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UNIVERSITY OF LOUISVILLE

THE SYSTEM BENZENE - METHYL ALCOHOL
PART II - SPECIFIC HEATS AND LIQUID ENTHALPIES

A Thesis
Submitted to the Faculty
of the Graduate School
of the University of Louisville
in Partial Fulfillment
of the Requirements
for the Degree of
MASTER OF CHEMICAL ENGINEERING

Department of Chemical Engineering

By

Harvey A. Rothenberg

1944

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THE SYSTEM BENZENE - METHYL ALCOHOL

PART II

SPECIFIC HEATS AND LIQUID ENTHALPIES

Harvey A. Rothenberg

Approved by the Examining Committee:

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September, 1944

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List of Symbols

Symbol	Explanation	Unit
C.E.	Calorimeter equivalent	calories/°C.
C _p	Specific Heat	calories/gram/°C.
E	Potential Difference	volts
H _r	Heat lost through radiation	calories
H _v	Heat lost by vaporisation	calories
I	Current	amperes
M	Weight of liquid in vessel	grams
o	Subscript indicating a period in which no heat is added to system	
Q	Heat added	calories
t ₁	Initial temperature of heating period	°C.
t ₂	Final temperature of heating period	°C.
Δt	Temperature difference	°C.
Δt _h	Temperature difference of heating period	°C.
Δt _{r(av)}	Average temperature difference of radiation period	°C.
W	Weight of mass whose temperature is changing	grams
⊙	Time	minutes

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ABSTRACT

This thesis presents data concerning the physical properties of the binary azeotropic system benzene-methanol.

The project is a continuation of a thesis by S. Rosenberg in 1941. Data are presented to show the variation of specific heats for liquid mixtures with respect to temperature and concentration. Curves are included, and the liquid enthalpies are deduced for mixtures at their boiling points.

Experiments were conducted in a small glass calorimeter which could be dismantled to facilitate rapid and precise weighing.

INTRODUCTION

Accomplishments in the field of distillation indicate that it is a well advanced science. However the success achieved by modern industry may not all be attributed to the application of sound theoretical reasoning. There are many instances in which the theory does not apply, and in such cases it has been necessary to resort to empirical relationships or so-called efficiency factors. Distillation column calculations are a good example.

The methods commonly used for the design of distillation equipment are subject to admitted limitations. The method of McCabe and Thiele (1) assumes constant molal overflow and cannot be used for other conditions. Gilliland (3) uses a relative volatility procedure where constancy of the value for one constituent is assumed for a number of consecutive plates. The method of Ponchon and Savarit (3) has been demonstrated to be the most accurate of calculation procedures, but even this has not been applied to azeotropic mixtures. This may have resulted from an almost complete lack of enthalpy data for this type of system.

Accordingly, it was the purpose of this investigation to examine a system in which an azeotropic mixture exists, and for which the McCabe-Thiele procedure gives inaccurate results, i.e. Benzene-Methyl Alcohol.

It was proposed to determine an accurate procedure for determination of certain heat quantities for the solution, and to present the results of these determinations on Benzene-Methyl Alcohol.

HISTORICAL

Previous to the initial investigation into this project by Rosenberg (4) in 1941, data on the physical properties of the system Benzene-Methyl Alcohol did not exist in the literature except for the pure constituents which are rather well identified in numerous handbooks and authentic tables. The specific heats of pure liquid methyl alcohol have been reported by many investigators over ranges of temperature up to 20°C., but values at higher temperatures appear to have been neglected.

In his research Rosenberg (4) has established densities, refractive indices, and boiling points over the complete range of liquid compositions, and has also determined the x-y (mol fraction) equilibrium data. At the same time he included results of his work on specific heats but admitted with its presentation that this information was of a doubtful nature and required additional evidence for confirmation.

When examined for methods for determining specific heats of liquid mixtures, the literature proved to be of no avail. An improved method was then evolved from an analysis of the procedure used by Rosenberg. Factors introducing a source of error were eliminated or reduced.

THEORETICAL

As signified by Robinson and Gilliland in their treatise on distillation (3), the mathematical theory of rectification of binary mixtures in a plate column was developed and applied by a Frenchman named Sorel (5). Although his method was rigorous, it was also complex; and several modifications were introduced in attempting to shorten it. As used today these are called the "usual simplifying assumptions" and are summarized as follows:

- (1) Radiation losses from the column are negligible.
- (2) The heat of mixing of the components both in the liquid and in the vapor are negligible.
- (3) The thermal properties of the components are similar so that the total mols of overflow and the total mols of vapor being transferred from plate to plate are substantially constant. However a different condition will exist in the sections of the column above and below the feed plate.

Probably the most common method in use at present is the graphical method developed by McCabe and Thiele (1). However it is derived on the basis of the usual simplifying assumptions and therefore would not apply to the system under consideration in this thesis.

The system Benzene-Methyl Alcohol is composed of two dissimilar materials. Benzene is polar and associating while the Methyl Alcohol is non-polar and non-associating. It would be expected that the condition of constant molal overflow would not be obtained up and down a column, and

a solution to the resulting condition must have an approach which is different from that normally used.

Such a solution should be found in the method offered by Ponchon and Savarit (3). There is a graphical method based entirely upon heat balances around each plate. The calculations require the representation of enthalpy vs. concentration curves both for the liquid and vapor. These curves should take into account the heat of mixing, sensible heats, and variation of latent heats, thus application of this method should be the most accurate. To date, however, it has not been tried except for the systems of simple type.

Liquid enthalpies may be obtained from specific heat data. The standard calorimetric method of obtaining specific heats of liquids is to apply a definite quantity of heat to a given amount of the liquid and measure the rise in temperature. Although this is precisely the manner in which Rosenberg proceeded, he found factors which introduced errors greater than the differences in specific heats of the mixtures.

The two liquids under consideration are relatively volatile. Furthermore the temperature range over which the investigation occurs, approaches the boiling points. The vaporization that takes place during the course of the proceedings must then be considered if any degree of accuracy is to be obtained. The heat of vaporization is extremely large in comparison to the specific heat, and therefore, although the loss of weight due to vaporization may be negligible from a material standpoint, it is very important from a heat standpoint. This provides two directions

of improvement, namely:

- (1) Limit the available vapor space by the shape of the vessel and confine it by allowing the liquid to fill the vessel as much as is practicable.
- (2) Adjust the method of calculation to minimize the effect of volatilization or to include it in correcting factors.

The fundamental relation for the specific heat determination can be expressed in the following equation:

$$C_P = \frac{Q}{W\Delta t} \quad (1)$$

in which the heat capacity at constant pressure of a substance is shown to be equal to the total heat input divided by the weight of material heated, and its temperature rise. In the case of a liquid, a portion of the heat must always be absorbed in raising the temperature of the confining vessel. Since the procedure necessitates the inclusion of other objects in the vessel, i.e. thermometer, stirrer, etc., all of which must absorb some heat, the heat effects of the total mass, exclusive of the liquid may be grouped together into one constant referred to as the "heat equivalent of the calorimeter." (C. E.)

The equation should therefore read

$$Q = WC_P\Delta t + (C.E.) \Delta t \quad (2)$$

Because of the differences in temperature between the liquid and its container and between the calorimeter and its surrounding

atmosphere, a portion of the heat is lost through radiation. In addition, the transition from liquid to vapor requires a quantity of heat to be absorbed. A true heat balance must take these factors into consideration, and so the conditions may be expressed for a unit time as

$$Q = W C_P \Delta t + (C.E.) \Delta t + H_R + H_V \quad (3)$$

Experimentally, the loss of heat due to radiation is usually determined by a measurement of the temperature drop of the system immediately preceding and immediately following the heating period. The average value thus obtained over a period of time equal to that during which the heat was applied is then added to the Δt during the run to give a total corrected Δt . This is essentially the procedure followed by Rosenberg. However results of his experiments showed that in many instances it was necessary to include in his computations an estimate of the amount of heat absorbed by vaporization, in order to obtain satisfactory results. Since it is difficult to predict such values within a reasonable degree of accuracy over a wide range of conditions, a method eliminating such a correction was desirable. An attack by a rate of heat flow method appeared advisable.

For any particular small increment of time the preceding heat balance could be expressed by the differential equation

$$\frac{dQ}{d\Theta} = W C_P \frac{dt}{d\Theta} + (C.E.) \frac{dt}{d\Theta} + \frac{dH_R}{d\Theta} + \frac{dH_V}{d\Theta} \quad (4)$$

It is significant here that although a slight loss of material results during the period of a run, giving rise to an appreciable effect in the term $\frac{dH_v}{d\Theta}$, W is very large and may be considered essentially constant in the term $WC_P \frac{dT}{d\Theta}$. Furthermore the magnitude of change in C_p with a variation of temperature is very small, and if the total change of temperature is limited to a small value, C_p may likewise be considered constant.

During the periods in which no heat is added, $\frac{dQ}{d\Theta} = 0$. Therefore

$$-\left(\frac{dH_R}{d\Theta} + \frac{dH_v}{d\Theta}\right) = WC_P \frac{dT_o}{d\Theta} + (C.E.) \frac{dT_o}{d\Theta} \quad (5)$$

where the subscript (o) indicates the rates of temperature change during a no-heat part of the cycle.

Substituting this equation into equation (4) results in the following:

$$\frac{dQ}{d\Theta} = WC_P \frac{dT}{d\Theta} + (C.E.) \frac{dT}{d\Theta} - WC_P \frac{dT_o}{d\Theta} - (C.E.) \frac{dT_o}{d\Theta} \quad (6)$$

where $\frac{dT}{d\Theta}$ and $\frac{dT_o}{d\Theta}$ are measured at the same temperature.

Factoring like terms reduces the equation to

$$\frac{dQ}{d\Theta} = [WC_P + (C.E.)] \frac{dT}{d\Theta} - [WC_P + (C.E.)] \frac{dT_o}{d\Theta} \quad (7)$$

or

$$\frac{dQ}{d\Theta} = [WC_P + (C.E.)] \left(\frac{dT}{d\Theta} - \frac{dT_o}{d\Theta} \right) \quad (8)$$

Since the entire range of the investigation is taken at temperatures exceeding that of the room, $\frac{dt_o}{d\Theta}$ will at all times have a negative slope, and the net result of equation (8) will be an addition of the two rates.

The effect of the vaporization is to cause a lowering of the temperature of the system by absorption of heat the same as would any loss by radiation, convection, etc. As is evidenced by the above analysis, the measurement of the rate of temperature drop during the no-heat period should then be a complete correction for the total of heat not utilized for raising the temperature of the liquid.

Although there exists a slight changing condition of the liquid during the time of the run, and since this change is aggravated by an increased time interval, $\left(\frac{dt_o}{d\Theta}\right)_t$ may be very closely approximated by the average slope of $\left(\frac{dt_o}{d\Theta}\right)_{t_1}$ and $\left(\frac{dt_o}{d\Theta}\right)_{t_2}$ where temperatures t_1 and t_2 are the initial and final temperatures of the heating period and are relatively close together.

The enthalpy or total heat content of a system, at any particular temperature and with reference to a given datum plane, is equal to the amount of heat which must be added to the system in order to cause its temperature to increase from that of the datum to the one in question. This may be expressed as

$$H = \int_{t_1}^{t_2} C_p dt \quad \text{under constant pressure.}$$

Although the evaluation of the integral may be determined from the equation of the specific heat vs. temperature curve, a simpler method

is to employ a graphical integration in which the area under this curve is obtained between the specified limits.

In accordance with the standard system of nomenclature 25°C . has been taken as the datum line and the boiling point of the liquid will be the upper limit in each case.

EXPERIMENTAL

MATERIALS

The substances used for experimental work were of high quality. Reagent grade Benzene was obtained from E. H. Sargent and Company, Chicago, Illinois. The methyl alcohol was C. P. grade, and it was obtained from the Peaslee-Gaulbert Paint Company, Louisville, Kentucky. In order to further insure the purity of these liquids, each was subjected to four batch distillations in which 10% of the product was rejected as heads and 10% as tails at each distillation. The resulting distillates were then absolutely colorless and constant boiling within $.01^{\circ}\text{C}$.

These materials were checked for refractive index and compared with identifying values in the literature. The boiling points were checked against previously unopened Merck reagents obtained from the laboratory. Results of the comparisons are shown:

Methanol

	Experimental	Merck Reagent	I. C. T.
Boiling Point @ 760 mm Hg.	64.5°C .	64.5°C .	64.1°C .
Refractive Index	1.3280^{25}		1.3276^{25}

Benzene

	Experimental	Merck Reagent	I. C. T.
Boiling Point @ 760 mm Hg.	80.3°C .	80.3°C .	80.1°C .
Refractive Index	1.4983^{25}		1.5016^{29}

The purified liquids were kept in tightly sealed glass containers, a rubber stopper being used for methanol while an aluminum foil-wrapped cork stopper was supplied for the benzene.

APPARATUS

Refractive indices were determined in all cases with the use of a standard Abbe refractometer employing a split prism maintained at constant temperature by a continual flow of water from a constant temperature bath.

For the determination of heat capacities an apparatus was especially prepared to satisfy the application. This consisted of a sufficiently insulated calorimeter with provision for stirring the liquid, measuring the temperature changes, and applying the heat; and an electrical heat source with accompanying panel for measuring quantities of energy supplied. In effect a 125 c.c. Erlenmeyer flask was equipped with two additional necks and slipped inside a large mouthed Dewar vacuum bottle of one pint capacity. Through aluminum foil wrapped cork stoppers in the necks of the Erlenmeyer, were extended the bulb of a sensitive thermometer, a glass stirring rod set in a glass bearing, and a length of double holed glass tubing containing the silver electrodes. A coil of fine nichrome wire was attached to the ends of the electrodes inside the vessel. The Dewar flask was then closed with a cork stopper which allowed the thermometer, stirrer, and electrodes to protrude. The unit was mounted on a ring stand, and an electric stirrer clamped to it. The stirring rod was connected to the motor drive through flexible rubber tubes.

A battery unit composed of four 1.5 volt Edison wet cells, connected in series, supplied the current. The current was varied by

an adjustable rheostat and passed through an ammeter, double-pole throw switch, and into the heating coil. A voltmeter was connected across the coil terminals. Time intervals were measured with a stop-watch. The accompanying sketch illustrates the arrangement.

Fig. 1 Diagram of Specific Heat Apparatus

PROCEDURE AND RESULTS

Before attempting a determination of unknown quantities, it was necessary to calibrate the apparatus. The calibration was carried out by subjecting the equipment to test runs under conditions which would exist during the analysis, but utilizing pure materials whose specific heats are accurately known. The materials selected were Benzene, Methyl Alcohol, and Carbon Tetrachloride, whose boiling points all fall within a limited range. By following this method it was possible to evaluate the term (C.E.) in the equation previously discussed, since all other items were known or measured.

The technique of both calibration and test processes included the following steps: First, a quantity of liquid placed in the removable portion of the calorimeter was carefully weighed with all items included and the vessel sealed. The equipment was assembled and the stirrer permitted to function. Temperatures were then recorded at fifteen-second intervals. After several minutes the switch was closed, completing the circuit, and current was allowed to pass through the coil. Values of potential drop and current were recorded. When a temperature rise of approximately one degree Centigrade had been reached the current was cut off. Temperature recordings were continued for several minutes or until an equivalent temperature drop had resulted. The stirrer was then disconnected and the inside vessel with its entire contents removed and reweighed.

For the determination of the specific heats of the mixtures, the composition was carefully checked immediately preceding and immediately following each run, by means of the refractive indices. Since this necessitated the withdrawal of a small amount of liquid each time, it was done in proper sequence with the weighings.

An example of this procedure follows with complete, observed experimental data, and the method employed to calculate the desired quantities. This run was made on a sample containing 40% Benzene, 60% Methanol (by volume).

Benzene-Methanol

DATA SHEET

Determination of Specific Heat

Run #33

Data:

Weight of flask and stirrer, etc., empty	C* + 9.5040g
Initial weight of flask + liquid	C + 99.8154g
Final weight of flask + liquid	C + 99.5650g
Loss in weight	0.2504g
Average weight of liquid	90.1862g
Refractive Index	1.3936
Voltage	3.52
Amperage	1.16

Temperatures @ 15 second intervals - (°C.)

1.)- 50.60	12.)- .65	23.)- .60
2.)- .50	13.)- .60	24.)- .74 (b)
3.)- .40	14.)- .52	25.)- .69
4.)- .30	15.)- .45 (a)	26.)- .60
5.)- .20	16.)- .59	27.)- .52
6.)- .11	17.)- .75	28.)- .46
7.)- .03	18.)- .91	29.)- .40
8.)- 49.94	19.)- 50.07	30.)- .34
9.)- .88	20.)- .20	31.)- .28
10.)- .80	21.)- .34	32.)- .21
11.)- .74	22.)- .48	33.)- .15

* C = counterbalance

(a) = current on

(b) = current off

Fig. 2 Typical Curve Showing Rate of Temperature Change During Run

The basic equation states

$$\frac{dQ}{d\Theta} = [WC_p + (C.E.)] \left(\frac{dt}{d\Theta} - \frac{dt_o}{d\Theta} \right)$$

$$\frac{dQ}{d\Theta} = \frac{EI}{4.182} \text{ calories/sec.} = \frac{60EI}{4.182} \text{ cal./min.}$$

Then
$$\frac{60EI}{4.182} = [WC_p + (C.E.)] \left(\frac{dt}{d\Theta} - \frac{dt_o}{d\Theta} \right)$$

or
$$C_p = \frac{\frac{60EI}{4.182 \left(\frac{dt}{d\Theta} - \frac{dt_o}{d\Theta} \right)} - C.E.}{W}$$

From figure 2

Initial radiation, etc., rate = -0.296 °C./min.

Final radiation, etc., rate = -0.256 °C./min.

Average radiation, etc., rate = -0.276 °C./min.

Heating rate = 0.580 °C./min.

$$C_p = \frac{\frac{60 \times 3.52 \times 1.16}{4.182 \times (0.580 + 0.276)} - 11.4}{90.1862}$$

$$C_p = 0.628 \text{ cal./gm./}^\circ\text{C.}$$

Temperature = 50 °C.

Concentration = 40% Benzene - 60% Methanol by volume

The calibration of the calorimeter was done with the use of the pure liquids, benzene, methyl-alcohol, and carbon tetrachloride. The data as observed are tabulated in Table I together with calculated values of calorimeter equivalents (C.E.) for the fourteen separate runs. In the calibration, the final mean value was 11.4 calories per degree, and only one value (14.7) deviated from the mean in a sufficient amount to be discarded as in probable error. Temperatures were varied from 30°C. to 50°C. in the separate determinations; but no consistent trend was observed, and the mean was taken without regard to the temperature of the run. The range 30°C. - 50°C. was chosen as it covered the desired experimental Cp range of the binary mixture.

Table II contains data obtained with mixtures of benzene and methyl-alcohol in concentrations of benzene varying from 10% by volume to 90% by volume. Temperatures were regulated during the runs to include the range 30°C. to 50°C. As the minimum boiling point of the binary mixture was only 57.2°C., determinations at temperatures over 50°C. were both unnecessary and extremely difficult.

A correlation of values obtained for 30°C. is shown in Figure 3 and are plotted in conjunction with values obtained directly and by extrapolation from accepted literature (2). Although the values do not fall directly on the postulated curve, the absolute deviation is small (maximum .027 cal./°C.). The curve is smooth and continuous showing no inflections even at the azeotropic point.

Table I Data for Calorimeter Calibration

Run No.	Material	E (Volts)	I (Amps)	M (Grams)	ΔT_h ($^{\circ}\text{C.}$)	$\Delta T_r(\text{av.})$ ($^{\circ}\text{C.}$)	T ($^{\circ}\text{C.}$)	Cp (cal/ $^{\circ}\text{C.}$)	C.E. (cal/ $^{\circ}\text{C.}$)
1	C_6H_6	3.50	1.23	105.02	0.860	0.232	40.	0.428	11.7
2	C_6H_6	3.46	1.22	104.96	0.810	0.277	50	0.436	10.0
3	C_6H_6	2.77	0.88	104.90	0.550	0.047	34.5	0.420	14.7*
4	CH_3OH	2.44	0.83	97.14	0.365	0.055	30	0.607	10.4
5	CH_3OH	2.75	0.86	97.08	0.300	0.163	40	0.618	13.2
6	CH_3OH	3.53	1.27	96.81	0.615	0.274	50	0.628	12.0
7	CH_3OH	2.48	0.79	86.55	0.378	0.059	30	0.607	11.9
8	CH_3OH	2.92	0.92	86.42	0.445	0.160	40	0.618	10.7
9	C Cl_4	2.55	0.78	176.19	0.518	0.080	30	0.206	11.5
10	C Cl_4	3.10	0.88	176.13	0.548	0.262	40	0.210	11.3
11	C Cl_4	3.42	1.01	175.86	0.610	0.366	50	0.213	13.3
12	C Cl_4	2.60	0.79	164.65	0.490	0.160	30	0.206	11.4
13	C Cl_4	2.93	0.89	164.60	0.560	0.237	40	0.210	12.4
14	C Cl_4	3.38	0.96	164.45	0.610	0.372	50	0.213	12.2

Mean value of (C.E.) = 11.4

*This value was discarded as the deviation from the mean value exceeded the probability of error and indicated some experimental discrepancy.

Table II Data for Specific Heat Determination

Run No.	C ₆ H ₆ (Vol.%)	T (°C.)	E (Volts)	I (Amps)	M (Grams)	Δt_h (°C.)	$\Delta t_{(av)}$ (°C.)	C.E. (Cal/°C.)	C _p (Cal/°C.)
15	10	30	2.63	0.89	89.80	0.460	0.028	11.4	0.637
16	10	30	2.72	0.92	81.65	0.500	0.111	11.4	0.582
17	10	40	2.80	0.95	89.75	0.400	0.180	11.4	0.606
18	10	50	3.00	1.06	89.64	0.440	0.220	11.4	0.641
19	20	30	2.61	0.86	96.39	0.448	0.042	11.4	0.563
20	20	30	3.15	1.05	86.70	0.665	0.119	11.4	0.568
21	20	40	2.96	1.07	96.36	0.490	0.170	11.4	0.600
22	20	50	2.95	1.07	96.26	0.360	0.255	11.4	0.651
23	30	30	2.92	1.02	94.49	0.588	0.065	11.4	0.570
24	30	40	2.97	1.04	90.44	0.485	0.187	11.4	0.601
25	30	50	4.30	1.57	89.05	1.130	0.285	11.4	0.639
26	40	30	3.55	1.27	95.28	1.000	0.052	11.4	0.524
27	40	30	2.90	0.98	90.54	0.498	0.142	11.4	0.578
28	40	30	3.07	0.99	90.07	0.533	0.123	11.4	0.606
29	40	40	3.53	1.27	93.97	0.753	0.260	11.4	0.563
30	40	40	3.26	1.04	90.44	0.498	0.230	11.4	0.610
31	40	40	3.30	1.07	90.00	0.530	0.200	11.4	0.640
32	40	50	4.21	1.48	92.86	1.019	0.328	11.4	0.591
33	40	50	3.52	1.16	90.19	0.580	0.276	11.4	0.628
34	40	50	3.90	1.29	89.84	0.700	0.338	11.4	0.643
35	50	30	3.20	1.11	92.26	0.773	0.078	11.4	0.525
36	50	40	3.65	1.23	90.98	0.800	0.234	11.4	0.561
37	50	50	4.32	1.53	90.85	1.070	0.355	11.4	0.605

Table II (Con't.)

Run No.	C ₆ H ₆	T	E	I	M	Δt_h	$\Delta t_r(\text{av})$	(C. E.)	Cp
38	60	30	3.15	1.08	95.28	0.695	0.089	11.4	0.534
39	60	40	3.48	1.24	94.20	0.770	0.207	11.4	0.555
40	60	50	4.09	1.48	94.07	1.028	0.298	11.4	0.574
41	70	30	3.85	1.34	97.58	1.170	0.095	11.4	0.480
42	70	40	3.95	1.40	96.45	1.000	0.186	11.4	0.573
43	70	50	3.80	1.36	96.31	0.854	0.285	11.4	0.556
44	80	30	3.07	0.98	90.76	0.680	0.099	11.4	0.483
45	80	40	2.50	1.14	90.72	0.755	0.252	11.4	0.502
46	80	50	3.82	1.32	90.61	0.830	0.383	11.4	0.530
47	90	30	3.24	1.01	96.33	0.748	0.116	11.4	0.444
48	90	40	3.78	1.25	95.60	0.955	0.245	11.4	0.473
49	90	50	3.90	1.44	94.58	1.000	0.393	11.4	0.491

Fig. 3 Specific Heats of Benzene-Methanol Mixtures at 30°C.

Figures 4 and 5 are similar plots of specific heats taken at 40° C. and 50°C. respectively. In these two curves, the maximum deviation (with the exception of one point) is only .02 cal./°C. Values were more consistent and regular although the shape of each curve was similar.

Fig. 4 Specific Heat of Benzene-Methanol Mixtures at 40°C.

Fig. 5 Specific Heat of Benzene-Methanol Mixtures at 50°C.

The curves from Figs. 3, 4, and 5 have been combined on Fig. 6 as a family to indicate the interrelationship of these specific heat data. It will be noted that the form is similar but that the methyl alcohol rich mixtures show a smaller increase in specific heat with temperature rise. This trend is more sharply exhibited in Figure 7 where the volume percentages are taken as the parameter and the specific heats are plotted against the temperature directly. The latter curves show an almost linear relationship between specific heats and temperatures for the same mixtures.

Enthalpy for a boiling liquid measured above 25°C. is defined as $\Delta H = \int_{25^{\circ}\text{C}}^{\text{B.P.}} C_p dt$. In the course of this investigation C_p has not been evaluated as an algebraic function of temperature and composition. However since the C_p values are now available at 30°, 40°, and 50°C., and since they fall into a regular family of curves with no apparent irregularity, graphical integration may be used for evaluation of the function.

The boiling point curve (Fig. 8) has been taken from data obtained by Rosenberg (4) and defines the upper limit of the specific heat integrals. Figure 9 presents the extrapolated specific heat curves with upper and lower limits set for evaluation. The data from this evaluation are presented in Table III. The calculation of molal enthalpies are illustrated by the following examples:

Mixture - 50% Benzene, 50% Methanol by volume

Boiling Point = 57.4°C. (from Figure 8)

Fig. 6 Comparison of Specific Heats of Benzene-Methanol Mixtures at 30°, 40°, and 50°C.

Fig. 7 Specific Heats of Benzene-Methanol
Mixtures at Varying Temperatures

Fig. 8 Boiling Point Curve for Benzene-Methanol Mixtures
Data from Rosenberg (4)

Fig. 9 Specific Heats for Benzene-Methanol Mixtures
at Varying Temperatures-Extrapolated

Table III Results of Graphical Integration for Enthalpies

Concentration % Benzene by Vol.	Boiling Point °C.	Area Under Curve (Cal./gm.)	Cal./mol (above 25°C.)
0	64.5	25.0	800
10	61.1	22.8	782
20	59.6	21.3	785
30	58.6	20.4	800
40	57.8	19.6	837
50	57.4	18.8	872
60	57.3	18.1	918
70	57.3	17.3	963
80	57.4	16.4	1010
90	57.8	15.4	1064
95	60.7	16.2	1190
97.5	64.5	17.5	1320
100	80.3	24.3	1895

Area under curve (Figure 9) = 18.8 cal./gm. = enthalpy/gm.

Ave. molecular weight = 46.4 (from figure 10)

Therefore enthalpy per mol of mixture

$$\Delta H_M = 18.8 \times 46.4 = 872 \text{ CAL/G.MOL}$$

Full evaluation of the enthalpies are shown in Figures 11 and 13 in terms of specific and molal enthalpies respectively. The latter necessitates the use of volume percent to mol percent conversions which have been expressed graphically in figure 12.

Fig. 10 Molecular Weights of Benzene-Methanol Mixtures

Fig. 11 Specific Enthalpies of Liquid Benzene-Methanol Mixtures

Fig. 12 Mol-Volume Relationships for Benzene-Methanol Mixtures

Fig. 13 Molal Enthalpies of Liquid Benzene-Methanol Mixtures

CONCLUSIONS AND RECOMMENDATIONS

A review of the data obtained in this investigation reveals some facts not particularly obvious from a previous knowledge of the characteristics of the system.

Specific heat curves show no definite break or reverse curvature throughout the entire composition range, and therefore conform to the group of other physical properties existing as continuous functions, namely, density, specific gravity, refractive index, etc. This fact is also emphasized by the regularity of the family grouping of constant composition curves of specific heat vs. temperature.

However in the determination of liquid enthalpies the extreme variations in the boiling point diagram produce a marked effect upon the resulting curves. By comparison it may be seen that when plotted on a volume basis, both the heat content and the boiling point curves follow a very definite downward trend with increasing percentages of benzene in the mixture until the very high concentrations are reached, at which point a sharp upward swing results. In the case of the enthalpy curve the slope is more negative and the point of inflection is therefore carried past the minimum boiling concentration and does not appear until the increase in boiling temperature is sufficient to overcome the decreasing enthalpy rate.

The effect of a decrease in enthalpy with an increase in the percent of benzene present is changed when expressed as a molar function. This is true because the molecular weight of benzene is so much greater than that of methanol. In this instance the heat content increases

gradually in a normal fashion until the rapid increase in boiling point again causes a rapid increase in enthalpy.

A function of this nature is not in conformity with existing enthalpy data for other systems, but some abnormality should be expected from the azeotropic nature of this system.

It should be noted that experimental values for the specific heat of pure methanol appears to be somewhat higher than values extrapolated from the literature. This would indicate that the upper end of the specific heat curves could be very slightly in error. However, without more conclusive data in this range there is no reason to doubt these experimental results. Moreover, the resulting influence of any error of this nature upon the enthalpy curve would be small.

In order to apply the method of Ponchon and Savarit to a distillation problem on this system, it is necessary to know one more relationship, i.e., vapor enthalpy vs. composition. Although the literature fails again to indicate a suitable procedure for this determination, it is believed that a procedure similar to that used for specific heat determinations would be applicable. In this instance, however, the heat of condensation would be measured calorimetrically. The same apparatus could then be used with but some slight adaptations.

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VITA

Harvey A. Rothenberg, son of Michael and Hannah Rothenberg was born on July 14, 1918 at Chicago, Illinois.

He attended O'Keeffe Grammar School and Hyde Park High School in Chicago, Illinois and upon graduation in February, 1936, he entered Armour Institute of Technology.

While at Armour Institute, he became a member of Rho Delta Rho social fraternity and the student chapter of the A. I. Ch. E. He was selected for membership in Phi Lambda Upsilon, national honorary chemical society, received letter awards in several sports and was elected to Honor "A", the honorary athletic society. During his undergraduate period he worked both for the NYA and as a student assistant in the Chemistry Department. In June, 1939, he was awarded the degree of Bachelor of Science in Chemical Engineering.

Accepting employment from Joseph E. Seagram & Sons, Inc., he worked at Lawrenceburg, Indiana, and in April, 1940, he was transferred to Louisville, Kentucky. With this company, he served as a production operator, production supervisor, War Production Board Assistant in converting grain distilleries to industrial alcohol production, and member of the Central and Plant Engineering Departments.

In September, 1940, he entered the evening division of Speed Scientific School of the University of Louisville, and received the degree of Master of Chemical Engineering in October, 1944.

In July, 1944, he was married to Anna L. Netherton in Louisville, Kentucky.