I. ABSTRACT

The heats of mixing at 25°C and 1 atmosphere have been determined for the binary liquid systems of ethanol-n-hexane, n-hexane-benzene, n-heptane-benzene, ethanol-n-heptane, ethanol-benzene and the ternary liquid systems of ethanol-benzene-n-hexane and ethanol-benzene-n-heptane. The specific heats have been determined for the two ternary systems at 25°, 35° and 45°C, and have been employed for calculation of ternary heats of mixing data at 35° and 45°C.

Brass calorimeters with thermistors as temperature sensing elements have been employed and the measurements are reported with an estimated accuracy of ± 1.2% for the binary and ± 2.4% for the ternary data.

Isenthalpic lines in calories per gram mole are prepared for the two ternary systems at 25°, 35° and 45°C, with the compositions expressed in mole fractions.

A comparison of the binary ΔH^m data with literature values provided a test of the reliability of the calorimeters. Where discrepancies existed in the literature among data for the binary systems, new data are established and compared. The ternary determinations, arranged along constant x_i/x_j lines, permitted a simple interpolation procedure.

The variation of the ternary heats of mixing with temperature indicated a non-linear effect.

Two methods, one for binary systems and the other for ternary systems, are proposed for extrapolating heats of mixing data over the complete concentration range from minimum data. For enthalpy of mixing, three experimental points are required as primary information for extrapolation of data of a binary system, whereas for a ternary system seven points are necessary. The methods, based on the Gibbs-Duhem equation may be employed for extrapolating other excess thermodynamic properties as well, and provide a consistent set of values.

A new approach has been successfully employed in the application of the quasi-lattice theory to heats of mixing data of binary systems, whereby a priori speculation of the interaction energy parameters is avoided. The specification of a separate $-\underset{|}{\mathrm{CH}}-$ contact allowed differentiation between molecules with branched and unbranched aliphatic chains. This has not been previously accomplished.

A set of quasi-lattice parameters has been obtained that provides representation of the heats of mixing data of benzene with a series of alkanes from C_5 to C_{13}, within an average percentage deviation of 3.6 per cent from the experimental values. The results obtained represent an improvement with respect to previous work.

II. ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to Dr. B.C.-Y. Lu, for his most valuable guidance and direction during this entire work.

Thanks are due to the members and staff of the Chemical Engineering Department for their assistance during this project. In particular the author would like to mention Messrs. Frank Giacobbi and Giuseppe Gasperetti for their help in preparation and setting up of the apparatus.

The author expresses his appreciation to Dr. R.F. Lama for helpful discussions and to Miss O. Boshko for indispensable help in preparation and arrangement of programs for the computer. In this connection thanks are due also to Mr. B. Boraydin and the staff of the computing centre.

Finally the author expresses his thanks to Mr. D. Poon, Mrs. Helen Chung and Mr. Jack Wang for their kind assistance.

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VI. NOMENCLATURE

a,b,c,a',b',	constants
A	molecule A
A_o, A_1, A_2	constants
B	molecule B
C	quasi-lattice parameter (Qx/2)(equations 31,32,34)
C	specific heat cal./(g)(^oC)(equations 50,51)
C'	specific heat cal./g.-mole ^oC (equations 55,56)
ch	- CH - type contact in the quasi-lattice theory
cl	- Cl type contact in the quasi-lattice theory
F	molal Gibbs free energy
G	any extensive molal property of a system
h	enthalpy of solution
$\overline{H}$	molal enthalpy (equation 11)
H	hydroxyl hydrogen type contact in the quasi-lattice theory
I, I_o, I_1	intercepts (equations 61, 62,63,65,66; figure 29)
I	aliphatic type contact in the quasi-lattice theory
I	current in amperes (equation 46)
J	the electrical equivalent of heat (4.184 Joules/cal.)
K	ratio of x_3/x_1 (figure 29)
K	constant for heater on calorimeter (1/4.184 R_H), (sample calculation)
L	relative partial molal enthalpy ($\overline{H} - H_{T,p}$)
M	molecular weight
n	number of components (equations 12,13,14)
n	number of different parameters C (equation 34)
n	number of moles of a component (equations 47,48,49,52,53,54)

n	number of carbons in n-alkane (equations 38,68)
O	oxygen type of contact in the quasi-lattice theory
q	total number of contacts on molecule A or B (equations 28,29)
P	pressure
Q	number of contact points in the quasi-lattice theory (equations 35, 37-40)
Q_c	electrical energy supplied to the calorimeter in calories (equations 43,46)
Q	heat absorbed on mixing, in calories (equations 43,47,48)
r	number of lattice sites for a molecule
R	gas constant
R	resistance of thermistors or heaters, ohms
S	slope of resistance-temperature curve for thermistors, $(R_T\beta/T^2)$
S	aromatic type contact in the quasi-lattice theory
S'	aliphatic contact on alkyl radical of aromatic compound
t	temperature ^{o}C
T	absolute temperature, ^{o}K
U	interaction energy, cal./g.-mole
V	volts
w	weight of component, grams
W	the heat equivalent of the calorimeter
x	liquid mole fraction
X	resistance measured by Wheatstone bridge (sample calculation)
X	function in the quasi-lattice theory (equations 31,34,35,36,39, 40,41)
$\underline{X}$	array of quasi-lattice functions X (equation 31)
Z	coordination number in the quasi-lattice theory

β	work function for thermistors
γ	liquid activity coefficient
Δ	indicates a property change as a result of mixing at constant T or P
η	quasi-lattice energy parameter, $e^{-U/RT}$
μ	chemical potential
θ	time, min.

Subscripts

A	molecule A
B	molecule B
B	binary mixture (equation 48)
B	benzene (equation 50)
c	refers to the calibration period (equations 43,46)
Cal	calorimeter
ch	refers to -CH- type contact, in the quasi-lattice theory
cy	refers to a cyclic molecule
H	hydroxyl-hydrogen contact, in the quasi-lattice theory
H-O	hydroxyl-hydrogen to oxygen type of interaction
H-S	hydroxyl-hydrogen to aromatic type of interaction
H-S'	hydroxyl-hydrogen to alkyl aliphatic type of interaction, aliphatic contact being on an aromatic compound
i,j,k	component i,j and k of mixture
ij	binary mixture of components i, and j
ijk	ternary mixture of components i,j, and k
i-i, i-j, j-j	types of interaction in the quasi-lattice theory
I	aliphatic type contact in the quasi-lattice theory
I-S	aliphatic to aromatic type interaction in the quasi-lattice theory

I-S'	aliphatic to alkyl aliphatic type interaction in the quasi-lattice theory
L	refers to liquid in calorimeter
m	indicates a mean value
N	number of moles of mixture (equations 15,17)
O	oxygen type contact in quasi-lattice theory
O-I	oxygen to aliphatic type interaction in quasi-lattice theory
O-I'	oxygen to alkyl aliphatic type interaction in quasi-lattice theory
O-S	oxygen to aromatic type interaction in quasi-lattice theory
O-S'	oxygen to alkyl aliphatic type interaction in quasi-lattice theory
p	constant pressure (equations 11,12,13,14,50,55,56)
p	number of kinds of contacts on molecule A (equations 31,32,34,35,36)
q	number of kinds of contacts on molecule B (equations 31,32,34,35,36)
soln	for the solution
S	aromatic type contact
S-S'	aromatic to alkyl aliphatic interaction in the quasi-lattice theory
x	at mole fraction x
x_1,x_2	indicate value of function at mole fraction x_1 and x_2
t	temperature °C
th	thermistor
T	total number of moles of binary or ternary system
T	temperature (equations 11,20-26)
1,2,3	components 1,2 and 3 of mixture
1	aromatic type of contact (equations 37,39-41)
2	aliphatic type contact (equations 38,39-41)

12	binary mixture of components 1 and 2
12	interaction between contact of type 1 and contact type 2 (equations 39-42)
13	binary mixture of components 1 and 3
23	binary mixture of components 2 and 3
123	ternary mixture of components 1, 2 and 3

Superscripts

A	molecule A
B	molecule B
E	excess property
M	mixing property
-	placed over a property indicates the partial molal property.

VII. INTRODUCTION

Heats of mixing data of liquids have been increasing in importance and demand. For the design and economic operation of several types of industrial equipment and for testing theories of solution, data concerning the heat effect associated with the mixing of liquids are constantly required. Neglect of such effects has been shown (15) to cause errors of 40%, for example, in distillation processes. Although the amount of data on heats of mixing of liquids has increased significantly for binary systems, the number of systems for which data are desirable is still large. Only a few ternary systems have been studied (11), (25), (35), (41), (53), and the number of multicomponent systems in the literature (41) for which data are reported, is still less.

Most of the studies were aimed at obtaining new data and developing new and more ideal calorimeters. The calorimeters presently in use are more sophisticated than earlier models. Most of the experimental difficulties have been overcome and there are several calorimeter designs that are satisfactory for experimental determination of heats of mixing of liquids. Some of the more important types are discussed under the review of calorimeters.

The experimental determination of heats of mixing has always been considered a very tedious and exacting operation for binary systems, and even more so for ternary and multicomponent systems. It is for this reason that engineers are always interested in obtaining the maximum amount of information from the minimum amount of experimental data. Efforts are also aimed at predicting heats of mixing of binaries and ternaries from analytical expressions derived from the molecular properties of the pure components. Success with such methods are dependent on further development of the theories of solutions and the models proposed for liquid structure.

In striving for economy in expenditure and resources there have been attempts to express ternary heats of mixing in terms of data for the binary systems and to minimise the number of experimental determinations necessary for providing data over the entire composition range for binary, and more assiduously, for ternary and multicomponent systems. The demand and usefulness of any correlation, graphical or analytical that allows attainment of the goals mentioned above are expressed by the engineering needs.

Objectives of this work

The following were the objectives of this research program:

1. The construction of a suitable calorimeter for the determination of heats of mixing of liquids.

2. A test of the reliability of the calorimeter.

3. Measurement of heats of mixing at 25°C for the binary systems of ethanol-n-hexane, n-hexane-benzene, n-heptane-benzene, ethanol-n-heptane and ethanol-benzene.

4. Measurement of heats of mixing at 25°C for the ternary systems of ethanol-benzene-n-hexane and ethanol-benzene-n-heptane.

5. Measurement of specific heats at 25°C, 35°C and 45°C for the ternary systems listed in 4.

6. Development of methods for extrapolating heats of mixing data of binary and ternary systems from a minimum of primary information.

7. Application of the quasi-lattice theory to heats of mixing data of binary systems to test the parameters proposed in an earlier investigation; to develop new parameters, and to overcome some of the difficulties that were evident from previous work.

VIII. LITERATURE REVIEW AND DISCUSSION

A. Heats of mixing of liquids

The discussion is restricted to the survey of data for the systems studied in this investigation.

1. Binary systems

ethanol-benzene

In the literature, heats of mixing of ethanol and benzene at 25°C are reported by Brown and Fock (8), Goates, Snow and James (23), Mrazek and Van Ness (45), Prigogine and Mathot (52), and Schnaible (61), (62), but there is some discrepancy between the data of Schnaible and the other authors. Data are also reported at 35° and 45°C by Brown and Fock (8) and Mrazek and Van Ness and at 45°C by Williamson and Scott (70).

ethanol-n-hexane

The heats of mixing of this system havebeen studied by Von Elbe (21) as a function of temperature and composition but the experimental data were not published. A graphical correlation between data for this system and those obtained for ethanol and n-heptane was given. Wolf, Pahlke and Wehage (71) reported data for this system. Brown, Fock and Smith (10) recently published data at 25°, 35° and 45°C but claimed only fair agreement with the data of Wolf et al.

ethanol-n-heptane

The heats of mixing of this system were studied by Von Elbe as a function of temperature. Brown, Fock and Smith (10) reported agreement with results of Savini and Van Ness (56) rather than Von Elbe (21). Numerical values were not published.

n-hexane-benzene

The data at 25°C reported for this system by Prigogine and Mathot (52) and Schnaible (61), (62) show some apparent discrepancy.

n-heptane-benzene

The data at 25°C of Lundberg (40) and Schnaible (61), (62) for this system are in fair agreement. Lundberg (40) reported data also at 50°C.

2. Ternary systems

No heats of mixing data existed in the literature for the two ternary systems ethanol-benzene-n-hexane or ethanol-benzene-n-heptane; for the few ternary systems studied (11), (25), (35), (41), (53), the number of experimental points was insufficient and the arrangement of the data unsuitable for any study of extrapolation.

B. Calorimetry and calorimeters

A general description of the application and techniques involved in calorimetry is given by Sturteyvant (64). Calorimeters of various descriptions, sizes and degree of complexity have been used previously with varying success.

The major sources of error in calorimetry are due to vaporisation and condensation effects caused by the change in vapor composition during mixing. In early designs of calorimeters (5), (12), (29), (69), a vapor phase was present and most of these authors appear to have ignored the correction necessitated by thermal effects due to changes in vapor composition. Later designs show that consideration was given to these errors and that efforts were taken to minimise the effects.

The calorimeter of Cheesman and Whittaker (19) in 1952 presented many desirable features. This was the first design to eliminate the necessity for correction due to a vapor phase. These authors used a plunger to pierce a tin-foil diaphragm separating two compartments containing the liquids. Further stirring was accomplished by slowly moving a magnet backwards and forwards, and this in turn caused an iron plunger to move in a similar manner in the liquid mixture. The cap of one compartment of the vessel carried a glass capillary sealed at the end remote from the cap, to allow for expansion and contraction during mixing. However, there was some degree of uncertainty as to the mixing in the capillary and a correction, for mass taking part in mixing, was necessitated. In 1952 Scatchard et al (59) used a horseshoe type tube as a mixing vessel with mercury separating the two components. By rotating the vessel, the mercury caused the liquids to mix.

In 1953 Tsao and Smith (67) employed a Dewar flask and the second component was added from a jacketed buret. This arrangement permitted very rapid determinations to be carried out. In 1954, Thacker and Rowlinson (66) used a calorimeter similar to that of Scatchard (59) but it was surrounded with a Dewar flask.

Adcock and McGlashan (1) in 1954 used the piercing membrane type calorimeter, with temperature measurement by thermocouple, where the reference temperature was taken as that of an identical apparatus simultaneously being used for blank determinations.

Cheesman and Ladner (13) in 1955, incorporated capillaries to allow for liquid expansion without the necessity of a vapor space. Brown and Fock (7) in 1955, employed a modified U-tube calorimeter, with mercury, initially separating the components, being used to cause mixing, on rotation of the mixing vessel.

Coops, Balk and Todd (16) in 1956, incorporated a circulating device in an isothermal calorimeter of the breaking-ampoule type. The liquids on mixing circulated through an annular path inside a spherical container; thermocouples were employed as temperature sensing elements. Moelwyn-Hughes and Missen (44) in 1957, used a similar calorimeter to that of Cheesman and Whittaker (14) in 1952. Schnaible, Van Ness and Smith (62) in 1957, used essentially the calorimeter proposed by Tsao and Smith (67) in 1953, with slight modification. Murti and Van Winkle (46) in 1958, used a similar type of calorimeter. Goates, Sullivan and Ott (25) in 1958 employed a stainless steel two-compartment calorimeter in the temperature range 10 to 40°C. The calorimeter of Ocon and Taboada (47) and (48) in 1959 was a 450 ml. Dewar flask with a bronze lid to support two thermometers, a heater, stirrer, pipette and an ether-cooling vessel. Hansen and Van Winkle (28) in 1960, used a calorimeter similar to that of Murti and Van Winkle (46) in 1958, both making use of thermocouples for recording temperature changes.

McGlashan and Morcum (42) in 1961, used a calorimeter similar to that of Adcock and McGlashan (1) in 1954 but with a few modifications. The calorimeter of Williamson and Scott (70) in 1960, was also similar to that of Adcock and McGlashan except that a thermistor was used as a temperature sensing element. Ratnam, Rao and Murti (53) in 1961, used essentially the same calorimeter as Murti and Van Winkle (46) in 1958. Findlay (22) in 1961, employed a calorimeter similar to that of Cheesman and Ladner (13) in 1955. Jessup and Stanley (31) in 1961, employed a Bunsen-type calorimeter in which the calorimetric medium is diphenyl ether. Prengle, Worley and Mauk (51) in 1961, used a Dewar type calorimeter which was similar in many respects to that of Tsao and Smith (67) in 1953. Brown and Fock (8) in 1961, designed a calorimeter similar to that reported by them in 1955, but with improvements, to eliminate various undesirable features. Thin corrugated diaphrams allowed changes in volume with minimum pressure changes. Mrazek and Van Ness (45) in 1961, developed a calorimeter with no vapor space, that allowed rapid determination of heats of mixing of endothermic liquid systems. In 1962 Otterstedt and Missen (50) used essentially the same calorimeter as that reported by Moelwyn-Hughes and Missen (44) in 1957. The principle characteristics of the calorimeter of Diaz Pena and Fernandez Martin (20) in 1963 were, the absence of a vapor phase and the use of small quantities of liquids (about 1 cc). Their calorimeter was developed from those of Das, Diaz Pena and McGlashan (18) in 1961 and Larkin and McGlashan (37) in 1961. Lundberg (40) in 1963 developed a calorimeter that allowed 4 determinations in a single run. This was designed for convenience and quick operation with reasonable accuracy. Except for accidental failure and possible anomalies at high dilutions two days were required for determination of heats of mixing of a mixture at a single temperature over the whole concentration range. The calorimeter contained four compartments formed by a shell of the shape of an inverted cup and by four vertical dividers. The four compartments were closed with a metal foil secured by a ring and crossbars. The metal foil for each compartment was ruptured in turn by depressing a knob. However, in order to rupture the diaphram, it was necessary to stop the stirring for about five seconds. The stirring apparatus rotated at 200 rpm. The calorimeter of Lama and Lu (36) in 1965 is basically similar to the earlier design of Cheesman and Whittaker (14) in 1952, without the capillaries, and modified for mixing powdered solids and liquids. This calorimeter was employed for endothermic and exothermic heat effects. The filling procedure ensured no vapor space prior to mixing of liquids. The mixing vessel was made of brass and a thermistor served as the temperature sensing element. Recently, in 1966, an isothermal dilution calorimeter was developed for measurement of endothermic heats of mixing, by Savini, Winterhalter, Kovach and Van Ness (57). The calorimeter could be used for integral as well as partial molal heats of mixing and compositions as low as 0.001 mole fractions could be investigated. Results could be obtained rapidly in a routine manner. This calorimeter was a refinement of an earlier design of Mrazek and Van Ness and consisted of a Dewar Flask with a specially designed feeding section employing mercury in its operation.

C. Methods of correlation, extrapolation and prediction of heats of mixing data

1. Correlation of heats of mixing data

a. Binary systems

In the literature, there are several empirical equations suggested for correlating heats of mixing data. For binary systems, Scatchard et al (60) proposed an equation for heat of mixing based on an analogy with excess free energy. Heats of mixing are expressed as a power series in $(x_i - x_j)$ as follows,

$$\Delta H_x^M = x_i x_j \quad A_o + A_1 (x_i - x_j) + A_2 (x_i = x_j)^2 + \ldots. \qquad (1)$$

where x_i and x_j are the mole fractions of components i and j respectively and the A's are constants which are functions of temperature and the properties of the system. The dissymmetry of the system and the accuracy of the experimental values determine the number of constants that fit the data. The constants are usually determined by the method of least squares.

Another equation developed by Boissonnas and Noordtzig (6) for non-polar systems is the following,

$$\frac{\Delta H_{12}}{x_1 x_2} = \overset{\infty}{H}_1 x_2 + \overset{\infty}{H}_2 x_1 \qquad (2)$$

An empirical modification (62), given below was found to fit data of non-polar systems, viz :

$$\frac{\Delta H}{x_1 x_2} = \overset{\infty}{H}_1 x_2 + \overset{\infty}{H}_2 x_1 - x_1 x_2 \left| \overset{\infty}{H}_1 - \overset{\infty}{H}_2 \right| \quad \ldots.$$

where $\left| \overset{\infty}{H}_1 - \overset{\infty}{H}_2 \right|$ represents the absolute value of $\overset{\infty}{H}_1 - \overset{\infty}{H}_2$.

These equations are satisfactory for systems involving non-polar components, only two constants being required to fit the data within two or three percent (62). For systems where at least one component is polar, even with a large number of constants, representation is unsatisfactory. It was pointed out (62) that in such cases a graphical correlation may be more expedient than an analytical one.

Graphical methods of correlation of binary heats of mixing data involve plots of $\frac{\Delta H_{12}}{x_1 x_2}$ versus x_1 or $x_1 x_2 / \Delta H_{12}$ versus x_1 suggested by Van Ness and Mrazek (63), if the former curve is not sufficiently linear.

b. Ternary systems

For ternary systems equations were proposed to express the heats of mixing in terms of the values of the constituent binaries. One such equation was originally developed by Scatchard et al (60) for ternary excess free energies in terms of volume fractions. Later Redlich and Kister (55) proposed a similar equation in terms of mole fractions. The form of the equation for heats of mixing, based on the above proposals is similar to that for free energy. In terms of mole fractions, ternary heats of mixing may be expressed by the following equation,

$$\begin{aligned}\Delta H^{M}_{1,2,3} = {} & x_1x_2\left[A_{o_{12}} + A_{1_{12}}(x_1-x_2) + A_{2_{12}}(x_1-x_2)^2 + \cdots\cdots\right] + \\ & x_1x_3\left[A_{o_{13}} + A_{1_{13}}(x_1-x_3) + A_{2_{13}}(x_1-x_3)^2 + \cdots\cdots\right] + \\ & x_2x_3\left[A_{o_{23}} + A_{1_{23}}(x_2-x_3) + A_{2_{23}}(x_2-x_3)^2 + \cdots\cdots\right]\end{aligned} \quad (3)$$

where $A_{o_{12}}$, $A_{o_{13}}$, $A_{o_{23}}$ etc., represent the constants in the corresponding equations for the constituent binaries.

Brown et al (9) have shown that this form of the equation is applicable for non-polar systems where the heats of mixing of the binaries are nearly symmetrical with respect to composition. When one of the components is polar, this equation does not provide satisfactory representation. To allow for this, Scatchard et al (59) suggested the modification of replacing the difference terms (x_1-x_2) and (x_1-x_3) by $(2x_1-1)$ where x_1 is the mole fraction of the polar component. The equation then becomes

$$\begin{aligned}\Delta H^{M}_{123} = {} & x_1x_2 \left[A_{o_{12}} + A_{1_{12}} (2x_1-1) + A_{2_{12}} (2x_1-1)^2 + \ldots\ldots \right] + \\ & x_1x_3 \left[A_{o_{13}} + A_{1_{13}} (2x_1-1) + A_{2_{13}} (2x_1-1)^2 + \ldots\ldots \right] + \\ & x_2x_3 \left[A_{o_{23}} + A_{1_{23}} (x_2-x_3) + A_{2_{23}} (x_2-x_3)^2 \quad \ldots\ldots \right] \end{aligned} \qquad (4)$$

where $2x_1-1 = x_1-x_2$ or $2x_1-1 = x_1-x_3$ according to the binary pair being considered. This equation has been found to give good agreement (58), (67), for two systems involving a polar component.

Another equation suggested by Tsao and Smith (67) may be expressed as follows,

$$\begin{aligned}\Delta H^{M}_{123} = {} & x_1x_2 \left[A_{o_{12}} + A_{1_{12}} (2x_1-1) + A_{2_{12}} (2x_1-1)^2 + \ldots\ldots \right] + \\ & x_1x_3 \left[A_{o_{13}} + A_{1_{13}} (2x_1-1) + A_{2_{13}} (2x_1-1)^2 + \ldots\ldots \right] + \\ & + (1-x_1)(x_2^{*})(1-x_2^{*}) \left[A_{o_{23}} + A_{1_{23}} (2x_2^{*}-1) + A_{2_{23}}(2x_2^{*}-1)^2 \ldots \right] \end{aligned} \qquad (5)$$

where $x_2^{*} = x_2/(x_2+x_3)$ and $2x_1-1 = x_1-x_2$ or x_1-x_3 according to the binary pair in question.

Mathieson and Thynne (41) proposed another equation for ternary heats of mixing of non-polar systems in terms of the values of the binaries, which may be expressed as follows,

$$\begin{aligned}\Delta H^{M}_{123} = {} & x_1x_2 \left[A_{o_{12}} + A_{1_{12}} (x_1-x_2-x_3/2) + A_{2_{12}} (x_1-x_2-x_3/2)^2 + \ldots\ldots \right] + \\ & x_1x_3 \left[A_{o_{13}} + A_{1_{13}} (x_1-x_3-x_2/2) + A_{2_{13}} (x_1-x_3-x_2/2)^2 + \ldots\ldots \right] + \\ & x_2x_3 \left[A_{o_{23}} + A_{1_{23}} (x_2-x_3) + A_{2_{23}} (x_2-x_3)^2 + \ldots\ldots \right] \end{aligned} \qquad (6)$$

Yet another equation, proposed by Knobeloch and Schwartz (35) may be expressed as follows,

$$\Delta H^{M}_{123} = \frac{\Delta_1 H_{123} + \Delta_2 H_{123} + \Delta_3 H_{123}}{3} \qquad (7)$$

where

$$\Delta_1 H_{123} = \frac{x_2}{x_2+x_3} \Delta_1 H_{12} + \frac{x_3}{x_2+x_3} \Delta_1 H_{13} + (1-x_1)^{\frac{1}{2}} \Delta_1 H_{23} \qquad (8)$$

$$\Delta_2 H_{123} = \frac{x_1}{x_1+x_3} \Delta_2 H_{12} + \frac{x_3}{x_1+x_3} \Delta_2 H_{23} + (1-x)^{\frac{1}{2}} \Delta_2 H_{13} \qquad (9)$$

$$\Delta_3 H_{123} = \frac{x_1}{x_1+x_2} \Delta_x H_{13} + \frac{x_2}{x_1-x_3} \Delta_3 H_{23} + (1-x_3)^{\frac{1}{2}} \Delta_3 H_{12} \qquad (10)$$

where $\Delta_1 H_{23}$ is the binary heat of mixing at a composition indicated by the intersection of the line from apex 1 to the base_{23} ; $\Delta_1 H_{12}$ and $\Delta_1 H_{13}$ are the binary heats of mixing for compositions given by the intersections of a line parallel to base_{23} and the side_{12} and side_{13} of the triangular composition diagram, respectively; $\Delta_2 H_{ij}$ and $\Delta_3 H_{ij}$ are similarly defined.

This equation was apparently developed from and used for very few data points (35) and was therefore not adequately tested. Furthermore computations at 9 binary compositions are required to establish a single ternary point.

The equations 3,4,5 and 6, described above, depend on the satisfactory representation of the heats of mixing of the constituent binaries, by a power series of the type discussed earlier. However for binary systems involving a polar component, even with a large number of constants the representation is unsatisfactory and this precludes any further attempts to use the above equations for correlation of ternary heats of mixing data.

2. Extrapolation and interpolation of heats of mixing data

For binary heats of mixing, the methods available for extrapolation and interpolation involve the use of graphical or analytical correlations. In order to obtain valid results with analytical correlations, satisfactory representation of the experimental data is necessary. Even so, these methods do not ensure a consistent set of data.

For ternary heats of mixing, it is necessary to resort to analytical representation for extrapolation and interpolation purposes. Because of the difficulties encountered in analytical representation, in the cases where one of the components of the ternary system is polar, a great demand exist for a graphical procedure that would allow extrapolation and interpolation of ternary heats of mixing data, in a consistent manner. In addition to this, it is desirable to establish the minimum number of experimental values that would be required for establishing heats of mixing data for ternary and multicomponent systems.

3. Prediction of heats of mixing data

In an effort to minimise expenditure of resources and time for establishing data when required, engineers have endeavoured to predict heats of mixing from the molecular properties of the pure components. Such endeavours involve application of a theory of solution and the specification of a model for liquid structure. The various theories of solutions, each with its own limitations, have been discussed and compared by Scott (63).

When the theories were developed and until recently there was not sufficient experimental data to allow adequate tests of the various models. With the heats of mixing data now available, efforts are aimed at testing the proposed models and establishing parameters that may provide a correlation with the molecular properties of the components. The parameters may then be used further to predict data for other systems.

The quasi-lattice theory in the form derived by Barker (3), (4), have been applied with some success by Goates, Snow and James (23) in describing the heats of mixing of ethanol with cyclohexane and both methanol and ethanol with benzene through the use of a "consistent and reasonable set of energy parameters".

Their procedure in the application of the theory to the ethanol-cyclohexane system consisted of varying one of the two energy parameters, the one of largest magnitude, to fit the maximum of the heat of mixing curve and finally adjusting the second smaller parameter to fit the shape of the curve as closely aspossible. The interaction of the hydroxyl-hydrogen and the oxygen occurs also in the systems of methanol or ethanol with benzene. The value for this interaction energy obtained from the first system was maintained for the alcohol-aromatic systems.

In the investigation (23), it was assumed that each hydrocarbon tetrahedron occupied one site of a fourfold coordinated lattice. The number of contact sites of the compounds were deduced directly from the structural formulas of the compounds. Goates, Snow and Ott (24), applied the theory further to a series of alcohols and aromatic hydrocarbons. For heats of mixing data they used the measurements reported by Mrazek and Van Ness (45) for alcohol-hydrocarbon systems, namely, the fifteen binary systems of methanol, ethanol, propanol, butanol and pentanol with benzene, toluene and ethylbenzene. They also applied the theory to free energies of mixing of the systems, methanol and benzene at 25°C using the equation proposed by Scatchard et al (59), ethanol and benzene at 45°C with the aid of the experimental data of Brown et al (9), and ethanol and toluene at 35°C using measurements of Kretchmer and Wiebe (34).

The calculated values for the three systems, agreed with the experimental results within 4-7 % but were generally low in all three cases. In the procedure (24) for fitting the experimental data, the general shape of the heats of mixing curve was established by the hydroxyl-hydrogen-aromatic and the oxygen-aromatic interaction energies. These were found to be important in determining the asymmetry of the curves. Then the height of the curve was adjusted by varying the aliphatic-aromatic interaction energy to produce the nearest fit. The same value was maintained for the hydroxyl-hydrogen-oxygen interaction energy. Examples of the extent of agreement were given only for the fitting of ΔH_x^M and ΔF_x^E data for ethanol and benzene at 25°C and 45°C respectively and for the fitting of ΔH_x^M data of propanol, butanol and amyl alcohol with ethylbenzene at 25°C.

It was pointed out (24), that "because one has so many parameters that he can, within reasonable limits, arbitrarily adjust, it is possible to fit a single set of ΔH_x^M experimental data with several combinations of energy values. To fit more than one system and yet maintain consistency among the constants used, limits very appreciably the number of ways of producing a satisfactory fit".

They found also (24), that the set of constants derived from a fitting of the heats of mixing data gave poor results in representing the free energy data. In studying the temperature effect on the energy parameters, they compared the calculated values of ΔH^M at X = 0.4 and proposed a 2-3% change in the interaction energies, U's, for each 10°C change in temperature. The temperature dependence of the energy parameters was of much less significance in the calculation of ΔF_x^E values than it was for ΔH_x^M .

Goates et al (24) concluded that "the generalised quasi-lattice model is useful for interpreting, and to some extent predicting a priori thermodynamic data of mixing in alcohol-hydrocarbon system." They suggested that by using the parameters proposed (24), semi-quantitative estimates with a ± 10% uncertainty was possible. Ott, Goates and Snow (49) further applied the theory to heats of mixing data for hydrocarbon-halogen-substituted hydrocarbon systems and to the hydrocarbon-hydrocarbon systems of benzene-n-hexane, benzene-n-heptane, benzene-cyclohexane and n-hexane-n-heptane.

They proposed a value of 70 cal./g.-mole for the aliphatic-aromatic interaction energy based on the average of those values producing the "best fit" of experimental data from the literature. For the criterion of "best fit", the average of the absolute values of the deviations at mole fractions 0.2, 0.4, 0.6, and 0.8, was used. For the aliphatic-aliphatic interaction a value of 1 cal./g.-mole was proposed. This result for the system n-hexane-n-heptane was claimed to serve as a test of the assumption of zero energy for interactions between I type contact points on different molecules. Energy values were also proposed for hydrocarbon-halogen interactions. An IBM-650 computer was employed for the rather lengthy computations. A figure illustrating the agreement obtained for a representative set, 7 of the 15 systems investigated, was given; however a comparison of the deviations was not reported.

Dacre and Benson (17) have applied the quasi-lattice theory to the heats of mixing data of methanol, ethanol, n-propanol, n-butanol and n-octanol with carbon tetrachloride. They found that the Barker model allowed calculation of the data for these systems with fair agreement. Sweeney and Rose (65) used the quasi-lattice theory of Barker in prediction of vapor-liquid equilibria for various alcohol-ester systems, such as methanol-methyl-acetate, ethanol-ethyl acetate, n-butanol-n-butylacetate, n-hexanol-n-hexyl acetate, and n-hexanol-methyl caproate. Successful results were obtained within the homologous series but only partial success with different type alcohol-ester mixtures.

The experimental results of McGlashan et al (42), for the heats of mixing and activity coefficients for the system n-hexane and n-hexadecane at several temperatures have been discussed by McGlashan, Morcum and Williamson (43) in terms of the lattice theory of mixtures of molecules of different sizes. This theory is outlined by Guggenheim (26,27). McGlashan et al considered three experimental mixing processes; (1) mixing at constant pressure, (2) mixing with zero volume change and (3) mixing at constant volume per element. Of these three, it was found that (3) corresponds more nearly, and (2) much more nearly than (1) to the mixing process implied by the lattice model. For lack of data only tentative comparison with the theory could be made for process (3). It was found also, that a choice of coordination number of Z = 4, 8, or 12 had no significant effect on their conclusions. Also no definite method for choice of elements was established, as a choice of $-CH_3$ and $-CH_2-CH_2-$, or $-CH_3$ and $-CH_2-$ or $-CH_2-CH_3$ and $-CH_2-CH_2-$ were equally valid.

These recent investigations are evidence of the growing interest and success in the application of the quasi-lattice theory.

IX. THEORETICAL CONSIDERATIONS

Heat of mixing

The term "heat of mixing", ΔH^M, is defined as the amount of heat absorbed or liberated per mole of mixture when pure components are mixed at constant temperature and pressure to form a solution. Hence

$$\Delta H^M = h_{soln} - x_1 (H_{T,p})_1 - x_2 (H_{T,p})_2 \qquad (11)$$

where h_{soln} is the enthalpy of the solution.

Thermodynamic considerations

Let G represent an extensive molal property, for example, enthalpy, of a homogeneous system and let ΔG represent the change in the property on mixing the pure components at constant temperature and pressure to form one mole of solution. Then

$$G = \sum_{i=1}^{n} x_i G_i + \Delta G \qquad (12)$$

According to Euler's theorem

$$G = \sum_{i=1}^{n} x_i \overline{G}_i \qquad (13)$$

where $\overline{G}_i$ represents the partial molal property of the component i. By combining equations 12 and 13, the following is obtained,

$$\Delta G = \sum_{i=1}^{n} x_i (\overline{G}_i - G_i) = \sum_{i=1}^{n} x_i \Delta \overline{G}_i \qquad (14)$$

This equation is also valid for excess thermodynamic properties of mixing. An excess thermodynamic property is defined as the difference between the thermodynamic property of mixing for the system being considered and that for an ideal solution at the same temperature, pressure and composition, namely

$$\Delta G^E = \Delta G - \Delta G^{ideal} \qquad (15)$$

An excess partial molal property for a component in solution is similarly defined by

$$\bar{G}_i^E = \bar{G}_i - \bar{G}_i^{ideal} \qquad (16)$$

Hence

$$\Delta \bar{G}_i^E = \Delta \bar{G}_i - \Delta \bar{G}_i^{ideal} \qquad (17)$$

When the property concerned is enthalpy, $\Delta H^{ideal} = 0$, and $\bar{H}_i^{ideal} = H_i$, therefore $\Delta H^E = \Delta H$, and $\Delta \bar{H}^E = \Delta \bar{H}_i$.

For a binary system at constant temperature and pressure the excess partial molal properties of mixing are related by the Gibbs-Duhem equation

$$\frac{dG_B}{dx_A} = -\left(\frac{x_A}{1-x_A}\right)\left(\frac{d\bar{G}_A}{dx_A}\right) \qquad (18)$$

or

$$\frac{d\Delta\bar{G}_B}{dx_A} = -\left(\frac{x_A}{1-x_A}\right)\left(\frac{d\,\Delta\bar{G}_A}{dx_A}\right) \qquad (19)$$

The Gibbs-Duhem equation may be applied to many different thermodynamic properties because of its generality. The equation in various forms is the accepted criterion for testing the thermodynamic consistency of data. The Gibbs-Duhem equation is applicable to any number of components of a system.

If equation 11 is differentiated partially with respect to x_1 and x_2, the following equations are obtained,

$$\frac{\partial(\Delta H^M_x)}{x_1} = \bar{H}_1 - (H_{T,p})_1 = L_1 \tag{20}$$

$$\frac{\partial(\Delta H^M_x)}{x_2} = \bar{H}_2 - (H_{T,p})_2 = L_2 \tag{21}$$

where $(H_{T,p})_i$ is the molal enthalpy of pure component i ; $\bar{H}_i$ is the partial molal enthalpy of component i in the solution at the same temperature and L_i is the relative partial molal enthalpy of component i, i.e., the heat absorbed per mole of component i at constant T and p when the pure component is dissolved in a large quantity of solution without a change in the composition of the solution.

Excess partial molal enthalpies may be obtained by the method of tangent and intercepts, involving the curves of ΔH^M versus x_1 or $\Delta H^M/x_1x_2$ versus x_1 as suggested by Van Ness and Mrazek (68). It has been shown recently (57) that partial molal enthalpies may be obtained by direct experimental measurements.

In a previous investigation, the following equations were proposed by Lu (38) for representing heats of mixing and relative partial molal enthalpies as functions of temperature,

$$\Delta H^M_N = a + bT \tag{22}$$

and

$$L_1 = a' + b'T \tag{23}$$

or

$$\Delta H^M_N = a + bT + cT^2 \tag{24}$$

and

$$L_1 = a' + b'T + c'T^2 \tag{25}$$

Evidence was summarised (38), supporting the linear variation of ΔH^M_x values as a function of temperature, for several systems. However, it was pointed out, also, that the linear relationship did not represent experimental data (0°-100°C) for the system ethanol-water, over the entire composition range. For alcohol concentrations higher than 28.1 mole %, the temperature effect was apparently more complicated at higher temperatures.

The experimental determination of the ternary heats of mixing as a function of temperature for the two systems of this investigation provides data to which the above equations may be applied and tested. In addition the results will be useful where expressions for the temperature dependence of the activity coefficients for the two ternary systems, are required. The temperature dependence is expressed by the equation

$$\frac{\partial \ln \gamma_1}{T} = \frac{(H_{T,p})_i - \overline{H}_i}{RT^2} = \frac{-L_i}{RT^2} \qquad (26)$$

C. The quasi-lattice theory of Barker and its application

1. The generalised quasi-lattice theory-application to thermodynamic excess properties.

The quasi-crystalline model for the liquid state is one approach to the theory of solutions and is based on a high degree of order such as in crystals but with some degree of disorder to represent the fluidity of the liquid state. The method has met with considerable success in the theory of polymer solutions (27).

Barker (3)(4) used the quasi-crystalline approach in predicting the excess free energy (and excess chemical potentials), entropy and heats of mixing for solutions of strongly associated substances such as alcohols in relatively non-polar substances such as chloroform and benzene.

The theoretical relations which form the basis for the predictions are expressed by a series of mathematical relations first derived by Barker. The mathematical equations are themselves based on a physical model describing the relative positions and interactions of the individual molecules in a mixture.

In the representation of the physical model each of the molecules immediately adjacent to one another in a mixture is considered to occupy a definite number of sites on a well-defined lattice. Each site so occupied is identified with a particular atom or group of atoms in a molecule. Each site is considered to have a certain coordination number which refers to the number of possible directions or surfaces of contact of the atoms at a given site, with other atoms of either the same molecule or a different molecule. The lattice must of course be three dimentional, to represent the liquid state, and the mathematical derivations are based on three dimensions.

A rigorous lattice picture would not result in a successful theory of solution, since it is obvious that extreme order does not exist in a liquid. This, however, is allowed for by setting up the rigorous order only for a given site on the lattice and its nearest-neighbour sites (those sites coordinated directly to a given site). In this way, there is short-range order but long-range disorder is allowed.

2. Lattice parameters

The generalized quasi-lattice model of Barker recognises different types of contact sites on a molecule. For example an alcohol molecule is considered to have three types of sites:

a) Hydrocarbon (designated as type I)

b) Hydroxyl hydrogen (designated as type H)

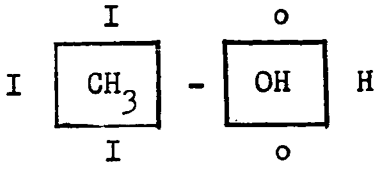
c) Oxygen (designated as type O)

Table 1

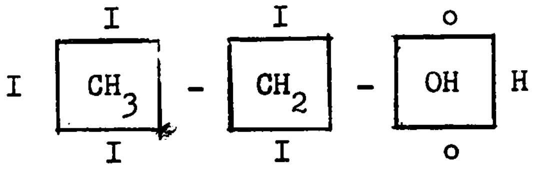
Literature values of the quasi-lattice parameters for various molecules based on the geometrical molecular structure.

Molecule	Ref.	Q_H	Q_O	Q_I	Q_s	Q_s'	C_{cl}	r
CH_3OH	(24)(25)	1	2	3	-	-	-	2
C_2H_5OH	(24)(25)	1	2	5	-	-	-	3
n-C_3H_7OH	(25)	1	2	7	-	-	-	4
n-C_4H_9OH	(25)	1	2	9	-	-	-	5
n-$C_5H_{11}OH$	(25)	1	2	11	-	-	-	6
C_6H_6	(24)(25)	-	-	-	12	-	-	4
$C_6H_5CH_3$	(25)	-	-	-	11	3	-	5
$C_6H_5C_2H_5$	(25)	-	-	-	11	5	-	6
n-C_6H_{14}	(49)	-	-	14	-	-	-	6
C_6H_{12}	(24)	-	-	12	-	-	-	4
C_7H_{16}	(49)	-	-	16	-	-	-	7
CCl_4	(17)(49)	-	-	-	-	-	12	5

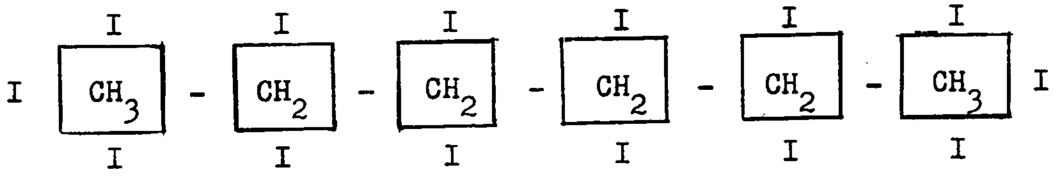
Illustration of lattice sites and types of interaction for alcohols and hydrocarbons



a. methanol



b. ethanol



c. n-hexane

Figure 1

Toluene and ethylbenzene for example, are considered to have two types, an aromatic hydrocarbon type (S) associated with the benzene ring and an aliphatic type (S') for the alkyl substituents. Benzene is treated as having only the aromatic (S) type site.

Application of the theory requires a knowledge of the number and type of sites on each molecule and the energies for all possible interactions of these sites. The number of sites for an alcohol molecule is usually calculated on the basis that each carbon and each oxygen atom occupy one position in a fourfold coordinated lattice. Atoms within the same molecule are considered as nearest neighbours. The remainder of sites available for contact with another molecule are represented by the letter Q. Subscripts to Q such as H, O, I, S, and S' or 1, 2, etc. refer to the type of site. The number and types of sites used in the literature (17), (24), (25), (49) are shown in Table 1. The number of types and number of lattice sites are illustrated for methanol, ethanol and n-hexane in Figure 1.

For the benzene-alcohol systems four types of sites, H, O, I, S are present resulting in ten interactions H-H, H-O, H-I, H-S, O-O, O-I, O-S, I-I, I-S and S-S. For the benzene-aliphatic hydrocarbon systems there are usually two types, I and S resulting in three interactions I-I, I-S and S-S. For systems involving toluene, and xylene, etc., the S' type included for the alkyl substituents introduces an additional five types of interactions namely H-S', O-S', I-S', S-S' and S'-S'.

3. Energy parameters

The energy of interaction, U_{i-j} is defined by the following equation,

$$U_{i-j} = \frac{1}{2}(i-i) + \frac{1}{2}(j-j) \qquad (27)$$

where i and j represent the various types of contact points such that one i-i contact and one j-j contact interact to produce two i-j contacts. By this definition the energy of interaction between like sites is zero, so that, for example $U_{H-H} = U_{O-O} = U_{I-I} = U_{S-S} = 0$ for the alcohol-benzene systems. Of the remaining six interactions for these systems, four (H-O, H-S, O-S, and I-S) are usually considered to be most significant either because the energies of interaction are expected to be relatively high as in the case of (H-O, H-S and O-S) or because the number of interactions of the particular type is large as in the case of the (I-S) type. The energy terms for the remaining two interactions H-I and O-I are considered to be zero.

In the literature (24), the interactions H-O, H-S and O-S were found to be more energetic than the H-I and O-I types. Also the interactions $U_{H-S'}$, $U_{O-S'}$ are considered to be similar to U_{H-I}, U_{O-I} and U_{I-I} and are assigned values of zero. The S-S' interaction is similar to that of I-S.

The number of contact points, q_A, q_B, are related to the number of lattice sites r and the coordination number z by the following equations

$$q_A Z = r_A Z - 2 r_A + 2 \qquad (28)$$

$$q_B Z = r_B Z - 2 r_B + 2 \qquad (29)$$

The number of contact points are further divided into classes according to type of contact so that Q_H^A represents the number of contacts of type H on the A molecule, and so on.

If in general, molecule A has p kinds of contacts and molecule B has q kinds, the various kinds of contacts may be numbered from 1 .... to (p+q) starting with the first p types for molecule A and then the q types for the molecule B.

The energy of interaction between contacts of types i and j is U_{i-j} cal./mole and is represented by the energy parameter η_{i-j} where

$$\eta_{ij} = e^{-U_{i-j}/RT} \qquad (30)$$

R is the gas constant, and T the absolute temperature ^{o}K.

The mathematical expressions developed by Barker (3), for the parameters X_i in the quasi-lattice theory are of the form

$$f_i(\underline{X}) = X_i\,(\eta_i\,\underline{X}) - C_i = 0 \qquad (31)$$

where $\underline{X}$ is the array $X_1, X_2, \ldots X_{p+q}$; η_i is the array $\eta_{i1}, \eta_{i2} \ldots \eta_{i(p+q)}$ and

$$C_i = Q_i \frac{x_i}{2} \qquad (32)$$

Q_i is the number of contacts of type i on the particular species A or B, and x_i is specified as follows

$$\begin{aligned} x_i &= x_A \quad \text{for} \quad 1 \leq i \leq p \\ &= x_B \quad \text{for } p+1 \leq i \leq p+q \end{aligned} \qquad (33)$$

The set of p+q equations $f_i\ (\underline{X}) = 0$ must be solved for the values of the p+q quantities $X_i \ldots X_{p+q}$ for a given concentration, x_p, x_q. An iterative process, the Newton-Raphson method is employed.

For the molecules A and B, the set of equations to be solved are as follows, where $n = p + q$

$$f_1 (X_1, X_2, \ldots X_n) = X_1 (\eta_{11} X_1 + \eta_{12} X_2 + \ldots \eta_{1n} X_n) - C_1 = 0$$

$$f_2 (X_1, X_2, \ldots X_n) = X_2 (\eta_{21} X_1 + \eta_{22} X_2 + \ldots \eta_{2n} X_n) - C_2 = 0$$

$$f_3 (X_1, X_2, \ldots X_n) = X_3 (\eta_{31} X_1 + \eta_{32} X_2 + \ldots \eta_{3n} X_n) - C_3 = 0$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$f_n (X_1, X_2, \ldots X_n) = X_n (\eta_{n1} X_1 + \eta_{n2} X_2 + \ldots \eta_{nn} X_n) - C_n = 0 \tag{34}$$

It should be mentioned here that $\eta_{ij} = \eta_{ji}$ and $\eta_{ii} = 1$.

4. Chemical potential

In terms of the solution of the above equations the chemical potential of a component is given by the following expressions :

$$\mu_i^E = RT \sum_i Q_i \ln (X_i / x_i X_i') + r_i (\frac{Z}{2} - 1) \ln (\frac{r_B x_B + r_A x_A}{r_i}) \tag{35}$$

where the following conditions hold for i.

i represents A for $1 \leqslant i \leqslant p$, and B for $p + 1 \leqslant i \leqslant q$; X_i' refers to the values of X_i when $x_A = 1$ and $x_B = 1$.

5. Heats of mixing

By the quasi-lattice theory the heat of mixing at a particular composition x is given by the following expression:

$$\Delta H^M = -RT \sum_{i=1}^{p-1} \sum_{j=i+1}^{p} (X_i X_j - x_A X_i' X_j') \eta_{ij} \ln \eta_{ij}$$

$$+ \sum_{i=p+1}^{q-1} \sum_{j=i+1}^{q} (X_i X_j - x_B X_i' X_j') \eta_{ij} \ln \eta_{ij}$$

$$+ \sum_{i=1}^{p} \sum_{j=p+1}^{q} (X_i X_j \eta_{ij} \ln \eta_{ij}) \qquad (36)$$

In applying the theory to heats of mixing, it is therefore necessary to specify the interaction energy U_{ij}, and the number of contacts on each molecule Q_i to allow solution of the equations for the parameters in the array $\underline{X}$.

A comparison of the calculated values of ΔH^M with experimental or literature values would determine the selection of parameters.

D. Application of quasi-lattice theory to benzene-n-alkane systems

Application of the quasi-lattice theory to heats of mixing of benzene and n-alkanes involves the assumption of the number of contacts for the benzene and the n-alkane molecules and the adjustment of one interaction energy of type U_{I-S}, to fit the experimental data. For aromatic hydrocarbons, the number of contact points is usually designated by Q_S and for saturated hydrocarbons, Q_I. In this investigation Q_1 and Q_2 are employed respectively. According to the geometrical molecular structure used in the literature (24), (25), (49), the values of Q_1 and Q_2 may be expressed as follows:

$$Q_1 = 12 \tag{37}$$

$$Q_2 = 2n + 2 \tag{38}$$

where n refers to the number of carbon atoms in the molecule concerned.

The equations 34 and 36 for calculating the heats of mixing values may be expressed as follows:

$$X_1 (X_2 \eta_{12} + X_1) = Q_1 x_1/2 \tag{39}$$

$$X_2 (X_2 + X_1 \eta_{12}) = Q_2 x_2/2 \tag{40}$$

$$\Delta H^M = - 2 RT (X_1 X_2 \eta_{12} \ln \eta_{12}) \tag{41}$$

where

$$\eta_{12} = e^{- U_{12}/RT} \tag{42}$$

U_{12} being the interaction energy.

X. EXPERIMENTAL DETAILS

A. Materials

1. Liquids

The list of pure liquids used in this investigation is given in Table 2 together with their grade, purity, and a comparison of measured and literature values of their refractive indices at 25°C. The liquids were used without further purification.

Table 2

Physical properties of the materials

Compound	Grade	Minimum* Purity (mole %)	Refractive Indices at 25°C Experimental	Lit. (a)
n-hexane	Research	99.9	1.37230	1.37226
n-heptane	Research	99.9	1.38525	1.38517
benzene	Spectrograde	99	1.49787	1.49790
ethyl alcohol	Pure absolute	99	1.35918	1.35914

* suppliers' data.
(a)Dow Chemicals Handbook.

2. Preparation of binary liquid mixtures

For a binary mixture of a particular composition, a predetermined volume of one component was measured into a dried and preweighed flask closed with a ground glass stopper. The flask with its contents was weighed and the weight was recorded. An amount of the second component, calculated from the weight of the first was then added to the flask, after which the weight was again recorded. The contents were mixed by shaking and the composition was calculated from the recorded weights.

3. Preparation of ternary liquid mixtures

The procedure was similar to that for binary mixtures. First a binary mixture was made up at a required composition in sufficient quantity. This mixture was then used for preparation of ternary mixtures, with a constant binary composition ratio, at required ternary mole fractions.

B. Calorimeter apparatus

The calorimers reviewed in Section VIII have shown a general improvement in design over the years as the various associated problems were solved. There are several designs, which are adequate for experimental heats of mixing of acceptable precision.

The calorimeter used in this investigation has several unique advantages for the determination of heats of mixing; in order of importance, these are:

(1) The heat associated with the breaking of the foil separating the compartments of the mixing cell is negligible.

(2) The design of the stirring mechanism makes it possible to accomodate several calorimeter jackets in the constant temperature bath.

(3) The brass jackets, unlike pyrex glass jackets, facilitate loading and unloading.

In addition to these advantages, there are others shared by other calorimeters:

(1) Mass losses to the outside are avoided.

(2) Small temperature changes may be accurately measured.

(3) Large volumes of liquids are not required for a determination.

Any apparent disadvantage of this calorimeter, for determination of heats of mixing, is also shared by other earlier improved calorimeters. The most significant of these common disadvantages is the rather lengthy time required for the adequate preparation of the mixing cell and the mixtures.

1. Details of assembly

A photograph of the assembly is given in Figure 2. Other important components of the assembly are shown in Figures 3,4,5,6 and 7.

a. The mixing cells

A sketch of a cell is shown in Figure 3.

The mixing vessels were made of two cylindrical parts of brass, which could be screwed together, with a tin foil diaphram, placed between teflon gaskets, separating the two compartments. Two threaded brass plugs carrying teflon gaskets for vacuum seal, closed the top and bottom of the calorimeters. In the lower section a gold-plated nail was used as a plunger to pierce the diaphram and to stir the liquids. On the outside of the lower portion of each vessel a length of silk covered manganin wire, gauge 26 was wound non-inductively and formed the heating coil. The coils were insulated from the metal of the vessel by a layer of glyptal cement which also served to hold them in place.

The temperature sensing element on each calorimeter was a Veco bead thermistor which was cemented on the outside of the lower or upper compartment with glyptal or epoxy resin. The resistances of the heating coils ranged from 9 to 25 ohms and were determined accurately in auxiliary experiments.

The voltage and current leads from the heating coils and also the

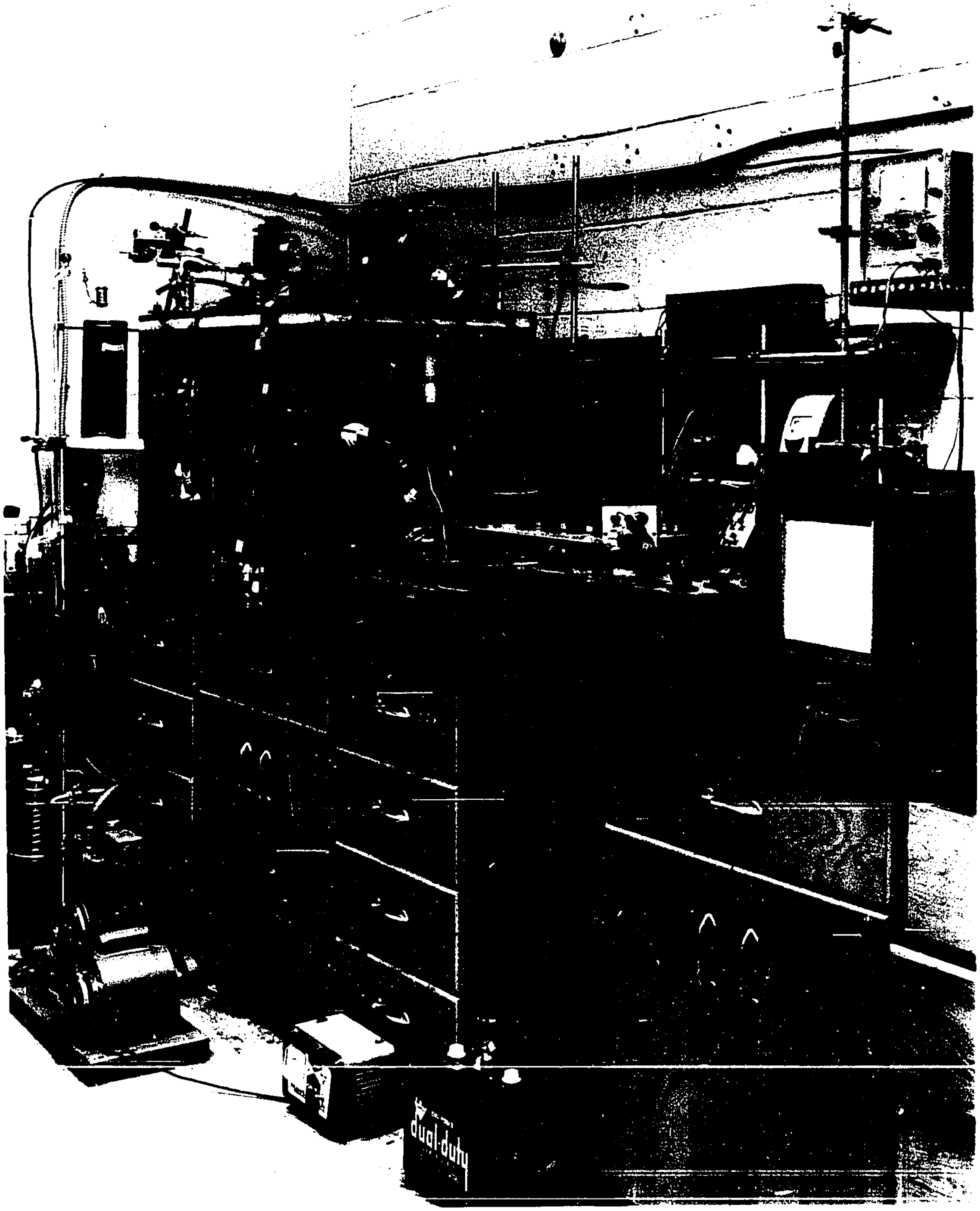
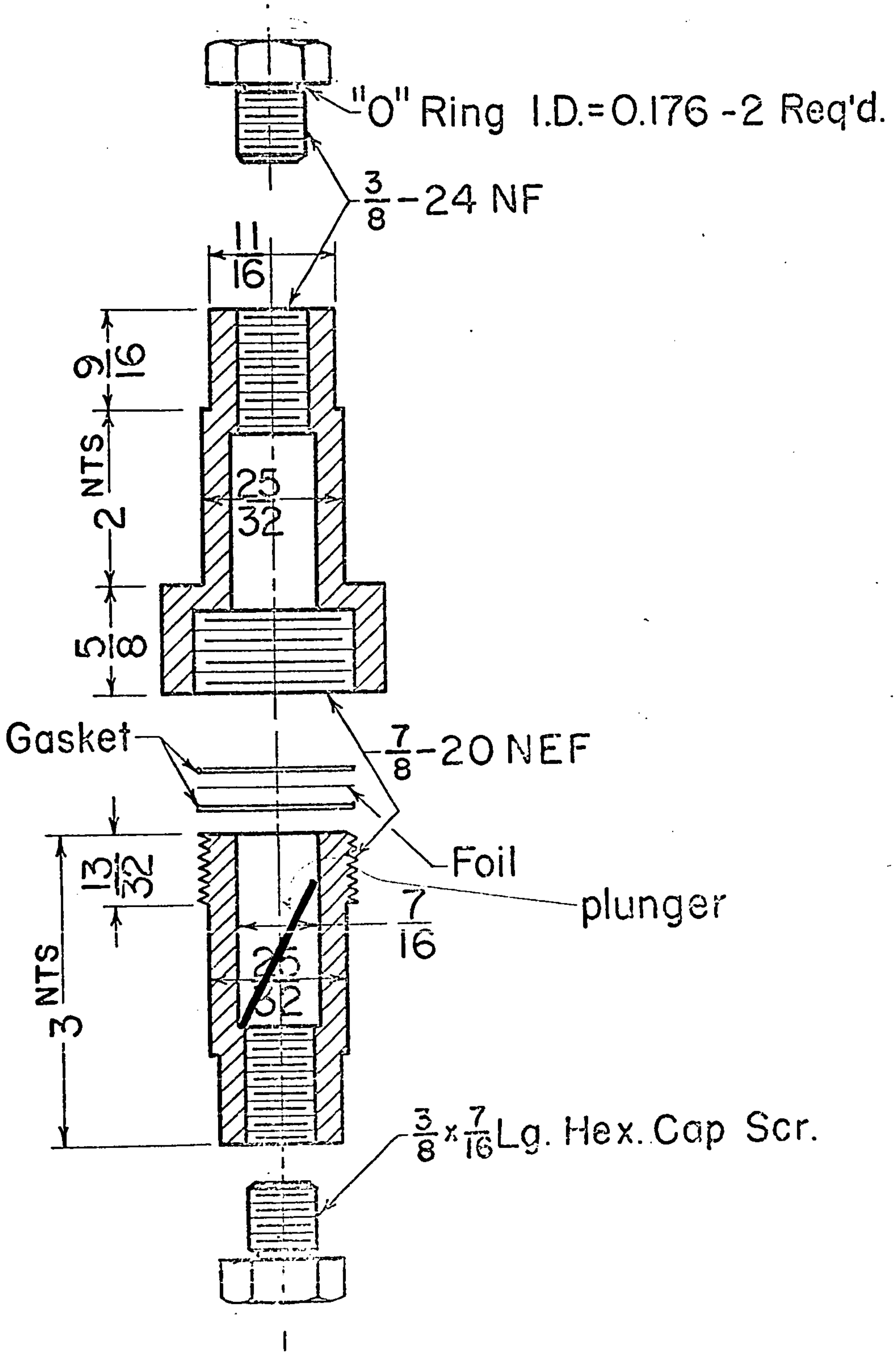


Figure 2. Calorimeter assembly

Figure 3. Mixing cell



two leads from the thermistors were soldered to the male portion of multiple pin connectors. The fine wires of the thermistors were carefully silver soldered to the leads.

b. Jackets

A sketch of a calorimeter jacket is shown in Figure 4. The jackets were constructed from 2 1/8" O.D. brass tube with a wall thickness of 1/8". The upper parts of the tubes were provided with flanges while the lower ends were closed with brass disks.

The lids of the jackets were flanges with two openings for connection of the jackets to the vacuum and the electronic systems. The vacuum outlets were made from 1/2" O.D. copper tube, about 6" long, and were soldered into one of the openings of the lid. The other opening of the lids carried 4" long copper tubes of 5/8" O.D. provided with Swagelok adapters and 8-point multiple hermetic seals for electrical connection.

Electrical insulation of the leads at the hermetic seals was accomplished with Glyptal resin, and the seals were maintained about 2 inches above the surface of the water in the constant temperature bath.

Corresponding leads, connected on both sides of the seal, provided a means of connection to the external circuits, from each jacket and calorimeter assembly. This connection was made at the main-junction multiple-pin connector to which the heating and measuring circuit were wired.

An O-ring, sitting on a rectangular groove in the lower flange rendered the interior of the jacket vacuum-tight when a 10-pound torque on four sealing bolts was applied across the two flanges.

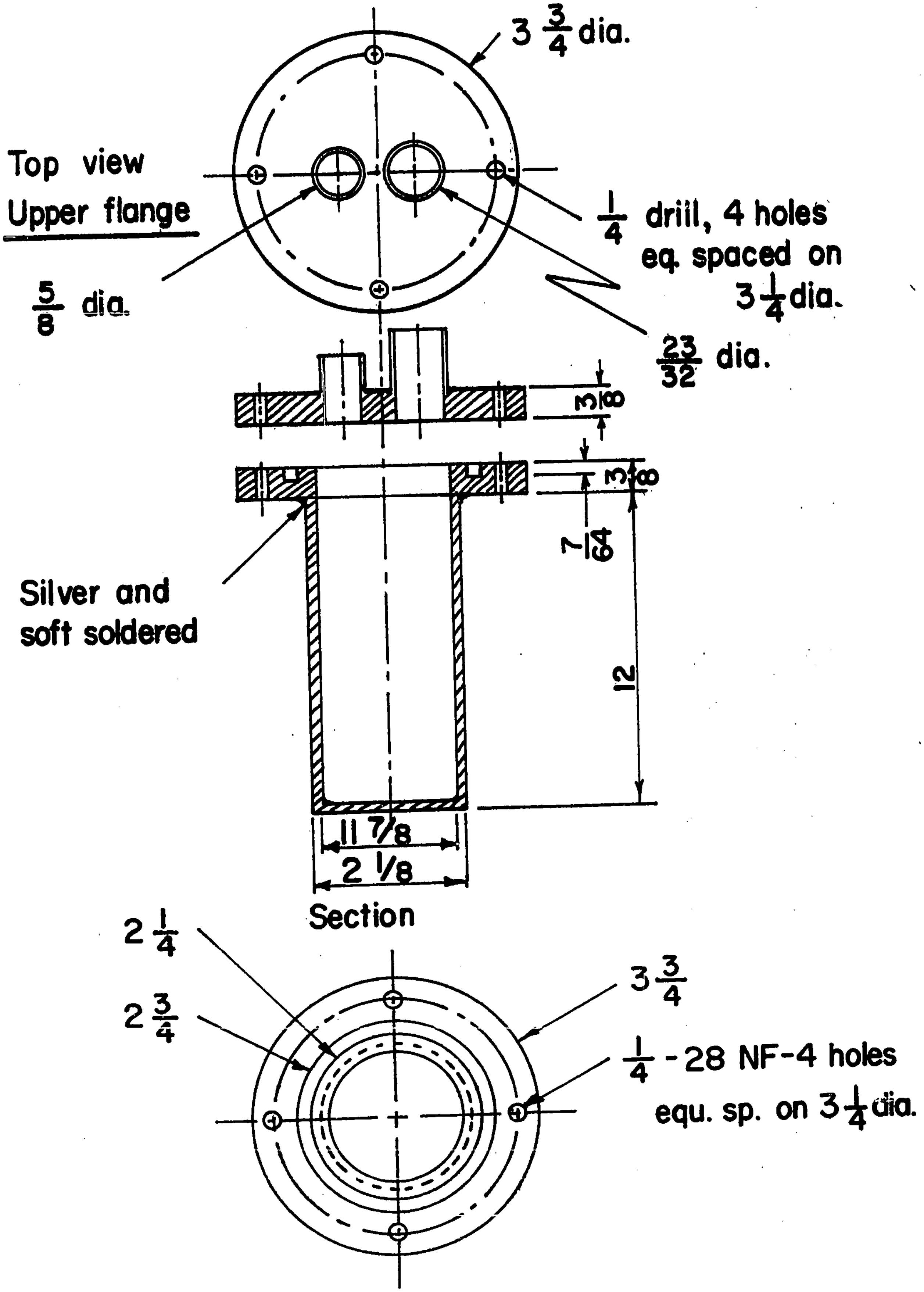


Figure 4. Jacket

c. Mixing and stirring - coil circuit

A sketch of the coil and coil-circuit is given in Figure 5. A solenoid, around and supporting the metal jacket in which each calorimeter was mounted, itself supported on a metal rack of brass in the constant temperature bath, provided a means of mixing the liquids in the two compartments, by causing the plunger to pierce the diaphram. Continued stirring during the mixing and calibration periods was maintained by breaking and reconnecting the circuit to the solenoid, about 40 times per minute. To accomplish this, a motor with a cam-actuating shaft, operating a microswitch, was employed.

The DC power for the solenoids was provided from a 110 volt AC source which was reduced by a variac transformer and then rectified in a resistance-capacitor circuit. The voltage across the solenoids was approximately 50 volts DC and the resistances of the coils ranged from 21 to 34 ohms.

The solenoids were positioned at a predetermined height with respect to the jacket and calorimeter on the inside, for effective rupture of the diaphram and efficient stirring.

The solenoid circuit was arranged with a main outlet into which any one of the solenoids could be plugged for operation.

d. Heating and measuring circuit

A sketch of the circuit for supplying energy, and measuring the energy supplied, to the calorimeter is shown in Figure 6.

The heating circuit consisted of 2 twelve volt lead-acid bateries, V_1 and V_2, connected in parallel; dummy resistors, VR, DR, and a standard

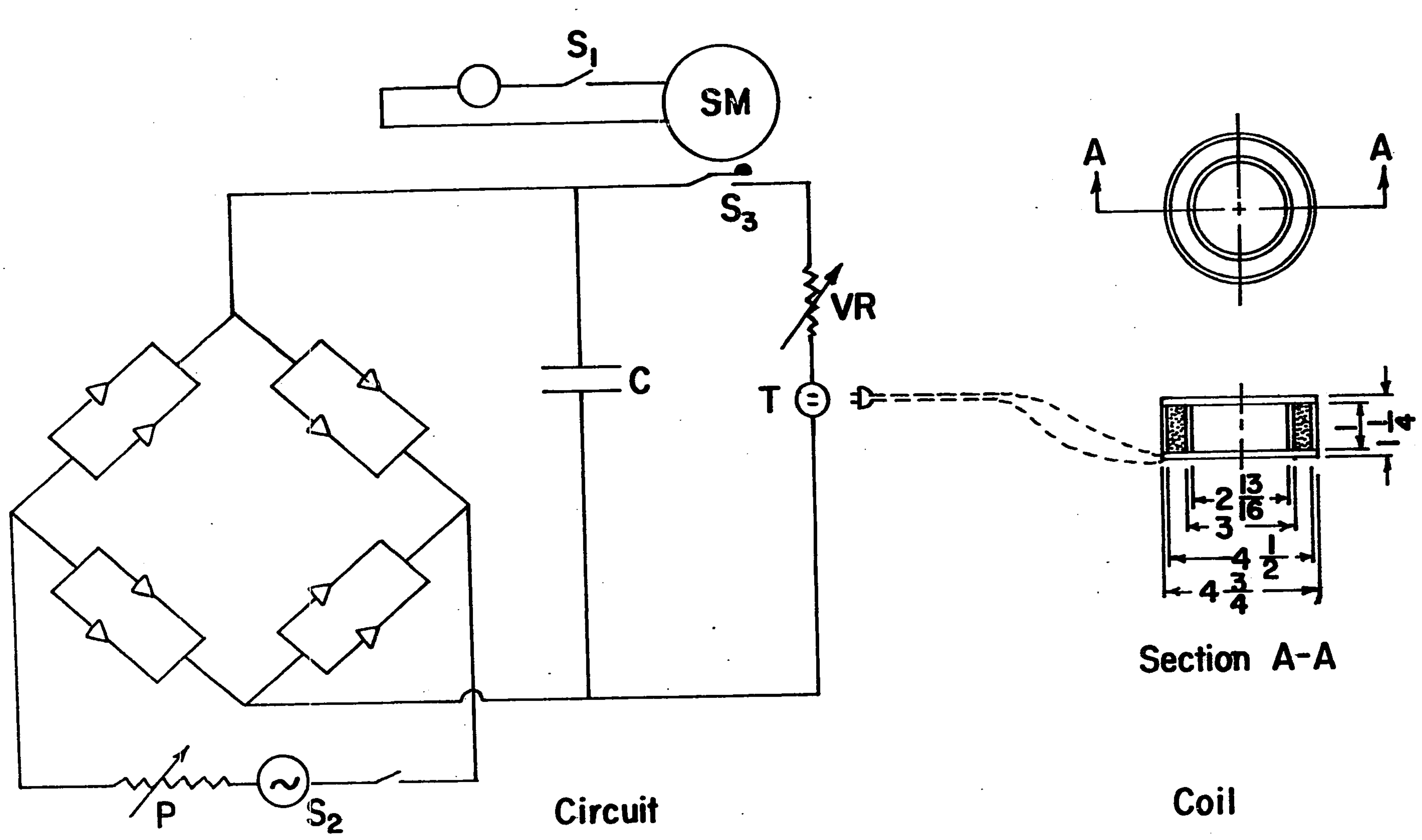
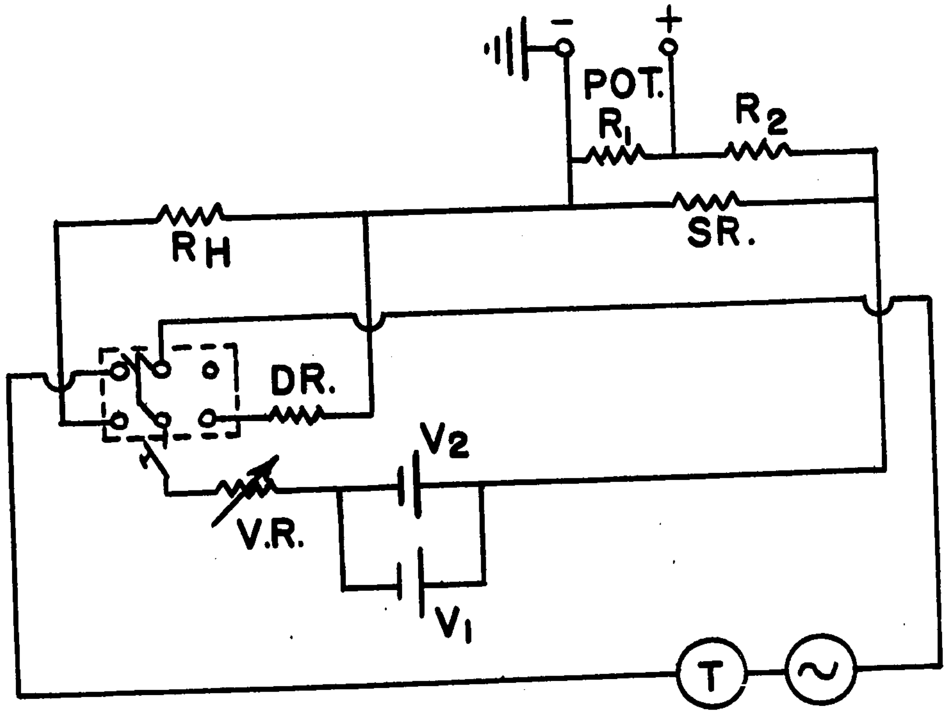


Figure 5. Coil and solenoid circuit

Figure 6.



Heater and Measuring Circuit

resistor SR of 40 ohms, wound from silk-covered manganin wire gauge 26. The standard resistor was kept in an oil bath. The dummy resistors VR and DR were used to discharge the batteries during non-heating periods and to adjust the circuit potential. The current through the heater R_H, of the order of 0.1 ampere, was calculated from the potential drop across the circuit with a standard resistor SR. This potential was determined by measuring a portion of the potential with the aid of a shunt, and a K_3 potentiometer, in conjunction with a high sensitivity galvanometer. A precision seconds timer T, synchronised with the heater circuit allowed measurements of the heating time to ± 0.05 sec. The timer was operated from the power mains at a frequency of 60 cycles/sec.

A 2-volt, lead acid storage battery served as the working cell for the K_3 potentiometer. The standard cell was certified by the National Bureau of Standards, Washington. The resistances of the heaters for the calorimeters, the standard resistor, the shunt, each with the necessary leads taken into account, were accurately measured to ± .005 ohms in auxiliary experiments with a Wheatstone bridge.

e. Thermistor circuit

A diagram of the thermistor bridge circuit for measuring temperature changes is given in Figure 7. When the electrical circuits to the calorimeter were completed by plugging in at the main junction, the thermistor on any calorimeter was incorporated in a Wheatstone bridge circuit arranged to provide a constant current. A 6-volt lead acid storage battery was employed as a power supply for the bridge. A 40,000 ohms variable resistor in series with the power supply maintained the current flowing through the thermistors at about 30 amps., in order to prevent undesirable dissipation of heat by the thermistors. The bridge unit provided external connections for, the

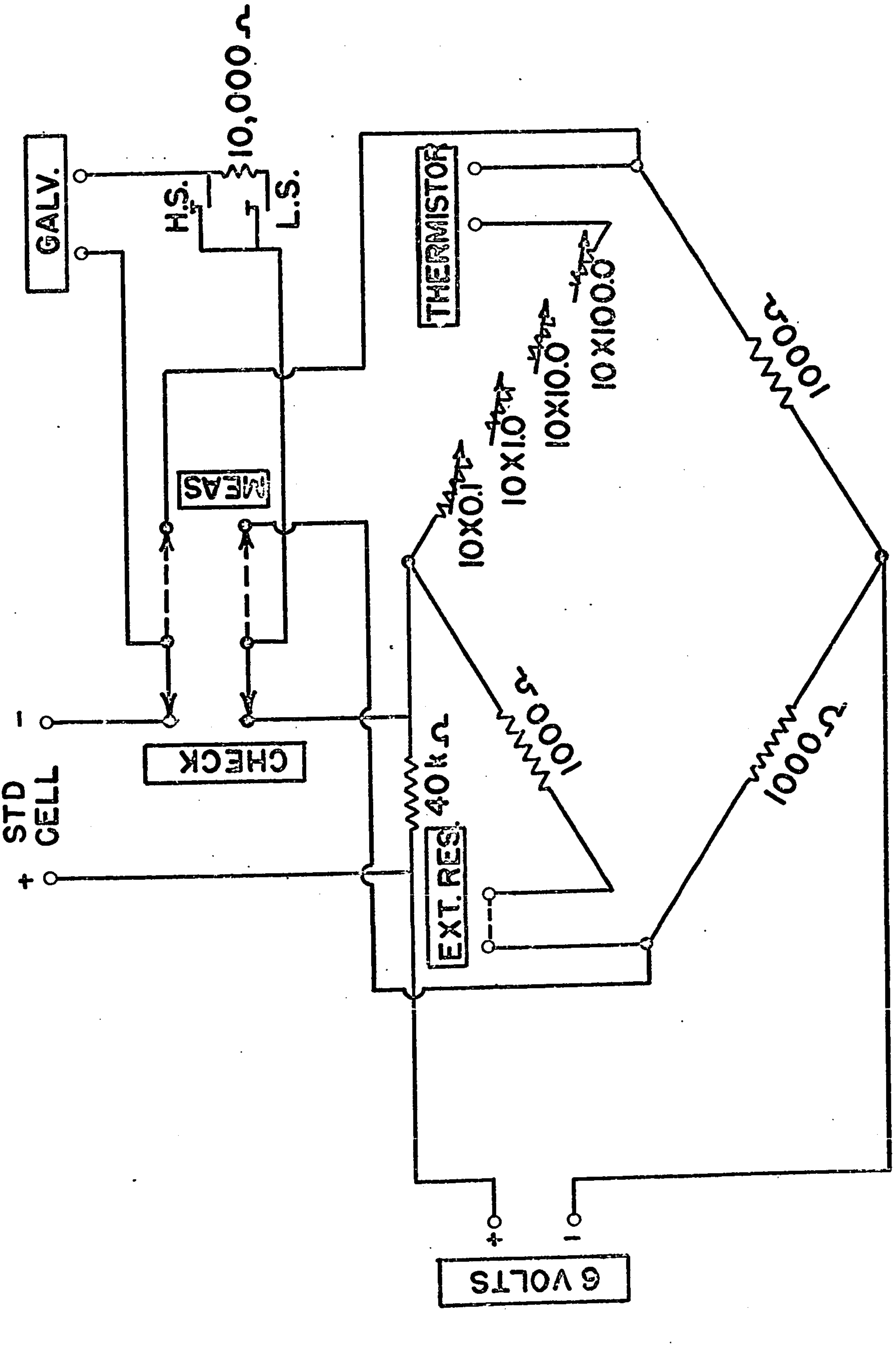


Figure 7. Thermistor Bridge Circuit

power supply, a standard cell, a thermistor and an auxiliary variable resistor, opposite to the arm containing the thermistor.

The thermistor bridge was calibrated, at the Division of Applied Physics of the National Research Council of Canada, and was found to have an accuracy of ± .01%. The external resistor, a decade box, was calibrated in an auxiliary experiment. The bridge was provided with coarse and fine adjustments, low and high sensitivity keys, with a switch that allowed a check to be made of the current, if necessary, prior to measurments with the bridge.

The thermistor bridge was initially set at balance. Variations of thermistor resistance due to temperature changes produced an imbalance in e.m.f. This output was fed to an electronic D-C Null Detector shown in Figure 2. The amplified D.C. voltage drove a 50 mv recorder with a chart speed of one inch per minute. The sensitivity of the circuit may be expressed as 4 mv per 0.001°C change in temperature. The D-C Null Detector provided three sensitivities from about 0.2 to 4 mv per 0.001°C. The recorder was used as a null instrument and the heat effects followed by the variation of thermistor resistance produced a trace on the recorder of millivolts versus time.

f. Thermistors

The thermistors used, were of nominal resistances of 500, 1,000 and 2,000 ohms. These were calibrated by the Division of Applied Physics, National Research Council of Canada. Values of the resistances at the corresponding temperatures for the entire temperature range to be used, allowed calculation of the thermistor characteristics given in Table 23. The theoretical basis for the calculations is given in the Appendix.

Prior to the calibration the thermistors were aged in an oven for about three weeks to ensure stability.

g. Coil

A sketch of the coil and accompanying circuit is given in Figure 5 with the coil circuit.

The coil was made from insulated copper wire No. 24B & S wound on a spool to give about 30-40 ohms. The spool consisted of a brass or aluminum cylinder with plexiglass flanges; the entire solenoid was waterproofed with Glyptal resin.

A brass ring, bolted onto the outside of the jacket, supported the jacket on the coil, which was insulated from the supporting ring and from the jacket with styrofoam.

h. The constant temperature bath

The bath was a 30 gallon rectangular glass tank, 30" x 15" x 20", insulated with 2 inches of Styrofoam, and further enclosed in a wooden box.

The control of the bath was maintained by two 750 watts calrod continuous heaters, two 750 watts calrod intermittent heaters, two coils providing a continuous cooling effect and a thermoregulator of the Fisher rotostat type. These units were symmetrically placed in the tank; the continuous heaters were placed at the center of the longer sides of the bath, the intermittent heaters at the shorter sides, while the cooling coils were wound symmetrically over the bottom of the tank. The cooling water entered the two cooling coils at the same rate from opposite sides of the bath.

Agitation of the bath was accomplished by two variable speed stirrers - Fisher Versatile type carrying 24" shafts with two sets of propellors, one set at the end of the shaft and the other set about 6" from the end. The blades of the propellors were bent in a manner to direct the heat as speedily as possible from the heaters to the thermoregulator which controlled the intermittent heaters.

With this arrangement the temperature of the bath was controlled to ± 0.005°C of any desired setting.

The temperature of the bath could be increased or decreased at will by adjusting the rotostat appropriately.

Beckman thermometers calibrated between 25°, 35° and 45°C at the Division of Applied Physics of the National Research Council were used to set the bath temperature to a desired value.

In the tank, a flanged brass ring, fixed with 3 screws externally around the jacket carrying the mixing vessel, and resting on the solenoids, was used to support the jacket. The solenoids were in turn supported on a brass bench, 18" long, 9" wide with legs about 7". The brass ring was insulated from the solenoids with styrofoam. The brass frame, carried cross bars to support 8 solenoids. The leads from each coil were long encugh to facilitate plugging into the common junction of the solenoid-actuating circuit, shown in Figure 5.

i. The vacuum system

The vacuum system is shown in Figure 2.

Vacuum was attained by means of a high vacuum, mechanical-diffusion type pump, with a capacity of 600 litres per minute at 10^{-4} mm Hg. The vacuum pump was connected to the pumping line with a 6" length of 1/2" diameter rubber tubing with a wall thickness of 1/4". The pumping line consisted of a length of pyrex glass tubing of 5/8" I.D., to which were attached, a trap cooled by liquid nitrogen and a Vacustat McLeod gauge.

The remainder of the pumping line consisted of an eight-outlet manifold, constructed from Swagelok union crosses, copper tubing and elbows, joined to the glass tubing with a vacuum rubber sleeve. The calorimeter jackets were connected with rubber sleeves, 2.54 cm O.D. and wall thickness of 0.82 cm.

The liquid nitrogen trap served the purposes, of protecting the system from mercury vapor, of condensing any escaping vapors in case of a leak, and of maintaining high vacuum.

2. Experimental procedure

a. Loading the calorimeter

This operation comprised essentially three phases: the first one being the weighing of the liquids to be mixed into the separate compartments of the mixing cell, the second was the positioning of the cell in the jacket, connecting the leads and closing the jacket for vacuum tightness, and the third was the mounting of the calorimeter jacket with its contents in the constant temperature bath. The procedure was as follows:

The calorimeters were cleaned with ether, dried with air. O-rings were replaced on the caps, and a tin foil diaphram was placed between the two gaskets at the center, separating the two compartments. The two parts of the calorimeter were tightened with a torque wrench to a predetermined torque at which the leakage was found to be negligible. The calorimeters were then filled successively. A calorimeter with the two plugs and stirrer was weighed empty. The stirrer was placed in the lower compartment of its calorimeter which was then tilted slowly to bring this compartment to the top for filling. Extreme care was necessary to prevent premature rupture of the diaphram by the plunger at this time. The compartment was then filled to the top, after which the brass plug was slowly screwed in, causing an overflow of excess liquid. This procedure eliminated any vapor space in the compartment, prior to mixing. The overflow was adsorbed by a piece of tissue while the plug was screwed in and tightened slightly. The calorimeter was then tilted cautiously to allow the stirrer to rest on the bottom instead of on the diaphram. The plug was tightened with the torque wrench as before. Any liquid remaining on the outside was removed with compressed air. The calorimeter was then weighed, placed in a dessicator under vacuum for 10-15 minutes and weighed again to test for leaks. If a leak was indicated the procedure was repeated with new O-rings and gaskets. The mass of the liquid was determined by difference.

The other compartment of the calorimeter was then filled with the second liquid in the same manner as outlined above and the weight of the unit, completely filled, was determined. The mass of the second liquid was determined also by difference.

A Fisher Gramatic balance was used for weighings and the weights were determined to ± .1 mg.

The calorimeter was then mounted in its metal jacket with the bottom resting on a rubber cushion in the jacket, and was kept in the center by two rings of cork or of rubber. The multiple-point pin carrying the 6 leads from the calorimeter was plugged into a similar receiving pin attached to the leads from the hermetic seal and fixed to the top of the metal jacket. The assembly was closed with an O-ring between the flanges of the top and bottom sections of the jacket, and held together with 1/4" brass bolts.

The continuity of the leads in the jacket was checked at this point and the jacket with the calorimeter inside was placed in the constant temperature bath, in which it was supported by the hollow casing of the solenoid. The temperature controller of the bath was adjusted for the desired temperature. The jacket was then connected to the vacuum manifold and was evacuated overnight while the system was allowed to reach thermal equilibrium. As many as eight calorimeters could be mounted at one loading.

b. Measurement of heat effects

Prior to mixing, the batteries were discharged, the DC Null Detector and the recorder were turned on. The degree of the vacuum, and the bath temperature, indicated by the McLeod Gauge and Beckman thermometer, respectively, were recorded. The vacuum was maintained at less than 10^{-3} mm. Hg.

One outlet from a jacket assembly in the bath was plugged in at the main junction to complete the electrical circuits to the calorimeter and the corresponding solenoid was plugged into the common outlet after it was ensured that the switch to energise the solenoid was open.

The zero of the DC Null Detector was adjusted at the highest sensitivity and the Wheatstone bridge was balanced at this position. The resistance of the variable resistor X of the bridge was recorded. This gave the initial resistance of the thermistor and provided a knowledge of the initial temperature of the calorimeter, and the temperature of the bath.

The zero of the DC Null Detector was adjusted, and the sensitivity was set at the second amplification. The reference trace on the recorder was followed for about 5 minutes. The variable resistor in the bridge was decreased by .2 ohms from the balance position causing the recorder pen to move to the left of the reference line. The solenoid was then energised, and the mixing process was started with the rupture of the diaphragm by the gold plated nail plunger.

The drop in temperature of the calorimeter due to the endothermic heat change, caused an increase in the resistance of the thermistor thus producing an output from the thermistor Wheatstone bridge. The output was amplified by the DC Null Detector and fed to the recorder. The changing output produced a trace on the recorder crossing the reference position. The variable decade resistor was changed periodically so that the trace on the recorder was made to cross the reference line, approximately every minute during initial and final rating periods and about 3 or 4 times per minute during the mixing or heating period. At each crossing of the reference position, the resistance(X) of the variable resistor in the bridge was recorded on the chart. At the end of the experiment the crossing points were timed in minutes from the chart. This was facilitated since the speed of the chart was 1 inch per minute and the rulings were 1/2" apart. The values of resistance (X) and minutes (Θ) were recorded and plotted.

After the mixing period, the energy equivalent of the calorimeter was determined by supplying a quantity of electrical energy while the calorimeter contents was stirred, to duplicate the change of resistance that occurred during the mixing. This is referred to as the calibration period.

A graphical method, making use of the variation of the resistance(X) with time, for the mixing and for the calibration, was employed for the determination of the corrected temperature rise. This involved the extrapolation of the initial and final rating periods to the time when the resistance of the thermistor was equal to the average of the values at the beginning and at the end of the heating and the calibration periods.

Typical plots of resistance change versus time for the heating and calibration periods are reproduced in Figure 8. Considering the mixing period the tin foil diaphragm was broken at B. The absorption of heat period BC, was completed in about 3-4 minutes. The final rating period DE was continued for 15 minutes after the peak was reached. The stirring effect is accounted for by BF. For the calibration, the initial and final rating periods are indicated by FG and IJ, respectively. GH represents the heating effect when energy is being supplied. The temperature changes corrected for heat losses, etc., are given by FC' for the mixing period, Figure 8a, and G'H' for the calibration period, Figure 8b. During this period the potential drop across the standard resistor was measured several times. After the heater was turned off, the mixing cell was allowed to come to steady state to establish the final rating period for about 15 minutes. The time during which the energy was supplied was read within 0.05 sec., directly from the electric timer, synchronised with the heater. The cell was later removed from the bath and weighed to check for losses. The dotted lines on the Figure 8 indicate the graphical extrapolations required for determination of resistance changes, and hence the temperature changes.

The heat Q^M absorbed on mixing of w_1 grams of component 1 with w_2 grams of component 2 was calculated from the equation

$$Q^M = Q_c \frac{\Delta T_m}{\Delta T_c} \qquad (43)$$

where Q_c is the amount of electrical energy supplied to the calorimeter, in calories;

ΔT_m is the corrected temperature change during mixing, in °C ;

ΔT_c is the corrected temperature change during electrical calibration in °C ;

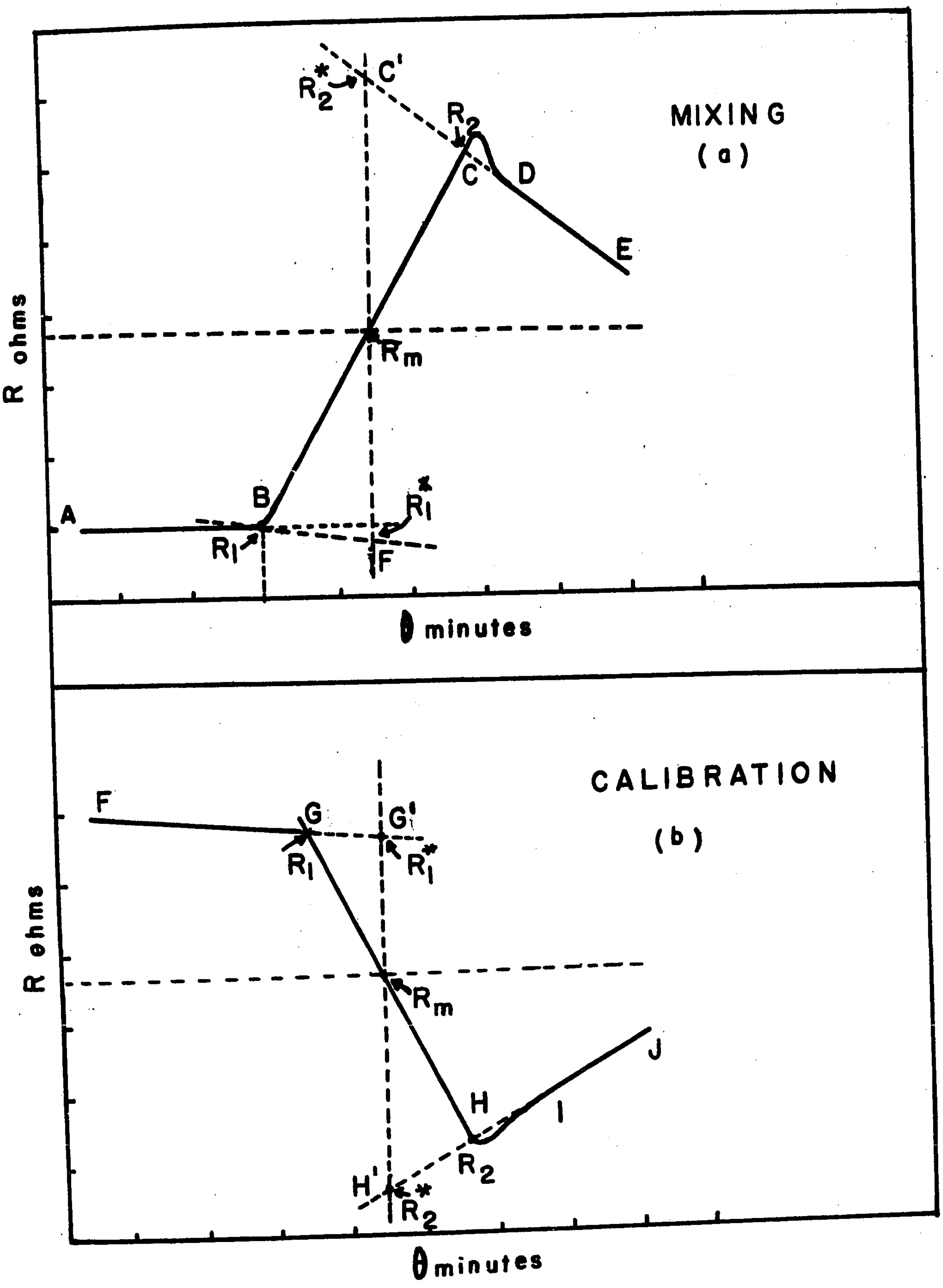


Figure 8. Typical resistance - time variation for experiments on heats of mixing

The temperature changes are calculated from the changes in the resistance of the thermistor by the following

$$\Delta T = \frac{\Delta R}{S_T} \tag{44}$$

where

$$S_T = \frac{R_T \beta}{T^2} \tag{45}$$

R_T being the resistance of the thermistor at temperature T ; β is the "work function" of the thermistor, in °K ; and T is the average temperature, in °K , over the change. The "work function", β is obtained from the calibration of the thermistor, and is further discussed in the appendix H.

The quantity of electrical energy supplied to the calorimeter, in calories, was determined from Joule's equation

$$Q_c = \frac{I^2 R_H \Theta}{J} \tag{46}$$

where I is the current in amperes, flowing through the heater resistance, R_H ;

Θ is the heating time, in seconds ;

and J is the electrical equivalent of heat (4.184 joules/cal.)

The heat of mixing two pure liquids is given by the expression

$$\Delta H^M = \frac{Q^M}{n_1 + n_2} \tag{47}$$

where Q^M is the heat absorbed on mixing, in calories ;

n_1 is the number of moles of component 1 ;

and n_2 is the number of moles of component 2.

When n_B moles of a binary mixture are mixed with one of the pure components the heat of mixing per mole of the resulting binary mixture is given by the equation

$$\Delta H^M = \frac{Q^M + (\Delta H^M)_B \times n_B}{n_T^o} \qquad (48)$$

where $(\Delta H^M)_B$ is the heat of mixing of the initial binary mixture ;

n_B is the number of moles of the initial binary mixture ;

n_T is the number of moles of the resulting binary mixture.

When n_B moles of a binary mixture of components 1 and 2 are mixed with n_3 moles of another pure component, the heat of mixing in calories per gram mole is still given by equation 48 above, except that

$$n_T = n_1 + n_2 + n_3 \qquad (49)$$

C. Determination of specific heats of ternary mixtures

1. Calibration of calorimeter vessels

The calorimeters were first calibrated with benzene at 25°, 35° and 45°C to establish their heat equivalents at these temperatures. Benzene was chosen because its specific heat as a function of temperature is reported in the literature (41). The experiments involved filling of the calorimeter with benzene, without the separating diaphragm and loading as previously outlined for a heat of mixing determinations. The procedure after this, was identical to that for an electrical calibration outlined previously. By establishing the temperature rise produced by a measurable quantity of electrical energy, in a mixing vessel containing benzene, the product of the mass of the calorimeter times its specific heat was determined. The heat equivalent W_c was further used in calculating the heat equivalent of the ternary mixtures ; the mass of the mixtures was known and so the specific heat in Cal./(g.)(°C) and Cal./(g.-mole)(°C) at a particular temperature could be calculated.

2. Preparation of ternary mixtures

First, a binary mixture of components 1 and 2 was prepared, in sufficient quantity, about 100 cc, at a desired mole fraction according to the procedure outlined previously. The ternary mixtures were then prepared by mixing calculated amounts of this binary mixture and the third component 3 in several stoppered flasks. The mole fraction of the ternary mixtures was calculated from the actual weights recorded. These ternary mixtures were used to fill the various calorimeters, calibrated for the specific heat determination.

3. Calculation of the specific heat of a ternary mixture

The heat equivalent W_{Cal} of a calorimeter at a particular temperature is given by the equation

$$W_{Cal} = \frac{Q_c}{\Delta T_c} - M_B C_{P_B} \qquad (50)$$

where Q_c is the energy supplied to the calorimeter and contents, in calories ;

ΔT_c is the corrected temperature rise produced, determined as previously outlined ;

M_B is the mass of benzene in the calorimeter, in grams ;

C_{P_B} is the specific heat of benzene at the required temperature, cal./(g.)(°C)

The specific heat C_{P_L}, in cal./(g.)(°C) of a ternary mixture of mass M_L is given by the following equation

$$C_{P_L} = \frac{1}{M_L} \quad \frac{Q_c}{\Delta T_c} - W_{Cal} \qquad (51)$$

where Q_c is the energy, in calories, supplied to the calorimeter and ternary mixture, calculated as previously outlined ;

ΔT_c is the corresponding temperature rise produced, also determined as before ;

W_{Cal} is the heat equivalent of the calorimeter at a particular temperature, in cal./°C.

If w_1, w_2, w_3 are the masses of the components 1, 2 and 3 and the corresponding molecular weights are M_1, M_2 and M_3 the specific heat, C_{P_L}' in cal./(g.-mole)(°C) of the ternary mixture is determined by the following equations

$$n_1 = \frac{w_1}{M_1} \quad ; \quad n_2 = \frac{w_2}{M_2} \quad ; \quad n_3 = \frac{w_3}{M_3} \qquad (52)$$

$$n_T = n_1 + n_2 + n_3 \qquad (53)$$

$$x_1 = \frac{n_1}{n_T} \quad ; \quad x_2 = \frac{n_2}{n_T} \quad ; \quad x_3 = \frac{n_3}{n_T} \qquad (54)$$

$$C_{P_L}' = C_{P_L} \quad (x_1 M_1 + x_2 M_2 + x_3 M_3) \qquad (55)$$

where n_1, n_2, n_3 are number of moles of components 1, 2, and 3,

x_1, x_2, x_3 are the mole fractions of the ternary mixture.

D. Calculation of heats of mixing at higher temperatures

The heats of mixing of the ternary systems at the higher temperatures of 35° and 45°C were calculated from the following equation

$$\Delta H_{x_1,x_2,t} = -\sum \int_{25}^{t} C_{P_i} \, dt + \Delta H_{x_1,x_2,25} + \int_{25}^{t} C_{P_{ijk}} \, dt \qquad (56)$$

where $\Delta H_{x_1,x_2T}$ is the ternary heat of mixing at composition x_1,x_2 and temperature $t^{\circ}C$, in cal./(g.-mole) ;

C_{P_i} is the specific heat, in cal./(g.-mole)($^{\circ}C$) of component i of the mixture ;

t is the temperature $35^{\circ}C$ or $45^{\circ}C$;

$\Delta H_{x_1,x_2,25}$ is the ternary heat of mixing at composition x_1,x_2 and at a temperature of $25^{\circ}C$;

and $C_{P_{ijk}}$ is the specific heat of the particular ternary mixture, in cal./(g.-mole)($^{\circ}C$).

To apply equation 56, $C_{P_i} = f(t)$ and $C_{P_{ijk}} = f(t)$ are required. Data for the specific heats of the individual components, i,j,k of the ternary mixtures are available in the literature (30). The value of $\int_{25}^{t} C_{P_{ijk}}\,dt$ was determined by graphical integration of the experimental data.

E. Calorimeter performance and precision

The results obtained for the heats of mixing of the binary systems were measures of the performance of the calorimeter. The experimental data are compared on $\Delta H/x_1,x_2$ versus x_1, plots with available values in the literature. Favourable agreement with the results of previous investigators attests to the reliability of the calorimeters. The plots are shown in Figures 9-13 and the results are discussed in a later section.

XI. RESULTS

A. Presentation of results

Results in tabular form are presented in the Appendices. Figures pertaining to the results are given in the appropriate section of this chapter.

1. Experimental data

a. Binary heats of mixing data at 25°C

The experimental data obtained for the binary systems are presented in Tables 3 to 7 in Appendix A and are compared with available values in the literature in Figures 9, 10, 11, 12 and 13 on plots of $\Delta H/x_1x_2$ versus x_1. A summary of deviations of literature ΔH^m values from those of this investigation is given in Table 8. The differences are expressed in terms of the maximum and the absolute average deviations as percentages. The latter one was calculated in terms of

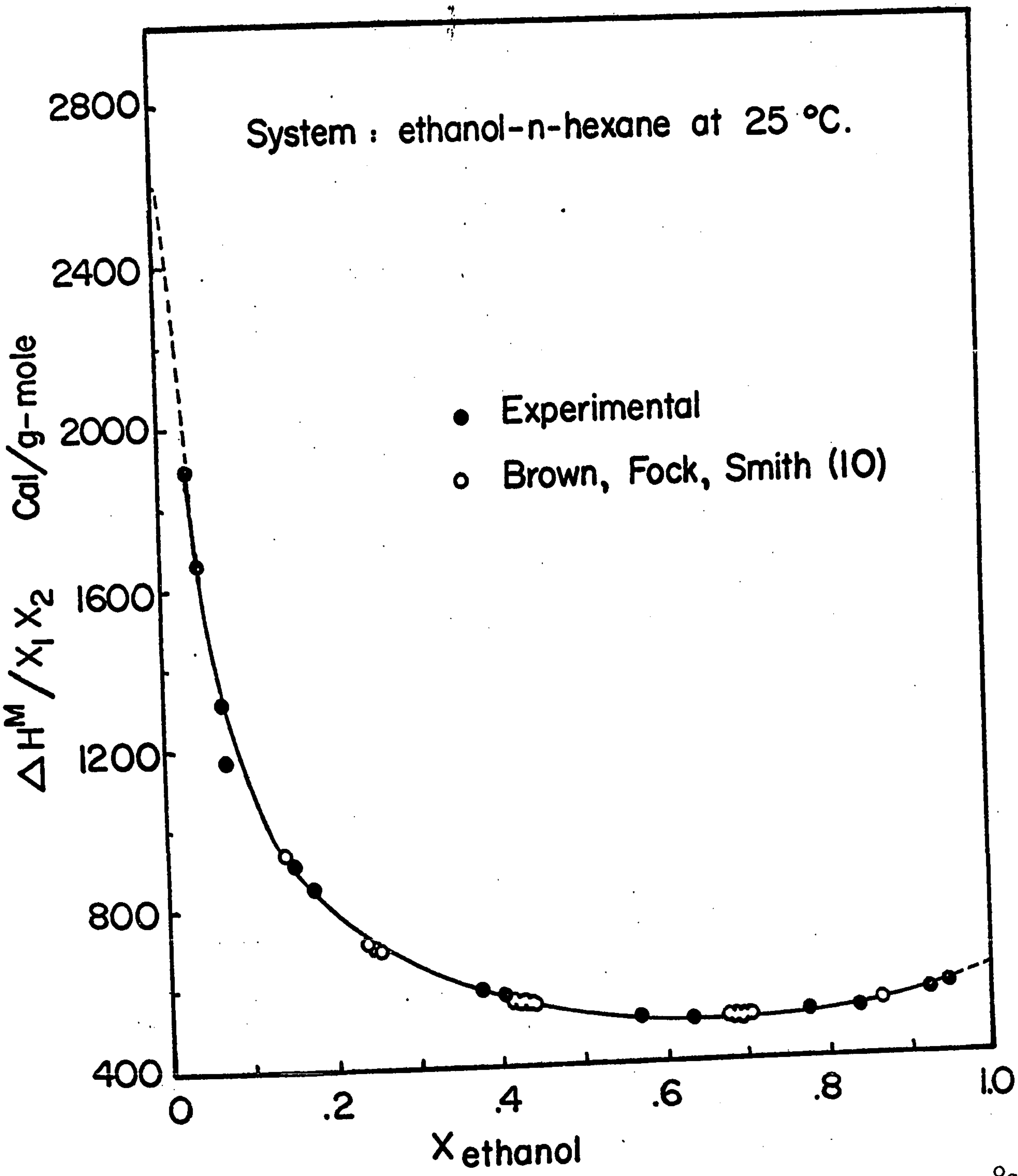
$$\left|\Delta H^m_{\text{Lit.}} - \Delta H^m_{\text{Authors}}\right| \Big/ \Delta H^m_{\text{Authors}}$$

from smoothed curves at 0.1 mole fraction intervals of x.

b. Ternary heats of mixing data at 25°C

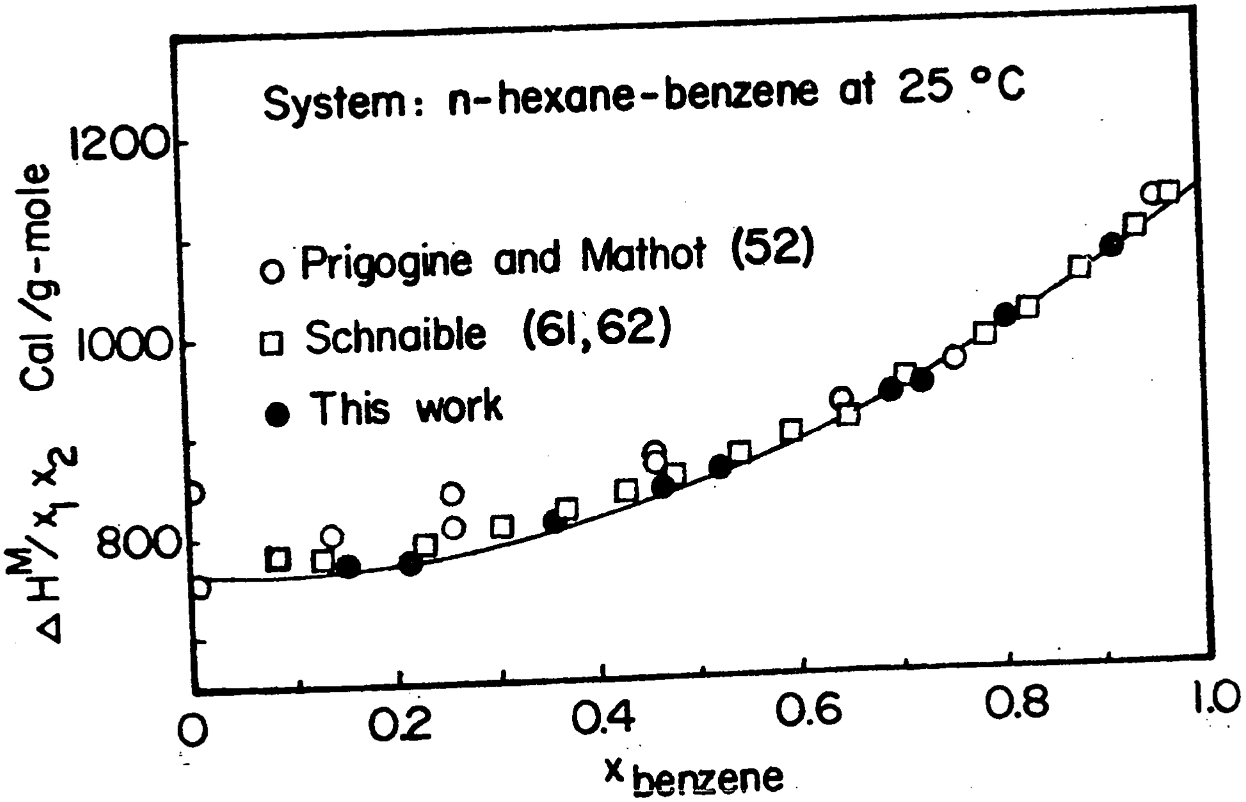
The experimental data for the ternary systems of ethanol-benzene-n-hexane and ethanol-benzene-n-heptane are given in Tables 9 and 10, respectively, in Appendix B. The compositions experimentally investigated are shown in Figures 14 and 15. In figures 16a and 16b, the ternary data for ethanol-benzene-n-hexane are plotted in terms of $\Delta H_{ijk} - (1-x_k)\,\Delta H_{ij}/x_k(1-x_k)$ cal./g.-mole versus x_k, for constant ratios of x_i/x_j. Figures 17a and 17b give similar results for the system ethanol-benzene-n-heptane.

Figure 9.



Heats of mixing values for the system ethanol-n-hexane at 25°C. Plot of $\Delta H^m/x_1x_2$ vs. x_1.

Figure 10.



Heats of mixing values for the system n-hexane-benzene at 25°C. Plot of $\Delta H^m/x_1x_2$ vs. x_1.

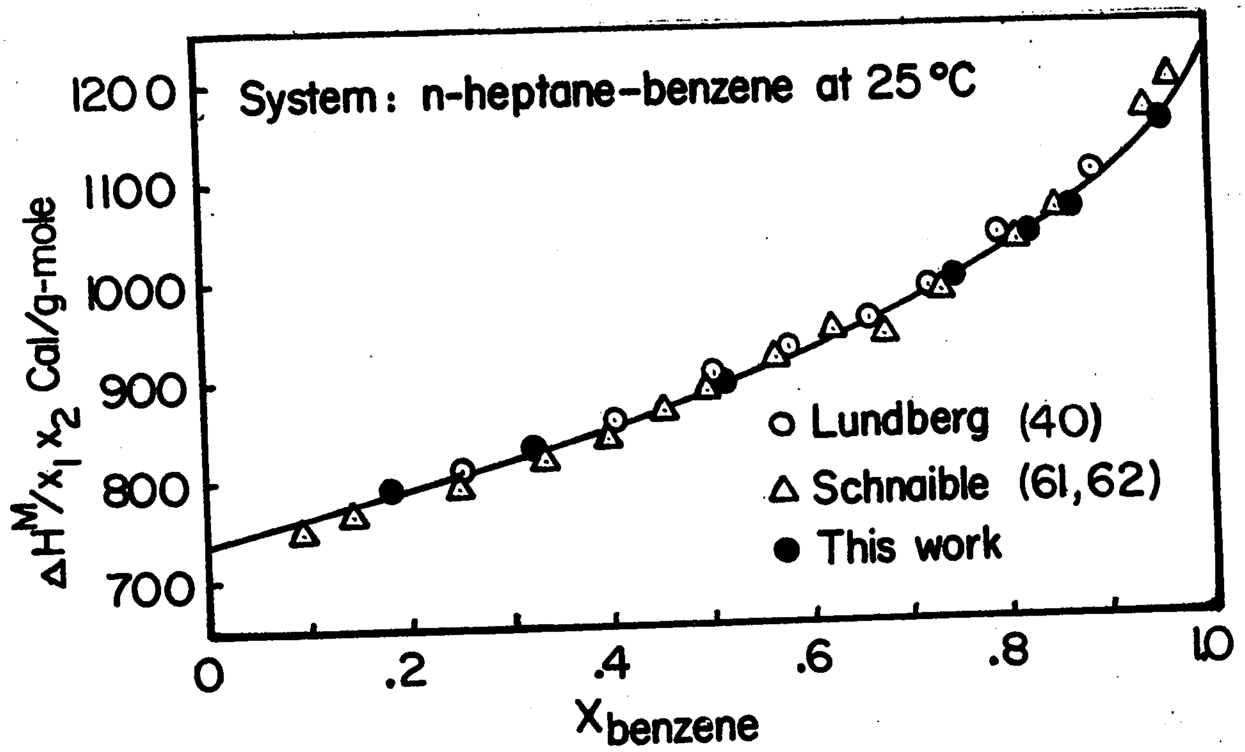


Figure 11. Heats of mixing values for the system n-heptane-benzene at 25°C. Plot of $\Delta H^m/x_1x_2$ vs. x_1.

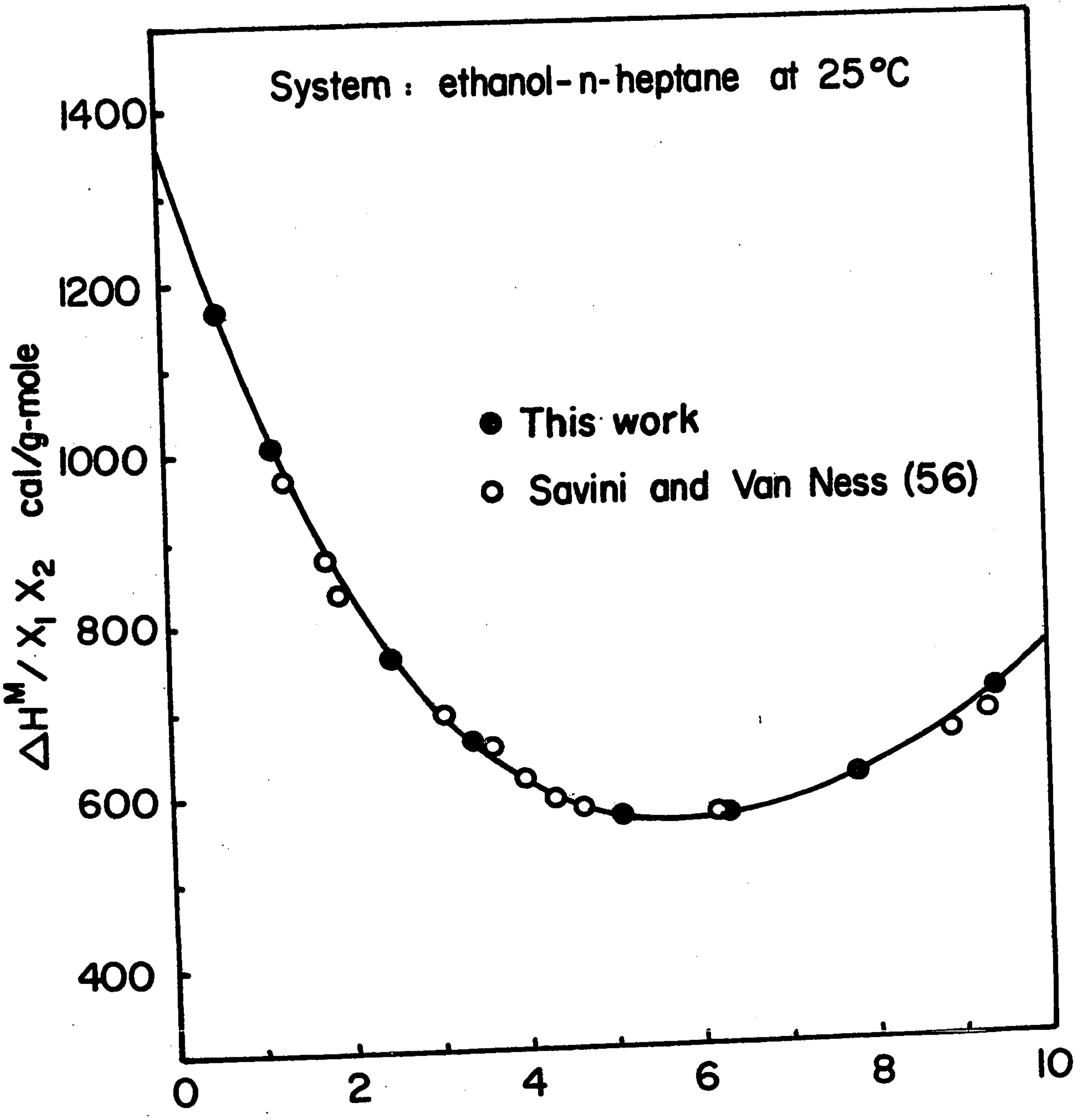


Figure 12. Heats of mixing values for the system ethanol-n-heptane at 25°C. Plot of $\Delta H^m/x_1x_2$ vs. x_1.

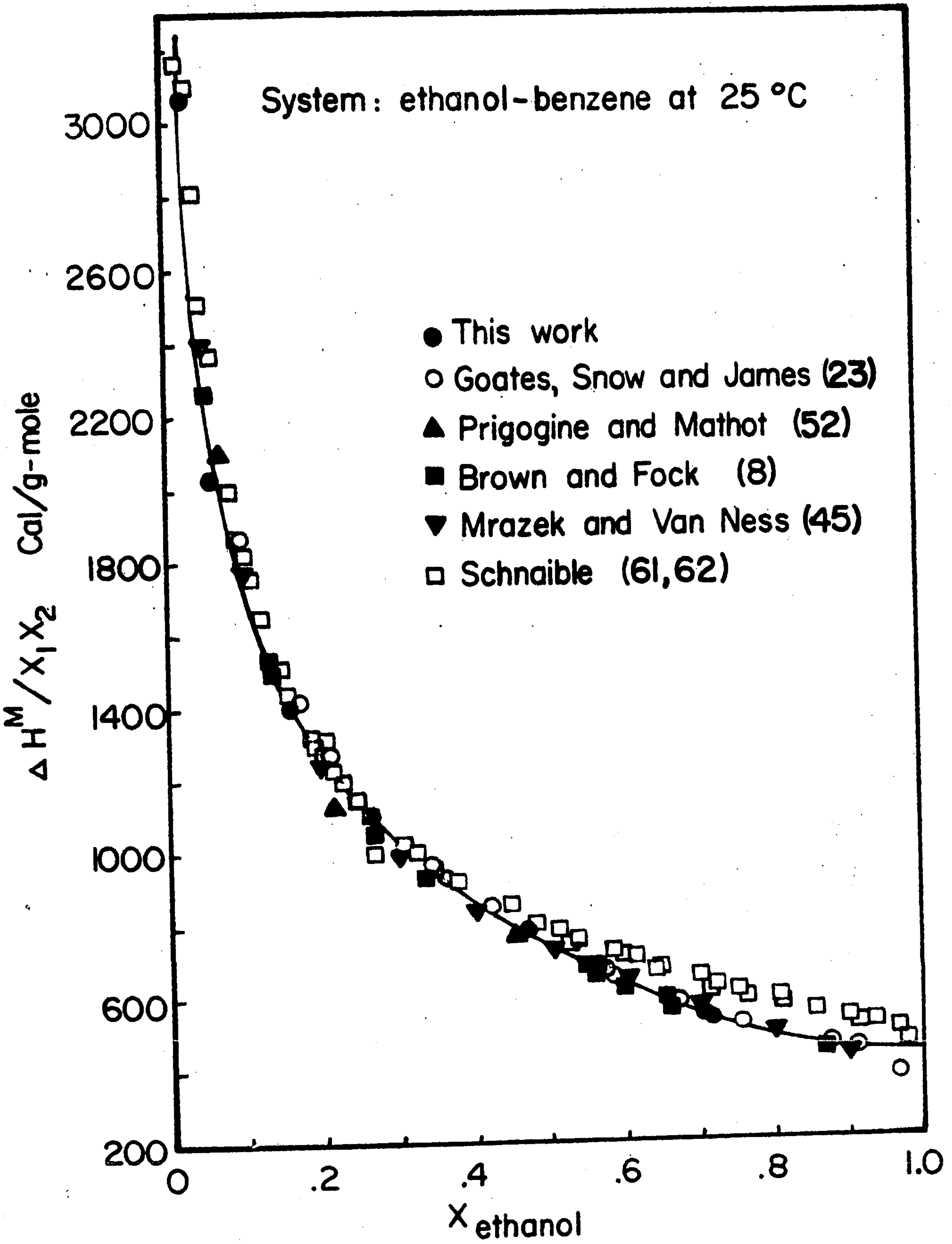


Figure 13. Heats of mixing values for the system ethanol-benzene at 25°C. Plot of $\Delta H^m/x_1x_2$ vs. x_1.

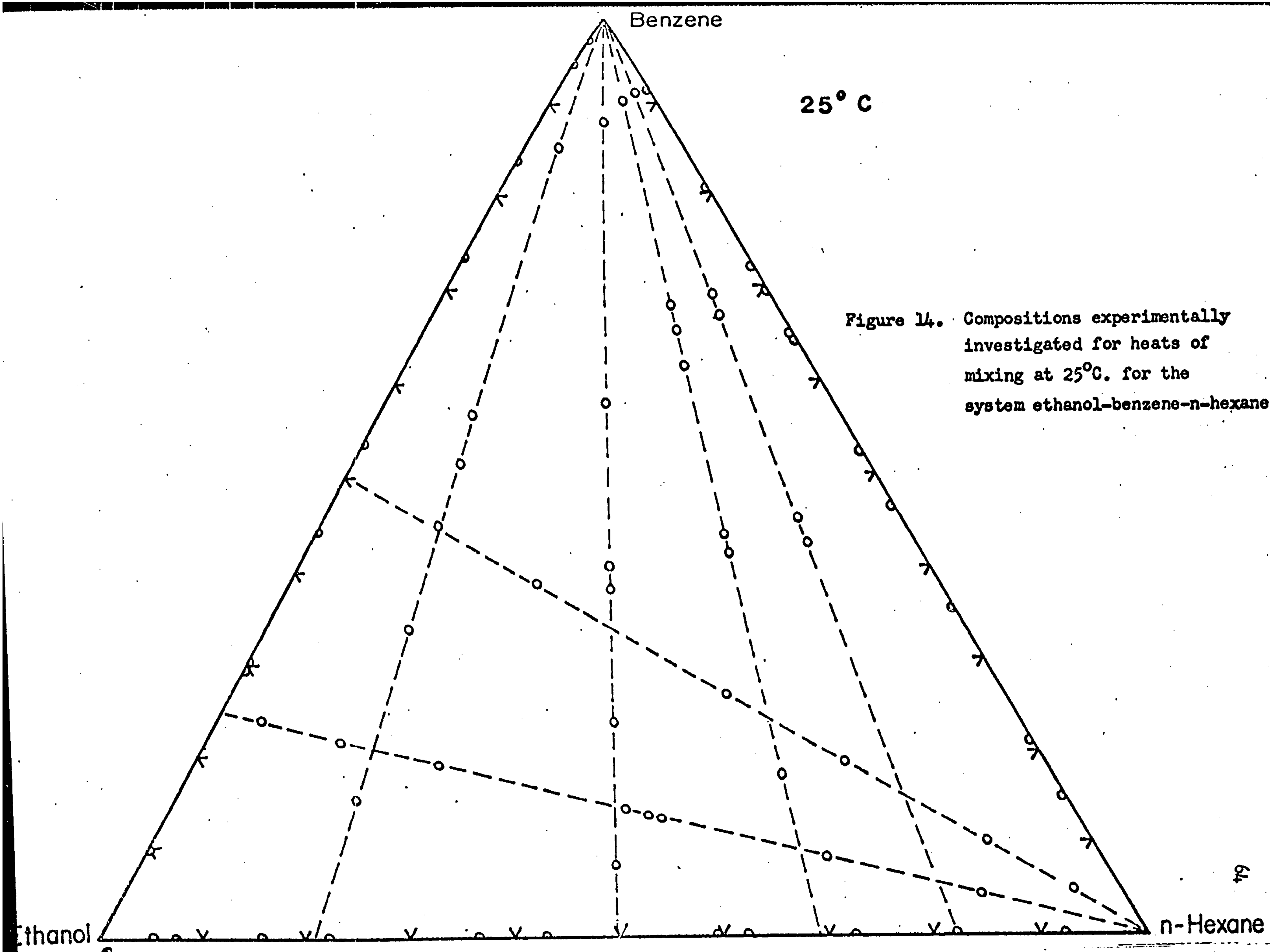


Figure 14. Compositions experimentally investigated for heats of mixing at 25°C. for the system ethanol-benzene-n-hexane.

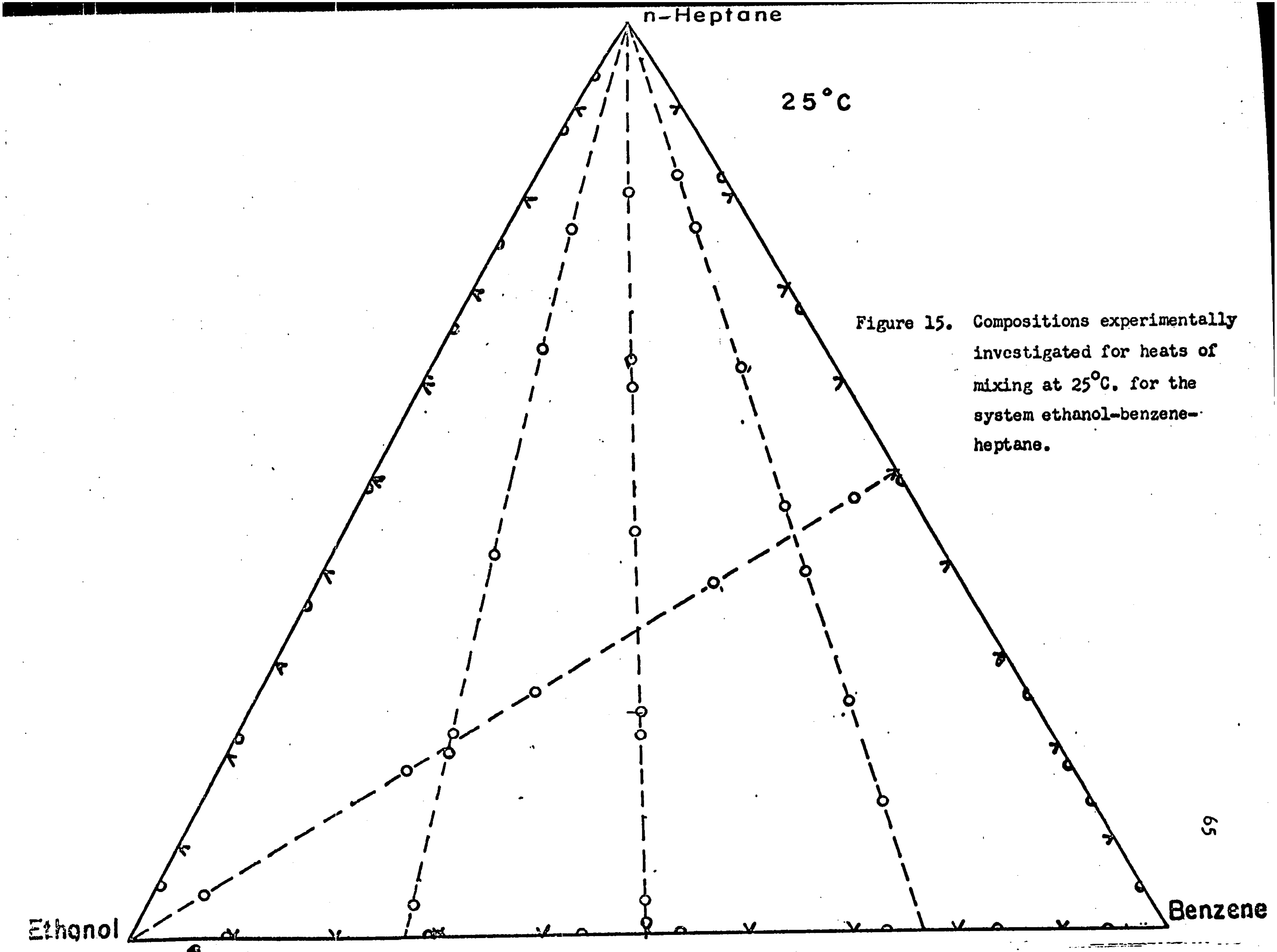


Figure 15. Compositions experimentally investigated for heats of mixing at 25°C. for the system ethanol-benzene-heptane.

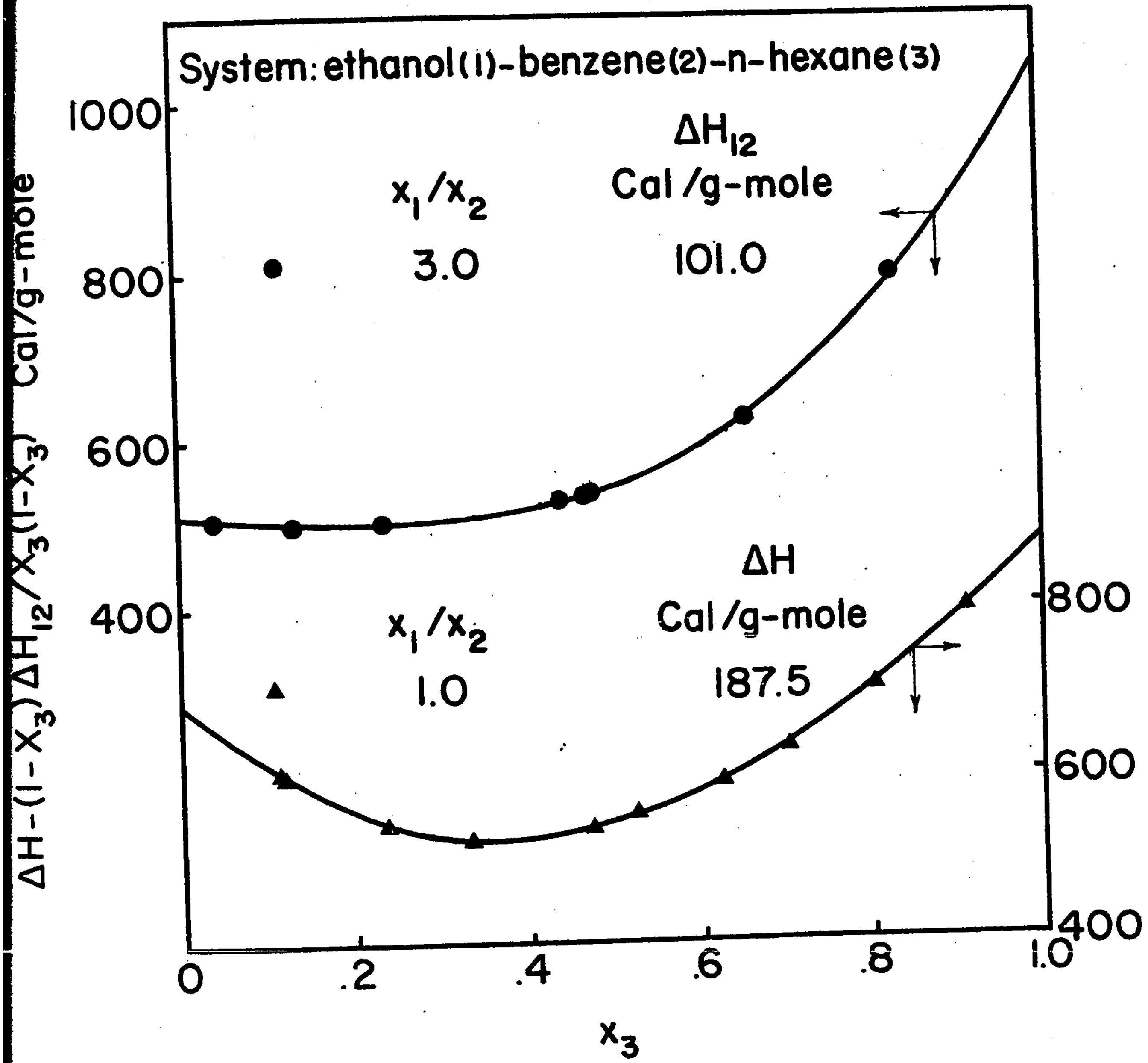
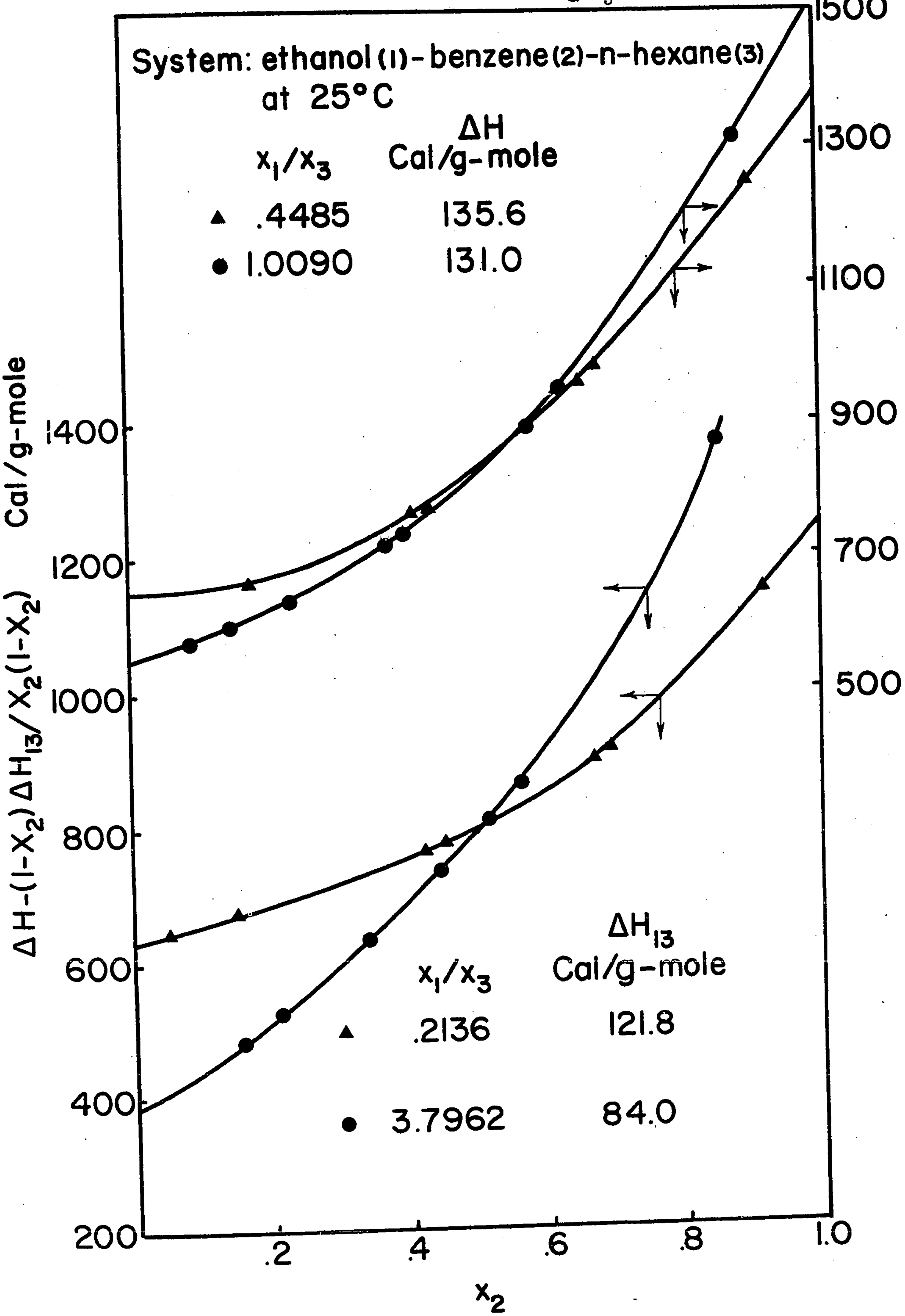


Figure 16a. Heats of mixing values for the system ethanol-benzene-n-hexane at 25°C., along constant x_i/x_j lines.

Figure 16b. Heats of mixing values for the system ethanol-benzene-n-hexane at 25°C., along constant x_i/x_j lines.



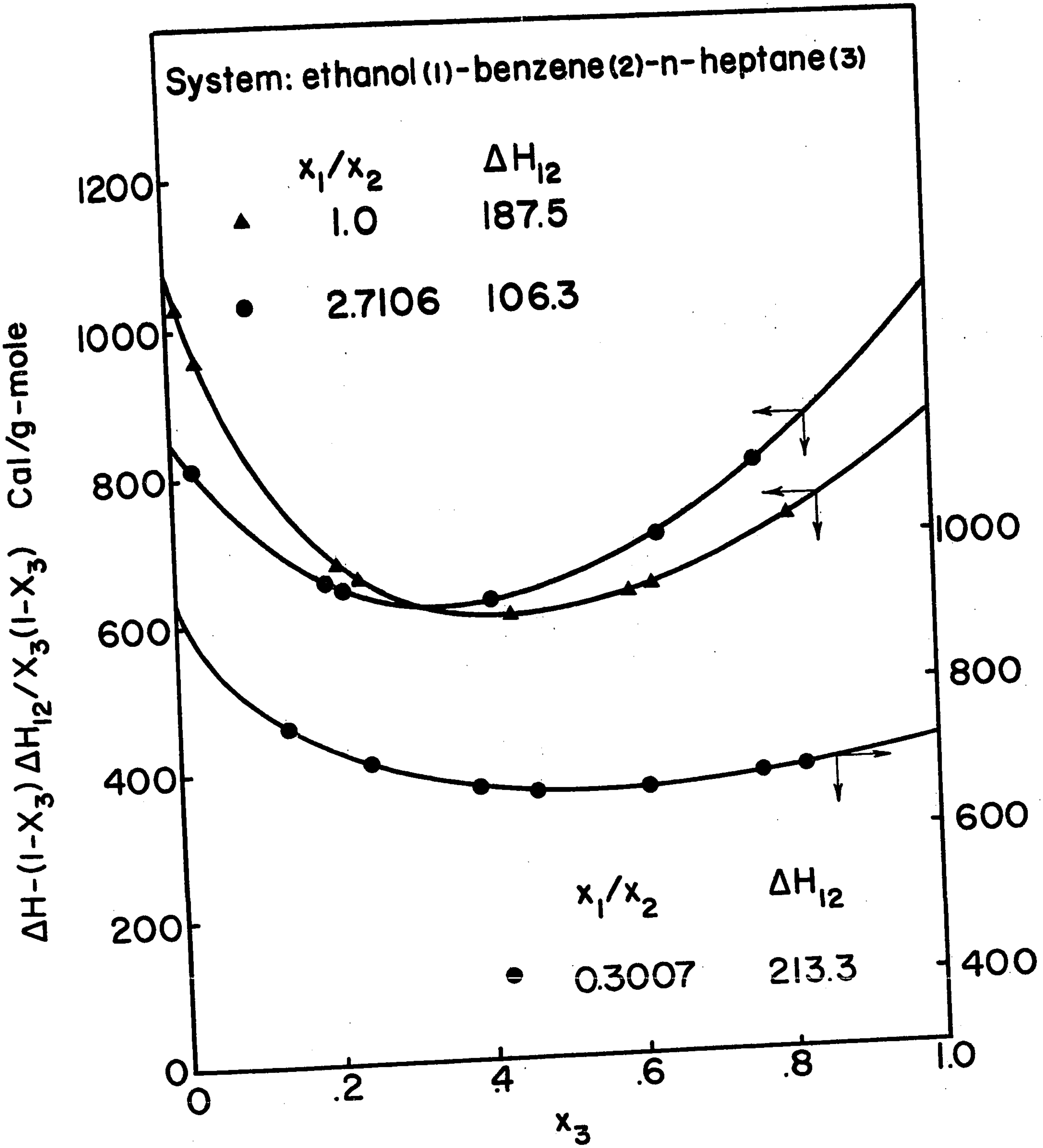
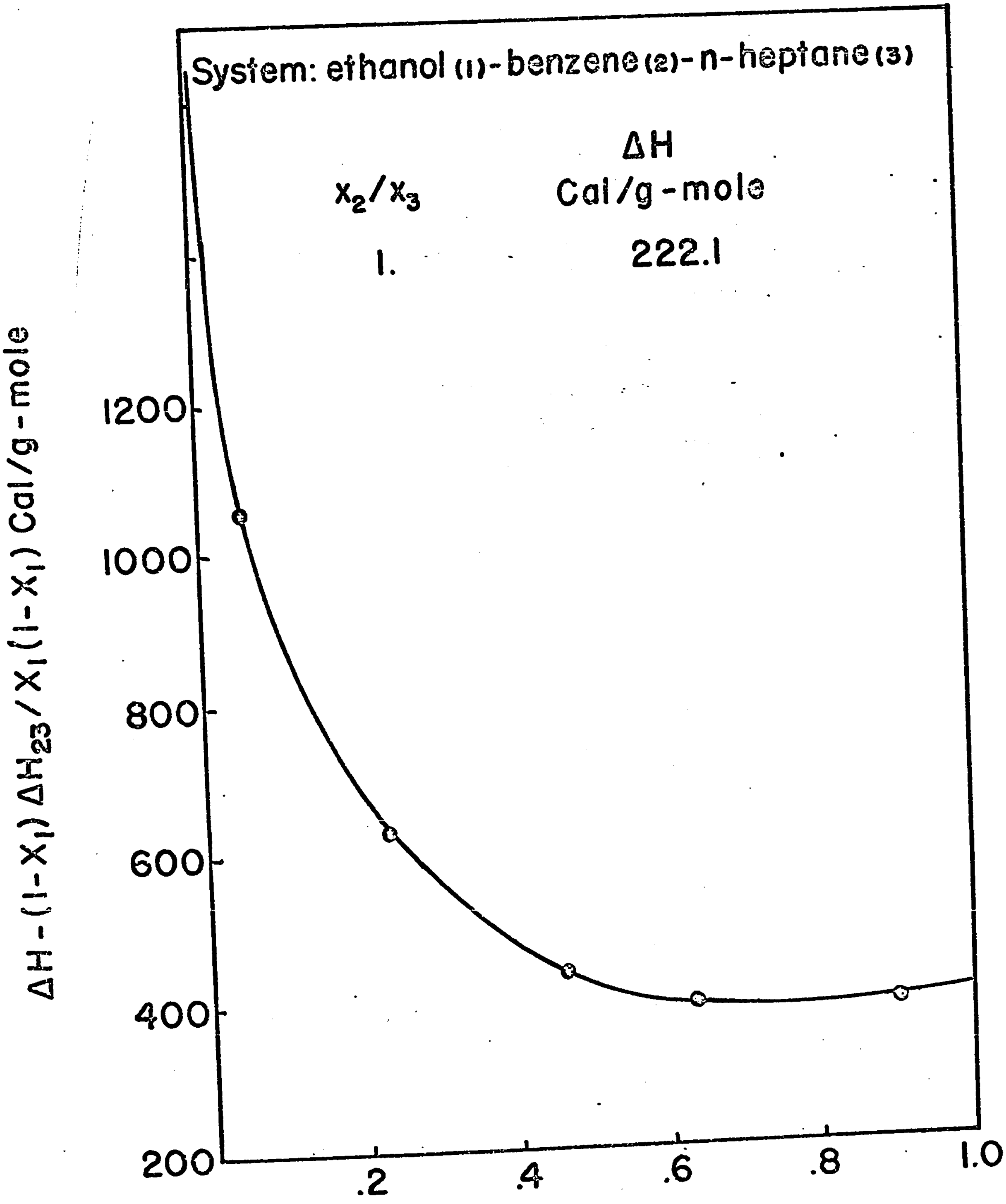


Figure 17a. Heats of mixing values for the system ethanol-benzene-n-heptane at 25°C., along constant x_i/x_j lines.

Figure 17b. Heats of mixing values for the system ethanol-benzene-n-heptane at 25°C., along constant x_i/x_j lines.



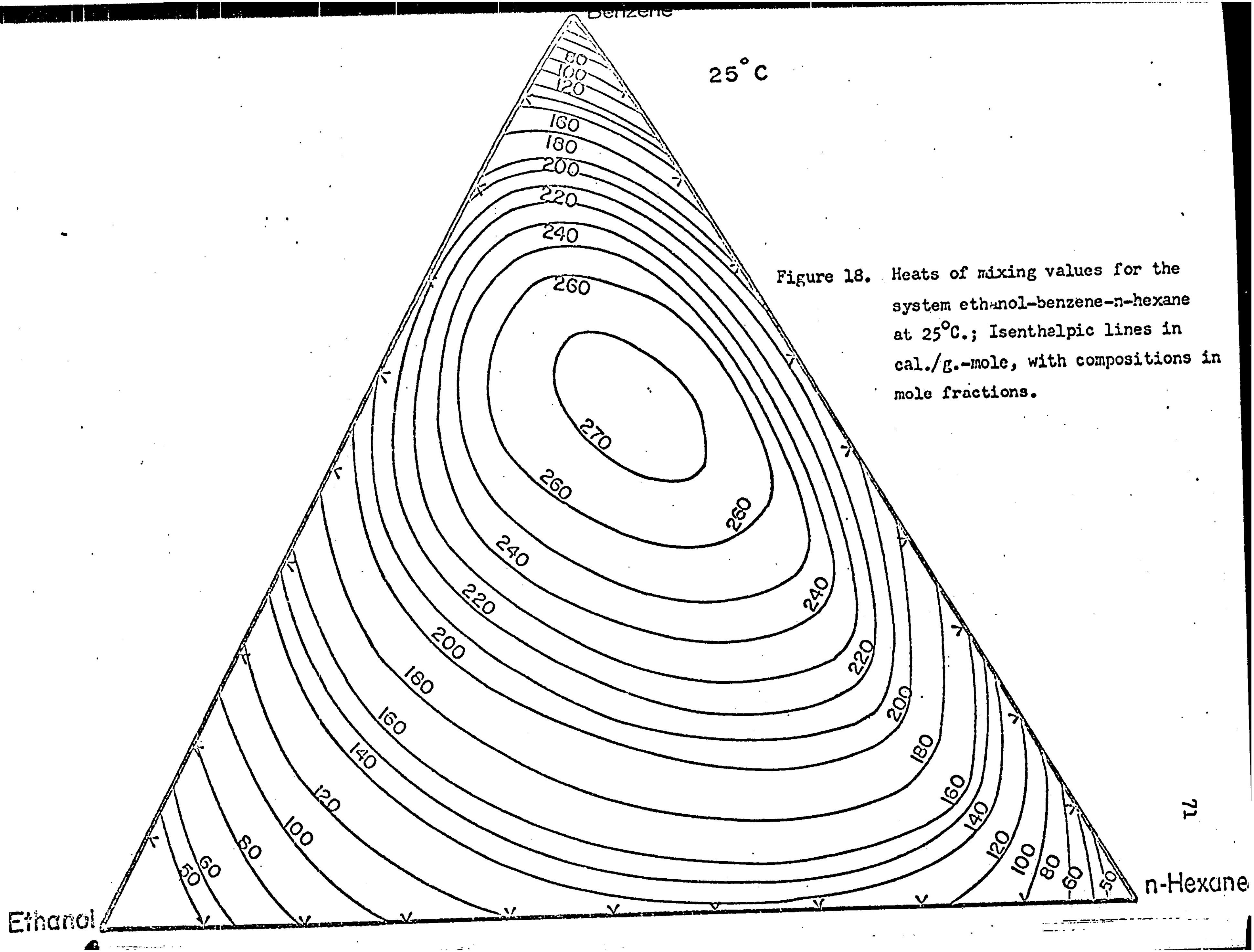


Figure 18. Heats of mixing values for the system ethanol-benzene-n-hexane at 25°C.; Isenthalpic lines in cal./g.-mole, with compositions in mole fractions.

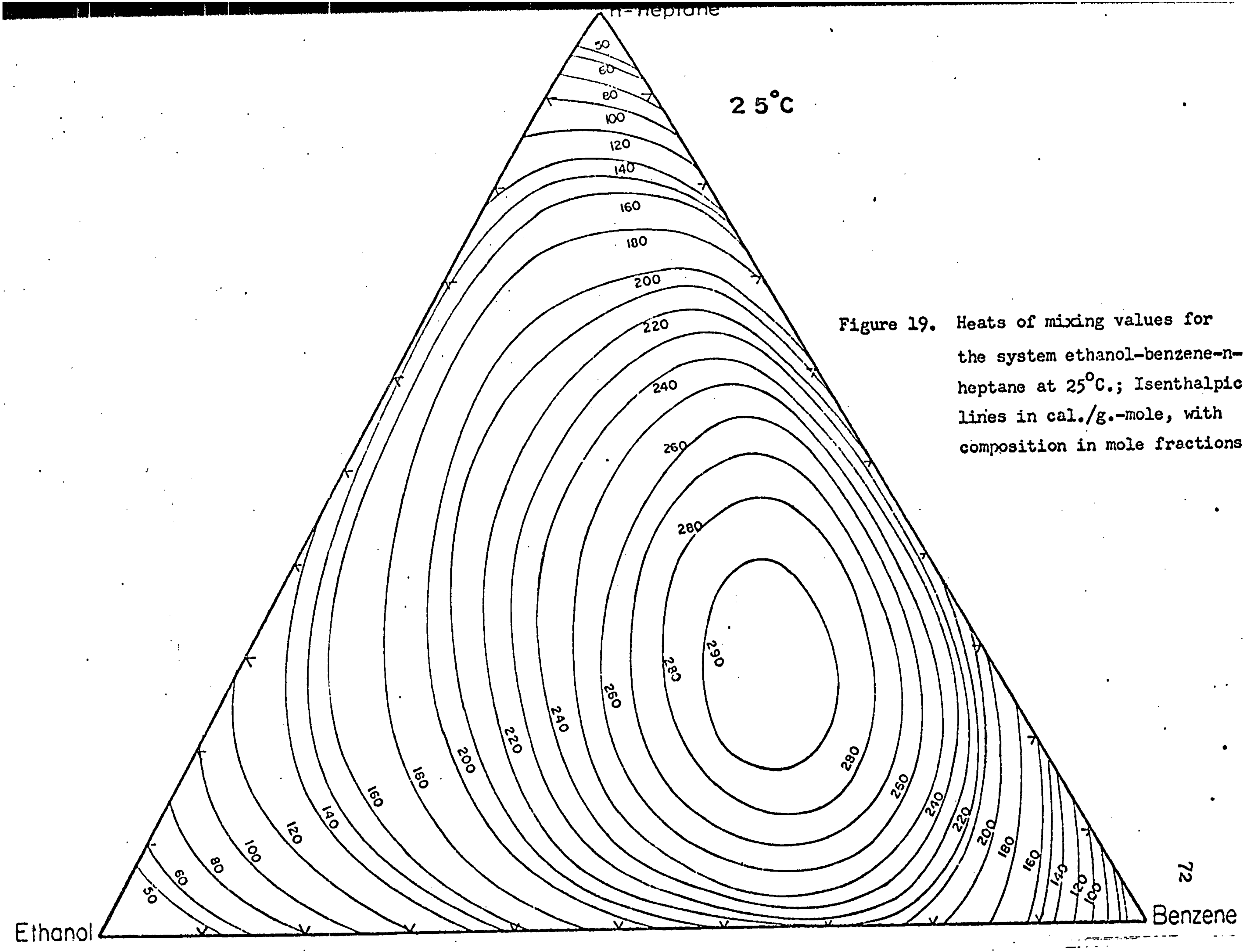


Figure 19. Heats of mixing values for the system ethanol-benzene-n-heptane at 25°C.; Isenthalpic lines in cal./g.-mole, with composition in mole fractions

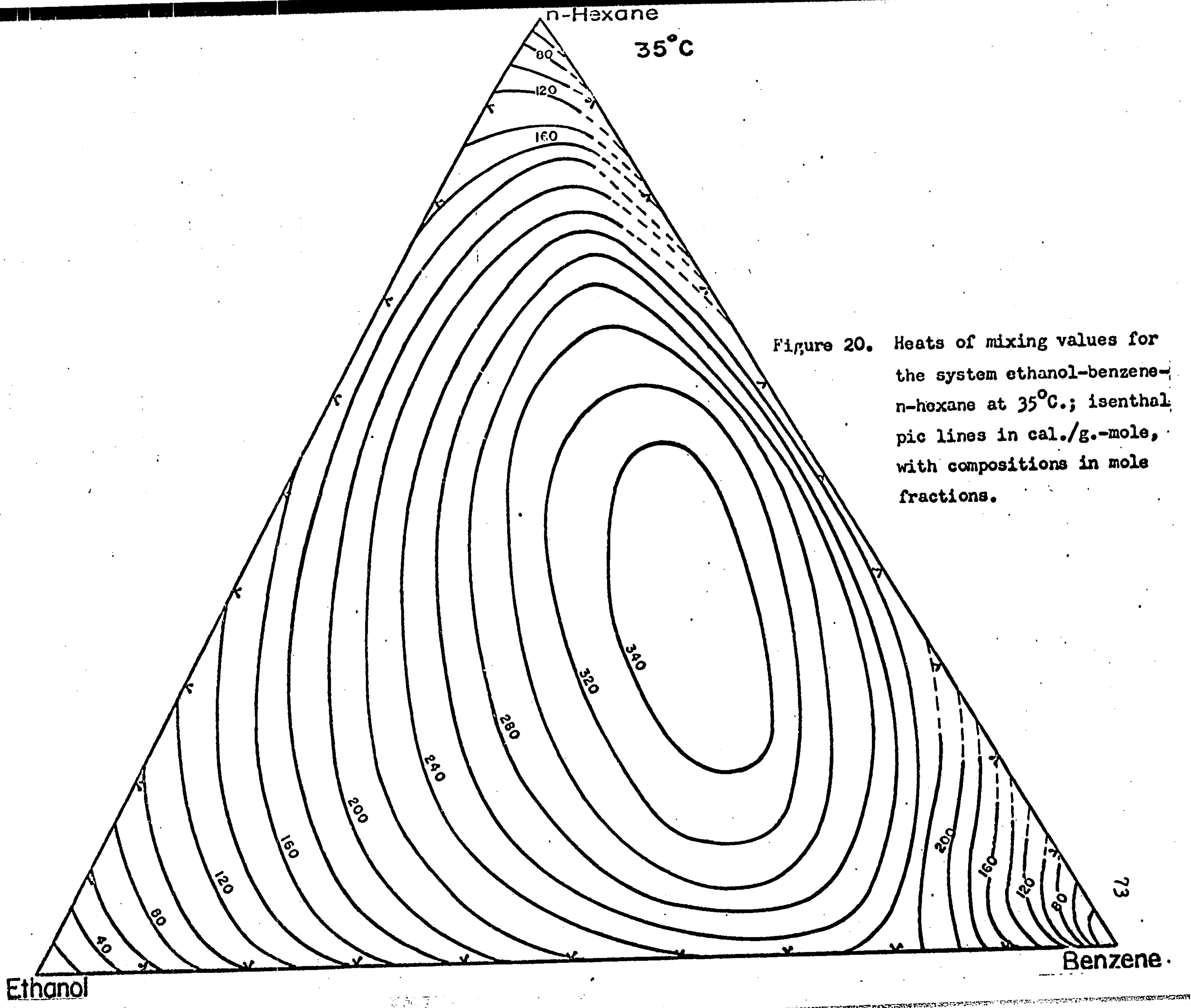


Figure 20. Heats of mixing values for the system ethanol-benzene-n-hexane at 35°C.; isenthalpic lines in cal./g.-mole, with compositions in mole fractions.

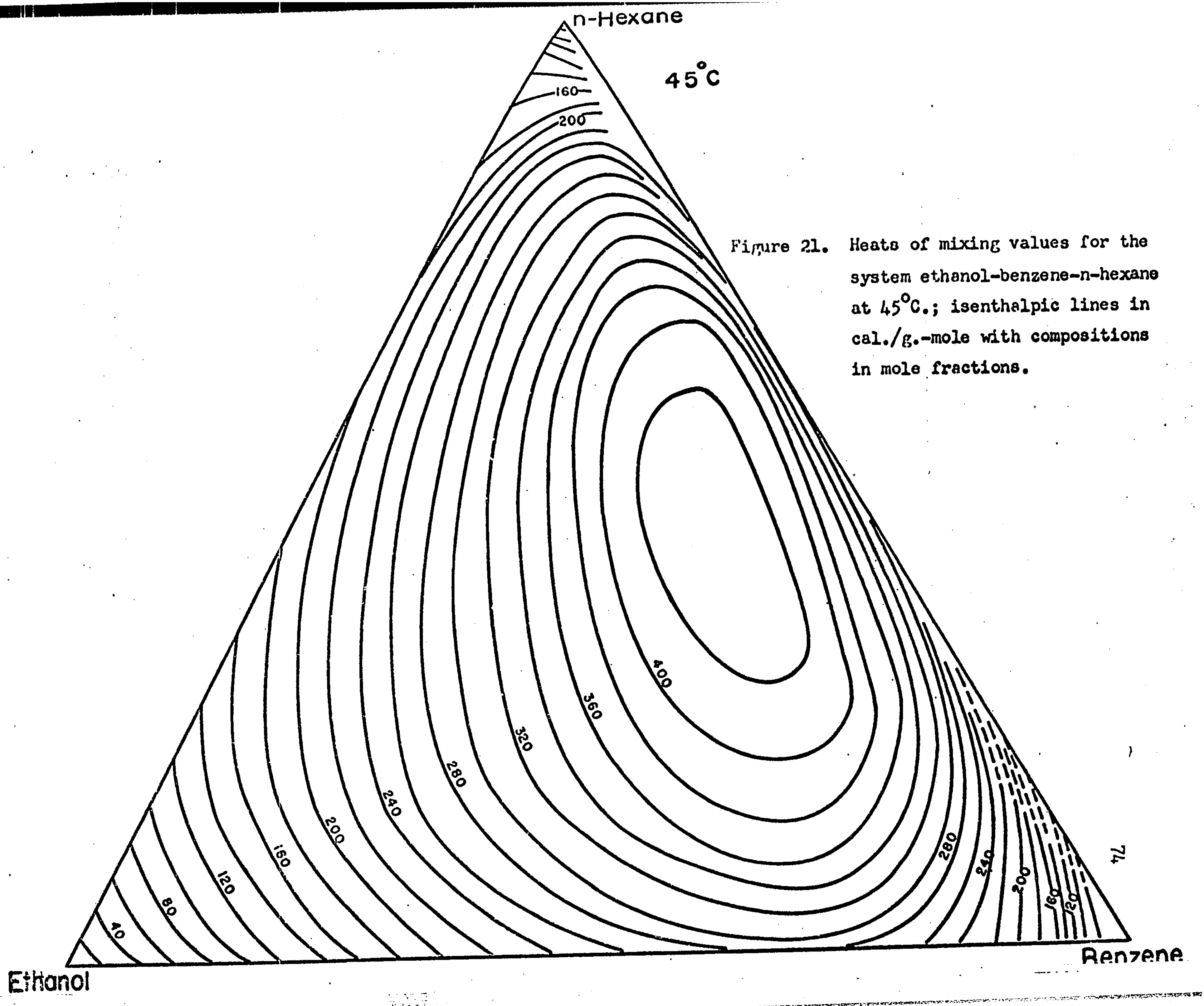


Figure 21. Heats of mixing values for the system ethanol-benzene-n-hexane at 45°C.; isenthalpic lines in cal./g.-mole with compositions in mole fractions.

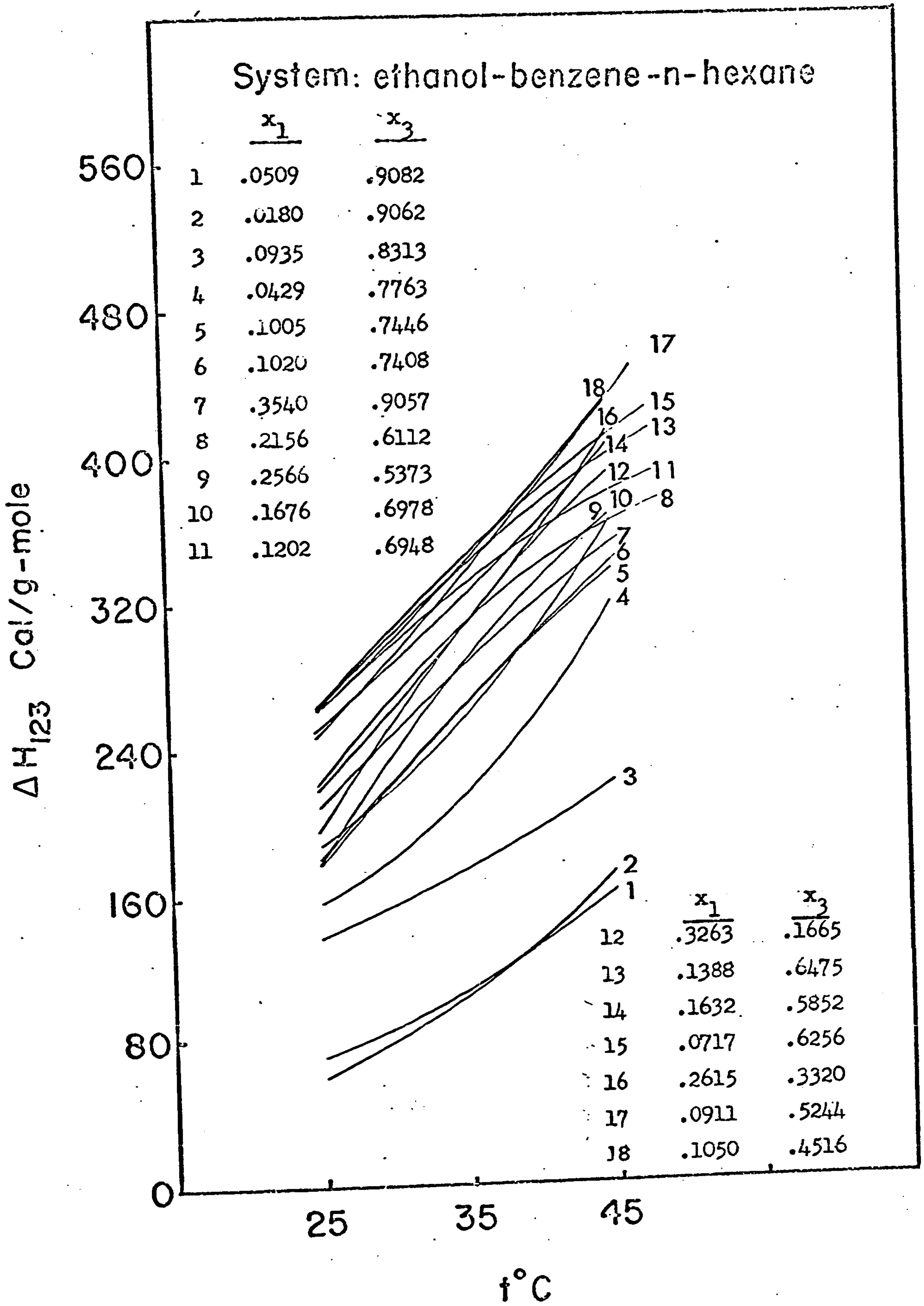


Figure 22. Variation of the heats of mixing of the system ethanol-benzene-n-hexane with temperature.

(ii) ethanol (1) - benzene (2) -n-heptane (3)

The ternary heats of mixing for this system, calculated at 35° and 45°C are presented in Table 16 of Appendix D in columns 4 and 5. Isenthalpic lines at 35° and 45°C are presented in Figures 23 and 24, respectively, for this system, and the temperature effect is illustrated in Figure 25.

3. Extrapolation of heats of mixing from minimum experimental data

a. Binary systems

The theoretical development of the proposed method is given, followed by a discussion of the application of the method in the extrapolation of heats of mixing data at 25°C of the binary system ethanol and benzene. The method is outlined in the discussion and is illustrated in Figure 26 for the heats of mixing of ethanol and benzene at 25°C. The extrapolated values of the partial molal enthalpies of mixing are plotted as $\Delta\bar{H}_1^M$ and $\Delta\bar{H}_2^M$ versus x_1. A comparison of predicted heats of mixing values with experimental data, at 25°C for the system ethanol-benzene, and ethanol-n-heptane is given in Figures 27 and 28, respectively, as plots of ΔH^M versus $x_{ethanol}$.

b. Ternary systems

The theoretical development of the proposed method is given, followed by a discussion of the application of the method in the extrapolation of heats of mixing data at 25°C of the ternary system ethanol (1) - n-heptane (2) - benzene (3).

The proposed method of extrapolation is illustrated in Figure 29. A comparison of experimental and extrapolated heats of mixing values for the ternary system ethanol (1) -n-heptane (2)-benzene (3) at 25°C is shown in Figure 30, along a constant x_3/x_2 line.

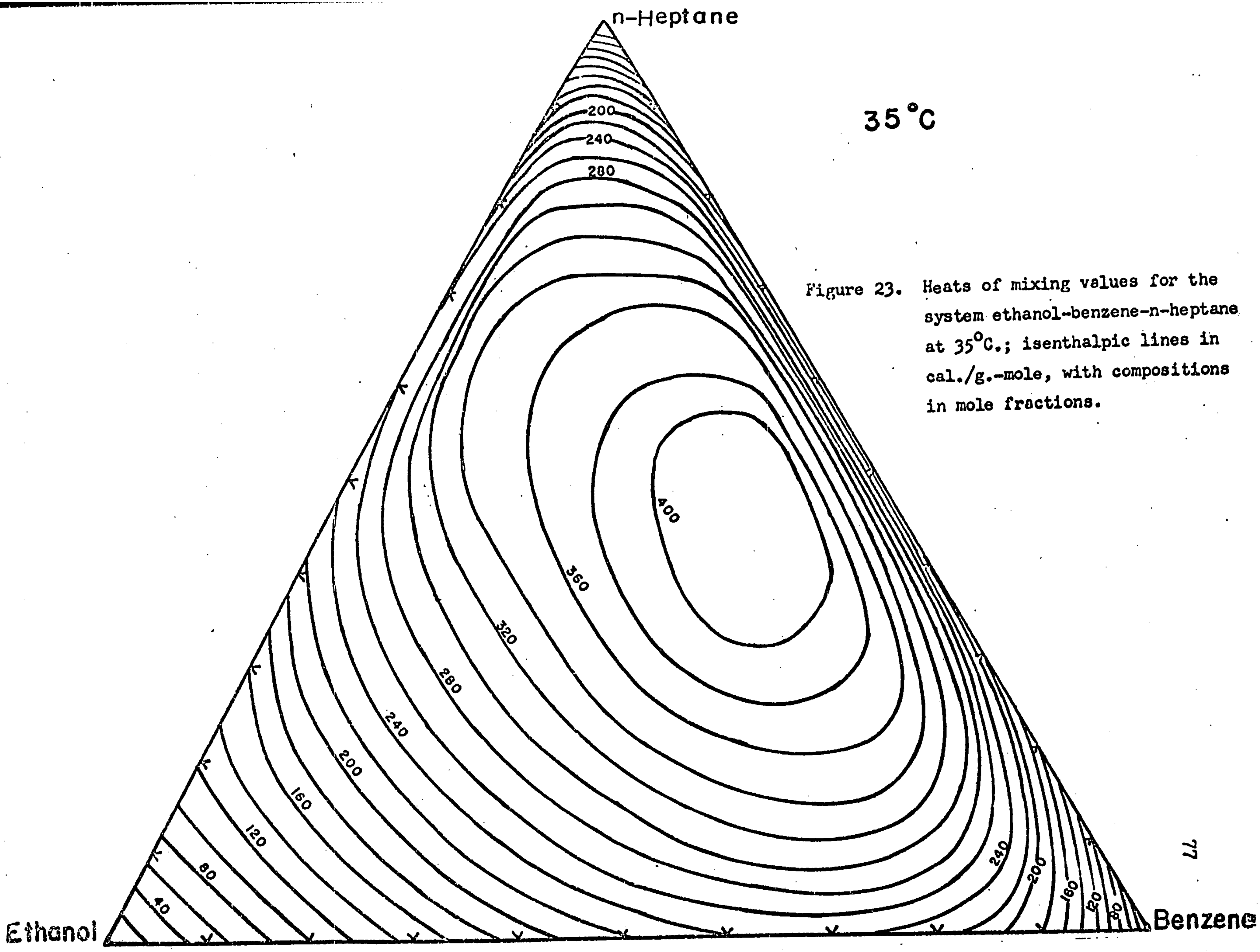


Figure 23. Heats of mixing values for the system ethanol-benzene-n-heptane at 35°C.; isenthalpic lines in cal./g.-mole, with compositions in mole fractions.

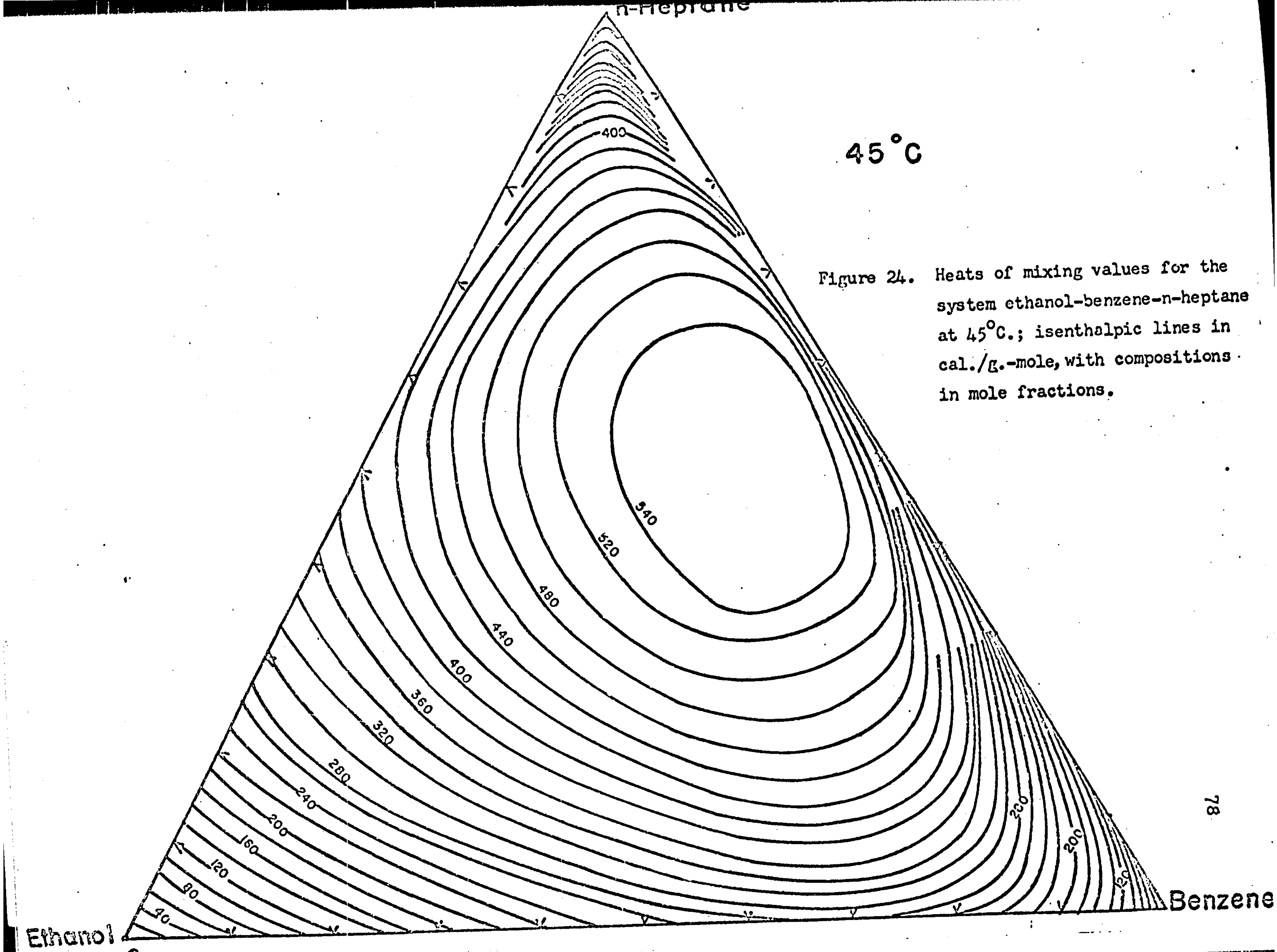


Figure 24. Heats of mixing values for the system ethanol-benzene-n-heptane at 45°C.; isenthalpic lines in cal./g.-mole, with compositions in mole fractions.

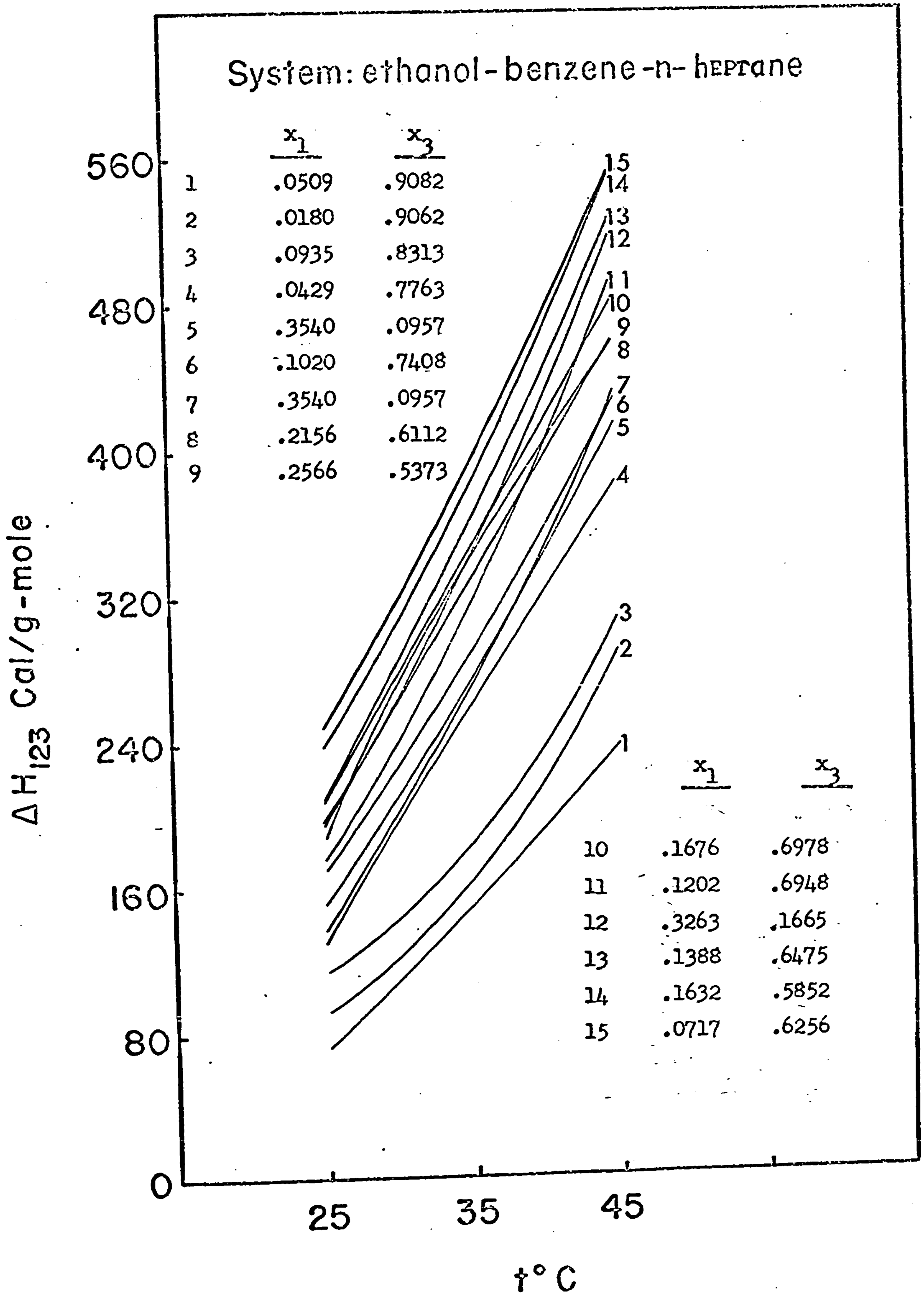


Figure 25. Variation of the heats of mixing of the system ethanol-benzene-n-heptane with temperature.

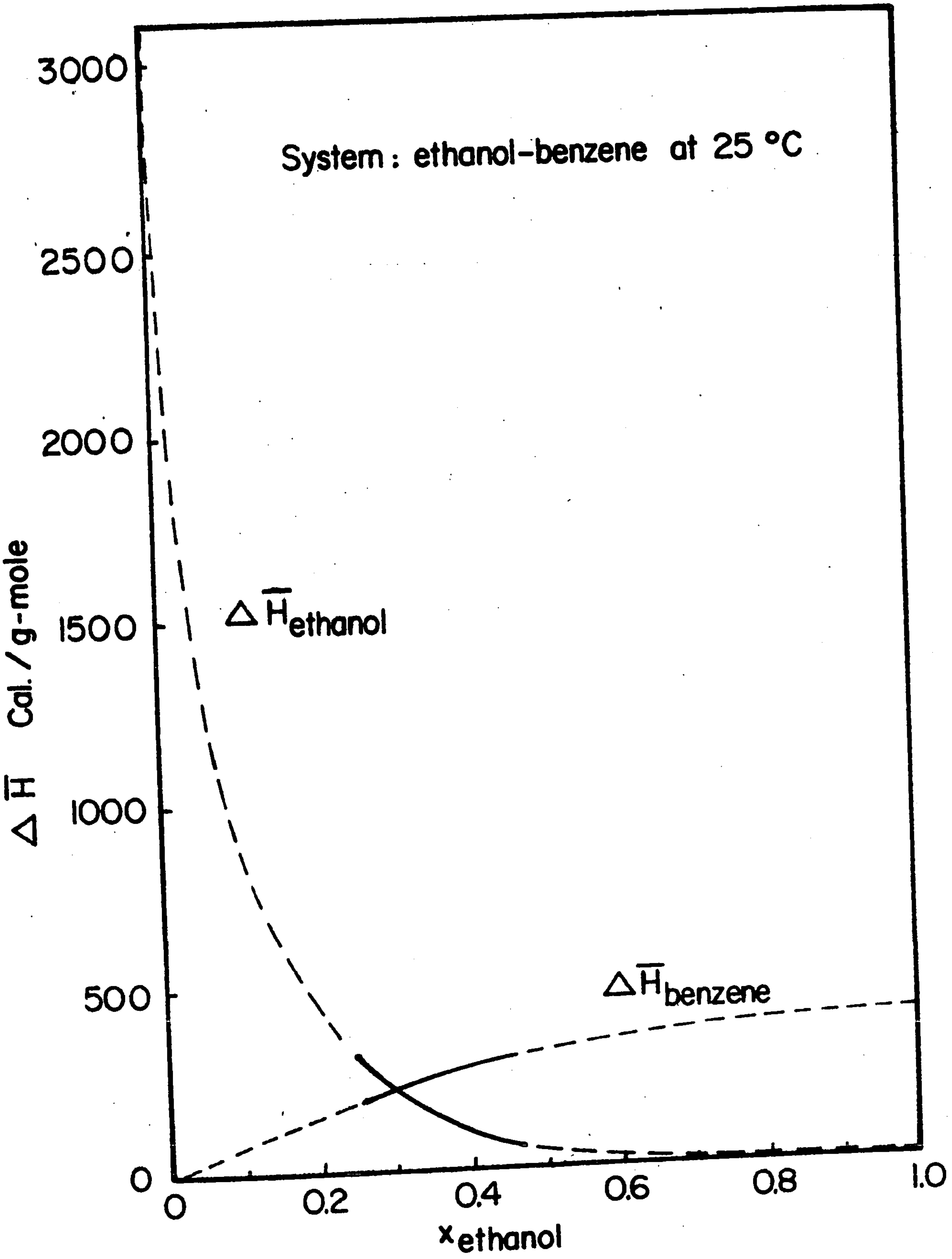


Figure 26. Extrapolated and partial molal enthalpies of mixing for the system ethanol-benzene at 25°C.
Plot of $\Delta\bar{H}^m_{\text{ethanol}}$ and $\Delta\bar{H}^m_{\text{benzene}}$ vs. x_{ethanol}

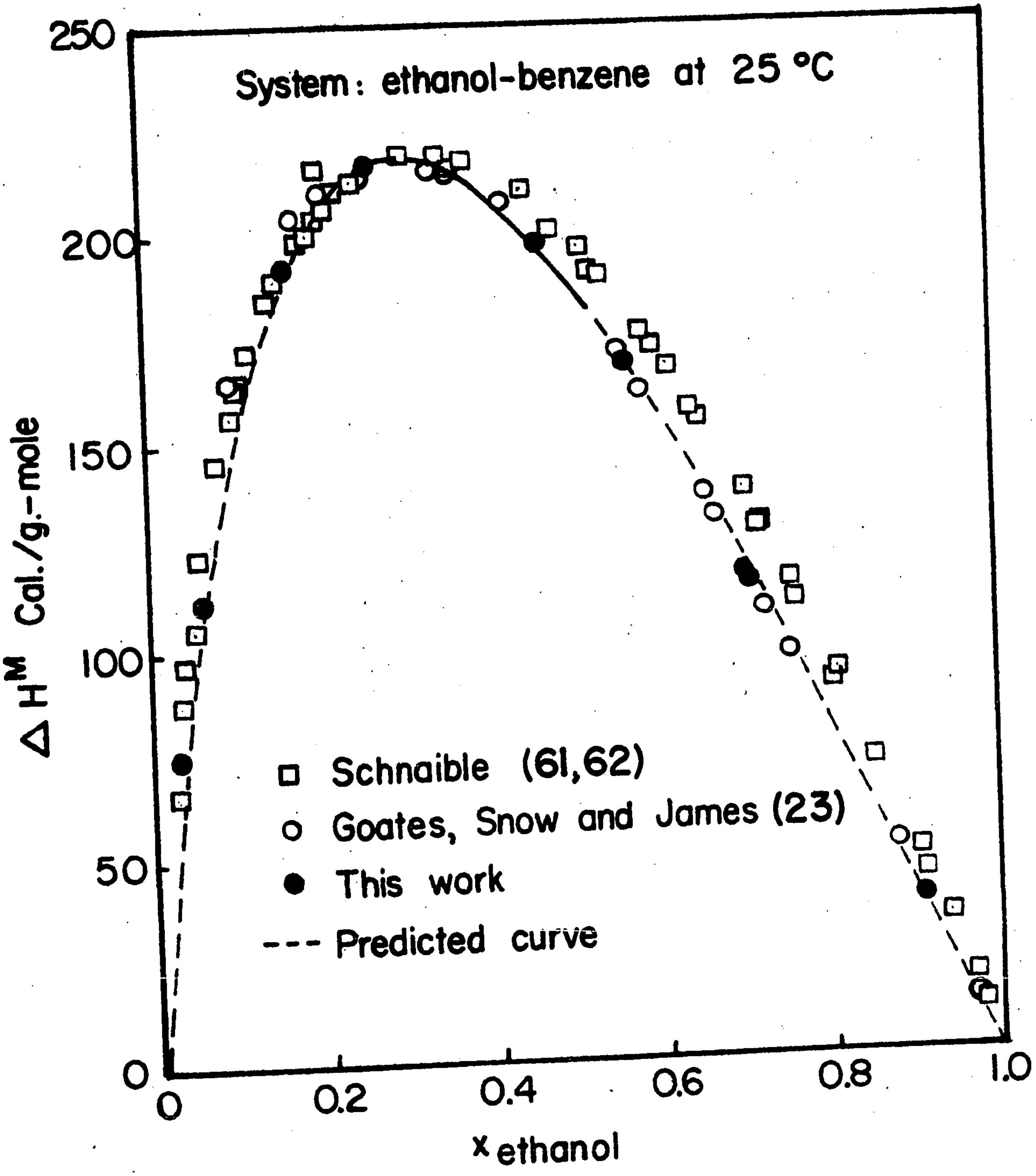


Figure 27. Comparison of predicted heats of mixing values with experimental data for the system ethanol-benzene at 25°C. Plot of ΔH^m vs. $x_{ethanol}$

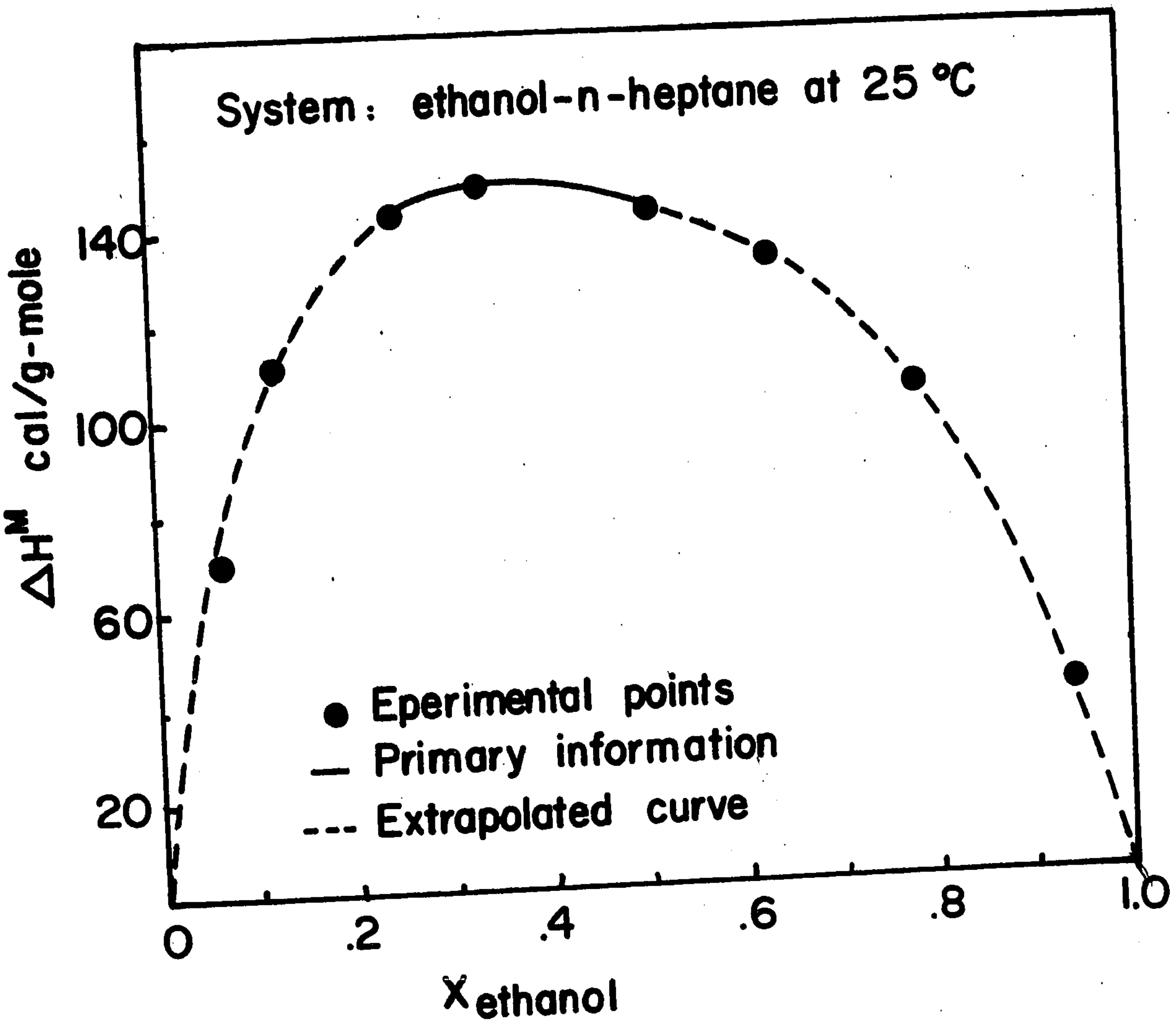


Figure 28. Comparison of predicted heats of mixing values with experimental data for the system ethanol-n-heptane at 25°C. Plot of ΔH^m vs. $x_{ethanol}$

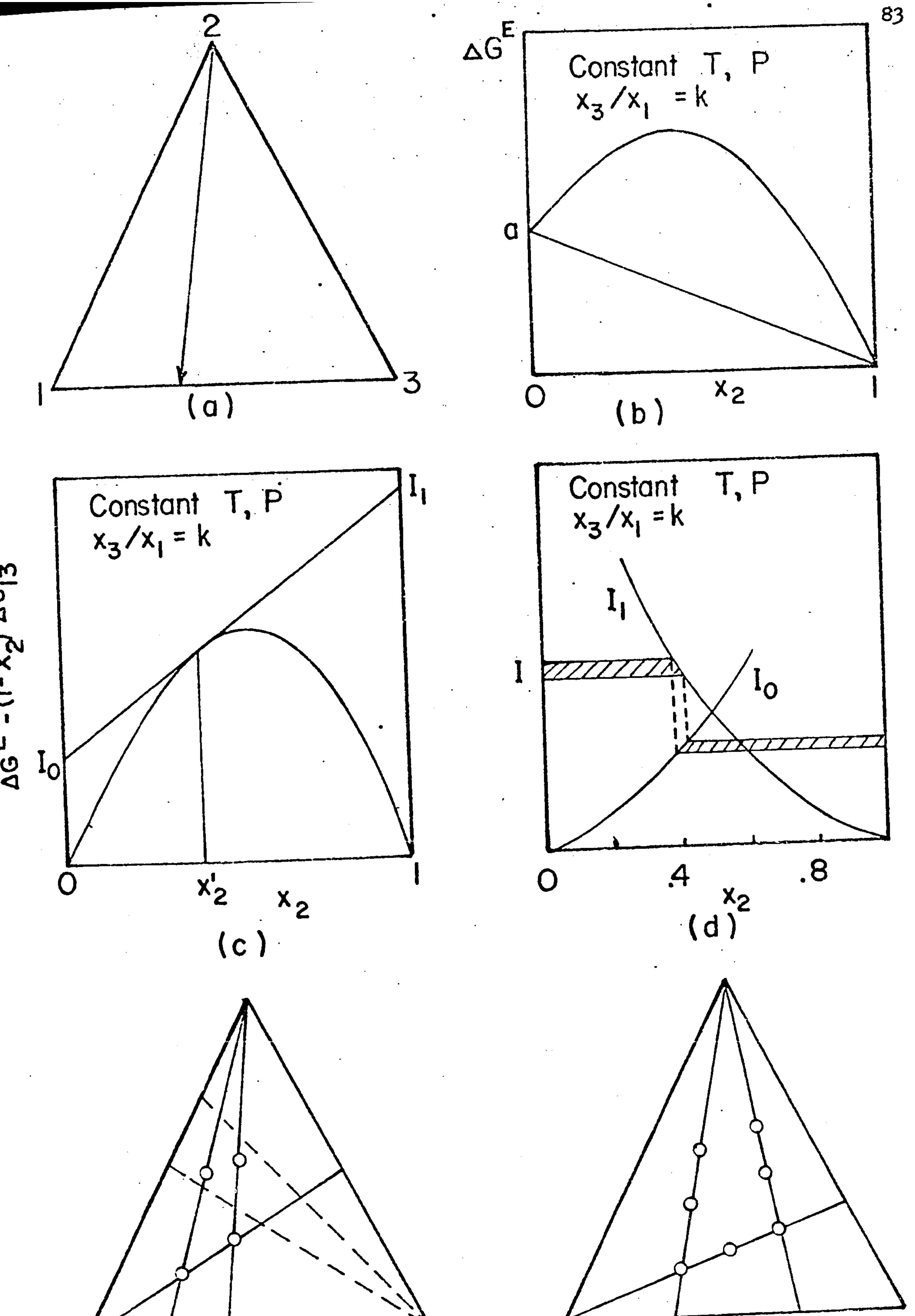


Figure 29. Illustration of proposed extrapolation method for ternary systems.

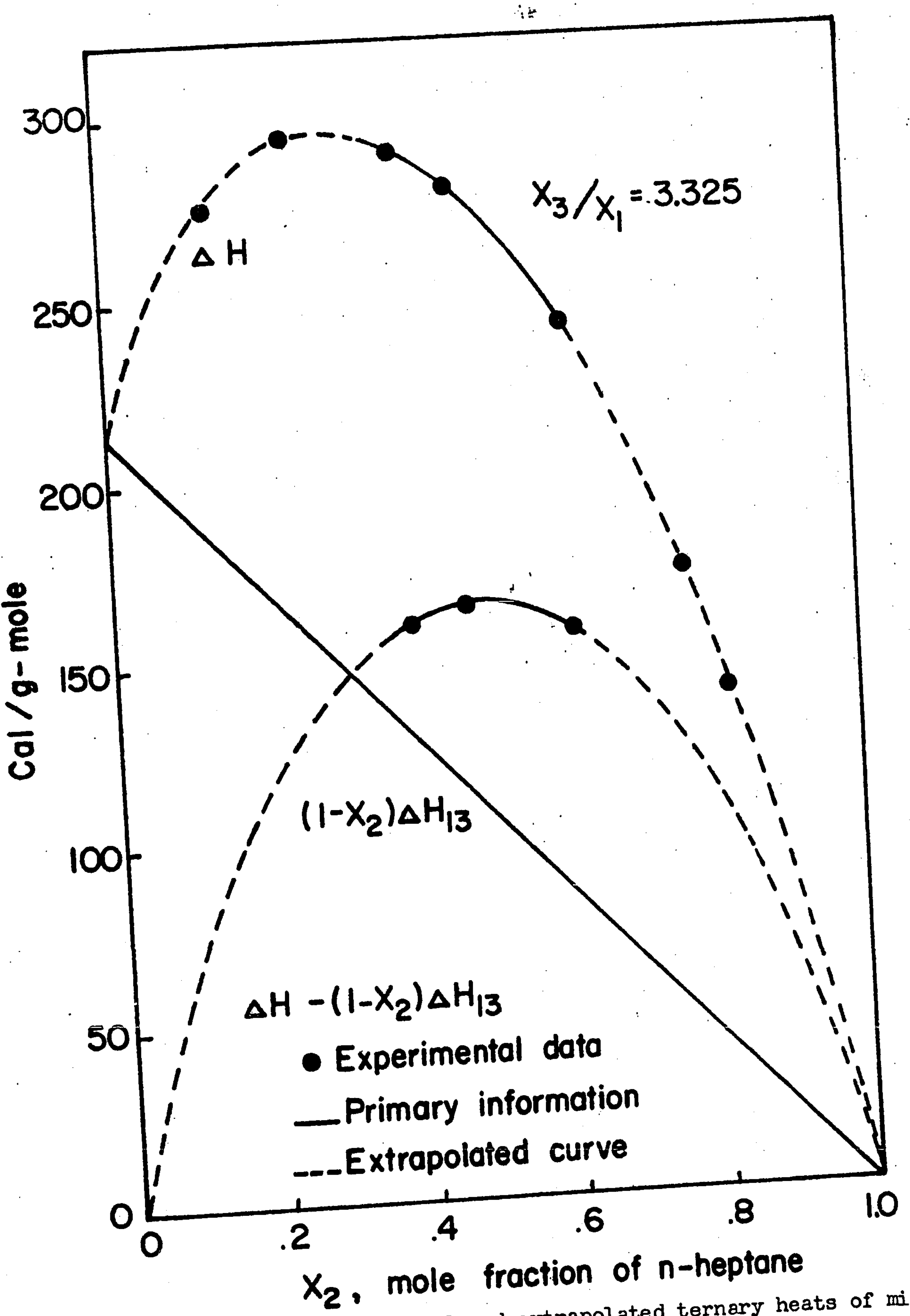


Figure 30. Comparison of experimental and extrapolated ternary heats of mixing values for the system ethanol (1)-n-heptane (2) - benzene (3) at 25°C., along a constant x_3/x_1 line.

4. Application of the generalised quasi-lattice theory of Barker to heats of mixing data

a. Testing of the parameters proposed in the literature and establishing energy values for various types of interactions by a new approach.

The discussion on the application of the quasi-lattice theory deals with previous work, the parameters and the criteria of "best-fit" used in earlier studies.. The new approach and new criteria for "best-fit" employed in this investigation are compared. The merits of the proposals of this investigation are pointed out.

The literature values of the quasi-lattice parameters for various molecules have been given in Table 1. An illustration of the arrangement of lattice sites and types of interaction was presented in Figure 1 for the alcohol molecules of methanol, ethanol and the hydrocarbon molecule, n-hexane. The types of interaction and the non-zero interaction energy values, proposed in the literature for various systems, are presented in Table 17, in Appendix E.

Quasi-lattice parameters, such as type and number of contacts, and number of lattice sites, specified in this investigation are given in Table 18, in Appendix E.

b. Specification of a $-\overset{|}{\mathrm{CH}}-$ contact for branched aliphatic chains

The assignment of the new $-\underset{|}{\mathrm{CH}}-$ type contact is discussed. An illustration of the arrangement for contact types and lattice sites proposed in this investigation for iso-propanol, iso-octane and 2,4-dimethylpentane is shown in Figure 31.

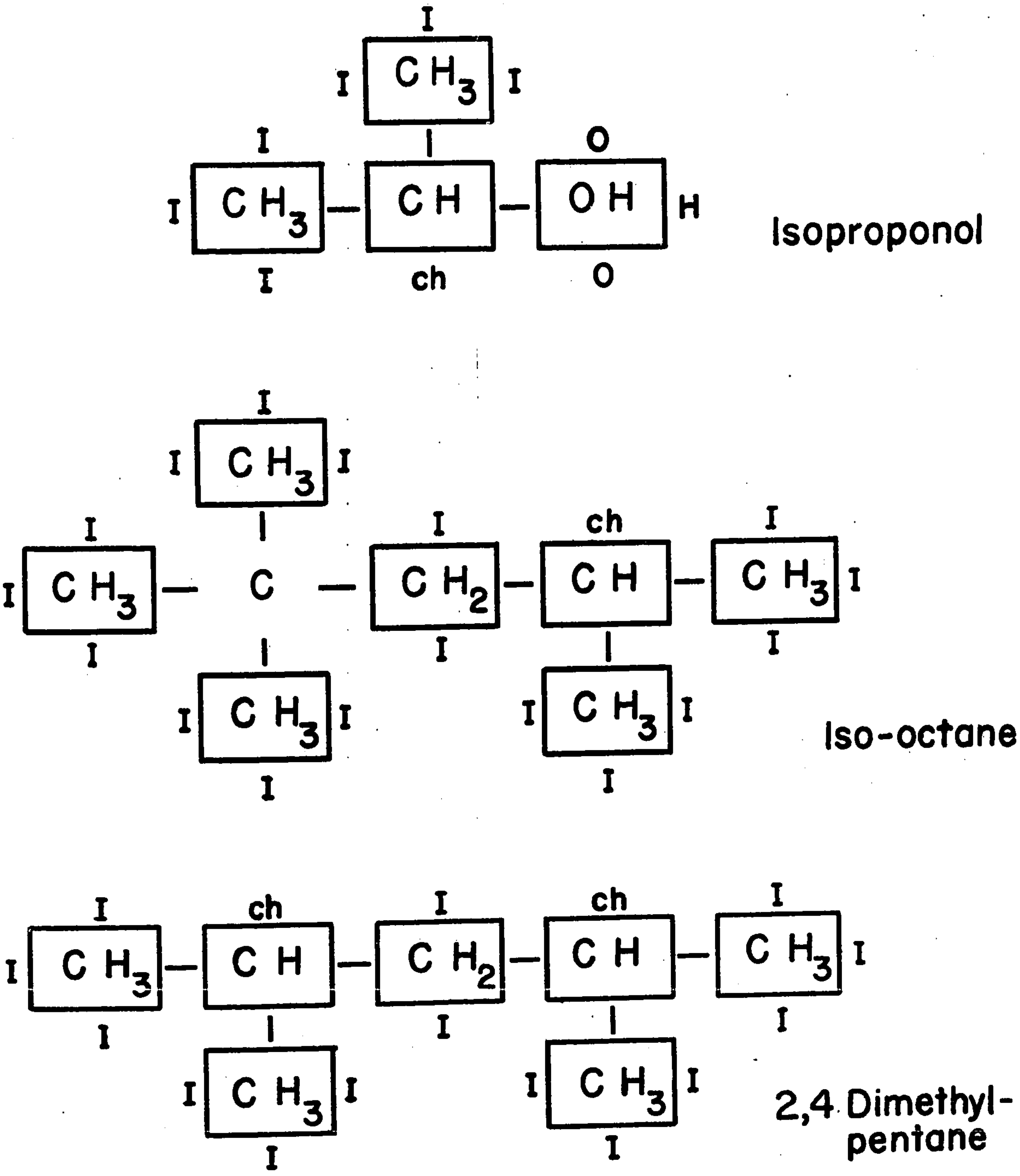


Figure 31. Illustration of contact types and lattice sites assigned for isopropanol, isooctane and 2,4 dimethylpentane.

The interaction energies and the corresponding deviations of predicted heats of mixing from experimental values are given in Table 19 of Appendix E for all systems studied in this investigation except those of benzene with n-alkanes. The presentation for these systems is outlined in the following section.

c. Quasi-lattice parameters to represent heats of mixing data of benzene-n-alkane systems, by a new approach.

This specific application of the quasi-lattice theory to the heats of mixing data of benzene-n-alkane systems is discussed.

A comparison of agreements between experimental ΔH^M values for the benzene-n-alkane systems and those calculated by the quasi-lattice theory are presented in Table 20, of Appendix F. The parameters suggested from the literature and those of this investigation are also given in Table 20. The extent of agreement is expressed in terms ofthe maximum and average absolute deviation in percent.

The "best-fit" energy values, U_{12} using the equations 37 and 38 for Q values, as suggested in the literature are presented in Table 21.

The results for evaluation of U_{12} and Q_2 values for the series of benzene-n-alkane systems, using $Q_1 = 12$ are presented in Table 22, showing the maximum and the avergage absolute deviations in percent. The ranges of Q_2 values with $Q_1 = 12$ and $U_{12} = 60, 61, 62$ and 63 cal./g.-mole are illustrated for the benzene-n-alkane systems in Figures 32, 33, 34 and 35, respectively.

A comparison of calculated and experimental ΔH^M values at 25°C for the n-alkanes with benzene is shown in Figure 36. Experimental

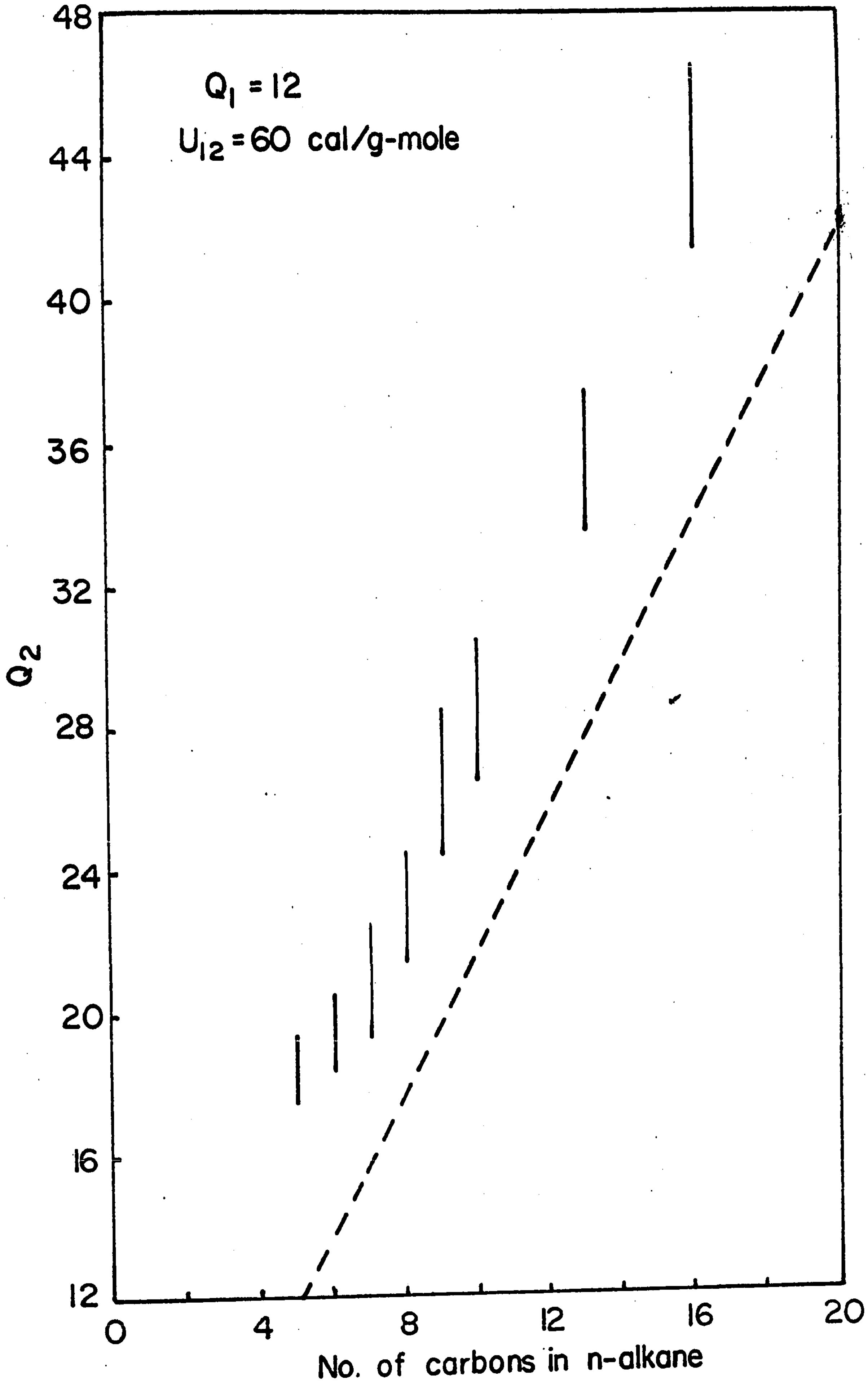


Figure 32. Range of Q_2 values with $Q_1 = 12$, $U_{12} = 60$ cal./g.-mole.

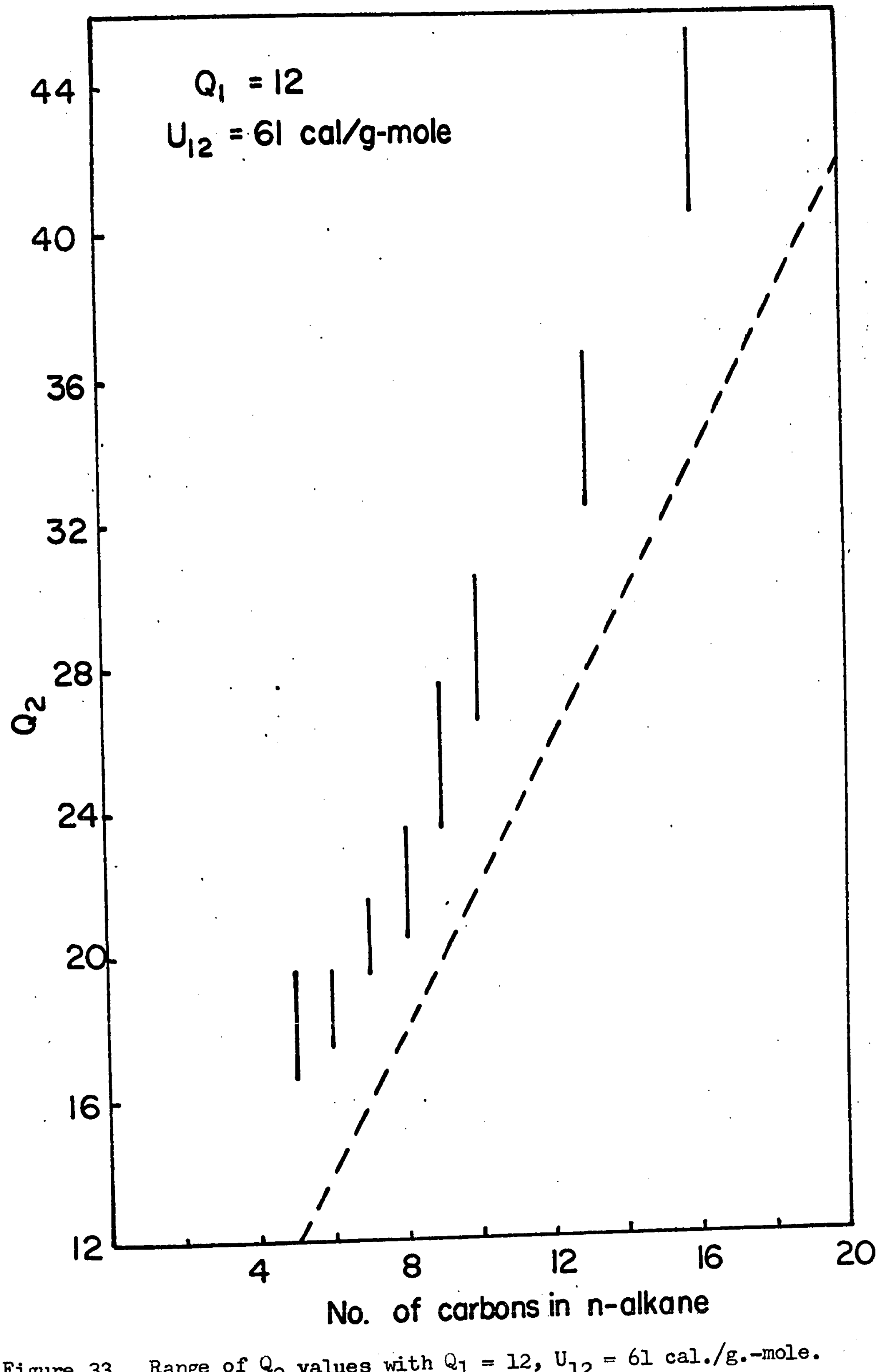


Figure 33. Range of Q_2 values with $Q_1 = 12$, $U_{12} = 61$ cal./g.-mole.

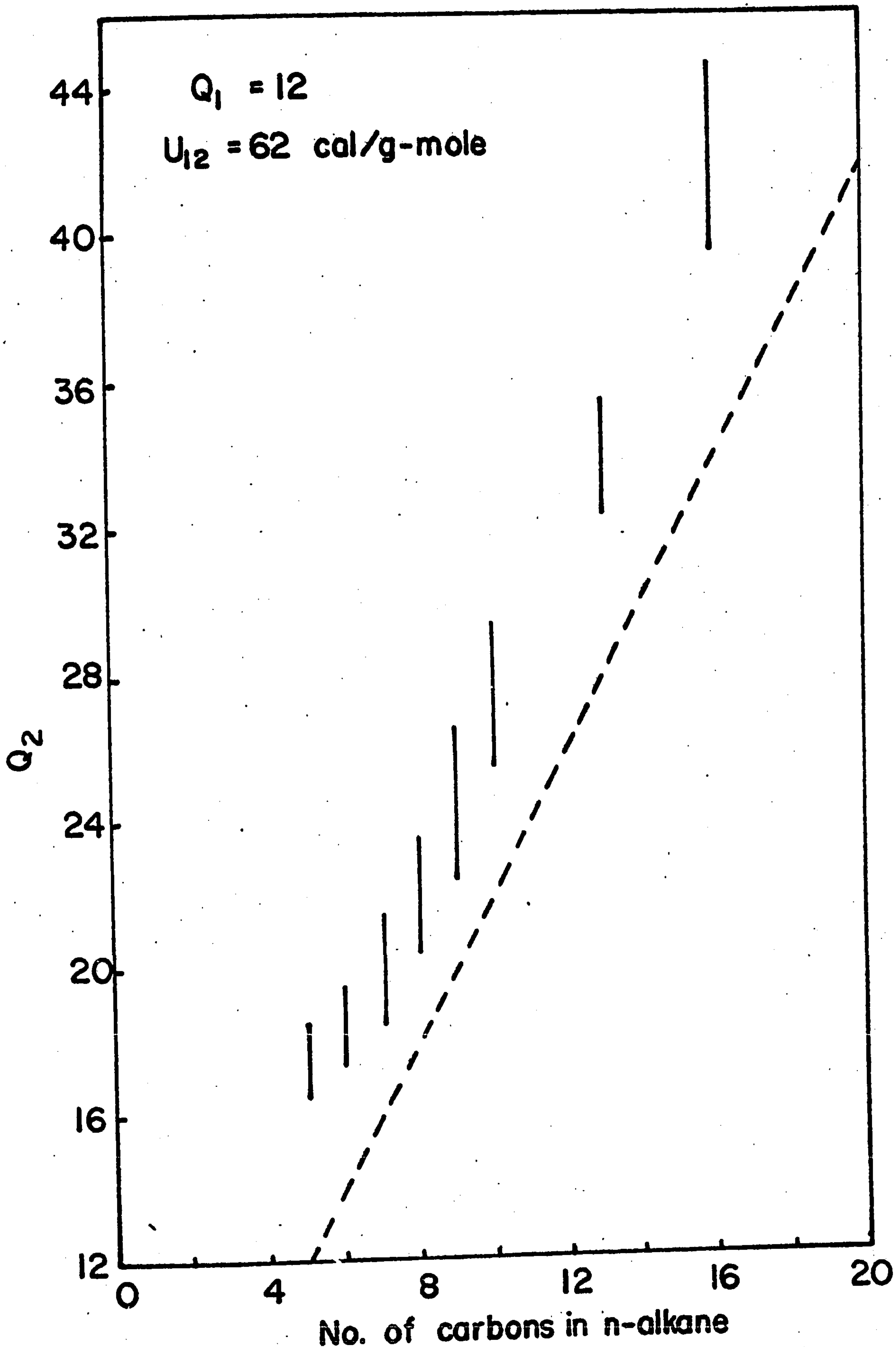


Figure 34. Range of Q_2 values with $Q_1 = 12$, $U_{12} = 62$ cal./g.-mole.

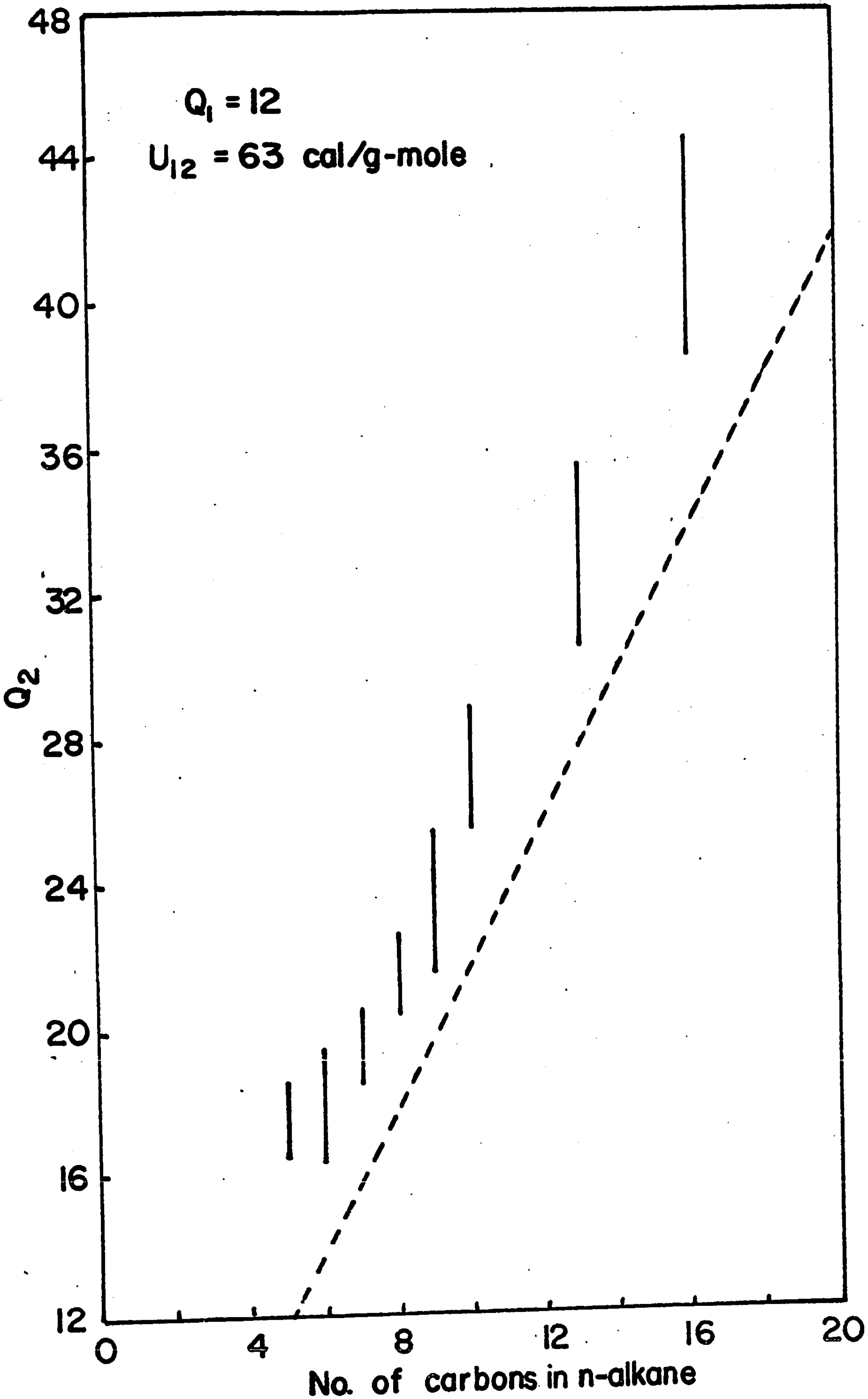


Figure 35. Range of Q_2 values with $Q_1 = 12$, $U_{12} = 63$ cal./g.-mole.

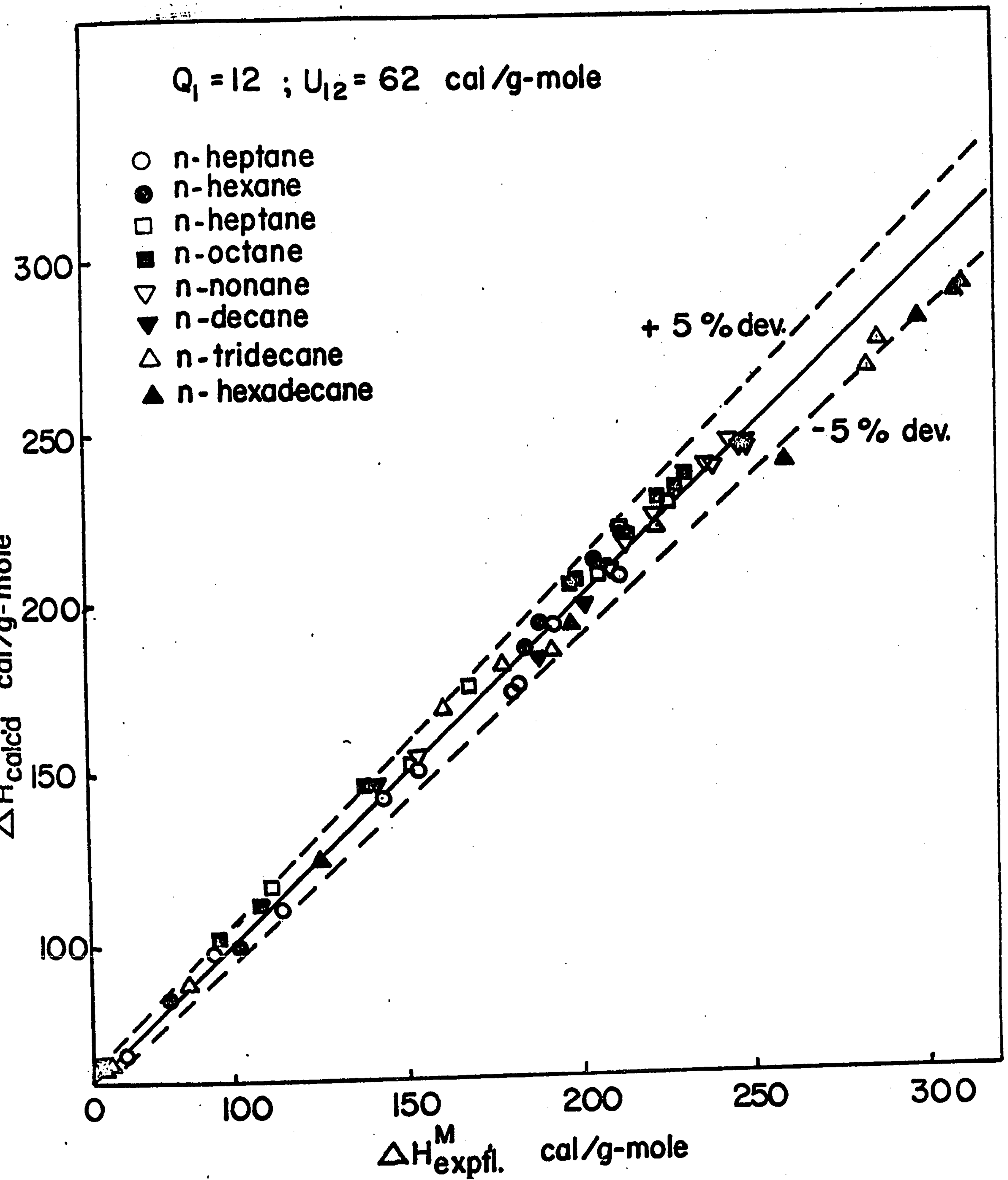


Figure 36. Comparison of calculated and experimental ΔH^m values at 25°C for n-alkanes with benzene.

values of ΔH^M are plotted versus ΔH^M values calculated with parameters proposed in this investigation.

B. Error analysis

1. Heats of mixing of binary systems

The sources of error in heats of mixing calorimetry are: a) the purity of the materials ; b) the uncertainty in the correction for the heat evolved in breaking and piercing the diaphragm ; c) the heat effects due to vaporization and condensation ; d) mechanical errors ; e) others.

These sources of error are discussed in the following paragraphs.

a. Purity of materials

In heats of mixing determinations, the purity of the materials have a significant effect on the results. The specifications of the materials used in this investigation are given in Table 2. The comparison of the refractive index measurements were in good agreement with literature values, and the materials were used without purification. No error in the final experimental values was attributed to the purity of the materials used.

b. Heat effect due to rupture of the diaphragm

Blanks tests with the same liquid in both compartments of the mixing cell indicated no heat effect due to action of the plunger on breaking and piercing the diaphragm.

c. Heat effect due to stirring

The heat effect due to stirring is accounted for as usual, in the graphical procedure employed for the determination of the thermistor resistance change during a mixing or calibration experiment. The correction is accomplished by extrapolating the fore- and after-period to the time at which the resistance change of the thermistor is half of the apparent overall change, Figure 8.

d. Heat effects due to vaporization and condensation

The greatest source of error in heats of mixing calorimetry is the vaporisation and condensation effects due to changes in the composition of any vapor phase. The design of the calorimeter vessels and the filling procedure were such that no vapor phase was present and hence this major source of error was eliminated.

e. Mechanical errors

These errors arise from the precision of the mechanical instruments used for measuring the various quantities, voltage, resistance, time and mass. The estimated percentage errors for these measurements are listed at the end of the section B.

f. Others

Other errors that must be taken into account are, the heat transfer to the surroundings and personal error in graphical extrapolations and estimations. These two errors amounted to about .5 percent.

The errors are listed as follows:

Errors	Max. %
Voltage measurements	± 0.05
Resistance measurements	± 0.01
Time measurements	± 0.03
Mass measurements	± 0.02
Heat transfer to surroundings	± 0.25
Graphical methods	± 0.25
Vaporisation and condensation effects	nil
Action of plunger	nil
Purity of materials	nil

For a heats-of-mixing determination the above measurements with the exception of those for mass must be repeated, once for the heat effect due to mixing and again for the calibration. The total maximum uncertainty thus becomes ± 1.18%

2. Heats of mixing of ternary systems

For the ternary heats of mixing a binary mixture, of known heats of mixing, was usually mixed with a third component. In addition to the errors due to the determination of the heat effect, there is the error inherent in the heats of mixing value of the binary mixture, and there is the error in mass measurements, for preparation of the binary mixture. These errors are listed below showing the estimated uncertainty in the final value.

Error	Max. %
Mass measurement	± .02
Binary Heats of mixing values	± 1.18
Experimental determination of heat effect	± 1.18
Total :	± 2.38

3. Specific heats of ternary mixtures

The errors involved in the determination of ternary specific heats are the same as those for a binary heats of mixing experiment plus an additional error from the preparation of the ternary mixture. The maximum uncertainty is therefore estimated to be ± 1.2 % .

4. Extrapolated values of heats of mixing

The agreement obtained between the extrapolated binary ΔH^M values and experimental data of this investigation, Figures 25, 26 and 28, indicates that the uncertainty in the extrapolated values is within the experimental uncertainty.

C. Discussion of results

1. Experimental

a. Binary heats of mixing data

One of the objectives of this work was to establish ternary heats of mixing data at $25^{\circ}C$ for the systems ethanol-benzene-n-hexane and ethanol-benzene-n-heptane. Some data existed in the literature for the constituent binaries of these ternary system. While for some of these binary systems there was agreement between data reported by different authors, for the other binary systems there was only partial agreement between data of different authors. Because of the discrepancies, experimental heats of mixing data for the binary liquid systems were established in this investigation. The comparison of these data with the literature values attested to the excellent performance of the calorimeters. Also reliable sets of values are provided, where discrepancies existed previously.

The summary of deviations of the ΔH^M values in the literature from those of this investigation, shown in Table 8, indicates excellent agreement with some of the previous investigators. The results are discussed separately for each system.

i. ethanol-n-hexane

The experimental results, Table 3, obtained in this investigation, agree well with the values reported by Brown, Fock and Smith (10) as shown in Figure 9, and by the small deviation of Table 8. However, the concentration range covered in this investigation extended into more diluted regions.

ii. n-hexane-benzene

The experimental data, Table 4, agree more or less with that reported by Schnaible as shown in Figure 10 and Table 8. They are slightly lower than those reported by Schnaible at low benzene concentrations.

iii. n-heptane-benzene

The experimental results, Table 5, agree fairly well with those reported in the literature (40),(61, 62). These results are compared in Figure 11.

iv. ethanol-n-heptane

A qualitative comparison, Figure 12, indicates that the results obtained in this investigation, Table 6, agree fairly well with those of Savini and Van Ness (56), and those of Brown, Fock and Smith (10).

v. ethanol-benzene

The experimental results, Table 7, obtained in this investigation, agree generally well with the literature values, with the exception of Schnaible's data, as shown in Figure 13. When all the heats of mixing data for this system are compared on a ΔH^M vs x_1 plot, the agreement between the values obtained in this study and the values reported by Goates, Snow and James (23) and Schnaible (61,62) in the maximum region is satisfactory. At high and low alcohol concentrations, discrepancies are observed.

b. Ternary heats of mixing data at 25°C

The ternary heats of mixing data obtained at 25°C for the two liquid systems ethanol-benzene-n-hexane and ethanol-benzene-n-heptane are the first set of heats of mixing data established for these systems, and represent one of the most comprehensive studies yet performed for heats of mixing of ternary system.

From a survey of previous work it is seen that not many ternary compositions were investigated for heats of mixing and that the experimental data were not arranged to permit any further studies but analytical representation, which was generally unsatisfactory, when the components were dissimilar, or when, at least one of the components was polar. In this study, the number of determinations far exceeds that of previous investigators. Furthermore the arrangement of the data, along constant x_i/x_j lines, provided a simple interpolation procedure and facilitated a study of the characteristics of the systems, for constant mole fraction ratios. The arrangement of the determinations in this study was accomplished by placing a pre-mixed binary of component 1 and 2, say, in one compartment of the calorimeter and the third component 3, in the other before the mixing process. The heat effect is then given by the quantity $\Delta H_{123} - (1-x_3)\ \Delta H_{12}$ cal./g.-mole.

i. ethanol (1) - benzene (2) -n-hexane (3)

The heats of mixing data at 25°C are presented in Table 9. The number of experimental determinations is 38, and the compositions experimentally investigated are shown in Figure 13, with lines of constant x_i/x_j ratios indicated by the dotted lines.

The computations, along lines of constant x_i/x_j, for the various quantities, $\Delta H_{123} - (1-x_3)\ \Delta H_{12}$, $\dfrac{\Delta H_{123} - (1-x_3)\ \Delta H_{12}}{x_3(1-x_3)}$, $(1-x_3)\ \Delta H_{12}$ and ΔH_{123} versus x_3 are given in Tables 11 a-f. Typical plots of the functions $\Delta H_{123} - (1-x_3)\ \Delta H_{12}$, $(1-x_3)\ \Delta H_{12}$ and ΔH_{123} versus x_3 are shown in Figure 28. It is seen that the curve of $\Delta H_{123} - (1-x_3)\ \Delta H_{12}$ versus x_3 is similar to the ΔH^M versus x_1 curve for binary heats of mixing. Values of $\Delta H_{123} - (1-x_3)\ \Delta H_{12}/x_3(1-x_3)$ versus x_3 were expected to have similar properties to the $\Delta H^M/x_1x_2$ versus x_1 curves for a binary system. Such curves for the various binary ratios presented in Figure 16 a and b, support the expectations. Isenthalpic lines in cal. /g.-mole are presented in Figure 18. The elliptical maximum region of the heat of mixing surface is indicated to be in a region richer in benzene but of approximately the same relative compositions of ethanol and n-hexane. The contour lines are closer for compositions progressively richer in benzene but farther apart and at about the same separation towards compositions richer in ethanol or n-hexane. Although the height of the maximum region occurs at a value lower than that for the system ethanol-benzene-n-heptane, the general shape of the contours is similar. The maximum region for the system ethanol-benzene-n-hexane rises to a value between 270 cal./g.-mole and 280 cal./g.-mole.

The experimental data for this system, with an illustration of the compositions investigated, and the isenthalpic lines have been reported (32).

ii. ethanol (1) - benzene (3) -n-heptane (2)

The heats of mixing data at 25°C for this system are presented in Table 10. There are 26 determinations and the compositions experimentally investigated are shown in Figure 15, with lines of constant x_i/x_j ratios indicated by the dotted lines. The computations along lines of constant x_i/x_j for the various quantities $\Delta H_{ijk} - (1-x_k)\,\Delta H_{ij}$, $\frac{\Delta H_{ijk} - (1-x_k)\Delta H_{ij}}{x_k(1-x_k)}$, $(1-x_k)\,\Delta H_{ij}$, and ΔH_{ijk} versus x_k are given in Tables 12 a-d. Typical plots of the functions are shown in Figure 28 for a value of $x_3/x_1 = 3.325$. It is seen that values of $\Delta H_{ijk} - (1-x_k)\,\Delta H_{ij}/x_k(1-x_k)$ versus x_k for this system also have similar properties to $\Delta H^M/x_1x_2$ versus x_1 curves for binary systems. Isenthalpic lines in cal./g.-mole are presented in the Figure 19. The contours are similar to those for the system ethanol-benzene-n-hexane but the maximum region occurs at a higher value, viz., between 290 cal./g.-mole and 300 cal./g.-mole.

c. Ternary specific heat data at 25°, 35° and 45°C

The ternary specific heat data for the liquid systems ethanol-benzene-n-hexane and ethanol-benzene-n-heptane are the first such data presented for these systems and have been used for calculation of the heats of mixing values at 35°C and 45°C. For these determinations, the calorimeters were calibrated with benzene. The experimental compositions investigated were the same for the three temperatures.

i. ethanol (1) - benzene (2) -n-hexane (3)

The specific heat data for this system is presented in Table 13. The number of experimental compositions is 19 and these were arranged along 3 lines of constant x_1/x_2 ratios. The results shown an increase in specific heats with increasing temperature at the compositions investigated.

ii. ethanol (1) - benzene (2) -n-heptane (3)

The specific heat data for this system is presented in Table 14. 16 experimental compositions have been investigated, arranged along 4 lines of constant x_1/x_2 ratios. An increase in specific heats with increase in temperature is also evident for the compositions investigated.

2. Interpolated and calculated data

a. Ternary heats of mixing values, interpolated at 25°C

The compositions experimentally investigated for the ternary specific heat determinations were different from those for the ternary heats of mixing determinations; also the constant binary ratio lines were not the same. This made it necessary to interpolate the experimental data, to obtain ternary heats of mixing values, at the compositions at which the specific heats were determined. The ternary interpolated heats of mixing values at 25°C were used with the specific heat data to calculate ternary heats of mixing values at 35°C and 45°C.

Because the ternary composition for the specific heat determinations were all arranged along lines of constant $x_{ethanol}/x_{benzene}$ ratios, only lines in this direction had to be considered, for interpolation. The procedure is outlined for the interpolation.

(1) Considering the vertex corresponding to 100% ethanol as 1, that for 100% benzene as 2 and that for 100% n-hexane as 3, values were read off from the ternary triangular diagram for the points of intersection x_i, x_j, x_k between existing lines of experimental data from vertex 1 or 2 to the opposite side, and the required composition line from vertex 3 to the opposite side.

(2) Using existing curves of $\frac{\Delta H_{ijk} - (1-x_k)\,\Delta H_{ij}}{x_k\,(1-x_k)}$ vs x_k and the appropriate ΔH_{ij} values, the value of ΔH_{123} for each of the points of intersection was determined.

(3) The value of ΔH_{12} for the particular line required was determined.

(4) Using the properties of $\frac{\Delta H_{ijk} - (1-x_k)\,\Delta H_{ij}}{x_k\,(1-x_k)}$ vs x_k curves, for each point of intersection along the line, the values of $\Delta H_{123} - (1-x_3)\,\Delta H_{12}/x_3\,(1-x_3)$ for the corresponding values of x_3 were calculated and plotted versus x_3

(5) From the curves of $\Delta H_{123} - (1-x_3)\,\Delta H_{12}$ vs x_3, the values of ΔH_{123} at the required compositions were determined.

The interpolated values are discussed below for each system.

i. ethanol-benzene-n-hexane

The interpolated values of heats of mixing at 25°C for the system ethanol-benzene-n-hexane are presented in column 3 of Table 15 of Appendix D. Heats of mixing values were calculated for the 19 experimental compositions at which the specific heat was determined.

ii. ethanol-benzene-n-heptane

The interpolated values of heats of mixing at 25°C for the system ethanol-benzene-n-heptane are presented in column 3 of Table 16 of Appendix D, for the 16 compositions at which the specific heats for this system were investigated.

b. Ternary heats of mixing values calculated at 35° and 45°C

The ternary heats of mixing at 35° and 45°C were calculated with the aid of the interpolated heats of mixing at 25°C, the experimental ternary specific heat data at 25°, 35° and 45°C, and the specific heat data as a function of temperature for the pure components, taken from the literature (30). With the aid of the methods of extrapolation proposed in this work, isenthalpic contours were prepared at 35° and 45°C for the two ternary systems. The contours at 25°, 35° and 45°C for each ternary system were further used in the investigation of the temperature effect on the heats of mixing of the ternary systems.

i. ethanol-benzene-n-hexane

The heats of mixing values, calculated at 45°C in Table 15, are greater than those at 35°C which in turn are greater than those at 25°C. The isenthalpic contours at 35° and 45°C, Figures 20 and 21, are prepared with the aid of the extrapolation techniques developed in this investigation. The general shape of the contours at 25°, 35°C, is similar, although a shift of the maximum region with temperature is apparent. As the temperature is increased, the maximum region moves to ternary compositions relatively more dilute in ethanol.

The temperature effect on the heats of mixing values for this system as indicated by Figure 22 is better represented by the non-linear equation proposed by Lu (38).

ii. ethanol-benzene-n-heptane

The general increase with temperature of the heats of mixing values for this system at 25°, 35° and 45° is apparent, in Table 16. The isenthalpic contours at 35° and 45°C, Figures 23 and 24, prepared also with the end of the extrapolation methods of this investigation, are similar to those at 25°C. A temperature shift of the maximum region towards compositions relatively more dilute in ethanol is observed, as the temperature is increased.

As for the ternary system discussed earlier, the temperature effect on the heats of mixing for the system ethanol-benzene-n-heptane as indicated by Figure 25, is better represented by the non-linear equation (38).

3. Extrapolation of binary heats of mixing from minimum data

a. Theoretical development of the proposed method

For a binary system at constant T and P, the excess partial molal enthalpy of mixing $\Delta\overline{H}^E$, of the two components are related by the Gibbs-Duhem equation

$$\frac{\partial \overline{H}_2^E}{\partial x_1} = -\left(\frac{x_1}{1-x_1}\right)\left(\frac{\partial \overline{H}_1^E}{\partial x_1}\right) \qquad (57)$$

It is seen from Equation 57 that at $X_1 = 0$ $(\frac{\partial \Delta\overline{H}_2^E}{\partial x_1}) = 0$, and similarly, at $x_1 = 1$, $(\frac{\partial \Delta\overline{H}_1^E}{\partial x_1}) = 0$. Furthermore, at $x_1 = 0$, $\Delta\overline{H}_2^E = 0$ and at $x_1 = 1$, $\Delta\overline{H}_1^E = 0$. Therefore, on a $\Delta\overline{H}^E$ vs x plot, both $\Delta\overline{H}^E$ curves approach their zero values with a horizontal tangency. This condition together with the modified Equation 57

$$(1 - x_1)(\frac{\partial \Delta\overline{H}_2^E}{\partial x_1}) \Delta x_1 = -x_1 (\frac{\partial \Delta\overline{H}_1^E}{\partial x_1}) \Delta x_1 \qquad (57a)$$

provide the basis for the extension method, and procedure previously proposed Deshpande and Lu (19) for vapor liquid equilibria may be followed. The extension method is limited to the situation where the excess partial molal enthalpy in question does not change sign over the complete concentration range. The partial molal enthalpies of mixing for the two components may be obtained using the procedure suggested by Van Ness and Mrazek (68) on a plot of $\Delta H^M/X_1X_2$ vs. X_1. The excess molal enthalpy of mixing, ΔH^E, is equal to the integral enthalpy of mixing per mole of solution, ΔH^M, as the enthalpy of mixing is zero for an ideal solution. Therefore the excess partial molal enthalpy of mixing $\Delta\overline{H}^E$ is equal to the partial molal enthalpy of mixing $\Delta\overline{H}^M$. Values for the partial molal enthalpies of mixing may be obtained, as outlined above, and may be extrapolated over the entire composition range, using the technique reported previously (19). The ΔH^M values may then be obtained from the extrapolated curves using the relationship

$$\Delta H^M = x_1 \Delta\overline{H}_1^M + (1 - x_1) \Delta\overline{H}_2^M \ldots\ldots \qquad (58)$$

Since the extrapolation is based on the Gibbs-Duhem equation, the method provides a set of thermodynamically consistent values.

It should be pointed out here that the proposed method is general because of the generality of the Gibbs-Duhem equation and so that the technique outlined above may be used for any excess thermodynamic property of mixing.

When the extensive molal property is enthalpy of mixing, as in our case, where the two excess partial molal properties at a given composition cannot be determined directly from a single measurement, a minimum of three experimental points is required for the extrapolation. If the property is Gibbs free energy of mixing, only two experimental points would be required. The method along with the heats of mixing data at 25°C for the binary systems has been reported (32).

b. Extrapolation of heats of mixing data at 25°C for the system ethanol and benzene.

The extension method is particularly useful for obtaining consistent data when, for a system at a given condition, several sets of data are available but do not agree with each other over the complete concentration range. The literature data for the heats of mixing of ethanol with benzene at 25°C, is a typical example of this situation. Since the agreement is good in the maximum region, it is useful to apply the extrapolation method to extend the data from this region to cover the complete concentration range. The extrapolation method of this investigation is illustrated in Figure 26 for the heats of mixing ethanol-benzene.

A small curve was drawn on a ΔH^M vs x_1 plot, from ethanol mole fraction $x_1 = 0.25$ to $x_1 = 0.46$ as shown in Figure 27, with emphasis given to the values obtained in this investigation and those reported by Goates et al (23). The partial molal enthalpies of mixing for the two components were obtained using the procedure suggested by Van Ness and Mrazek (68) on a $\Delta H^M/X_1X_2$ vs X_1 plot. The values obtained for the partial molal enthalpy of mixing were then plotted on a large size graph paper and extrapolated over the complete concentration range, using the technique reported previously. The extrapolated curves are shown in Figure 26. The ΔH^M values were then calculated using equation 58 and the extrapolated ΔH^M values are shown in Figure 27 by the dotted line, indicating a set of thermodynamically consistent values, which agree very well with the data obtained in this investigation for ethanol-benzene. Figure 28, shows similar results for ethanol-n-heptane at 25°C.

4. Extrapolation of ternary excess properties from minimum data

a. Theoretical development of the proposed method

For a ternary system at constant temperature and pressure,

$$\Delta G^E = x_1 \Delta \bar{G}_1^E + x_2 \Delta \bar{G}_2^E + x_3 \Delta \bar{G}_3^E \qquad (59)$$

which may be differentiated partially with respect to x_2 at constant x_1/x_3 provided that the experimental compositions investigated follow the constant ratio lines, Figure 29a. On including the Gibbs-Duhem equation into the consideration, the following is obtained

$$\left(\frac{\partial \Delta G^E}{\partial x_2}\right)_{x_1/x_3} = \frac{\Delta \bar{G}_2 - \Delta G^E}{1 - x_2} \qquad (60)$$

On a ΔG^E vs x_2 plot, Figure 29 b, $\Delta G^E = 0$ at $x_2 = 1$ and $\Delta G^E = a = \Delta G_{13}^E$ at $x_2 = 0$. The quantity ΔG_{13}^E is the excess thermodynamic property of the binary solution 1-3, and is a constant at a given x_1/x_3 ratio. If $\Delta G^E - (1 - x_2) \Delta G_{13}^E$ is plotted versus x_2, Figure 29c the shape of the curve reduces to that for a binary system. At $x_2 = x_2^1$, let $\Delta G^E - (1 - x_2) \Delta G_{13}^E = A$; if I_oI_1 is the tangent at A with intercepts

I_o and I_1 at $x_2 = 0$ and $x_2 = 1$ respectively, it may readily be shown from the geometry and Equation 60 that

$$I_1 = \Delta\bar{G}_2^E \qquad (61)$$

it is the excess partial molal property of component 2 in the ternary solution, and

$$I_o = \frac{\Delta G^E - x_2 \Delta\bar{G}^E}{(1-x_2)} - \Delta G_{13} = \frac{x_1 \Delta\bar{G}_1^E + x_3 \Delta\bar{G}_3^E}{1 - x_2} - \Delta G_{13} \qquad (62)$$

Furthermore, it may readily be shown that

$$x_2 \frac{\partial I_1}{\partial x_2} + (1 - x_2) \frac{\partial I_o}{\partial x_2} = 0 \qquad (63)$$

For the purpose of comparison, Equation 63 may be rearranged into the form of that for a binary system (Equation 57), namely

$$x_2 \frac{\partial \Delta\bar{G}_2^E}{\partial x_2} + (1-x_2) \frac{\partial \left[\frac{1}{1+k}(\Delta\bar{G}_1^E + k\,\Delta\bar{G}_3^E)\right]}{x_2} = 0 \qquad (64)$$

where $k = x_3/x_1$. The properties of Equation 63 are identical to those of Equation 60. On an I vs x_2 plot, $I_1 = 0$ at $x_2 = 1$ and $I_o = 0$ at $x_2 = 0$, and both I_o and I_1 approach their zero values with horizontal tangency, Figure 29d. Equation 63 may be rearranged to give

$$x_2 \frac{\partial I}{\partial x_2} \Delta x_2 = -(1 - x_2) \frac{\partial I_o}{\partial x_2} \Delta x_2 \qquad (65)$$

so that stepwise integrations may be carried out to extrapolate both curves over the complete concentration range using the procedure outlined for binary systems. From the extrapolated curves the ΔG^E values for the ternary system may then be calculated using the relationship

$$\Delta G^E = x_2 I_1 + (1 - x_2) + (1 - x_2) \Delta G_{13} \qquad (66)$$

If the excess thermodynamic property under consideration is the excess free energy of mixing, the ΔF^E values along a constant x_i/x_j line may be predicted from two experimental points. However in order to extrapolate the ΔF^E and the μ_i^E values over the complete ternary concentration range, a minimum of 4 isothermal experimental points is required. These 4 points would provide ΔF^E values of the ternary solutions along three solid lines. Extrapolation along any constant x_i/x_j line crossing the original three is then possible, if the three known ΔF^E values are used to provide intercepts for the above procedure to be followed. The pressure effect on μ_i^E is neglected and the μ_i^E values may be calculated from the extrapolated curve.

When the excess thermodynamic property under consideration is excess enthalpy of mixing, the same procedure may be followed with the only difference that a minimum of 7 experimental points is required as the primary information for obtaining the H values over the complete concentration range. Intercepts required in the extrapolation procedure may be obtained by the method of Van Ness and Mrazek (68).

b. Extrapolation of heats of mixing data at 25°C for the ternay system ethanol-n-heptane-benzene

The proposed extrapolation method is illustrated in Figure 29. The results of the application of the method to heats of mixing data for ethanol (1)-n-heptane (2)-benzene (3) are shown in Figure 30. The extrapolation is carried out along a constant x_1/x_3 line, and the primary information is indicated by the solid line in Figure 30. The dotted line indicates the values obtained by the extrapolation procedure. The agreement is very satisfactory.

The method, along with the ternary data for the system ethanol-benzene-n-heptane has been published (39).

The proposed method is naturally subject to the same limitation as that for the binary systems, namely, it is limited to the situation where the excess partial molal properties concerned do not change sign along the constant x_i/x_j lines. It may also be mentioned that the proposed method can be readily applied to quaternary systems, provided proper concentration surfaces and lines are taken.

5. Application of the generalised quasi-lattice theory of Barker to heats of mixing data

a. Testing of the parameters proposed in the literature and establishing energy values for various types of interactions by a new approach

The generalised quasi-lattice theory of Barker (3), (4) has been tested in this investigation, along with previously proposed quasi-lattice parameters for various molecules, based on the geometrical characteristics. From the results obtained it appears that the theory does have some merit in describing the heats of mixing of several systems, and quantitative significance, for some of the interaction energies, is becoming more apparent.

The parameters proposed in previous work (24), (25), (49) viz, number of contacts of the various types and the number of lattice sites r, Table 2, were based on the geometrical molecular structure of the component molecules. The types of interaction and the non-zero energy values are presented by Goates et al (24), (25) and Ott et al (49). In selecting quasi-lattice parameters that accorded the best fit of the experimental data, these authors used a criterion that did not distinguish between absolute deviations of relatively small magnitudes but of unacceptably high percentage. This situation would occur for the comparisons in the dilute regions. Notwithstanding the significance of the work of these authors (24), (25) and (49), their choice of criterion of "best fit" was unsatisfactory.

The criteria of "best fit" employed in this investigation for selecting parameters are a) the smallest average percentage absolute deviation together with b) the smallest maximum percentage deviation. These criteria give proper weight to the deviations for any composition.

Furthermore, in this investigation, a different approach was employed, for establishing parameters for the quasi-lattice theory, that provided agreement, with the experimental data. With this approach, a priori speculation for the values of the parameters, was avoided. The Barker quasi-lattice computations and the comparisons with experimental data were carried out on the IBM 1620 computer. The primary information to the computer consisted of a) the experimental data and corresponding compositions in mole fractions; b) quasi-lattice parameters, such as the number of lattice sites, and the number of contacts for each type, based on geometrical characteristics of the molecules; c) ranges for each of the non-zero interaction energies specified by an initial value, U_o, a final value, U_f and a value ΔU for incremental changes between U_o and U_f; and other quantities such as temperature, etc... Calculations of the heats of mixing were performed, with the above quasi-lattice parameters of the input data, for all combinations of incremental values of the set of interaction energies.

For every calculation, comparisons were made with the experimental data; the average percentage absolute deviation and the maximum percentage deviation were calculated. The sets of parameters were recorded, when a maximum average percentage deviation less than or equal to a given value was obtained. These sets were then further analysed to ascertain which set or sets produced the smallest "maximum average percentage absolute deviation" and the smallest "maximum percentage deviation".

Quasi-lattice parameters, not previously specified, but assigned in this investigation, given in Table 18, are based on the geometrical molecular structure for the various molecules. The interaction energies for the various types of contacts and the corresponding deviations obtained for the systems investigated, presented in Table 19, illustrate the values obtained with the new criteria. The energy values are expressed as $U \pm \Delta U/2$ cal./g.-mole.

b. Specification of a $-\underset{|}{\mathrm{CH}}-$ contact for branched aliphatic chains

It was mentioned in previous work (49), that the theory and the data available did not permit attempts at differentiation between normal and branched chain hydrocarbons. In this investigation, assignment of a type of contact, different from that of the $-\mathrm{CH_2}-$ and $-\mathrm{CH_3}$, for the $-\underset{|}{\mathrm{CH}}-$ group, of the branched molecules of iso-octane, 2,4-dimethypentane and iso-propanol, provided excellent agreement between the calculated and experimental data for the systems i-octane-n-octane, cyclohexane-i-octane, benzene-i-octane and iso-propanol-benzene. An illustration of the types of contact and lattice sites specified for the branched molecules is given in Figure 31. The results of the fitting are indicated in Table 19. These systems were fitted within an average percentage deviation of 3.2 and a maximum percentage deviation of 8.8.

c. Quasi-lattice parameters to represent heats of mixing data of benzene-n-alkane systems, by a new approach

Values of the parameters associated with the quasi-lattice theory were evaluated with the new approach, using the experimental heats of mixing data at 25°C for the systems benzene-n-pentane, benzene-n-hexane, benzene-n-heptane, benzene-n-octane, benzene-n-nonane, benzene-n-decane, benzene-n-tridecane and benzene-n-hexadecane. For heats of mixing of n-pentane, n-decane and n-tridecane with benzene, the experimental data of Jones et al (33), were used. The data used for benzene-n-hexane were determined in this investigation and reported (32). Data for the other system were available from the literature (40), (61).

Using the literature model for benzene, the values obtained for the parameters for the n-alkanes that resulted in the "best fit" of the experimental data, were different from those reported in the literature. A set of parameter values was selected which permitted the evaluation of heats of mixing values for binary benzene-n-alkane systems within an average absolute deviation of 3.6%, with the exception of the system benzene-n-hexdecane.

In previous application of the quasi-lattice theory to heats of mixing of benzene with n-hexane and with n-heptane (49), equations 37 and 38 were employed for the Q values and an average value of U_{12} = 70 cal./g.-mole was obtained. When these values were applied to other benzene-n-alkane systems, it was found, however, that the agreement between the calculated and experimental heats of mixing values was not as good as expected. As shown in Table 20 the maximum deviation may be as high as 20%, and the average absolute deviation, 12%. Using equations 37 and 38, the values of U_{12} that resulted in the "best fit" of the experimental data for the systems tested are listed in Table 21. The U_{12} values vary from 66 to 74. The "best fit" is defined as the one that gave the lowest average absolute deviation from the experimental points.

In this investigation, it was decided to use $Q_1 = 12$ and to determine the suitable values for Q_2 and U_{12} from the experimental data, such that the average absolute deviation would be about 3.5% and the maximum deviation, 6%. Computations were performed on an IBM 1620 computer. The integers obtained in this manner for Q_2 and U_{12} are listed in Table 22.

Although there were a few interaction energies outside of the range 60-63 cal./g.-mole that would meet the above criteria, this range was selected so that data for all systems would allow comparable agreement. With this range, the average absolute deviation and the maximum deviation obtained for the system benzene-n-hexadecane are somewhat higher than the above criteria as shown in Table 22. It seems that for this system, a higher U_{12} value would be more desirable. The range of Q_2 values corresponding to the four U_{12} values as listed in Table 22 are presented in Figures 32-35, in which the dotted lines represent the literature Q_2 values. In Figure 36, the calculated heats of mixing values for the eight binary systems are compared with the experimental values using

$$Q_1 = 12 \tag{67}$$

$$Q_2 = 17 + 2(n - 5)$$

and

$$U_{12} = 62 \text{ cal./g.-mole}$$

The dotted lines represent 5% deviations. With the exception of the system benzene-n-hexadecane, the average absolute deviations obtained are less than 3.6% and the maximum deviations, 6.3%, and the agreement is better than that obtained by using the literature parameter values. It should be mentioned that similar agreement may be obtained by means of different combinations of Q_1, Q_2 and U_{12} values. It is also obvious that different Q_2 and U_{12} ranges may be obtained in the above evaluations if one uses a Q_1 value other than 12. Despite these empirical aspects, it is also evident that the theory could be employed for evaluating thermodynamic properties of solutions. A better method for determining the number of contact points is, however, very much in demand.

XII. SUMMARY

A. Heats of Mixing

1. A calorimeter has been constructed and operated successfully in determination of heats of mixing of five binary and two ternary liquid systems.

2. Experimental data, at 25°C, are obtained for the binary systems ethanol-n-hexane, n-hexane-benzene, n-heptane-benzene, ethanol-n-heptane and ethanol-benzene, and the ternary systems of ethanol-benzene-n-hexane and ethanol-benzene-n-heptane.

3. The excellent agreement of the binary heats of mixing data, with literature results from other improved calorimeters, attest to the reliability of the calorimeters in this investigation. Where discrepancy existed previously, new data are established.

4. The heats of mixing at 25°C for the system ethanol-benzene-n-heptane are greater than those for ethanol-benzene-n-hexane.

5. The arrangement of the ternary data along constant x_i/x_j lines provided a means of simple extrapolation and facilitated a study of the characteristics of the systems for constant binary mole fraction ratios.

6. Plots of ternary heats of mixing in terms of the quantities $\Delta H_{ijk} - (1-x_k)\,\Delta H_{ij}$ vs x_k are similar to the curves of ΔH_{ij}^M vs x_i for binary systems.

7. Plots of ternary heats of mixing in terms of the quantities $\Delta H_{ijk} - (1-x_k)\,\Delta H_{ij} / (1-x_k)\,x_k$ are similar to the curves of $\Delta H_{ij}^M / x_i x_j$ vs x_i for binary systems.

8. Isenthalpic curves at 25°C, in terms of cal./g.-mole, have been prepared for the ternary systems ethanol-benzene-n-hexane and ethanol-benzene-n-heptane. The compositions are in mole fractions.

9. The maximum region of the heat of mixing surfaces for both systems is of elliptical shape and is indicated to be in region richer in benzene, but of approximately the same relative compositions, of ethanol and n-hexane, or ethanol and n-heptane.

10. The ternary heats of mixing surfaces, fall off steeply, for compositions progressively richer in benzene, but less steeply and at about the same rate, towards compositions richer in ethanol or n-hexane, for the former ternary system and towards compositions richer in ethanol or n-heptane for the latter.

11. The general shape of the contours is similar for the two ternary systems. However the maximum region of the heats of mixing surface for ethanol-benzene-n-hexane occurs at a value between 270 cal./g.-mole and 280 cal./g.-mole. The corresponding region for the system ethanol-benzene-n-heptane occurs at a higher value between 290 cal./g.-mole and 300 cal./g.-mole.

B. Interpolated and calculated ternary heats of mixing

1. Heats of mixing values at 25°C and at the mole fractions investigated for the ternary specific heats, have been determined by interpolation of the experimental heats of mixing data at 25°C for the systems ethanol-benzene-n-hexane and ethanol-benzene-n-heptane.

2. Ternary heats of mixing values at 35° and 45°C for the systems ethanol-benzene-n-hexane and ethanol-benzene-n-heptane have been calculated with

the aid of the interpolated ternary heats of mixing data at 25°C, the experimental specific heat data as determined at three temperatures, 25°, 35°, 45° and the specific heat data as a function of temperature for the pure components, taken from the literature.

3. Isenthalpic contours at 35°C and 45°C are prepared for the systems ethanol-benzene-n-hexane and ethanol-benzene-n-heptane, with the aid of the ternary heats of mixing calculated at 35°C and 45°C, and the extrapolation methods developed in this investigation.

4. The general shape of the contours for each system for the temperatures 25°, 35° and 45°C are similar, but as the temperature is increased, there is a definite shift of the peak of the heats of mixing surface towards a region relatively more dilute in the polar component, ethanol.

5. The temperature effect on the heats of mixing for the ternary systems is better represented by the non-linear equation proposed by Lu (38).

C. Extrapolation of binary heats of mixing from minimum data

1. A general method based on the Gibbs-Duhem equation is proposed for extrapolating binary heat of mixing. Because of the generality of the Gibbs-Duhem equation to other excess properties, the method may be applied to other thermodynamic excess functions.

2. The method requires a minimum of three experimental points, when the two excess partial molal properties at a given composition cannot be determined directly from a single measurement, such as enthalpy or volume.

3. When the two excess partial molal properties of mixing at a given composition can be obtained directly from a single measurement, two experimental points are required.

4. The extension method is particularly useful for obtaining consistent data when there is discrepancy between several sets of data, over a section of the concentration range.

5. The extrapolation method is illustrated for the heats of mixing at $25^{o}C$ for the ethanol-benzene system, and a set of thermodynamically consistent values is indicated, which agree very well with the data obtained in this investigation.

D. Extrapolation of ternary heats of mixing from minimum data

1. A method, based on the Gibbs-Duhem equation, is proposed for extrapolating ternary heats of mixing over the complete concentration range from a minimum of primary information.

2. Seven ternary experimental points are required for those thermodynamic properties whose three excess partial molal quantities at a given composition cannot be directly evaluated from a single measurement, such as excess enthalpy of mixing, assuming that the necessary binary data is available.

3. The extrapolation method is a generalisation of, and an extension to ternary system of, a method previously reported for binary vapor-liquid equilibrium data.

4. The extrapolation is carried out along constant binary ratio lines and is illustrated for the system ethanol (1) -n-heptane (2)-benzene (3) along a constant x_1/x_3 line. Excellent agreement is obtained between extrapolated and experimental data.

5. The limitation of this method is the same as for the binary system, namely, it is limited to the situation where the excess partial molal heats of mixing do not change sign along the constant x_i/x_j lines.

6. The method may also be applied to quaternary and higher systems provided that proper concentration surfaces and lines are taken.

7. Because of the generality of the Gibbs-Duhem equation with respect to other excess functions the extrapolation technique developed for ternary heats of mixing, may be applied to other thermodynamic excess properties.

8. In the case of a thermodynamic property, such as Gibbs free energy of mixing, where one single measurement determines the three excess partial molal quantities, only four ternary experimental points are required besides the binary data.

E. Application of the generalised quasi-lattice theory of Barker to heats of mixing data of various systems, by a new approach

1. The generalised quasi-lattice theory of Barker, have been applied to heats of mixing data for several systems, in a test of the theory itself and the previously proposed quasi-lattice parameters for various molecules, based on the geometrical characteristics.

2. The results support the contention that the theory appears to have some merit in describing the heats of mixing of several systems and some quantitative significance, for the interaction energies, is becoming more apparent.

3. A separate $-\underset{|}{\mathrm{C}}\mathrm{H}-$ type contact, has been specified for branched molecules and the results indicated that differentiation between branched and unbranched molecules was accomplished.

4. The new $-\underset{|}{\mathrm{C}}\mathrm{H}-$ type contact gave satisfactory agreement between the calculated and experimental heats of mixing for the systems, i-octane-n-octane, cyclohexane-i-octane, benzene-i-octane and isopropanol-benzene.

5. In testing the merits of the quasi-lattice theory for representing heats of mixing, the criteria of "best fit" employed in this investigation, for selecting parameters, unlike that of previous authors, gave proper weight to the deviations obtained at any composition.

6. The "best fit" criteria, employed for this study are a) the smallest <u>average percentage absolute deviation</u> and b) the smallest <u>maximum percentage deviation</u>.

7. To establish the values of the interaction energies in the quasi-lattice application in this study, a new approach was employed, which avoided a priori speculation of the energy parameters.

8. For this approach, the input data contained ranges for each of the non-zero interaction energies specified by an initial value, U_o, a final value U_f and a value ΔU for the incremental changes between U_o and U_f.

9. Calculations and comparisons were made on an IBM 1620 computer for all combinations of incremental values of interaction energies, to establish the set of parameters which produced the smallest "average percentage absolute deviation" together with the smallest, "maximum percentage deviation".

10. Quasi-lattice parameters, not previously specified, were assigned for the first time in this investigation for several molecules, based on their geometrical molecular characteristics.

F. Application of the quasi-lattice theory to heats of mixing data of benzene-n-alkanes systems by a new approach

1. Quasi-lattice parameters were evaluated from the experimental heats of mixing data at 25°C, for the eight systems, benzene-n-pentane, benzene-n-hexane, benzene-n-heptane, benzene-n-octane, benzene-n-nonane, benzene-n-decane, benzene-n-tridecane and benzene-n-hexadecane.

2. With the literature model for benzene, the values of the parameters for the n-alkanes that produced the "best fit" of the experimental data were found to be different from those reported previously.

3. A set of parameter values was selected, with which the heats of mixing values for the binary benzene-n-alkane systems were evaluated within an average absolute deviation of 3.6% and a maximum deviation of 6%, with the exception of the system benzene-n-hexadecane.

4. The parameters selected are expressed by the following: $Q_1 = 12$, $Q_2 = 17 + 2\ (n - 5)$ and $U_{12} = 62$ cal./g.-mole.

XIII. CONCLUSIONS

A. Heats of mixing

1. The calorimeter employed in this investigation provides heats of mixing of acceptable precision and may be used to obtain data on other binary and ternary systems.

2. The heats of mixing values at 25°C and 1 atm. of the ternary system ethanol and benzene with n-alkanes apparently increases with increasing chain length or molecular weight of the aliphatic molecule, and the isenthalpic curves prepared for the two ternary systems are similar in the shape of the contours.

3. A three constant equation of the form $a + bT + cT^2$ rather than one with two constants will better represent the temperature effect of the heats of mixing of the two ternary systems.

B. Extrapolation of binary heats of mixing from minimum data.

1. The method proposed for extrapolating heats of mixing of binary liquid systems establishes a thermodynamically consistent set of values and is applicable to other binary excess properties of mixing.

2. In addition, because only three experimental points are required for extrapolating a property such as enthalpy or volume of mixing and two points, for a property such as Gibbs free energy of mixing, the extension method provides a reliable and time saving means for obtaining consistent values of the property in question, over the complete concentration range.

C. Extrapolation of ternary heats of mixing from minimum data

1. The method proposed for extrapolating heats of mixing of ternary systems is applicable to other ternary excess thermodynamic properties of mixing, and the extrapolated results constitute a thermodynamically consistent set of values.

2. Since only seven ternary experimental points are required for extrapolating a property such as enthalpy or volume, of a ternary system, and four ternary points for a property such as Gibbs free energy, the extension method provides a reliable and time saving means for obtaining values of the ternary excess property in question, over the complete concentration range.

3. The extrapolation method is a generalisation of, and extension to ternary system of, a method previously reported for binary vapor-liquid equilibrium data, and hence, is subject to the same limitation, viz., it is applicable to the situation where the excess partial molal properties in question do not change sign along the constant x_i/x_j lines.

4. Provided that proper concentration surfaces and lines are taken, the method may be applied to quaternary and higher systems.

D. Testing of the generalised quasi-lattice theory of Barker

1. The quasi-lattice theory appears to have some merit in describing the heats of mixing of several systems; and some quantitative significance, for interaction energies, is becoming more apparent.

2. With a separate $-\underset{|}{\mathrm{C}}\mathrm{H}-$ type contact, specified for branched aliphatic molecules, differentiation between branched and normal molecules is possible. This is exemplified in the satisfactory agreement obtained,

between the calculated and experimental heats of mixing for the systems, i-octane-n-octane, cyclohexane-i-octane, benzene-i-octane and isopropyl alcohol-benzene.

3. In testing the merits of the quasi-lattice theory for representing heats of mixing data, the criteria of "best fit" employed in this investigation for selecting parameters, vig., a) the smallest average percentage absolute deviation and b) the smallest maximum percentage deviation, unlike that previously used in the literature, give proper weight to the deviations obtained at any composition.

4. In establishing the values of the interaction energies in the quasi-lattice application, the new approach, as was used in this investigation, avoids a priori speculation of the energy parameters, because the input data consisted of ranges for each of the non-zero interaction energies, specified by an initial value, U_o, a final value, U_f, and a value ΔU for the incremental changes between U_o and U_f.

5. Calculations and comparisons, carried out on the IBM 1620 computer, for all combinations of incremental values of the interaction energies, allowed testing of the entire ranges of the energy parameters. Closer approximation is provided by the reduction in ΔU values.

E. Application of the quasi-lattice theory to heats of mixing data of benzene-n-alkane systems.

1. Quasi-lattice parameters that produced the "best fit" of the experimental heats of mixing data at 25°C for the systems benzene-n-pentane, benzene-n-hexane, benzene-n-heptane, benzene-n-octane, benzene-n-nonane, benzene-n-decane, benzene-n-tridecane and benzene-n-hexadecane, were found to be different from those reported in the literature, assuming the literature model for benzene.

2. The quasi-lattice parameters, viz., $Q_1 = 12$, $Q_2 = 17 + 2\ (n-5)$ and $U_{12} = 62$ cal./g.-mole where n represents the number of carbons in a n-alkane molecule, allow evaluation of the heats of mixing at 25°C., within an average absolute deviation of 3.6% and a maximum deviation of 6% from experimental values, for the series of n-alkanes and benzene mentioned above.

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XIV. APPENDICES

A. Binary heats of mixing data

Table 3

Heats of mixing data for the system ethanol (1) -n-hexane (2) at 25°C.

x_1	ΔH^M cal./g.-mole
0.0395	71.9
0.0497	78.5
0.0726	78.3
0.0730	89.1
0.1509	116.7
0.1773	124.6
0.2707	129.5
0.3757	139.6
0.4043	138.6
0.5680	123.7
0.6318	116.6
0.7749	87.0
0.8399	69.3
0.9526	37.9
0.9483	27.3

Table 4

Heats of mixing data for the system n-hexane (2) benzene (1) at 25°C.

x_1	ΔH^M cal./g.-mole
0.1519	102.9
0.2136	129.8
0.3575	185.5
0.4678	209.7
0.5242	213.5
0.6427	207.5
0.6497	205.2
0.6957	196.1
0.7211	189.3
0.8075	155.3
0.9157	82.8

Table 5

Heats of mixing data for the system n-heptane (2) benzene (1) at 25°C.

x_1	ΔH^M cal./g.-mole
0.1806	116.2
0.3261	181.4
0.5119	222.7
0.7485	187.4
0.8248	150.3
0.8614	127.2
0.9532	51.4

Table 6

Heats of mixing data for the system ethanol (1) -n-heptane (2) at 25°C.

x_1	ΔH^M cal./g.-mole
0.0638	69.9
0.1255	110.5
0.2506	143.1
0.3407	148.5
0.5108	142.2
0.6368	131.4
0.7815	104.3
0.9412	39.9

Table 7

Heats of mixing data for the
system ethanol (1) - benzene (2) at 25°C.

x_1	ΔH^M cal./g.-mole
0.0250	75.2
0.0586	112.0
0.1615	190.9
0.2673	216.5
0.4668	197.0
0.5602	168.4
0.7018	117.0
0.7074	114.8
0.9058	37.8

Table 8

A summary of deviations of binary ΔH^M values in the literature from those of this investigation.

System	Ref.	Deviation in ΔH^M, %	
		Avg. abs. dev.	Max. dev.
Ethanol-n-hexane	(10)	1.1	1.8
Benzene-n-hexane	(52)	1.3	3.3
"	(61)(62)	1.1	2.6
Ethanol-benzene	(8)	2.5	9.0
"	(23)	2.0	9.9
"	(45)	3.2	10.3
"	(52)	7.2	11.3
"	(61)(62)	9.8	22.7

B. Ternary heats of mixing data

Table 9

Ternary heats of mixing data for the system ethanol (1) - benzene (2) -n-hexane (3) at 25°C.

x_1	x_2	ΔH^M cal./g.-mole
0.4449	0.4449	226.2
0.3814	0.3814	241.2
0.2630	0.2630	233.5
0.2620	0.2620	233.5
0.8850	0.8850	210.2
0.0994	0.0994	149.5
0.0450	0.0450	82.0
0.2557	0.1742	208.4
0.1822	0.4123	274.5
0.1750	0.4353	277.7
0.1073	0.6536	273.4
0.1195	0.6143	280.4
0.0991	0.6802	265.9
0.0296	0.9045	120.7
0.4614	0.0757	161.5
0.3841	0.2352	215.7
0.3129	0.3770	250.2
0.3009	0.4009	254.6
0.2122	0.5774	272.4
0.0601	0.8804	153.4
0.6709	0.1501	133.0
0.5237	0.3383	198.2
0.3846	0.5141	242.9
0.3444	0.5648	249.5
0.1165	0.8528	183.6
0.7172	0.2389	117.7
0.6513	0.2170	145.0
0.5722	0.1906	167.7
0.4203	0.1401	186.4
0.4017	0.1338	186.9
0.3914	0.1305	186.7
0.2586	0.0862	175.0
0.1312	0.0437	132.4
0.1011	0.4255	256.9
0.0964	0.4520	259.9
0.0581	0.6699	239.5
0.0543	0.6916	232.8
0.0154	0.9122	102.9

Table 10

Ternary heats of mixing data for the
system ethanol (1) - n-heptane (2) - benzene (3) at 25°C.

x_1	x_3	ΔH^M cal./g.-mole	x_1	x_3	ΔH^M cal./g.-mole
0.4933	0.4933	198.6	0.1714	0.0633	168.0
0.4801	0.4801	216.4	0.1988	0.6611	275.2
0.3909	0.3909	261.6	0.1731	0.5758	293.2
0.3793	0.3793	262.0	0.1403	0.4666	290.1
0.2803	0.2803	253.4	0.1237	0.4115	279.4
0.2033	0.2033	227.8	0.0897	0.2982	240.3
0.1885	0.1885	227.8	0.0543	0.1805	172.1
0.0986	0.0986	151.3	0.0413	0.1374	138.3
0.7057	0.2603	129.2	0.0560	0.4770	265.1
0.5841	0.2155	189.6	0.2374	0.3813	283.1
0.5691	0.2101	193.9	0.4672	0.2664	226.6
0.4261	0.1572	213.5	0.6382	0.1809	170.7
0.2639	0.0973	200.8	0.9032	0.0484	55.4

Table 11a

Heats of mixing data for the system ethanol (1) - benzene (2) -n-hexane (3) at 25°C.

$x_1 = .5$; $x_1/x_2 = 1$; $\Delta H_{12} = 187.5$ cal./g.-mole

	cal./g.-mole			
x_3'	$Q_{m_{12}}$	$\frac{Q_{m_{12}}}{x_3'(1-x_3')}$	$(1-x_3')\Delta H_{12}$	ΔH_{123}
.1102	59.3	605	166.9	226.2
.1160	61.7	602	165.8	227.5
.2372	98.2	543	143.0	241.2
.3310	116.1	524	125.4	241.5
.4740	134.9	541	98.6	233.5
.4760	135.2	542	98.3	233.5
.5260	139.6	560	88.9	228.5
.6230	139.5	594	70.7	210.2
.8012	112.2	702	37.3	149.5
.9100	65.1	795	16.9	82.0
.7000	133.1	634	56.3	189.4

Table 11b

Heats of mixing data for the system ethanol (1) - benzene (2) -n-hexane (3) at 25°C.

$x_1 = .75$; $x_1/x_2 = 3.0$; $\Delta H_{12} = 101.0$ cal./g.-mole

x_3'	$Q_{m_{12}}$	$\frac{Q_{m_{12}}}{x_3'(1-x_3')}$	$(1-x_3')\Delta H_{12}$	ΔH_{123}
	cal./g.-mole			
.0439	21.2	506	117.7	96.5
.1317	57.3	501	145.0	87.7
.1640	68.6	500	153.0	84.4
.2372	90.7	501	167.7	77.0
.4260	128.5	526	186.5	58.0
.4396	129.8	527	186.4	56.6
.4645	132.8	534	186.9	54.1
.4781	134.0	537	186.7	52.7
.6270	140.5	601	175.0	37.7
.6552	141.2	625	175.0	34.8
.8251	114.7	795	132.4	17.7
.7787	126.3	733	148.7	22.4

Table 11c

Heats of mixing data for the

system ethanol (1) - benzene (2) -n-hexane (3) at 25°C.

x_1 = .1760; x_1/x_3 = .2136; ΔH_{13} = 121.8 cal./g.-mole

	cal./g.-mole			
x_2'	$Q_{m_{13}}$	$\frac{Q_{m_{13}}}{x_2'(1-x_2')}$	$(1-x_2')\Delta H_{13}$	ΔH_{123}
.0550	33.6	64.6	115.1	148.7
.1500	85.9	674	103.5	189.4
.4255	186.9	765	70.0	256.9
.4520	193.2	780	66.7	259.9
.6699	199.3	901	40.2	239.5
.6916	195.2	915	37.6	232.8
.9122	92.0	1149	10.7	102.7

Table 11d

Heats of mixing data for the

system ethanol (1) - benzene (2) -n-hexane (3) at 25°C.

$x_1 = .3099$; $x_1/x_3 = .4485$; $\Delta H_{13} = 135.6$ cal./g.-mole

	cal./g.-mole			
x_2'	$Q_{m_{13}}$	$\frac{Q_{m_{13}}}{x_2'(1-x_2')}$	$(1-x_2')\Delta H_{13}$	ΔH_{123}
.0930	55.5	65.8	123.0	178.5
.1742	95.3	662	112.0	207.3
.2370	122.8	679	103.5	226.3
.4123	182.2	752	79.7	261.9
.4353	188.7	768	76.6	265.3
.6536	215.8	953	47.0	262.8
.6143	216.5	914	52.3	268.8
.6802	213.4	981	43.4	256.8
.9045	107.7	1247	13.0	120.7

Table 11e

Heats of mixing data for the

system ethanol (1) - benzene (2) -n-hexane (3) at 25°C.

x_1 = .5022; x_1/x_3 = 1.009; ΔH_{13} = 131.0 cal./g.-mole

	cal./g.-mole			
x_2'	$Q_{m_{13}}$	$\frac{Q_{m_{13}}}{x_2'(1-x_2')}$	$(1-x_2')\Delta H_{13}$	ΔH_{123}
.0757	40.4	578	121.1	161.5
.1440	74.4	602	112.1	186.5
.2352	115.5	642	100.2	215.7
.3345	154.3	693	87.2	241.5
.3770	168.6	718	81.6	250.2
.4009	176.1	733	78.5	254.6
.5774	216.8	888	55.4	272.2
.6220	222.0	944	49.5	271.5
.8804	137.7	1308	15.7	153.4

Table 11f

Heats of mixing data for the system ethanol (1) - benzene (2) -n-hexane (3) at 25°C.

$x_1 = .7915$; $x_1/x_3 = .3796$; $\Delta H_{13} = 84.0$ cal./g.-mole

	cal./g.-mole			
x_2	$Q_{m_{13}}$	$\frac{Q_{m_{13}}}{x_2'(1-x_2')}$	$(1-x_2)\ \Delta H_{13}$	ΔH_{123}
.1501	61.6	483	71.4	133.0
.2090	86.8	525	66.2	153.0
.3383	142.6	637	55.6	198.2
.4420	181.2	735	46.3	227.5
.5141	202.1	809	40.8	242.9
.5648	212.9	866	36.6	249.5
.8528	171.2	1364	12.4	183.6

Table 12a

Heats of mixing data for the system ethanol (1) - benzene (2) -n-heptane (3) at 25°C.

$x_1 = .5$; $x_1/x_2 = 1$; $\Delta H_{12} = 187.5$ cal./g.-mole

	cal./g.-mole			
x_3	$Q_{m_{12}}$	$\frac{Q_{m_{12}}}{x_3'(1-x_3')}$	$(1-x_3')\Delta H_{12}$	ΔH_{123}
.0135	13.6	1024	185.0	198.6
.0398	36.4	953	180.0	216.4
.2182	115.0	674	146.6	261.6
.2414	119.8	654	142.2	262.0
.4394	148.3	602	105.1	253.4
.5935	151.6	628	76.2	227.8
.6230	150.1	639	70.7	220.8
.8028	114.3	722	37.0	151.3

Table 12b

Heats of mixing data for the system ethanol (1) - benzene (2) -n-heptane (3) at 25°C.

$x_1 = .7305$; $x_1/x_2 = 2.7106$; $\Delta H_{12} = 106.3$ cal./g.-mole

	cal./g.-mole			
x_3'	$Q_{m_{12}}$	$\frac{Q_{m_{12}}}{x_3'(1-x_3')}$	$(1-x_3')\Delta H_{12}$	ΔH_{123}
.0340	26.5	807	102.7	129.2
.2004	104.6	653	85.0	189.6
.2203	111.0	646	82.9	193.9
.4167	151.5	623	62.0	213.5
.6388	162.4	704	38.4	200.8
.7653	143.1	797	24.9	168.0

Table 12c

Heats of mixing data for the system ethanol (1) - benzene (2) - n-heptane (3) at 25°C.

$x_1 = .2312$; $x_1/x_2 = .3007$; $\Delta H_{12} = 213.3$ cal./g.-mole

	cal./g.-mole			
x_3'	$Q_{m_{12}}$	$\frac{Q_{m_{12}}}{x_3'(1-x_3')}$	$(1-x_3')\Delta H_{12}$	ΔH_{123}
.1401	91.8	762	183.4	275.2
.2511	133.3	709	159.7	293.2
.3931	160.6	673	129.5	290.1
.4648	165.2	664	114.2	279.4
.6121	157.5	664	82.7	240.3
.7652	122.0	679	50.1	172.1
.8213	100.2	683	38.1	138.3

Table 12d

Heats of mixing data for the

system ethanol (1) - benzene (2) -n-heptane (3) at 25°C.

$x_2 = .5$; $x_2/x_3 = 1.$; $\Delta H_{23} = 222.1$ cal./g.-mole

		cal./g.-mole		
x_1'	$Q_{m_{23}}$	$\frac{Q_{m_{23}}}{x_1'(1-x_1')}$	$(1-x_1')\Delta H_{23}$	ΔH_{123}
.0560	55.9	1057	209.2	265.1
.2374	114.0	629	169.1	283.1
.4672	108.6	436	118.0	226.6
.6382	90.6	392	80.1	170.7
.9032	33.6	387	21.8	55.4

C. Specific heats of the ternary systems

Table 13

Ternary specific heat data

System: ethanol (1) - benzene (2) -n-hexane (3)

x_1	x_3	c_p, cal./(g)(°C)		
		25°C	35°C	45°C
0.0180	0.9062	0.6403	0.6822	0.7027
0.0429	0.7763	0.7032	0.7539	0.7985
0.0717	0.6256	0.7035	0.7589	0.8013
0.0911	0.5244	0.6864	0.7332	0.7795
0.1050	0.4516	0.6684	0.7115	0.7579
0.0509	0.9082	0.5468	0.6633	0.7621
0.0935	0.8313	0.5592	0.6701	0.8025
0.1676	0.6978	0.5783	0.6701	0.7964
0.2156	0.6112	0.5831	0.6562	0.7822
0.2566	0.5373	0.5836	0.6500	0.7633
0.2615	0.3320	0.6100	0.6195	0.6254
0.2986	0.2374	0.5915	0.6001	0.6087
0.3263	0.1665	0.5751	0.5861	0.5938
0.3540	0.0957	0.5537	0.5675	0.5761
0.1005	0.7446	0.6318	0.6362	0.6400
0.1020	0.7408	0.6332	0.6381	0.6413
0.1202	0.6948	0.6382	0.6416	0.6465
0.1388	0.6475	0.6395	0.6453	0.6497
0.1633	0.5852	0.6381	0.6452	0.6495

Table 14

Ternary specific heat data

System: ethanol (1) - benzene (2) -n-hexane (3)

x_1	x_3	c_p, cal./(g)(°C)		
		25°C	35°C	45°C
0.1008	0.8906	0.6462	0.6545	0.6628
0.1797	0.8049	0.6825	0.6935	0.7021
0.2352	0.7446	0.6975	0.7075	0.7186
0.3087	0.6648	0.7052	0.7182	0.7295
0.0131	0.9120	0.5923	0.6335	0.6821
0.0385	0.7408	0.6400	0.6935	0.7475
0.0453	0.6948	0.6420	0.6935	0.7445
0.0616	0.5852	0.6351	0.6871	0.7335
0.0759	0.8308	0.6501	0.6956	0.7421
0.1274	0.7159	0.6701	0.7185	0.7650
0.1507	0.6639	0.6725	0.7198	0.7683
0.2120	0.5273	0.6672	0.7081	0.7515
0.0745	0.9041	0.6253	0.6402	0.6566
0.2237	0.7122	0.7179	0.7586	0.7968
0.2947	0.6208	0.7229	0.7699	0.8087
0.3519	0.5473	0.7212	0.7685	0.8026

D. Ternary heats of mixing at 25°C (interpolated), 35° and 45°C (calculated).

Table 15

Ternary heats of mixing values for the system ethanol (1) - benzene (2) -n-heptane (3).

x_1	x_3	ΔH^M values, cal./g.-mole Interpolated 25°C	Cal'd 35°C	Cal'd 45°C
0.0180	0.9062	60.1	104.0	170.1
0.0429	0.7763	155.2	215.3	318.2
0.0717	0.6256	202.7	304.1	410.4
0.0911	0.5244	245.2	334.4	428.6
0.1050	0.4516	262.6	339.6	430.1
0.0509	0.9082	72.1	108.2	160.2
0.0935	0.8313	136.4	173.4	220.5
0.1676	0.6978	186.2	284.0	364.6
0.2156	0.6112	207.4	284.3	350.1
0.2566	0.5373	218.1	304.6	360.2
0.2615	0.3320	259.2	343.0	408.3
0.2986	0.2374	261.3	337.7	396.9
0.3263	0.1665	260.2	328.4	379.4
0.3540	0.0957	249.3	307.3	348.1
0.1005	0.7446	180.4	263.0	335.9
0.1020	0.7408	176.5	263.6	340.3
0.1202	0.6948	177.9	286.4	366.8
0.1388	0.6475	195.8	303.6	389.4
0.1632	0.5852	250.9	320.3	404.2

Table 16

Ternary heats of mixing values for the system ethanol (1) - benzene (2) -n-heptane (3).

x_1	x_3	ΔH^M values, cal./g.-mole Interpolated 25°C	Cal'd 35°C	Cal'd 45°C
0.1008	0.8906	92.7	165.0	292.4
0.1797	0.8049	133.2	263.8	385.5
0.2352	0.7446	152.5	275.1	415.9
0.3087	0.6648	171.5	290.3	431.8
0.0131	0.9120	73.8	152.1	240.2
0.0385	0.7408	176.9	315.9	494.4
0.0453	0.6948	197.1	339.1	517.6
0.0616	0.5852	238.1	379.2	553.3
0.1507	0.6639	209.9	361.7	529.2
0.2120	0.5273	249.5	392.1	550.3
0.1274	0.7159	191.6	342.2	461.2
0.0759	0.8308	139.5	271.7	434.7
0.2947	0.6208	208.8	346.2	483.2
0.0745	0.9041	115.5	185.3	310.4
0.2237	0.7122	199.3	332.0	463.5
0.3519	0.5473	207.4	344.6	482.0

E. Quasi-lattice parameters, interaction energies and corresponding deviations between literature and calculated values of heats of mixing for various binary systems.

Table 17

Types of interaction and non-zero energy values proposed in the literature for various systems.

System	Ref.	Interactions and energy values				
		O-H	I-S	H-S	O-S	S-S'
ethanol-cyclohexane	(23)	-3200	49	-	-	-
methanol-benzene	(23)	-3200	82	-410	-210	-
ethanol-benzene	(23)	-3200	81	-545	-300	-
propanol-benzene	(24)	-3200	87	-545	-300	-
butanol-benzene	(24)	-3200	82	-545	-300	-
amylalcohol-benzene	(24)	-3200	75	-545	-300	-
methanol-toluene	(24)	-3200	82	-430	-155	82
ethanol-toluene	(24)	-3200	75	-615	-215	75
propanol-toluene	(24)	-3200	92	-615	-215	92
butanol-toluene	(24)	-3200	89	-615	-215	89
amylalcohol-toluene	(24)	-3200	72	-615	-215	72
methanol-ethylbenzene	(24)	-3200	82	-450	-110	82
ethanol-ethylbenzene	(24)	-3200	75	-670	-185	75
propanol-ethylbenzene	(24)	-3200	95	-670	-185	95
butanol-ethylbenzene	(24)	-3200	89	-670	-185	89
amylalcohol-ethylbenzene	(24)	-3200	75	-670	-185	75
benzene-n-hexane	(49)	-	68	-	-	-
benzene-n-heptane	(49)	-	72	-	-	-
benzene-cyclohexane	(49)	-	71	-	-	-
		O-H	H-cl	I-I	S-cl	
methanol-carbon tetrachloride	(17)	-5000	25	-1400	-	-
ethanol-carbon tetrachloride	(17)	-5000	0	-1800	-	-
n-propanol-carbon tetrachloride	(17)	-5000	13	-1800	-	-
n-butanol-carbon tetrachloride	(17)	-5000	17	-1800	-	-
n-octanol-carbon tetrachloride	(17)	-5000	7	-1800	-	-
CCl_4 -benzene	(49)	-	-	-	9	-
CCl_4 -cy - C_6H_{12}	(49)	-	14	-	-	-
		I-I'				
n-hexane-n-heptane	(49)	1				

Table 18

Quasi-lattice parameters specified in this investigation based on geometrical characteristics ; type and number of contacts, number of lattice sites.

Molecule	Q_H	Q_O	Q_I	Q_S	Q_{ch}	r
n-C_8H_{18}	-	-	18	-	-	8
n-C_9H_{20}	-	-	20	-	-	9
n-$C_{10}H_{22}$	-	-	22	-	-	10
n-$C_{13}H_{28}$	-	-	28	-	-	13
n-$C_{16}H_{34}$	-	-	34	-	-	16
i-C_8H_{18}	-	-	17	-	1	7
CH_3-cy-C_6H_{12}	-	-	14	-	-	5
$CH_3CH(CH_3)CH_2CH(CH_3)CH_3$	-	-	14	-	2	7
$C_6H_5CH_3$	-	-	3	11	-	5
n-$C_6H_{13}OH$	1	2	13	-	-	7
n-$C_{10}H_{21}OH$	1	2	21	-	-	11
n-$C_8H_{17}OH$	1	2	17	-	-	9
i-C_3H_7OH	1	2	6	-	1	4

Table 19

Quasi-lattice energy values and corresponding deviations for all systems studied in this investigation*.

	Exp'tl data		Non-zero interaction Energy values			
System	Ref.	Temp. °C			Avg.abs. dev.%	Max. dev.%
			I-ch			
i-octane-n-octane	(40)	25	74 ± .5		1.3	2.4
			I_{cy}-I	I_{cy}-ch		
cyclohexane-i-octane	(40)	25	12.0±.5	28± .5	3.2	8.8
cyclohexane-n-heptane	(40)	25	17.4±.5	-	5.1	12.2
cyclohexane-n-hexane	(40)	25	15.0±.25	-	11.3	23.3
			I-S	S-I'		
benzene-cyclohexane	(45)	25	69 ± .5		1.4	4.4
toluene-n-heptane	(40)	25	70 ± 1.0	90± 1	6.3	14.5
toluene-n-hexadecane	(40)	25	68 ± .25	90±.25	2.7	5.5
m-xylene-n-heptane	(40)	25	64 ± .25	60±.25	4.4	9.3
			I-S	S-ch		
benzene-i-octane	(40)	25	60 ± .25	299±.5	.83	2.8
			H-O	I-I'		
ethanol-n-hexane	(10)	25	-3400±100	38±.5	1.2	2.1
n-propanol-n-hexane	(10)	25	-3120± 10	20±.5	1.1	2.1
n-butanol-n-hexane	(10)	25	-3400±100	17± 1	3.0	5.7
n-hexanol-n-hexane	(10)	25	-3600±100	21± 1	4.0	15.9
n-octanol-n-hexane	(10)	25	-3680± 10	15±.5	2.8	5.6

the following interactions were assigned zero values, H-I', O-I, O-I' and I-I'.

Table 19 (cont'd)

	Exp'tl data		Non-zero interaction Energy values			
System	Ref.	Temp. °C	H-O H-O' H'-O' H'-O	I-I'	Avg.abs. dev.%	Max. dev.%
methanol-n-butanol	(20)	25	-3200	32	3.6	9.9
methanol-n-hexanol	(20)	25	-3200	49	3.1	9.5
methanol-n-octanol	(20)	25	-3200	61	2.4	6.6
methanol-n-decanol	(20)	25	-3200	70	3.1	10.2

the following interactions were assigned zero values, H-I, H-H', H-I', O-I, O-O', O-I', I-H', I-O', H'-I' and O'-I'.

	Ref.	Temp. °C	I-S	S-ch	H-O	H-S	O-S	Avg. abs. dev. %	Max. dev. %
i-propanol-benzene	(45)	25	98±2	700±25	-3700±250	-200±100	-250±25	1.6	6.8

the following interactions were assigned zero values, I-ch, H-I, H-ch, O-I and O-ch.

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* number of contacts and lattice sites based on geometrical molecular characteristics.

F. Results of the application of the quasi-lattice theory to heats of mixing data of alkanes with benzene.

Table 20

Comparison of agreements between experimental ΔH^M values for benzene-n-alkane systems and those calculated by the quasi-lattice theory.

n-alkane	No. of observations	Q_2		U_{12}		Avg. abs.dev.%		Max. Dev.%	
		Lit.	This Work	Lit.	This Work	Lit.	This Work	Lit.	This Work
n-pentane	9	12	17	70	62	11.9	2.4	19.5	4.0
n-hexane	6	14	19	70	62	4.8	2.4	11.9	3.3
n-heptane	6	16	21	70	62	3.2	2.2	7.0	5.4
n-octane	9	18	23	70	62	6.4	3.6	16.3	6.3
n-nonane	7	20	25	70	62	3.8	0.8	9.7	1.4
n-decane	8	22	27	70	62	4.6	2.0	13.2	3.7
n-tridecane	9	28	33	70	62	6.1	2.7	14.6	5.7
n-hexadecane	6	34	39	70	62	0.5	4.9	1.0	7.7

Table 21

"Best fit" values of U_{12} using Equations 37 and 38 for Q values.

n-alkane	U_{12} cal./g.-mole	avg. abs. dev. %
n-pentane	74	10.3
n-hexane	71	4.8
n-heptane	69	3.6
n-octane	66	5.3
n-nonane	68	3.2
n-decane	69	4.7
n-tridecane	67	5.7
n-hexadecane	70	0.5

Table 22

Evaluation of U_{12} and Q_2 values for benzene-n-alkane systems using $Q_1 = 12$

			Deviation in ΔH^M values	
n-alkane	U_{12}	Q_2	Avg. abs. dev. %	Max. dev. %
n-pentane	60	18	1.9	3.4
		19	1.3	4.3
	61	17	3.5	5.4
		18	1.0	2.4
		19	2.8	6.0
	62	17	2.4	4.0
		18	1.6	4.1
	63	17	1.8	4.9
		18	3.0	5.7
n-hexane	60	18	2.8	5.5
		19	1.4	4.9
	61	18	2.8	5.5
		19	1.4	4.9
	62	18	1.4	4.0
		19	2.4	3.3
	63	17	1.8	5.8
		18	1.4	2.5
		19	3.3	4.4
n-heptane	60	20	2.9	4.2
		21	1.7	2.6
		22	2.9	6.0
	61	20	1.4	2.7
		21	1.8	3.8
	62	19	2.4	3.5
		20	.9	1.4
		21	2.2	5.4
	63	19	1.0	2.0
		20	1.7	3.0

Table 22 (continued)

n-alkane	U_{12}	Q_2	Deviation in ΔH^M values	
			Avg. abs. dev. %	Max. dev. %
n-octane	60	27	3.3	5.8
		28	2.5	3.5
		29	1.8	6.2
	61	21	3.1	5.3
		22	1.6	4.1
		23	2.0	4.6
	62	21	2.5	5.3
		22	1.8	5.8
		23	3.6	6.3
	63	21	2.3	6.9
		22	3.2	7.5
n-nonane	60	25	2.3	3.1
		26	1.7	1.2
		27	.8	2.1
		28	2.1	4.2
	61	24	2.4	4.0
		25	.5	1.6
		26	.8	1.6
		27	2.3	3.7
	62	23	3.0	5.1
		24	1.1	2.5
		25	.8	1.4
		26	2.3	3.2
	63	22	3.2	6.3
		23	1.7	3.6
		24	1.0	2.3
		25	2.3	3.0

Table 22 (continued)

n-alkane	U_{12}	Q_2	Deviation in ΔH^M values	
			Avg. abs. dev. %	Max. dev. %
n-decane	60	27	3.3	5.8
		28	2.5	3.5
		29	1.8	6.2
		30	2.0	9.5
	61	27	2.5	4.3
		28	1.7	4.7
		29	2.5	8.0
		30	3.4	11.2
	62	26	2.7	5.3
		27	2.0	3.7
		28	1.7	6.3
		29	3.4	9.7
	63	26	2.2	4.8
		27	1.8	5.3
		28	3.2	8.0
n-tridecane	60	34	3.2	7.4
		35	2.4	6.1
		36	2.6	4.9
		37	2.9	7.3
	61	33	3.2	7.2
		34	2.5	5.9
		35	2.6	4.7
		36	2.9	6.4
	62	33	2.7	5.7
		34	2.8	4.6
		35	3.2	5.4
	63	32	3.5	5.7
		33	3.0	5.8
		34	3.3	6.2

Table 22 (continued)

n-alkane	U_{12}	Q_2	Deviation in ΔH^M values Avg. abs. dev. %	Max. dev. %
n-hexadecane	60	42	5.3	9.4
		43	5.1	9.0
		44	5.2	8.6
		45	5.3	8.3
		46	5.5	9.4
	61	41	4.7	8.7
		42	4.6	7.9
		43	4.7	7.5
		44	4.8	7.4
		45	4.9	9.3
	62	39	4.9	7.7
		40	4.2	7.3
		41	4.0	6.9
		42	4.1	6.5
		43	4.2	7.2
		44	4.3	9.1
	63	39	3.7	6.3
		40	3.5	5.8
		41	3.6	5.4
		42	3.7	6.8
		43	3.8	8.8
		44	4.2	10.7

G. Sample calculations

1. Heat of mixing at 25° from experimental observation

a. Weighing and filling :

Weight of calorimeter empty	147.3981 gms.
Weight of calorimeter + benzene	156.2006 gms.
Weight of benzene	8.8025 gms.
Moles of benzene	.11269
Weight of calorimeter + benzene + ethanol	157.2009 gms.
Weight of ethanol	1.0003 gms.
Moles of ethanol	.02171
Total moles (benzene + ethanol)	.13440
Mole fraction of ethanol	.1615
Mole fraction of benzene	.8385
x_1x_2	.13541
Weight of calorimeter on completion of experiment	157.1996 gms.

b. Observations during experiment :

i. Mixing

$X_o = 965.1 \quad R_o = 496.9$

θ_m	R_m	θ_m	R_m	θ_m	R_m
0-9	496.9	12.61	513.4	19.40	516.5
10.71	498.4	12.82	515.4	20.29	516.1
10.91	500.4	13.11	517.4	21.28	515.6
11.14	501.4	13.45	518.4	23.54	514.7
11.60	503.4	15.05	515.4	25.21	514.0
11.75	505.4	15.80	518.1	26.34	513.5
11.91	507.4	16.60	517.6	27.54	513.0
12.14	509.4	17.50	517.2	28.70	512.1
12.31	511.4	17.22	516.9	31.17	511.5

ii. Calibration

V_m = .65449 volts ; θ = 156.5 secs.

θ_c(mins)	R_c(ohms)	θ_c(mins)	R_c(ohms)
0-6	505.3	19.52	499.8
7.2	505.2	19.90	498.8
9.75	505.1	20.3	497.8
12.64	505.0	23.28	498.0
15.86	504.9	26.0	498.3
17.21	504.8	28.59	498.6
18.05	503.8	32.50	499.0
18.40	502.8	35.95	499.3
18.78	501.8	40.86	499.7
19.11	500.8	45.10	500.0

C. Calculations and observations from R-θ plots :

i. Temperature change during mixing period

R_1 = 496.90 R_2 = 519.02

$$R^M = \frac{R_1 + R_2}{2} = \frac{496.90 + 519.02}{2} = \frac{1015.92}{2} = 507.96$$

S = 17.25 ohms/°C

$$\Delta R^M = R_2^* - R_1^* = 519.50 - 496.77 = 22.73 \text{ ohms}$$

$$\Delta T^M = \frac{\Delta R^M}{S} = \frac{22.73}{17.25} = 1.31768^\circ C = 1.3177$$

ii. Temperature change during calibration

$$R_1 = 504.82 \qquad R_2 = 497.94$$

$$R_{Cm} = \frac{R_1 + R_2}{2} = \frac{497.94 + 504.82}{2} = \frac{1002.76}{2} = 501.38 \text{ ohms}$$

$$S = 16.98 \text{ ohms/}^{o}C$$

$$\Delta R_c = R_1^* - R_2^* = 504.78 - 497.85 = 6.93 \text{ ohms}$$

$$\Delta T_c = \frac{\Delta R_c}{S} = \frac{6.93}{16.98} = 0.40812^{o}C$$

d. Energy dissipated during calibration

$$Q = I_H^2 R_H \theta' \text{ joules}$$

$$= \frac{I_H^2 R_H \theta'}{4.184} \text{ calories}$$

$$= (V_m.f)^2 \frac{R_H}{4.184} . \theta'$$

$$= V_m^2 \theta' \text{ x } (\frac{R_H}{4.184} .f^2) = V_m^2 \theta' .K_{cal.}$$

$$= .65449^2 \text{ x } 156.45 \text{ x } .11857$$

$$= .42835 \text{ x } 156.45 \text{ x } .11857$$

$$= 67.015 \text{ x } .11857$$

$$= 7.9459 \text{ calories}$$

$$H_C = \frac{Q_c}{\Delta T_c} = \frac{7.9459}{.040812} = 19.4695 \text{ cal./}^{o}C$$

$$Q^M = H_c \text{ x } \Delta T^M = 19.4695 \text{ x } 1.3177$$

$$= 25.653 \text{ calories}$$

$x_E = .1615$, $x_B = .8385$, $n_T = .13440$, $x_1x_2 = .13541$

$$\Delta H_M = \frac{Q_M}{n_T} = \frac{25.653}{.13440} = 190.87 \text{ cal./g.-mole}$$

$$\frac{\Delta H_M}{x_1x_2} = \frac{190.87}{0.13541} = 1409.57 = 1409.6$$

Heats of mixing of ethanol and benzene at a mole fraction of .1615 ethanol is 190.9 cal./g.-mole.

2. Heats of mixing at higher temperatures

System: ethanol (1) - benzene (2) -n-hexane (3)

Calculation of ΔH^M_{35} at $x_1 = .3540$, $x_2 = .5503$, $x_3 = .0957$.

By interpolation, ΔH^M_{25} at this mole fraction = 249.3

$x_1 M_1 = 16.31$ gms; $x_2M_2 = 42.98$ gms; $x_3M_3 = 8.25$ gms; $\sum x_iM_i = 67.54$ gms.

By graphical intergration of literature data of specific heats as a function of temperature

$$\int_{25}^{35} c_{p_{ethanol}}\,dt = 5.969 \text{ cal./gm} \quad ; \int_{25}^{35} c_{p_{benzene}}\,dt = 4.144 \text{ cal./gm} \quad ;$$

$$\int_{25}^{35} cp_{n\text{-hexane}}\,dt = 5.466 \text{ cal./gm}$$

From the experimental values of the ternary specific heats at 25°, 35° and 45° by graphical integration $\int_{25}^{35} c_{p_{123}}\,dt = 5.605$ cal./gm

Considering one mole of solution of the ternary mixture, the heat of mixing at 35°C at this mole fraction

$$\Delta H^M_{35} = - x_1M_1 \int_{25}^{35} c_{p_{ethanol}}\,dt - x_2M_2 \int_{25}^{35} c_{p_{benzene}}\,dt$$

$$- x_3M_3 \int_{25}^{35} c_{p_{n\text{-hexane}}}\,dt + \Delta H^M_{25} + \sum x_1M_1 \int_{25}^{35} c_{p_{123}}\,dt$$

$$= 307.3 \text{ cal./g.-mole}$$

H. Calibration of thermistors

Thermistors are thermally sensitive resistors whose resistance decreases exponentially with increased temperature,

$$\frac{R}{R^{o}} = e^{\beta(1/T - 1/T^{o})} \qquad (70)$$

where R is the thermistor resistance, in ohms, at temperature $T^{o}K$;

R^{o} is the thermistor resistance, in ohms, at temperature

T ^{o}K ; and

is the work function, in ^{o}K

Over a limited temperature range, β may be considered constant and may be used in Equation 70 for interpolation purposes.

An important distinction between thermistors and other resistance materials is the extreme sensitivity of thermistors to relative minute changes of temperature. The change of thermistor resistance with temperature is obtained by differentiating Equation 70 with respect to T,

$$\frac{dR}{dT} = \frac{\beta \times R}{(T)^2} \qquad (71)$$

The temperature coefficient of resistance (α) is the ratio of dR/dT to the resistance of the thermistor at a specified temperature,

$$\alpha = \frac{1}{R}\,\frac{dR}{dT} = \frac{\beta}{T^2} \qquad (72)$$

Table 23 shows the values of β determined from calibrations of thermistor resistance as a function of temperature.

Table 23

Thermistor		Work function
No.	R_{25}	β 25°K
1	1082.5	3496
2	505.5	3015
3	1070.9	3123
4	993.5	3452
5	989.4	3390
6	939.0	3416
7	959.1	3492
8	585.6	3609

I. List of items with manufacturers and, or suppliers.

I. List of items with manufacturers or suppliers

Item	Manufacturer or supplier
1. Chemicals	
a. Gases	Union Carbide Ltd., Linde Gases Division, Ottawa, Ont.
b. Benzene, Spectroquality Reagent, 99 mole %	Matheson, Coleman and Bell, Norwood (Cincinnati), Ohio.
c. Ethyl alcohol, 'Pure Absolute', 99 mole %	Consolidated Alcohols Ltd., P.O.Box 372, Terminal "A", Toronto, Ont.
d. n-hexane, n-heptane, Research Grade, 99.9 mole %.	Phillips Petroleum Co., Special Products Division, Bartlesville, Oklahoma.
2. Refractive Index Measurements	
a. Precision Refractometer, Cat. Nos. 33-45-02-01 Nos. 33-45-03.	Bausch and Lomb, Optical Company, Rochester 2, N.Y.
b. Haake Ultratherm Pump, Cat. No. 13-874-110.	Fisher Scientific Co., Ltd., 8505 Chemin Devonshire, Town of Mount Royal, Mtl 9.
c. Balance Gramatic, precision of ± 0.2 mg., Cat. No. 1-910-4 X 3.	
3. Mixing Cells	
a. O-rings	Precision Rubber Product Co., Ste-Thérèse de Blainville, Que.
b. Tin foil and teflon	Canus Equipment Ltd, 340 Gladstone Ave., Ottawa 2, Ont.
c. Thermistors, Veco, Cat. No. 32A12, 31A2, 32A75.	Rocke International Corp., 13 East 40th Street, New York 16, N.Y.
d. Manganin wire, size 26, about 1.1 ohms/foot.	Hawkesbury Wire Co., Ltd., Hawkesbury, Ont.

Item	Manufacturer or supplier
4. Jackets	
a. Hermetic seals, Cat. No. 406/8/C	Quality Hermetics Ltd., 45 Hollinger Rd., Toronto, Ont.
5. Thermostatic Bath	
a. Thermoregulator, Rotostat Differential, Cat. No. 15-180-15.	Fisher Scientific Co. Ltd., 8505 Chemin Devonshire, Town of Mount Royal, Que.
b. Transistor Relay, Cat. No. 13-991-80-V2.	"
c. Stirrers, heavy duty, variable speed, non-sparking. Cat. No.14-497V4	"
d. Heaters, Immersion, 750 watts, Cat. No.11-463-5V4.	"
e. Beckman thermometer	"
6. Calorimeter Vacuum System	
a. Vacuum pump Welsch, Mechanical & Diffusion type Cat. No.1-102V1.	"
b. Metal to glass seal	The O.H. Johns Glass Co., Ltd., 219 Broadview Avenue, Toronto 8, Ont.
c. Vacustat 2G, range 1 to 10^{-3} mm/Hg.	Edwards High Vacuum, Canada Ltd.
d. Vacuum leak tester	Fisher Scientific Co. Ltd. 8505 Chemin Devonshire, Town of Mount Royal, Que.
7. Thermistor Circuit	
a. Wheatstone bridge S.K. 4970.	Tinsley Instruments, Smith Falls, Ont.
b. 2-volt batteries, 'Exide Type', Cat. No.52819.	Keyes Supplies Co., Ltd., 80 Bayview Road, Ottawa, Ont.
c. K-3 Potentiometer	Leeds and Northrup Canada Ltd, 465 Victoria Avenue, St.Lambert, Que.

Item	Manufacturer or supplier
7. Thermistor Circuit (cont'd)	
d. Electronic D.C. Null Detector, Cat. No.9834-1.	Leeds and Northrup Canada Ltd., 465 Victoria Avenue, St.Lambert, Que.
e. Recorder, Speedomax H, response time: 1 sec., chart speed: 60 in./hr.	"
8. Heater Circuit	
a. Volt box, Cat. No.83417	Central Scientific Co. of Canada Ltd., Ottawa, Ont.
b. Galvanometer, type SR4, sensitivity: 200 mm/ a.	Tinsley Instruments Ltd., Smith Falls, Ont.
c. Standard cell, saturated type 1149.	"
d. Precision electric timer	Precision Scientific Co., Chicago, Ill.
e. Connectors	Cesco Electronics Ltd., 1300 Carling Avenue, Ottawa, Ont.
9. Coil circuit	
a. Synchronous Motor	General Electric, Ottawa, Ont.
b. Microswitch, 10A 125/250 VAC, Licon 11-204.	Licon, Chicago, Ill.