

STUDY OF THE HEAT CAPACITY OF
MORPHOLINE-WATER MIXTURES

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MORPHOLINE-WATER MIXTURES

by

ROBERT FREDERICK SCHMUCK

Bachelor of Science

University of California

Berkeley, California

1938

and

RALPH ANDRES BROWN

Bachelor of Science

Hamline University

St. Paul, Minnesota

1939

Submitted to the Department of Chemistry
Oklahoma Agricultural and Mechanical College
In Partial Fulfillment of the Requirements

For the degree of

MASTER OF SCIENCE

1941

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APPROVED BY:

H. M. Trimble

Chairman, Thesis Committee

J. R. Wood

Member of the Thesis Committee

Otto M. Smith

Head of the Department

D. C. M. Intosh

Dean, Graduate School

ACKNOWLEDGEMENT

The authors wish to acknowledge the financial assistance rendered by the Oklahoma Agricultural and Mechanical College through graduate assistantships which made this work possible.

We wish to thank Mr. Dale McKinney for the preparation of diagrams and curves.

Especially do the authors wish to express their sincere appreciation for the supervision, expert advice, and kind assistance which were given by Dr. H. M. Trimble, under whose direction this work was accomplished.

PREFACE

The applications of heat capacity data to thermodynamic considerations are manifold. Some applications are: the calculation of the change in heat content of a system whose temperature is changed, the derivation of free energy equations, the empirical relationship between heat capacities and temperature, and the determination of entropies. The partial heat capacities of the constituents of a mixture, that is, the contributions which they severally make to its total heat capacity, have been shown to be related to the degree of association or dissociation between these constituents. Thus they promise to be of great value in formulating an adequate theory of the solution state. Much of the work yet to be done in connection with the thermodynamics of solutions requires data upon such properties for a basis. Few such data are to be found in the literature. Partial heat capacities also provide the only satisfactory values for use in calculating such quantities as heats of mixing, heats of dilution, and, to a considerable degree, heats of reaction in solution.

A part of the work in physical chemistry at Oklahoma A. and M. College recently has been concerned with developing apparatus and with determining the heat capacities of various mixtures and compounds, and our work is part of this program.

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INTRODUCTION

The method used in making calorimetric determinations depends to a great extent upon the nature of the material which is being studied. Substances or mixtures which are volatile, which react with metals that are ordinarily used in the construction of calorimeters, or which react with components of the atmosphere, have not been examined very extensively. In particular, the range of temperature covered has been very limited. Such substances, then, offer a promising field for heat capacity studies.

The usual method for determining heat capacities involves the supplying of a known quantity of heat, generally by electrical heating, to the body whose heat capacity is desired, and noting the temperature rise accompanying the influx of heat. This method generally is applicable for non-volatile substances and those which do not become contaminated by contact with air. For those which suffer these limitations, this method is unsuitable.

The flow method involves passing the material under examination at a constant rate over a heating coil where heat is imparted to it at a constant rate. Its temperature is measured before and after passing over this coil, and its heat capacity may be found from the measured values (1). Its application for our purpose is certainly possible, but the apparatus necessary is complex, cumbersome, and costly, also the experimental determinations are difficult. It, too, is not well suited to our work.

Spectroscopic methods have been utilized very successfully in obtaining empirical heat equations for individual gases (2). Indeed,

they promise to be much more useful for gases than any others, but they require extensive knowledge of the behavior of the gas molecules; knowledge which must often be drawn from theoretical rather than from experimental evidence. It may be that such methods can be applied also to liquids, though this has not yet been done. It would seem, however, that the difficulties of interpretation would be very great with mixtures. In spite of their promise, these methods are yet far from practical for our purpose.

The method of mixtures has long been used in determining the heat capacities of metals, of minerals, and of solids in general. It involves heating the object to some desired temperature, and then dropping it into a calorimeter where it cools, raising the temperature of the calorimeter. The heat capacity of the object is readily found from its weight, the temperature interval through which it falls, and the change in heat content of the calorimeter. It has seldom been applied to the determination of the heat capacities of liquids. Among the recent workers in this field are K. J. Frederick and J. H. Hildebrand (3) (4) (5). The apparatus as here employed is essentially a modification of that which they developed. It has been found well suited to our purposes.

Morpholine, a cyclic secondary amine with the formula $\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{NH}$ is a relatively new compound which has commanded much interest, and has many interesting industrial possibilities. It finds use as an emulsifying agent and as a solvent. It is soluble in water in all proportions, and its mixtures with this substance may be of as much interest from a theoretical standpoint as those of dioxan, which it resembles in some ways. Morpholine and its aqueous solutions are liquids of just the type for which we have planned to develop apparatus and heat capacity methods:

they react readily with CO_2 to form a carbamic acid; morpholine itself absorbs water readily from the air; these liquids readily corrode many metals when in contact with atmospheric oxygen; and their volatilities are such as to prohibit heat capacity studies in open vessels over wide ranges of temperature.

APPARATUS AND MATERIALS

Morpholine

We obtained our morpholine from the Union Carbide and Carbon Corporation. It was refluxed over sodium for several hours to purify it, and then was ready to be distilled. We checked the boiling point of the morpholine with our thermocouple, as it distilled, and found that it was constant at 127.0°C. The atmospheric pressure during the distillation was 740 mm. The boiling point as given in the literature is 127.1°C for this pressure.

Water

Distilled water was employed for each individual run. For the morpholine-water mixtures, CO₂ free water was used. The CO₂ was expelled by boiling the water which was then cooled in CO₂ free air.

Pyrex glass

Capsules made from pyrex glass tubing were used, as this glass has a very small temperature coefficient of expansion, and is resistant to chemical attack (6). Quartz, gold, platinum, or tantalum capsules are suitable, but they were not available.

Literature investigation indicated that the heat capacity of pyrex glass is an unknown quantity. Frederick and Hildebrand (7) (8), and De Vries (9) present three different heat capacity equations. Subsequent correspondence with the Corning Glass Works (10) verified this inconsistency, for they state that there is no definite known value or equation for the specific heat of pyrex glass.

This laboratory (unpublished work), has obtained a specific heat equation for pyrex tubing which differs from those already mentioned. It

seems possible that a discrepancy in Engle's (11) heat capacity values for pure morpholine may have resulted from using a published value which was not valid for the pyrex tubing he employed. This work gave further evidence upon this matter. A table comparing the various equations which have been found for the heat capacities of pyrex glass will be presented later.

Heaters

Two heaters of the type shown in Figure I were employed. Their temperatures were controlled by means of built-in mercury thermoregulators, operating through relays of the usual type. The source of electrical energy for controlling the heaters was a battery of Edison cells. From day to day the smaller heater, which we used for temperatures around 50°C and 80°C, maintained temperatures so constant that the readings of its thermocouple did not vary from the mean by more than 9 microvolts. This is equivalent to a change of approximately 0.20°C. The larger heater, which we used for the two higher temperatures, would vary from the mean by not more than 8 microvolts, corresponding to a change of 0.18°C.

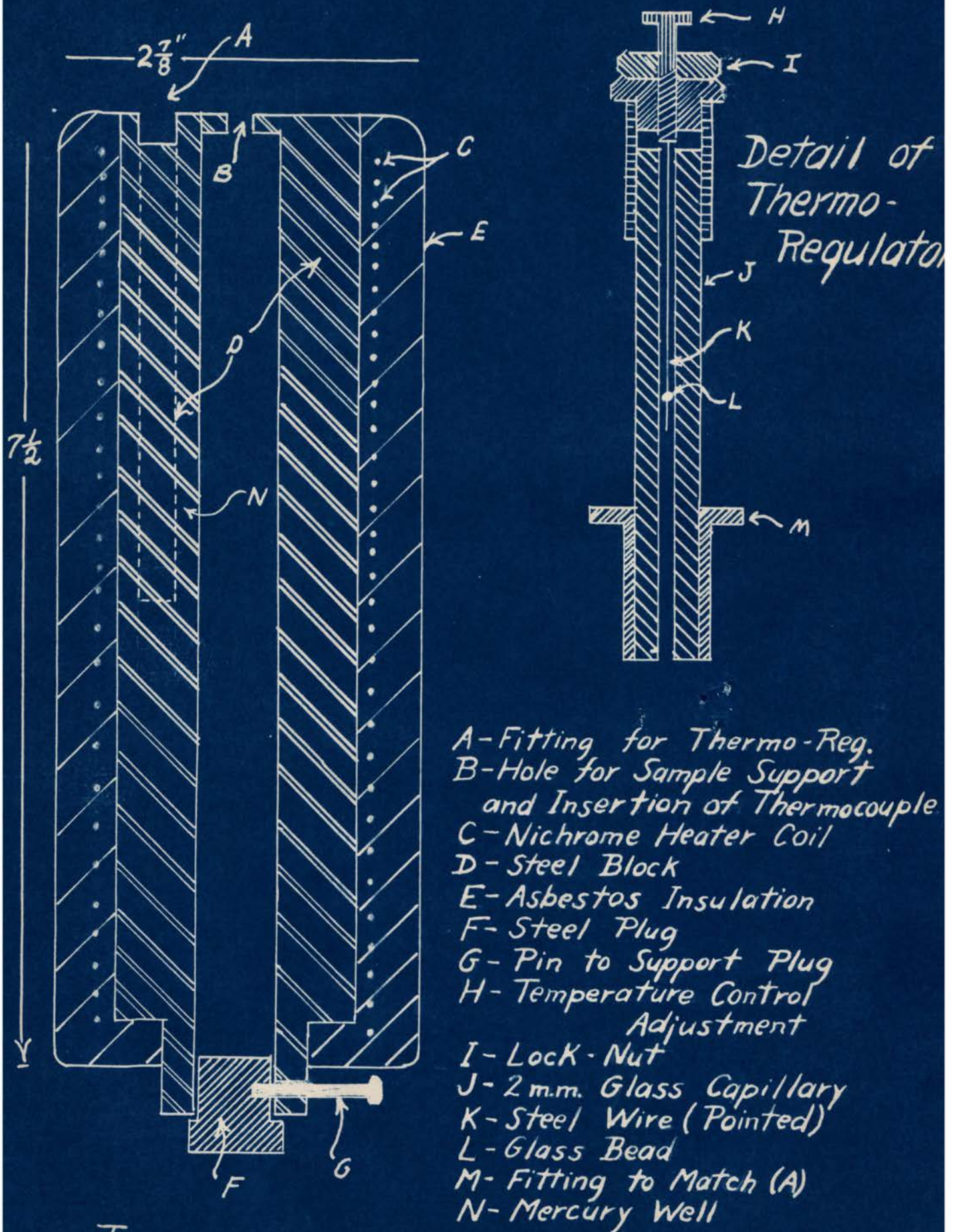
Calorimeter

The calorimeter used was of the submerged type and is shown in Figure II. The calorimeter container was constructed of copper. Next to the container, and separated by an annular space provided by a bakelite insulator, was a convection shield. The 450 ml. calorimeter cup of nickel plated brass fitted into a bakelite insulator which rested in the convection shield. The lid was fitted with tubes which held, respectively, a Beckmann thermometer, an opening for the introduction of a sample, and bearings for a stirrer shaft, which was of glass. The calorimeter was made water proof with the use of Number 6 water pump lubricant spread on the bearing surface where the lid and container joined. Changing the grease about every third time sufficed to insure a water proof connection.

Constant Temperature Water Bath

The water bath, in which the calorimeter was submerged, was a 25-liter galvanized iron cylindrical container. This was kept at a constant

Cross Section of Heater

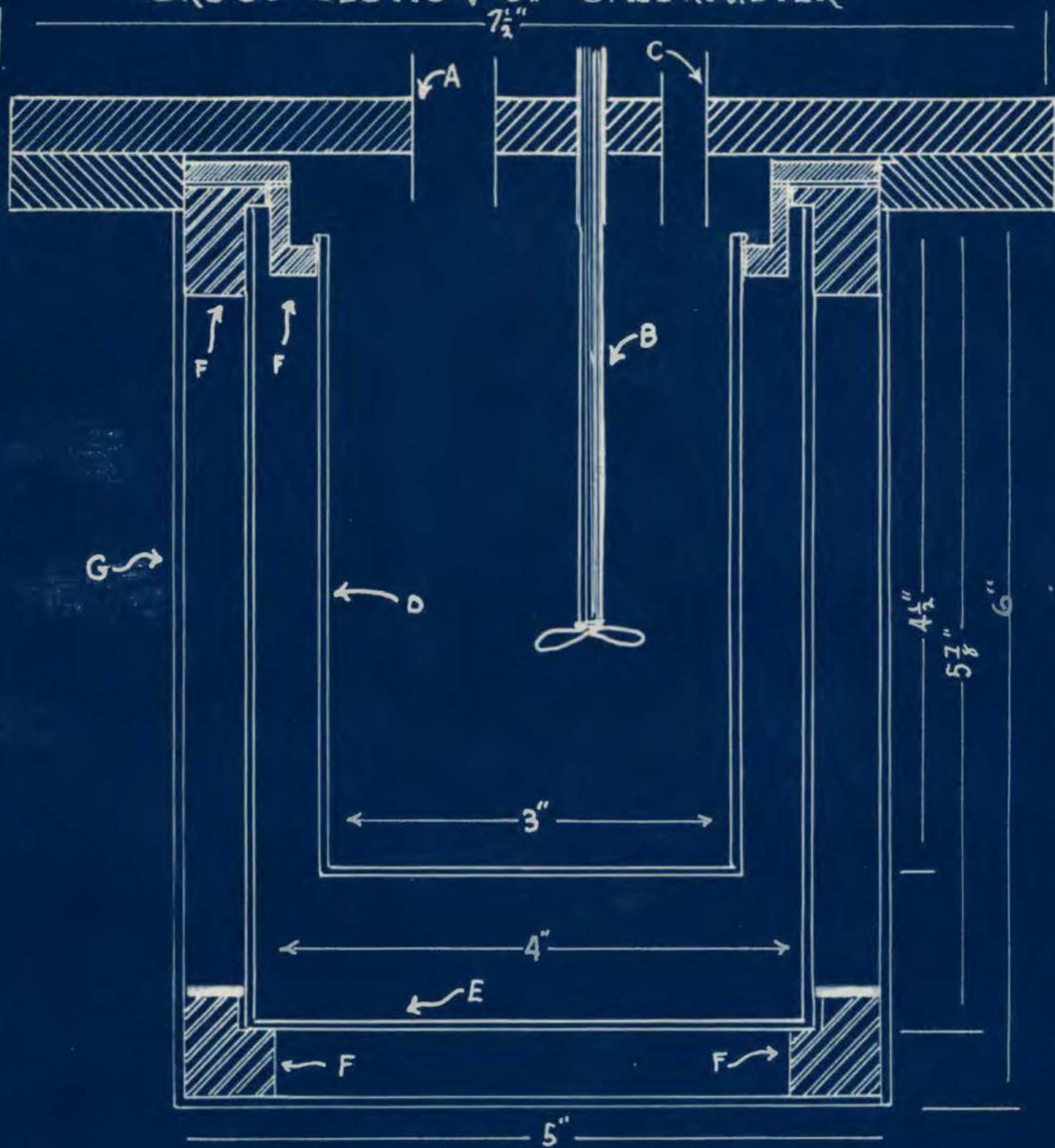


- A-Fitting for Thermo-Reg.
- B-Hole for Sample Support and Insertion of Thermocouple
- C-Nichrome Heater Coil
- D-Steel Block
- E-Asbestos Insulation
- F-Steel Plug
- G-Pin to Support Plug
- H-Temperature Control Adjustment
- I-Lock-Nut
- J-2 m.m. Glass Capillary
- K-Steel Wire (Pointed)
- L-Glass Bead
- M-Fitting to Match (A)
- N-Mercury Well

Figure 1

CROSS SECTION OF CALORIMETER

3



- A- sample Insertion Tube
- B- Stirrer
- C- Thermometer tube
- D- Calorimeter Cup
- E- Convection Shield
- F- Bakelite Ring Spacers.
- G- Calorimeter Container

Figure II

temperature by means of an electric stirrer and an electric heater regulated by an automatic mercury regulator and relay.

Beckmann Thermometer

A Beckmann thermometer calibrated by the Bureau of Standards was used to measure the temperature change in the calorimeter. The thermometer was tapped just before making each reading to keep the mercury thread from sticking to the sides of the capillary tube. The temperatures were read to 0.001°C. with the aid of a magnifying lens. Three thermometer corrections were used to obtain the temperature change in the calorimeter as measured by the Beckmann thermometer. These corrections were:

- (1) Stem correction from calibration table.
- (2) Emergent stem correction which was evaluated by use

of the following equation:

$$E. S. C. = 0.00016 \times d(t_1 + t_2 + S - t_3) \text{ where,}$$

d = temperature difference observed on the thermometer.

t_1 = reading of the Beckmann when the sample was dropped into the calorimeter cup.

t_2 = maximum or minimum reading of the Beckmann after the sample was dropped into the calorimeter cup.

S = zero setting of the Beckmann in °C.

t_3 = room temperature in °C.

- (3) Setting factor for the zero setting of the Beckmann.

In this work the zero setting of the thermometer was 28°C. This factor was 0.0022.

Thermocouples

Two single junction thermocouples were employed in this work. One,

used as a standard, was calibrated by the Bureau of Standards by comparing it with a standard platinum resistance thermometer at -50°C , 0°C , 50°C , 100°C , and 150°C . The other was used for measuring the temperatures of the electric heaters which supplied energy to heat the samples. The couples, approximately one meter in length, were constructed of 30 mil copper and constantan wire after the manner described by Trimble (12). An ice bath assembled in a thermos bottle served as a cold junction vessel. The E. M. F. readings of the two thermocouples, each with one junction in the ice bath and the other junction in boiling benzene (80°C), boiling water (100°C), or boiling chlorobenzene (132°C), were compared at these three points. After these comparisons were made, it appeared that the E. M. F. across the working thermocouple at 50°C was about 6 microvolts less than the standard at this same temperature. At 100°C the difference was -4 microvolts, and at 150°C it was -6 microvolts.

Using the standard thermocouple tables in International Critical Tables, we calculated the differences between the E. M. F.'s of the standard thermocouple and the accepted values at 50°C , 100°C , and 150°C . The differences between the E. M. F.'s of the working thermocouple and the accepted values at 50°C , 100°C , and 150°C were then found by utilizing the results of the comparison we had made between the standard and the working thermocouples. By plotting the latter differences against the E. M. F. readings that covered the range we used, we obtained a correction curve for the working thermocouple. Adding this difference as found for any E. M. F. to the observed E. M. F. itself, the corrected value was found. The corresponding temperature was then read from our curves. Consider, for example, that the E. M. F. reading

of the thermocouple was 4292 microvolts. Referring to the correction curve for that particular E. M. F. reading, the reading was seen to be 31 microvolts lower than that of the standard table for that temperature. Adding 31 to 4292 gives the corrected E. M. F. reading. Reading from a large scale graph made by plotting temperature against International Critical Tables E. M. F. readings, it is found that an E. M. F. of 4323 microvolts corresponds to a temperature of 101.01°C, which is the temperature of the hot terminal point of the thermocouple.

The working thermocouple was checked periodically with the boiling point of benzene or of water and was found to give unvarying E. M. F. readings.

Potentiometer

A type K₂ potentiometer was used in measuring the potential differences generated by the thermocouple. Potentiometer readings varied from about 2,000 to 6,000 microvolts. A Weston type cell was used as a standard of E. M. F. in setting the potentiometer.

EXPERIMENTAL

In starting the experimental part of this study, the heat capacity of the calorimeter was first determined. Since the manipulations and methods of calculation from the data secured were essentially the same in all our calorimetric determinations, this determination will be discussed in some detail.

A cylinder of pure copper, weighing 106.20 grams, was suspended in the heater which had been set at some desired temperature. While it was heating up, we prepared the calorimeter. Water had been brought to the temperature of the water bath, 30°C., in a volumetric flask which had been found to deliver 411.9 grams of water at this temperature. The meniscus was adjusted to the mark, the contents of the flask were discharged into the calorimeter can, and the calorimeter was assembled and put into the water bath. Preliminary tests showed that the copper block came to the temperature of the heater in an hour or less. Just before the expiration of this time, a half dozen or more readings of the temperature by means of the thermocouple were made. When these checked satisfactorily, the calorimetric determination proper was started. The first rating period was followed, making readings each minute until five or six consecutive readings showed that the calorimeter temperature was constant or changing regularly. On the even minute, the bottom of the heater was allowed to drop, the heater was turned into position over the calorimeter, and the copper block was quickly lowered into the calorimeter. Readings were then resumed and continued until six or more readings in the final rating period showed that the calorimeter temperature was again

changing at a regular rate. A typical series of readings is given in Table I below:

Table I

Thermocouple Readings Microvolts	Time (Minutes)	Beckmann Reading	Temperature Change
3761	0	0.773	
3761	1	0.778	0.005
3761	2	0.784	0.006
3761	3	0.788	0.004
3761	4	0.793	<u>0.005</u>
3761	5	Sample dropped, Average =	0.005
3761 = Mean	6	2.168	
$\frac{28}{3789}$ = Correction	7	2.167	0.001
Temperature: 89.50°C (heater)	8	2.163	0.004
Setting of Beckmann Thermometer: 28.00°C	9	2.160	0.003
Room Temperature: 21°C	10	2.158	0.002
Weight of Copper	11	2.154	0.004
Block: 106.20 grams	12	2.153	0.001
	13	2.150	<u>0.003</u>
		Average	0.003

The calculations were performed as follows:

$$\text{Reading at start: } 0.793 + 0.005 \text{ (average rise per minute)} \\ + 0.008 \text{ (scale correction)} = 0.806^\circ$$

$$\text{Reading at end: } 2.168 + 0.003 \text{ (average fall per minute)} \\ + 0.009 \text{ (scale correction)} = \underline{2.180^\circ}$$

$$\text{Uncorrected rise: } 1.374^\circ\text{C}$$

$$\text{Emergent stem correction: } 0.00018 \times 1.4 (1 + 2 + 28 - 21) = 0.002^\circ$$

$$\text{Setting correction: } 0.0022 \times 1.374 = \underline{0.003^\circ}$$

$$1.379^\circ\text{C}$$

The lowest temperature reached by the copper block = highest corrected temperature reached in the calorimeter =

$$2.180^\circ + 28.00^\circ = 30.18^\circ\text{C}$$

Fall in temperature of copper block: 89.50°C to 30.18°C

The heat lost by the copper block in falling from 89.50°C to 30.18°C must be equal to the heat gained by the calorimeter. The heat capacity per gram of copper is given by the expression:

$$C_p = 0.09076 + 0.0000415 t \text{ calories (13)}$$

Integrating, we find that the change in heat content of the copper block is

$\Delta H = 0.09076 (t_2 - t_1) + 0.00002075 (t_2^2 - t_1^2)$ calories per gram where t_2 is the temperature of the heater, and t_1 is the lowest temperature which the block reaches in the experiment. Thus we have:

Weight of copper block x change in heat content per gram =

heat capacity of calorimeter x corrected rise

$$\text{or: } 106.20 \times [0.09076 (89.50 - 30.18) + 0.00002075(89.50^2 - 30.18^2)] \\ = \text{heat capacity} \times 1.379$$

Solving for the heat capacity, it is found that it is 426.5 calories per

degree.

In this work we used 427.8 ± 2.3 as the heat capacity of the calorimeter, this being the average of eighteen runs with the copper block. After almost completing the measurements, we made two runs with the copper block, and obtained heat capacities of 428.6 calories and 425.9 calories, which values check the former ones within experimental error.

The heat capacity can also be found directly. The weight of the nickel plated brass cup was 140.8 grams, and the weight of the water that was used was 411.9 grams. Considering the heat capacity of brass per gram as being 0.09 (14), and using Roth's value for the heat capacity of water per gram at 30°C (15), the heat equivalent as calculated theoretically is 424.6 calories. This is a satisfactory agreement; if the stirrer and thermometer were considered, a higher theoretical value would result. The fractions of these parts, whose temperature changes with that of the calorimeter, cannot be estimated so the above value, found experimentally, was used in our calculations.

The next experimental step was to find equations representing the heat capacity of pyrex glass over the temperature range 0°C to 125°C. To do this, a sample of pyrex glass was ground up and put into a capsule which was then dried, sealed, and provided with a ring formed from the upper part of the capsule by which it could be suspended.

The calorimetric experiments with these samples were just like those described above. We found that with this ground glass, about 1.5 hours was required to obtain temperature equilibrium, and it was also reached more slowly in the calorimeter. Otherwise, these experiments

offered no new features. An ice bath was used for the 0°C determination, and the heaters were set for the approximate points 50°C, 80°C, 100°C, and 125°C. Satisfactory determinations on the pyrex samples usually required three runs for each temperature, and more than three runs at zero were used in getting heat capacity values at this point. Leaving the pyrex samples in the ice bath for longer time intervals did not seem to enhance the accuracy of the measurements.

The corrections to the Beckmann readings, and the temperature change in the sample were calculated as in the example of Table I. The heat given to the calorimeter was found by multiplying its heat capacity by the corrected temperature rise which occurred in it. For one of the pyrex samples which weighed 26.86 grams it was found that:

$\Delta H/\text{gram pyrex}$ for the temperature interval 84.92°C to 28.86°C was:

$$287.9 \text{ calories}/26.86 = 10.72 \text{ calories/gram}$$

To facilitate the calculations to be made later, we corrected the change of heat content measured above, to that which would have been found if the sample had fallen to exactly 30°C. This assumes a linear relationship between ΔH and temperature. Thus in the above case:

$$10.72 \text{ calories}/(84.92^\circ\text{C} - 28.86^\circ\text{C}) = x/(30.00^\circ\text{C} - 28.86^\circ\text{C})$$

$$x = 0.22 \text{ calories}$$

Therefore: $\Delta H/\text{gram pyrex}$ (for the interval 84.92°C to 30.00°C)

$$10.72 - 0.22 = 10.50 \text{ calories}$$

To simplify the calculations which follow, $\Delta H/\text{gram}$ was used on the basis of a fall in temperature, from the maximum temperature of the sample when heated, to 0°C. Thus ΔH from temperature t to 30°C added to ΔH from 0°C to 30°C gives ΔH from t to 0°C. These values are shown in Tables II and III.

Table II

Sample I

Heat required to raise one gram pyrex from 0°C to t°C.

Temp.	$\Delta H/\text{gr.}$	Temp.	$\Delta H/\text{gr.}$	Temp.	$\Delta H/\text{gr.}$
30	5.332	59.04	10.60	97.40	18.66
30	5.295	59.08	10.49	97.50	18.63
30	5.290	59.20	10.61	97.70	18.61
30	5.246	84.74	15.86	97.60	18.50
30	5.232	84.85	16.01	127.70	24.66
30	5.162	84.85	15.78	127.40	24.85
Ave.=5.260±.072		84.92	15.76	127.49	24.92

The empirical equation derived from the plot of the data in Table II is: (1) $\Delta H/\text{gram pyrex} = 0.167t + 0.000350t^2 - 0.000000780t^3$.

Table III

Sample II

Heat required to raise one gram pyrex from 0°C to t°C.

Temp.	$\Delta H/\text{gr.}$	Temp.	$\Delta H/\text{gr.}$	Temp.	$\Delta H/\text{gr.}$
30	5.215	52.84	9.573	97.44	18.57
30	5.299	53.00	9.447	97.75	18.69
30	5.351	53.20	9.608	127.49	25.24
30	5.372	84.85	16.000	127.60	24.79
Ave.=5.309±.094		84.90	15.88	127.62	24.91

The empirical equation derived from the plot of the data in Table III is: (2) $\Delta H/\text{gram pyrex} = .167t + 0.000296t^2 - 0.000000545t^3$

The above empirical equations give values of ΔH that compare favorably

with experimental values.

Figure III illustrates the apparatus that was used in purifying morpholine and preparing its mixtures with water. The condenser, A, was placed in the flask, B, and the morpholine refluxed. Then the condenser was removed, a ground glass stopper was placed in the neck of flask, A, and the desired quantity of morpholine distilled into the flask, C. Capsules were made from the pyrex tubing in the form of short test tubes with constricted necks. Such a capsule, D, was sealed in a ground glass joint, E, and this vessel was weighed. Then a quantity of carbon dioxide free water was added, and the vessel was again weighed. With this weighed amount of water in the capsule, the ground glass joint, E, was fitted into H. The other end of this delivery tube replaced the flask, B, at I. Air pressure then was applied at the point indicated to force some of the morpholine from C into the Capsule, D, in which was the weighed amount of water. A removable ground glass stopper fitted at E, so that after a definite amount of morpholine had been added, the stopper could be inserted, and the solution thoroughly mixed. The weight of the vessel, with the water and morpholine in it, was now found. The percentage composition of the mixture could then be calculated. The capsule was immersed in an acetone-dry ice bath in order to freeze the mixture and lower its vapor pressure, and the capsule was then sealed at G. Another weighing gave the weight of the sample as used in the experiment.

After sufficient runs were made, the capsule was reweighed as a check, a small hole was pierced in the capsule with an oxygen torch, and the liquid removed. As the weight of the capsule with the mixture

Apparatus for Purifying Morpholine and Preparing Mixtures

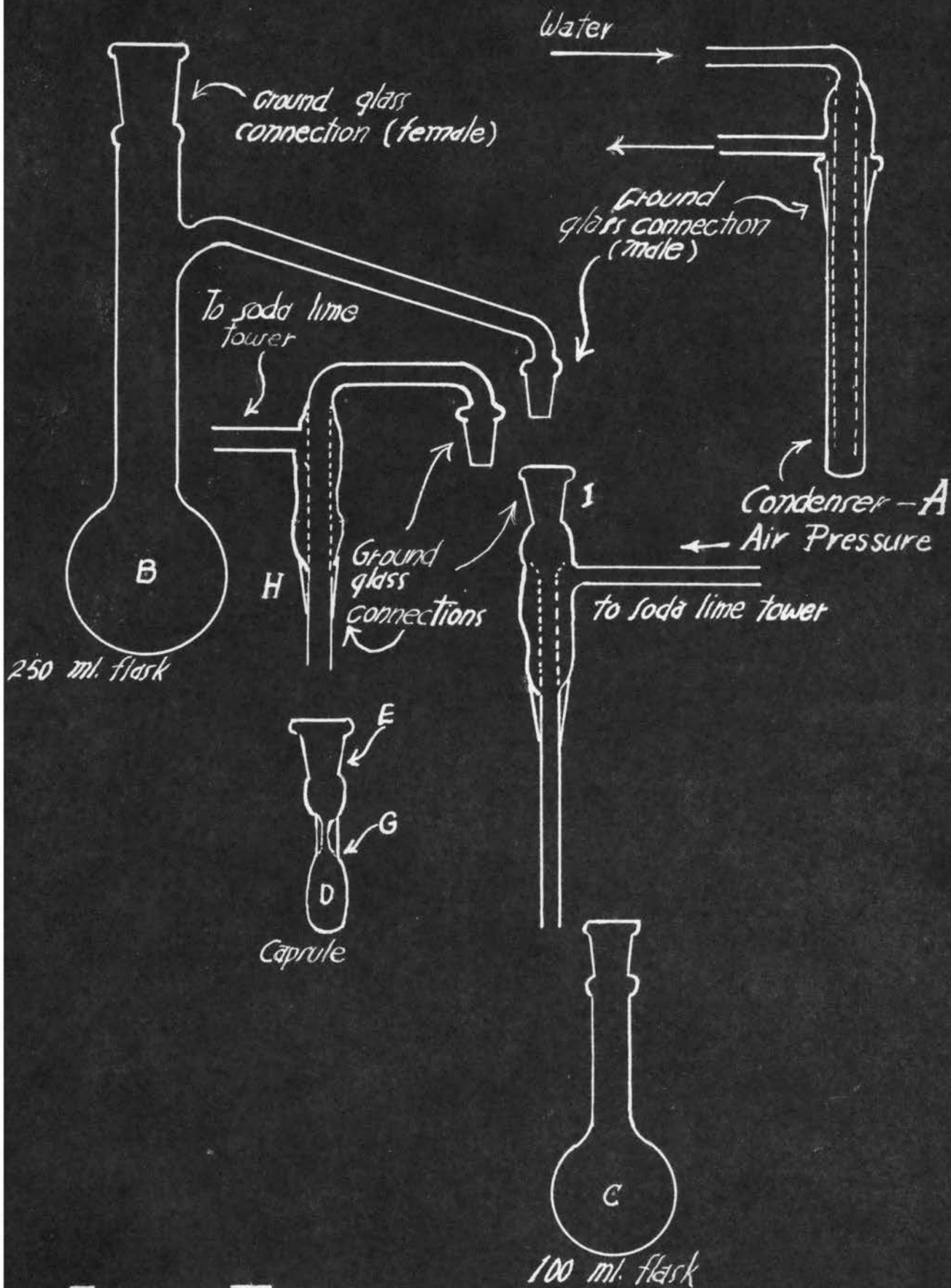


Figure III

enclosed was known, the weight of the mixture was obtained by finding the weight of the empty capsule. Table IV shows the weights of the capsules we worked with, the weights of the mixtures, and the composition of each expressed in per cent, mole fractions, and molality. Eight such samples of varying composition were obtained. Care was exercised at all times to make any changes rapidly, and to insure the absence of any carbon dioxide or moisture.

The following table tabulates data upon the capsules and the mixtures contained in each.

Table IV
Make Up of The Morpholine-Water Samples

Sample	Weight of Capsule	Weight of Morph.-water	Per cent Water	Mole Fraction Water	Molality H ₂ O in Morpholine
II-6	13.89 g.	10.37 g.	81.09	0.954	238.2
II-5	12.42 g.	9.045 g.	75.04	0.935	167.0
I-5	13.42 g.	9.953 g.	66.95	0.907	112.5
I-4	13.47 g.	10.19 g.	61.09	0.884	87.22
II-4	12.48 g.	9.831 g.	49.36	0.825	54.15
I-3	13.59 g.	10.77 g.	39.71	0.761	36.60
II-2	11.95 g.	8.229 g.	28.19	0.655	21.80
I-6	13.65 g.	10.66	17.77	0.511	12.01

Determinations of the heat capacities of each of the eight mixtures were made in the same manner as in the case of the pyrex glass. However, in calculating the change of heat content for each mixture, the corresponding ΔH for the pyrex capsule had to be subtracted from the total

change of heat content. The ΔH for the pyrex glass was read directly from the experimental curves.

The results are given in Tables V to XIII inclusive. In each case the heat evolved per gram of mixture on passing from temperature t° to 0°C is given. The curves in Figure IV were plotted from the data presented in the above tables, and Table XIII tabulates the empirical heat capacity equations found for each mixture.

Table V

Experimental Values for Morpholine-Water Mixture I-6

Temp. ($^\circ\text{C}$)	$\Delta H/\text{gram}$	Temp. ($^\circ\text{C}$)	$\Delta H/\text{gram}$	Temp. ($^\circ\text{C}$)	$\Delta H/\text{gram}$
0.00	0.00	50.30	29.10	100.66	61.99
30.00	16.64	78.90	46.97	124.73	79.61
30.00	16.67	79.13	47.15	124.78	79.26
30.00	17.01	100.43	61.75	124.89	80.18
50.18	28.92	100.50	61.60		

Table VI

Experimental Values for Morpholine-Water Mixture II-2

Temp. ($^\circ\text{C}$)	$\Delta H/\text{gram}$	Temp. ($^\circ\text{C}$)	$\Delta H/\text{gram}$	Temp. ($^\circ\text{C}$)	$\Delta H/\text{gram}$
0.00	0.00	50.90	32.80	101.51	70.47
30.00	18.96	50.96	32.59	101.29	70.12
30.00	19.52	65.10	42.27	101.49	101.49
30.00	19.72	80.71	54.55	120.91	120.91
30.00	18.78	81.35	53.66	128.24	92.72
				128.81	91.63

Table VII

Experimental Values for Morpholine-Water Mixture I-3

Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$
0.00	0.00	50.13	35.59	100.51	75.72
30.00	20.88	50.18	35.43	100.57	76.00
30.00	20.82	78.88	56.51	124.78	97.45
		79.10	56.26	124.80	97.54

Table VIII

Experimental Values for Morpholine-Water Mixture II-4

Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$
0.00	0.00	65.22	51.07	126.20	104.55
30.00	22.44	80.43	63.01	127.06	103.74
30.00	22.85	80.57	63.37	127.55	105.06
30.00	22.72	100.80	81.01		
50.58	40.30	101.00	80.97		
53.10	40.30	101.61	81.89		

Table IX

Experimental Values for Morpholine-Water Mixture I-4

Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$
0.00	0.00	50.11	40.85	100.45	86.18
30.00	24.47	50.13	41.03	100.55	86.91
30.00	24.68	78.83	65.60	124.60	108.68
30.00	23.67	78.88	66.17	124.89	109.96
30.00	23.95				

Table X

Experimental Values for Morpholine-Water Mixture I-5

Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$
0.00	0.00	78.96	67.73	100.45	88.42
30.00	24.43	79.10	68.91	100.57	88.03
30.00	24.72	85.76	73.67	120.92	107.59
50.16	41.52			124.82	111.25
50.22	41.89				
50.13	41.58				

Table XI

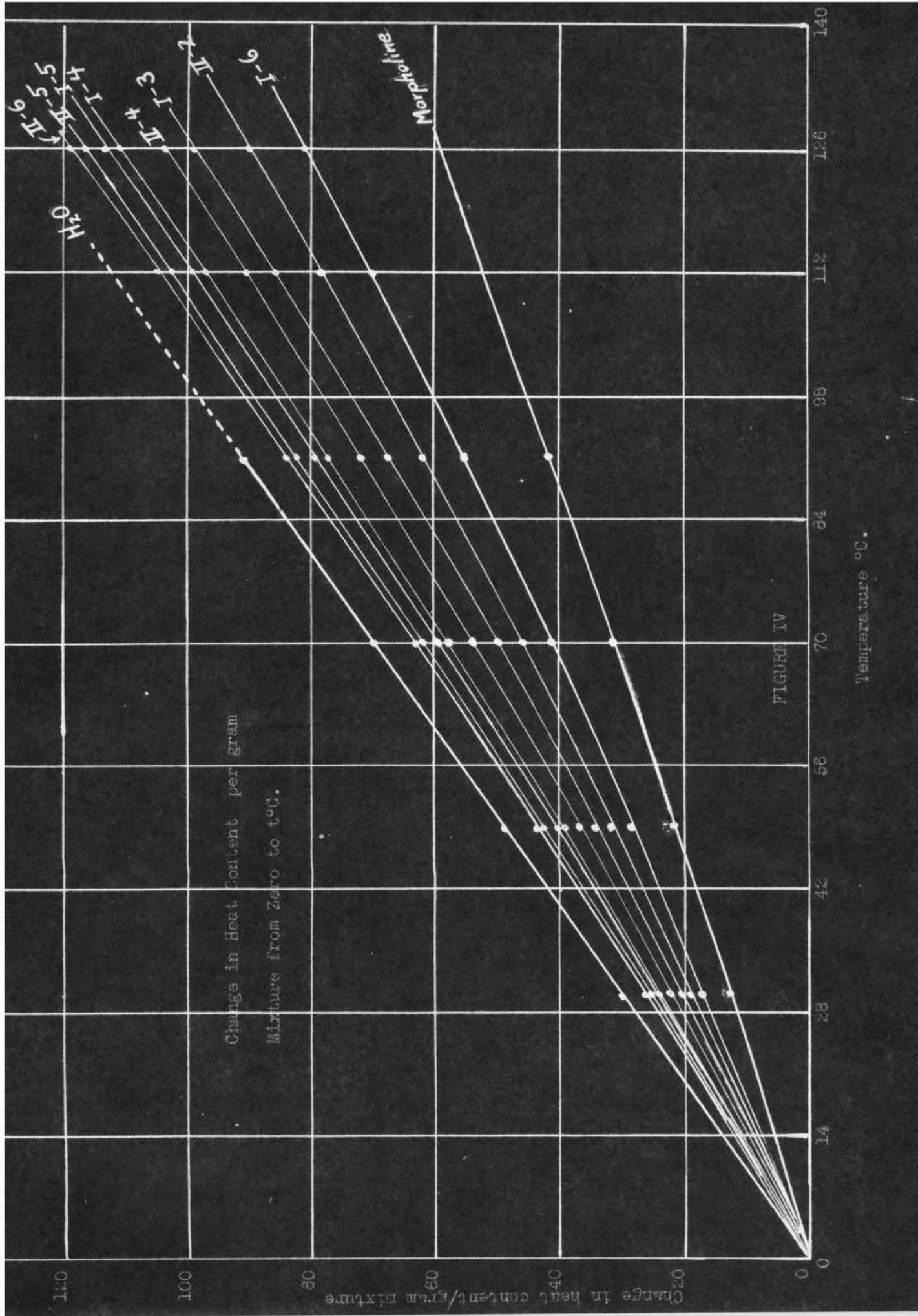
Experimental Values for Morpholine-Water Mixture II-5

Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$
0.00	0.00	78.28	71.09	126.04	116.76
30.00	26.70	80.57	72.19	126.79	126.79
30.00	25.77	80.61	72.04	127.35	127.35
30.00	26.15	81.19	72.92	127.62	117.75
50.74	44.36	81.42	73.71		
50.77	44.45	101.01	91.87		
50.86	44.22	101.01	91.85		
51.21	44.58				
53.28	47.38				

Table XII

Experimental Values for Morpholine-Water Mixture II-6

Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$	Temp. (°C)	$\Delta H/\text{gram}$
0.00	0.00	50.18	45.13	100.50	94.27
30.00	27.43	50.31	45.28	100.74	94.59
30.00	27.36	79.10	72.23	127.35	119.44
30.00	27.27	79.16	72.76	127.49	120.12
		85.54	79.25		



Change in Heat Content per gram
Mixture from Zero to t°C.

FIGURE IV

Temperature °C.

Table XIII

: Table : Per cent: Equations representing change of heat con-
 Mixture: Number : Water : tent per gram from 0°C to temp. t°C (ΔH),
 : : : and heat capacity per gram (C) 0° to 125°C

I-6	V	17.77	$\Delta H = 0.545t + 0.000581t^2 + 0.00000310t^3$ $C = 0.545 + 0.000762t + 0.00000930t^2$
II-2	VI	28.19	$\Delta H = 0.638t + 0.0000833t^2 + 0.00000444t^3$ $C = 0.638 + 0.0001666t + 0.00001332t^2$
I-3	VII	39.71	$\Delta H = 0.681t + 0.000235t^2 + 0.00000405t^3$ $C = 0.681 + 0.000470t + 0.00001215t^2$
II-4	VIII	49.56	$\Delta H = 0.748t + 0.000208t^2 + 0.00000315t^3$ $C = 0.748 + 0.000416t + 0.00000945t^2$
I-4	IX	61.09	$\Delta H = 0.800t + 0.000250t^2 + 0.00000270t^3$ $C = 0.800 + 0.000500t + 0.00000810t^2$
I-5	X	66.95	$\Delta H = 0.817t + 0.000300t^2 + 0.00000220t^3$ $C = 0.817 + 0.000600t + 0.00000660t^2$
II-5	XI	75.04	$\Delta H = 0.860t + 0.000288t^2 + 0.00000150t^3$ $C = 0.860 + 0.000576t + 0.00000450t^2$
II-6	XII	81.09	$\Delta H = 0.900t + 0.000129t^2 + 0.00000138t^3$ $C = 0.900 + 0.000258t + 0.00000414t^2$

The data on the heat capacity of morpholine are by Trimble (18), and those on the heat capacity of water from the equations are by Roth (15). They are represented in the curve of Figure IV.

DISCUSSION AND CONCLUSIONS

The degree of error in the experimental procedure was small. The predominant errors in calorimetric determinations are discussed fully by White (16). The greatest errors are those resulting from thermal leakage, heat of stirring, the variable evaporation of water, and the temperature change measurement. It was estimated that the above errors did not exceed $\pm .1\%$ in all. The capsules could not be filled completely with the liquid mixture because of the danger of bursting when used at higher temperatures. The vapor space above the liquid never exceeded one milliliter. At the higher temperatures, of course, part of the mixtures vaporized. This vapor condensed when the capsule was dropped into the calorimeter, giving up a certain amount of heat. However, this quantity of heat was negligible. The temperature of the heater was measured to within $\pm .10^{\circ}\text{C}$ and as the temperature range through which the samples changed was never less than 20°C , and usually much greater, the error involved would not be greater than $\pm 0.50\%$. The values for the heat capacity of the calorimeter did not vary by more than $\pm 0.53\%$. The accuracy was estimated as being within $\pm 0.53\%$.

At 0°C the degree of accuracy was not so high, due probably to the method of getting the sample to that temperature. The ice bath used to bring the sample to 0°C did not vary in temperature of course, but the sample to be cooled was in a chamber with air containing water vapor and condensation of water occurred on the outside walls of the capsule. This would result in a higher change of heat content for the

sample because of the additional cold water present. The error for the 0°C determination of both the pyrex glass and the morpholine-water mixtures was $\pm 1.0\%$. Attempts to reduce the moisture content of the air surrounding the capsule by forcing it into the chamber through soda lime towers did not improve the results. Evidently the amount of error found in ice bath determinations would decrease if a more successful means for ensuring the presence of water free air were devised.

A comparison of heat capacity values obtained by various experimenters for pyrex glass is of interest. Table XIV gives such a comparison. The values given for the author's work are based on equations obtained by differentiation of equations (1) and (2) above. This comparison seems to indicate that pyrex glass varies enough in composition to require determination of its heat capacity whenever it is used in this type of work.

The heat capacity curves in Figures V, VI, VII, and VIII, indicate that the heat capacities of the mixtures are higher than the mean of the heat capacities of the pure components. Partial molal heat capacities, expressed by the symbol \bar{C} , indicate the apparent heat capacities per mole for each component in a mixture. Partial molal heat capacities of water and morpholine were found by the method of intercepts as described by Lewis and Randall (17). The curves of Figure V, found by plotting heat capacity against per cent by weight of water at 0°, 30°, 50°, 80°, 100°, and 125°C were used for this purpose. A two-inch glass cube was used to obtain tangents to the curves. When its edge was placed at the desired point on the curve and the curve as viewed through the glass appeared as an unbroken line, a line drawn along the edge of the

cube was perpendicular to the tangent at that point. The tangent then was drawn through the point and its intercepts on the respective ordinates for pure water and pure morpholine were read. Thus we secured the partial heat capacities per gram for the two substances at 0, 25, 50, 75, and 100 per cent of water. The partial molal heat capacities, \bar{C} , of the components were calculated by multiplying the partial heat capacities per gram of each substance by its molecular weight. Table XV summarizes the partial molal heat capacities found.

Table XIV

A Comparison of Heat Capacity Data for Pyrex Glass

Temp. °C	Frederick Hildebrand : 25°C-175°C : Equation 1 :	Frederick Hildebrand : 25°C-150°C : Equation 2 :	De Vries : 25°C-175°C : Equation 3 :	Unpublished : Values : 0°C-125°C : Equation 4 :	Brown : Schmuck : 0°C-125°C : Equation 5 :	Brown : Schmuck : 0°C-125°C : Equation 6 :
0				0.163	0.167	0.167
25	0.190	0.186	0.186	0.182	0.185	0.181
50	0.193	0.188	0.193	0.195	0.196	0.193
75	0.202	0.192	0.201	0.206	0.207	0.202
100	0.209	0.197	0.209	0.217	0.214	0.210
125	0.215	0.204	0.217	0.226	0.218	0.215

$$(1) \quad C_p = 0.1141 + 0.0002532t \quad (7)$$

$$(2) \quad C_p = 0.186 + 0.000055 (t - 25) + 0.00000115 (t-25)^2 \quad (8)$$

$$(3) \quad C_p = 0.1839 + 0.0005134 (t - 20^\circ) \quad (9)$$

$$(4) \quad C_p = 0.168 + 0.000306t - 0.000001167t^2 \quad (10)$$

$$(5) \quad C_p = 0.167 + 0.000700t - 0.00000254t^2$$

$$(6) \quad C_p = 0.167 + 0.000592t - 0.00000164t^2$$

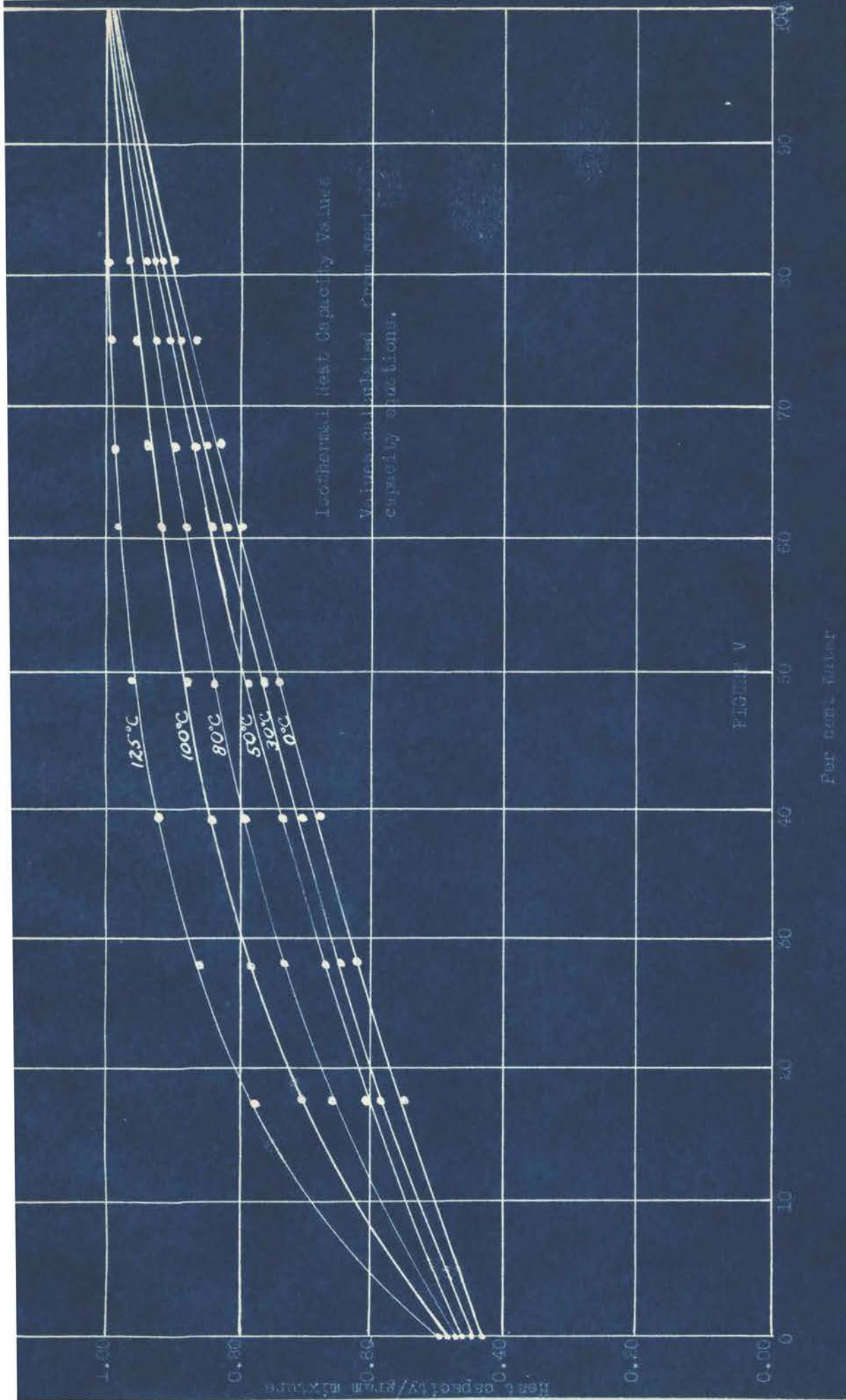
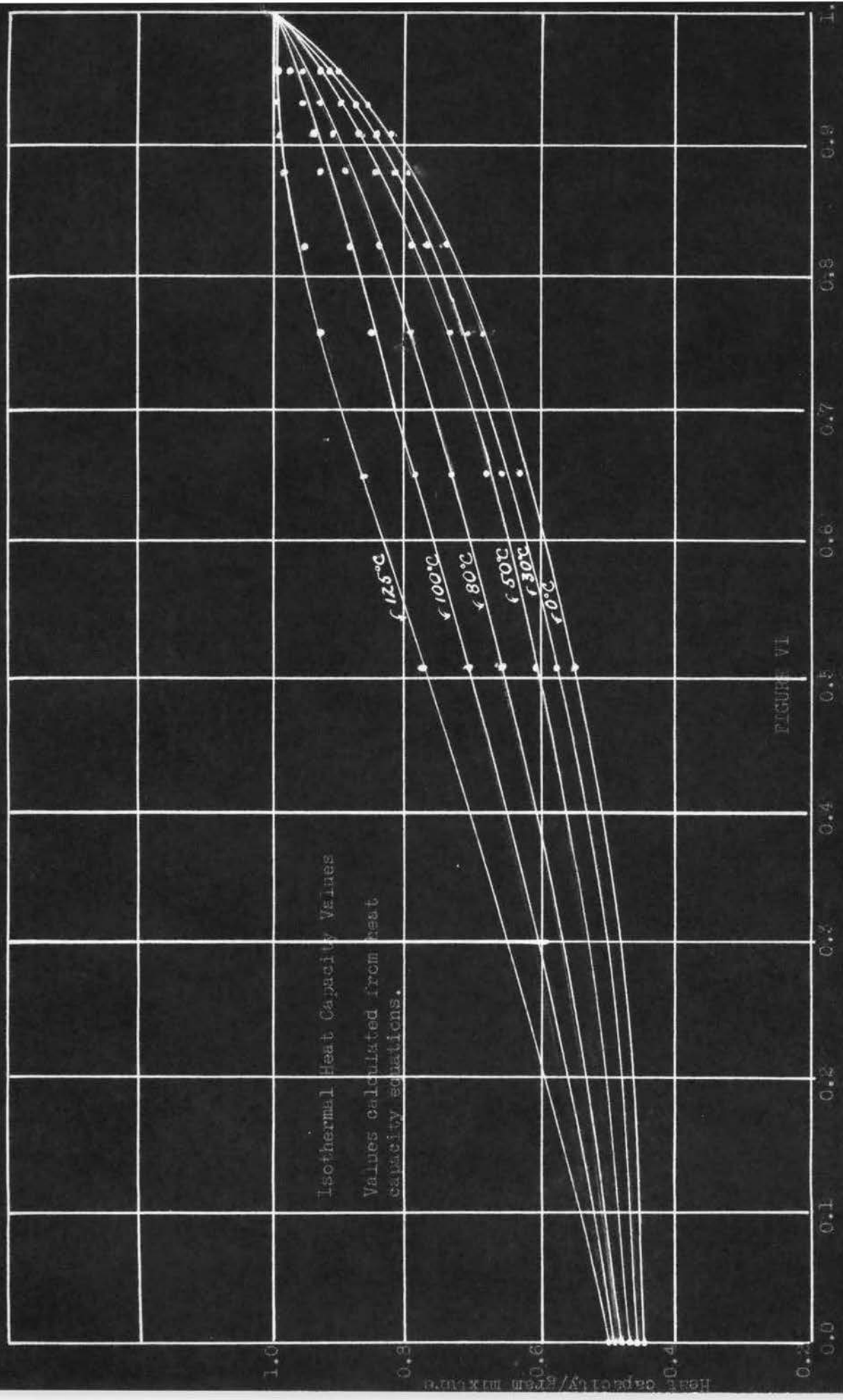


FIGURE V

Isothermal Heat Capacity Values
 Values calculated from ment...

Per cent Water

Heat capacity/gram mixture



Isothermal Heat Capacity Values
 Values calculated from heat
 capacity equations.

FIGURE VI

Mole Fraction Water

1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0

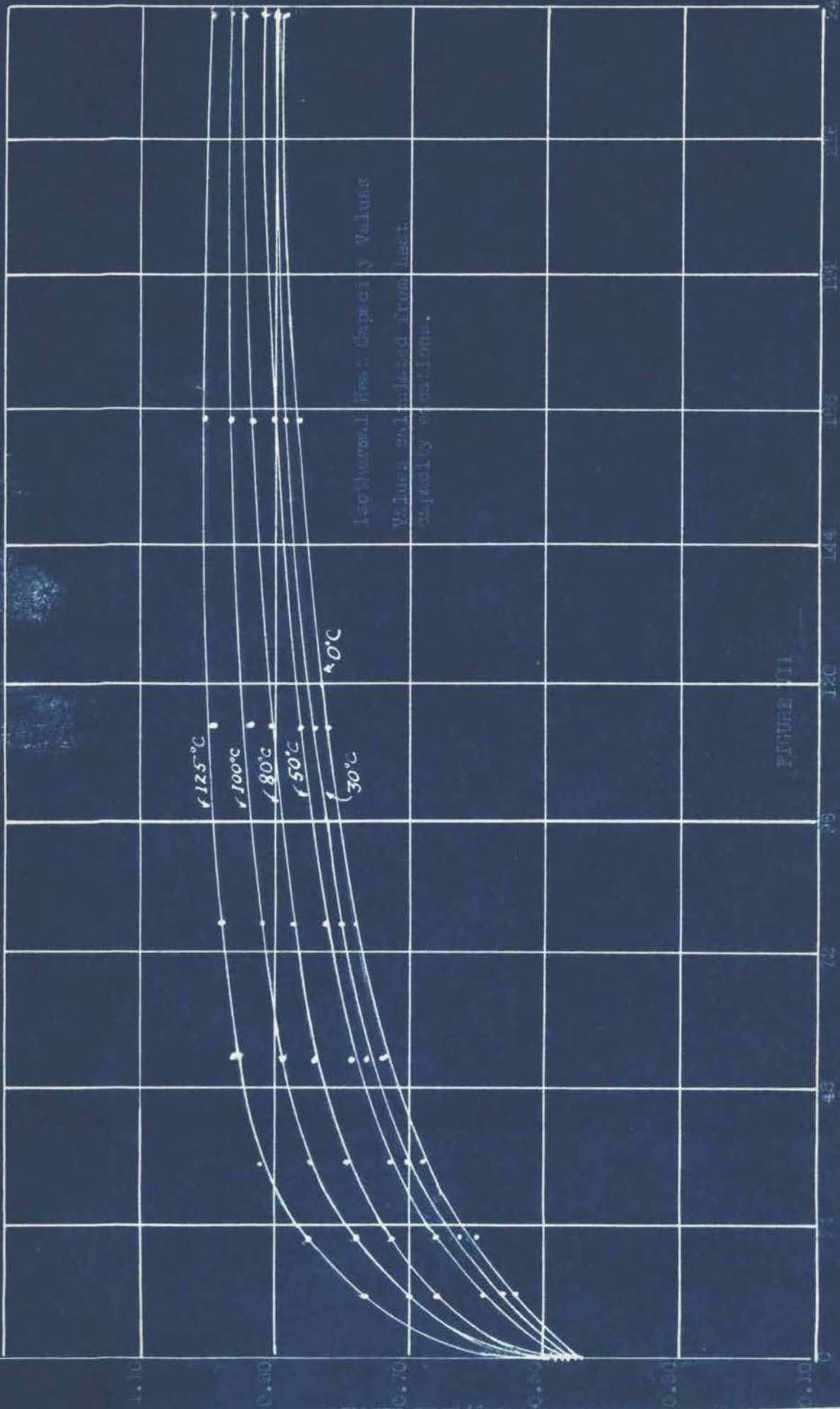


FIGURE III

Isothermal Heat Capacity Values
Values evaluated from heat capacity simulation.

Relativity Water in Mosquito Larvae

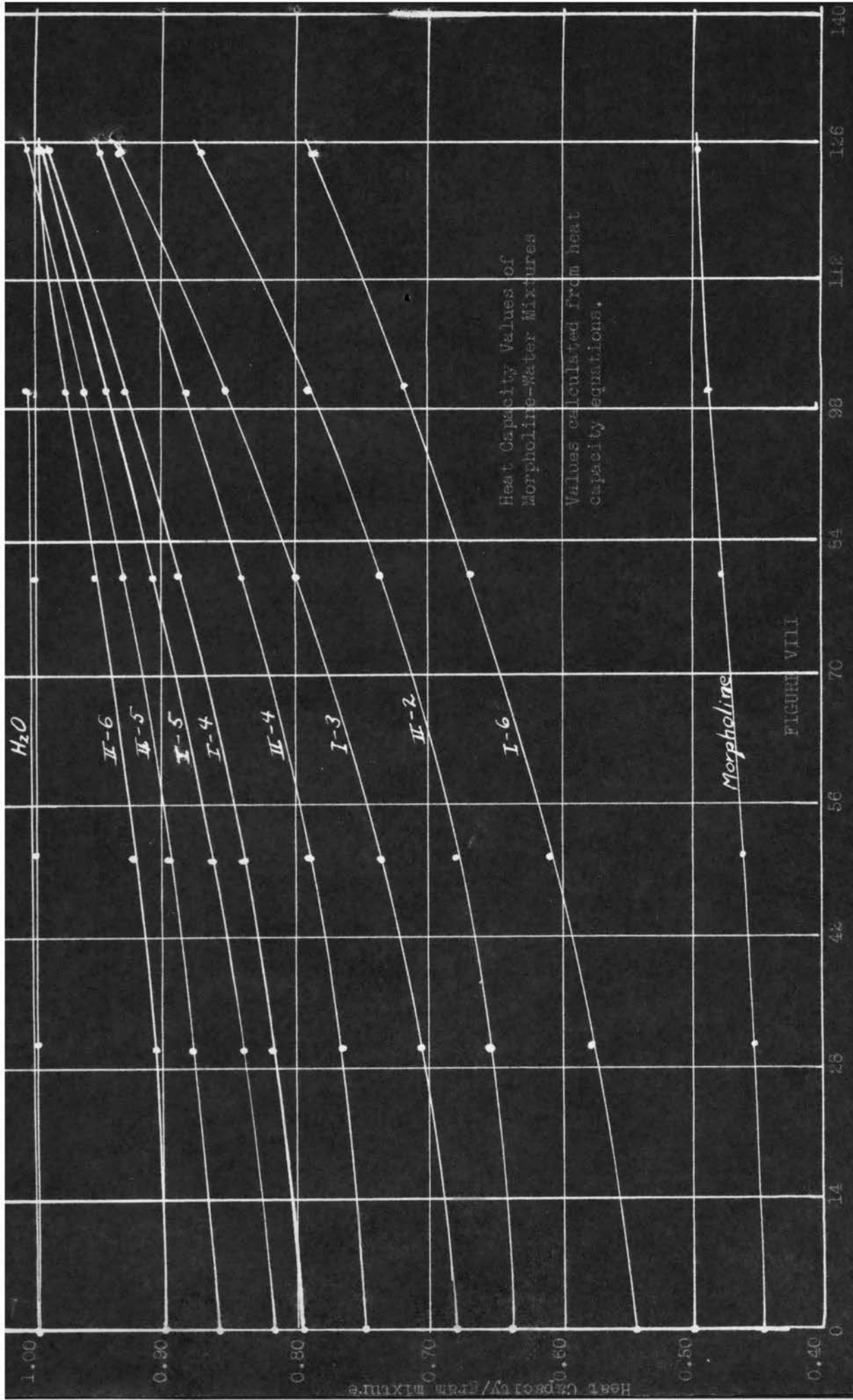


FIGURE VIII
temperature °C.

Table XV

Partial Molal Heat Capacities of Morpholine and Water

Per Cent:						
Water :	Morpholine			Water		
Heat Capa-:	Heat Capa-:	Heat Capa-:	Heat Capa-:	Heat Capa-:	Heat Capa-:	Heat Capa-:
city/gram :	\bar{C}	$\bar{C} - C$	city/gram :	\bar{C}	$\bar{C} - C$	city/gram :
At 0°C						
0.0	.445	38.72	0.00	1.100	19.80	1.67
25.0	.457	39.76	1.04	1.078	19.40	1.27
50.0	.470	40.89	2.17	1.019	18.34	0.21
75.0	.457	39.76	1.13	1.008	18.14	0.01
100.0	.450	39.15	0.43	1.007	18.13	0.00
At 30°C						
0.0	.457	39.76	0.00	1.236	22.25	4.29
25.0	.469	40.80	1.04	1.138	20.48	2.52
50.00	.489	42.54	2.76	1.043	18.77	0.81
75.0	.493	42.89	3.13	1.014	18.25	0.29
100.0	.512	44.54	4.78	.998	17.96	0.00
At 50°C						
0.0	.465	40.46	0.00	1.405	25.29	7.33
25.0	.490	42.33	2.17	1.151	20.72	2.76
50.0	.542	47.15	6.69	1.050	18.90	0.94
75.0	.579	50.37	9.91	1.010	18.18	0.22
100.0	.597	51.94	11.48	.998	17.96	0.00

Table XV
-continued-

Partial Molal Heat Capacities of Morpholine and Water

Per Cent:						
Water :		Morpholine			Water	
:Heat Capa-:		:Heat Capa-:			:	
:city/gram :		:city/gram :			:	
	\bar{C}	$\bar{C} - C$		\bar{C}	$\bar{C} - C$	
At 80°C						
0.0	.476	41.41	0.00	1.835	33.03	14.99
25.0	.548	47.68	6.27	1.253	22.19	4.15
50.0	.629	54.72	13.31	1.073	19.51	1.27
75.0	.690	60.30	18.89	1.020	18.36	0.32
100.0	.698	60.73	19.32	1.002	18.04	0.00
At 100°C						
0.0	.484	42.11	0.00	2.780	50.04	31.91
25.0	.598	52.03	9.92	1.290	23.22	5.09
50.0	.692	60.20	18.09	1.090	19.62	1.49
75.0	.782	63.03	25.92	1.025	18.45	0.32
100.0	.877	76.30	34.99	1.007	18.13	0.00
At 125°C						
0.0	.493	42.89	0.00	3.520	63.36	45.09
25.0	.660	57.42	14.53	1.412	24.42	6.15
50.0	.823	71.60	28.71	1.092	19.66	1.39
75.0	.950	82.65	39.76	1.015	18.27	0.00
100.0	.967	84.13	41.24	1.015	18.27	0.00

The mixing of morpholine with water is an exothermic process (19, 20). This indicates that there is chemical combination between them. It has been suggested that a dihydrate, $C_4H_9ON \cdot 2H_2O$ is formed in a solution containing 70% morpholine and 30% water (20). The results of our experiments furnish further evidence for chemical combination between the two components of this mixture.

It will be noted in Table XV that the partial molal heat capacities for morpholine and water in all their mixtures are greater than their respective molal heat capacities. Data are tabulated in Table XV for the mixtures at various temperatures and the differences are given in the respective columns headed $\bar{C} - C$. Williams and Daniels (21) give two possible explanations for such a situation. One explanation has it that one or both of the components is associated in the pure state, and that these complexes are broken down when they are mixed. As a result, there are more molecules in the mixture than there were in the pure components from which the mixture was formed, and therefore its heat capacity is greater. Pure water is known to be highly associated, and there seems every reason to believe that pure morpholine is also. The dissociation of a compound, however, absorbs heat. The fact that heat is evolved when water and morpholine are mixed indicates that something more than simple dissociation of one or both of the components occurs.

The second explanation for the increase of the partial molal heat capacities of water and morpholine on mixing holds that one or more chemical compounds form between the components; and that a greater quantity of heat is required to raise the temperature of a given quantity of the

mixture through one degree than would be required by its components, taken together, for a similar temperature change, because these compounds are to some extent dissociated in the process. This, we believe, is the more probable of the two explanations. It may be, indeed, that there is preliminary dissociation of water when these substances are mixed, followed by combination of these dissociation products to form intermolecular compounds. If so, the exothermal energy change in the latter process must exceed the endothermal energy change in the former. The changes in heat capacity undoubtedly involve vibration and resonance effects of complex nature as well as kinetic translations and simple dissociations, so one cannot hope for any simple explanation of the phenomenon. Nevertheless, the heat capacity results, taken together with the fact that heat is evolved on mixing, furnish strong evidence for the existence of intermolecular compounds in these mixtures. This work can give no information as to their nature.

It is of interest to note that the increase of partial molal heat content, $\bar{U} - C$, is greater for a given mixture the higher the temperature. Thus it may be seen from Table XV that this difference is 2.17 calories per mole at 0°C for morpholine in a mixture containing 50% of it by weight. This difference increases regularly up to 125°C where it has risen to 28.71 calories for this component in the same mixture. The $\bar{U} - C$ values for water also show a progressive increase with rising temperature. This may be due to a greater degree of compound dissociation at higher temperatures. However, the full explanation of these facts is difficult or impossible in the present state of our knowledge.

Undoubtedly, evidence from the study of many other properties of this system must be at hand before the molecular makeup of its mixtures can be elucidated.

SUMMARY

The heat capacities of pyrex glass and morpholine-water mixtures have been determined employing the method of mixtures. The results have been presented in tables and graphs. In the case of pyrex glass, a comparison with other existing data has been presented. Empirical equations for the change of heat content with temperature of pyrex glass and the mixtures have been formulated. Partial molal heat capacities obtained for the components of the mixture lend support to the belief that compound formation or association occurs on mixing.

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BIOGRAPHIES

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Ralph Andres Brown was born at Glenwood, Minnesota, on April 19, 1917. He was graduated from Glenwood High School in June, 1935. He received his undergraduate training at Hamline University in St. Paul, Minnesota, and was graduated with the Bachelor of Science Degree in June, 1939. From September 1939 to June 1941, he served as a Graduate Assistant in the Chemistry Department of Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma.

Robert Frederick Schmuck was born at Buffalo, New York, on October 23, 1916. He attended schools in the following cities during the first eight years of his schooling: Buffalo, New York; Saginaw, Michigan; Bremerton, Washington; Longview, Washington; Salem, Oregon; and Sante Fe, New Mexico. He was graduated from Santa Fe High School in May, 1934. His first year of college was taken at Humboldt State College, Arcata, California, and the next three years at the University of California, Berkeley, California, from which he was graduated in May of 1938 with a degree of Bachelor of Science in Chemistry. From July, 1938 to September, 1939, he was employed by the Martin Oil Company of Pheonix, Arizona. From September, 1939, to June, 1941, he did graduate work in chemistry, and was a Graduate Assistant in the Department of Chemistry at Oklahoma Agricultural and Mechanical College, Stillwater, Oklahoma.

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