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The heat of mixing of diactone alcohol and water at 25 C

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THE HEAT OF MIXING
OF DIACETONE ALCOHOL AND WATER
AT 25°C

BY

FREDERIC M. KONRAD

A THESIS
SUBMITTED TO THE FACULTY OF
THE DEPARTMENT OF CHEMICAL ENGINEERING
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Abstract

A calorimeter of twin design with auxillary apparatus was built for measuring the heat of mixing with a maximum error of $\pm 1.0\%$. Reliability of the apparatus was tested with the benzene-methanol system and gave results comparable to those of other investigators with apparatus of different design.

The heat of mixing of diacetone alcohol and water was measured at 25°C over the entire concentration range. A peak value of 238 cal/mole solution was obtained at 0.67 mole fraction water the mixing of two moles water with one of diacetone alcohol.

Specific heat of diacetone alcohol-water mixtures was also measured at 25°C with the same apparatus.

APPROVAL OF THESIS

FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

NEWARK, NEW JERSEY

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INTRODUCTION

Enthalpy changes due to mixing of liquids is an important factor in many industrial processes. The effect in distillation design calculations by the Ponchon enthalpy method is well known. Several methods (10,12,14) for predicting heat of mixing from vapor pressure data, latent heat of vaporization, and volume changes give orders of magnitude but usually vary considerably from the real value.

This work was undertaken to design equipment for determining the heat of mixing and to obtain data for testing correlations with other properties.

Diacetone alcohol has found use as a solvent for the separation of hydrocarbon mixtures. The alcohol is recovered by washing the hydrocarbon with water and purified by distillation. Recently an investigation⁽¹⁾ of the vapor-liquid equilibrium of diacetone alcohol and water indicated wide divergence from ideality and suggested large heat effects due to mixing. Data were obtained for this system at 25°C which can be used to test correlations of the heat of mixing with other physical properties of the system. These methods are reviewed and provide a basis for further investigation.

THEORETICAL

A number of methods have been proposed and tested for calculating the heat of mixing based on the physical properties of the pure components and the characteristics of the solution.

Vold⁽²²⁾ tested Hildebrands⁽²⁾ general solubility equation with carbon tetrachloride solutions by assuming regular solutions (one involving no entropy change when a small amount of one of its components is transferred from an ideal solution of the same composition and the total volume remains unchanged).

$$\Delta H = \frac{N_1 V_1 N_2 V_2}{N_1 V_1 + N_2 V_2} \left[\left(\frac{E_1^*}{V_1} \right)^{1/2} - \left(\frac{E_2^*}{V_2} \right)^{1/2} \right]^2 = \frac{N_1 V_1 N_2 V_2}{N_1 V_1 + N_2 V_2} D_{12}^2$$

E_1^* and E_2^* = energies of vaporization of the two pure liquids to an infinitely dilute value

N_1 and N_2 = mole fractions of components

V_1 and V_2 = molal volume of the pure liquids

D_{12}^2 = square of the difference between the square roots of the internal pressure of the two liquids

Vold concluded that satisfactory results could be obtained if a single determined value was used to evaluate the vaporization energy term. It was also shown that fair agreement was obtained for

tetrachloride mixtures when the parameter D_{12}^2 was calculated from E°/V values.

Scatchard^(14 - 18) has calculated the thermodynamic functions of mixtures, including the free energy and entropy of mixing, from vapor-liquid equilibrium data for a number of systems. The heat of mixing at constant volume is the sum of the free energy and entropy of mixing. It was assumed that $\left[F_x^E \right]$

$$H_x^M = F_x^E + TS_x^E$$

varied linearly over the temperature range studied (20°C to 50°C) and that the entropy was a linear function of temperature

$$S_x^E (tm) = \frac{F_x^E (t_1) - F_x^E (t_2)}{t_2 - t_1}$$

Free energy values were calculated from excess chemical potentials of the pure components. These values were based on vapor-liquid equilibrium and vapor pressure data for a binary mixture over the entire composition range at two different temperatures

$$\mu_1^E = RT \ln P_{y1}/P_1x_1 + (B_1 - V_1) (P - P_1)$$

$$\mu_2^E = RT \ln P_{y2}/P_2x_2 + (B_2 - V_2) (P - P_2)$$

where	V_1 and V_2	= molal volume of each component
	x_1 and x_2	= mole fractions in liquid
	y_1 and y_2	= mole fractions in vapor
	P	= vapor pressure of solution
	P_1 and P_2	= vapor pressure of pure components
	B_1 and B_2	= characteristic temperature function of each component calculated from theory of corresponding states

These equations were used to calculate the heat of mixing benzene-methanol solutions⁽¹⁴⁾ (Table IV) and although the values were significantly higher than values actually measured by Scatchard⁽¹⁴⁾ the same asymmetry is shown with a maximum at 70 mole percent benzene.

The change in slope of a log log plot of solution vapor pressure versus the vapor pressure of a pure component was used as a basis for calculating the partial molal heat of dilution by Othmer⁽¹¹⁾. A second paper⁽¹²⁾ gives a correlation of the partial molal heat of solution with activity coefficient and latent heat of vaporization.

$$\log \gamma_1 = \frac{H_1}{L_1} (\log p_1^\circ) + C$$

γ = activity coefficient of component

H_1 = partial heat of solution of component

L_1° = molal latent heat of vaporization

p_1° = vapor pressure of pure component at given temperature

This method yielded values about 10% higher than experimental for the hydrochloric acid-water system.

Mertes and Colburn⁽¹⁰⁾ used a similar method to determine the heat of dilution of furfural-hydrocarbon mixtures

$$\frac{d \log \gamma_1}{d (1/T)} = \frac{L_1}{2.303 R}$$

where L_1 = partial molal heat of solution

γ_1 = activity coefficient

EXPERIMENTAL

HEAT OF MIXING DETERMINATION

Calorimeter Design

The calorimeter was of twin design where mixing was carried out in one vessel and the second was used as a temperature reference. Mixing heats were compared to those of a known amount of electrical energy. For endothermal mixing the process was isothermal; electrical energy was supplied to compensate for the heat of mixing and the temperature was held constant. In exothermic work the rate of heating due to mixing was observed and subsequently duplicated in the same apparatus. Design and operation followed the recommendations of Swietoslawski⁽²⁰⁾. Twin design and the method of comparative measurement negates such errors as heat input due to agitation, vaporization and condensation, radiation, and rate of conduction and eliminates the application of doubtful corrections.

Calorimeter Proper

A diagram of the calorimeters is shown in Fig. 1. Silvered, vacuum jacketed, Dewar flasks each holding about 1600 ml. were used as the calorimeters. An 18 gauge copper collar 3/4" x 3/4" was sealed around the lip of each flask for support in the submarine can. Bakelite ERL-3003 epoxy resin with 25% HR-18793 amine hardner was used for sealing; the cement also served as an insulation

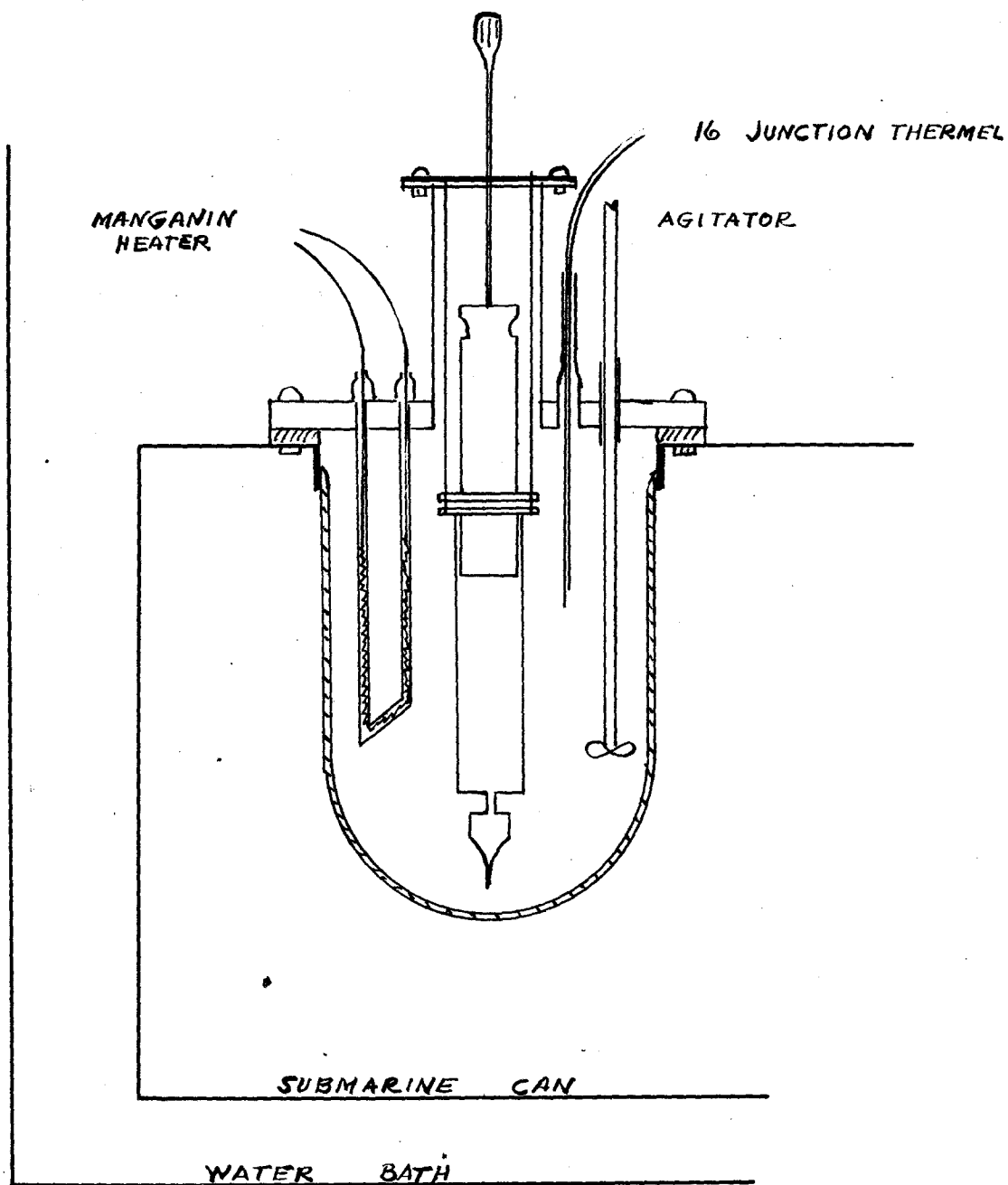
barrier. A brass cover plate $1\frac{1}{4}$ " x $7\frac{1}{2}$ " O.D. containing parts for the heater, agitator, mixing pipette and thermel was bolted through the collar with a $1\frac{1}{4}$ " Garlock rubber gasket to make a water tight seal and to serve as an insulation barrier. The calorimeters were bolted to the top of an 18 gauge copper submarine can 10 " x 15 " x 18 " through two $6\frac{7}{8}$ " dia. holes, 10 inches from center to center. A $1\frac{1}{4}$ " Garlock rubber gasket was used between the calorimeter collar and the can to make a water light seal.

Heater leads and the glass heating jacket was sealed through $1\frac{1}{4}$ " brass compression fittings and $1\frac{1}{4}$ " Saran tubing with epoxy resin. The 16 junction thermel was sealed through the cover with a $1\frac{1}{2}$ " compression fitting with copper tubing in the same manner. The jacket did not extend down into the calorimeter so that the thermocouple junctions were in direct contact with the liquid to give rapid response.

A $3\frac{3}{8}$ " ground glass shaft and bearing with a 1" Teflon paddle was used for agitation. The bearing was sealed through the cover with epoxy cement. A glass tube surrounded the bearing and shaft to the water level of the bath to insure a water tight seal. The agitators were turned at 100 R.P.M. with an electronic controlled variable speed d.c. motor. The shaft was split with a piece of rubber pressure tubing inserted to act as an insulation barrier. No significant change in temperature differential or temperature rise in the calorimeters was noted after agitation for eight hours. Dow-Corning

FIG 1

DIAGRAM OF CALORIMETER



Silicone grease was used to lubricate the bearing. The lower end of the bearing was not in contact with liquids in the vessel.

Hypodermic syringes holding 100 ml. were used to introduce the second liquid. They entered the calorimeter through a 6" x 2" I.D. brass tube which extended above the cover plate and was soldered to the center of the plate with a lap joint. The 6" tube was necessary to contain the plunger when the syringe was full of liquid. The syringe barrel was suspended down into the liquid by 1/8" bronze rods from a 3" brass cover plate which bolted to a 3/4" collar soldered to the top of the tube. The 1/8" rods were fastened to the syringe barrel with Teflon collars.

A 22 gauge needle was used on the syringe. During the course of the work difficulty was encountered with premixing of the liquids by diffusion through the needle. This was eliminated by sealing the needle with Dow-Corning silicone grease. Blank tests indicated no heat effects due to the grease with the systems employed.

The syringe plunger was operated with a 1/8" bronze rod cemented to the top of the plunger which extended through the cover plate and above the water level of the bath. The plunger rod was sealed through the cover with vinyl tubing. All reagents were weighed; the syringe was used only as a dispensing apparatus.

The submarine can was immersed in a constant temperature water bath controlled to $25.00 \pm 0.01^{\circ}\text{C}$. A "Magna-Set" thermoregulator and a mercury switch electronic relay were used for temperature control by regulating the heat supplied by three 200 watts nichrome heaters encased in copper tubing. Each heater was five feet long and insured rapid heat dissipation over a large surface. The bath contained about 30 gallons of water and was agitated with an Aminco centrifugal pump mixer.

Heating circuit

The heat of mixing was compared to the heat supplied by a manganin coil. The coil was made by wrapping six feet of #38 manganin wire on a glass $1/8"$ rod. The coil was sealed in a U-shaped 5 mm x 450 mm glass tube filled with kerosene. Resistance of the coil at 25°C was 66.62 ohms measured with a Wheatstone bridge. Copper leads (#20 wire) were soldered to the coil and extended 7 cm. into each end of the glass tube. A constant six volt circuit was supplied by a Mallory full wave selenium rectifier, Model 65AC6. Input to the rectifier was maintained constant with a Raytheon type VR-C 112 CP voltage stabilizer operating at 60 watts, 60 cycles and a 100% power factor. Output was 115 volts for line variations of 95 to 130 volts. The circuit also included a 120 ohm Bechro variable rheostat, a Weston Model 1 direct current milliammeter (Serial #60413) with a .320 ohm resistance on the 150 ma. range, and a relay switch

FIG 2.



- A

VOLTAGE STABILIZER

- Ⓑ

SELENIUM RECTIFIER 110V.A.C. \rightarrow 6V.D.C.

- C

MILLIAM METER

- (d)

100 OHM VARIABLE RESISTOR

- E

RELAY SWITCH

- F

MANGANIN HEATER

- 

TIMER SWITCH

- (H)

ELECTRIC TIMER.

(H.B. Instrument Co. No. 7970) connected in series with the manganin coil. The relay coil was connected in parallel with an electric timer graduated to 0.2 seconds so that the heating circuit was opened and closed simultaneously with starting and stopping of the timer. A toggle switch was also placed in series with the heating circuit so that the timer could be used without applying heat to the calorimeter. The manganin heater had an energy input of 10.73 cal/min. at 106 milliamperes. A circuit diagram is shown in Fig. 2.

Thermoelectric circuit

Temperature differentials between calorimeters was measured with a Leeds and Northrup type K-2 potentiometer using a type A Leeds and Northrup galvanometer as a null instrument. The potentiometer has a five meter manganin slide wire graduated to 0.1 microvolts. A 200 ohm external damping resistance was used with the galvanometer which had a 15.9 ohm internal resistance, 4.7 sec. period, and a 35 ohm critical damping resistance. Sensitivity of this instrument was 0.27 microvolts per millimeter on a scale at one-half meter. This is equivalent to 0.00084°C per mm scale deflection with the 16 junction #24 gauge chromel-alumel thermopile. Junctions were made with silver solder and borax flux. The thermopile had an electromotive force of 323.2 microvolts per $^{\circ}\text{C}$.

When measuring endothermal heats this apparatus was used as a null instrument for the temperature was held constant by balancing with a constant heat input. For exothermic mixing the temperature rise was recorded and was subsequently duplicated by electrical heating.

Reagents

Diacetone alcohol used in these studies was obtained from the Fisher Scientific Co. (cat. no. D-17) and contained about 15% acetone. It was purified by fractional distillation in a two inch I.D. column, 60 inches high filled with 1/4" stainless steel Cannon protruded packing. The distillation was carried out at 15 mm. Hg and a reflux ratio of nine. A "heart" cut was taken which represented 51% of the original material and had a boiling range of 60.7 to 61.8°C at 15 mm. Hg. Density and refractive index measurements are shown in Table I.

Demineralized water boiled to expel dissolved gases was used in the diacetone alcohol-water studies.

Anhydrous methanol was obtained by distillation of a C.P. grade over magnesium methoxide and collected under a dry nitrogen atmosphere. Reagent benzene was dried by distillation. Properties of these reagents are also shown in Table I. All densities were measured with a pycnometer at 25°C and referred to water at 4°C. The refractive index of these reagents was measured with a Bauch and Lomb Abbe' refractometer.

TABLE I
REAGENT PROPERTIES

		<u>Diacetone</u> <u>alcohol</u>	<u>Water</u>	<u>Methanol</u>	<u>Benzene</u>
Refractive Index D ²⁵	(experimental)	1.4215	1.3328	1.3270	1.4988
	(literature)	1.4235 @20 (8)	1.3323 (4)	1.3277 (4)	1.4979 (5)
		1.4300 @ 9 (3)			
Density (25/4)	(experimental)	0.9286	-	0.7851	0.8725
	(literature)	0.9306 (3)	-	0.7859 (6)	0.8729 (7)

Benzene-Methanol Calibration

Benzene-methanol was used to determine the reliability of the equipment for two reasons: (1) the reagents were made readily available in pure form, and (2) confirmatory data has been obtained on this system by a number of investigators. The heat of mixing was determined by charging benzene to the calorimeter and methanol to the pipette and the system was allowed to attain thermal equilibrium. The solvents were preheated to 25°C by storing them in the constant temperature bath at least 24 hours prior to charging. Eight hours were usually required before the calorimeter came to equilibrium after charging. A 50 mole percent solution was used in the reference calorimeter. Equilibrium was assumed when the differential was maintained at ± 0.5 microvolts between calorimeters.

During the determination the pipette was discharged and heat was supplied by the manganin coil simultaneously. The rate of discharge was regulated so as to maintain the temperature differential within $\pm 0.005^\circ\text{C}$. After addition of all of the methanol the syringe was flushed twice by drawing solution back into the chamber and discharging it. After flushing, the temperature differential was restored to the original value before mixing. By this procedure the required heating time could be determined within ± 0.05 minutes which is equivalent to 0.5 calories. The bulk of the measurements were 100 calories or greater so that the timing error was $\pm 0.5\%$ or less.

Subsequent solutions and a series of measurements were made by withdrawing a known amount of the last solution equivalent to the next methanol charge. All solvents and solutions were weighed to 0.1 g. The amount of heat removed with the solutions withdrawn was subtracted from the total heat observed in the next measurement to give the net heat of mixing. Solution concentrations and heat of mixing calculations are shown in the Appendix.

The initial results determined at 30°C are shown in Table II and are plotted in Fig. 3. along with values of Williams⁽²³⁾ and Scatchard⁽¹³⁾ and were low with respect to previous work. The measurements were repeated at 25°C to determine the effect of temperature; the Williams data was for 25°C and Scatchard's values were measured at 20°C. Similar low results were obtained (Table III). It was noted that in some cases exceptionally long periods of time were required to attain thermal equilibrium after charging and suggested that some premixing may have taken place due to diffusion through the hypodermic needle. This loss would accumulate in a series of measurements and account for the low results.

The measurements at 25°C were repeated with the hypodermic needle sealed with Dow-Corning Silicone grease to prevent diffusion during the time necessary to establish equilibrium. Blank tests with both solvents indicated no heat effects due to the small amount of grease (ca. 10

TABLE II

HEAT OF MIXING OF BENZENE-METHANOL
SOLUTIONS; DATA SHOWING THE EFFECTS OF DIFFUSION

<u>Exp.</u> <u>No.</u>	<u>Mole Fraction</u> <u>Benzene</u>	<u>Heat of</u> <u>Solution</u> (Cal/Mole Sol'n)
1	0.953	79
2	.905	111
3	.838	137
4	.747	143
5	.669	143
6	.596	135
7	.527	124
21	.456	77
20	.425	75
19	.396	71
18	.362	60
17	.329	51
16	.297	42
15	.265	32
14	.241	26
13	.210	22
12	.161	18
11	.127	13
10	.093	10
9	.060	6
8	.030	3

TABLE III

HEAT OF MIXING OF BENZENE-METHANOL
SOLUTIONS AT 25°C: DATA SHOWING THE
EFFECT OF DIFFUSION

<u>Exp. No.</u>	<u>Mole Fraction Benzene</u>	<u>Heat of Solution</u>
22	0.908	123
23	.831	140
24	.725	146
25	.631	141
26	.549	131
27	.484	121

FIGURE 3
HEAT OF MIXING OF BENZENE
METHANOL SOLUTIONS SHOWING
THE EFFECT OF DIFFUSION
THROUGH THE SYRINGE NEEDLE

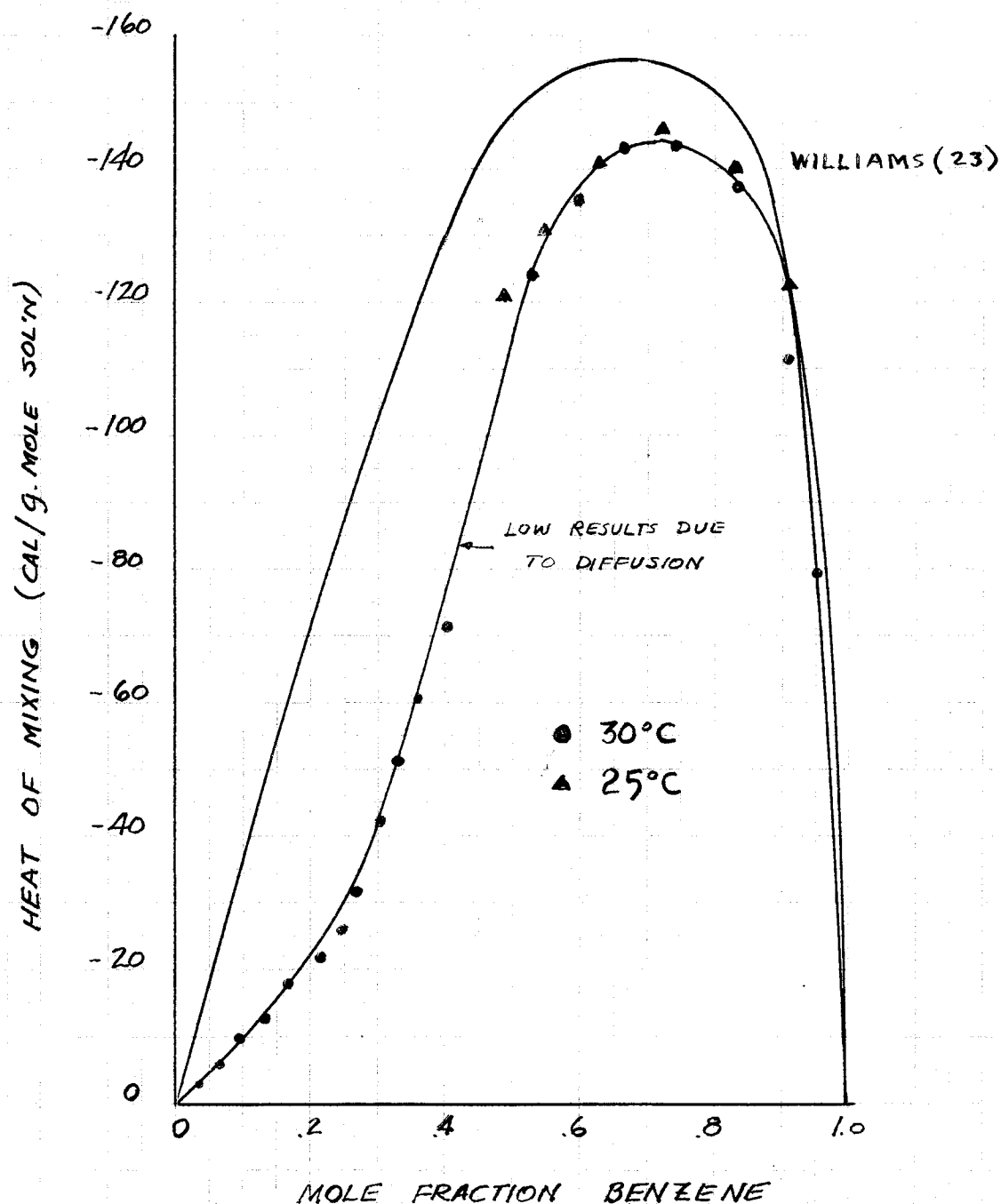


FIG 4

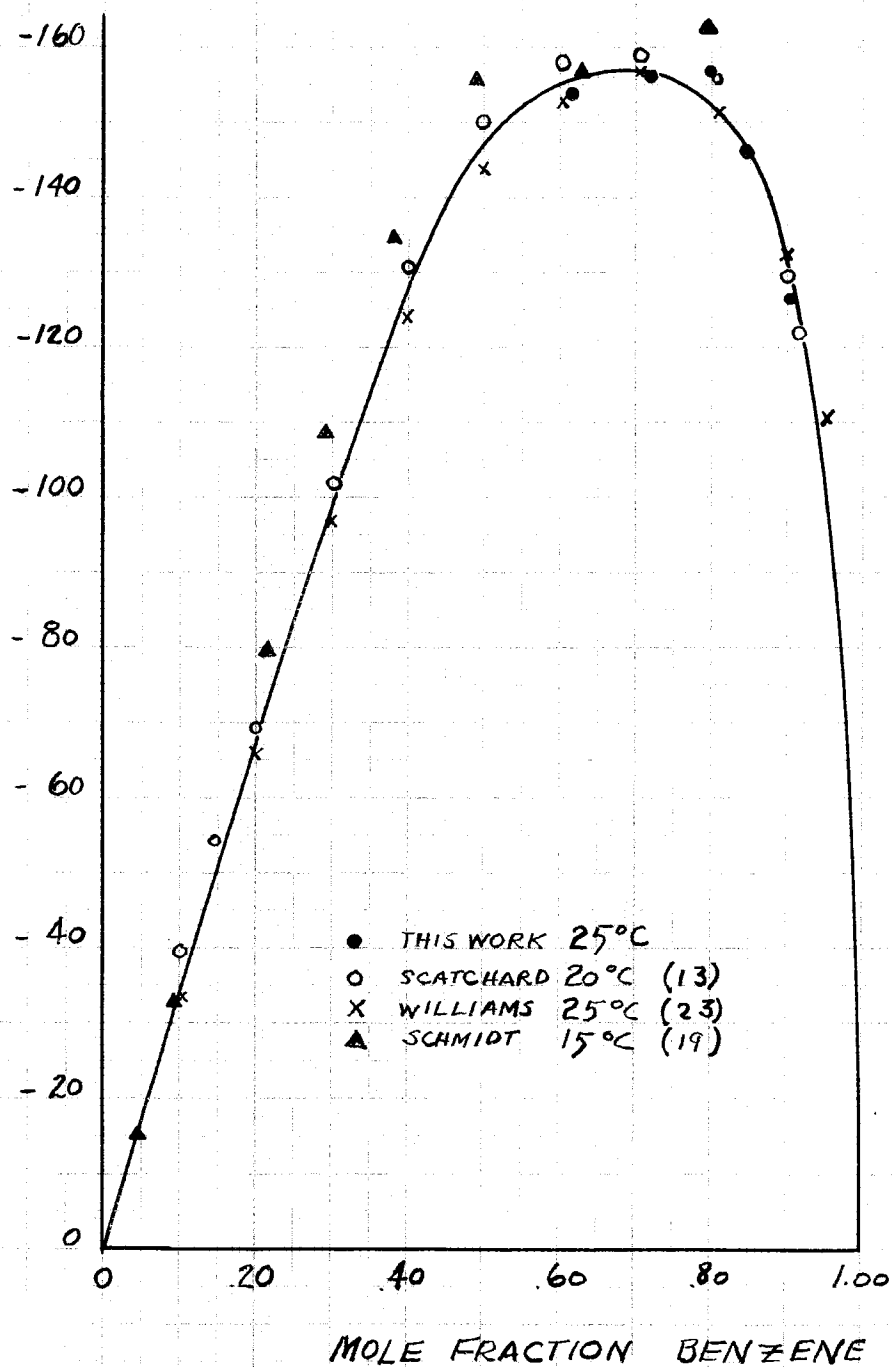
HEAT OF MIXING
BENZENE - METHANOL

TABLE IV

HEAT OF MIXING FOR BENZENE-METHANOL;
 COMPARISON OF THIS WORK WITH OTHER INVESTIGATORS
 (Conc. in Mole Fraction Benzene; ΔH in Cal/Mole Solution)

THIS WORK		SCATCHARD (13)		WILLIAMS (23)		SCATCHARD (14*)		SCHMIDT (19)		WOLF (24)	
Conc.	$\Delta H_{25^\circ C}$	Conc.	$\Delta H_{20^\circ C}$	Conc.	$\Delta H_{25^\circ C}$	Conc.	$\Delta H_{45^\circ C}$	Conc.	$\Delta H_{15^\circ C}$	Conc.	$\Delta H_{20^\circ C}$
-	-	0.1	40.0	0.1	33.0	0.1	56	.044	15.0	-	-
-	-	0.2	69.6	0.2	66.0	0.2	99	.093	33.0	-	-
-	-	0.3	102	0.3	97.0	0.3	139	.146	54.5	-	-
-	-	0.4	131	0.4	124	0.4	180	.215	80.0	0.25	75
-	-	0.5	150	0.5	144	0.5	220	.292	109	-	-
.612	154	0.6	158	0.6	153	0.6	254	.381	135	-	-
.710	156	0.7	159	0.7	157	0.7	268	.487	156	0.50	155
.787	157	0.8	156	0.8	151	0.8	247	.618	157	-	-
.836	146	-	-	-	-	0.9	167	.790	163	0.75	192
.910	126	0.9	129	0.9	132						
.911	122			0.95	110						

*Calculated Values

milligrams). These repeat measurements which gave results consistent with those of Scatchard and Williams are shown in Table IV. The values are plotted against benzene concentration in Fig. 4. A peak value of 157 cal./mole solution was obtained at 70 mole percent benzene as compared to Scatchard's value of 159 @ 20°C, Williams' at 157 also at 25°C, and Schmidt's 163 at 15°C. The data was also confirmed by Thacker and Rowlinson⁽²¹⁾ at 25°C.

Diacetone Alcohol-Water System

The mixing of diacetone alcohol and water at 25°C gives a exothermic effect. In these studies water was added to diacetone alcohol over a predetermine length of time (usually one to two hours) and the rate of temperature rise was recorded and plotted. The solution was then allowed to cool back to 25°C by placing a cold finger in place of the pipette and running 20°C water through it. The pipette was replaced and equilibrium was again established. Heat was then applied at a rate to give a temperature rise equivalent to that obtained during the mixing. Typical heating curves are shown in Figures 5 and 6. The heating and mixing exotherms were duplicated fairly accurately; the area under the curves shown agree within 2.5%. However the negligible effect of varying the heating and mixing time significantly was demonstrated by repeating the heating in experiment 29 at 7.03 cal./min. At this rate the heating time was 83 minutes as compared to 54.3 minutes at 10.63 cal./min. and gave a heat of mixing

FIG 5
TYPICAL HEATING CURVE

EXPERIMENT 29

10.90 MOLES SOLUTION
5.50 MOLE % WATER

HEATING RATE - 10.63 CAL./MIN
HEATING TIME - 54.3 MIN
HEAT OF MIXING - 577 CAL.

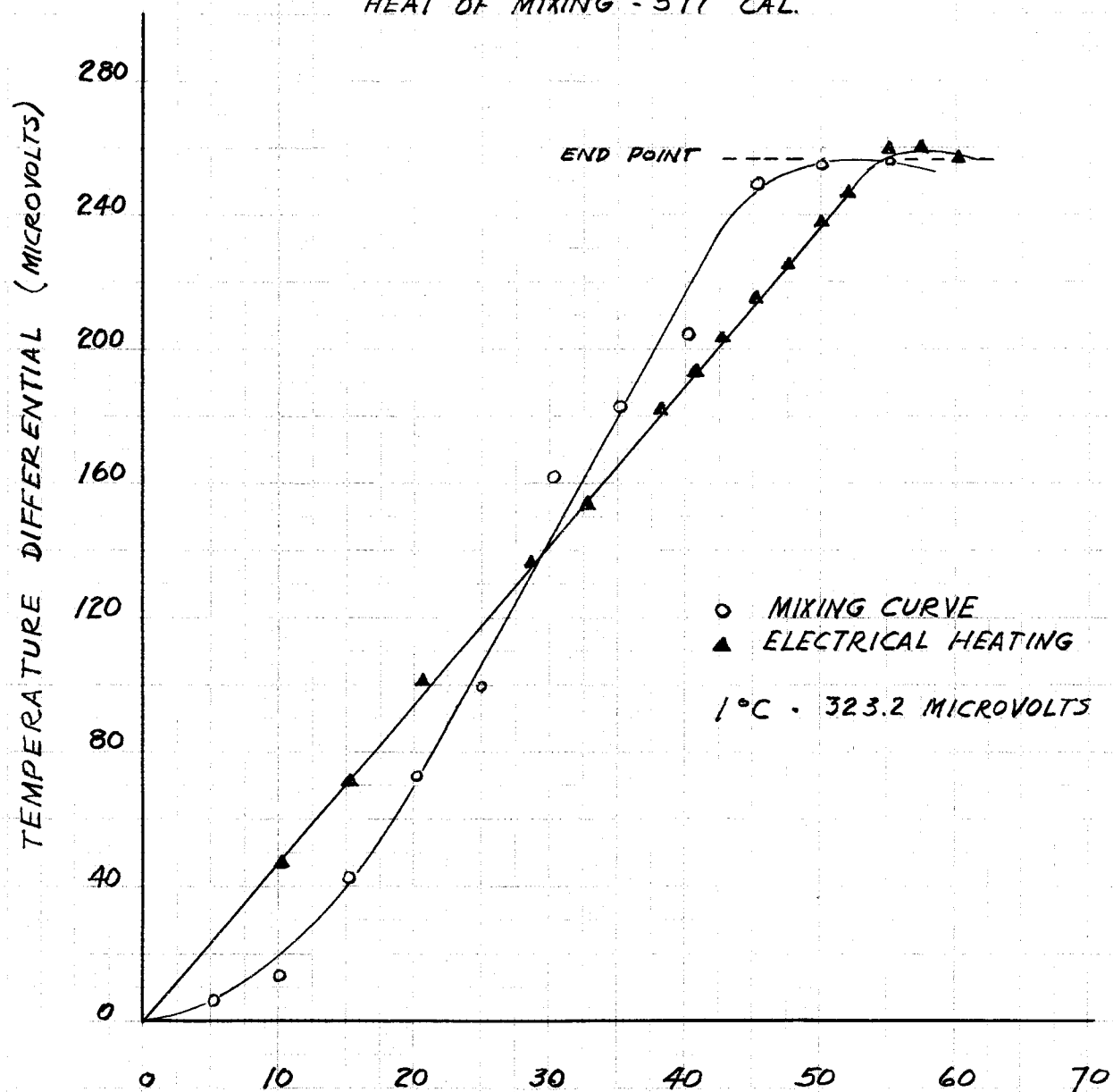


FIG 6 TYPICAL HEATING CURVE

EXPERIMENT 44

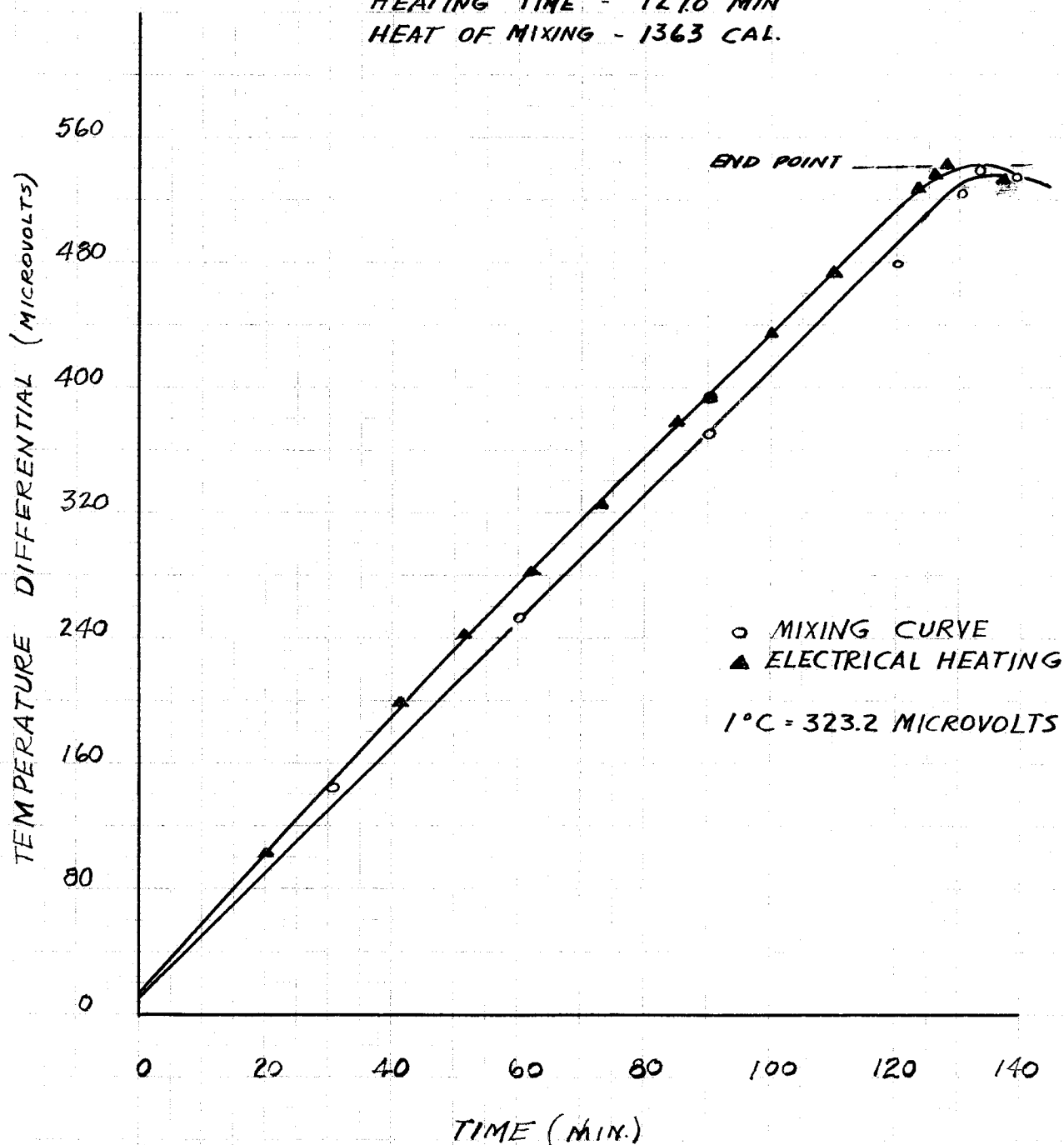
15.96 MOLES SOLUTION

52.88 MOLE % WATER

HEATING RATE - 10.65 CAL/MIN.

HEATING TIME - 1270 MIN

HEAT OF MIXING - 1363 CAL.



result of 583 cal. as compared to 577 cal. at 10.63 cal./min. This is only a 1% deviation for a 35% deviation in heating time.

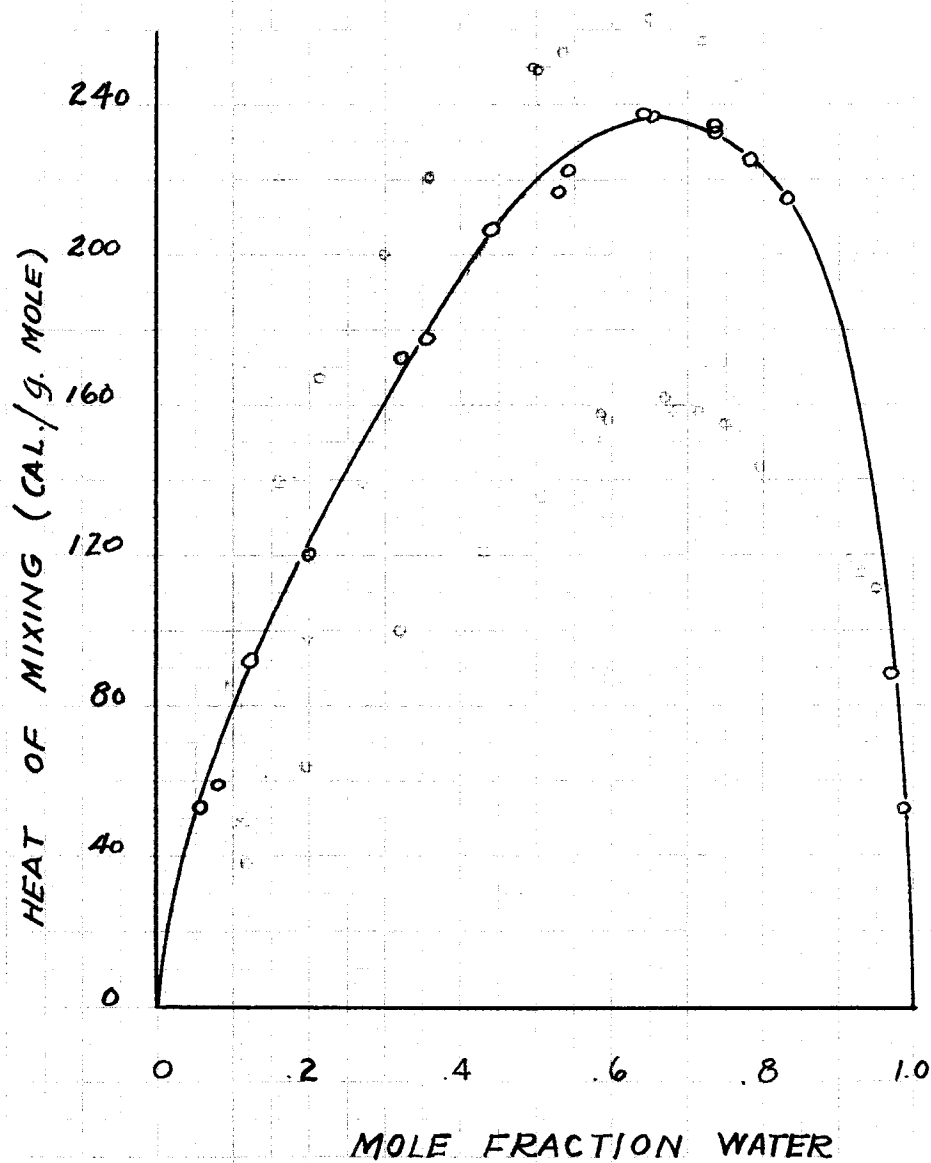
A series of measurements covering the entire composition range was run in duplicate. Solutions were prepared in a manner similar to the benzene-methanol experiments (Series A, B, C). In series D diacetone alcohol was added to water. Concentrations and heat of mixing calculations are shown in the Appendix. A peak value of 238 cal./mole solution was obtained at 0.67 mole fraction water which corresponds to a ratio of two moles of water to one mole of diacetone alcohol (Table V and Fig. 7).

TABLE VHEAT OF MIXING OF DIACETONE ALCOHOL-WATER
SOLUTIONS AT 25°C

<u>Series</u>	<u>Experiment No.</u>	<u>Mole Fraction Of Water</u>	<u>Heat Of Mixing (Cal/Mole)</u>
A	29	0.055	53
B	32	0.080	59
A	30	0.121	92
B	33	0.198	120
B	34	0.323	173
C	43	0.357	178
B	35	0.441	207
C	44	0.529	217
B	36	0.538	223
C	45	0.646	237
B	38	0.727	235
C	46	0.729	233
B	39	0.784	226
B	40	0.826	216
D	42	0.969	89
D	41	0.985	53

FIG. 7

HEAT OF MIXING
DIACETONE ALCOHOL-WATER
SOLUTIONS AT 25°C



Specific Heat of Diacetone
Alcohol Water Solutions @ 25°C

The time temperature curves which were used to determine the heat of mixing were also employed to determine the specific heat of diacetone alcohol water solutions. The thermal equivalent of the calorimeter (325.1 cal/°C) was determined by heating a known weight of distilled water for fifty minutes and noting the temperature rise. The heat capacity of the calorimeter was equal to the total heat input from the heating coil minus the heat taking up by the water (specific heat of water 0.9989). Temperature rise for the first fifty minutes was likewise read off of each heating curve for the diacetone alcohol water solutions; typical curves are shown in Figures 5 and 6. Total energy inputs were calculated from the current density for the first fifty minutes. Net heat to the solution was taken as the difference between total input minus the heat to the calorimeter. The specific heat in cal./°C g. solution was calculated from the net heat input. These values are shown in Table VI. The function of specific heat of the solution with respect to water concentration is shown in Figure 8.

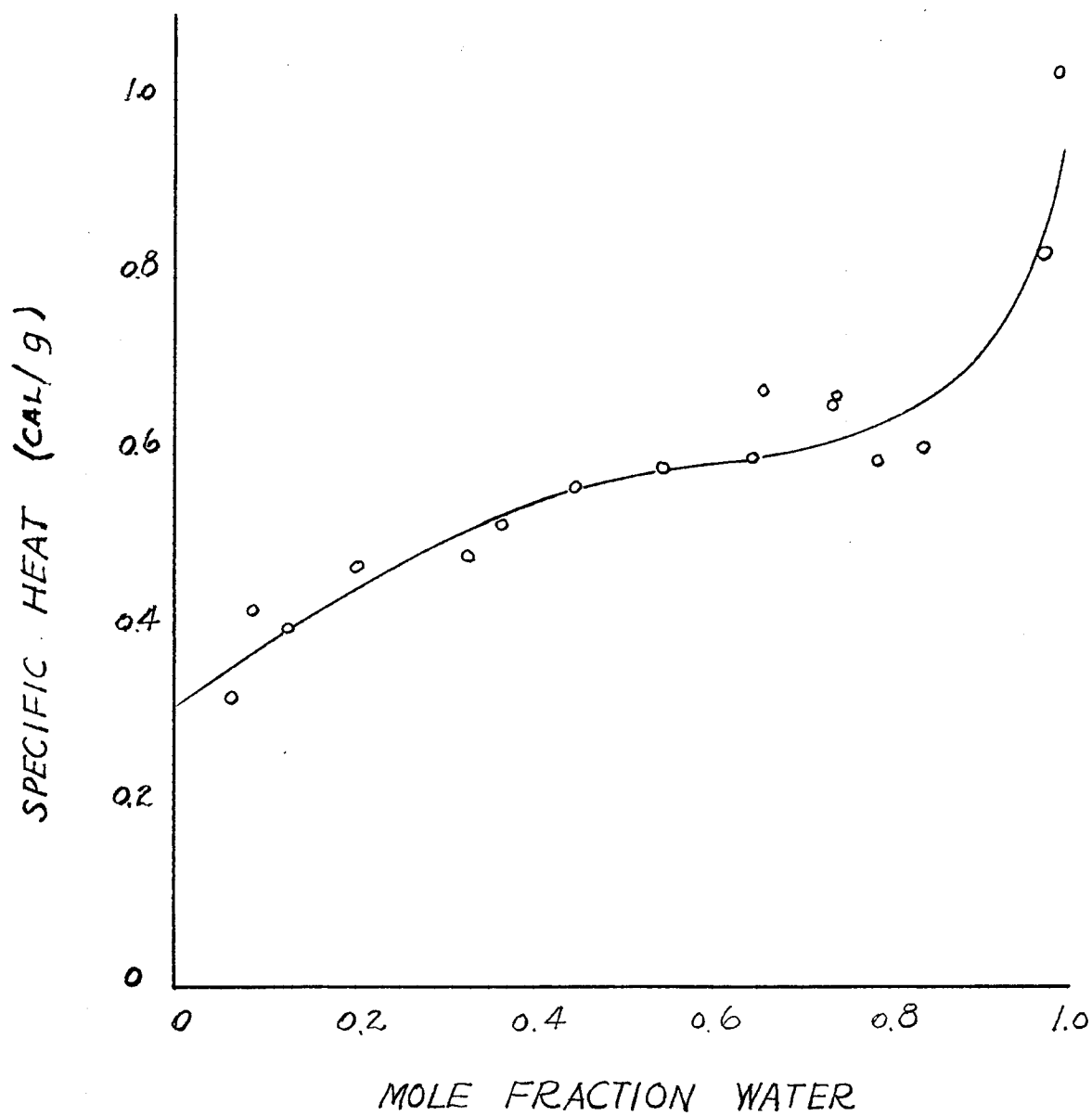
This was the first measurement of the specific heat of these solutions. A value of 1.04 at 0.984 mole fraction water indicated a maximum in the region of low diacetone alcohol concentration. The lower primary alcohols also exhibit maximum points at the lower concentrations in water solution^(12A).

TABLE VI

SPECIFIC HEAT OF DIACETONE ALCOHOL-WATER
SOLUTIONS AT 25°C

Exp. No.	Mole Fraction Water	Specific
		Heat Cal./°C-g Sol'n
29	0.055	0.332
32	0.080	0.431
30	0.121	0.412
33	0.198	0.480
34	0.323	0.493
43	0.357	0.527
35	0.441	0.570
36	0.538	0.590
37	0.639	0.600
45	0.646	0.677
38	0.727	0.662
46	0.729	0.670
39	0.784	0.593
40	0.826	0.611
42	0.969	0.823
41	0.984	1.037

FIGURE 8
SPECIFIC HEAT OF
DIACETONE ALCOHOL - WATER
SOLUTIONS
AT 25°C



Conclusions

A sensitive apparatus was built for determining the heat of mixing of liquids and it was estimated to give reliable results with an error of less than $\pm 1\%$. The endothermal heat of mixing values of benzene and methanol at 25°C cited in the literature were confirmed. It was shown that specific heat data may be obtained with the same apparatus.

The heat of mixing of diacetone water solutions was determined for the first time over the entire composition range and showed a positive maximum (exothermic) heat of 238 cal/mole solution at 67 mole percent water and suggested the association of two moles of water with one mole of diacetone alcohol.

The specific heat of diacetone alcohol water solutions was also measured over the entire range of composition.

Recommendations

The heat of mixing data for diacetone alcohol water solutions suggests the formation of an addition complex by hydrogen bonding. Badger and Bauer⁽¹⁾ have shown by spectroscopic methods that diacetone alcohol in 18 mole percent carbon tetrachloride solution consists of about 75% of molecules with internal hydrogen bonds. This would indicate that the heat of mixing represents the net heat change due to destruction of intramolecular and intermolecular hydrogen bonds and the formation of hydrogen bonds between water and diacetone alcohol.

Searles and Tamres^(19A,20A) have been able to correlate the donor ability of aromatic hydrocarbons with heat of mixing measurements and shifts in the OD bond with methanol-d solutions. Heat of mixing has also been used to show the differences in donor ability of oxygen, nitrogen, sulfur, and halogens^(7A).

Since the complex formation is a function of the hydroxyl concentration, the concentration and heat of mixing should correlate with the cohesive energy density (\mathcal{J}) or internal energy of the pure components. Cohesive energy density may be expressed by the following equation:

$$\mathcal{J} = \frac{H}{V} - RT$$

H = heat of vaporization (cal./mole)

R = gas constant (cal./°K)

T = absolute temperature (°K)

V = molal volume (cc./mole)

Additional heat of mixing data at other temperatures would be desirable to test the equation and to determine the effect of temperature on the peak value and its position with respect to concentration. Solid-liquid phase diagram and spectroscopic studies would also be of interest in the elucidation of the existence of the addition complex.

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APPENDIX

TABLE I

DIACETONE ALCOHOL-WATER SOLUTIONS
FOR SERIES "A" EXPERIMENTS

<u>Experiment</u> <u>No.</u>	<u>C₆H₁₂O₂</u> <u>Charged</u> (g)	<u>H₂O</u> <u>Charged</u> (g)	<u>Net</u> <u>C₆H₁₂O₂</u> (g)	<u>Net</u> <u>H₂O</u> (g)	<u>Total</u> <u>Weight</u> (g)	<u>Total</u> <u>Moles</u>	<u>Mole</u> <u>Fractions</u> <u>H₂O</u>
29	1197	10.8	1197	10.8	1207.8	10.90	0.0550
30	-	14.8	1197	25.6	1222.6	11.72	0.1212

TABLE II
 DIACETONE ALCOHOL-WATER
 HEAT OF MIXING DATA FOR
 SERIES "A" EXPERIMENTS (25°C)

Exp. No.	Total Moles Sol'n	Temp. Rise (°C)	H E A T I N G D A T A				ΔH Heat of Mixing (Cal)	Σ ΔH (Cal)	ΔH Net (Cal)	ΔH (Cal/Mole)
			I (ma)	R (ohms)	t (Min)	Rate (Cal/Min)				
29	10.90	0.791	105.5	66.62	54	10.631	574	574	574	52.7
30	11.72	0.611	105.0	"	48	10.530	505	1079	1079	92.1

TABLE III

DIACETONE ALCOHOL-WATER SOLUTIONS
FOR SERIES "B" EXPERIMENTS

Experiment No.	$C_6H_{12}O_2$ Charged (g)	H_2O Charged (g)	Sol'n Removed (g)	$C_6H_{12}O_2$ Removed (g)	H_2O Removed (g)	Net $C_6H_{12}O_2$ (g)	Net H_2O (g)	Total Weight (g)	Total Moles	Mole Fraction H_2O
32	1005	13.6	-	-		1005	13.6	1019	9.40	0.0798
33	-	24.8	-	-		1005	38.4	1043	10.78	0.1976
34	-	33.6	69.5	66.9	2.6	938.1	69.4	1008	11.91	0.3233
35	-	43.6	37.5	34.9	2.6	903.2	110.5	1014	13.91	0.4407
36	-	49.2	67.5	60.1	7.4	843.1	152.3	995	15.71	0.5379
37	-	76.7	35.4	30.0	5.4	813.1	223.6	1037	19.41	0.6394
38	-	102.4	98.2	77.0	21.2	736.1	304.8	1041	23.26	0.7274
39	-	97.3	117.0	82.7	34.3	653.4	367.8	1021	26.05	0.7839
40	-	103.1	98.7	63.1	35.2	590.2	435.4	1026	29.25	0.8263

TABLE IV

DIACETONE ALCOHOL-WATER HEAT OF MIXING
DATA FOR SERIES "B" EXPERIMENTS (25°C)

Exp. No.	Moles Sol'n	Temp. Rise (°C)	HEATING DATA				ΔH Heat of Mixing (Cal)	Σ ΔH (Cal)	ΔH Removed (Cal)	Σ ΔH Removed (Cal)	ΔH Net (Cal)	ΔH (Cal/Mole)
			I (ma)	R (ohms)	t (Min)	Rate (Cal/Min)						
32	7.98	0.733	106.0	66.62	52	10.73	558	558	-		558	59
33	19.76	0.902	105.5	"	70	10.63	740	1298	-		1298	120
34	32.33	1.015	106.0	"	79	10.73	848	2146	86	86	2059	173
35	44.07	0.985	106.0	"	83	10.73	891	3037	77	163	2874	207
36	53.79	0.903	106.0	"	77	10.73	826	3863	191	354	3509	223
37	63.94	1.253	106.0	"	116	10.73	1245	5108	125	479	4629	238
38	72.67	1.417	106.0	"	118	10.73	1266	6374	438	917	5457	235
39	78.37	1.139	105.0	"	99	10.53	1043	7417	613	1530	5887	226
40	82.60	1.021	105.9	"	92.5	10.71	991	8408	569	2099	6309	216

TABLE V

DIACETONE ALCOHOL-WATER SOLUTIONS
FOR SERIES "C" EXPERIMENTS

<u>Experiment</u> <u>No.</u>	<u>C₆H₁₂O₂</u> <u>Charged</u>	<u>H₂O</u> <u>Charged</u>	<u>Sol'n</u> <u>Removed</u>	<u>C₆H₁₂O₂</u> <u>Removed</u>	<u>H₂O</u> <u>Removed</u>	<u>Net</u> <u>C₆H₁₂O₂</u>	<u>Net</u> <u>H₂O</u>	<u>Total</u> <u>Weight</u>	<u>Total</u> <u>Moles</u>	<u>Mole</u> <u>Fraction</u> <u>H₂O</u>
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)		
41	92.3	963	-	-	-	92.3	963	1055	54.2	0.9854
42	96.1	-	96.8	8.5	88.3	179.9	875	1055	50.1	0.9691

TABLE VI

DIACETONE ALCOHOL-WATER HEAT OF MIXING
DATA FOR SERIES "C" EXPERIMENTS (25°C)

<u>Exp.</u> <u>No.</u>	<u>Moles</u> <u>Sol'n</u>	<u>Temp.</u> <u>Rise</u> (°C)	<u>H E A T I N G D A T A</u>				ΔH	Σ	ΔH	Σ	ΔH	
			<u>I</u>	<u>R</u>	<u>t</u>	<u>Rate</u>	<u>Heat of</u> <u>Mixing</u> (Cal)	<u>ΔH</u> (Cal)	<u>Removed</u> (Cal)	<u>ΔH</u> <u>Removed</u> (Cal)	<u>Net</u> (Cal)	<u>ΔH</u> (Cal/Mole)
41	54.24	2.040	105.5	66.62	269	10.63	2860	2860	-	-	2860	52.7
42	50.10	1.569	105.5	"	173	10.63	1839	4699	262	262	4437	88.6

TABLE VII
DIACETONE ALCOHOL-WATER SOLUTIONS
FOR SERIES "D" EXPERIMENTS

<u>Experiment</u> <u>No.</u>	<u>C₆H₁₂O₂</u> <u>Charged</u> (g)	<u>H₂O</u> <u>Charged</u> (g)	<u>Sol'n</u> <u>Removed</u> (g)	<u>C₆H₁₂O₂</u> <u>Removed</u> (g)	<u>H₂O</u> <u>Removed</u> (g)	<u>Net</u> <u>C₆H₁₂O₂</u> (g)	<u>Net</u> <u>H₂O</u> (g)	<u>Total</u> <u>Weight</u> (g)	<u>Total</u> <u>Moles</u>	<u>Mole</u> <u>Fraction</u> <u>H₂O</u>
43	944	81.5	-	-	-	944	81.5	1026	12.65	0.3573
44	-	76.7	77.0	70.9	6.1	873	152.1	1025	15.96	0.5288
45	-	84.8	117.5	100.1	17.4	773	219.4	992	18.84	0.6465
46	-	93.0	94.4	73.5	20.9	700	291.6	991	22.21	0.7290

TABLE VIII

DIACETONE ALCOHOL-WATER HEAT OF MIXING
DATA FOR SERIES "D" EXPERIMENTS (25°C)

Exp. No.	Moles Sol'n	Temp. Rise (°C)	HEATING DATA				ΔH Heat of Mixing (Cal)	Σ ΔH (Cal)	ΔH Removed (Cal)	Σ ΔH Removed (Cal)	ΔH Net (Cal)	ΔH (Cal/Mole)
			I (ma)	R (ohms)	t (Min)	Rate (Cal/Min)						
43	12.65	3.156	105.6	66.62	212	10.65	2258	2258	-		2258	178
44	15.96		106.0	"	127	10.73	1363	3621	170		3451	216
45	18.84		102.0	"	141	10.00	1410	5031	396	556	4465	237
46	22.21		105.6	"	107	10.65	1140	6171	425	991	5180	233

TABLE IX

METHANOL-BENZENE SOLUTIONS
FOR SERIES "E" EXPERIMENTS

Experiment No.	C_6H_6 Charged	CH_3OH Charged	Sol'n Removed	C_6H_6 Removed	CH_3OH Removed	Net C_6H_6	Net CH_3OH	Total Weight	Total Moles	Mole Fraction C_6H_6
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)		
1	1096	22.5	-	-	-	1096	22.5	1118	14.73	.953
2	-	24.8	-	-	-	1096	47.3	1143	15.51	.905
3	-	38.3	39.8	38.2	1.6	1058	84.0	1142	16.16	.838
4	-	58.8	75.9	70.3	5.6	988	137.2	1125	16.92	.747
5	-	59.3	64.4	56.5	7.9	931	188.6	1120	17.81	.669
6	-	66.6	47.7	39.7	8.0	891	247.2	1138	19.13	.596
7	-	72.6	115.6	90.5	25.1	801	294.7	1096	19.45	.527

TABLE X
BENZENE-METHANOL HEAT OF MIXING
DATA FOR SERIES "E" EXPERIMENTS (30°C)

Exp. No.	Moles Sol'n	<u>H E A T I N G D A T A</u>				Heat of Mixing (Cal)	Σ	γ	Σ	ΔH Net (Cal)	ΔH (Cal/Mole)
		<u>I</u> (ma)	<u>R</u> (ohms)	<u>t</u> (Min)	<u>Rate</u> (Cal/Min)		<u>ΔH</u> (Cal)	<u>ΔH</u> Removed (Cal)	<u>ΔH</u> Removed (Cal)		
1	14.73	106	66.62	109.0	10.73	1170	1170	-	-	1170	79
2	15.51	106	"	51.3	10.73	551	1721	-	-	1721	111
3	16.16	106	"	51.3	10.73	551	2272	60	60	2212	137
4	16.92	105	"	34.0	10.53	358	2630	147	207	2423	143
5	17.81	105	"	24.7	10.53	260	2890	139	346	2544	143
6	19.13	105	"	13.9	10.53	146	3036	108	454	2582	135
7	19.45	105	"	9.1	10.53	95	3131	262	716	2415	124

TABLE XI

METHANOL-BENZENE SOLUTIONS
FOR SERIES "F" EXPERIMENTS

Exp. No.	C_6H_6 Charged (g)	CH_3OH Charged (g)	Sol'n Removed (g)	C_6H_6 Removed (g)	CH_3OH Removed (g)	Net C_6H_6 (g)	Net CH_3OH (g)	Total Weight (g)	Total Moles	Mole Fraction C_6H_6
8	79.5	1042	-	-	-	79.5	1042	1121	33.54	0.030
9	76.8	-	66.3	4.7	61.6	151.6	980	1132	32.54	0.060
10	86.7	-	78.1	10.5	67.6	227.8	913	1141	31.41	0.093
11	83.6	-	154.5	30.8	123.6	280.6	789	1070	28.22	0.127
12	78.2	-	120.0	31.5	88.5	327.4	701	1028	26.06	0.161
13	78.6	-	140.0	44.6	95.4	388.0	605	993	23.86	0.210
14	81.0	-	-	-	-	469.0	605	1074	24.89	0.241
15	84.7	-	70.5	30.8	39.7	496.3	566	1062	24.00	0.265
16	80.6	-	78.3	36.6	41.7	540.3	524	1064	23.27	0.297
17	85.0	-	-	-	-	625.3	524	1149	24.36	0.329
18	86.0	-	140.1	76.2	63.9	635.1	460	1095	22.48	0.362
19	88.6	-	124.8	72.4	52.4	651.3	408	1059	21.06	0.396
20	78.3	-	67.3	41.4	25.9	788.2	382	1070	20.72	0.425
21	85.6	-	72.7	46.8	25.9	727.0	356	1083	20.40	0.456

TABLE XII

BENZENE-METHANOL HEAT OF MIXING
DATA FOR SERIES "F" EXPERIMENTS (30°C)

Exp. No.	Moles Sol'n	HEATING DATA				ΔH Heat of Mixing	Σ ΔH	ΔH Removed	Σ ΔH Removed	ΔH Net	ΔH
		I (ma)	R (ohms)	t (Min)	Rate (Cal/Mole)	(Cal)	(Cal)	(Cal)	(Cal)	(Cal)	(Cal/Mole)
8	33.54	105.5	66.62	9.8	10.63	104	104	-	-	104	3
9	32.54	105.0	"	8.2	10.53	86	190	6	6	184	6
10	31.41	105.2	"	13.9	10.57	147	337	13	19	318	10
11	28.22	105.9	"	7.9	10.71	85	422	43	62	360	13
12	26.06	106.0	"	13.4	10.73	144	566	40	102	464	18
13	23.86	105.9	"	12.3	10.65	131	697	63	165	532	22
14	24.89	105.0	"	11.6	10.53	122	819	-	165	654	26
15	24.00	105.0	"	15.1	10.63	161	980	43	208	772	32
16	23.27	105.6	"	25.0	10.65	266	1246	57	265	981	42
17	24.36	105.9	"	25.2	10.71	270	1516	-	265	1251	51
18	22.48	105.6	"	24.6	10.65	262	1778	152	417	1361	60
19	21.06	105.6	"	28.3	10.65	301	2079	155	572	1507	71
20	20.72	105.2	"	14.1	10.57	149	2228	96	668	1560	75
21	20.40	105.6	"	10.6	10.65	112	2340	106	774	1566	77

TABLE XIII

METHANOL-BENZENE SOLUTIONS
FOR SERIES "G" EXPERIMENTS

<u>Exp.</u> <u>No.</u>	<u>C₆H₆</u> <u>Charged</u>	<u>CH₃OH</u> <u>Charged</u>	<u>Sol'n</u> <u>Removed</u>	<u>C₆H₆</u> <u>Removed</u>	<u>CH₃OH</u> <u>Removed</u>	<u>Net</u> <u>C₆H₆</u>	<u>Net</u> <u>CH₃OH</u>	<u>Total</u> <u>Weight</u>	<u>Total</u> <u>Moles</u>	<u>Mole</u> <u>Fraction</u> <u>C₆H₆</u>
	(g)	(g)	(g)	(g)	(g)	(g)	(g)	(g)		
22	1104	46.1	-	-	-	1104	46.1	1150	15.57	0.908
23	-	43.3	76.8	73.7	3.1	1030	86.3	1117	15.88	0.831
24	-	68.6	77.1	71.1	6.0	959	149.0	1108	16.93	0.725
25	-	75.6	77.0	66.6	10.4	893	214.2	1107	18.12	0.631
26	-	79.7	80.3	64.8	15.5	828	278.4	1106	19.30	0.549
27	-	77.6	80.3	60.1	20.2	768	335.8	1104	20.31	0.484

TABLE XIV

BENZENE-METHANOL HEAT OF MIXING
DATA FOR SERIES "G" EXPERIMENTS (25°C)

Exp. No.	Moles Sol'n	HEATING DATA				Heat of Mixing (Cal)	Σ ΔH (Cal)	ΔH Removed (Cal)	Σ ΔH Removed (Cal)	ΔH Net (Cal)	ΔH (Cal/Mole)
		I (ma)	R (ohms)	t (Min)	Rate (Cal/Min)						
22	15.57	105.5	66.62	180.0	10.63	1914	1914	-	-	1914	123
23	15.88	105.6	"	41.6	10.65	443	2357	128	128	2229	140
24	16.93	106.0	"	36.4	10.73	390	2747	154	282	2465	146
25	18.12	105.6	"	23.6	10.65	252	2999	172	454	2545	141
26	19.30	105.5	"	16.1	10.63	171	3170	185	639	2531	131
27	20.31	106.0	"	10.4	10.73	112	3282	184	823	2459	121

TABLE XV

METHANOL-BENZENE SOLUTIONS
FOR SERIES "H" EXPERIMENTS

<u>Exp.</u> <u>No.</u>	<u>C₆H₆</u> <u>Charged</u> (g)	<u>CH₃OH</u> <u>Charged</u> (g)	<u>Sol'n</u> <u>Removed</u> (g)	<u>C₆H₆</u> <u>Removed</u> (g)	<u>CH₃OH</u> <u>Removed</u> (g)	<u>Net</u> <u>C₆H₆</u> (g)	<u>Net</u> <u>CH₃OH</u> (g)	<u>Total</u> <u>Weight</u> (g)	<u>Total</u> <u>Moles</u>	<u>Mole</u> <u>Fraction</u> <u>C₆H₆</u>
49	1001	40.4	-	-	-	1001	40.4	1041	14.07	.910
50	-	40.4	-	-	-	1001	80.8	1082	15.33	.836
51	-	80.4	84.7	78.4	6.3	923	154.9	1078	16.64	.710
52	-	78.3	83.2	71.2	12.0	851	221.2	1073	17.80	.612
53	1080	43.7	-	-	-	1080	43.7	1124	15.19	.911
54	-	76.1	-	-	-	1080	119.8	1200	17.57	.787

TABLE XVI

BENZENE-METHANOL HEAT OF MIXING
DATA FOR SERIES "H" EXPERIMENTS (25°C)

Exp. No.	Moles Sol'n	HEATING DATA				ΔH Heat of Mixing (Cal)	Σ ΔH (Cal)	ΔH Removed (Cal)	Σ ΔH Removed (Cal)	ΔH Net (Cal)	ΔH (Cal/Mole)
		I (ma)	R (ohms)	t (Min)	Rate (Cal/Min)						
49	14.07	105.8	66.62	165.5	10.69	1769	1769	-	-	1769	126
50	15.33	105.5	"	44.4	10.63	472	2241	-	-	2241	146
51	16.64	105.5	"	49.6	10.63	527	2768	176	176	2592	156
52	17.80	105.5	"	32.2	10.63	342	3110	200	376	2734	154
53	15.19	106.5	66.62	171.6	10.83	1859	1859	-	-	1859	122
54	17.57	106.3	"	81.3	10.79	877	2756	-	-	2756	157

TABLE XVIISPECIFIC HEAT CALCULATIONSHeat Capacity of Calorimeter

Weight of Water Charged	=	1229 g
Heating Time	=	50 Min.
Heating Rate	=	10.30 Cal./Min.
Temperature Rise	=	0.3311 °C
Total Heat Input	=	515.0 Cal.
Heat Uptake by Water	=	<u>406.9</u> Cal.
Heat Uptake by Calorimeter	=	108.1 Cal.
Heat Capacity of Calorimeter	=	325.1

Specific Heat of Diacetone Alcohol Water Solution
(Exp. No. 29)

Solution Charged	=	1208 g
Heating Time	=	50 Min.
Heating Rate	=	10.63 Cal/Min.
Temperature Rise	=	0.732 °C
Total Heat Input	=	531.5 Cal.
Heat Uptake by Calorimeter	=	<u>237.9</u> Cal.
Heat Uptake by Solution	=	293.6 Cal.
Specific Heat of Solution	=	0.332

TABLE XVIII

SPECIFIC HEAT DATA FOR DIACETONE ALCOHOL-WATER SOLUTIONS

Exp. No.	Mole Fraction Water	Weight Solution (g)	Temperature Rise		Heat Input Rate (Cal./Min)	Total* Heat Input (Cal)	Heat to Calorimeter (Cal)	Net Heat to Solution (Cal)	Specific Heat of Solutions (Cal/g.°C)
			Microvolts	°C					
29	.055	1208	236.5	0.732	10.63	531.5	237.9	293.6	0.332
32	.080	1019	227	0.702	10.73	536.5	228.3	308.2	0.431
30	.121	1223	205	0.634	10.53	526.5	206.9	319.6	0.412
33	.198	1045	208	0.644	10.63	531.5	209.2	322.3	0.480
34	.323	1008	211	0.653	10.73	536.5	212.2	324.3	0.493
43	.357	1025	199	0.616	10.65	532.5	200.1	332.3	0.527
35	.441	1014	192	0.594	10.73	536.5	193.1	343.4	0.570
36	.538	995	190	0.588	10.73	536.5	191.1	345.4	0.590
37	.639	1037	183	0.566	10.73	536.5	184.0	352.5	0.600
45	.646	993	162	0.501	10.00	500.0	163.0	337.0	0.677
38	.727	1040	171	0.529	10.73	536.5	172.0	364.5	0.662
46	.729	991	174	0.538	10.65	532.5	175.0	357.5	0.670
39	.784	1020	183	0.566	10.53	536.5	184.1	342.4	0.593
40	.826	1025	182	0.563	10.71	535.5	183.1	352.4	0.611
42	.969	1055	144	0.446	10.63	531.5	144.8	386.7	0.823
41	.984	1055	121	0.374	10.63	531.5	121.7	409.8	1.037

*For 50 Minute Heating Time