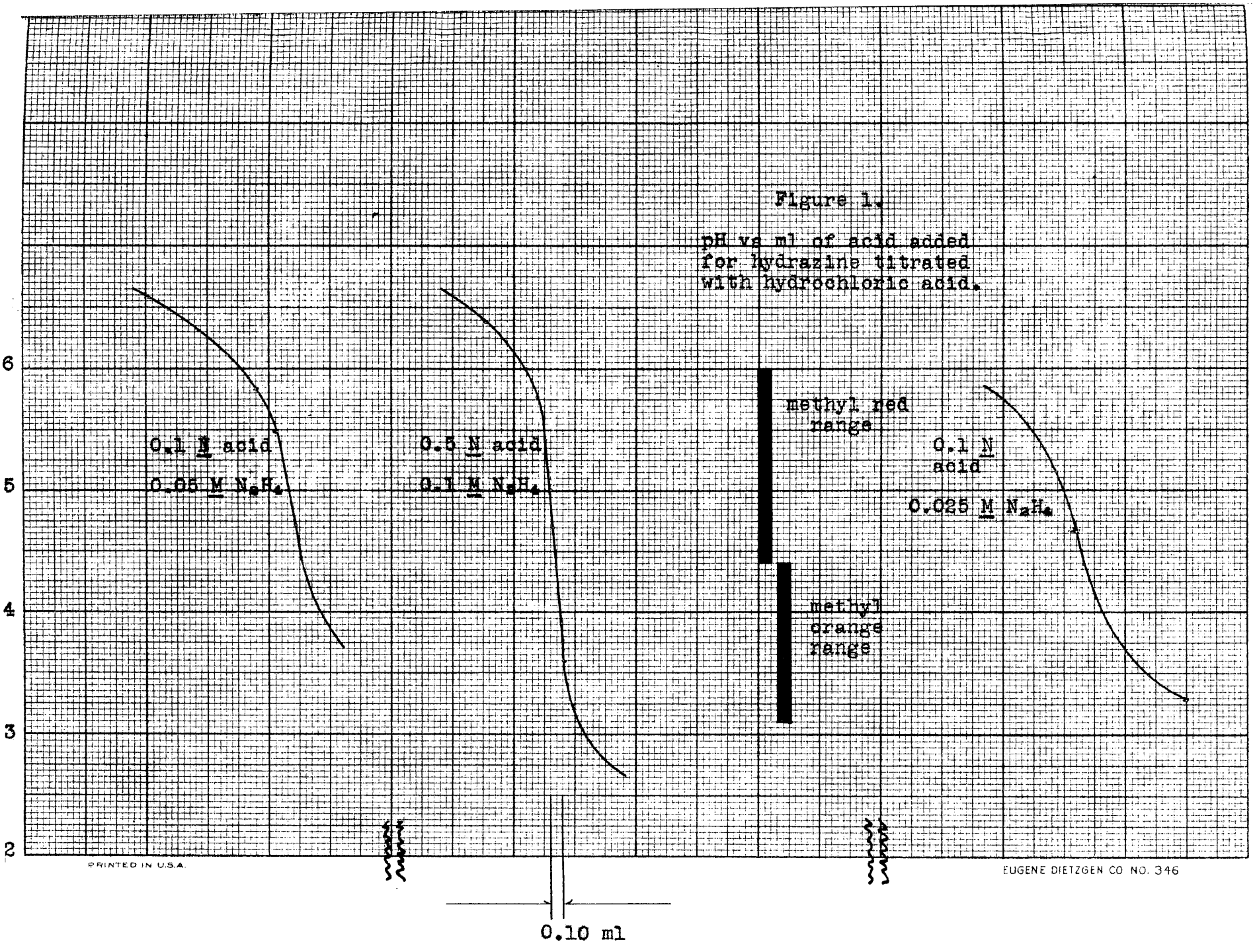
Figure 1.
pH vs ml of acid added for hydrazine titrated with hydrochloric acid.
6
5
4
3
2
0.1 N acid
0.05 M N_2H_4
0.5 N acid
0.1 M N_2H_4
methyl red range
0.1 N acid
0.025 M N_2H_4
methyl orange range
0.10 ml
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true inflection point falls in the lower (more acid) range of methyl red, and in the upper (more basic) range of methyl orange. Results of analyses using both indicators appear in Table 1. The samples were taken using the micro pipet technique described earlier and weighed about 0.6 grams each.

Table 1

Titration of 0.2 M hydrazine with 0.5 N HCl

% N_2H_4		Indicator
99.88 100.00 99.90	99.93 av.	methyl orange to color of pH 4 buffer
99.94 99.83	99.88 av.	methyl red to color of pH 4.5 buffer

Combination acidimetric and iodate method

In the presence of ammonia or other base, the acid method will not indicate the true amount of hydrazine. However, combination of the acidimetric with an oxidimetric method on any one sample, in that order, yields a procedure for determining both total base and hydrazine. For example, a hydrazine solution after titration with standard acid can be titrated using the iodate method. The difference in the two titres gives a measure of the amount of other basic components that are present.

To check the accuracy of this method, a synthetic mixture was prepared containing a known amount of ammonia and hydrazine. In a weight buret, 35.4587 g. of 53.67% hydrazine was mixed with 4.8630 g. of 17.86% ammonia. The contents of the buret were thoroughly mixed and four samples were taken using the micro pipet

technique previously mentioned. The results are recorded in Table 2.

Table 2

Analyses of a synthetic sample containing 44.23% N_2H_4 and 2.87% NH_3 by the combination acid and iodate method

Sample wt.,g.	ml. of 0.3992 N HCl	ml. of 0.1004 M KIO_3 for 100/250 aliquot	%N_2H_4 obsd.	% NH_3 obsd.
0.5908	22.96	32.48	44.22	2.92
0.5909	22.94	32.51	44.26	2.87
0.5927	23.03	32.57	44.21	2.92
0.5908	22.95	32.51	44.26	2.88

Direct iodate, using solvent (1)

$$N_2H_4 + KIO_3 + 2HCl \longrightarrow KCl + ICl + N_2 + 3H_2O$$

In the presence of concentrated hydrochloric acid (4 N or above) hydrazine can be titrated directly with standard iodate solution. The addition of iodate is continued until the iodine color is discharged. Actually, the initial reaction involves reduction of iodate to iodine. The latter is subsequently oxidized by additional iodate to ICl, resulting in the disappearance of the iodine color. Partial reactions can be written representing these various steps.

$$N_2H_4 \longrightarrow N_2 + 4H^+ + 4e^-$$

$$5e^- + IO_3^- + 6H^+ \longrightarrow 3H_2O + \tfrac{1}{2}I_2$$

$$\tfrac{1}{2}I_2 + Cl^- \longrightarrow ICl + e^-$$

A few ml. of $CHCl_3$ or CCl_4 is added to dissolve the iodine, the end point being reached when the solvent layer is decolorized.

A sample of Merk's "Suitable for Micro Analysis" hydrazine sulfate was recrystallized and dried at 110° C and then titrated using a 0.4000 N (0.1000 M) solution of Baker's KIO_3. Duplicate analyses were made, the second sample containing 0.5 g. NH_4Cl/g. $N_2H_4.H_2SO_4$. Results of these test runs indicated 100.1 and 100.0% purity of the hydrazine sulfate. These experiments confirmed the literature claims (2) to the effect that the presence of ammonium salts does not interfere with this procedure.

Since reagent iodate occasionally contains some periodate, it is recommended that each new bottle be checked against recrystallized hydrazine sulfate. Recrystallized potassium dichromate and potassium iodate were compared and the iodate was used to analyze the recrystallized hydrazine sulfate. Results agreeing to within one part in a thousand were obtained. Thereafter, each new bottle of reagent iodate was checked against the hydrazine sulfate.

Since the end point depends on the appearance of iodine and its subsequent disappearance by oxidation to ICl, it is necessary to keep the normality of HCl within certain limits, preferably between 3 and 5. The importance of this requirement was demonstrated by the following experiment: one-hundred ml. of concentrated hydorchloric acid (12 N) containing KIO_3 and an excess of hydrazine was progressively diluted with water and shaken with 5 ml. of CCl_4. The results appear in Table 3. It will be noted that ICl is sufficiently stable in concentrated hydrochloric acid (presumably as ICl_2^-) that it is not reduced to iodine by hydrazine unless the concentration of hydrochloric acid is less than 7-8 N. However, the reaction between hydrazine and iodate (in HCl) to form ICl_2^-

occurs immediately. The influence of hydrochloric acid concentration on this reaction seems to have escaped attention by previous workers.

Table 3

Effect of HCl normality on the reduction of ICl by hydrazine

Normality of HCl	Remarks
12	N_2 evolution and formation of ICl observed immediately. No iodine color in solvent, aqueous solution yellow.
8.3	Appearance of faint iodine color in solvent, aqueous Solution yellow.
7.2	Definite iodine color in solvent, aqueous solution slightly brown.
6.8	Deep iodine color in solvent, aqueous solution brown.

Reagents required

Concentrated HCl, standard KIO_3, $CHCl_3$ or CCl_4.

Procedure

To a glass-stoppered flask containing the solution of the sample add 20% more than an equal volume of concentrated HCl (12 N) and 5 ml. of CCl_4. Add standard iodate solution until the aqueous layer begins to change from a dark brown color to a light yellow. At this point add the iodate dropwise and shake the solution vigorously after the addition of each drop. When the iodine color is completely discharged from the solvent layer, the end point has been reached. The final normality of HCl should be between 3 and 5.

Direct Iodate with internal indicator (9)

The procedure is the same as given above for direct iodate using solvent, except that a water-soluble dye is used instead of the solvent. Amaranth and Brillant Ponceaux 5R having British Colour Index numbers 184 and 185, respectively, are satisfactory for this purpose. (These dyes are known under the National Aniline Co. names of Wool Red, 40F, and Brilliant Scarlet, 3R). A 0.2% aqueous solution of either of these indicators is made up; three to five drops are sufficient to give a distinct end point in 250 ml. of solution. The dyes are not affected by hydrochloric acid, iodine, or iodine monochloride under conditions of the titration, but are readily destroyed by a trace of iodate in 3-5 N HCl at temperatures above 30° C. The heat of dilution of concentrated HCl to 5-6 N is sufficient to raise the temperature above this permissible minimum. The addition of the indicator is delayed until the end point is approached, that is, until the iodine color begins to lighten. The iodate analyses presented in Table 2, page 7, were obtained using this method.

Indirect iodate method (2)

$$4H^+ + 5N_2H_4 + 4IO_3^- \longrightarrow 5N_2 + 2I_2 + 12H_2O \quad (A)$$

$$6H^+ + 5I^- + IO_3^- \longrightarrow 3I_2 + 3H_2O \quad (B)$$

The oxidation of hydrazine to nitrogen by iodate proceeds slowly in neutral or alkaline solution but is rapid and quantitative in acid solution. Both hydrazine and iodide ions reduce iodate to iodine; the hydrazine sample in acid solution is treated with an excess of iodate and the excess iodate is determined by

addition of potassium iodide. The liberated iodine is then titrated with thiosulfate. In 0.5-2 N sulfuric acid, reaction (A) is complete in three minutes. Addition of iodate dropwise to hydrazine solution, or the reverse addition, has no effect on the accuracy. In alkaline solution, however, the reaction does not give quantitative results.

Reagents required

KI, starch solution, standard KIO_3, standard $Na_2S_2O_3$, 4 N sulfuric acid.

Procedure

To a given volume of standard iodate, 30-50% in excess of that needed to oxidize the hydrazine, add an equal volume of 4 N sulfuric acid. Add the hydrazine sample to the solution. After five minutes add potassium iodide in excess and titrate the liberated iodine with thiosulfate.

Direct iodine method (1)

$$N_2H_4 + 3I_2 \longrightarrow 4HI + N_2$$

Hydrazine can be titrated directly with standard iodine solution if the pH is regulated to 7.0-7.4 and if the last drops of iodine solution are added at intervals of a few seconds. At a pH lower than 7 the reaction is quantitative but very slow. If the pH is greater than 7.5 the method gives low results. Using 0.1 N I_2 solution, one drop will give to 200 ml. of the solution a perceptible yellow color that is permanent for several minutes. Against a good light and a white background the end point is easily discernible.

The presence of ammonium salts was found to have no effect, since triplicate analyses used 32.96, 33.00, 32.99 ml. of standard I_2 (last sample contained 0.5 g. NH_4Cl).

In experiments by the author, no reagent blank was subtracted since 150 ml. of water containing 0.5 g. KI (amount present after a normal titration) and adjusted to pH 7.0-7.2 with $NaHCO_3$ required but 0.02 ml. of standard iodine solution.

Reagents required

Standard I_2, standard $Na_2S_2O_3$, $NaHCO_3$.

Procedure

A hydrazine sample is diluted to ca 150 ml. in a 600 ml. beaker containing pH meter electrodes and a stirrer. Solid $NaHCO_3$ is added until the pH has been adjusted to 7.0-7.2 and standard iodine solution is added. Additional $NaHCO_3$ is added whenever necessary to maintain the pH in the desired range. When the yellow color begins to linger for a fraction of a second, the rate of iodine addition is decreased to one drop/five seconds. At the equivalent point the color will persist for several minutes. Reference has already been made to the fact that hydrazine is readily oxidized by air at a pH above 7. In carrying out this procedure it would be desirable to eliminate this possible source of error, by introducing nitrogen gas into the container.

Indirect iodine method (2)

The oxidation of hydrazine by iodine occurs rapidly in alkaline solution. To prevent errors resulting from the formation of

iodate, a large excess of iodine is used and the iodine is added to the hydrazine solution before addition of the alkali. Errors due to loss of hydrazine from alkaline solution are reduced by rapid addition of the iodine. Following the recommended order of addition, an accuracy of 0.2% is achievable.

Reagents required

Standard iodine, standard thiosulfate, 2 N NaOH, 3 N H_2SO_4, starch solution.

Procedure

The hydrazine sample is placed in a glass-stoppered flask, an excess of standard iodine solution is added, followed by an excess of alkali. After two minutes the solution is acidified and the residual iodine titrated with thiosulfate.

Direct permanganate method (1)

$$5N_2H_4 + 4MnO_4^- + 12H^+ \longrightarrow 5N_2 + 16H_2O + 4Mn^{++}$$

In boiling 1 N HCl solution hydrazine can be titrated with $KMnO_4$. The author found that the end point faded rapidly. The procedure is not recommended.

Reagents required

4 N HCl, standard $KMnO_4$.

Procedure

To 40 ml. of 0.1 N hydrazine solution add 30 ml. of 4 N HCl solution, heat to boiling and titrate with 0.1 N $KMnO_4$ until the solution is pink. The end point is fleeting.

Indirect permanganate method (1)

$3N_2H_4 + 4MnO_4^- \longrightarrow 4MnO_2 + 3N_2 + 4OH^- + 4H_2O$ (alkaline solution)

Kolthoff (1) claimed to have achieved excellent results by the oxidation of hydrazine in alkaline solution with excess permanganate and back titration of the excess in acid solution using KI and thiosulfate. The author found, however, that the permanganate method was subject to erratic variations, amounting frequently to 1% and occasionally to as much as 3-5%. The deviations on duplicate titrations were often as large as 0.5-1%. In comparison with results obtained by the iodate and iodine methods, the errors using the $KMnO_4$ method were always negative, i.e., gave lower values for hydrazine content. Kolthoff based his claims on the analyses of a standard solution of hydrazine sulfate, whereas hydrazine solutions of widely differing concentrations, some containing acid and others only free hydrazine, were analyzed in checking the method.

In an effort to determine the cause for the observed discrepancies, the order of addition of reagents was varied; that is, hydrazine was added to alkaline permanganate rather than the recommended procedure in which permanganate is added to the alkaline hydrazine solution. Since iodine is subject to oxidation to iodate in alkaline solution, the addition of KI was delayed until after acidification. However, the method still gave results which would frequently deviate 1% or more without apparent reason. It was concluded that the method is capable of giving reproducible results only if carefully standardized and repeated exactly under those conditions. Typical results are presented in Table 4.

Table 4

Percentage N_2H_4 in samples analyzed by $KMnO_4$, KIO_3, and I_2 methods

$KMnO_4$	I_2	KIO_3	% Difference based on iodate
96.9	99.4	99.4	-3.5 (a)
98.2	99.4	99.4	-1.2 "
97.4	99.3		-2.0 "
99.1	99.4		-0.3 (b)
10.04		10.02	+0.2 "
11.63		12.00	-3.1 "
13.39		13.55	-1.2 "
19.68		19.75	-0.35 "

(a) Order of addition: NaOH, $KMnO_4$, N_2H_4, H_2SO_4, KI.

(b) Order of addition: N_2H_4, NaOH, $KMnO_4$, KI, H_2SO_4.

Reagents required

Standard $KMnO_4$, standard $Na_2S_2O_3$, 4 N NaOH, 4 N H_2SO_4, KI, and starch solution.

Procedure

An excess of standard $KMnO_4$ is placed in a 500 ml. conical flask containing the hydrazine solution and ten ml. of 4 N NaOH. Since the reduction in alkaline solution yields MnO_2, the normality is three-fifths that in acid solution. After 30-45 minutes, 2 g. of KI is added and the solution is acidified with 20 ml. of 4 N H_2SO_4. The liberated iodine is titrated with thiosulfate.

Bromate method (1,10,11)

This method is essentially similar to the iodate procedure.

If the titration is carried out at room temperature and indigo or methyl orange is used to detect free bromine at the end point, an excess of bromate is required. The excess can be determined iodimetrically. In the presence of 6 N HCl the reaction is quantitative if begun in boiling solution. Reference (11) mentions the use of phosphomolybdic acid as indicator.

Ferricyanide-cerimetric method (12)

$$N_2H_4 + 4K_3Fe(CN)_6 + 4KOH \longrightarrow 4K_4Fe(CN)_6 + 4H_2O + N_2$$

The oxidation is accomplished by adding excess ferricyanide in basic solution, acidifying with HCl and determining the amount reduced using standard ceric sulfate. The amount of excess alkali was found to be without effect. The final acidity should be less than 1.8 N in HCl. It is stated that oxidation of hydrazine is not complete if insufficient excess ferricyanide is added. However, a large excess of ferricyanide must be avoided since the end point cannot then be seen easily.

Reagents required

Standard ceric sulfate, 6 N HCl, 0.5 M $K_3Fe(CN)_6$, 0.5 M $FeCl_3$, 6 N NaOH.

Procedure

Dilute 35 ml. of 0.1 N hydrazine solution to 60 ml. in a 250 ml. conical flask, add 10 ml. of 0.5 M $K_3Fe(CN)_6$ solution, followed by 10 ml. of 6 N NaOH. Shake gently for one-half minute and allow to stand for two minutes. Add 30 ml. of 6 N HCl and titrate with standard 0.1 N ceric sulfate solution until the green color just

disappears and the solution assumes a brown color. Add 2-3 drops of 0.5 M $FeCl_3$ solution just before the end point for a sharper color change.

Sodium-p-toluolsulfonchloramide methods (13)

The use of Chloramine-T, (name given above) is described in reference (13) and involves a potentiometric titration of hydrazine solutions using that reagent. A modification is to substitute Chloramine-T for iodine and proceed as in the direct iodimetric analysis.

Bromine and hypochlorous acid methods (2)

For the sake of completeness, two other methods are mentioned, bromine oxidation and hypochlorous acid oxidation. In the former, excess standard bromine solution is added to a dilute acid solution of hydrazine and the excess treated with KI after two minutes. The iodine is titrated with standard thiosulfate solution. The hypochlorous acid method involves addition of the hydrazine sample to a buffer of mono- and di-sodium phosphate (pH 7) followed by addition of excess standard hypochlorous acid. After five minutes, KI and sulfuric acid are added and the iodine titrated as before with thiosulfate.

C. SUMMARY

1) A survey has been made of methods recorded in the literature for the quantitative determination of hydrazine. The advantages and disadvantages of these various procedures have been considered and the most promising methods subjected to experimental

study.

2) Excellent and reproducible results were obtained using either a) the direct iodine, or b) the direct iodate method with solvent or with indicator.

3) The direct acid titration of free hydrazine with 0.5 N HCl to either the methyl red or methyl orange end point, followed by iodate oxidation, is a useful combination where ammonia and/or other basic constituents are present.

4) The use of micro pipets is recommended for the analysis of concentrated hydrazine solutions.

5) Prompt acidification of hydrazine samples prior to analysis is recommended to avoid carbon dioxide or moisture absorption, or loss of hydrazine by air oxidation.

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PART II. PREPARATION OF ANHYDROUS HYDRAZINE

PART II. PREPARATION OF ANHYDROUS HYDRAZINE

A. INTRODUCTION

The interest in anhydrous hydrazine for possible use as a jet propulsion fuel prompted the author to undertake first, a critical survey of recorded procedures for the dehydration of hydrazine hydrate, and secondly, an experimental study, based on certain theoretical premises, of an improved process for the production of anhydrous hydrazine. Although a considerable number of investigations have dealt with the preparation of anhydrous hydrazine, there seems to be doubt concerning the efficacy of the various recorded procedures. In many instances a method recommended by one investigator has not been found suitable by another.

The starting material used by previous investigators has been (in most instances) hydrazine hydrate, ranging in composition from 85-100% $N_2H_4.H_2O$. A variety of dehydrating agents such as barium oxide, sodium hydroxide, potassium hydroxide, and calcium oxide has been used in conjunction with procedures of varying complexity. Long refluxing with the dehydrating agent has usually been recommended, followed by repeated distillation either in vacuum or in an inert atmosphere. These steps have occasionally been followed by fractionally freezing to produce anhydrous hydrazine, usually in poor yield.

B. HISTORICAL

Dehydration of hydrazine hydrate with barium oxide and with barium hydroxide

Barium oxide was first used (1890) by Curtius and Schultz (1) in an unsuccessful attempt to prepare anhydrous hydrazine from the hydrate. DeBruyn (2) later succeeded by refluxing the hydrate with excess barium oxide at 110-120° C for several hours, followed by distillation at 100-150 mm. To distil over the last quantities of hydrazine it was necessary to reduce the pressure to 40-50 mm. and increase the temperature. The distillate, which still contained 3-4% water, was redistilled from half its weight of barium oxide in an atmosphere of hydrogen at a pressure of 150-200 mm. Ebler and Krause (3) obtained 93% hydrazine after refluxing the hydrate for 12 hours with twice its weight of barium oxide and subsequent vacuum distillation. Repetition of this treatment, followed by fractional freezing, increased the concentration to 99.7% hydrazine.

In 1911 Hale and Shetterly (4) investigated several methods for the preparation of anhydrous hydrazine. The hydrate was refluxed with excess barium oxide in an all-glass apparatus for one-half to one hour at the boiling point (ca 114°C) using a Vigreux column as a reflux condenser. Thereafter, the pressure was reduced to 20-300 mm. and the distillate collected in a current of hydrogen. In a typical experiment, 150 ml. of hydrazine hydrate and 415 g. of crushed barium oxide yielded 92 g. of 99.83% hydrazine. Welsh (5) modified this procedure to the extent of using a water-cooled Vigreux column as a more efficient condenser during the reflux period. Partially dehydrated hydrazine hydrate was boiled for three hours with a 50% excess of barium oxide and thereafter distilled in an atmosphere of hydrogen to yield a distillate containing 99.7% N_2H_4. This method has been used by other investigators

6,7) who report preparation of material containing 99.6% N_2H_4 (7); no data of the yield is given. More recently Giguere and Rundle (8) prepared 99.4% N_2H_4 by repeated refluxing and distillation from barium oxide followed by two fractional freezing steps.

Hale and Shetterly (4) investigated the effectiveness of barium hydroxide as a dehydrating agent. One distillation increased the concentration from 64% N_2H_4 (amount present in $N_2H_4.H_2O$) to 78%; redistillation of this product gave an additional increase up to 88%. Distillation of a mixture consisting of 91.5 g. of 82.5% N_2H_4 and 400 g. $Ba(OH)_2$ gave a product containing 93.1% N_2H_4. Redistillation of this material with fresh barium hydroxide yielded two fractions, the most concentrated containing 96% N_2H_4.

Dehydration of hydrazine hydrate with sodium hydroxide

Raschig (9) claims to have prepared anhydrous hydrazine in substantially quantitative yield by the following procedure: equal quantities of sodium hydroxide and hydrazine hydrate were heated to 113° (approximately the boiling point of N_2H_4). The temperature was slowly raised to 150° and the vapor condensed, taking precautions that it did not contact organic matter. From 100 g. of $N_2H_4.H_2O$, he obtained 60 g. of distillate; no analysis of the product is given.

Raschig's method was studied in more detail by Hale and Shetterly (4). After heating 250 g. of hydrazine hydrate with an equal weight of sodium hydroxide at the boiling point for two hours, the mixture was distilled and four fractions collected. The fractions weighed 50,54, 55 and 10 g., and contained 98.6, 97.5, 95.0

and 87.0% N_2H_4, respectively. In a similar experiment using fused sodium hydroxide, three fractions were collected weighing 25, 23, and 21 g. and containing 99.3, 98.1 and 98.1% N_2H_4, respectively.

After partially dehydrating the hydrate by sodium hydroxide (Raschig's method), Welsh and Broderson (10) found it necessary to use barium oxide in order to eliminate the last traces of water. Friedrichs (11) distilled hydrazine from sodium hydroxide after refluxing the mixture for several hours, then redistilled twice from BaO*, and finally resorted to fractional freezing to achieve 99.9% N_2H_4. No data concerning the yield are given. Gilbert (12) prepared 99-100% N_2H_4 by dehydrating the hydrate with sodium hydroxide in an all-glass apparatus. The product was subjected to fractional freezing to yield 99.90% N_2H_4. Kahovec and Kohlrausch (13) also prepared hydrazine using sodium hydroxide and hydrazine hydrate; no analyses are given, but the boiling range, 114.9-115.7°C, is somewhat higher than the accepted value for anhydrous hydrazine, 113.5° C (14).

Dehydration of hydrazine hydrate with potassium hydroxide

Wenner and Beckman (15) prepared anhydrous hydrazine from hydrazine hydrate and fused potassium hydroxide by the following method (which, they state, is superior to the barium oxide procedure): the hydrate was refluxed for three hours with fused potassium hydroxide in an atmosphere of hydrogen. Hydrazine was then

*Redistillation from barium oxide was accomplished in an allglass apparatus. The hydrazine was progressively distilled by cooling the receiver bulb with dry ice-alcohol and heating the other. When one-half the hydrazine had distilled over, the bulb containing the residue was sealed off. Two of these sealed-off flasks exploded subsequently after a period of exposure to ordinary daylight. Analysis of gas in an unexploded bulb indicated the presence of hydrogen.

distilled in a stream of hydrogen at pressures from 30-100 mm. repetition of this distillation (three times) gave 98.9% N_2H_4. Semesheen (16) used this method and obtained a product, boiling at 113.4°C (761.5 mm.). This figure compares well with the accepted value of 113.5°C (14). Bamford (17) reported the preparation of anhydrous hydrazine by repeated refluxing of hydrazine hydrate with potassium hydroxide and vacuum distillation. Bushnell, Hughes, and Gilbert (18) prepared anhydrous hydrazine using both barium oxide and potassium hydroxide as dehydrating agents; they state that barium oxide is the more efficient dehydrating agent, although a greater loss of material is entailed in its use.

Miscellaneous methods

An interesting method, historically, is the reaction of hydrazine hydrochloride with sodium methylate in anhydrous methanol (2). After filtration of the precipitated sodium chloride, the hydrazine and methanol were separated by fractional distillation. The ammonolysis of hydrazine sulfate in liquid ammonia (19) is said to give substantially anhydrous hydrazine. Since ammonium sulfate is insoluble in liquid ammonia it can be separated easily from the liquid phase consisting of ammonia and hydrazine. Simple evaporation of ammonia leaves a residue of hydrazine. Pleskow (20) fractionated the ammonia-hydrazine extract over barium oxide under reduced pressure and then vacuum distilled the hydrazine.

Stähler (21) attempted to use calcium oxide as a dehydrating agent. Two-hundred grams of the hydrate was heated to 120°C with 700 g. of calcium oxide. Even after raising the temperature to

145-150°C, little hydrazine was obtained. Distillation proceeded gradually, but decomposition also occured, since the product contained ammonia. However, Barrick (22) prepared anhydrous hydrazine by the method of Hale and Shetterly (4) with final drying over freshly prepared calcium oxide and high vacuum distillation.

Dschawachow (23) investigated the equilibrium for the system: hydrazine-boric acid. Upon heating to 250-260°C, $(N_2H_4)_2(H_2B_4O_7)_3$ decomposes into $(N_2H_4)_2(B_2O_3)_6$, the latter dissociating into B_2O_3 and N_2H_4 above 260°C. He stated that this procedure could be used to prepare anhydrous hydrazine. Stolle' and Hofmann (24) claimed that hydrazinocarbonic acid or its hydrazine salt could be heated with barium oxide or calcium oxide to yield hydrazine. An attempt to carry out this experiment using a 100 g. quantity resulted in a violent explosion.

Stolle' (25) dehydrated hydrazine solutions by the addition of sodium amide in molar proportions to the water present, followed by distillation. An excess of the amide is to be avoided, since the explosive material, sodium hydrazide, is formed by reaction of hydrazine with sodium amide. Schlenk and Weichselfelder (26) removed traces of water still present in hydrazine dehydrated by the Raschig procedure (9) by the addition of sodium metal. The hydrazine was removed slowly by vacuum distillation. The residue, containing some sodium hydrazide, exploded violently on contact with air or moisture.

C. DISCUSSION OF THE LITERATURE

It is obvious from the foregoing literature survey that some

confusion exists concerning the best method of preparing anhydrous hydrazine. However, there are some salient features which may be discussed under the following headings:

a) Removal of water from hydrazine hydrate by chemical combination, e.g., with barium oxide or calcium oxide.

b) Reduction of the vapor pressure of water using materials which form hydrates of low vapor pressure, e.g., sodium hydroxide, potassium hydroxide, and barium hydroxide.

c) Time of reflux before distillation of hydrazine.

d) Distillation in an inert atmosphere and/or at reduced pressure.

e) Repetition of the above steps.

f) Fractional freezing.

Procedure (a) involves the difficulty of mixing a liquid with more than its weight of solid and subsequent distillation from this heterogeneous mass. Poor heat transfer and mechanical entrapment are obvious disadvantages of this procedure, and could account for the reported loss of material (18). The long period of refluxing undoubtedly serves to establish equilibrium in (a) where an excess of solid reagent is used. Barium hydroxide forms solid hydrates and its use is therefore encumbered by the disadvantages cited for procedures given under (a). In addition, these hydrates possess high vapor pressures even at ordinary temperature ranges, and for that reason barium hydroxide cannot be considered an effective dehydrating agent. However, in the case of sodium hydroxide, the reason for long refluxing is a little more obscure, since (within a great range of concentration) sodium hydroxide, hydrazine and

water form a completely liquid system. Operation (d) assumes importance because of the ease of oxidation of hydrazine and its inherent instability, thermodynamically, toward decomposition into its elements. (Bamford (17) reported explosions produced by sparking hydrazine vapor at 100°C). The necessity for (e,f) obviously results from the inefficiency of the previous steps.

D. THEORETICAL

After a careful study of the literature, it was decided to investigate more fully the use of sodium hydroxide for the dehydration of hydrazine hydrate. Two obvious advantages of its successful use would be: a) its low cost relative to the other dehydrating agents, and b) the ease of distillation from a completely liquid system. The Na^+ ion is smaller than the K^+ ion, which would lead one to expect that a hydrate of sodium hydroxide should have a lower vapor pressure at a given temperature than the corresponding hydrate of potassium hydroxide. This is equivalent to stating that sodium hydroxide might be expected to be a better dehydrating agent than potassium hydroxide, both on a weight and molar basis. This prediction is verified by data (27) appearing in Table 1.

At the melting point of $NaOH.H_2O$ (64.3°C) the vapor pressure is 0.3 mm., while that of hydrazine is 108 mm. (28). Assuming that equilibrium would favor complete conversion to $NaOH.H_2O$, it should be possible to add sodium hydroxide (in molar proportions to the water present) to a hydrazine-water solution and distill substantially anhydrous hydrazine from a system which is completely liquid above 64.3°C. Of course, the freezing point of the monohydrate would be depressed somewhat, due to solubility of hydrazine in this

phase. Reference is made to the fact that the addition of sodium hydroxide up to the eutectic composition (1.33 $NaOH:1H_2O$) m.p., 61.5°C, produces an additional vapor pressure lowering (see Table 1).

The following equilibrium reaction

$$NaOH(s) + N_2H_4.H_2O(liq.) \rightleftharpoons NaOH.H_2O(liq.) + N_2H_4(liq.)$$

can be assumed to favor the formation of the products on the right. Sufficient free energy data are not available to allow estimation of the equilibrium constant. However, the large differences in heats of hydration,

$$N_2H_4(liq.) + H_2O(liq.) \longrightarrow N_2H_4.H_2O(liq.)$$

$$\Delta H_{298}^{\circ} = -1.80 \text{ Kcal (18)}$$

$$NaOH(s) + H_2O(liq.) \longrightarrow NaOH.H_2O(s)$$

$$\Delta H_{291}^{\circ} = -5.01 \text{ Kcal (29)}$$

indicate that this is a fair assumption.

On this basis, then, proper adjustment of the $NaOH:H_2O$ ratio should make it possible to use technical caustic soda if allowance is made for the water content of the latter. There is no theoretical advantage for using fused sodium hydroxide. Furthermore, equilibrium in this liquid system should be attained rapidly, and thus no advantage would result from long refluxing prior to distillation. It is felt that variations in concentration of hydrazine as effected by methods reported in the older literature were not caused by the dehydrating agent, but by another factor, apparently unrecognized previously, namely, rectification of the vapor after evaporation from the liquid phase.

Theoretically, it seemed highly probable that consideration of the factors outlined above would lead to the development of a suitable method for the preparation of anhydrous hydrazine. An experi-

Table 1

Solubility of the alkali hydroxides and the vapor pressures of their hydrates (27)

Temp., °C	Vapor pressure, mm. Hg	Solid phase	Solubility, g. MOH/100 g. H_2O
20	0.61	$NaOH.H_2O$	109
30	0.91	"	117.5
40	1.2	"	129
50	1.3	"	145
60	1.0	"	174
62.5	0.7	"	190.7
64.0	0.4	"	211
64.3	0.3	$NaOH.H_2O$ m.p.	222.3
64.0	0.16		240*
62.5	0.06		269
61.5	0.035	(Eutectic)	295
80	0.075	NaOH	314
100	0.25	"	338
150	4.4	"	416
30	2.4	$KOH.2H_2O$	126
32.5	2.2	" and $KOH.H_2O$	135
40	3.3	$KOH.H_2O$	
50	5.5	"	140
60	9.1	"	
80	21	"	161
100	40	"	178

*The apparent discontinuity in solubility arises because of the solubility of NaOH in liquid $NaOH.H_2O$.

mental study was therefore undertaken to evaluate the following points:

a) The feasibility of distilling hydrazine from the three component system $NaOH-H_2O-N_2H_4$, using $NaOH:H_2O$ ratios (on a molar basis) of one or greater.

b) Substitution of technical caustic soda for C.P. or fused sodium hydroxide.

c) Distillation at temperatures above the melting point of the $NaOH:H_2O$ eutectic (61.5°C).

d) Distillation, as in (a), using a fractionating column.

E. EXPERIMENTAL

Apparatus

Pyrex-glass apparatus with standard taper connections was used throughout this investigation. The tapers were lubricated by carefully applying silicone grease to the top one-third only. A liter, round-bottom flask, fitted with a 24/40 taper was used as the still pot. It was heated by a glascol heating mantle, the temperature of the latter being controlled by a Variac transformer. A thermocouple well was sealed into the side of the flask and extended nearly to the bottom. To prevent spray from contaminating the distillate, an ordinary condenser (uncooled) was mounted vertically. From the top, connection was made to a water-cooled condenser, and a thermometer was inserted at this junction to indicate the vapor temperature. A fraction cutter was used to collect the distillate, provision being made to evacuate the receivers and to allow sampling without interruption of distillation.

Reduced pressure (ca 90 mm.) was maintained during distillation

with either a water aspirator or a vacuum pump. The latter was actuated by a relay and manometer. Since the aspirator functioned satisfactorily it was used in all but the first two runs. The vacuum was adjusted manually by bleeding air into the system (at the pump) by means of a capillary and stop-cock. A two-liter ballast flask was inserted to cushion sudden pressure changes. The pressure was read using a Germann (30) type barometer.

Procedure

This sequence was followed in all runs: the apparatus was flushed with nitrogen and stoppered. A quantity of analyzed hydrazine hydrate* (ca 85% $N_2H_4.H_2O$) was weighed quickly into the distilling flask. The requisite amount of sodium hydroxide was weighed out as quickly as possible into a tared bottle. After the flask had been inserted into the heating mantle, the sodium hydroxide was added. The flask was then connected to the distillation apparatus and the system evacuated to approximately 90 mm. Since the heat of reaction is sufficient to raise the temperature to about 45°C, the flask must be connected immediately to the distillation apparatus to avoid hydrazine losses. Sufficient heat was then applied externally to begin distillation (61-62°C).

Distillation from a hydrazine solution containing reagent sodium hydroxide and water in equimolar quantities.

Following the procedure outlined above, hydrazine hydrate and reagent sodium hydroxide were mixed and three fractions were distilled from the mixture.

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*Fairmount Chemical Co., Inc., 600 Ferry St., Newark, N. J.

Run 1

Materials used

a) 366 g. $N_2H_4.H_2O$: (85.5% $N_2H_4.H_2O$) — 300 g. N_2H_4, 6.25 moles; 166 g. H_2O, 9.22 "

b) 386 g. NaOH: minimum assay 97%) — 374 g. NaOH, 9.36 "

assuming 1% H_2O — 3.9 g. H_2O, 0.22 "

Total: 6.25 moles N_2H_4 9.44 moles, H_2O, 9.36 moles NaOH.

Ratio: moles NaOH:moles H_2O = 0.99

Operating Data

Pressure, mm., Hg	Pot temp., °C	Vapor temp., °C	
94	63	62	
96	63	63	Fraction (1)
88	63	61	
88	63	61	
88	63	61	
90	73	63	Fraction (2)
88	75	64	
88	79	65	
88	84	66	Fraction (3)
88	89	67	

Fraction (1) 106.6 g., 98.4% N_2H_4.

Fraction (2) 61.4 g., 97.9% N_2H_4.

Fraction (3) 27.3 g., 90.4% N_2H_4.

Total recovery: 94.8% of theoretical.

The hydrazine analyses were made by the iodate method of Smith and Wilcox (31) using a weight buret or micro pipet. The hydrazine was transferred, immediately after weighing, into an excess of hydrochloric acid to prevent air oxidation. (See Part I, page 4).

After about 170 g. of distillate had been collected, the temperature of the still rose rapidly. The last fraction, collected during this temperature interval, was of lower hydrazine content. This observation was used in later runs to determine at which

temperature to cut the last fraction which was invariably of lower hydrazine content.

Distillation from a hydrazine solution containing reagent sodium hydroxide and water in a molar ratio of 1.2:1.0

The following experiment was performed to evaluate the effect of increasing the $NaOH:H_2O$ mole ratio to a value larger than one. The materials and apparatus were the same as in Run 1, distillation occuring at pressures from 90-105 mm.

Run 2

a) 366 g. $N_2H_4.H_2O$:

Materials used

200 g. N_2H_4, 6.25 moles

166 g. H_2O, 9.22 moles

b) 471 g. NaOH:

457 g. NaOH, 11.43 moles

(Assuming 1% H_2O) 4.7 g. H_2O, 0.26 moles

Total: 6.25 moles N_2H_4, 11.43 moles NaOH, 9.48 moles H_2O.

Ratio: moles NaOH:moles H_2O = 1.21.

Operating Data

Fraction (1) 107.4 g., 98.4% N_2H_4. Pot temperature 62°C.

Fraction (2) 81.2 g., 97.3% N_2H_4. Pot temperatures 62-66°C.

Fraction (3) 6.7 g., 93.7% N_2H_4. Pot temperatures 66-87°C.

Total recovery: 95.4% of theoretical.

Comparison of Run 1 with Run 2 shows that there is an advantage to increasing the mole ratio $NaOH:H_2O$ from 0.99 to 1.21. As indicated in Table 1, the ratio of $NaOH:H_2O$ at the $NaOH.H_2O$-NaOH eutectic is 1.33.

The melting points of $NaOH.H_2O$ and N_2H_4 are 64.3 and 1.8°C, respectively. It was thought that solid $NaOH.H_2O$ might precipitate on cooling a solution as prepared in Run 1, leaving concentrated N_2H_4 in solution. A composition corresponding to that used in Run 1 was heated until complete solution occured. Examination revealed the presence of two liquid phases, the upper phase being about one-fifth the volume of the lower phase. Upon cooling to approximately 65°C, the lower phase began to crystallize. Further cooling resulted in formation of a semi-solid mass. The ternary system $NaOH$-N_2H_4-H_2O was subsequently investigated in detail at various temperatures. The data appear in Part III of this thesis.

Distillation from a hydrazine solution containing technical caustic soda and water in equimolar quantities

Technical NaOH (Merck, U.S.P., approximately 95%) was used in all subsequent experiments.

Run 3

Materials used

a) 372 g. $N_2H_4.H_2O$: (Assay 84.3% $N_2H_4.H_2O$) — 301 g. N_2H_4, 6.26 moles; 171 g. H_2O, 9.50 "

b) 450 g. technical NaOH: (about 95%) — 428 g. NaOH, 10.68 "

Assuming 5% H_2O — 22.5 g. H_2O, 1.25 "

Total: 6.26 moles N_2H_4, 10.68 moles NaOH, 10.75 moles H_2O.

Ratio: moles NaOH: moles H_2O = 1.0.

Operating Data

Fraction (1) 98.0 g., 98.0% N_2H_4. Pot temperature 63-65°C, pressure 98-105 mm.

Fraction (2) 69.7 g., 99.1% N_2H_4. Pot temperature 65-75°C, pressure 109-110 mm.

Fraction (3) 45.3 g., 78.8% N_2H_4. Pot temperature 75-97°C, pressure reduced to 19 mm.

Total recovery: 100% of theoretical

Fraction (1) was collected at the rate of 3 g./min., and fraction (3) was also collected rapidly. Fraction (2) was collected slowly.

Run 4 was a duplicate of Run 3 except that distillation was allowed to proceed very slowly, 1½ hours being required to collect fraction (1).

Run 4

Operating Data

Fraction (1) 101.8 g., 99.0% N_2H_4. Pot temperatures 60-64°C, pressures 91-105 mm.

Fraction (2) 68.6 g., 98.8% N_2H_4. Pot temperatures 64-69°C, pressures 102-105 mm.

Fraction (3) 32.1 g., 91.7% N_2H_4. Pot temperatures 69-94°C, pressures 98-102 mm.

Total recovery: 98.5% of theoretical.

Distillation using a fractionating column.

A fractionating column was constructed of 12 mm. (i.d.) pyrex tubing. At the base, it was drawn down to form a drip-tip with appropriate vapor holes. A short length of 25 mm. tubing was sealed to the column above the drip-tip and a 24/40 taper was sealed to the other end of this large tubing. The column was packed to a

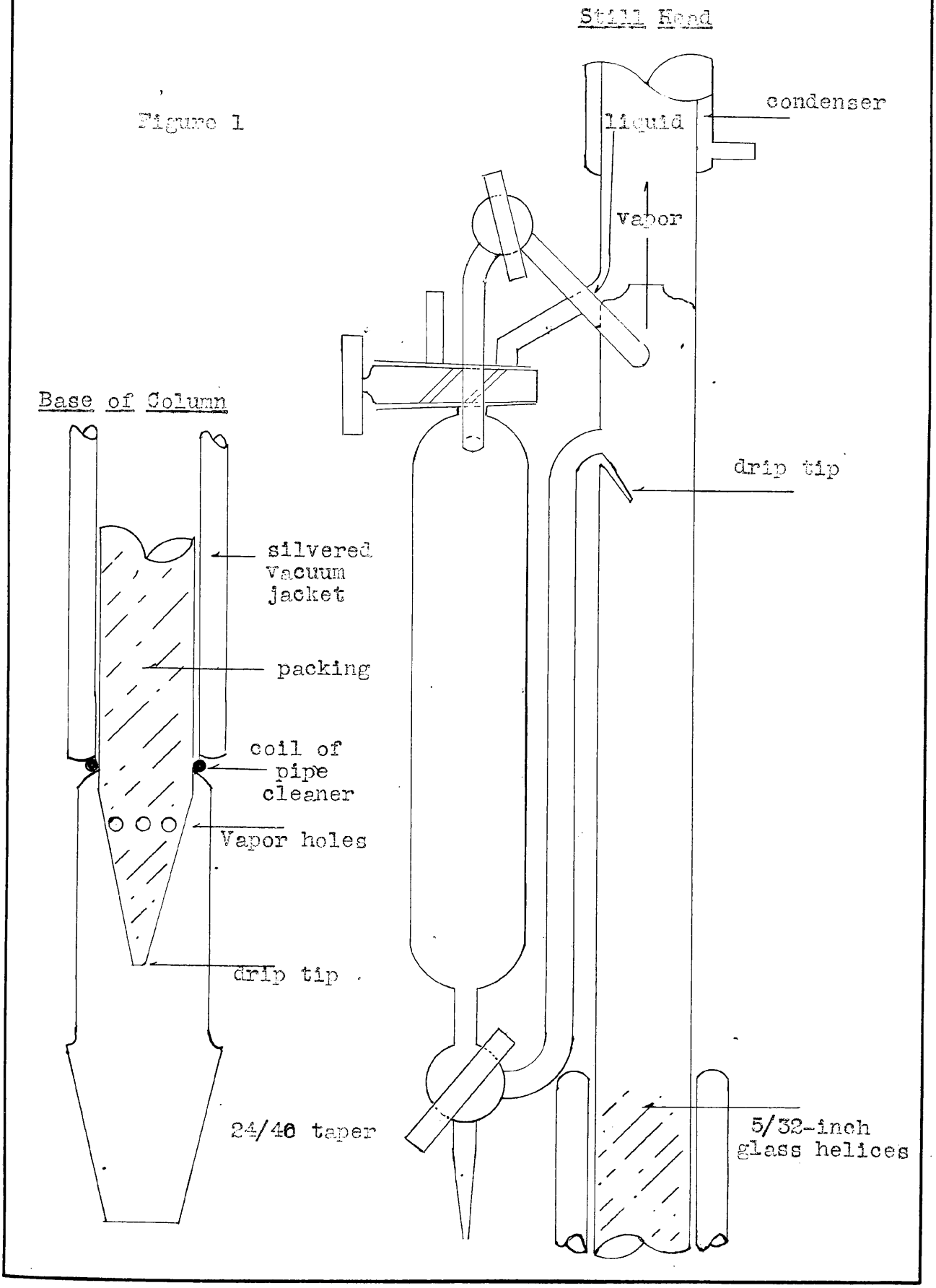
height of 92 cm. with 5/32-inch glass helices. After packing, the column was placed within a silvered vacuum jacket, 92 cm. in length. The jacket rested on the 25 mm. extension at the base of the column, direct glass-glass contact being avoided by the use of a coil of pipe cleaner as a cushion.

The column was operated at total reflux, all the condensate being returned to the column. A take-off head, illustrated in Figure 1, was constructed so that all the condensate was required to pass through a 35 ml. reservoir before being returned to the top of the packing. The liquid passed in the top of the reservoir and was returned to the column by a constant-level syphon operating from the bottom of the reservoir. In this manner the column was operated at the maximum fractionating efficiency. Distillation was allowed to proceed until the column had been operating (with the reservoir full) for approximately one hour. By a system of stop cocks, the reservoir was emptied without interruption of distillation. Subsequent samples were collected at approximately one-half hour intervals.

Run 5

Materials used: see Run 3.

Figure 1


Still Head
condenser
liquid
vapor
drip tip
Base of Column
silvered vacuum jacket
packing
coil of pipe cleaner
Vapor holes
drip tip
24/40 taper
5/32-inch glass helices

Operating Data

Pressure, mm. Hg	Pot Temp., °C	Time	Remarks
100	61	0 min	
100	61	10 "	
92	62	25 "	Two liquid phases;
93	62	35 "	
94	61	1 hr,20 "	Fractions combined to
94	61	1 hr,55 "	give fraction (1),
87	64	2 hr,30 "	100.1 g.
84	65	2 hr,45 "	Two liquid phases, upper
86	64	3 hr,10 "	phase slightly yellow.
84	64	3 hr,30 "	Fractions combined to
80	65	3 hr,50 "	give fraction (2), 57.7g.
78	72	4 hr,10 "	One phase, pot tempera-
78	90	4 hr,25 "	ture increased rapidly.
78	95	4 hr,35 "	Fractions combined for
			fraction (3), 32.4 g.

Fraction (1) 100.1 g., 99.9% N_2H_4.

Fraction (2) 57.7 g., 99.9% N_2H_4.

Fraction (3) 32.4 g., 99.7% N_2H_4.

Total recovery: 94.6% of theoretical.

On standing (closed) overnight, a few ml. of liquid drained from the column, and the packing was still visibly wet. The holdup in the column undoubtedly amounted to several grams. Of course, this amount would be of less significance if larger quantities were distilled, or several runs were made in succession. It should be noted that the poorest fraction contained 99.7% N_2H_4, whereas, without fractionation, the concentration of the poorest fraction varied from 78-93%. Furthermore, the freezing point of fraction (3) was found to be + 1.7°C (corrected) which agrees with the accepted value for anhydrous hydrazine (12,16).

An observation port, located at the junction of the two liquid phases, made it possible to note the disappearance of the upper phase as distillation progressed. After approximately 80% of the

amount of hydrazine originally present had distilled over, there remained only one phase. Thereafter, the temperature of the pot rose rapidly and the distillation rate decreased markedly.

The hydrazine-water system has a maximum boiling point at a composition corresponding to 58.5% hydrazine and 41.5% water (33). The boiling point of hydrazine hydrate (64% N_2H_4, 36% H_2O) is 118.5°C (32) while that of hydrazine is 113.5°C. Fractional distillation of a solution containing more than 58.5% hydrazine will result in the removal of hydrazine-rich material until the mixture of maximum boiling composition referred to has been reached. Scott (33) has shown that in the vapor state, hydrazine hydrate is largely dissociated into N_2H_4(g) and H_2O (g) at 99°C and 366 mm., the dissociation being essentially complete at 138°C and 744 mm. Distillation at lower pressures would favor dissociation of any hydrazine hydrate molecules in the vapor state, if indeed they exist.

Rectification of the vapor from a hydrazine-water-sodium hydroxide composition is extremely efficient, especially when a column is operated on total reflux. As demonstrated in the distillation without fractionation, the initial distillate contains about 99% hydrazine. If this material were fractionated, the vapor in equilibrium with liquid of such composition would be still richer in hydrazine. In a packed fractionating column, where all the condensate is returned to the top of the packing, the liquid at the top approaches pure hydrazine while the hydrazine-poorer material washes to the bottom of the column. However, under equilibrium conditions, the water content of the material on the first theoretical plate above the still cannot exceed the low value fixed by the

vapor pressure of water over the $NaOH-H_2O-N_2H_4$ solution in the still. As a consequence, the column is continually supplied with high concentration hydrazine, and if a reservoir is placed so as to allow all the distillate to pass through, but retaining a part, its contents will rapidly approach 100% hydrazine.

F. SUMMARY

1. Anhydrous hydrazine has been obtained in essentially quantitative yield by fractional distillation (at ca 80-100 mm.) from a hydrazine solution containing sodium hydroxide and water in equimolar quantities. The distillation was carried out at or above the melting point of sodium hydroxide monohydrate.

2. At temperatures higher than approximately 60°C, the system is completely liquid, allowing efficient heat transfer and rapid achievement of equilibrium.

3. Within certain concentration ranges, this liquid system consists of two liquid phases.

4. Distillation without fractionation, i.e., simple distillation, makes it possible to remove approximately 80% of the hydrazine present in 85% hydrazine hydrate as a product of 97-99% purity, provided equimolar amounts of sodium hydroxide and water are present in the mixture. The remaining 20% of hydrazine may be obtained as a product containing up to 90% N_2H_4.

5. Distillation as in (4) but using a mole ratio $NaOH:H_2O$ of 1.21 increases somewhat the concentration of hydrazine in the distillate, particularly of the last 20%.

6. Technical caustic soda was substituted successfully for fused or reagent sodium hydroxide, allowance being made for the water content of the technical material.

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PART III. PHASE EQUILIBRIA IN TERNARY SYSTEMS CONTAINING HYDRAZINE

PART III. PHASE EQUILIBRIA IN TERNARY SYSTEMS CONTAINING HYDRAZINE

A. INTRODUCTION

The preparation of anhydrous hydrazine by the sodium hydroxide procedure (see Part II of this thesis) involves the distillation of hydrazine from a solution which contains water and sodium hydroxide in equimolar quantities. During the early stages of this investigation it was observed that 85% hydrazine hydrate and sodium hydroxide form two liquid phases when heated to approximately 60°C. Since this phenomenon had not been reported previously, it was decided to investigate quantitatively the hydrazine-water-sodium hydroxide system as a function of temperature. In addition, hydrazine, water and a) potassium hydroxide and b) potassium carbonate were studied quantitatively at a single temperature. A qualitative study using still other compounds was made in an unsuccessful attempt to find another ternary system exhibiting two liquid phases in the temperature range from 25-100°C.

It was not entirely unexpected that hydrazine (H_2NNH_2) should be salted out of water by the addition of sodium hydroxide, since the same phenomenon is exhibited by ethylene diamine ($H_2NCH_2CH_2NH_2$) (1). Above atmospheric pressure, ammonia, water and sodium hydroxide also form two liquid phases (2).

B. HISTORICAL

The representation of a three component system using triangular coordinates was first proposed by Gibbs (3). A brief discussion of the salient features of this method of depicting phase relation-

ships in such systems is appropriate at this point. It is a characteristic of the equilateral triangle that the sum of perpendiculars from any point within the triangle to the three sides is equal to the height. It is convenient to set the sum of the weights (or molar amounts) of the three components equal to one-hundred and divide the height of the triangle into one-hundred parts. Lines are drawn parallel to the three sides and any composition can be located by measuring the percentage of each component from the base opposite the corner representing the pure component. This is demonstrated in Figure 1, where the point P represents a mixture containing 70% C, 15% A, and 15% B.

More complex equilibria, where several phases are present, can be treated according to the method of Tammann (4). For purposes of illustration, the case of three phases coexisting in equilibrium may be treated, using Figure 1. If N_1, N_2, and N_3 grams of the three phases of compositions V_1, V_2, and V_3, respectively, are mixed, the over-all composition corresponds to V_4. This point is the center of gravity of the triangle V_1 V_2 V_3. The calculation is made as follows: the line connecting V_1 and V_2 is regarded as a lever, with the masses N_1 and N_2 on the appropriate ends. In order that the lever may balance there must be a fulcrum F such that $N_2 \times \overline{V_2F} = N_1 \times \overline{V_1F}$. The composition F is now connected by a line through V_3. A similar situation exists so that $(N_1 + N_2) \times \overline{FV_4} = N_3 \times \overline{V_3V_4}$. The following proportion also holds:

$$\overline{FV_4}:\overline{FV_3} = \frac{N_3}{N_1 + N_2 + N_3}$$

An additional feature of the equilateral triangle is demonstrated by the line $\overline{OB}$ in Figure 1. All compositions along this

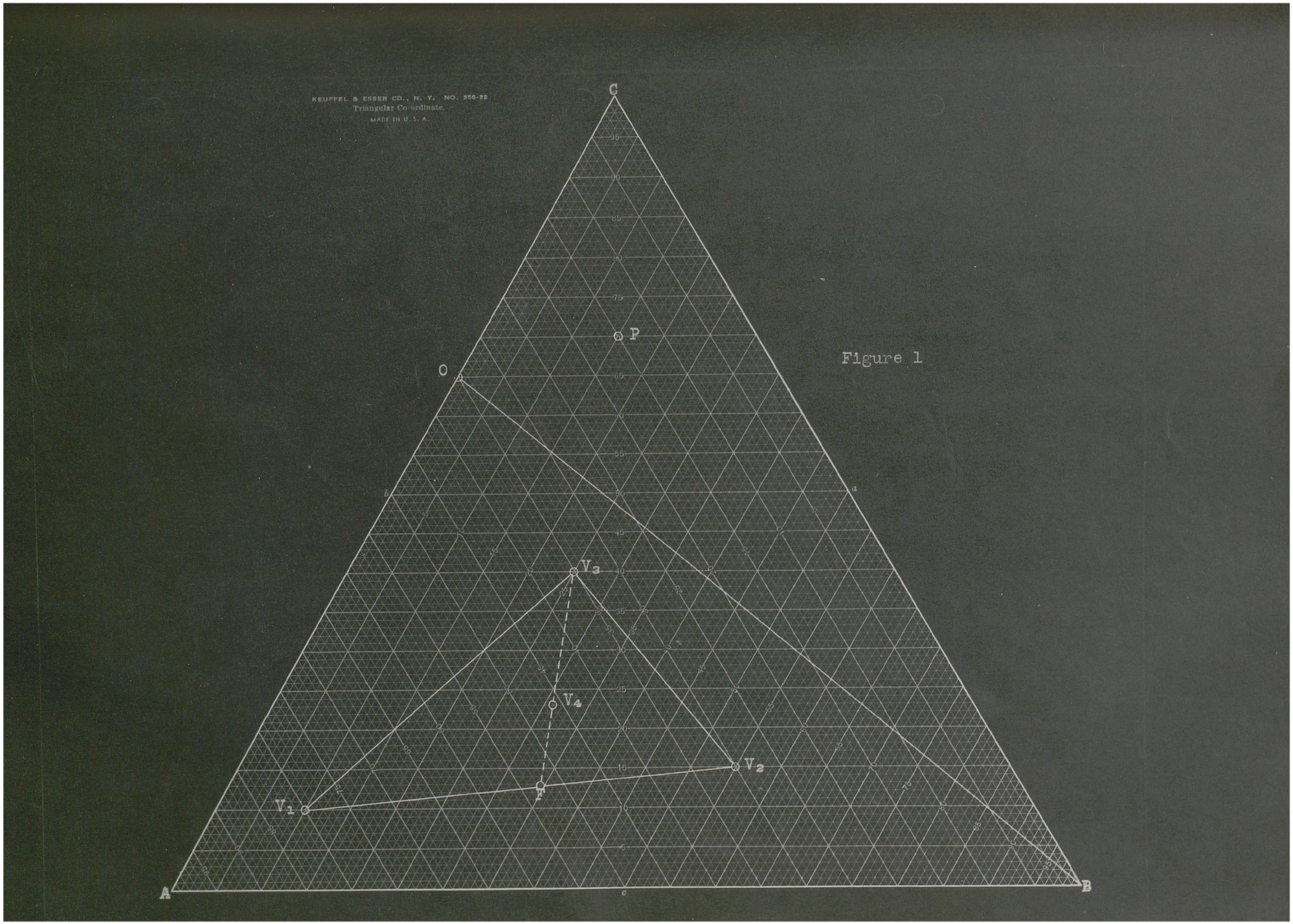

KEUFFEL & ESSER CO., N. Y. NO. 358-32
Triangular Co-ordinate
MADE IN U.S.A.
C
A
B
P
O
V1
V2
V3
V4
a
b
c

Figure 1

line represent a fixed ratio of A:C with varying amounts of component B.

If a solid is precipitated from a three component liquid system, it is often difficult to free the precipitate of adhering mother liquor, thus making accurate analysis impossible. An elegant way of overcoming this difficulty was proposed by Schreinemakers (5). This method is depicted in Figure 2. The precipitate, with adhering mother liquor, is analyzed to give a composition corresponding to the point D. The liquid with which it is in equilibrium is also analyzed to give the point E. A line is drawn between the points E and D and extrapolated until it intersects the side of the triangle at F to give the composition of the solid phase. According to the lever rule, the wet solid of composition D is composed of liquid E and solid F of proportions $\overline{DF}$ and $\overline{DE}$, respectively. Any other pair of analyses, e.g., H and G, would extrapolate to the same point, provided the same solid phase (in the example, 50% A, 50% B) is precipitated. Of course, if the precipitate is a compound containing all three components, then two pairs of analyses would be necessary and the extrapolated lines would intersect at some point in the interior of the triangle.

The system hydrazine-water-sodium hydroxide belongs to a class in which the two liquid components are miscible throughout a wide range of concentrations, while the solid component is only very slightly soluble in one liquid but very soluble in the other. Water and hydrazine are completely miscible in all proportions, while sodium hydroxide is insoluble in anhydrous hydrazine.

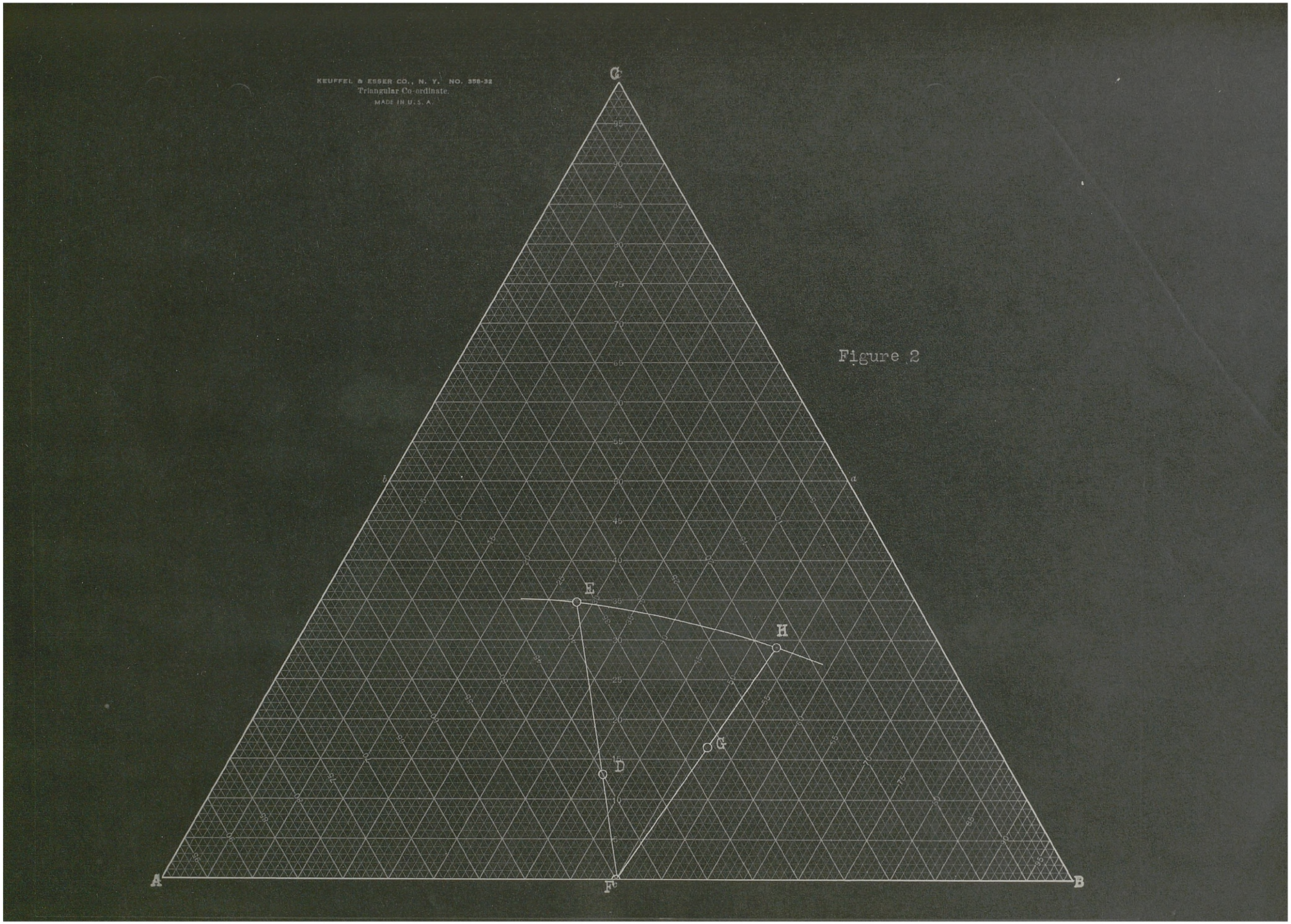

KEUFFEL & ESSER CO., N. Y. NO. 358-32
Triangular Co-ordinate.
MADE IN U. S. A.
C
A
B
E
H
G
D
F
a
b

Figure 2

C. EXPERIMENTAL

Apparatus

The heating bath consisted of a pyrex jar (21x26 cm.) around which was wound a nichrome ribbon of 10 ohms resistance. This resistance winding was insulated with asbestos and was connected in series with a variable resistance. Heating by this coil was continuous and was adjusted so that the desired bath temperature could not be reached using this heater alone. A Sargent Zero-Current Relay unit with thermostat and heater was used in intermittent operation to bring the temperature to the desired point. The variation in bath temperature did not exceed 0.1°C.

Stanolind mineral oil, U.S.P. heavy grade, was used as the bath liquid. Stirring was sufficiently vigorous so that temperature gradations throughout the bath did not exceed 0.1°C. The temperature was read using a Rascher and Betfold thermometer, graduated in 0.1 degree divisions. It was calibrated at the ice-point, the transition point of sodium sulfate decahydrate, and at the boiling point of water. After suitable correction for emergent stem (6) and the barometric pressure, a smooth curve was drawn through the three points and the proper corrections were applied to the apparent temperature readings. The temperatures appearing in the following pages are all corrected values.

The equilibrium studies were made using a closed pyrex cell (18x3.5 cm.) with stirring accomplished by means of a solenoid stirrer patterned after the one used by Booth and Martin (7). The solenoid was wound using 250 feet of 20 gage copper wire (3.5 ohms total) wound around a 3/4 inch hollow spool. Current (from the

110 V. A.C. line) was supplied to this solenoid through two 600 watt cone heaters connected in series. The current was interrupted by a 24 rpm motor* which operated a cam and furnished 48 pulses per minute to the stirrer. The stirrer was made of 3 mm. tubing wound into a spiral in the upper end of which an iron nail, sheathed in glass, had been sealed. This end was drawn up into the field of the solenoid when it was energized. The stirring rate was sufficient to produce the desired mixing of the two liquid phases. More rapid stirring caused foaming of the mixture.

Analytical procedure

Reference was made in Part I to the fact that free hydrazine is oxidized by atmospheric oxygen. Sodium hydroxide catalyzes this oxidation when present in certain concentration ranges. It was consequently necessary to take suitable precautions in sampling the mixtures to prevent contact with the atmosphere during weighing and analysis. Furthermore, crystals usually precipitated from samples on cooling, making it necessary to withdraw samples at the temperature of the bath.

Consideration of the above factors made it necessary that a procedure be used to effect the following:

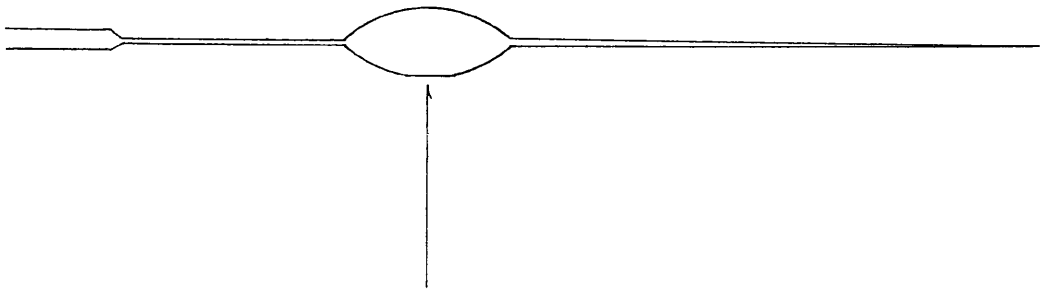
1. Sampling at the bath temperature.
2. Protection of the sample from oxygen and moisture.
3. Sampling of the lower phase without contamination from the upper phase.
4. Prevention of sample loss or change during crystallization on cooling to room temperature.

*Merkel-Korff Gear Company, 213 N. Morgan Street, Chicago, Illinois

The conditions listed above were met by the use of the pipet illustrated in Figure 3. The pipets were made of thin glass, weighed about 0.5 grams each, and had a capacity of about 1 ml. The capillary ends prevented any significant sample change either by oxidation or by absorption of carbon dioxide and water. After cooling to room temperature, the fullpipets were weighed and then crushed beneath the surface of oxygen-free water in a nitrogen atmosphere. The pipets were never filled completely, since it was difficult to crush them (when full) after the sample had solidified. The pipets were heated before being introduced into the equilibrium mixture and were allowed to come to the temperature of the bath before the sample was withdrawn. A 1 ml. hypodermic syringe was used to draw the liquid up into the pipets. When a sample of the lower phase was taken, the plunger of the hypodermic syringe was depressed slowly as the end of the pipet was being lowered through the upper phase, causing a tiny stream of bubbles to leave the capillary tip and preventing any liquid from entering.

The analytical procedure has already been discussed in Part I. Use was made of the combination acid-iodate method proposed by the author. The pipets were crushed beneath 50 ml. of oxygen-free water in a nitrogen atmosphere in 500 ml. Erlenmeyer flasks. The resulting solutions were titrated immediately with standard 0.5 M HCl to the methyl orange end point. This acid titration gave the total base present. The entire sample, or an aliquot, was then titrated with 0.1000 M iodate to give the amount of hydrazine directly. After allowance had been made for the acid equivalent of hydrazine, the percentage of sodium hydroxide was obtained by

Figure 3



Bottom flat to prevent rolling during weighing and crushing operations

difference. The percent of water was obtained as a second difference. Examples of the reproducibility of this method appear in Table 1.

Table 1

Duplicate analyses of samples containing hydrazine, water and sodium hydroxide

Sample	% N_2H_4	%NaOH	%H_2O	Temperature
Upper phase	90.0	2.4	7.6	70.0°C
(45 min. apart)	90.0	2.5	7.5	
lower phase	7.75	65.2	27.0	"
(1 hour apart)	7.75	65.4	26.8	
upper phase	70.5	12.2	17.3	"
(30 min. apart)	70.4	12.0	17.6	
lower phase	23.6	45.8	30.6	"
(30 min. apart)	23.8	45.8	30.4	
upper phase	77.5	9.3	13.2	60.0°C
(different run)	77.4	9.0	13.6	
lower phase	19.0	51.4	29.6	"
(different run)	19.0	51.2	29.8	

Based on the results summarized in Table 1, it can be seen that analytical results are subject to comparitively small errors with maximum deviations of the following order of magnitude: $\pm$ 0.1% for N_2H_4; $\pm$ 0.2% for NaOH; and $\pm$ 0.4% in the water values. The percentage of water is subject to the maximum error since its determination is based on two differences. In the tables that follow, the values for the percentage of water are rounded to the nearest 0.5%.

System, hydrazine-water-sodium hydroxide at 100°C

Using the techniques and apparatus discussed in the previous

sections, the system consisting of reagent sodium hydroxide, anhydrous hydrazine and distilled water was investigated at 100°C. The results of this investigation are summarized in Table 2 and are presented graphically in Figure 4.

Several separate runs were necessary since it was impossible to perform all of the necessary dilutions or additions using a cell of the indicated dimensions. Fresh materials were used at the beginning of each run. However, no decomposition was observed except during one attempt to study mixtures containing only a few percent hydrazine and 70% NaOH. A trial mixture of approximately this composition was made by the addition of anhydrous hydrazine to a saturated solution of sodium hydroxide in water. The mixture darkened quickly and gas evolution was noticed. On the other hand, a mixture consisting of 98% hydrazine and solid sodium hydroxide was stirred for several hours; the liquid phase was found to give identical analyses both before and after treatment.

Table 2

System, hydrazine-water-sodium hydroxide at 100°C

	Phase	%N_2H_4	%NaOH	%H_2O	Remarks
1)	upper	93.7	2.4	5.0	Limiting composition
	lower	5.7	70.3	24.0	of the two liquid phases
2)	lower	6.3	69.7	24.0	Two liquid phases
3)	upper	59.0	19.1	22.0	"
	lower	32.9	37.8	29.5	
4)	upper	87.5	3.0	9.5	"
	lower	9.2	62.9	28.0	
5)	upper	80.6	6.4	13.0	"
	lower	15.5	54.4	30.0	
6)	upper	70.6	11.6	18.0	"
	lower	23.3	46.1	31.0	

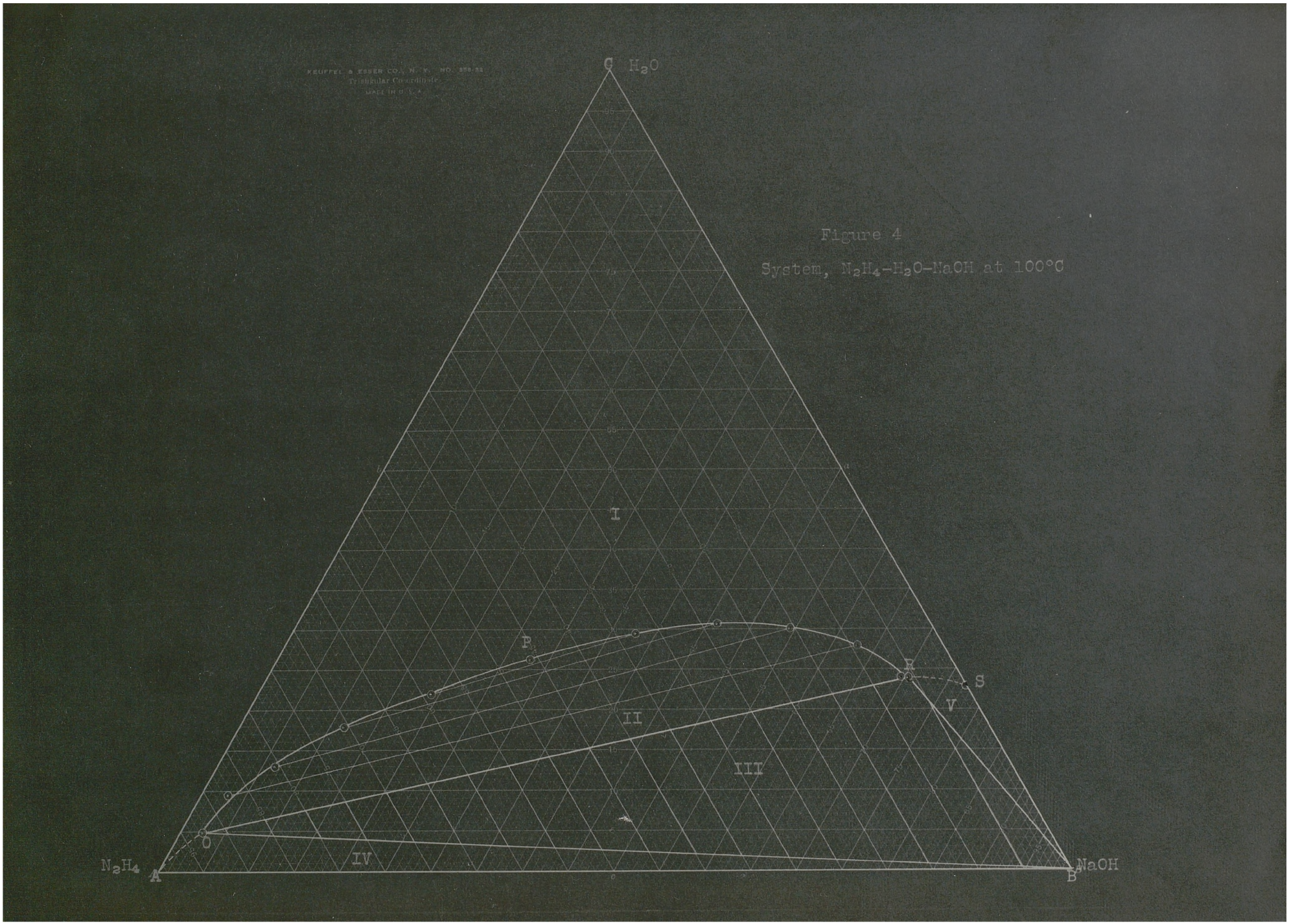


Figure 4

System, N_2H_4–H_2O–NaOH at 100°C

7)	- - -	45.9	27.9	26.0 *Composition of plait point

*The composition of the plait point was determined by the interpolation method given in the International Critical Tables (8).

In Figure 4 the letters have the following significance: region I is the region of complete miscibility, there being only one liquid phase and no solid phase. Region II is bounded by the binodal curve OPR and represents a two liquid phase region in which the compositions of the conjugate liquid phases vary from the limiting values O and R up to the plait point P, where the compositions of the two liquids become identical. Region III (shaded area) is a three phase region, in which the two liquid phases with the compositions represented by the points O and R are in equilibrium with solid sodium hydroxide. The equilibrium amounts of the phases are governed by the lever rules discussed on page 43 in connection with Figure 1. Regions IV and V are two phase regions in which solid sodium hydroxide is in equilibrium with saturated solutions of compositions indicated by the dotted lines AO and RS. The line AO represents the solubility of sodium hydroxide in concentrated hydrazine (above 92.7% N_2H_4), while the line RS depicts the solubility of sodium hydroxide in water containing a few percent of hydrazine. The point S gives the solubility of sodium hydroxide in water at 100°C.

System, hydrazine-water-sodium hydroxide at 90°C

The analytical results obtained for this system appear in Table 3 and are depicted in Figure 5. The designations and relationships in Figure 5 are those previously discussed in connection with Figure 4.

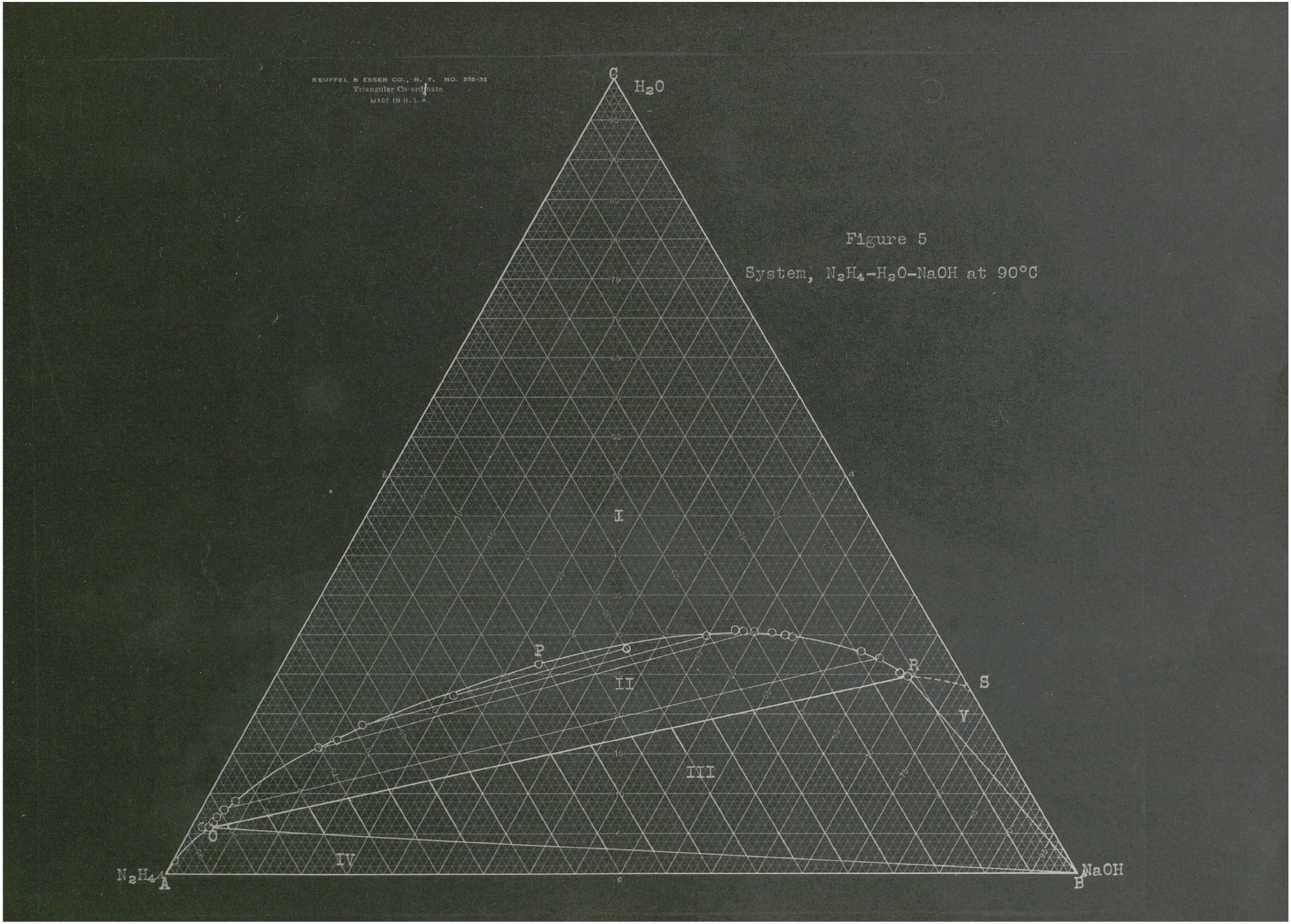


Figure 5

System, N_2H_4-H_2O-NaOH at 90°C

Table 3

System, hydrazine-water-sodium hydroxide at 90°C

	Phase	%N_2H_4	%NaOH	%H_2O	Remarks
1)	liquid	92.9	0.9	6.0	One liquid phase in equilibrium with solid sodium hydroxide
	"	93.0	1.2	6.0	
2)	"	98.1	0.1	2.0	"
3)	upper	57.0	20.8	22.0	Two liquid phases
	lower	35.0	36.9	28.0	
4)	upper	68.9	12.6	18.5	"
	lower	25.3	44.9	30.0	
5)	lower	21.0	48.6	30.5	"
6)	lower	18.0	51.8	30.0	"
7)	lower	15.9	54.2	30.0	"
8)	upper	93.2	2.0	6.0	Limiting composition of the two liquid phases; solid phase present on cooling from 100°C.
	lower	5.9	69.3	25.0	
9)	upper	91.6	2.1	6.5	Two liquid phases
	lower	6.4	68.4	25.0	
10)	upper	90.8	2.3	7.0	"
11)	upper	89.5	2.6	8.0	"
	lower	7.8	65.2	27.0	
12)	upper	87.7	3.4	9.0	"
	lower	9.3	62.8	28.0	
13)	upper	72.6	10.8	16.5	"
	lower	21.9	47.8	30.5	
14)	upper	75.1	9.2	15.5	"
	lower	19.9	49.8	30.5	
15)	lower	16.6	53.4	30.0	"
16)	- - -	45.6	28.2	26.0	Composition of plait point, interpolated

System, hydrazine-water-sodium hydroxide at 70°C

The analytical results for this system are presented in Table 4 and are plotted in Figure 6. The ternary system was first investigated at this temperature. In order to check the analytical and sampling procedures and to determine if equilibrium is reached quickly, duplicate samples were taken for many of the compositions. The phase areas and designations which appear in Figure 6 are similar to those appearing in Figure 4; the discussion is identical.

System, hydrazine-water-sodium hydroxide at 60°C

Examination of the curves presented for the system at 100°, 90°, and 70°C, and of the data for limiting compositions O and R and plait points (Table 6) at these temperatures, reveals only a very slight change in the shape of the binodal curves OPR with temperature. It is interesting, therefore, that the values listed in Table 5 and plotted in Figure 7 show a significant decrease in the extent of the binodal curve at 60°C. Furthermore, a new crystalline phase, $NaOH.H_2O$, m.p., 64.3°C, is the stable solid phase in equilibrium with the liquids O and R, and a second three phase area is noted.

One very important practical reason for undertaking a study of the ternary system, N_2H_4-H_2O-NaOH, was to determine if concentration of hydrazine could be effected economically by bringing about separation of a hydrazine-rich phase. Since 85% $N_2H_4.H_2O$ is a commercially available material, the effect of adding increasing amounts of sodium hydroxide to it may be discussed in terms of the data presented graphically in Figure 7. Actually, a

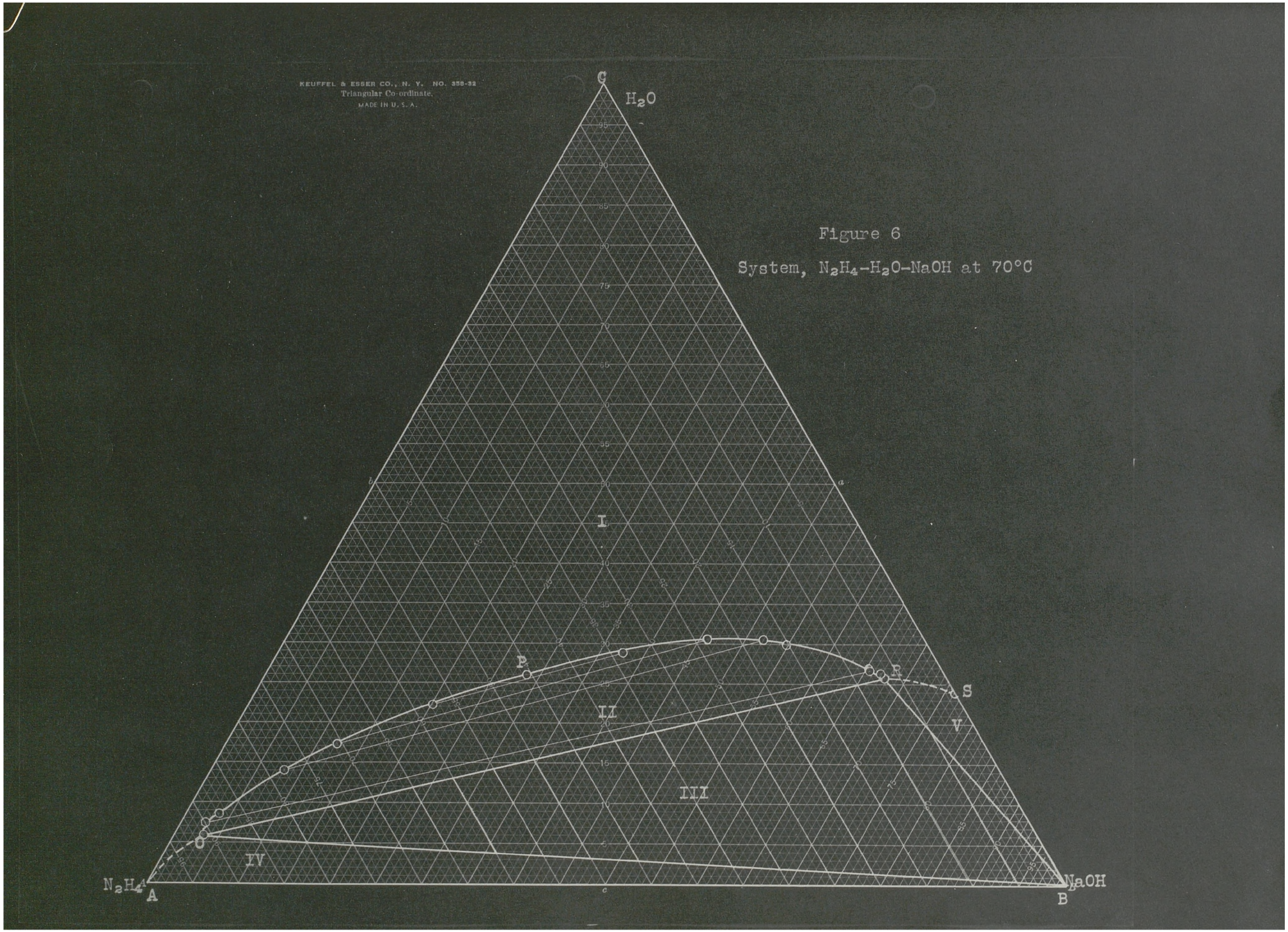


Figure 6

System, N_2H_4-H_2O-NaOH at 70°C

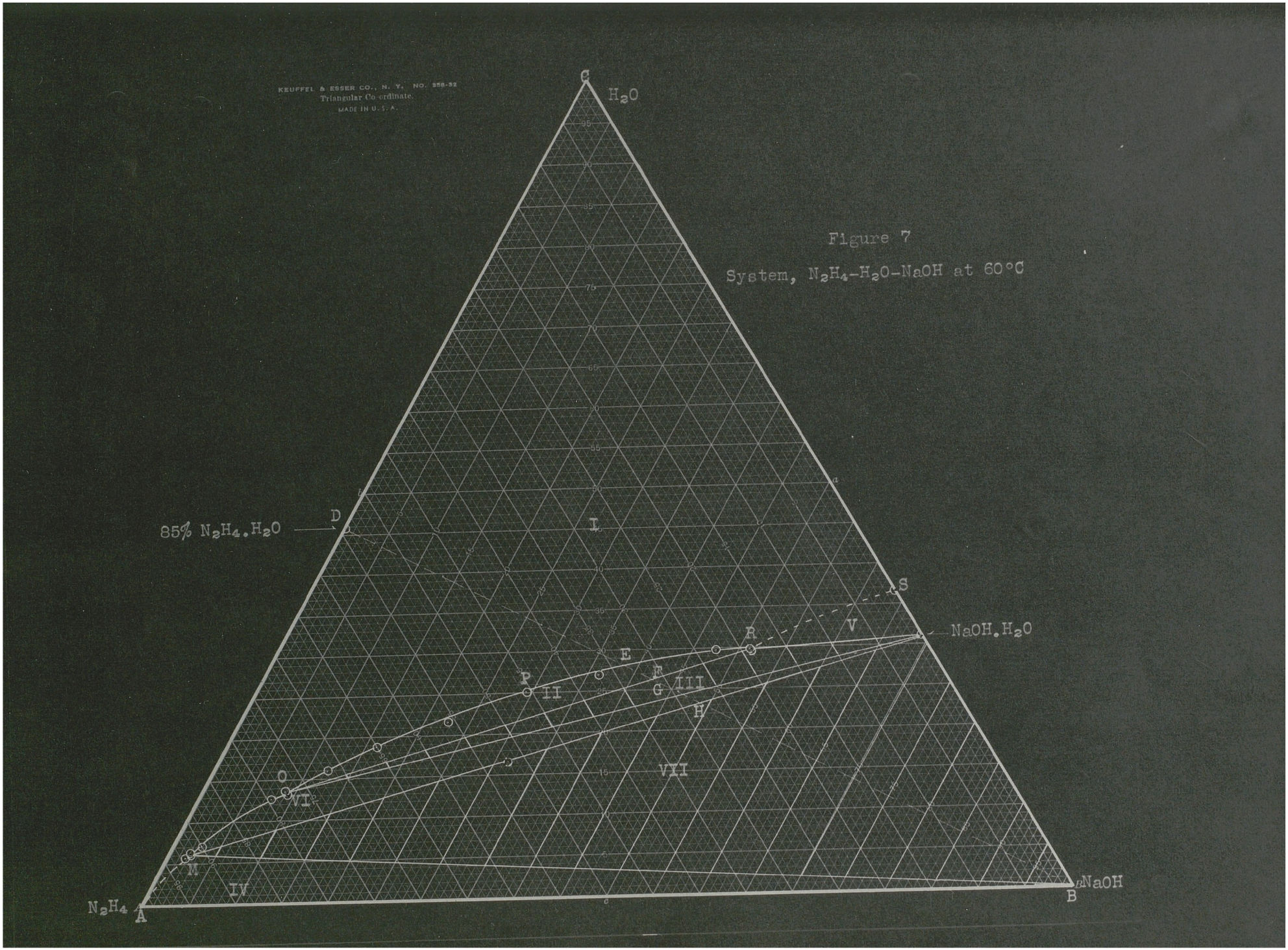


Figure 7

System, N_2H_4–H_2O–NaOH at 60°C

Table 4

System, hydrazine-water-sodium hydroxide at 70°C

	Phase	%N_2H_4	%NaOH	%H_2O	Remarks
1)	upper	90.9	3.2	6.0	Limiting composition of the two liquid phases; mixture cooled from 100°C, solid present
	lower	6.7	67.6	25.5	
2)	upper	57.7	20.1	22.0	Two liquid phases
	lower	33.6	37.5	29.0	
3)	lower	6.8	66.9	26.5	"
4)	lower	15.2	54.9	30.0	"
5)	upper	87.9	3.6	8.5	"
	lower	9.0	63.0	28.0	
6)	upper	90.0	2.4	7.5	Duplicates, "
	upper	90.0	2.5	7.5	
	lower	7.8	65.2	27.0	
	lower	7.8	65.4	27.0	
7)	upper	78.0	8.0	14.0	Two liquid phases
	lower	17.5	52.0	30.5	
8)	upper	70.5	12.2	17.5	Duplicates, "
	upper	70.4	12.0	17.5	
	lower	23.6	45.8	30.5	
	lower	23.8	45.8	30.5	
9)	- - -	45.4	28.5	26.0	Composition of plait point, interpolated

Table 5

System, hydrazine-water-sodium hydroxide at 60°C

	Phase	%N_2H_4	%NaOH	%H_2O	Remarks
1)	upper	55.8	23.7	21.5	Two liquid phases
	lower	36.7	36.3	27.0	
	lower	36.8	36.2	27.0	
2)	upper	65.0	16.3	18.5	"
3)	upper	71.7	12.3	16.0	"
	lower	22.9	47.4	29.5	
4)	upper	77.5	9.3	13.0	Limiting composition of
	lower	19.0	51.4	29.5	conjugate liquid phases
5)	upper	77.4	8.9	13.5	Duplicate, "
	lower	19.0	51.2	30.0	
6)	liquid	79.6	7.8	12.5	One liquid phase in equilibrium with solid NaOH.H_2O
7)	liquid	91.4	2.0	6.5	Limiting composition of
	liquid	91.4	2.3	6.5	the liquid phase in equi-
	liquid	91.6	2.3	6.0	librium with NaOH and NaOH.H_2O
8)	liquid	90.0	3.0	7.0	*Pair of analyses for the
	wet solid	52.0	31.4	16.5	Schreinemakers' method for composition of solid phase
9)	liquid	92.6	1.8	5.5	One liquid phase in equilibrium with NaOH
10)	- - -	45.5	29.6	25.0	Interpolated composition of plait point

*Extrapolation gave 70.2% NaOH; the theoretical value for NaOH.H_2O is 69.0%

Table 6

Summary of plait points and limiting compositions of conjugate liquid phases

Temp., °C	Material	%N_2H_4	%NaOH	%H_2O
100	upper phase	92.7	2.4	5.0
90	" "	92.2	2.0	6.0
70	" "	90.9	3.2	6.0
60	" "	77.5	9.3	13.0
100	lower phase	5.7	70.3	24.0
90	" "	5.9	69.3	25.0
70	" "	6.7	67.6	25.5
60	" "	19.0	51.4	29.5
100	plait point	45.9	27.9	26.0
90	" "	45.6	28.2	26.0
70	" "	45.4	28.5	26.0
60	" "	45.5	29.6	25.0

more efficient separation would occur at 100°C, but the complexity of the system at 60°C justifies the discussion of the effects at this temperature. The 85% hydrate material is represented by the point D, and the line $\overline{DE}$ represents changes which occur as increasing amounts of sodium hydroxide are added to composition D. Overall compositions represented by the line $\overline{DE}$ up to the point where it intersects the binodal curve OPR at E consist of but one liquid and no solid phase. The interval $\overline{EF}$ represents compositions which separate into two liquid phases, but no solid phase. Over the interval $\overline{FG}$ the two liquid phases O and R are present together with a precipitate of solid $NaOH.H_2O$. At G, phase R has disappeared, leaving only liquid of composition O and solid $NaOH.H_2O$. During the interval $\overline{GH}$, solid $NaOH.H_2O$ is in equilibrium with solutions of hydrazine of compositions indicated by the curve $\overline{OM}$. In the interval $\overline{MB}$, solid NaOH, solid $NaOH.H_2O$ and a hydrazine solution corresponding to point M are in equilibrium.

System, hydrazine-water-sodium hydroxide at 50°C

The two liquid phase region does not exist at this temperature; relationships are represented by a simple solubility curve. Obviously, in the temperature range 50-60°C this solubility surface intersects the surface representing the conjugate liquid phases.

The analysis of samples taken at 50°C was complicated by the gelatinous nature of the $NaOH.H_2O$ precipitate. Because of the poor settling properties of the precipitate it was necessary to resort to another means of sampling the liquid phase. A piece of alundum extraction thimble was sealed into the end of a length of 6 mm. glass tubing. This tube was inserted into the slurry and the liquid

was allowed to filter through the alundum into the hollow tube. A sample of this liquid was then taken using the pipet technique previously described by the author. The scatter of values obtained using this technique is greater than found previously. The data appear in Table 7 and are plotted in Figure 8.

Table 7

System, hydrazine-water-sodium hydroxide at 50°C

	Phase	%N_2H_4	%NaOH	%H_2O	Remarks
1)	liquid	45.9	26.2	28.0	Saturated liquid
2)	"	23.1	40.4	36.5	"
3)	"	87.8	3.7	8.5	"
4)	"	39.3	29.4	31.5	"
5)	"	60.0	17.2	23.0	"
6)	"	94.0	1.5	4.5	"
7)	"	83.1	7.4	9.5	Schreinemakers' method for composition of solid phase
	solid (wet)	51.4	30.5	18.0	
8)	liquid	93.1	1.7	5.0	"
	solid (wet)	46.2	35.9	18.0	

System, hydrazine-water-potassium hydroxide at 50°C

Hydrazine hydrate and potassium hydroxide were heated to 100°C and cooled slowly to room temperature. Only one liquid phase was observed in the range 100-25°C. The system was investigated quantitatively at 50°C. The data are presented in Table 8 and in Figure 9. Solid potassium hydroxide monohydrate is the stable phase at this temperature, the Schreinemakers' method giving a value of 75.2% KOH which compares well with the theoretical value of 75.7% KOH for $KOH.H_2O$.

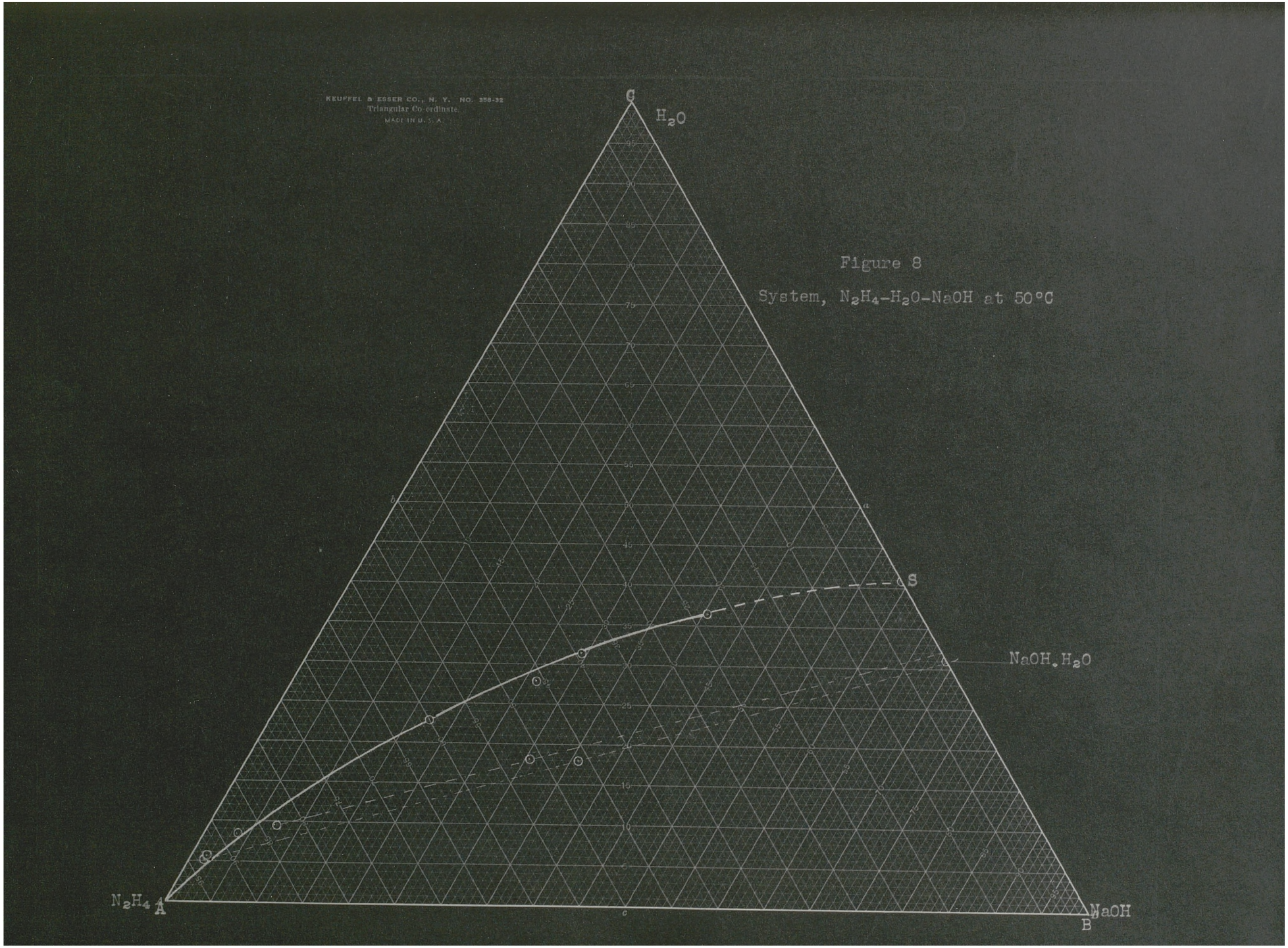


Figure 8

System, N_2H_4–H_2O–NaOH at 50°C

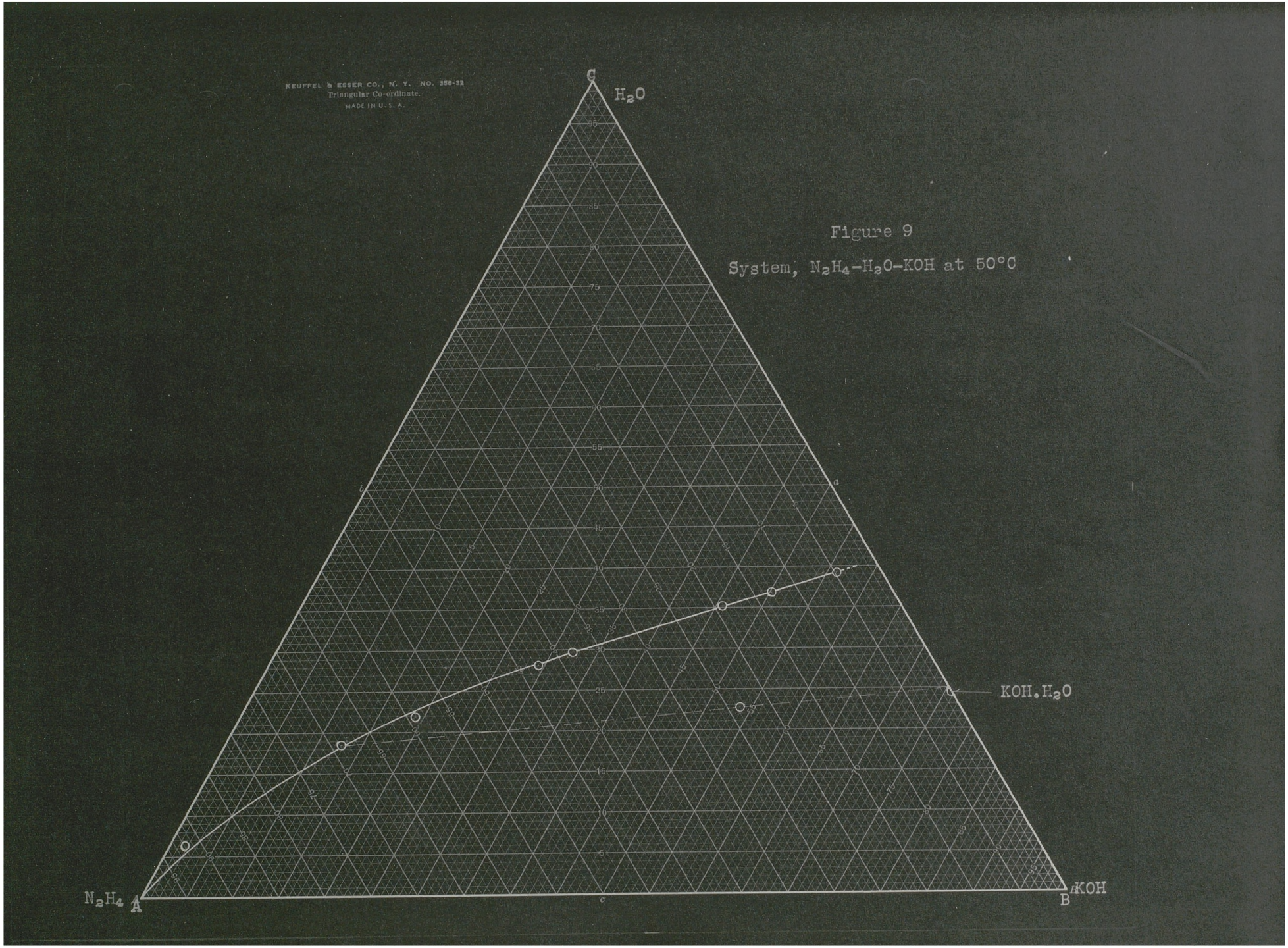


Figure 9

System, N_2H_4–H_2O–KOH at 50°C

Table 8

System, hydrazine-water-potassium hydroxide at 50°C

	Phase	%N_2H_4	%KOH	%H_2O	Remarks
1)	liquid	91.9	1.8	6.5	Saturated liquid
2)	"	59.1	19.1	22.0	"
3)	"	38.2	32.2	29.5	"
4)	"	19.1	45.6	35.5	"
5)	"	13.0	50.2	37.0	"
6)	"	4.8	56.0	39.0	"
7)	"	68.8	12.8	18.5	"
8)	"	33.7	53.8	12.5	Schreinemakers' method
	solid (wet)	42.7	29.3	28.0	for composition of solid

System, hydrazine-water-potassium carbonate at 50°C

The system hydrazine hydrate and potassium carbonate was investigated qualitatively over the temperature range 25-100°C in the search for conjugate liquid phases. Only one liquid phase was found. The system was investigated quantitatively at 50°C. The data appear in Table 9 and in Figure 10. The solid phase in equilibrium with the saturated liquid was found to be $K_2CO_3.3/2H_2O$; extrapolation using the Schreinemakers method gave exactly the theoretical composition for this hydrate.

Qualitative investigations

An unsuccessful attempt was made to find another ternary system (involving hydrazine and water as two of the components) which would exhibit the phenomenon of conjugate liquid phases in the temperature interval 25-100°C. Several substances were tried in a

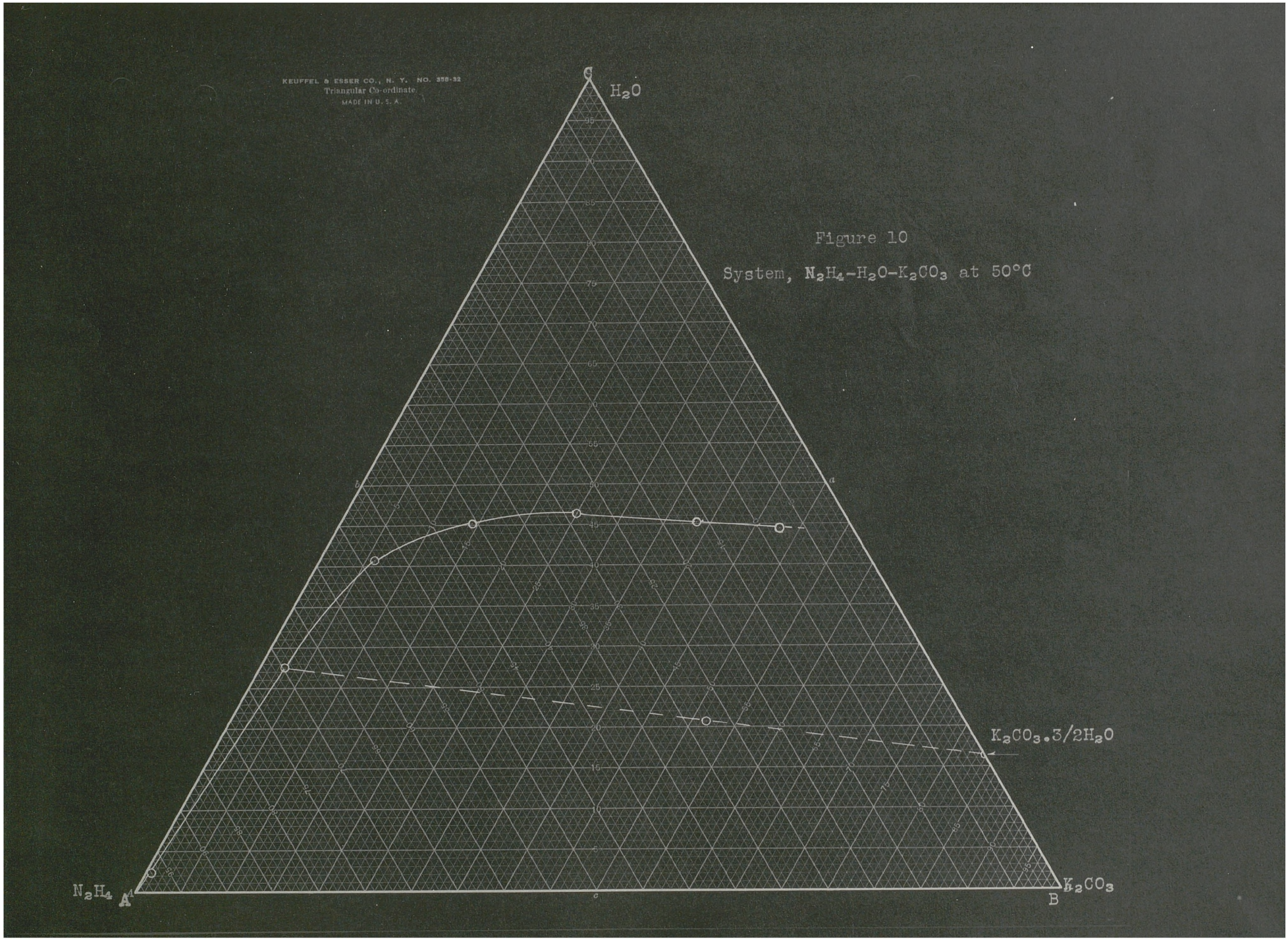


Figure 10

System, N_2H_4-H_2O-K_2CO_3 at 50°C

Table 9

System, hydrazine-water-potassium carbonate at 50°C

	Phase	%N_2H_4	%K_2CO_3	%H_2O	Remarks
1)	liquid	97.0	0.6	2.5	Saturated liquid
2)	"	53.4	6.0	40.5	"
3)	"	7.6	47.9	44.5	"
4)	"	16.2	38.5	45.5	"
5)	"	28.7	25.0	46.5	"
6)	"	40.5	14.3	45.0	"
7)	"	69.8	2.7	27.5	Schreinemakers' method
	solid (wet)	27.7	51.7	20.5	for composition of solid

Table 10

Qualitative investigations

Material	Liquid phases
Na_3PO_4	one
Na_2CO_3	"
Na_2SO_4	"
K_2CO_3	"
KOH	"

qualitative manner. The material under test was placed in the equilibrium tube at 100°C. Sufficient 85% hydrazine hydrate was added to just dissolve the solid, and then a slight excess of the solid was added. The mixture was cooled slowly to room temperature with constant stirring and observed at 10° intervals. None of the materials listed in Table 10 were observed to effect separation into two liquid phases.

D. DISCUSSION

In general, a ternary system has four variables, temperature, pressure, and mole fraction of two of the three components. In the present study, pressure was not a variable, being always equal to the atmospheric pressure. Use of triangular coordinates allows the representation of all possible three component mixtures in one plane. Temperature may be represented by the third dimension. Thus, with pressure constant, the temperature dependence of ternary systems can be represented using a solid prism, with the height representing the temperature. Isothermal planes through this prism allow planar representation of data presented in Part III of this thesis. It is obvious that these isothermal planes intersect a surface, and it is the trace of this surface on the isothermal plane that gives the curves which have been presented.

The preparation of anhydrous hydrazine by distillation from an aqueous solution which contains sodium hydroxide was presented in Part II. It was observed during the distillation at constant pressure that the temperature of the still contents increased only a few degrees while approximately 80% of the hydrazine was being collected. Thereafter, the temperature of the still rose rapidly,

and the rate of hydrazine distillation decreased sharply. Observation showed that these effects occured when the last amounts of the upper phase had disappeared.

According to the Phase Rule, $F = C + 2 - P$, a two-component system, consisting of two liquid phases and a vapor phase, is univariant. At a given temperature such a system has a fixed pressure. Distillation at a fixed pressure (T constant) occurs until one liquid phase disappears. A three component system, having two liquid phases and a vapor phase, is bi-variant. There are, however, three variables, temperature, pressure, and the percent of one component. Thus, removal of a component by distillation at constant pressure is accompanied by a temperature change.

In view of this discussion, it becomes necessary to explain why a rapid temperature change during distillation did not occur until after the upper phase had disappeared. Examination of the tie lines in Figure 6 shows that they slant sharply toward the hydrazine apex. It was shown in Figure 1 that compositions along a line that passes through a corner of the triangle involve only a change in the amount of that component. Since removal of hydrazine causes the composition of the residue to move approximately parallel to the tie lines in the two liquid phase region, it is apparent that the composition of the conjugate phases will not change rapidly, but that the amount of upper phase will steadily decrease until the composition of the residue has moved past the curve PR into field I.

However, a slight temperature increase was noted; consequently the explanation offered in the preceeding paragraphs is not com-

pletely valid. The situation actually involves a small temperature increase, and consequently the still composition moves not only away from the hydrazine apex but upward along the temperature axis as well. Actually, the slopes of the tie lines and the extent of the binodal curves are almost identical for the temperature range 70-100°C as demonstrated in Figures 4, 5, and 6. Data for the limiting compositions, O and R, and the plait point P, also lead to the same conclusion (Table 6). In the temperature range, 70-100°C, the surface representing the compositions of the conjugate liquid phases rises essentially vertically. Therefore, over this temperature range, the behaviour of the still composition on the removal of hydrazine can be represented (as a first approximation) on an isothermal plot.

A method of extreme simplicity and convenience in determing the exact over-all composition resulting from the addition of sodium hydroxide to an aqueous hydrazine solution of any composition is illustrated in Figure 11. If the molar proportions of water and sodium hydroxide are to be 1:1, corresponding to $NaOH.H_2O$, a line $\overline{DA}$ is drawn from 69% NaOH through the hydrazine apex. Compositions along this line represent the addition of hydrazine to $NaOH.H_2O$. A line is then drawn from the point E representing any particular hydrazine-water composition (in the example 53% N_2H_4) through the sodium hydroxide apex. Compositions along this line represent the addition of sodium hydroxide to a hydrazine-water solution of composition E. The intersection of these two lines at F gives the exact composition of the mixture, obtained by the addition of sufficient sodium hydroxide to the hydrazine-water

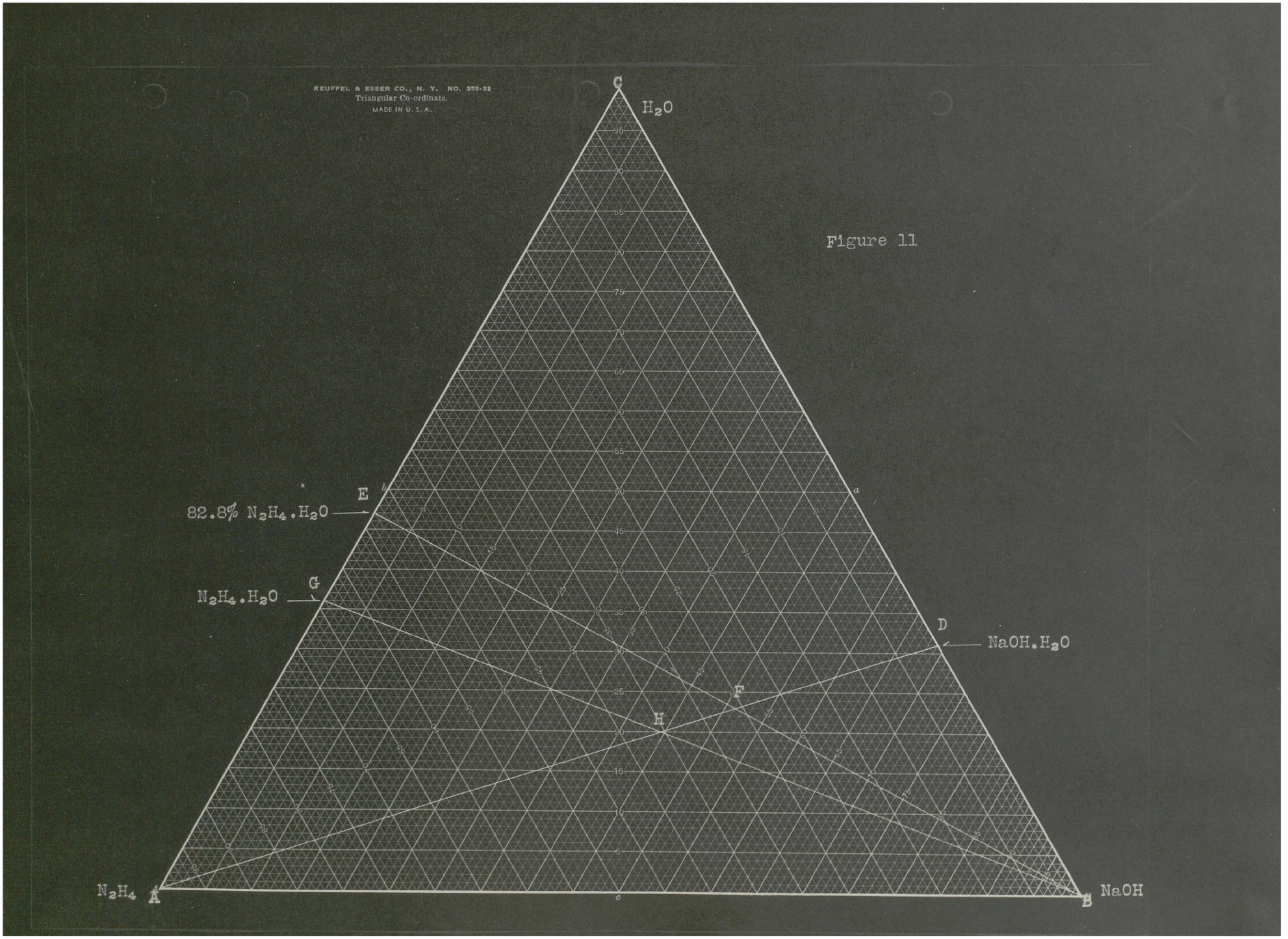

KEUFFEL & ESSER CO., N. Y. NO. 358-32
Triangular Co-ordinate.
MADE IN U. S. A.
C
H_2O
E
82.8% $N_2H_4.H_2O$
G
$N_2H_4.H_2O$
D
$NaOH.H_2O$
F
H
N_2H_4
A
B
NaOH
a
b
c

Figure 11

solution to yield a $NaOH:H_2O$ mole ratio of one. This shows that the final composition must contain 51.2% NaOH. An initial composition corresponding to G would intersect the line $\overline{AD}$ at H and would require 44.6% NaOH in the final mixture in order that sodium hydroxide and water be present in equimolar quantities. Although self evident, this method of quick calculation has not appeared elsewhere, to the author's knowledge. It amounts to the graphical solution of two simultaneous equations in triangular coordinates.

E. SUMMARY

1. The system hydrazine-water-sodium hydroxide has been studied quantitatively at 50, 60, 70, 90, 100°C.

2. At temperatures from approximately 60°C to the boiling point this system exhibits two liquid phases, within certain concentration ranges.

3. At 50°C, a simple solubility curve is observed, with $NaOH.H_2O$ in equilibrium with a saturated solution containing hydrazine, water and sodium hydroxide.

4. The effect of these conjugate liquid phases on the preparation of hydrazine by distillation from a hydrazine, water, sodium hydroxide mixture has been discussed.

5. A quantitative study of the systems, hydrazine-water-potassium hydroxide and hydrazine-water-potassium carbonate was made at 50°C. Neither system gives evidence for formation of two liquid phases.

6. A qualitative study was made in the temperature interval 25-100°C in an unsuccessful attempt to find another hydrazine-water ternary system exhibiting two liquid phases.

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VITA

The author was born on February 5, 1919, in Springfield, Illinois, and attended the public schools of that city until his graduation from Feitshans High School in February, 1937. In the fall of that year he entered the James Millikin University at Decatur, Illinois, having been awarded a scholarship. During his senior year at Millikin he served as an assistant in Chemistry. Upon graduation in 1941 with the degree of Bachelor of Arts, he shared first honors and received his degree Summa Cum Laude.

He entered the graduate school of the University of Illinois in September, 1941, on a graduate fellowship, and received the degree of Master of Science in Chemistry in 1942. Between 1942 and 1946 he served as a research chemist on the Plutonium Project.

In 1946 he was awarded a National Research Council Fellowship, making it possible for him to complete his doctorate training. He is a member of the following societies: the American Chemical Society, Sigma Xi, Phi Lambda Upsilon, Alpha Chi Sigma, and the Kappa Society (Millikin).