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THERMODYNAMICS OF BINARY POLAR LIQUID MIXTURES

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CONTENTS

Page

CHAPTER - I : INTRODUCTION

CHAPTER -II : EXPERIMENTAL

CHAPTER - III : RESULTS AND DISCUSSIONS

CHAPTER - I : INTRODUCTION

INTRODUCTION

A great deal of experimental work has been done on the thermodynamic properties of liquid mixtures of non-electrolytes. Many theories have been put forward to explain the properties of binary mixtures of non-polar liquids. However, as yet there is no generally satisfactory theory which can correlate the thermodynamic properties of mixtures of polar liquids from those of its pure components. In the absence of such a development, the present emphasis is to determine experimentally the thermodynamic excess properties of binary systems of polar liquids in the hope that the data thus collected will be useful in the formulation and testing of theories which may attempt to predict the binary mixture properties from those of the pure components. The increasing use of alcohols and amines in many industrial processes as well as the theoretical interest in the nature of associated solutions have greatly stimulated the need for extensive informations on thermodynamic properties of alcohols, amines and their mixtures.

In a different project in the laboratory we had to give information on the physical and thermodynamic properties of butyl alcohols and butyl amines and their mixtures. Since both the amines and alcohols have proton donar and proton acceptor group, it is expected that there will be a significant degree of hydrogen bonding both in their pure state as well as in their binary mixtures. It is now fairly well established that the energy of a hydrogen bond may be considered to be sum of four terms[1] viz. (a) electrostatic energy, (b) dispersive energy, (c) exchange repulsion and (d) delocalisation energy due to electron transfer from a proton acceptor to a proton donar. One cannot however easily estimate the contribution of each of these forces to the overall energy of the hydrogen bond either experimentally or by exact theoretical calculations. It will therefore be useful to investigate how the energy of the hydrogen bond varies with the chemical nature of the proton acceptor and/or a proton donar. We have, in this investigation, undertaken the measurement of the thermodynamic excess properties of mixtures of n-butyl amine with water, methanol, ethanol, 1-propanol and 1-butanol, and to find out as to how the energy of the hydrogen bond varies with the increase in the chainlength of the n-alcohols from C_1 to C_4 from the determination of the calorimetric heats of mixing and vapour liquid equilibria.

The difference between any thermodynamic function X of mixing (denoted by superscript m) for a real system and the corresponding value for an ideal solution at the same temperature, pressure and composition is called the thermodynamic excess function (denoted by superscript E).

$$X^E = X^m_{\substack{(\text{real solution})\\(\text{at } T,P,x\quad)}} - X^m_{\substack{(\text{ideal solution})\\(\text{at } T,P,x\quad)}} \quad \ldots. \quad (1)$$

Therefore for an ideal solution, all excess functions are zero. The excess functions may be positive or negative for a real solution. When the excess Gibb's free energy, G^E, of a solution is greater than zero, the solution is said to exhibit a positive deviation from ideality; whereas if it is less than zero, the deviation from ideality is said to be negative. The excess free energy of mixing for a binary mixture containing x and (1-x) mole fractions of two components is given by the relation :

$$\begin{aligned} G^E &= G^m_{(\text{real})} - G^m_{(\text{ideal})} \\ &= RT\left[x \ln \gamma_1 x + (1-x) \ln \gamma_2 (1-x)\right] \\ &\qquad - RT\left[x \ln x + (1-x) \ln (1-x)\right] \\ &= RT\left[x \ln \gamma_1 + (1-x) \ln \gamma_2\right] \quad \ldots. \quad (2) \end{aligned}$$

where γ_1 and γ_2 are the activity coefficients of the two components.

The relation between the excess functions are exactly the same as those between the total functions e.g.

$$G^E = H^E - TS^E \quad \ldots. \quad (3)$$

$$A^E = U^E - TS^E \quad \ldots. \quad (4)$$

$$H^E = U^E + PV^E \quad \ldots. \quad (5)$$

and the partial derivatives of the functions are analogous to those of total functions for example

$$\left[\frac{\partial G^E}{\partial P}\right]_{T,x} = V^E \qquad \ldots. \quad (6)$$

$$\left[\frac{\partial G^E}{\partial T}\right]_{P,x} = -S^E \qquad \ldots. \quad (7)$$

$$\left[\frac{\partial (G^E/T)}{\partial (1/T)}\right]_{P,x} = H^E \qquad \ldots. \quad (8)$$

$$\left[\frac{\partial H^E}{\partial T}\right]_{P,x} = C_p^E \qquad \ldots. \quad (9)$$

C_p^E is defined by the equation

$$C_p^E = C_p - x\,C_{p_1}^o - (1-x)\,C_{p_2}^o \qquad \ldots. \quad (10)$$

where C_p, $C_{p_1}^o$ and $C_{p_2}^o$ are the heat capacities of the solution, pure component 1 and pure component 2 respectively. In other words, C_p^E is the difference between the mean molar heat capacity of the solution and the sum of the heat capacities of the pure components to form one mole of solution before mixing.

The values of the excess functions e.g. S^E, H^E etc. can be readily derived in terms of the activity coefficient γ, and mole fraction x by an appropriate thermodynamic formulae, as for example,

$$H^E = \frac{\partial (G^E/T)}{\partial (1/T)} = -RT^2 \left[\frac{x \, \partial \ln \gamma_1}{\partial T} + (1-x) \frac{\partial \ln \gamma_2}{\partial T} \right] \qquad \ldots\ (11)$$

The molar heat content (enthalpy) of mixing ΔH^m of a binary system is defined by the equation

$$\Delta H^m_{(T,P,x)} = H_{(T,P,x)} - (1-x)\, H_{(T,P,0)} - x\, H_{(T,P,1)} \qquad \ldots\ (12)$$

where $H_{(T,P,x)}$ is the enthalpy at temperature T, and pressure P of one mole of the mixture containing mole fraction x of one of the components[2]. Hence,

$$H^E = \Delta H^m_{(real)} - \Delta H^m_{(ideal)} \qquad \ldots\ (13)$$

But, $\Delta H^m_{(ideal)} = 0$. Hence,

$$H^E = \Delta H^m \qquad \ldots\ (14)$$

Although, in principle, one can obtain the value of H^E or ΔH^m from the variation of the excess molar Gibb's free energy G^E as a function of temperature as given by the equation (8) or (11); but the data obtained by this procedure often lead to a value of H^E of uncertain accuracy[2,3]. The precise value of the heat of mixing can be obtained only by a direct calorimetric measurement. Moreover the heats of mixing can be obtained much more quickly from the direct calorimetric experiments than from the temperature coefficient of the Gibb's free energy of mixing. The activity coefficients of the components and hence the free energy of mixing can be obtained by various methods[4]. The determination of the isothermal vapour liquid equilibrium is the most commonly used method for the determination of the free energy of mixing. The combination of the calorimetric data on heats of mixing at several temperatures with the vapour pressure data is therefore used for the high precision determination of the excess properties viz. H^E, S^E, G^E and C_p^E.

The thermodynamic excess properties of alcohols with benzene and other aromatic hydrocarbons[5-17], with normal alkanes[18-24] and with carbon tetrachloride[25-27] have been studied by a number of workers. Although there is a general agreement that the alcohols undergo self association due to hydrogen bond formation in their pure state as well as in their solutions in non-polar solvents, and that the degree of self association decreases with the increase of the dilution of the alcohols; yet there is no agreement about the type and the energy of self association of alcohols. The mixing of the alcohols with non-polar hydrocarbon solvents is accompanied by an absorption of heat. This has been attributed to the breaking of alcohol-alcohol hydrogen bonds in the self-associated alcohol species as a result of the dilution of the alcohol. Van Ness and co-workers[22] have shown that the energy associated with the breaking of the alcohol-alcohol bonds decreases slightly with the increase of the chain-length in the n-alcohols. Brown and co-workers[19] have correlated the excess enthalpy of mixing, H^E with the ratio of the hydroxyl group to the total number of carbon atoms in the mixture and explained the relative changes in the thermodynamic properties of the alcohol + hydrocarbon systems with the changes in composition, solvent and temperature. Missen and co-workers[27] showed that H^E and G^E values of alcohol + CCl_4 systems are generally positive but in some cases (e.g. methanol + CCl_4 at low temperatures) they become negative in certain regions of concentration indicating a significant alcohol-CCl_4 interactions. The value of TS^E for most of the alcohol + CCl_4 systems are negative at low temperature. However, in very dilute alcohol region, they have been found to be mostly positive.

Thermodynamic excess properties of alcohol + water systems have been studied widely. Frank and Ives[29] have reviewed the structural properties of monohydric alcohol-water mixtures. It has been observed that at 25°C for the mixtures of methanol or ethanol with water

$$G^E > 0 > H^E > TS^E$$

and with the increase of temperature, H^E becomes positive in the alcohol-rich regions. The values of H^E for mixture of

1-propanol or 1-butanol with water are negative in low alcohol concentrations but becomes positive at higher alcohol mole fractions. This behaviour has been attributed to the fact that both water and alcohols are present in the highly structured state and that the water is more structured than the alcohols. Alexander and Hill[30] determined the heats of solution of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol and 2-methyl propan-2-ol with water at low concentrations between 5° and 35°C. In all these cases the results could be adequately represented by a quadratic dependence of the heats of solution on temperature. Arnett et al.[31] have reported the values of the excess heat capacities at 25°C of twentyone low molecular weight alcohols from pure liquid standard state to their high dilution in water, C_p^E for alcohol + water systems are positive and their magnitude is dependent on the size of the alcohol molecules. Branching, unsaturation or ring closure of the alcohol component in the alcohol + water mixtures reduce the magnitude of C_p^E. However, branching of the alcohols has a reverse effect if a gaseous standard state is used instead of a pure liquid state. Belousov and Ponner[32] determined the values of the excess enthalpies of mixing of water with iso-propanol, n-butanol, iso-butanol and sec-butanol. Ramaldo and Ruel[33] determined the heats of mixing of fourteen binary mixtures of alcohols e.g. $C_2 + (C_3, C_4, C_8, C_{10})$; $C_3 + (C_5, C_8, C_{10})$; $C_5 + (C_8, C_{10})$ at 20°, 25° and 30°C and investigated the applicability of the extension of the principle of congruence to the data. Polak[34] et al. have reported the values of G^E, H^E, TS^E and V^E for the four binary mixtures of methanol with n-butanol, isobutanol, sec.-butanol and tert-butanol and have attributed to the observed differences in the excess thermodynamic properties in terms of the differences in the hydrogen bonding and the shape of the component molecules. The same group of authors in their previous studies[35-38] on thermodynamic properties of binary mixtures of alcohols showed that the ddviation from an ideal behaviour increases with the increase in the differences of the molecular weights of the alcohols. Goodwin and Newsham[39] have reported the enthalpies of mixing of 1-propanol + 1-butanol binary and water + 1-propanol + 1-butanol ternary systems.

Thermodynamic excess properties of a number of mixtures of amines with non-polar solvents have been reported[40-48]. Primary and secondary amines have both a proton donar and proton acceptor group. They therefore also undergo self association through hydrogen bonding in a manner similar to that found for the alcohols. It is generally agreed that the degree of self association in amines is much smaller than that present in the corresponding alcohols. The heats of mixing of normal aliphatic amines with hydrocarbons have been observed to be positive and attributed to the breaking of amine-amine bonds on dilution with the hydrocarbons. The type and mode of association of the normal aliphatic amines in pure state or in its solution with hydrocarbons is still debatable, a ~~solu~~ situation similar to that found for the alcohols. Wolff and co-workers[41] in their analysis of the vapour pressure isotherms from -55° to +20°C for (C_1-C_3) n-primary aliphatic amines in non-polar aliphatic hydrocarbon solvents have assumed the existence of monomers, dimers, trimers and tetramers. They have shown that the association of the amines decreases with an increase in the chainlength of the amines and with an increase in the temperature. The longer chainlength hydrocarbons exert a smaller dilution effect than the hydrocarbon with a shorter chainlength. Deshpande and Pandya[47], have measured the heats of mixing of aniline with benzene, carbontetrachloride and chlorobenzene and have compared the experimental results with those calculated from the Prigogine's average potential theory. They found a good agreement between the observed and the calculated values. Vinogradov and Linnel[49] showed that pyridine and pyrrole react together to form 1:1 complex. Their calorimetric investigation showed that $\triangle H$ for the formation of the pyridine-pyrrole complex is -3.8 Kcal/mole. Matzen and Kuskova[50] reported the values of H^E at 15° for triethyl amine + water system, while Davidson and coworkers[51-53] have reported the values of the excess free energy of mixing of several alkyl substituted amines with water. Copp and Everett[54] determined the excess thermodynamic properties of mixing of triethyl amine and diethylamine with water and found the values of H^E and TS^E to be negative but G^E as positive. Hepler and Fenby[55] measured the heats of mixing of triethylamine + chloroform system at 25° and 35°C and interpreted the results in term of 1:1 complex formation. They proposed a model from which it was possible to obtain the equilibrium constant and the molar enthalpy of complex formation from the H^E values at one temperature.

Findlay and co-workers[56,57] have studied the thermodynamic properties of binary mixtures of (C_1-C_4) n-alcohols with triethyl amine and with pyridine. They observed that for triethyl amine + (C_1-C_4) n-alcohols

$$V^E < 0, \quad G^E > 0, \quad TS^E < H^E < 0.$$

Methanol + triethylamine mixture was found to have the highest value of H^E as compared to values of H^E for other (C_2-C_4) alcohol + triethylamine mixtures. They found that the thermodynamic excess properties of mixtures of pyridine with (C_2-C_4) n-alcohols did not follow any pattern[57]. As for example, the value of TS^E is positive for 1-propanol + pyridine and 1-butanol + pyridine systems but negative for ethanol + pyridine system in the entire concentration range. H^E is negative for ethanol + pyridine system, positive for 1-butanol + pyridine system for the entire concentration range, but for the 1-propanol + pyridine system, H^E is negative in alcohol-rich region and positive in the pyridine-rich region. The difference in the thermodynamic excess properties of these two systems have been attributed[57] to the weaker alcohol-amine bonds in the pyridine-alcohol complexes as compared to the triethylamine-alcohol complexes. It has been observed that the strength of the alcohol-pyridine bond decreases in the order :

$$\text{ethanol} > \text{1-propanol} > \text{1-butanol}$$

although this result is in conflict with the results of the same group of workers, obtained earlier by infrared spectroscopy[58]. Orszagh et al.[59] have reported the values of H^E, G^E and TS^E for the mixtures of pyridine with 1-butanol, 1-pentanol and 1-hexanol at different temperatures. Kamarov and coworkers[60-62] studied the vapour liquid equilibrium of binary and ternary mixtures of butylamines with 1-butanol and with water. They reported the formation of heteroazeotrope in the mixtures of butylamines with water. They also observed that $n\text{-}Bu_2NH + 1\text{-}BuOH$ system shows positive deviation while $n\text{-}BuNH_2 + 1\text{-}BuOH$ system shows negative deviation from ideality. Nakanishi and coworkers[63-65] have studied the thermodynamic excess properties of alcohols with various liquids including n-butylamine. They observed a tangential azeotrope in the methanol + n-butylamine system. In the study of binary mixture of methanol with n-butylamine, with diethylamine and with triethylamine, they observed the following decreasing order of the excess functions:

$$H^E < TS^E < G^E < 0$$

for binary mixtures of methanol with n-butylamine and diethylamine and

$$TS^E < H^E < 0 \;; \quad G^E > 0$$

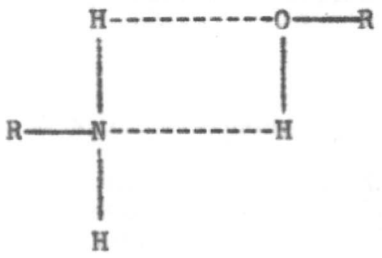
for binary mixtures of methanol with triethylamine. The magnitude of H^E for this system followed the order

$$Et_2NH > n\text{-}BuNH_2 > Et_3N.$$

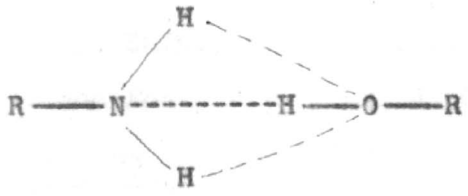
Murakami and Fujishiro[66] measured the heats of mixing of 1-butanol + n-butylamine system at 25°C and found the strength of the amine-alcohol hydrogen bond to be -8.03 Kcal/mole. Ratkovics and coworkers[67-69] recently have reported the thermodynamic excess properties of n-alcohols with n-butylamine, diethylamine and triethyl amine and have interpreted their results in term of complex formation between alcohol (A) and amine (B) of the type AB and A_jB_j. P. Huyskens, Th. Zeegers-Huyskens and coworkers[70-74] have investigated the nature of interaction between alcohols and amines by i.r., n.m.r. spectroscopic, vapour pressures and dipole moment studies. They determined calorimetrically[70] the enthalpy of hydrogen bond formation between ethanol, 1-butanol and sec-butanol with n-butylamine, diethylamine and triethylamine, in carbontetrachloride and cyclohexane media. They observed that the enthalpies of hydrogen bond formation between any amine (say n-butylamine) with the above three alcohols are equal within their experimental accuracy (-7.5 ± 0.3 Kcals/mole), but the enthalpy of hydrogen bond formation ($\triangle H_{12}$) between any alcohol (say n-butanol) with the three amines follows the order :

	$n\text{-}BuNH_2$ >	Et_2NH >	Et_3N
$\triangle H_{12}$(Kcal/mole)	(-7.48)	(-5.48)	(-4.86)

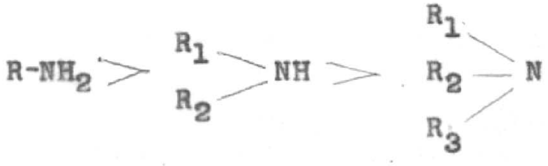
The same order is valid for mixtures of other alcohols with these three amines. P. Huyskens and Th. Zeegers-Huyskens[72] found that the n.m.r. spectra of the mixtures of n-butylamine and 1-butanol and their solution in benzene showed a common peak for both the $-NH_2$ group of the amine and the $-OH$ group of the alcohol. This was attributed to the fast exchange between protons arising as a result of the formation of the complex $R-NH_2-HO-R$, where $R = n$-C_4H_9. The proton shift of this complex was situated at about 2 p.p.m. from the H_2O proton peak. This was taken as an indication of a non-ammoniacal structure of the complex. They estimated the characteristic time of the exchange of the proton between the $-NH_2$ and $-OH$ groups to be smaller than 2×10^{-5} seconds, from the shape of the common peak. Conductivity data at high concentrations of the n-butylamine showed that the time of passage through the ionic RNH_3^+ form is greater than 2×10^{-4} second. They therefore concluded that the major part of proton exchange takes place directly through the formation of non-dissociated amine-alcohol complex RNH_2-HOR without passing through the ionic form, RNH_3^+. Such a behaviour suggested the existence of a non-linear hydrogen bond between the primary amines and alcohol. Two possibilities of the structure were envisaged; (a) a structure with two hydrogen bonds between O and N, with a possibility of a coordinated migration of the protons between two equilibrium positions



and (b) a structure with three hydrogen bonds where the three protons are situated approximately at the same distance from the N-O line;



one of the protons being closer to the oxygen while the two other being nearer to the nitrogen atom. The tertiary amines like Et_3N can only form a linear hydrogen bond with the alcohols. The observed order of the strength of the hydrogen bond between alcohols and amines viz.



$$R\text{-}NH_2 > R_1R_2NH > R_1R_2R_3N$$

was attributed to the formation of the non-linear hydrogen bonds.

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CHAPTER - II : EXPERIMENTAL

EXPERIMENTAL

1. CALORIMETRIC DETERMINATION OF HEATS OF MIXING OF LIQUIDS :

There has been a great deal of development since 1950 in the design of the calorimeters for the measurement of the heats of mixing of liquids. McGlashan[1] has reviewed the importance of various factors which should be taken into consideration in the design of such a calorimeter. It has been pointed out that, besides the requirement of the attainment of prompt thermal equilibrium, it is desirable to eliminate the vapour space in contact with the liquids and at the same time keep provision for the expansion or the contraction of the liquids on mixing. A number of such calorimeters have been described in literature e.g. Brown and coworkers[2,3], McGlashan and coworkers[4,5], Mrazek and Van Ness[6] and others[7-10].

In the present investigation, we have made use of a twin-type calorimeter, similar to that described by Adcock and McGlashan[4] with some minor modifications. In such a calorimeter it is not necessary to minimise the heat leakage but a provision is made to compensate for the heat of the reaction by supplying an equivalent quantity of heat. The direct measurement of temperature is avoided and instead a measurement is made of the quantity of heat supplied to compensate for the heat change produced as a result of the mixing of the liquids.

The calorimeter assembled in this investigation is shown schematically in Fig. 1(a) with the left-hand compartment of the calorimeter as assembled and the right-hand compartment of the calorimeter dismantled. The calorimeter consists of two identical double jacketed pyrex glass vessels A_1 and A_2 with B-55 male ground joints. The outer jackets are connected to side tubes at the end of which are provided B-14 male ground glass joints used for connection to the vacuum system for evacuation of the jackets. The vessel in which liquids are mixed inside the stainless steel bell is designated as the "reaction vessel" A_1, and the other similar vessel where compensation for the heat evolved is provided is called as the "reference vessel" A_2. The design of the stainless steel bell is shown schematically in Fig. 1(b). Both the vessels can be closed by a double cap D, fitted with B-55 female ground joints. The cap D has three openings at the top to accommodate (1) the upper parts of the stainless steel bells, (2) the heater leads E and (3) the leads I of the thermistor T used as the heat sensing elements.

The stainless steel bell B, which hold one of the liquids to be mixed over mercury surface and without vapour space has two stirrer blades and a sharp pointer G, for breaking the glass bulb L. A stainless steel clamp C holds the glass bulb L, formed by blowing one end from a 9 mm O.D. glass tube, in position. This bulb L has a capacity of about 1.5 to 2 ml

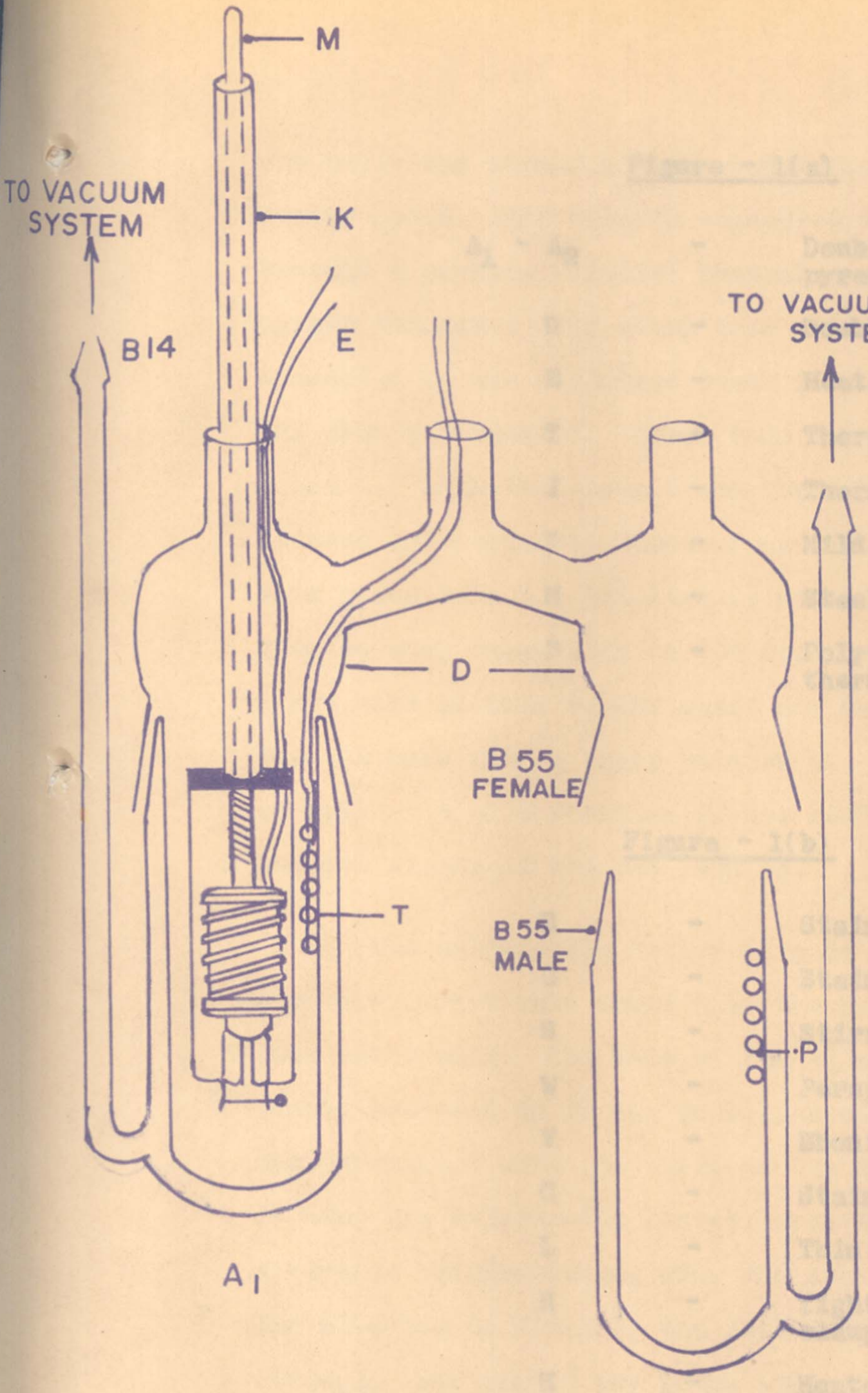


FIG. 1 (a)

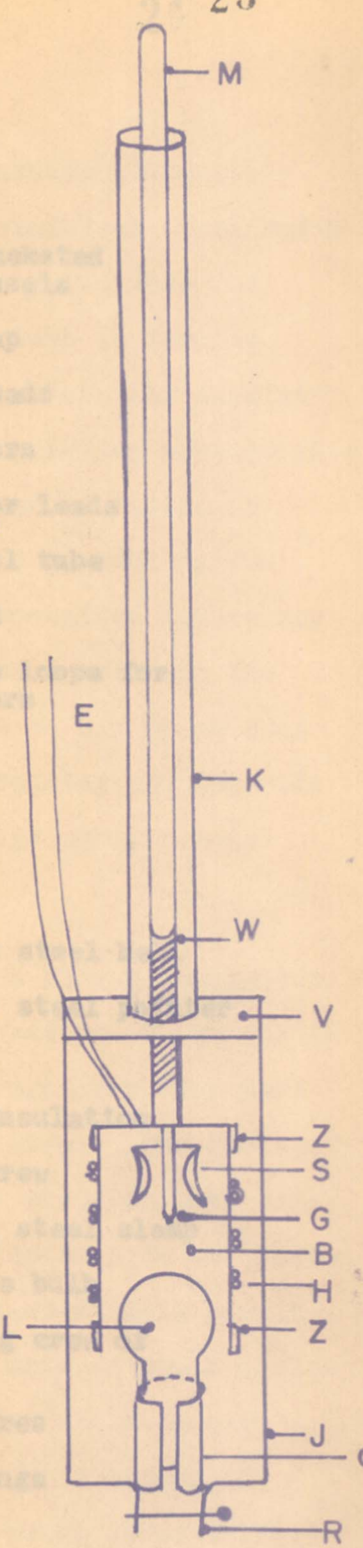


FIG. 1 (b)

THE CALORIMETER

Figure - 1(a)

A_1 - A_2 - Double jacketed pyrex vessels

D - Double cap

E - Heater leads

T - Thermistors

I - Thermistor leads

K - Mild steel tube

M - Steel rod

P - Polythene loops for thermistors

Figure - 1(b)

B - Stainless steel bell

G - Stainless steel pointer

S - Stirrer

W - Perspex insulation

V - Ebonite crew

C - Stainless steel clamp

L - Thin glass bulb

R - Tightening crew of clamp

H - Heater wires

Z - Teflon rings

and holds the second liquid over mercury surface without vapour space. The bell is connected to a stainless steel rod M through a perspex (lucite) thermal insulation W. This rod passes through a mild steel tube K and the tube in turn is connected to two stainless steel rods J via thermally insulating ebonite medium V. These rods hold the clamping arrangements C and R. Both the clamp C and the bell B can be raised or lowered independently whenever necessary for puncturing the thin glass bulb L. The liquids which are contained separately over mercury substrates in the stainless steel bell and the glass bulb without vapour space can be made to mix by puncturing the bulb with a sharp pointer G. The raising and lowering as well as a slow rotation of the bell brings about a homogeneous mixing of the two liquids.

The calorimeter heater is made from a 38 swg constantan wire non-inductively wound over the upper surface of the stainless steel bell. The ends of the 38 swg constantan wire were finely soldered to 28 swg enamelled copper wires. The whole of the constantan wire and parts of the copper wires at both ends, forming the calorimeter heater, were inserted in a 24 swg teflon sleevings before winding over the stainless steel bell surface. The sleeving is fixed to the bell with the help of small teflon rings Z. The use of any adhesive was avoided since in our earlier design of the calorimeter, following the method of Adcock and McGlashan[4], it was found that n-butyl amine reacted with practically all the adhesives available to us. The heater leads E were taken out of the glass vessel through the side tubes of the double cap D.

A matched pair of thermistors obtained from M/s. Tempo Semiconductors, Bombay, each having a normal resistance of 33 K ohms at room temperature was used as the temperature sensing elements. The resistance of the thermistors were matched to ± 1% by the manufacturers. Their resistance matching was further checked at different intervals of temperature within the range 25^{o} to 50^{o}C. The pair of thermistors in which the difference of resistances at any particular temperature within the above range did not exceed ± 1% was used. The thermistor leads were soldered to a two core shielded wire and the soldered portion were covered with an epoxy resin. The shielded wires were taken out through the middle opening of the double cap D. The thermistors were suitably mounted into the polythene loops P placed on the inner wall of the double jacketed vessels A_1 and A_2 in such a way that their positions are not disturbed when the stainless steel bell is rotated.

Constant Temperature Bath

The calorimeter is mounted in a copper bath filled with water and provided with an efficient electrically driven stirrer and a 60 watts electric bulb used for heating the bath whenever necessary. The copper bath in turn is immersed in a larger cubical thermostat of about 60 gallons capacity. The thermostat is thermally lagged on the five sides and covered with a wooden lid. The temperature of the thermostat can be controlled to $\pm 0.01^{\circ}C$ by means of a coiled type mercury-toluene thermoregulator coupled with a 200 watts heater and an electronic relay arrangement. Variation in the fixed temperature of the outer thermostat by $\pm 0.01^{\circ}C$ did not produce corresponding changes in the inner copper bath in which the calorimeter was dipped. In addition, any fluctuation of the temperature of the inner copper bath, expected to produce equivalent heat effects in the two identical halves of the calorimeter.

Electrical Circuit

The electric current through the calorimeter heater required for the compensation of the heat evolved during mixing of the liquids is provided from two 2-volts lead accumulators as shown in the electrical circuit diagram (Fig. 2). Here H_1 and H_2 are the calorimeter heaters for the reaction vessel and the reference vessel respectively. H_3 is the dummy heater kept outside the calorimeter system through which the current from the lead accumulator is passed for about an hour for the stabilisation of the current. In order to find the value of the current through the heater H_1 and H_2 required for heat compensation, the potential across the standard 10 ohms resistance R_1 in series with the heater is measured. R_2 is a resistance box which is used for adjusting the current through the heater circuit. Z is the mercury commutator for starting and stopping the electronic timer and the calorimeter heater at the

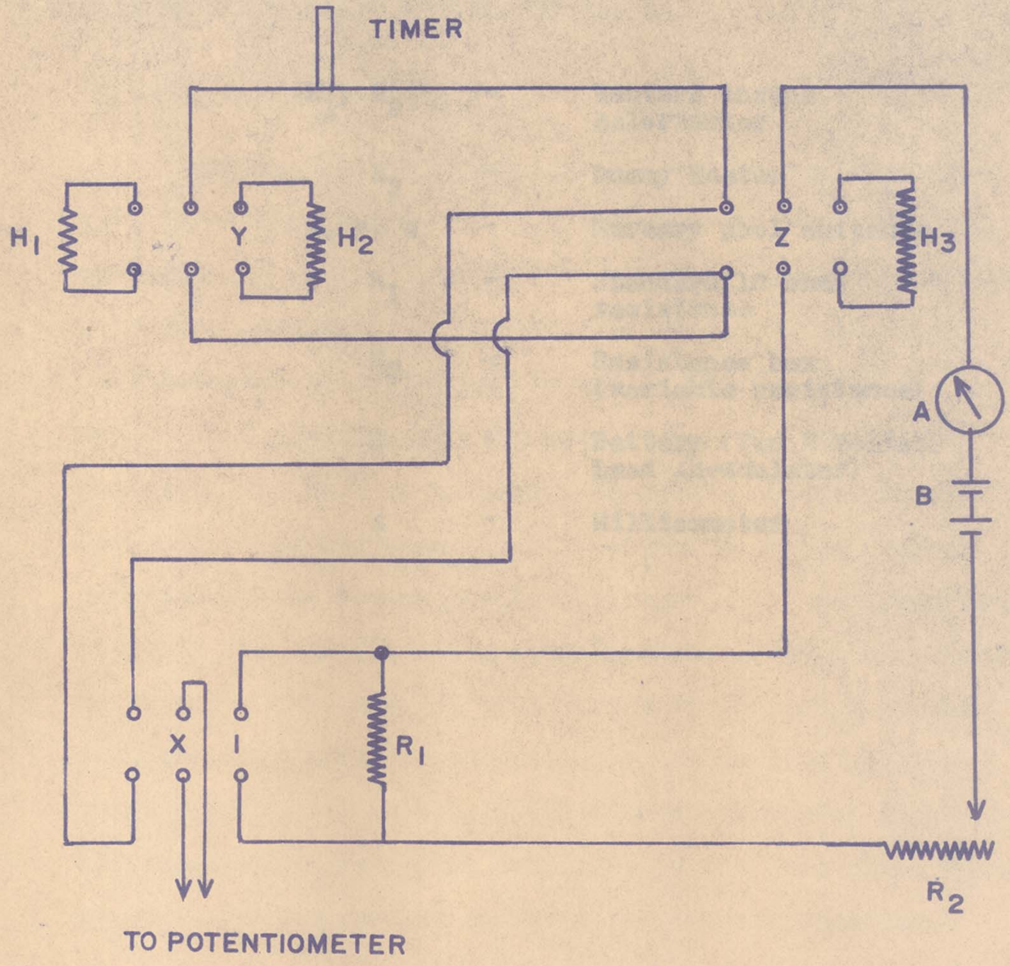


FIG. 2

ELECTRICAL CIRCUIT

Figure - 2

H_1, H_2 - Heaters inside calorimeter

H_3 - Dummy Heater

x, y, z - Mercury pool switches

R_1 - Standard 10 ohms resistance

R_2 - Resistance box (variable resistance)

B - Battery (Two 2 Volts Lead Accumulator)

A - Milliammeter

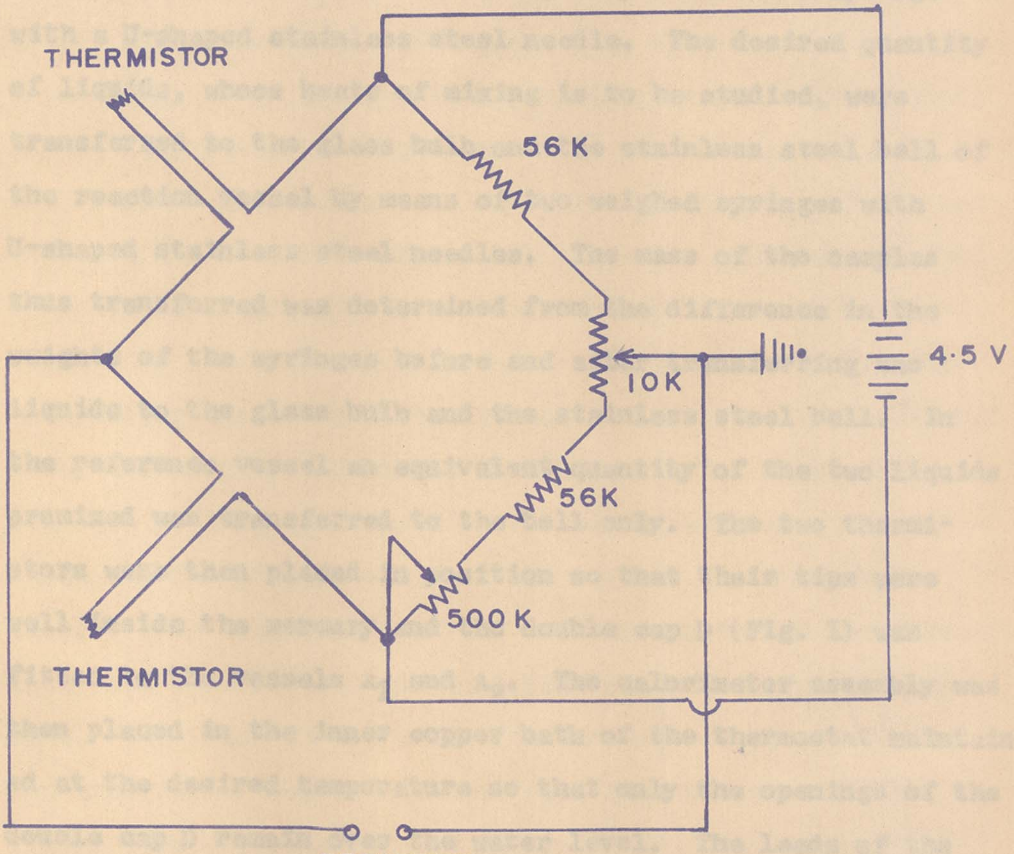
same time. A milliammeter A connected in series with the accumulators indicates the steady current passing through the heating coil. The resistances of the heaters were rechecked once in a week as a routine measure.

Thermistor Bridge Circuit

The two matched thermistors form the two arms of a D.C. Wheatstone bridge circuit shown in Fig. 3. The other two arms are made of two 56 KΩ resistances in series with a 10 KΩ wire wound potentiometer. A 500 Ω wire wound potentiometer is introduced in one of the two 56 K ohm arms for a finer adjustment. The output from the Wheatstone bridge is fed to a 25 millivolt Honeywell potentiometer recorder. The recorder point is adjusted at the desired position by the manupulation of a coarse 10 K variable resistance and finally for finer adjustment by a 500 ohm variable resistance. The thermal equilibrium is indicated by the straight line trace of the recorder pen parallel to the chart paper. Any change in resistance thereafter in one of the thermistors causes an imbalance in the Wheatstone bridge circuit and is recorded on the potentiometer recorder.

Method of Measurement of Heats of Mixing

Equal amount of pure mercury was filled in the double jacketed reaction and reference vessels of the calorimeter heater. The bells and the glass bulbs are placed in position



THERMISTOR BRIDGE CIRCUIT

FIG. 3.

such that when fitted properly the bell is completely dipped in mercury. The air trapped inside the glass bulb and the bell in both the vessels was removed by means of a syringe with a U-shaped stainless steel needle. The desired quantity of liquids, whose heats of mixing is to be studied, were transferred to the glass bulb and the stainless steel bell of the reaction vessel by means of two weighed syringes with U-shaped stainless steel needles. The mass of the samples thus transferred was determined from the difference in the weights of the syringes before and after transferring the liquids to the glass bulb and the stainless steel bell. In the reference vessel an equivalent quantity of the two liquids premixed was transferred to the bell only. The two thermistors were then placed in position so that their tips were well inside the mercury and the double cap D (Fig. 1) was fitted to the vessels A_1 and A_2. The calorimeter assembly was then placed in the inner copper bath of the thermostat maintained at the desired temperature so that only the openings of the double cap D remain over the water level. The leads of the thermistors were connected to the bridge circuit (Fig. 3) and the heaters H_1 and H_2 were connected to the electrical circuit (Fig. 2). The thermostat was then covered with the wooden lid and the whole assembly was kept as such for about five hours to ensure thermal equilibrium. The calorimeter was then connected through B-14 ground joint to the vacuum system and the space between the two walls of the vessels A_1 and A_2 was evacuated. The calorimeter was left as such for about one hour before the run was started. In the meantime the heating current was stabilised by running through the dummy heater. The recorder was then switched on. The thermal equilibrium of the entire assembly was indicated by the recorder pen trace parallel to the length of the chart paper. The liquids in the calorimeter were then mixed by puncturing the glass bulb L with the pointer G and by mildly rotating, raising and lowering the stainless steel bell (Fig. 1). The heat evolved as a result of mixing of the two liquids was indicated by the deflection of the recorder points. The current through the calorimeter heater and the electronic timer were then switched on by the mercury commutator Z. The potential drop across a standard 10 ohms resistance was measured simultaneously to determine the precise value of the current 'i' through the heater. The commutator 'Z' was switched on to the dummy heater side when the recorder pen came back near the original base line. The time 't' for which the current was passed through the calorimeter heater was then read from the electronic timer. The stirring in both the vessels was continued until the recorder pen traced a straight line parallel to the length of the recorder chart. The recorder was then turned off. In most cases the final parallel line traced by the recorder pointer did not coincide with the original base line of the recorder and differed by a small separation Δ_1 (see Fig. 4) which required a correction to get the exact value of the heat compensation.

The entire system was then allowed to cool down to the bath temperature. The recorder was turned on. In order to determine the correction factor for the inexact compensation Δ_1, the heater current through the calorimeter was then turned on for a time nearly equal to that required for an earlier compensation experiment (Fig. 4). The recorder was kept on until~~l~~ it again traced a line parallel to the recorder chart paper. The separation Δ_2, between the initial and final traces of the recorder during this calibration experiment was then related to the quantity of heat supplied to the calorimeter heater obtained from its resistance r, current i' and time t'. The heat of mixing ΔH^m per mole of the mixture corrected for inexact compensation was then calculated by the equation :

$$\Delta H^m = \frac{i^2 rt}{(n_1 + n_2)} \pm \frac{\Delta_1 \, i'^2 r.t'}{\Delta_2 \, (n_1 + n_2)} \text{ joules/mole.} \qquad (1)$$

where the current is expressed in amperes, the resistance in ohms and the time in seconds, n_1 and n_2 are the number of moles of the two components. The correction term in the expression (1) is positive in case of under compensation (as in Fig. 4a) and negative in case of over compensation (see Fig. 4b).

In the procedure described above, if the time required for the heat compensation is large, (say > 100 sec.) there is a possibility of some leakage of heat in spite of the evacuation

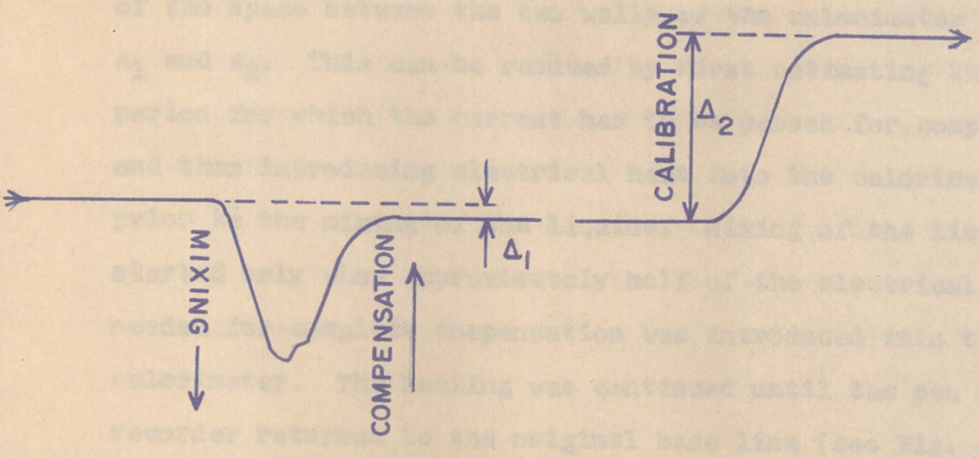


FIG. 4 (a)

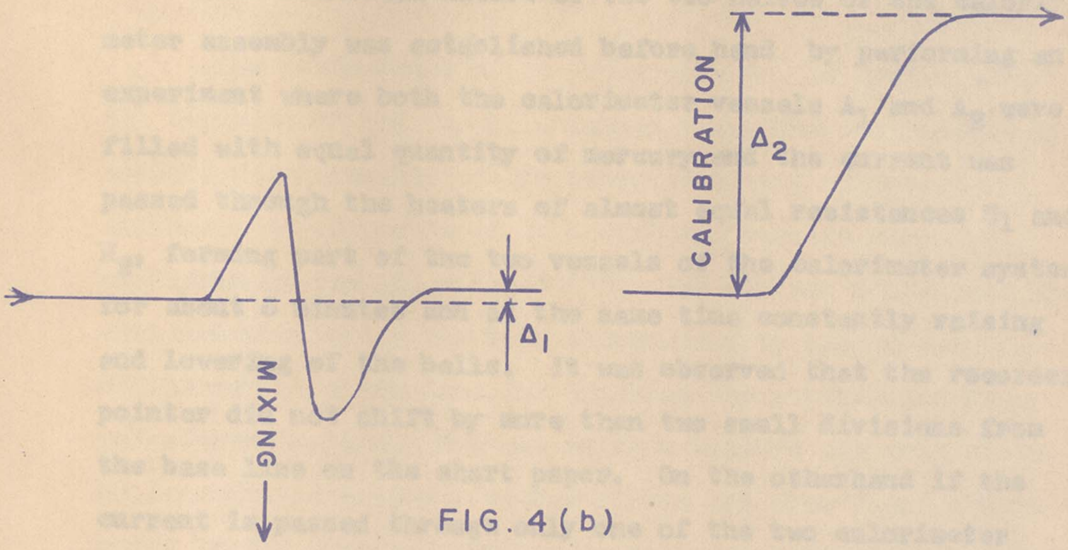


FIG. 4 (b)

RECORDER TRACE FOR HEAT COMPENSATION

of the space between the two walls of the calorimeter vessels A_1 and A_2. This can be reduced by first estimating the period for which the current has to be passed for compensation and then introducing electrical heat into the calorimeter prior to the mixing of the liquids. Mixing of the liquids was started only when approximately half of the electrical energy needed for complete compensation was introduced into the calorimeter. The heating was continued until the pen of the recorder returned to the original base line (see Fig. 4b). Correction for the unexact heat compensation was applied in the usual way by performing a calibration experiment as described above.

The identical nature of the two halves of the calorimeter assembly was established before hand by performing an experiment where both the calorimeter vessels A_1 and A_2 were filled with equal quantity of mercury and the current was passed through the heaters of almost equal resistances H_1 and H_2, forming part of the two vessels of the calorimeter system for about 5 minutes and at the same time constantly raising and lowering of the bells. It was observed that the recorder pointer did not shift by more than two small divisions from the base line on the chart paper. On the otherhand if the current is passed through only one of the two calorimeter heaters for the same period, the recorder pen shifts almost to its full length i.e. 200 small divisions indicating that the mismatching of the two halves is less than one per cent. If the position of the two matched thermistors are interchanged and a similar simultaneous heating of the two calorimeter heaters H_1 and H_2 is undertaken the direction of the small shift in the position of the recorder pen is reversed indicating that the small difference observed in the apparent heat capacities of the two arms of the twin calorimeter system can be mainly attributed to the mismatching of the two thermistors (± 1%).

By performing a series of experiments where only thin glass bulbs are broken in both the vessels one after the other in the absence of the liquids to be mixed, it has been observed that the heat effect due to breaking of the bulb is not detectable in the recorder.

The performance of the twin calorimeter system and the accuracy of the result obtained therefrom was checked by comparing the results of the heats of mixing of methyl alcohol + water system at 25°C with the results already available in the literature[11,12]. The mixture of Benzene and carbontetrachloride has been recommended by Larkin and McGlashan[5] as a standard for checking the performance of a calorimeter system. But use of this mixture was criticised by Bennett and Benson[9], Watts, Clarke and Glew[13] and others owing to the slow reaction of carbontetrachloride with mercury. Recently Ahmed[14] has recommended n-hexane + cyclohexane system as a standard for checking the performance of a heat of mixing calorimeter system.

Our choice of an exothermic reaction of mixing of CH_3OH and H_2O as a standard rather than an endothermic reaction as chosen by others[15,16] was dictated by the knowledge that in an endothermic reaction the heat compensation is carried out in the mixing vessel itself and hence any difference in the heat capacities of the calorimeter vessels or the matching of the thermistor pair resistances in the calorimeter system, if present, will not be detected in the results of the heats of mixing. It is therefore appropriate to use an exothermic reaction as a standard for calibration of the calorimeter if it is to be used for determining the exothermic heats of mixing. In addition both methyl alcohol and water can be easily obtained in the pure state. They have widely different densities so that they are as difficult to mix as any pair for which the heat of mixing is to be determined. They have in addition widely different vapour pressures and the magnitude of the heat of mixing is comparable with those of the systems to be studied by us.

The results obtained on the heats of mixing of the $CH_3OH + H_2O$ system at 25°C summèrised in Table-1 are in good agreement with those obtained by Lama and Benzamin[11] and Benzamin and Benson[12] as shown in Fig. 5.

Table 1 : **Heats of mixing of CH_3OH-H_2O system at 25°C**

x_1 = Mole fraction of CH_3OH in the mixture

$\triangle H^m$ is expressed in Calories per mole of mixture.

Present work		Literature value (Ref. 11)		Literature value (Ref. 12)	
x_1	$\triangle H^m$	x_1	$\triangle H^m$	x_1	$\triangle H^m$
0.0376	- 57.31	0.0287	- 46.0	0.02916	- 47.77
0.0535	- 79.40	0.0492	- 76.8	0.08310	-119.4
0.1002	-136.20	0.0495	- 77.3	0.1029	-139.5
0.1284	-159.45	0.0674	- 98.1	0.1091	-145.2
0.1677	-178.20	0.0973	-130.6	0.1725	-187.3
0.1765	-186.30	0.1253	-155.3	0.2045	-198.4
0.2277	-206.81	0.1468	-169.4	0.2949	-212.3
0.3130	-209.60	0.1903	-189.6	0.3233	-211.7
0.3438	-207.63	0.2041	-193.7	0.3864	-207.6
0.4809	-193.49	0.2463	-202.9	0.4786	-195.7
0.7220	-142.25	0.3562	-203.7	0.5978	-172.5
0.7685	-125.99	0.3955	-201.9	0.6785	-152.3
0.8725	- 72.80	0.4689	-191.5	0.7684	-123.3
		0.5566	-175.4	0.8614	- 83.9
		0.6598	-151.6	0.9528	- 32.65
		0.7823	-114.7		
		0.7990	-106.8		
		0.9348	- 40.8		

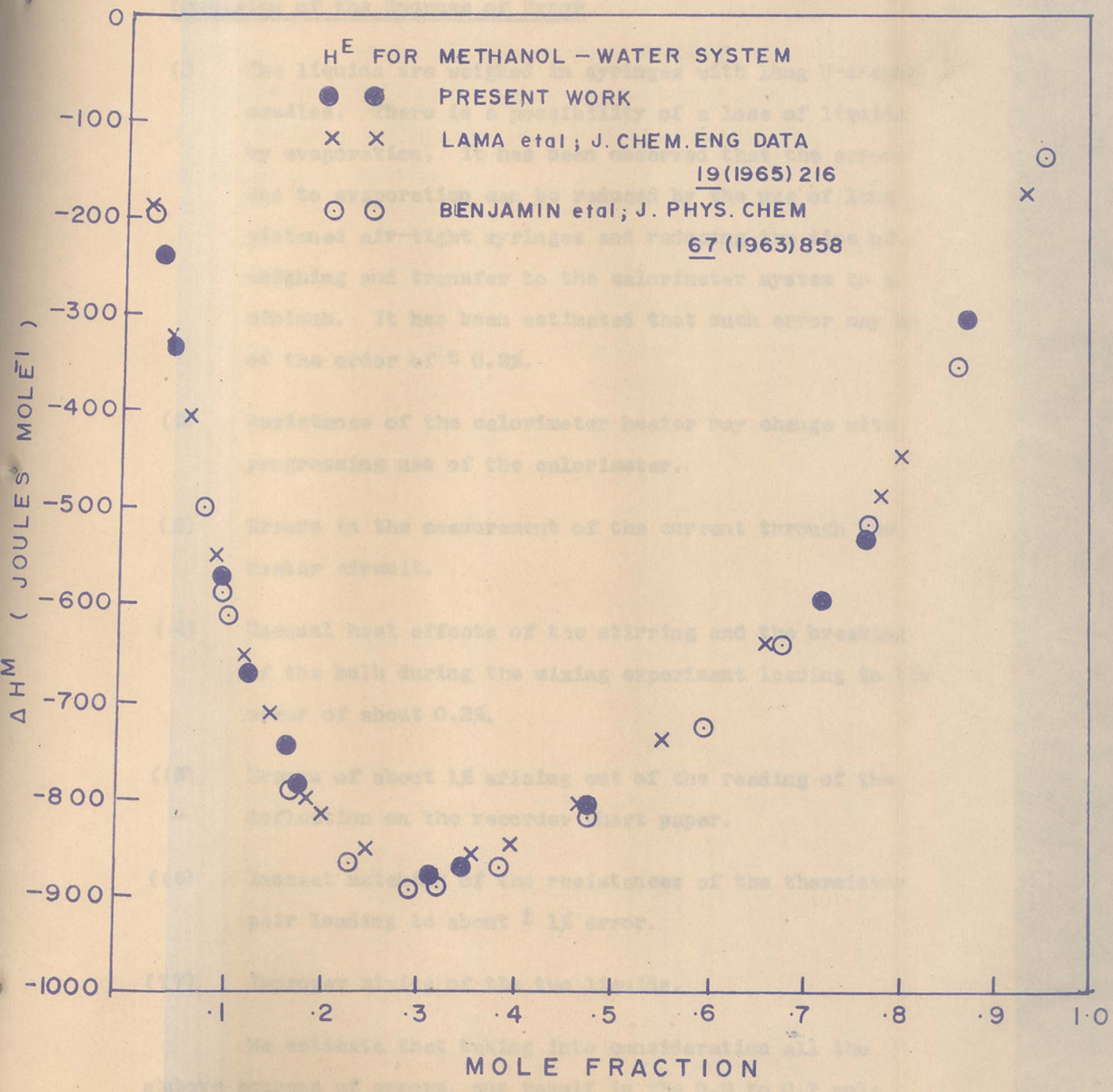

H^E FOR METHANOL – WATER SYSTEM
● ● PRESENT WORK
× × LAMA etal ; J. CHEM. ENG DATA 19 (1965) 216
⊙ ⊙ BENJAMIN etal ; J. PHYS. CHEM 67 (1963) 858
ΔHM (JOULES MOLE⁻¹)
0
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
·1
·2
·3
·4
·5
·6
·7
·8
·9
1·0
MOLE FRACTION

FIG. 5

Discussion of the Sources of Error

(1) The liquids are weighed in syringes with long U-shaped needles. There is a possibility of a loss of liquids by evaporation. It has been observed that the errors due to evaporation can be reduced by the use of long pistoned air-tight syringes and reducing the time of weighing and transfer to the calorimeter system to a minimum. It has been estimated that such error may be of the order of ± 0.2%.

(2) Resistance of the calorimeter heater may change with progressing use of the calorimeter.

(3) Errors in the measurement of the current through the heater circuit.

(4) Unequal heat effects of the stirring and the breaking of the bulb during the mixing experiment leading to the error of about 0.2%.

(5) Errors of about 1% arising out of the reading of the deflection on the recorder chart paper.

(6) Inexact matching of the resistances of the thermistor pair leading to about ± 1% error.

(7) Improper mixing of the two liquids.

We estimate that taking into consideration all the above sources of errors, our result in the 0.3 to 0.7 mole fraction range may have uncertainties upto a maximum of ± 2%.

The result in the extreme range of concentration may have larger uncertainties of ± 3%, since we did not have with us a suitable microvolt amplifier to measure very small changes in the imbalance of the wheatstone bridge arising out of very small heat changes.

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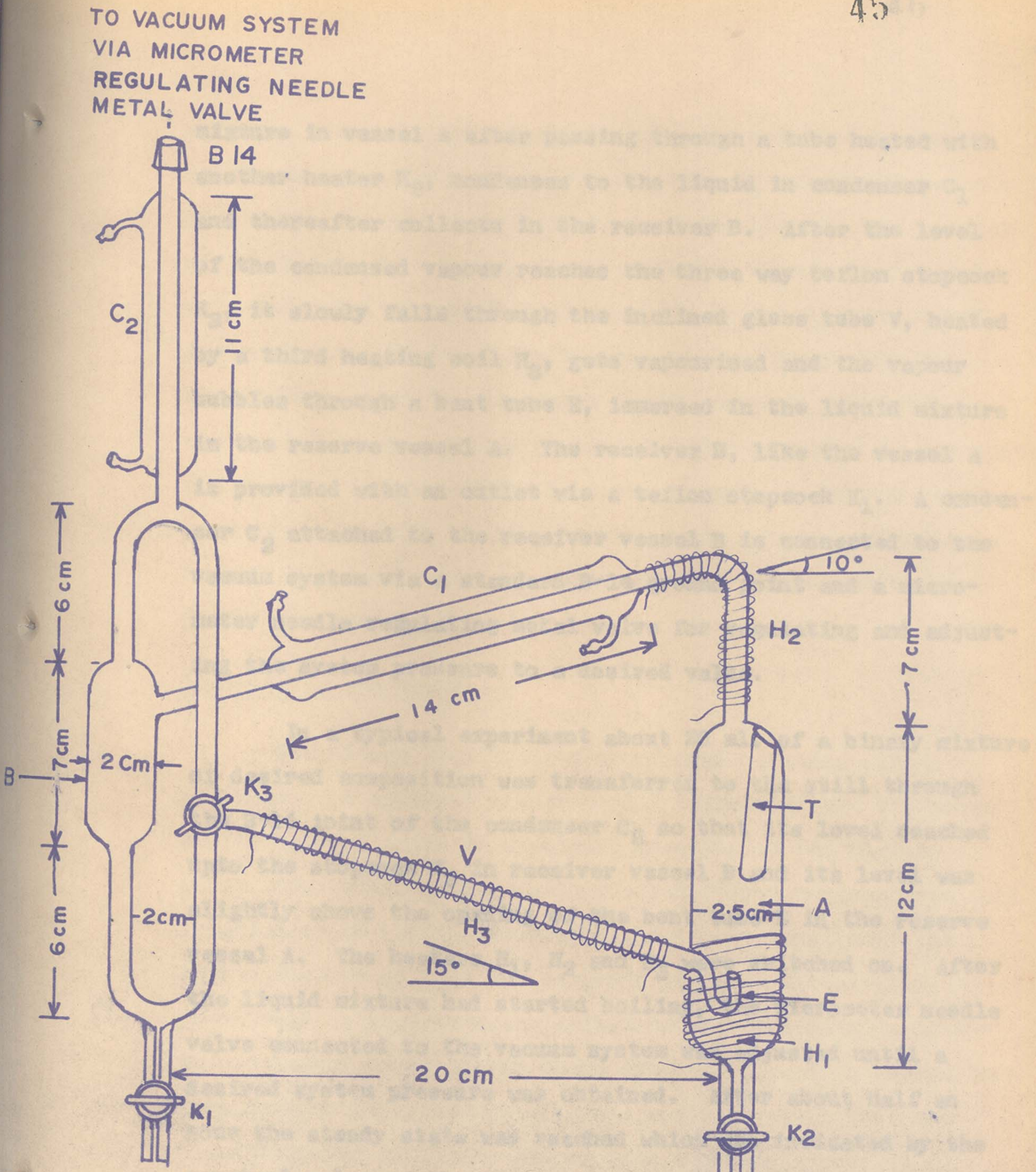
2. DETERMINATION OF EXCESS FREE ENERGY OF MIXING OF LIQUIDS :

The most commonly used method for the determination of the excess free energy of mixing involves isothermal determination of the vapour liquid equilibrium either by a static method or by a dynamic recirculating method. The static method has the advantage that it measures a true equilibrium, it is precise, it can also be used at very small pressures. In addition, it is equally suitable for binary mixtures of liquids with wide differences in their boiling points. Further, the method is rapid because measurement can be made at a series of temperatures with a single analysis of the overall liquid composition. The true liquid composition at any temperature is calculated by successive approximation from the values of the total pressure, the total volume and the total quantity of each component in the liquid and in the vapour phases. There are several methods for the calculation of the equilibrium vapour composition. This is done by direct integration of the first order differential equation derived from the Gibbs-Duhem equation to obtain a best fit to the experimental vapour pressure data and hence requires the ready availability of a digital computer.

In the recirculating still method for the determination of the vapour liquid equilibria, both the liquid and the vapour phases are circulated at whatever rate they are generated until a steady state is reached. Both the liquid and vapour compositions are determined experimentally. The recirculating still method is also capable of giving precise values of the excess free energy of mixing compared to those obtained on the static equilibrium still for a binary mixture~~s~~ of liquids with boiling points not far different from each other. We have made use of this method because digital computation facilities are not easily available to us. A large number of recirculating stills with various degrees of sophistication for the determination of the vapour liquid equilibrium have been described in the literature and reviewed by Hala et al.[17] We have made use of a modified Jones-Colburn recirculating still[18] mainly because it was possible for us to conduct experiments with very small quantities of liquids ($\sim$ 20 ml.) and also obtain a thermal equilibrium in a comparatively short period of about half an hour.

The recirculating still used by us for measurement of vapour liquid equilibria is shown in Fig. 6. It is made of pyrex glass and consists of a reserve vessel A containing liquid mixture part of which is electrically heated by the heater H_1. The rest of the portion used as disengaging chamber for the liquid and vapour phases is thermally insulated with an asbestos rope. A thermometer or a calibrated thermocouple used for measuring the equilibrium temperature is dipped in silicone oil contained in a thermometer pocket T, whose lower end is always above the liquid level in the reserve vessel A. The reserve vessel is fitted with an outlet via a teflon stopcock K_2. The vapour generated from the heated liquid



MODIFIED JONES-COLBURN STILL

FIG. 6.

mixture in vessel A after passing through a tube heated with another heater H_2, condenses to the liquid in condenser C_1 and thereafter collects in the receiver B. After the level of the condensed vapour reaches the three way teflon stopcock K_3, it slowly falls through the inclined glass tube V, heated by a third heating coil H_3, gets vapourised and the vapour bubbles through a bent tube E, immersed in the liquid mixture in the reserve vessel A. The receiver B, like the vessel A is provided with an outlet via a teflon stopcock K_1. A condenser C_2 attached to the receiver vessel B is connected to the vacuum system via a standard B-14 ground joint and a micrometer needle regulating metal valve for regulating and adjusting the system pressure to a desired value.

In a typical experiment about 20 ml. of a binary mixture of desired composition was transferred to the still through the B-14 joint of the condenser C_2 so that its level reached upto the stopcock K_3 in receiver vessel B and its level was slightly above the opening of the bent tube E in the reserve vessel A. The heaters H_1, H_2 and H_3 were switched on. After the liquid mixture had started boiling, the micrometer needle valve connected to the vacuum system was adjusted until a desired system pressure was obtained. After about half an hour the steady state was reached which was indicated by the constant value of the temperature and the system pressure. The pressure difference on the manometer was read by a cathetometer. Room temperature and atmospheric pressure were noted. The heater switches were put off. Partial vacuum in the circulating still was completely released. Stopcock K_3 was simultaneously rotated to cut off the circulation of the liquid. The samples of the liquid from vessel A and condensed vapour from vessel B were collected through teflon stopcock K_2 and K_1 respectively for analysis. The equilibrium pressure is determined from the difference of the barometer reading and the manometer reading after appropriate corrections for expansion of mercury and for the difference in the room temperature and the temperature of calibration of the cathetometer. A value of 'g' equal to 978.59 cm/sec^2 valid for Poona was used in the calibration of the pressure.

Analysis of the Sample

The binary liquid mixtures of n-butyl amine with alcohols were analysed either by (1) Potentiometric titration of the n-butyl amine in a weighed quantity of the mixture after dissolving in water with a standardised hydrochloric acid solution or by (2) the determination of the density of the liquid mixture at 25°C and deriving its composition from the previously determined relationship between the density of the amine-alcohol mixtures and their composition. Both the methods gave results in agreement with one another except that the potentiometric titration method gave inaccurate results in the composition of the binary mixtures with very large amine/alcohol ratios, possibly due to the increased loss of the amine by evaporation during weighing, transfer and titration of the of the mixture. In such cases compositions were determined by density method.

Determination of Density

Density of the liquids were measured by the use of a Lipkin-type pycnometer of about 3.5 ml. capacity. The pycnometer shown in Fig. 7 consisted of a U-shaped pyrex capillary tube with a small bulb A in one of its arms. The other arm at the top was bent at an angle of 45° to facilitate the filling of the liquid in the pycnometer. Two reference marks R_1 and R_2 were made on the two capillary tube arms of the pycnometer, one slightly above the bulb and the other on the same level on the other arm. In order to determine the volume of the liquid in the pycnometer upto the marks R_1 and R_2, the entire capillary range was calibrated at different temperatures initially in terms of height of pure water above the marks versus the mass/volume of the water taken in the pycnometer after applying appropriate correction in the weights due to buoyancy and the weight of air in the empty pycnometer. The plot of height versus volume (shown in Fig. 8 and obtained from the results shown in Table 2) is a straight line, which apart from the calibration also confirms the uniformity of the diameter of the capillary tube of the pycnometer.

The washed and dried pycnometer was weighed empty, filled with the liquid whose density was to be measured. It was then placed in a thermostatic bath maintained at 25° ± .01°C.

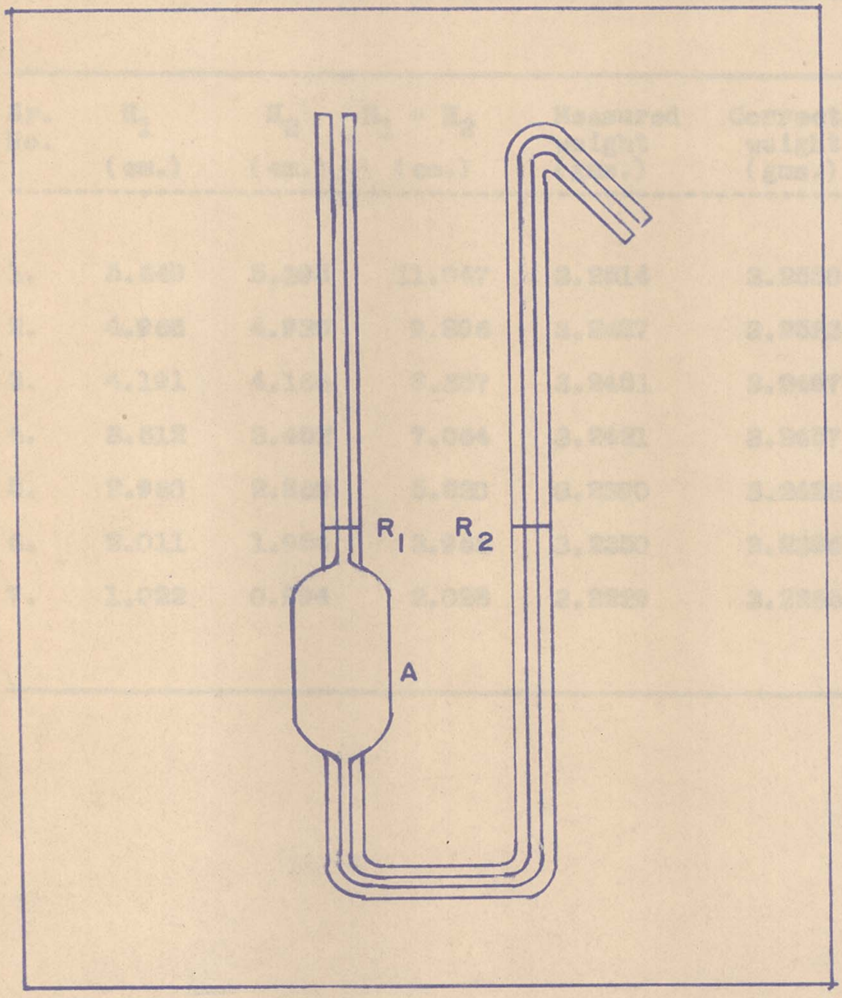
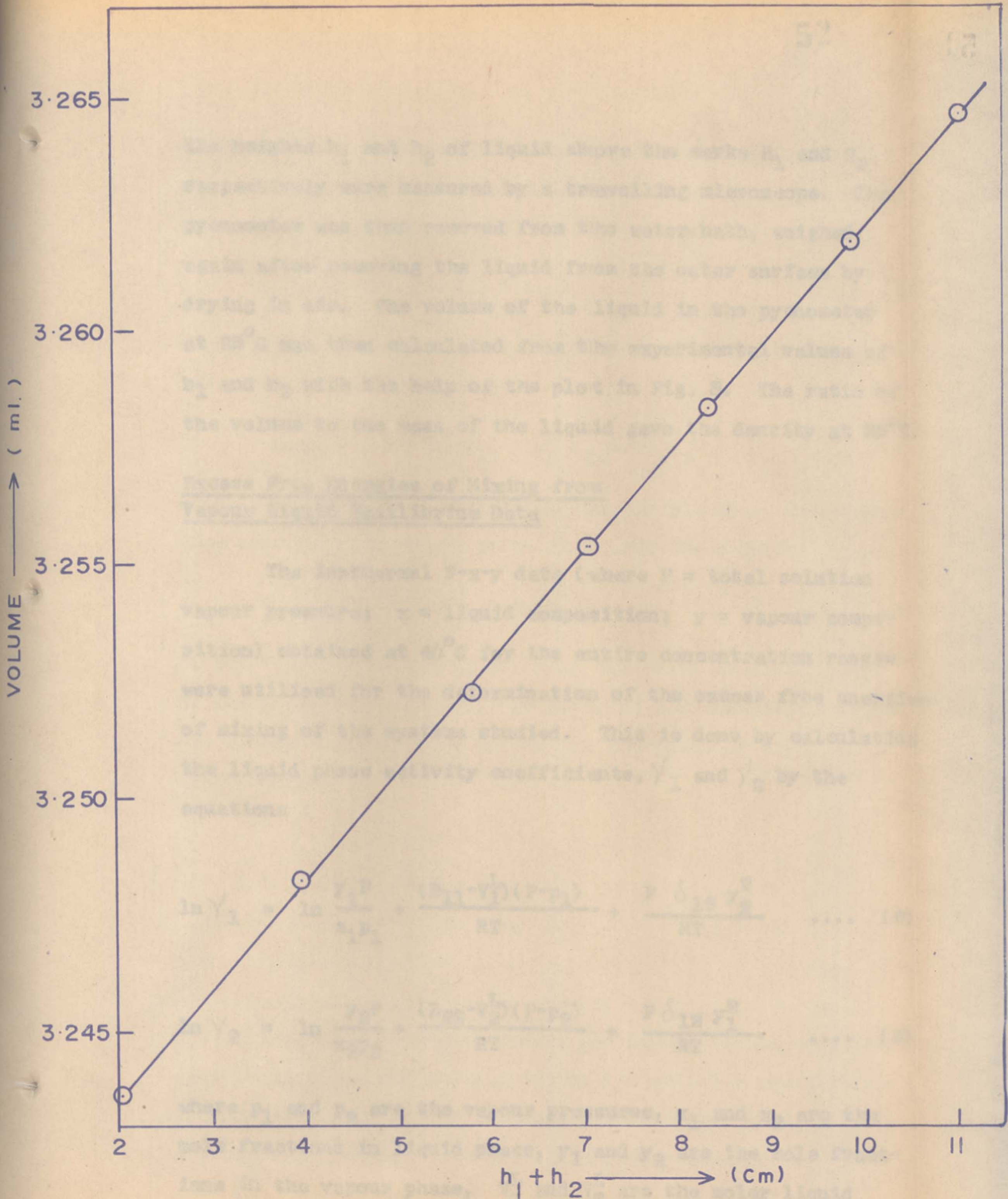


FIG.7. PYCNOMETER

Table 2 : Calibration of pycnometer at 25°C

Sr. No.	H_1 (cm.)	H_2 (cm.)	$H_1 + H_2$ (cm.)	Measured weight (gms.)	Corrected weight (gms.)	Volume (ml.)
1.	5.649	5.398	11.047	3.2514	3.2550	3.26465
2.	4.966	4.930	9.896	3.2487	3.2523	3.26194
3.	4.191	4.166	8.357	3.2451	3.2487	3.25833
4.	3.612	3.452	7.064	3.2421	3.2457	3.25532
5.	2.960	2.860	5.820	3.2390	3.2426	3.25221
6.	2.011	1.954	3.965	3.2350	2.2386	3.24820
7.	1.022	0.994	2.028	3.2229	3.2265	3.24361



CALIBRATION OF PYCNOMETER

FIG. 8

The heights h_1 and h_2 of liquid above the marks R_1 and R_2 respectively were measured by a travelling microscope. The pycnometer was then removed from the water bath, weighed again after removing the liquid from the outer surface by drying in air. The volume of the liquid in the pycnometer at 25°C was then calculated from the experimental values of h_1 and h_2 with the help of the plot in Fig. 8. The ratio of the volume to the mass of the liquid gave the density at 25°C.

Excess Free Energies of Mixing from Vapour Liquid Equilibrium Data

The isothermal P-x-y data (where P = total solution vapour pressure; x = liquid composition; y = vapour composition) obtained at 40°C for the entire concentration ranges were utilised for the determination of the excess free energies of mixing of the systems studied. This is done by calculating the liquid phase activity coefficients, γ_1 and γ_2 by the equations :

$$\ln \gamma_1 = \ln \frac{y_1 P}{x_1 p_1} + \frac{(B_{11}-V_1^L)(P-p_1)}{RT} + \frac{P\,\delta_{12}\,y_2^2}{RT} \quad \ldots\ldots (2)$$

$$\ln \gamma_2 = \ln \frac{y_2 P}{x_2 p_2} + \frac{(B_{22}-V_2^L)(P-p_2)}{RT} + \frac{P\,\delta_{12}\,y_1^2}{RT} \quad \ldots\ldots (3)$$

where p_1 and p_2 are the vapour pressures, x_1 and x_2 are the mole fractions in liquid phase, y_1 and y_2 are the mole fractions in the vapour phase, V_1^L and V_2^L are the moler liquid volumes of the components (1) and (2) respectively. B_{11} and B_{22} are the second virial coefficients of the pure components (1) and (2) respectively and

$$\delta_{12} = 2B_{12} - B_{11} - B_{22} \qquad \ldots. \quad (4)$$

where B_{12} is the second virial cross coefficient of the mixture and given by the expression

$$B_{12} = (B - y_1^2 B_{11} - y_2^2 B_{22})/2y_1y_2 \qquad \ldots. \quad (5)$$

where B is the virial coefficient of the mixture. The excess free energy of mixing is calculated from the equation

$$G^E = RT\,(x_1 \ln \gamma_1 + x_2 \ln \gamma_2)\,. \qquad \ldots. \quad (6)$$

If the vapour ~~pressure~~ phase is an ideal gas which is mostly true at low pressures, the last two terms of the equations (2) and (3) become insignificant and we get the commonly used expressions :

$$\gamma_1 = \frac{y_1 P}{x_1 p_1} \qquad \ldots. \quad (7)$$

and

$$\gamma_2 = \frac{y_2 P}{x_2 p_2} \qquad \ldots. \quad (8)$$

The experimental values of the second virial coefficients at 40°C required for calculation of the activity coefficients are not available in the literature for n-butyl amine and n-propanol, although the values of B_{11} for ethanol have been determined by three groups of workers[19-21]. These values however show wide variation (see Table 3). The value of B_{11} for 1-propanol has been determined experimentally in the temperature interval 105°- 150°C by Cox[22]. He has also given an expression for calculating the virial coefficient of 1-propanol as a function of temperature.

$$\log_{10}(-B_{11}) = 12.491 - 3.7 \log_{10} T.$$

The values of the second virial coefficients for ethanol, 1-propanol and n-butyl amine used for the calculation of the activity coefficients were determined from the Pitzer Curl[23] equation recommended for slightly polar liquids. According to this equation

$$B = \frac{RT_c}{P_c} \left\{ (0.1445 + 0.073\,\omega) - (0.0330 - 0.46\,\omega)\,T_r^{-1} - (0.1385 + 0.50\,\omega)\,Tr^{-2} - (0.0121 + 0.097\,\omega)\,T_r^{-3} - 0.0073\,\omega\,T_r^{-8} \right\} \quad \ldots. \quad (9)$$

where R is the molar gas constant, T_c and P_c are critical temperature and critical pressure; ω, the accentric factor which is a macroscopic measure of the extent to which the force field around the molecule deviate from spherical symmetry and is found by equation

$$\omega = -\log(P_r)_{T_r=0.7} - 1 \quad \ldots. \quad (10)$$

P_r and T_r are reduced pressures, P/P_c and reduced temperature T/T_c respectively.

Table 3 : Values of second virial coefficient at different temperatures

Substance	Temperature °C	Values of second virial coefficient				
		Ref.21	Ref.19	Ref.20	Present calculation	Ref.22
Ethanol	40	-2134	-2500*	-3800	-1136	-
	60	-1285	-1522	-1990	-	-
	80	- 938	- 941	-1330	-	-
1-Propanol	40	-	-	-	-1665	-1808*
	115	-	-	-	-	- 913
	120	-	-	-	-	- 781
	135	-	-	-	-	- 619
	150	-	-	-	-	- 606
n-Butyl amine	40	-	-	-	-1496	-

* Extrapolated values at 40°C

Other expressions for the calculation of the second virial coefficients of associating liquids as for example those of Black[24,25], or O'Connell and Prausnitz[26] were not used for want of appropriate constants required for the liquids.

The effect of second virial coefficient on excess free energy of mixing is small particularly at low pressure at which we worked i.e. in the range of 52 mm to 188 mm of mercury. Any error arising out of differences in the actual value of the second virial coefficient and those calculated from the Pitzer Curl equation may therefore be neglected. The calculated values of the second virial coefficients are also given in Table 3 along with the data already available.

The value of δ_{12} used in the equations (2) and (3) and defined by the equation (4) requires the knowledge of the second virial cross coefficient B_{12} of the mixture and is not available in the literature. Although this value also can be theoretically calculated by using O'Connell and Prausnitz[26] method, but some of the data required for the calculation were difficult to obtain. Some of the workers faced with similar problem have assumed that the vapour phases are ideal. This makes $B_{12} = \frac{1}{2} (B_{11} + B_{22})$, and hence $\delta_{12} = 0$; consequently the third term of the equations (2) and (3) also becomes zero. We have assumed B_{12} to be a geometric mean of B_{11} and B_{12} viz. $B_{12} = (B_{11} \times B_{22})^{\frac{1}{2}}$ as has been done by

Boublikove and Lu[27] etc.

The value of molar volume V^L at 40°C are given in Table-4.

Testing Equilibrium Data for Thermodynamic Consistency

A fundamental thermodynamic equation used for testing the reliability of experimental vapour liquid equilibrium data is

$$RT \sum x_i \, d\ln \gamma_i + \left(\frac{H^E}{T}\right) dT - V^E \, dP = 0 \qquad \text{.... (11)}$$

where R is the gas constant, T is the temperature in degree Kelvin, x_i is the mole fraction of component in the liquid mixture, γ_i is the activity coefficient of component i in the liquid mixture (the standard state being defined as that of pure component), H^E is the excess molar heat of mixing, P is the pressure of the system and V^E is the excess molar volume of mixing of the liquids. The activity coefficient of component i in the binary liquid mixture is given by equation (2). For isothermal conditions at temperature near or below the normal boiling point of the components the term $\left(\frac{H^E}{T}\right) dT$ in equation (11) is zero and the term $V^E \, dP$ is usually negligible so that for binary mixture,

$$x_1 \, d\ln \gamma_1 + x_2 \, d\ln \gamma_2 = 0 \qquad \text{.... (12)}$$

Several tests for the reliability of experimental vapour liquid equilibrium data have been suggested in terms of explicit

Table 4 : Molar volumes of the substances at 40°C

Substance	Molar volumes (m.L)
Ethanol	59.6
1-Propanol	76.0
n-Butyl amine	102.0

algebraic expressions derived for equation (12) above. Such tests can be used to establish the reliability of experimentally measured vapour compositions, liquid composition and vapour pressure data. These tests are however useless for assessment of data generated by means of equation (12) if the y-x data are calculated from the p-x data.

In 1947 Herington[28] developed a thermodynamic tests for the internal consistency of the experimental vapour liquid equilibrium data as given by equation 13.

$$\int_0^1 \log \frac{\gamma_1}{\gamma_2}\, dx_1 = 0 \qquad \ldots. \quad (13)$$

which means, the algebraic area bounded by $x_1 = 0$ and $x_1 = 1$ in plot of $\log \frac{\gamma_1}{\gamma_2}$ versus x_1 should be zero. Additional details of the method of treatment of data have also been given by several authors[29-31]. Several criticisms[32,33] have however been voiced against the wide use of equation (13). However, Herington[34] has shown that in practice neither of the objections raised above limit the usefulness of the equation (13). The performance of the Jones-Colburn still used by us was checked by an actual vapour liquid equilibrium experiment with ethanol + water system at 50°C, comparing the results with those available in the literature[35,36] and subjecting these results to a thermodynamic consistency test. The vapour liquid equilibrium data on ethanol-water system at 50°C obtained by us are given in Table 5 and those already available in the literature in Tables 6 and 7. The x-y diagrams are plotted in Fig. 9. The plots of $\log \frac{\gamma_1}{\gamma_2}$ versus x_1 are shown in Fig. 10. Our data show a

percentage deviation of 1.4 per cent compared to 4.8 per cent from data of Dulitskaya[35] and 23 per cent for the data of Udo
Utvenko[36].

Table 5 : Vapour liquid equilibrium of ethanol (1) and water (2) at 50°C. (Present work)

Sr. No.	x_1	y_1	P (mm.of Hg)	$\log \gamma_1/\gamma_2$
1	0	0	92.51	-
2	0.0267	0.2371	108.66	0.6767
3	0.0743	0.4127	138.34	0.5649
4	0.1333	0.5225	170.22	0.4746
5	0.2174	0.5817	187.71	0.3218
6	0.2795	0.6096	192.64	0.2274
7	0.3673	0.6332	199.98	0.0941
8	0.4317	0.6500	202.48	0.0106
9	0.5660	0.7000	200.72	-0.1247
10	0.6641	0.7394	215.49	-0.2206
11	0.7802	0.8064	211.44	-0.3080
12	0.8308	0.8454	222.87	-0.3308
13	0.9070	0.9070	225.41	-0.3775
14	1.000	1.000	220.6	-

Table 6 : **Vapour liquid equilibrium of ethanol (1) and water (2) at 50°C.** (Literature value - Ref.35)

Sr. No.	x_1	y_1	P (mm.of Hg)	$\log \gamma_1/\gamma_2$
1	0	0	92.51	-
2	0.0956	0.4796	154.50	0.5630
3	0.1600	0.5384	173.30	0.4085
4	0.2500	0.5749	187.00	0.2306
5	0.3360	0.5934	193.30	0.0820
6	0.4870	0.6509	202.80	-0.0843
7	0.7455	0.7859	216.30	-0.2795
8	1.000	1.000	220.6	-

Table 7 : Vapour liquid equilibrium of ethanol (1) and water (2) at 50°C. (Literature value - Ref.36)

Sr. No.	x_1	y_1	P (mm.of Hg)	$\log \gamma_1/\gamma_2$
1	0	0	92.51	-
2	0.0290	0.2080	115.70	0.5666
3	0.1100	0.4390	161.00	0.4240
4	0.2460	0.5210	187.90	0.1456
5	0.4510	0.6230	204.80	-0.0739
6	0.5810	0.6850	213.40	-0.1761
7	0.6820	0.7400	218.10	-0.2545
8	0.8620	0.8700	222.80	-0.3473
9	0.8850	0.8910	222.90	-0.3512
10	0.9260	0.9290	223.00	-0.3577
11	0.9470	0.9450	223.10	-0.4100
12	1	1	220.6	-

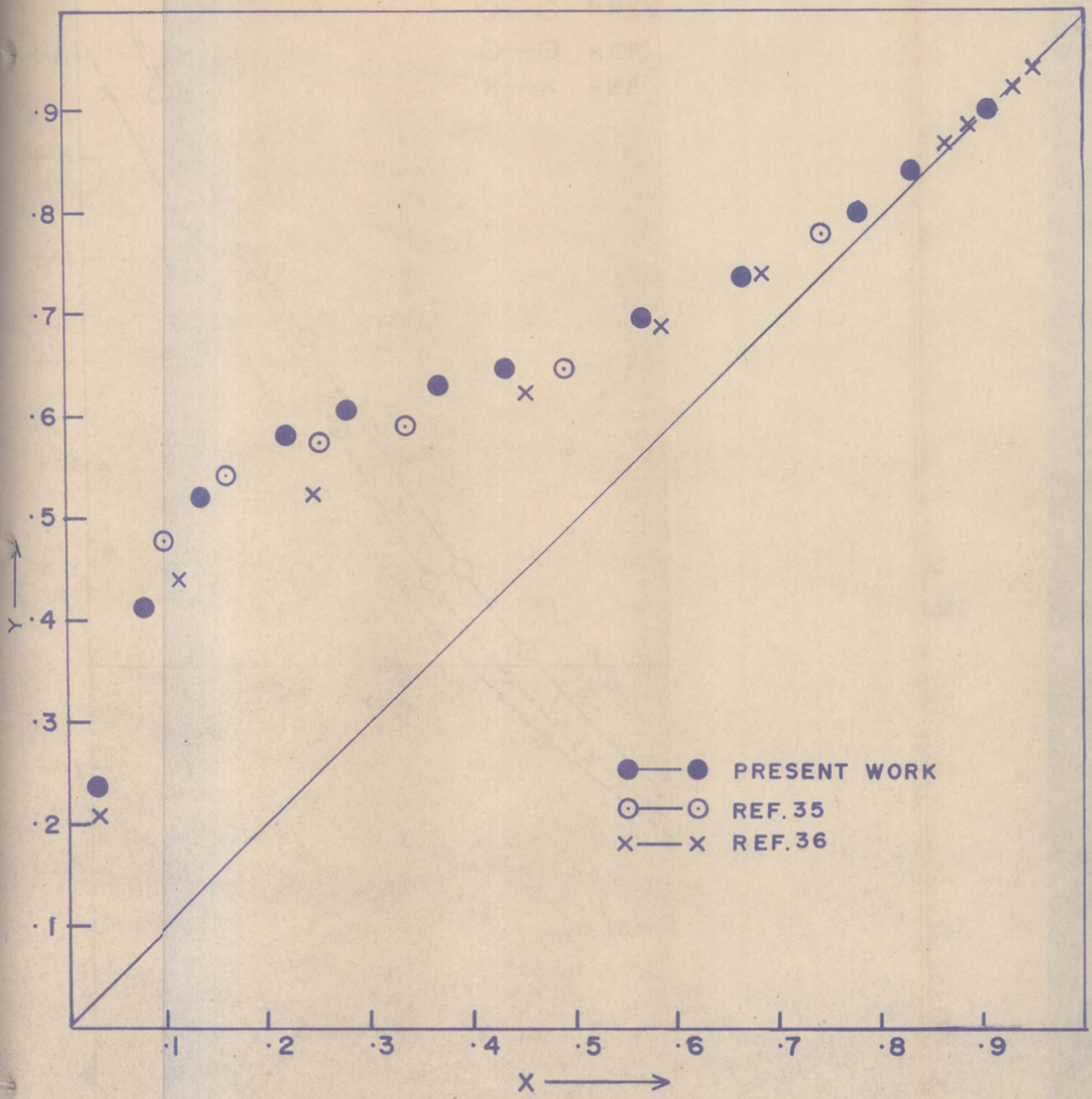


FIG.9. X-Y DIAGRAM FOR ETHANOL-WATER SYSTEM
AT 50°C

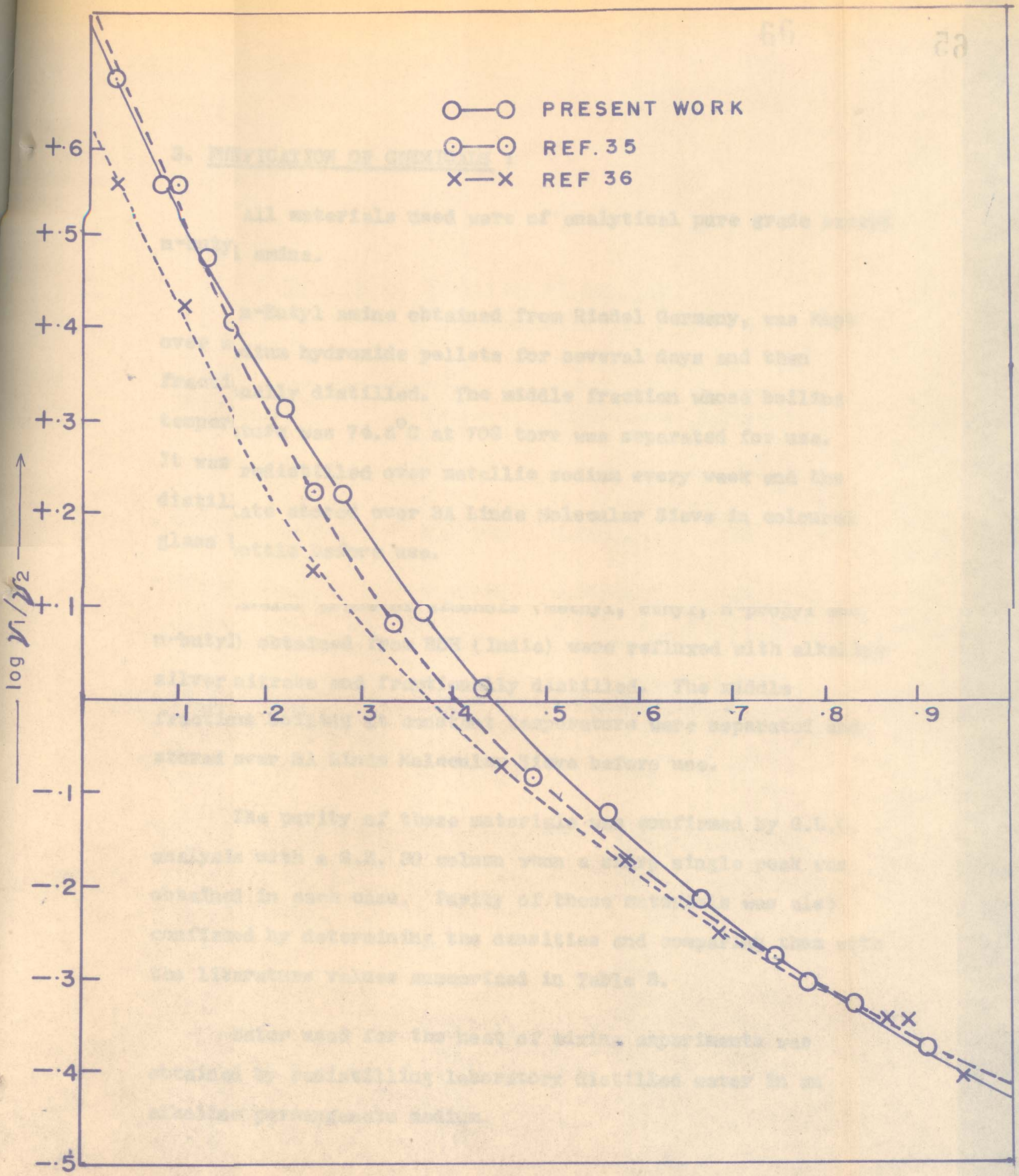


FIG 10. THERMODYNAMIC CONSISTANCY TEST; ETHANOL+WATER SYSTEM AT 50°C

3. PURIFICATION OF CHEMICALS :

All materials used were of analytical pure grade except n-butyl amine.

n-Butyl amine obtained from Riedel Germany, was kept over sodium hydroxide pellets for several days and then fractionally distilled. The middle fraction whose boiling temperature was 74.6°C at 708 torr was separated for use. It was redistilled over metallic sodium every week and the distillate stored over 3A Linde Molecular Sieve in coloured glass bottle before use.

Analar grade of alcohols (methyl, ethyl, n-propyl and n-butyl) obtained from BDH (India) were refluxed with alkaline silver nitrate and fractionally distilled. The middle fractions boiling at constant temperature were separated and stored over 3A Linde Molecular Sieve before use.

The purity of these materials was confirmed by G.L.C. analysis with a S.E. 30 column when a sharp single peak was obtained in each case. Purity of these materials was also confirmed by determining the densities and comparing them with the literature values summerized in Table 8.

Water used for the heat of mixing experiments was obtained by redistilling laboratory distilled water in an alkaline permanganate medium.

Table 8 : Densities of the pure materials at 25°C

Substance	Present work	Literature value	Reference
n-Butyl alcohol	0.80580	0.80583	37
n-Propyl alcohol	0.79955	0.79950	38
Ethyl alcohol	0.78503	0.78508	39
Methyl alcohol	0.78673	0.78675	40
n-Butyl amine	0.73310	0.73308	41

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CHAPTER - III : RESULTS AND DISCUSSIONS

RESULTS AND DISCUSSIONS

The heats of mixing of n-butyl amine with water, methanol, ethanol, 1-propanol and 1-butanol were measured at 25°C and 40°C throughout the entire range of concentration.

The results on the heats of mixing, H^E, for the system water (1) – n-butyl amine (2) at 25°C and 40°C are given in Tables 9 and 10 respectively. These tables give the details of the quantities in gms. of water (1) and n-butyl amine (2) taken in the calorimeter assembly for mixing, x_1, the mole fraction of water in the mixture, $H^E (= \Delta H^m)$, the observed heat of mixing in Joules per mole of the mixture, H^E/x_1 and H^E/x_1x_2 in Kilo Joules per mole where x_2 is the mole fraction of n-butyl amine. The mixing of water with n-butyl amine is an exothermic reaction throughout the entire range of concentration. The plot of H^E versus x_1 has the shape of a parabola. The values of the H^E at the maxima at 25° and 40°C are -3.48 and -3.36 KJ/mole at water mole fraction of 0.522 and 0.547 respectively. It may be observed from Fig. 11 that an increase in the temperature from 25°C to 40°C brings about a small decrease in the magnitude of the exothermic heat of mixing of the water+n-butyl amine system. Though we have reported the heats of mixing for the water-rich region of the binary mixture upto $x_1 = 0.97$, we have not reported the results for $x_1 < 0.23$. The molecular weight of water is very small as compared to that of n-butyl amine. The estimated error arising out of the uncertainty in the weight of water taken in the very small water mole fraction region of the concentration range together with the small value of the heat of mixing in this range, as well as, the probability of an inhomogeneous mixing of a very small quantity of water in a very large quantity of n-butyl amine, brings about a large uncertainty in our results in this region of the concentration.

The values of H^E versus x_1 have been fitted by the method of least squares in a Redlich Kister equation of the type

$$H^E \text{ (KJ mole}^{-1}\text{)} = (1-x_2)\, x_2 \left[B + C\,(1-2x_2) + D\,(1-2x_2)^2\right] \qquad \ldots\ (1)$$

where B, C and D are constants whose values have been summarized in Table 20. The values of H^E as a function of x, derived by equation (1) and represented by the continuous lines for both 25° and 40°C in Fig. 11 are in very good agreement with the experimental results. There are no reports in the literature of an earlier work on the heats of mixing of the water—n-butyl amine system.

Table 9 : Heats of Mixing of Water—n-Butyl amine at 25°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction of 1st component	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.1766	2.3060	0.2373	-2148.1	-9.052	-11.868
2	0.2228	2.1405	0.2972	-2523.5	-8.491	-12.080
3	0.2505	2.0805	0.3285	-2746.7	-8.361	-12.451
4	0.2925	1.8028	0.3973	-3031.7	-7.631	-12.658
5	0.4242	1.7550	0.4954	-3401.1	-6.865	-13.604
6	0.3871	1.1405	0.5797	-3396.0	-5.858	-13.941
7	0.5703	1.1752	0.6635	-3111.0	-4.689	-13.932
8	0.8003	0.9843	0.7676	-2577.8	-3.358	-14.450
9	1.0408	0.9207	0.8212	-2123.0	-2.585	-14.462
10	1.2433	0.6144	0.8916	-1427.1	-1.601	-14.773
11	2.0843	0.3390	0.9615	- 675.8	-0.703	-18.265

Table 10 : Heats of Mixing of Water—n-Butyl amine at 40°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction of 1st component	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.2293	2.1346	0.3039	-2437.5	-8.021	-11.523
2	0.2775	1.9046	0.3719	-2913.1	-7.833	-12.471
3	0.2377	1.5959	0.3771	-3004.2	-7.967	-12.789
4	0.2639	1.3191	0.4484	-3136.8	-7.000	-12.682
5	0.2875	1.4217	0.4511	-3185.5	-7.062	-12.865
6	0.3216	1.2064	0.5200	-3370.2	-6.481	-13.502
7	0.3450	1.1990	0.5390	-3498.6	-6.491	-14.080
8	0.4311	1.1891	0.5957	-3368.3	-5.654	-13.987
9	0.5157	1.0406	0.6682	-3028.8	-4.533	-13.661
10	0.6750	1.0462	0.7239	-2739.4	-3.784	-13.706
11	0.9080	0.8837	0.8075	-2326.0	-2.880	-14.964
12	1.0377	0.8320	0.8352	-1927.5	-2.320	-14.004
13	1.0614	0.8346	0.8379	-1861.1	-2.221	-13.703
14	1.4900	0.4958	0.9243	- 927.2	-1.003	-13.251

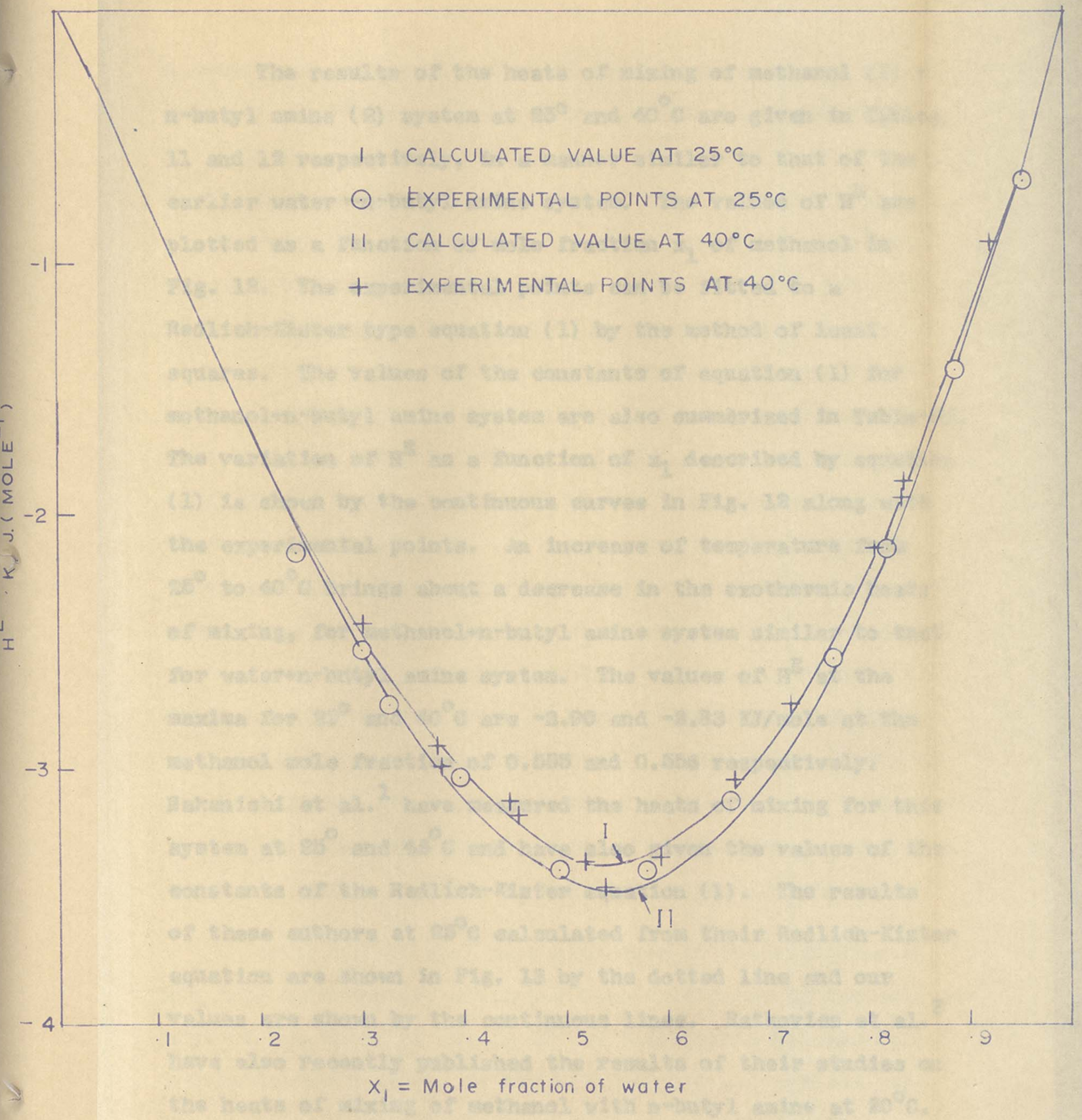


FIG. 11 HEATS OF MIXING OF WATER n-BUTYLAMINE SYSTEM

The results of the heats of mixing of methanol (1) + n-butyl amine (2) system at 25° and 40°C are given in Tables 11 and 12 respectively, in a manner similar to that of the earlier water—n-butyl amine system. The values of H^E are plotted as a function of mole fraction x_1 of methanol in Fig. 12. The experimental points can be fitted to a Redlich-Kister type equation (1) by the method of least squares. The values of the constants of equation (1) for methanol+n-butyl amine system are also summàrized in Table-20. The variation of H^E as a function of x_1 described by equation (1) is shown by the continuous curves in Fig. 12 along with the experimental points. An increase of temperature from 25° to 40°C brings about a decrease in the exothermic heats of mixing, for methanol+n-butyl amine system similar to that for water+n-butyl amine system. The values of H^E at the maxima for 25° and 40°C are -3.90 and -3.83 KJ/mole at the methanol mole fraction of 0.555 and 0.556 respectively. Nakanishi et al.[1] have measured the heats of mixing for this system at 25° and 45°C and have also given the values of the constants of the Redlich-Kister equation (1). The results of these authors at 25°C calculated from their Redlich-Kister equation are shown in Fig. 13 by the dotted line and our values are shown by the continuous lines. Ratkovics et al.[2] have also recently published the results of their studies on the heats of mixing of methanol with n-butyl amine at 20°C.

A comparison of the values of H^E corresponding to any mole fraction at 40° and 25°C from our results and at 45° and 25° from the data of Nakanishi et al.(1) shows that an increase in the exothermic heats of mixing of the methanol+n-butyl amine system for a 5° decrease in temperature below 25° is expected to be $\lesssim 1\%$ (Table 13), a value less than the limits of the estimated variation of 2% in our experimental results. It is therefore not unreasonable to compare our results on the heats of mixing of methanol+n-butyl amine system at 25° with those of Ratkovies et al.[2] at 20°C. Fig. 13 shows such a comparison where the results of the Hungarian workers are shown by ~~filled~~ circles. It may be observed that there is a close agreement between our data and those of Ratkovics et al. except in a very small region (x_1 = 0.45 to 0.67) near the maxima, where the exothermic heats of mixing reported by the Hungarian workers are about 5% larger than those obtained by us. The results of Nakanishi et al.[1] on the heats of mixing for this system are lower than those obtained by us throughout the entire range of concentration. The differences range from 1% at the maxima to 7% at x_1 = 0.8 as shown in Table 13.

Nakanishi et al.[1] have also used in their studies a twin type calorimeter, which has been calibrated by the measurement of the heats of mixing of the endothermic Benzene+Carbon tetrachloride system. It has been pointed out earlier (page 38) that in an endothermic heat of mixing experiment with a twin-calorimeter system, the electrical heating required for the

Table 11 : Heats of Mixing of Methyl alcohol—n-Butylamine at 25°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction of 1st component	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.2084	2.0513	0.1883	-1949.8	-10.355	-12.760
2	0.2158	1.9189	0.2043	-2028.4	- 9.929	-12.475
3	0.3315	1.8267	0.2929	-2861.3	- 9.769	-13.816
4	0.4232	1.8757	0.3399	-3122.6	- 9.187	-13.915
5	0.6436	1.9244	0.4329	-3666.6	- 8.470	-14.935
6	0.7563	1.9110	0.4746	-3806.6	- 8.021	-15.263
7	0.6153	1.1913	0.5411	-3860.3	- 7.134	-15.547
8	0.8734	1.1206	0.6402	-3765.0	- 5.881	-16.348
9	1.0626	0.8755	0.7348	-3270.0	- 4.450	-16.778
10	1.4360	0.7171	0.8205	-2471.5	- 3.012	-16.779
11	1.6470	0.5617	0.8700	-1904.0	- 2.189	-16.834
12	1.6410	0.3072	0.9242	-1230.2	- 1.331	-17.549

Table 12 : **Heats of Mixing of Methyl alcohol—n-Butyl amine at 40°C**

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction of 1st component	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.1887	1.9080	0.1842	-1771.3	- 9.616	-11.785
2	0.2876	1.6446	0.2853	-2710.2	- 9.499	-13.292
3	0.4425	1.3519	0.4277	-3493.2	- 8.167	-14.270
4	0.5826	1.1372	0.5387	-3713.1	- 6.893	-14.942
5	0.7878	1.0078	0.6409	-3641.2	- 5.681	-15.821
6	0.9378	0.8769	0.7094	-3360.4	- 4.737	-16.297
7	0.9147	0.8288	0.7159	-3319.0	- 4.636	-16.318
8	1.1633	0.7787	0.7732	-2925.8	- 3.784	-16.676
9	1.3780	0.7334	0.8111	-2447.3	- 3.017	-16.301
10	1.6004	0.3482	0.9130	-1260.5	- 1.381	-15.875

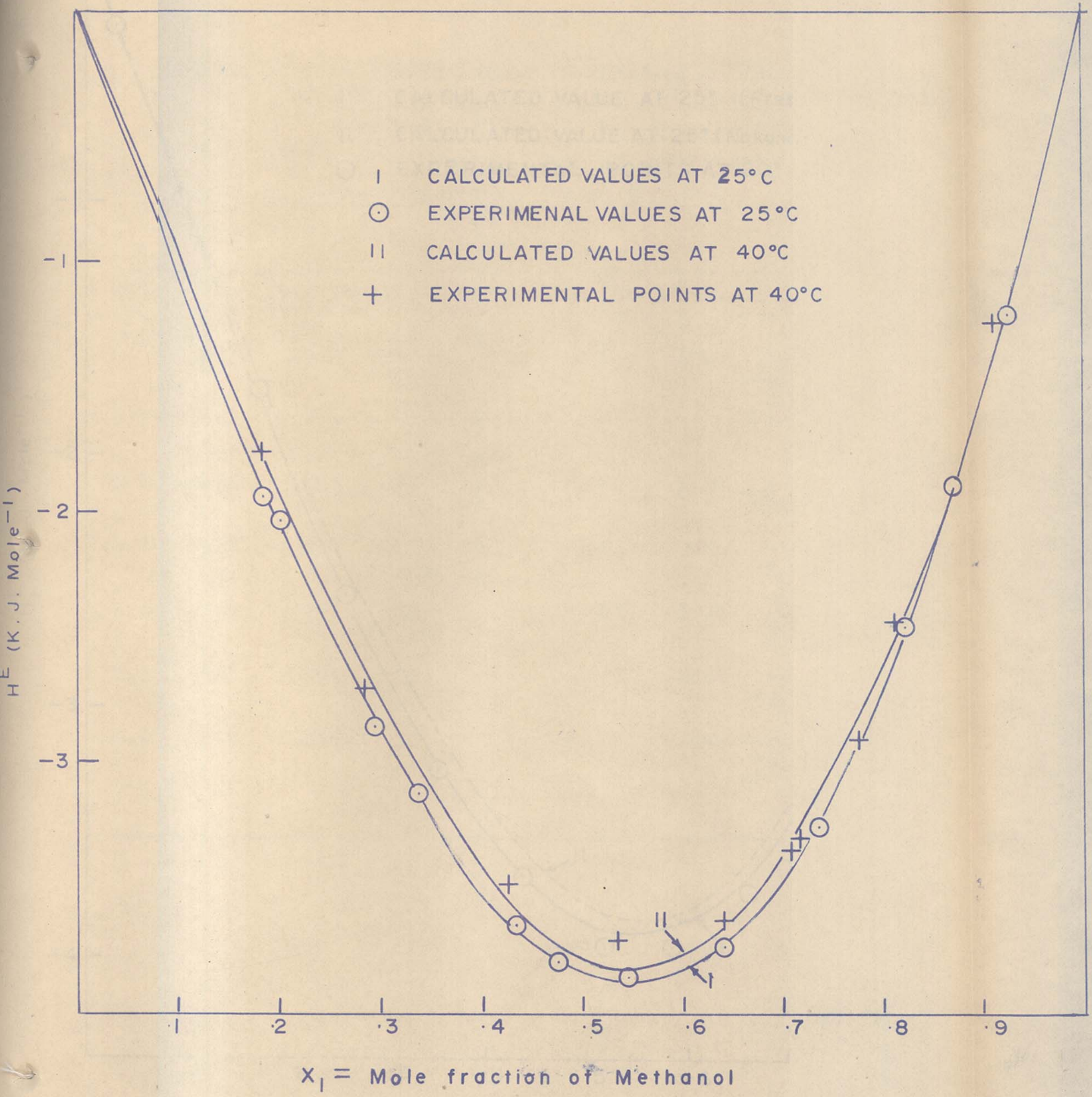


FIG. 12. HEATS OF MIXING OF METHANOL-n-BUTYLAMINE SYSTEM

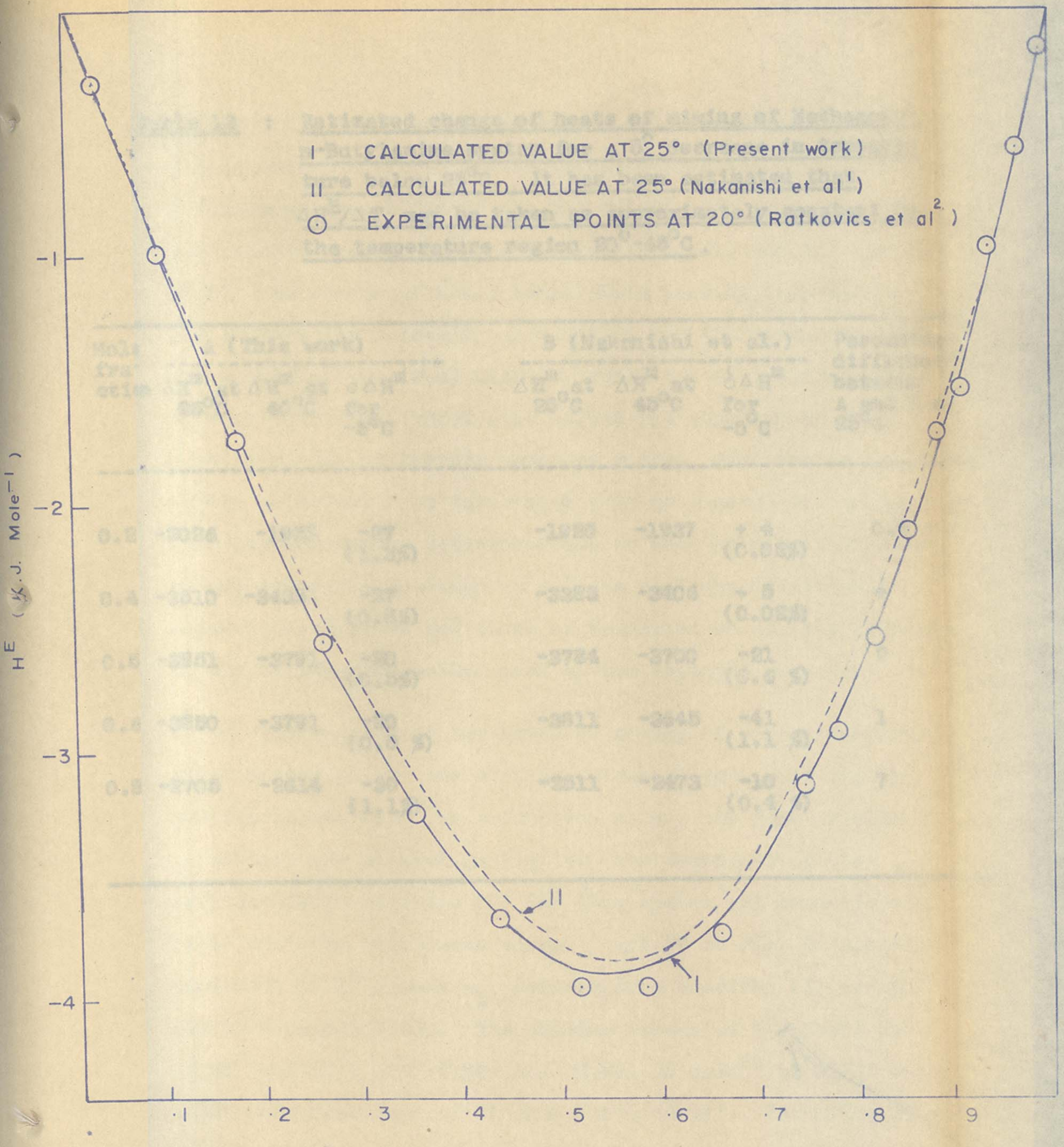


FIG.3. HEATS OF MIXING OF METHANOL - n- BUTYLAMINE SYSTEM

Table 13 : Estimated change of heats of mixing of Methanol—n-Butylamine system for a 5° decrease in temperature below 25°C. It has been estimated that $\Delta H^E/\Delta T$ may be taken as approximately constant in the temperature region 20°-45°C.

Mole fraction	A (This work)			B (Nakanishi et al.)			Percentage difference between A and B at 25°C
	ΔH^m at 25°C	ΔH^m at 40°C	$\delta\Delta H^m$ for -5°C	ΔH^m at 25°C	ΔH^m at 45°C	$\delta\Delta H^m$ for -5°C	
0.2	-2026	-1928	-27 (1.3%)	-1920	-1937	+ 4 (0.02%)	0.5
0.4	-3510	-3435	-27 (0.8%)	-3385	-3406	+ 5 (0.02%)	4
0.5	-3851	-3791	-20 (0.5%)	-3784	-3700	-21 (0.6 %)	2
0.6	-3850	-3791	-20 (0.5 %)	-3811	-3645	-41 (1.1 %)	1
0.8	-2705	-2614	-30 (1.1%)	-2511	-2473	-10 (0.4 %)	7

determination of the heat of mixing is carried out in the mixing vessel itself. In such a situation, the exact matching of the heat capacities of the two calorimeter vessels, i.e. the reaction vessel and the reference vessel, and the matching of the resistance of their temperature sensing thermistors are in fact not necessary as required for the measurement of the exothermic heats of mixing. Hence any such difference, if they exist, and which will affect the accuracy of the results of the exothermic heats of mixing, will not be detected if the calorimeter is calibrated with an endothermic system like Benzene+carbon tetrachloride, as done by Nakanishi et al.[1] We are therefore inclined to believe that the differences between our results and those of Nakanishi et al. may be traced to the calibration method used by the Japanese workers.

The results on the heats of mixing of ethanol+n-butyl amine system at 25° and 40°C are given in Tables 14 and 15 and the values of H^E as a function of x_1, the mole fraction of ethanol are plotted in Fig.14. The constants of the Redlich-Kister equation (1) for this system are summarized in Table 20. The continuous curves I and II in Fig. 14 show the variation of H^E versus x_1, derived from equation (1) for 25° and 40°C respectively. The maximum values of H^E (Table 21) at 25° and 40°C are -2.995 and -2.901 KJ mole^{-1} at 0.545 and 0.551 mole fractions of ethanol respectively. Ratkovics et al.[2] have recently reported the results of their measurement of the heats of mixing of this system at 20°C. We have estimated that for the ethanol + n-butyl amine system, like the methanol + n-butyl amine system, a decrease of temperature from 25° to 20°C is likely to bring about an increase of ~1% in the exothermic heat of mixing, a value within the estimated limits of our experimental error of 2%. We can therefore compare our results on the heats of mixing at 25°C with those of Ratkovics et al. at 20°C (Fig. 14). It may be observed that although there is a close agreement between our results and those of the Hungarian workers for ethanol mole fraction region $> .65$ the values of the exothermic heats of mixing obtained by Ratkovics et al. differ by as much as 4% from our experimental results in the lower mole fraction region.

The results of the heats of mixing for 1-propanol + n-butyl amine system at 25° and 40°C are given in Tables 16 and 17 respectively and the values of H^E as a function of x_1, the mole fraction of 1-propanol are plotted in Fig. 15 along with the values (continuous lines) calculated from Redlich-Kister equation (1). The values of the constants calculated by the method of the least squares are summàrized again in Table 20. For the system 1-propanol + n-butyl amine, the maximum heats of mixing obtained at 25° and 40°C are -3.079 KJ per mole and -2.839 KJ per mole at the propanol mole fraction 0.534 and 0.526 respectively. The only result on the heat of mixing for this system available in the literature is by Ratkovics et al. at 20°C. It may be pointed out that for this system the decrease in $|-H^E|$ with an increase in temperature from 25° to 40°C,

Table 14 : Heats of Mixing of Ethyl alcohol– n-Butyl amine system at 25°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction of 1st component	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.2100	1.8830	0.1504	-1318.0	- 8.764	-10.315
2	0.4997	2.0896	0.2752	-2135.0	- 7.758	-10.702
3	0.7227	2.1252	0.3506	-2546.3	- 7.263	-11.183
4	0.8153	1.9086	0.4041	-2736.6	- 6.772	-11.365
5	0.7834	1.3797	0.4741	-2953.2	- 6.229	-11.846
6	0.9774	1.1499	0.5744	-2958.7	- 5.151	-12.101
7	1.1792	1.1786	0.6137	-2885.4	- 4.702	-12.170
8	1.3006	0.9578	0.6831	-2736.4	- 4.006	-12.639
9	1.4243	0.8731	0.7214	-2624.6	- 3.638	-13.058
10	0.8869	1.7232	0.7552	-2377.5	- 3.148	-12.858
11	1.6490	0.5990	0.8138	-1941.5	- 2.386	-12.817
12	1.7151	0.4612	0.8551	-1645.7	- 1.925	-13.282
13	2.0520	0.2733	0.9226	- 850.7	- 0.922	-11.915

Table 15 : Heats of Mixing of Ethyl alcohol–n-Butyl amine system at 40°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction of 1st component	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.2257	2.2479	0.1375	-1158.8	-8.428	- 9.771
2	0.5447	2.0335	0.2984	-2213.3	-7.417	-10.570
3	0.7733	2.1216	0.3665	-2580.7	-7.041	-11.114
4	0.6212	1.4914	0.3980	-2636.8	-6.625	-11.005
5	0.7864	1.3646	0.4778	-2806.5	-5.874	-11.248
6	0.9325	1.4191	0.5106	-2917.0	-5.713	-11.673
7	1.0349	1.3165	0.5552	-2888.1	-5.202	-11.693
8	1.0400	1.0036	0.6216	-2875.3	-4.626	-12.225
9	1.2885	0.9794	0.6762	-2682.0	-3.966	-12.247
10	1.4977	0.8259	0.7422	-2400.7	-3.243	-12.549
11	1.3802	0.5960	0.7862	-2085.2	-2.652	-12.405
12	2.0250	0.3380	0.9049	-1102.8	-1.219	-12.814

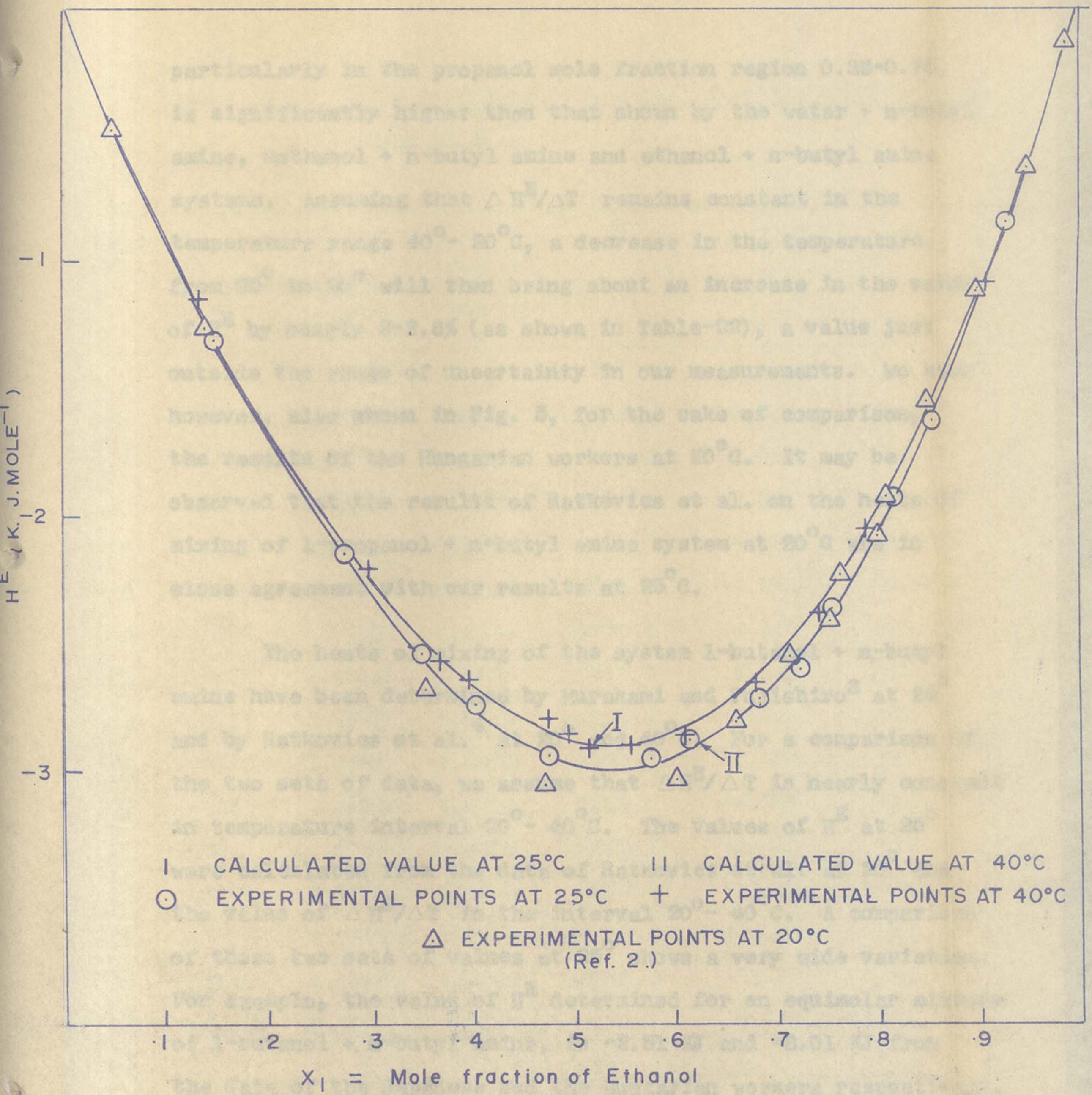


FIG. 14. HEATS OF MIXING OF ETHANOL — n-BUTYLAMINE SYSTEM

particularly in the propanol mole fraction region 0.35-0.75, is significantly higher than that shown by the water + n-butyl amine, methanol + n-butyl amine and ethanol + n-butyl amine systems. Assuming that $\triangle H^E/\triangle T$ remains constant in the temperature range 40°- 20°C, a decrease in the temperature from 25° to 20° will then bring about an increase in the value of H^E by nearly 2-2.6% (as shown in Table-22), a value just outside the range of uncertainty in our measurements. We have however, also shown in Fig. 5, for the sake of comparison, the results of the Hungarian workers at 20°C. It may be observed that the results of Ratkovics et al. on the heats of mixing of 1-propanol + n-butyl amine system at 20°C are in close agreement with our results at 25°C.

The heats of mixing of the system 1-butanol + n-butyl amine have been determined by Murakami and Fujishiro[3] at 25° and by Ratkovics et al.[4] at 20° and 40°C. For a comparison of the two sets of data, we assume that $\triangle H^E/\triangle T$ is nearly constant in temperature interval 20°- 40°C. The values of H^E at 25° were calculated from the data of Ratkovics et al. at 20° and the value of $\triangle H^E/\triangle T$ in the interval 20°- 40°C. A comparison of these two sets of values at 25° shows a very wide variation. For example, the value of H^E determined for an equimolar mixture of 1-butanol + n-butyl amine, is -2.51 KJ and -3.01 KJ from the data of the Japanese and the Hungarian workers respectively. We therefore redetermined the heats of mixing for the system

Table 16 : Heats of Mixing of n-Propyl alcohol--n-Butyl amine system at 25°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction of 1st component	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.1628	1.9896	0.0906	- 784.7	-8.661	- 9.523
2	0.4665	1.8721	0.2327	-1824.4	-7.840	-10.215
3	0.6602	1.7475	0.3150	-2378.7	-7.551	-11.023
4	0.7416	1.9101	0.3209	-2422.7	-7.550	-11.118
5	0.8205	1.6702	0.3742	-2724.8	-7.282	-11.635
6	0.9628	1.7178	0.4056	-2787.6	-6.873	-11.562
7	0.9094	1.3944	0.4425	-3017.7	-6.820	-12.232
8	0.9117	1.2287	0.4746	-3105.3	-6.543	-12.451
9	0.9485	1.2389	0.4828	-3083.1	-6.386	-12.347
10	1.4897	1.3511	0.5730	-3004.7	-5.244	-12.180
11	1.5967	1.0950	0.6396	-2829.1	-4.423	-12.273
12	1.5595	0.8206	0.6982	-2678.4	-3.836	-12.712
13	1.7424	0.7382	0.7418	-2313.3	-3.118	-12.080
14	1.7818	0.4650	0.8234	-1742.2	-2.116	-11.982
15	2.1635	0.2917	0.9003	-1009.1	-1.121	-11.237

Table 17 : Heats of Mixing of n-Propyl alcohol—n-Butyl amine system at 40°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction x_1	ΔH^m $(J.mole^{-1})$	$\Delta H^m/x_1$ $(KJ.mole^{-1})$	$\Delta H^m/x_1x_2$ $(KJ.mole^{-1})$
1	0.2637	2.0674	0.1344	-1160.2	-8.632	- 9.976
2	0.3563	2.0586	0.1740	-1393.9	-8.011	- 9.700
3	0.3360	1.2376	0.2484	-1910.8	-7.692	-10.234
4	0.5550	1.2595	0.3518	-2538.2	-7.215	-11.132
5	0.9123	1.4008	0.4420	-2796.6	-6.324	-11.336
6	0.9753	1.1198	0.5146	-2902.9	-5.641	-11.621
7	1.1808	1.0964	0.5673	-2742.3	-4.834	-11.170
8	0.9863	0.7200	0.6251	-2701.6	-4.322	-11.531
9	1.6055	0.8547	0.6957	-2470.7	-3.551	-11.671
10	1.7826	0.5765	0.7914	-1868.5	-2.361	-11.317
11	2.1210	0.4224	0.8594	-1410.4	-1.641	-11.675
12	2.2556	0.2539	0.9154	-963.4	-1.052	-12.447

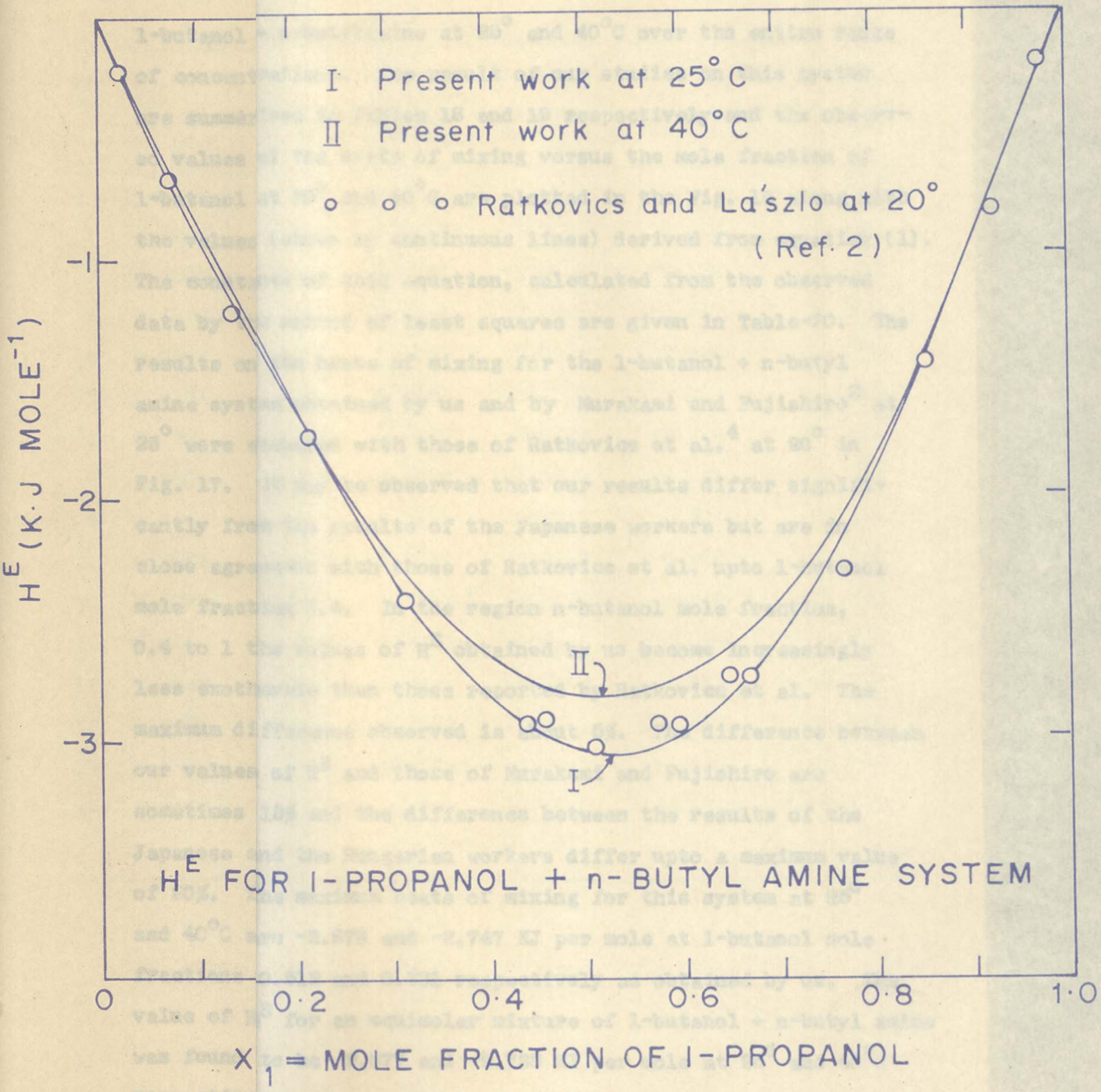

I Present work at 25° C
II Present work at 40° C
o o o Ratkovics and La´szlo at 20°
(Ref. 2)
-1
-2
-3
H^E (K.J MOLE^{-1})
II
I
H^E FOR 1-PROPANOL + n-BUTYL AMINE SYSTEM
0
0·2
0·4
0·6
0·8
1·0
X_1 = MOLE FRACTION OF 1-PROPANOL

Fig 15

1-butanol + n-butylamine at 25° and 40°C over the entire range of concentrations. The result of our studies on this system are summârised in Tables 18 and 19 respectively and the observed values of the heats of mixing versus the mole fraction of 1-butanol at 25° and 40°C are plotted in the Fig. 16 along with the values (shown by continuous lines) derived from equation (1). The constants of this equation, calculated from the observed data by the method of least squares are given in Table-20. The results on the heats of mixing for the 1-butanol + n-butyl amine system obtained by us and by Murakami and Fujishiro[3] at 25° were compared with those of Ratkovics et al.[4] at 20° in Fig. 17. It may be observed that our results differ significantly from the results of the Japanese workers but are in close agreement with those of Ratkovics et al. upto 1-butanol mole fraction 0.4. In the region n-butanol mole fraction, 0.4 to 1 the values of H^E obtained by us become increasingly less exothermic than those reported by Ratkovics et al. The maximum difference observed is about 5%. The difference between our values of H^E and those of Murakami and Fujishiro are sometimes 15% and the difference between the results of the Japanese and the Hungarian workers differ upto a maximum value of 20%. The maximum heats of mixing for this system at 25° and 40°C are -2.879 and -2.747 KJ per mole at 1-butanol mole fractions 0.512 and 0.531 respectively as obtained by us. The value of H^E for an equimolar mixture of 1-butanol + n-butyl amine was found to be -2.877 and -2.738 KJ per mole at 25° and 40°C respectively, as compared to the values 2.51 and 3.01 KJ per mole

Table 18 : Heats of Mixing of n-Butyl alcohol–n-Butyl amine system at 25°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction of 1st component	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.1736	2.0308	0.0778	-750.6	-9.649	-10.463
2	0.2603	1.8885	0.1197	-1098.6	-9.178	-10.426
3	0.4873	1.8045	0.2106	-1799.1	-8.547	-10.827
4	0.5907	1.5510	0.2732	-2199.1	-8.050	-11.076
5	0.7705	1.5300	0.3320	-2460.2	-7.410	-11.093
6	0.9721	1.1495	0.4549	-2862.9	-6.293	-11.545
7	1.1895	1.1815	0.4984	-2905.4	-5.829	-11.621
8	1.1682	1.0822	0.5158	-2788.3	-5.406	-11.165
9	1.3852	1.0227	0.5784	-2888.7	-4.994	-11.845
10	1.3288	0.8852	0.5970	-2830.4	-4.741	-11.764
11	1.9440	1.0255	0.6516	-2659.8	-4.082	-13.835
12	1.8940	0.7860	0.7039	-2286.6	-3.249	-10.973
13	2.0680	0.5866	0.7767	-1947.1	-2.507	-11.227
14	1.7226	0.3274	0.8385	-1640.7	-1.957	-12.118
15	2.0410	0.1703	0.9220	- 748.8	-0.8121	-10.412

Table 19 : Heats of Mixing of n-Butyl alcohol – n-Butyl amine System at 40°C

Sr. No.	Wt. of 1st component in gm.	Wt. of 2nd component in gms.	Mole fraction x_1	ΔH^m (J.mole^{-1})	$\Delta H^m/x_1$ (KJ.mole^{-1})	$\Delta H^m/x_1x_2$ (KJ.mole^{-1})
1	0.1775	2.2320	0.0728	- 625.3	-8.589	- 9.264
2	0.2646	2.2719	0.1031	- 878.0	-8.516	- 9.495
3	0.3025	2.0957	0.1246	-1103.4	-8.856	-10.116
4	0.4735	1.9964	0.1896	-1549.6	-8.176	-10.085
5	0.7038	1.8845	0.2694	-2015.1	-7.480	-10.254
6	0.7668	1.9720	0.2774	-1944.6	-7.010	- 9.701
7	0.7245	1.5147	0.3207	-2167.2	-6.758	- 9.948
8	0.8071	1.2611	0.3871	-2420.0	-6.252	-10.200
9	0.9817	1.5106	0.3907	-2477.9	-6.342	-10.409
10	0.7563	1.0040	0.4264	-2681.4	-6.288	-10.963
11	1.0601	1.1119	0.4847	-2787.8	-5.752	-11.161
12	1.0577	1.0414	0.5005	-2732.6	-5.460	-10.993
13	0.8725	1.0722	0.5480	-2802.1	-5.113	-11.312
14	1.1688	0.8504	0.5756	-2778.5	-4.827	-11.374
15	1.6532	0.9295	0.6370	-2585.2	-4.058	-11.180
16	1.7952	0.6919	0.7191	-2412.6	-3.355	-11.944
17	1.8942	0.7130	0.7238	-2120.7	-2.930	-10.609
18	2.0622	0.6018	0.7718	-1974.1	-2.558	-11.209
19	2.3040	0.3726	0.8591	-1464.2	-1.704	-12.096
20	2.4785	0.2191	0.9178	- 768.5	-0.837	-10.187

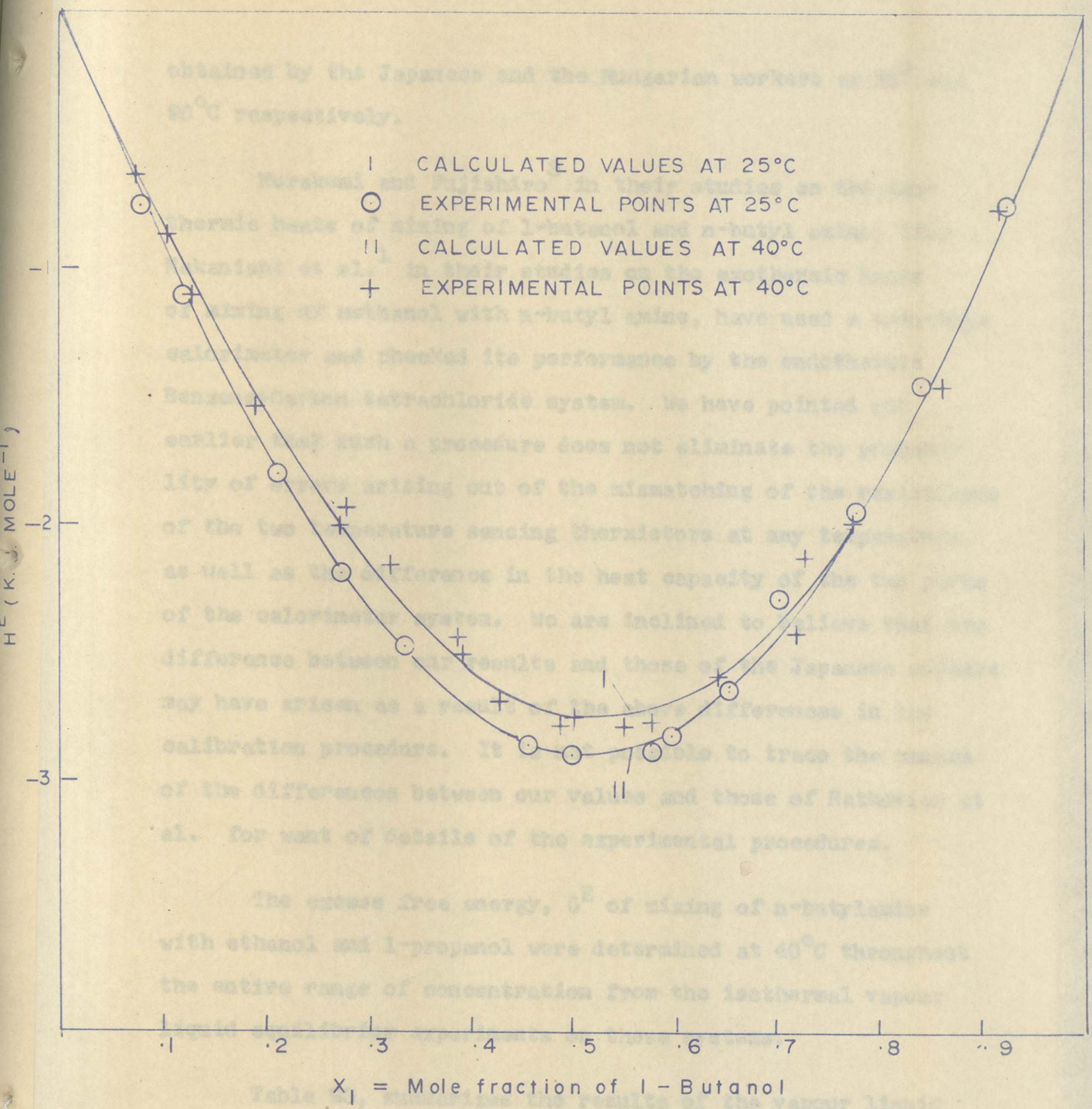


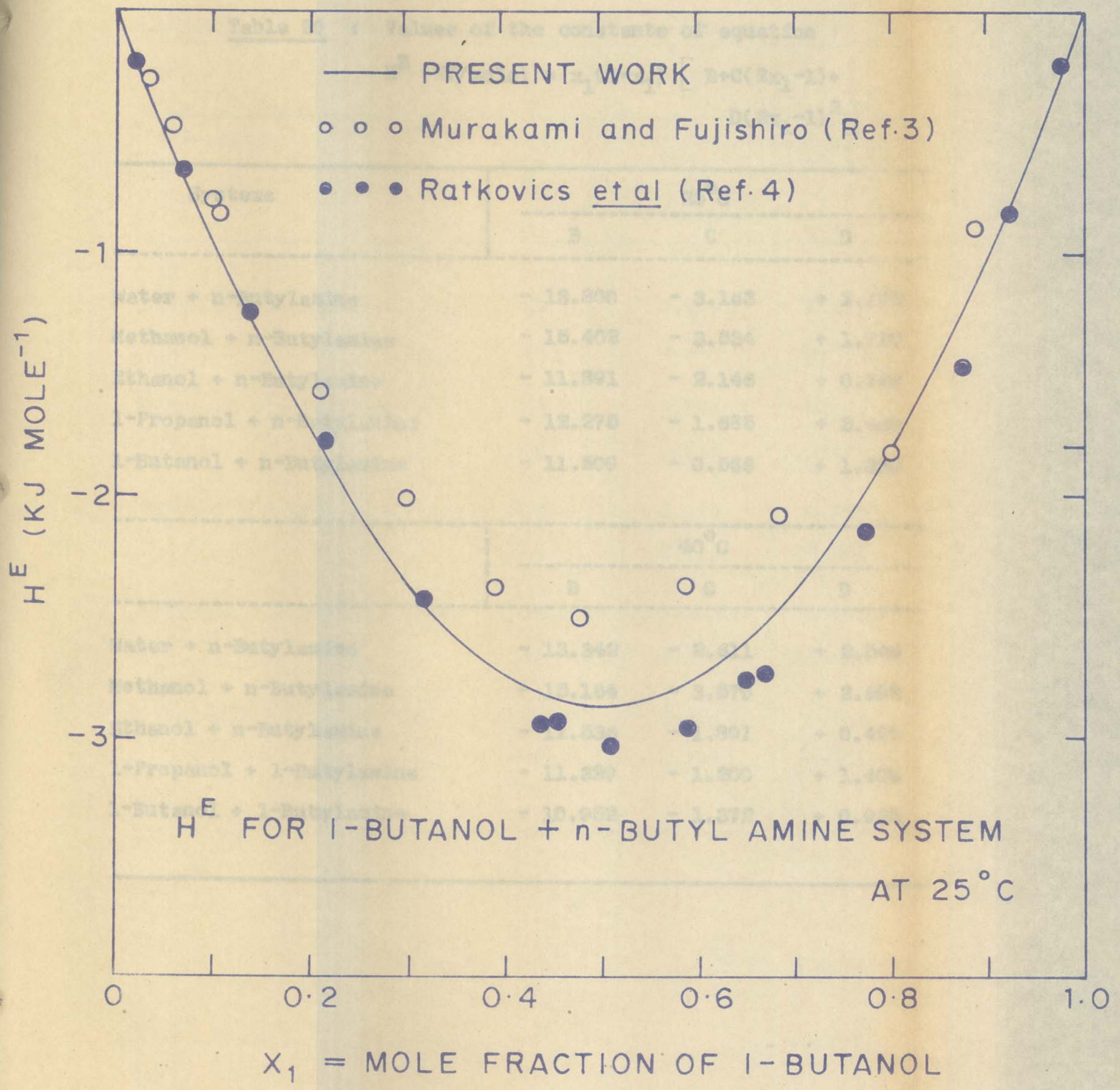
FIG. 16. HEATS OF MIXING OF 1-BUTANOL + n-BUTYLAMINE SYSTEM

obtained by the Japanese and the Hungarian workers at 25° and 20°C respectively.

Murakami and Fujishiro[3] in their studies on the exothermic heats of mixing of 1-butanol and n-butyl amine, like Nakanishi et al.[1] in their studies on the exothermic heats of mixing of methanol with n-butyl amine, have used a twin-type calorimeter and checked its performance by the endothermic Benzene+Carbon tetrachloride system. We have pointed out earlier that such a procedure does not eliminate the probability of errors arising out of the mismatching of the resistances of the two temperature sensing thermistors at any temperature, as well as the difference in the heat capacity of the two parts of the calorimeter system. We are inclined to believe that the difference between our results and those of the Japanese workers may have arisen as a result of the above differences in the calibration procedure. It is not possible to trace the causes of the differences between our values and those of Ratkovics et al. for want of details of the experimental procedures.

The excess free energy, G^E of mixing of n-butylamine with ethanol and 1-propanol were determined at 40°C throughout the entire range of concentration from the isothermal vapour liquid equilibrium experiments on these systems.

Table 23, summarizes the results of the vapour liquid equilibrium studies at 40°C for the ethanol + n-butylamine



—— PRESENT WORK
○ ○ ○ Murakami and Fujishiro (Ref·3)
● ● ● Ratkovics et al (Ref·4)
-1
-2
-3
H^E (KJ MOLE^{-1})
H^E FOR 1-BUTANOL + n-BUTYL AMINE SYSTEM AT 25 °C
0
0·2
0·4
0·6
0·8
1.0
X_1 = MOLE FRACTION OF 1-BUTANOL

Fig. 17

Table 20 : Values of the constants of equation :

$$H^E\ (\mathrm{KJ/mole}) = x_1(1-x_1)\left[B+C(2x_1-1)+D(2x_1-1)^2\right]$$

Systems	25°C		
	B	C	D
Water + n-Butylamine	- 13.800	- 3.163	+ 3.172
Methanol + n-Butylamine	- 15.402	- 3.534	+ 1.720
Ethanol + n-Butylamine	- 11.891	- 2.146	+ 0.740
1-Propanol + n-Butylamine	- 12.275	- 1.685	+ 3.469
1-Butanol + n-Butylamine	- 11.509	- 0.566	+ 1.335

	40°C		
	B	C	D
Water + n-Butylamine	- 13.342	- 2.611	+ 2.546
Methanol + n-Butylamine	- 15.164	- 3.570	+ 2.698
Ethanol + n-Butylamine	- 11.536	- 1.891	+ 0.427
1-Propanol + 1-Butylamine	- 11.329	- 1.200	+ 1.406
1-Butanol + 1-Butylamine	- 10.952	- 1.372	+ 0.935

Table 21 : The Maximum Value of H^E and position of Maxima

Systems	Temperature ^oC	Maximum value of H^E KJ/mole	Corresponding value of x_1
Water + n-Butylamine	25	- 3.476	0.522
	40	- 3.361	0.547
Methanol + n-Butylamine	25	- 3.900	0.555
	40	- 3.834	0.556
Ethanol + n-Butylamine	25	- 2.995	0.545
	40	- 2.901	0.551
1-Propanol + n-Butylamine	25	- 3.073	0.534
	40	- 2.839	0.526
1-Butanol + n-Butylamine	25	- 2.879	0.512
	40	- 2.747	0.531

Table 22 : Percentage deviation for 5 degrees decrease in temperature below 25°C

System	Mole fraction	ΔH^m at 25°C	ΔH^m at 40°C	Deviation for 5° decrease	Percentage
Ethanol— n-Butylamine	0.2	-1654	-1640	- 5	0.3 %
	0.4	-2744	-2674	-23	0.8 %
	0.5	-2973	-2884	-30	1 %
	0.6	-2950	-2855	-31	1 %
	0.8	-2066	-2003	-21	1 %
Propanol— n-Butylamine	0.2	-1602	-1616	+ 5	0.3 %
	0.4	-2831	-2648	-61	2.2 %
	0.5	-3069	-2832	-78	2.6 %
	0.6	-2993	-2763	-77	2.6 %
	0.8	-1926	-1854	-24	1.3 %
1-Butanol— n-Butylamine	0.2	-1710	-1567	-48	2.7 %
	0.4	-2722	-2554	-56	2.1 %
	0.5	-2877	-2738	-46	1.8 %
	0.6	-2777	-2685	-31	1.1 %
	0.8	-1819	-1830	+ 4	0.2 %

binary mixture. In the first three columns, the compositions x_1 and y_1 of the equilibrium liquid and vapour phases respectively and the total pressure P are listed. The activity coefficients $\log \gamma_1$ and $\log \gamma_2$ determined by equations (2) and (3) (p.52) are given in columns 4 and 5 respectively. The excess Gibb's free energy

$$G^E = (x_1 \ln \gamma_1 + x_2 \ln \gamma_2) RT \qquad .... \quad (2)$$

are given in the last column where x_1 is the mole fraction of n-butyl amine in the equilibrium liquid phase and $x_2 = (1-x_1)$. The x-y diagram and the P-x-y plots for the system n-butyl amine + ethanol, shown in Figs. 8 and 9 respectively indicate the presence of an azeotrope at 0.32 mole fraction of n-butylamine. No work on the vapour liquid equilibria for this system has so far been reported in the literature. The thermodynamic consistency of the vapour liquid equilibrium results was checked by the symmetrical area test. The plots of $\log \gamma_1/\gamma_2$ vs x_1 are shown in Fig. 20. The absolute value of the integral $\int_0^1 \log(\gamma_1/\gamma_2) dx_1$ over the ranges for which the integral is positive and negative are 51.0 cm^2 and 49.0 cm^2. This indicates a percentage deviation of 2%. The plot of G^E versus x_1, the mole fraction of n-butyl amine in the liquid phase is shown in Fig. 24. It may be observed that the excess free energy of mixing is negative throughout the concentration range ~~of~~ and the minimum value of G^E is found to be -835 Joules/mole at 0.46 mole fraction of the amine.

Table 23 : Excess Free Energy of Mixing for n-BuNH$_2$(1) – Ethyl alcohol(2) System at 40°C

Sr. No.	Mole fraction of 1st component in liquid x_1	Mole fraction of n-Butylamine in vapour y_1	Total solution vapour pressure P in mm.	Log γ_1	log γ_2	G^E in J.mole^{-1}
1	0.1202	0.0708	123.24	-0.4093	-0.0123	-355.19
2	0.2037	0.1603	118.30	-0.3011	-0.0307	-507.63
3	0.2939	0.2838	115.53	-0.2226	-0.0577	-628.23
4	0.3835	0.4263	115.99	-0.1598	-0.0933	-703.04
5	0.4409	0.5224	119.45	-0.1195	-0.1177	-701.26
6	0.5355	0.6641	128.47	-0.0685	-0.1586	-653.03
7	0.6020	0.7451	136.66	-0.0429	-0.1847	-587.88
8	0.6970	0.8422	146.56	-0.0233	-0.2441	-535.21
9	0.8214	0.9312	162.60	-0.0065	-0.3302	-380.58
10	0.8864	0.9640	172.19	-0.0001	-0.3901	-262.81
11	1.0000	1.0000	187.50*	0	0	0
12	0	0	134+	0	0	0

* Pure n-butylamine

\+ Pure ethanol

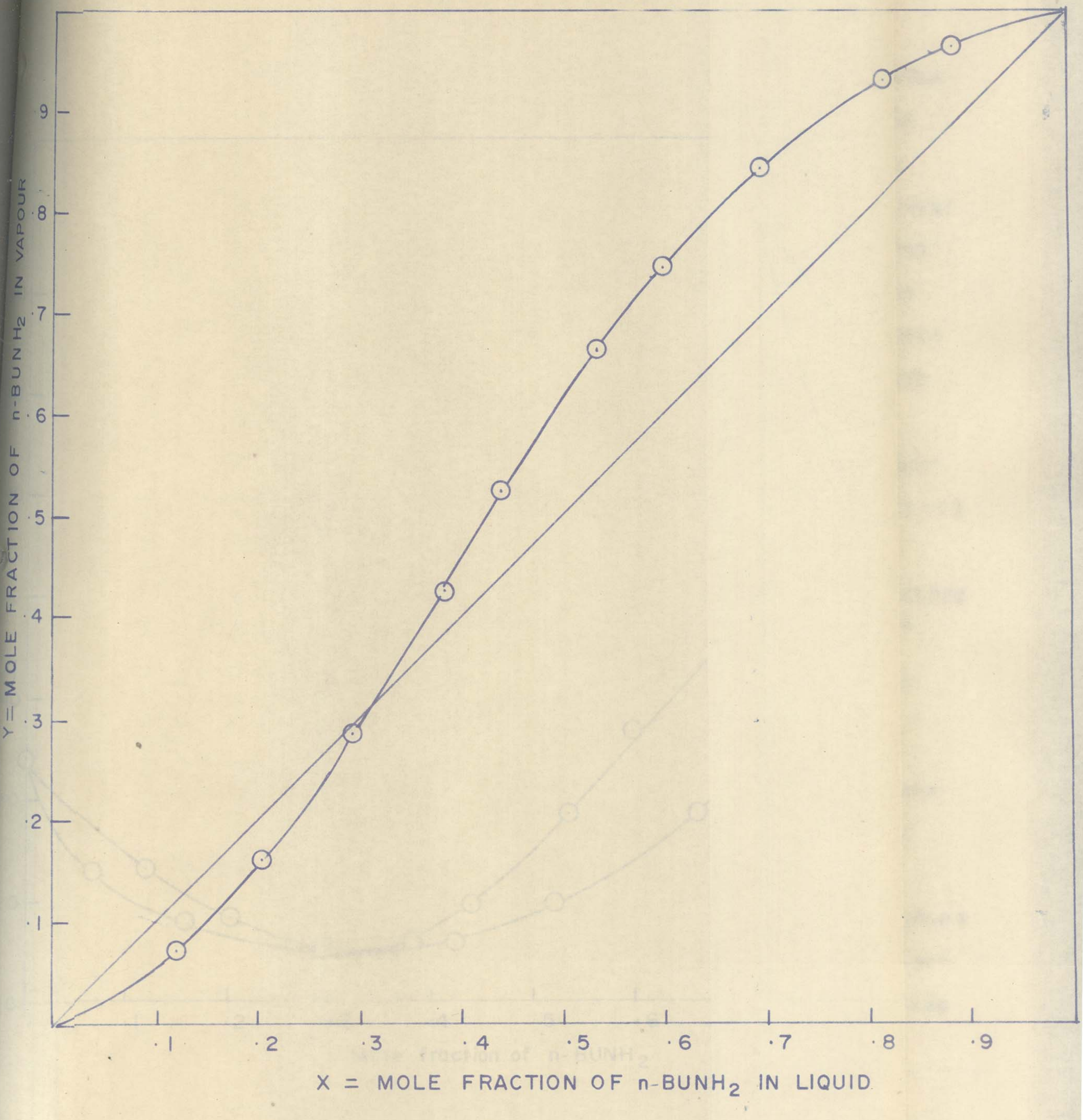


FIG 18: X–Y DIAGRAM ; n-BUNH$_2$ + EtOH SYSTEM AT 40°C

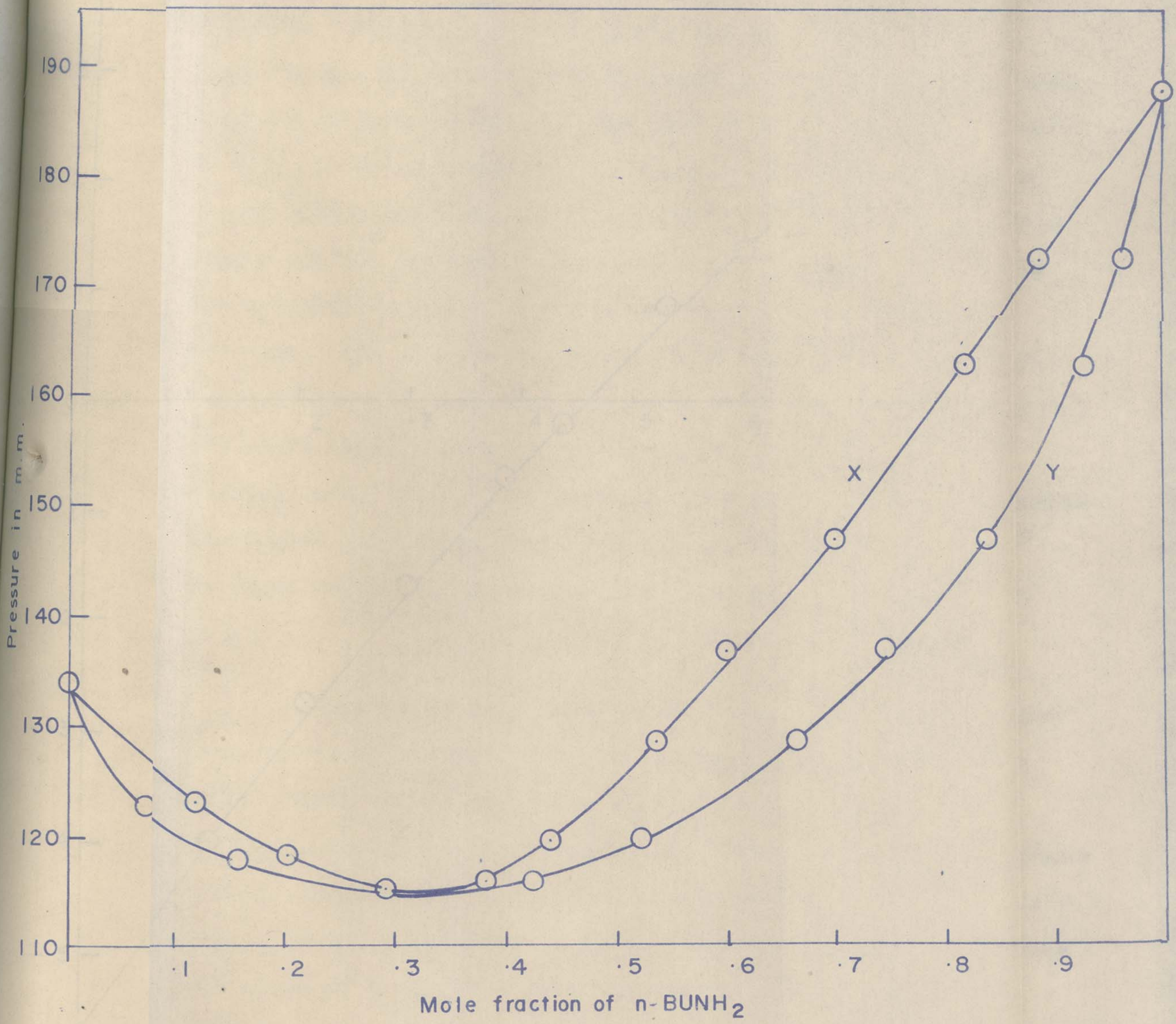


FIG 19. P-X,Y DIAGRAM FOR n-BUNH$_2$+ EtOH SYSTEM AT 40°C

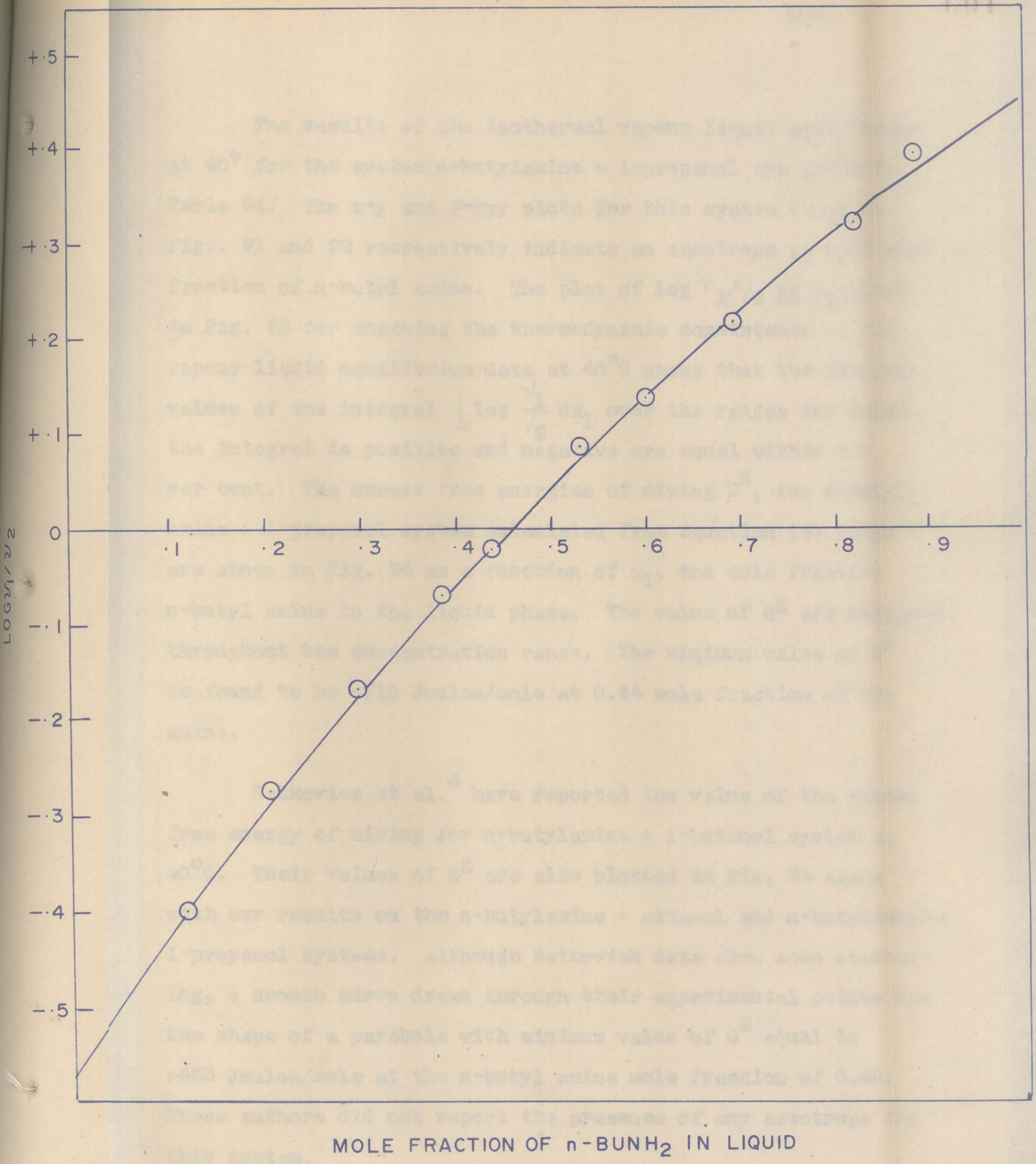


FIG 20 CONSISTENCY TEST : n-BUNH$_2$+ EtOH SYSTEM AT 40°C

The results of the isothermal vapour liquid equilibrium at 40^{o} for the system n-butylamine + 1-propanol are given in Table 24. The x-y and P-x,y plots for this system shown in Figs. 21 and 22 respectively indicate an azeotrope at 0.09 mole fraction of n-butyl amine. The plot of log γ_1/γ_2 vs x_1 given in Fig. 23 for checking the thermodynamic consistency of the vapour liquid equilibrium data at 40^{o}C shows that the absolute values of the integral $\int_0^1 \log \frac{\gamma_1}{\gamma_2} dx_1$ over the ranges for which the integral is positive and negative are equal within 2.9 per cent. The excess free energies of mixing G^E, for n-butylamine + 1-propanol system calculated from equation (6) (page 53) are shown in Fig. 24 as a function of x_1, the mole fraction n-butyl amine in the liquid phase. The value of G^E are negative throughout the concentration range. The minimum value of G^E is found to be -710 Joules/mole at 0.44 mole fraction of the amine.

Ratkovics et al.[4] have reported the value of the excess free energy of mixing for n-butylamine + 1-butanol system at 40^{o}C. Their values of G^E are also plotted in Fig. 24 along with our results on the n-butylamine + ethanol and n-butylamine + 1-propanol systems. Although Ratkovics data show some scattering, a smooth curve drawn through their experimental points has the shape of a parabola with minimum value of G^E equal to -455 Joules/mole at the n-butyl amine mole fraction of 0.48. Those authors did not report the presence of any azeotrope for this system.

Table 24 : Excess free energy of mixing for n-Butylamine(1)-n-Propyl alcohol(2) System at 40°C

Sr. No.	Mole fraction of n-BuNH$_2$ in liquid x_1	Mole fraction of n-BuNH$_2$ in vapour y_1	Total solution vapour pressure P in mm.	log γ_1	log γ_2	G^E J.mole^{-1}
1	0.0404	0.0383	52.37	-0.5723	-0.0051	-167.95
2	0.1139	0.1304	52.50	-0.4894	-0.0131	-403.84
3	0.2329	0.3474	56.29	-0.3444	-0.0450	-687.94
4	0.2766	0.4367	60.11	-0.2913	-0.0551	-720.32
5	0.3880	0.6426	70.59	-0.2010	-0.1104	-872.75
6	0.4900	0.7850	87.09	-0.1247	-0.1615	-860.27
7	0.5890	0.8785	105.41	-0.0736	-0.2335	-839.35
8	0.6897	0.9315	124.40	-0.0455	-0.2892	-726.26
9	0.7300	0.9510	133.77	-0.0299	-0.3430	-686.21
10	0.7842	0.9682	145.20	-0.0180	-0.3984	-600.34
11	0.8494	0.9818	158.27	-0.0083	-0.4474	-446.30
12	0.8811	0.9870	164.15	-0.0073	-0.4757	-377.70
13	1.0000	1.0000	187.50*	0	-	0
14	0	0	53.1‡	-	-	-

* Pure n-Butylamine

‡ Pure 1-Propanol

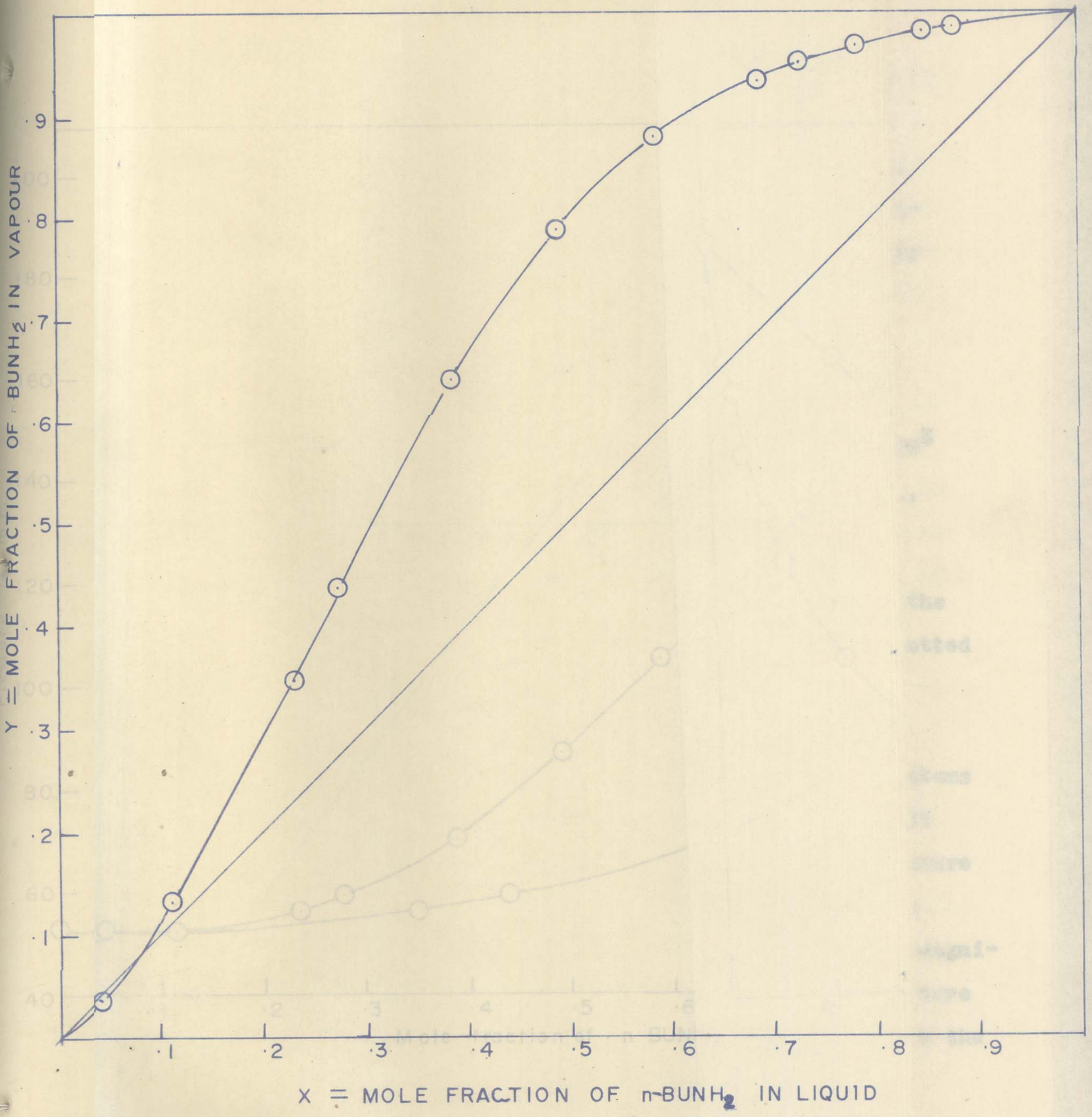


FIG 21. X–Y DIAGRAM: n-$BUNH_2$ + 1-PrOH SYSTEM AT 40°C

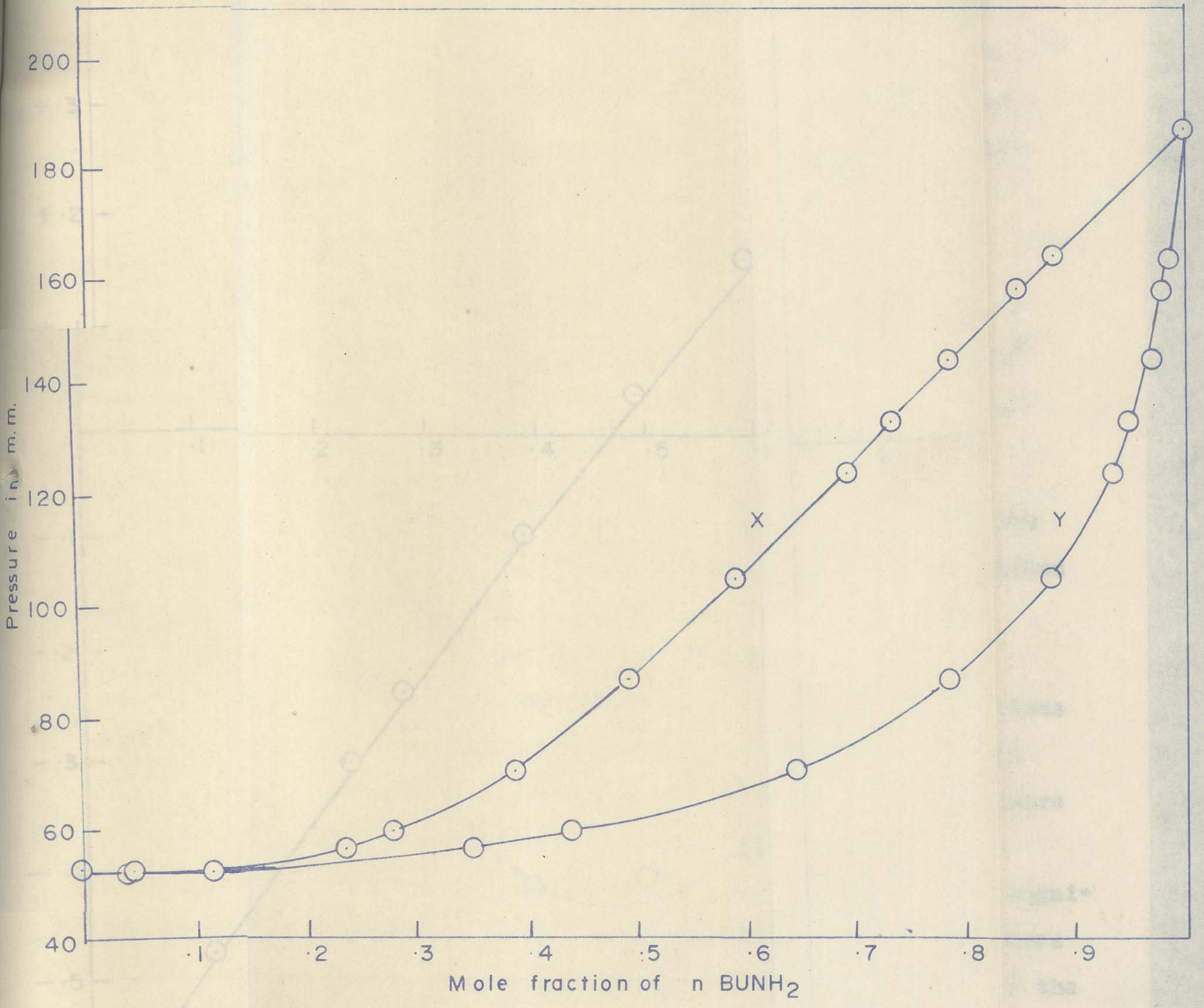


FIG 22. P-X,Y DIAGRAM FOR n-BUNH$_2$+1-PrOH SYSTEM AT 40°C

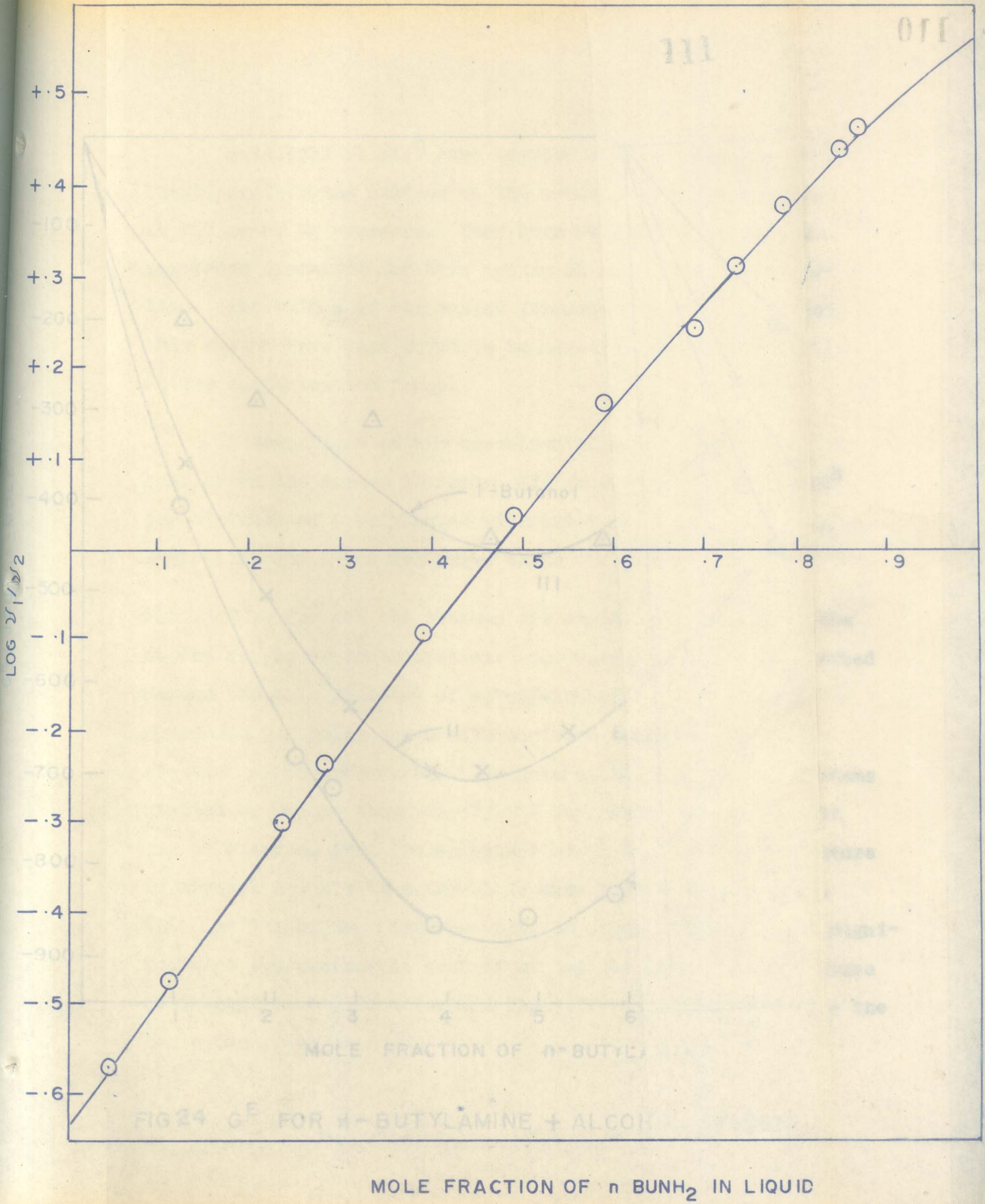


FIG 23. CONSISTENCY TEST: n-BUNH$_2$ + 1-PrOH SYSTEM AT 40°C

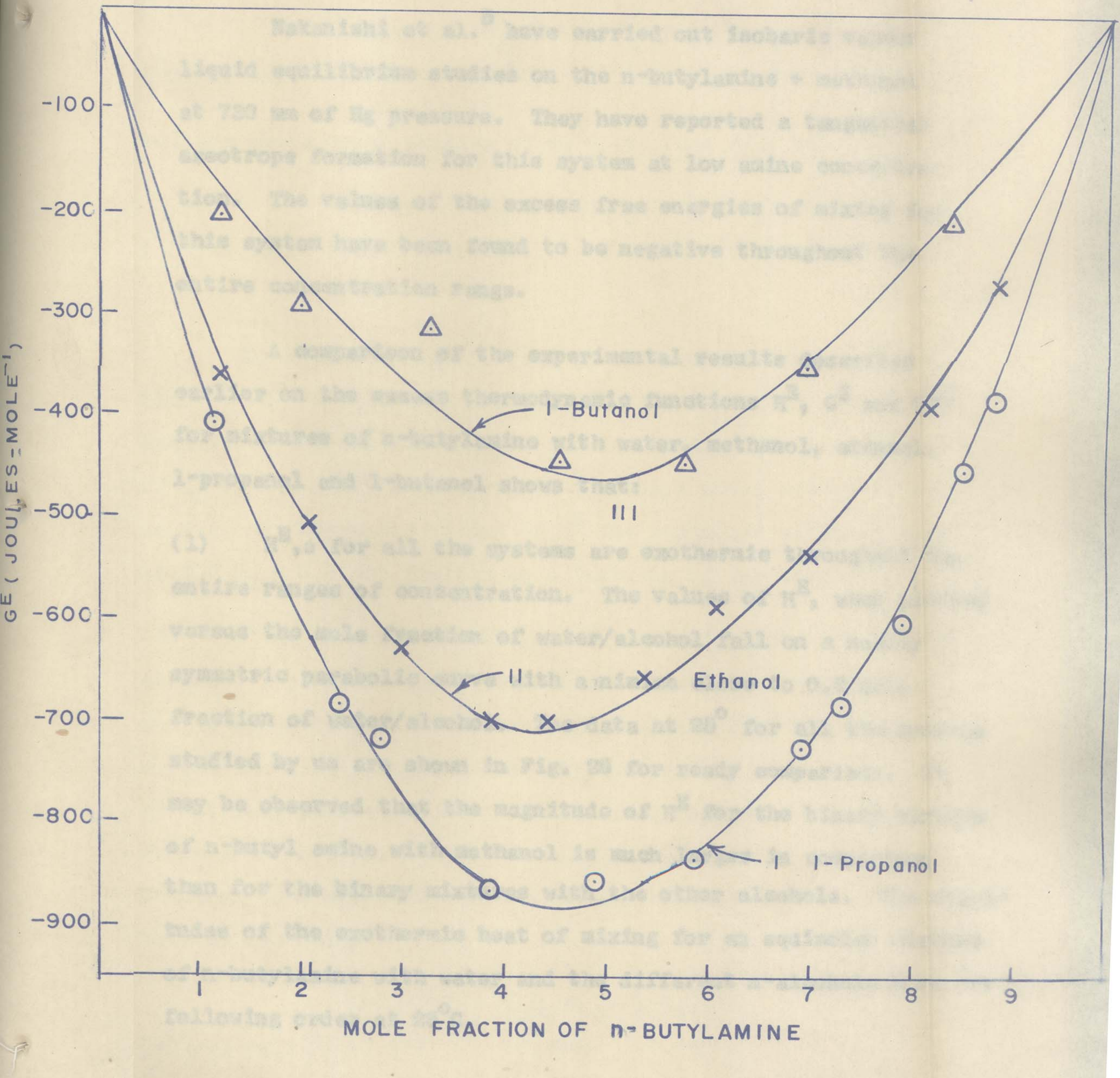


FIG 24. G^E FOR n-BUTYLAMINE + ALCOHOL SYSTEMS AT 40°C

Nakanishi et al.[5] have carried out isobaric vapour liquid equilibrium studies on the n-butylamine + methanol at 730 mm of Hg pressure. They have reported a tangential azeotrope formation for this system at low amine concentration. The values of the excess free energies of mixing for this system have been found to be negative throughout the entire concentration range.

A comparison of the experimental results described earlier on the excess thermodynamic functions H^E, G^E and TS^E for mixtures of n-butylamine with water, methanol, ethanol, 1-propanol and 1-butanol shows that:

(1) H^E,s for all the systems are exothermic throughout the entire ranges of concentration. The values of H^E, when plotted versus the mole fraction of water/alcohol fall on a nearly symmetric parabolic curve with a minima close to 0.5 mole fraction of water/alcohol. The data at 25° for all the systems studied by us are shown in Fig. 28 for ready comparison. It may be observed that the magnitude of H^E for the binary mixture of n-butyl amine with methanol is much larger in comparison than for the binary mixtures with the other alcohols. The magnitudes of the exothermic heat of mixing for an equimolar mixture of n-butylamine with water and the different n-alcohols have the following order at 25°C.

Water $<$ CH_3OH $>$ 1-C_3H_7OH $>$ C_2H_5OH $>$ 1-C_4H_9OH
($-H^E$/KJ mole^{-1})(3.450) (3.850) (3.069) (2.973) (2.877)
..... (a)

but the above order changes at 40°C to (see Fig. 38)

Water $<$ CH_3OH $>$ C_2H_5OH $>$ 1-C_3H_7OH $>$ 1-C_4H_9OH
($-H^E$/KJ mole^{-1})(3.445) (3.791) (2.973) (2.832) (2.738)
..... (b)

The effect of an increase in the temperature on H^E shows that $\frac{d}{dT}(H^E) = C_p^E$, is a positive quantity although small in magnitude, for all the systems studied by us. The largest value of C_p^E is observed for 1-propanol + n-butyl amine system as shown in Fig. 29, where the values of H^E for equimolar mixtures as well as for $x_1 = 0.7$ are plotted as a function of the temperature.

(2) G^E at 40°C for the binary mixtures of n-butyl amine with ethanol, 1-propanol and 1-butanol are negative throughout the entire range of concentrations. The values of G^E when plotted versus the mole fraction of n-butyl amine fall also on nearly symmetrical parabolic curves with maxima close to the 0.5 mole fraction of n-butyl amine. The magnitude of $-G^E$ for equimolar mixtures of n-butylamine with ethanol, 1-propanol and 1-butanol follows the order :

1-C_3H_7OH $>$ C_2H_5OH $>$ 1-C_4H_9OH
($-G^E$/KJ mole^{-1}) (0.877) (0.690) (0.450)
.... (c)

The values of TS^E at 40°C of these systems, calculated from relations $TS^E = H^E - G^E$, when plotted versus the mole fraction of alcohol shown in Figs. 25, 26 and 27 also fall on parabolic curves with minima close to 0.5 mole fraction of alcohols. The values of TS^E are negative throughout the entire concentration range and their magnitude for equimolar mixtures of the amine + alcohol follows the order :

	$1\text{-}C_4H_9OH >$	$C_2H_5OH >$	$1\text{-}C_3H_7OH$
$(-TS^E/KJ\ mole^{-1})$	(2.29)	(2.28)	(1.95)

.... (d)

(3) the values of the thermodynamic excess properties for the systems where both the values of G^E and H^E have been determined are in the following order :

$$-H^E > -TS^E > -G^E \quad \text{and} \quad G^E < 0 \qquad \text{.... (e)}$$

According to Ott et al.[6] and McKinnon and Williamson[7] the positive excess heat capacity for a binary mixtures shows the existence of a specific attractive interaction between the solute and the solvent molecules. The positive excess heat capacities for binary mixtures of n-butylamine with n-alcohols/water coupled with pronounced exothermic heats of mixing may therefore be taken as an evidence of complex formation between water/alcohol and n-butylamine molecules. The symmetry of the H^E, TS^E and G^E curves (Figs. 25, 26 and 27) and the V^E (Ref.8) curves (Fig. 30) with minima at about x = 0.5, further suggests that the interaction in all these cases is mainly of 1:1 type, although the presence of more complicated interactions $A_i\ B_j$ (A = Alcohol, B = Amine) cannot be ruled out.

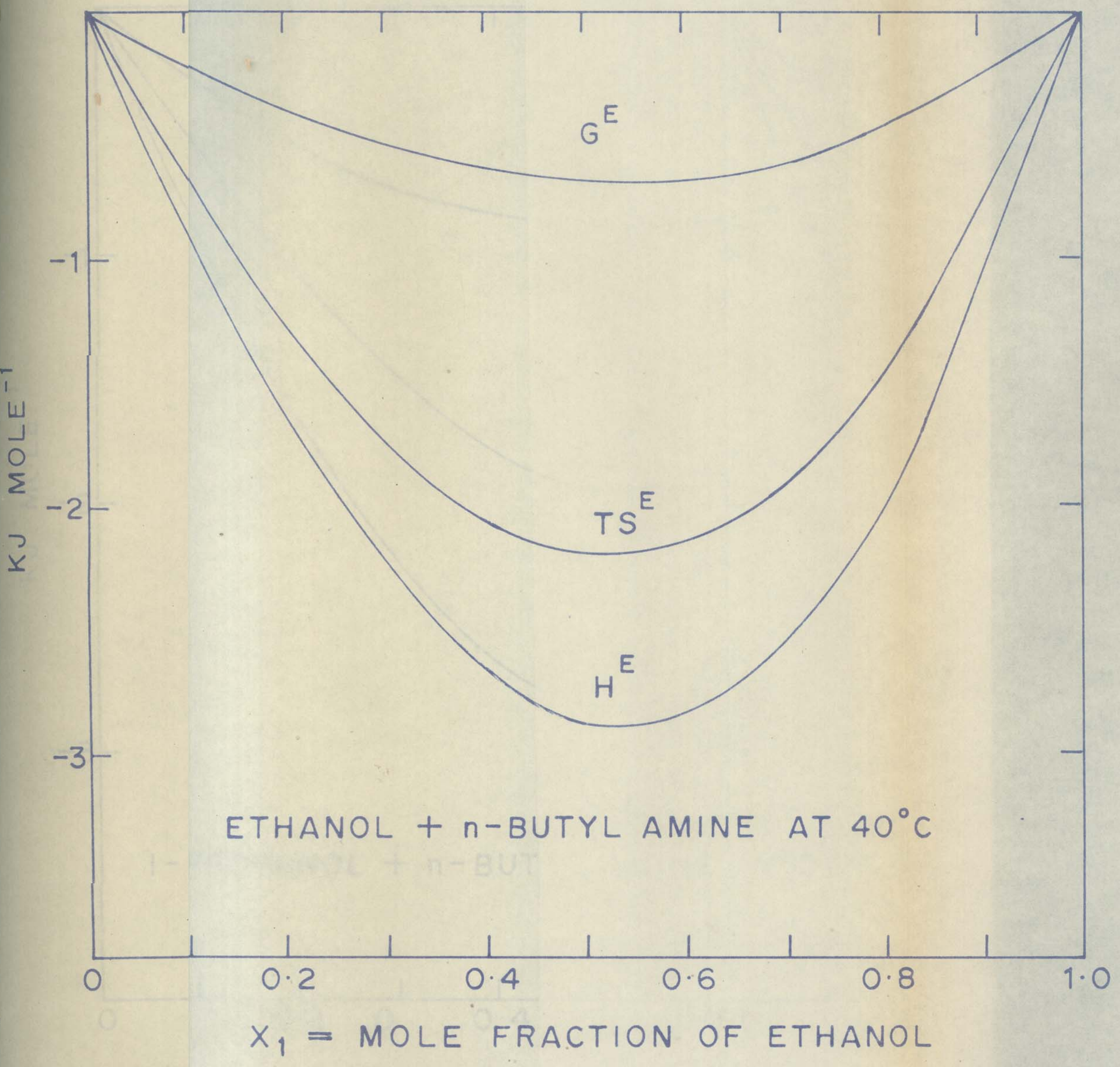

G^E
TS^E
H^E
ETHANOL + n-BUTYL AMINE AT 40°C
KJ MOLE^{-1}
-1
-2
-3
0
0·2
0·4
0·6
0·8
1·0
X_1 = MOLE FRACTION OF ETHANOL

Fig. 25

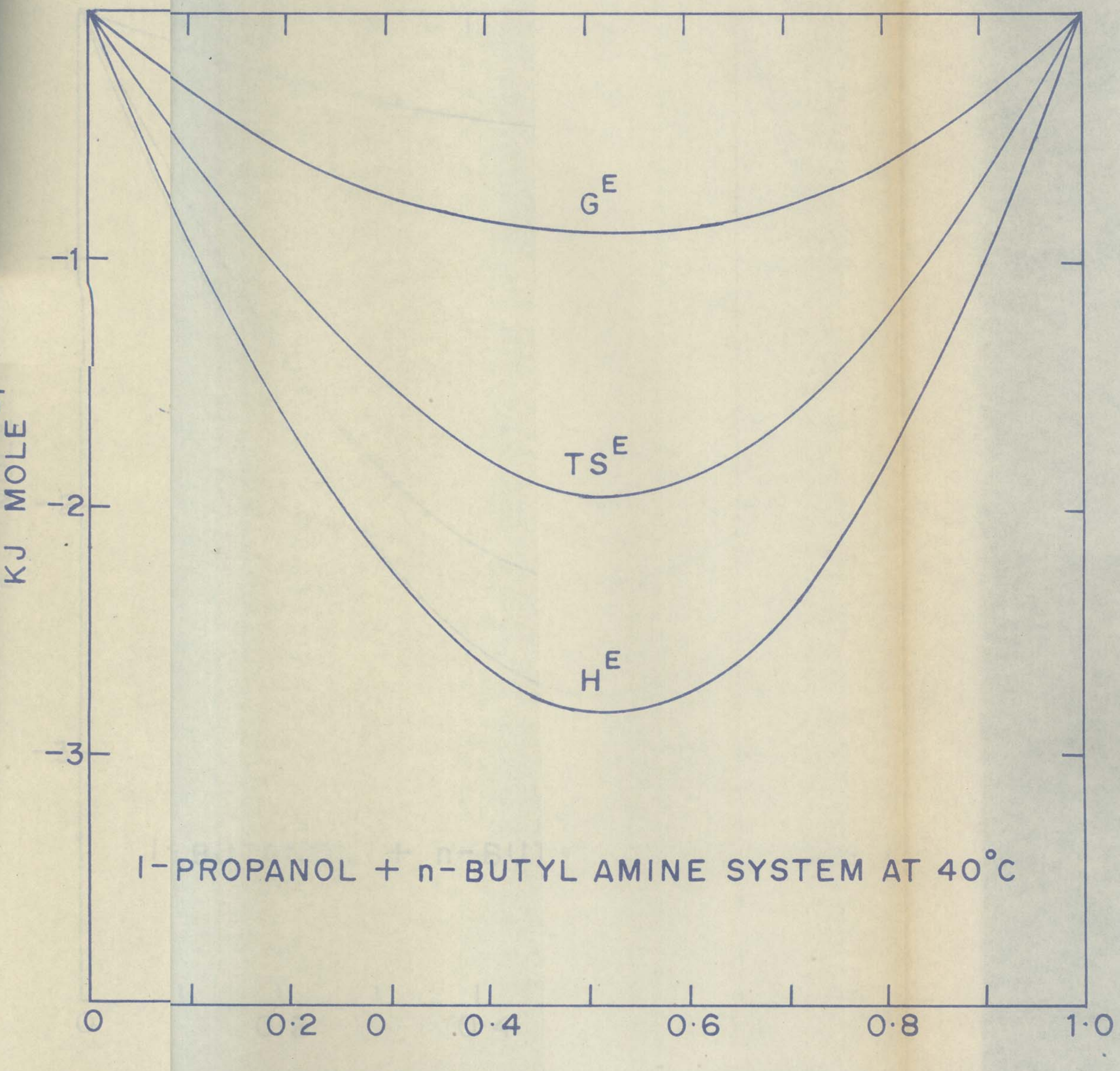

G^E
TS^E
H^E
-1
-2
-3
KJ MOLE^{-1}
1-PROPANOL + n-BUTYL AMINE SYSTEM AT 40°C
0
0·2
0
0·4
0·6
0·8
1·0
X_1 = MOLE FRACTION OF 1-PROPANOL

Fig. 26

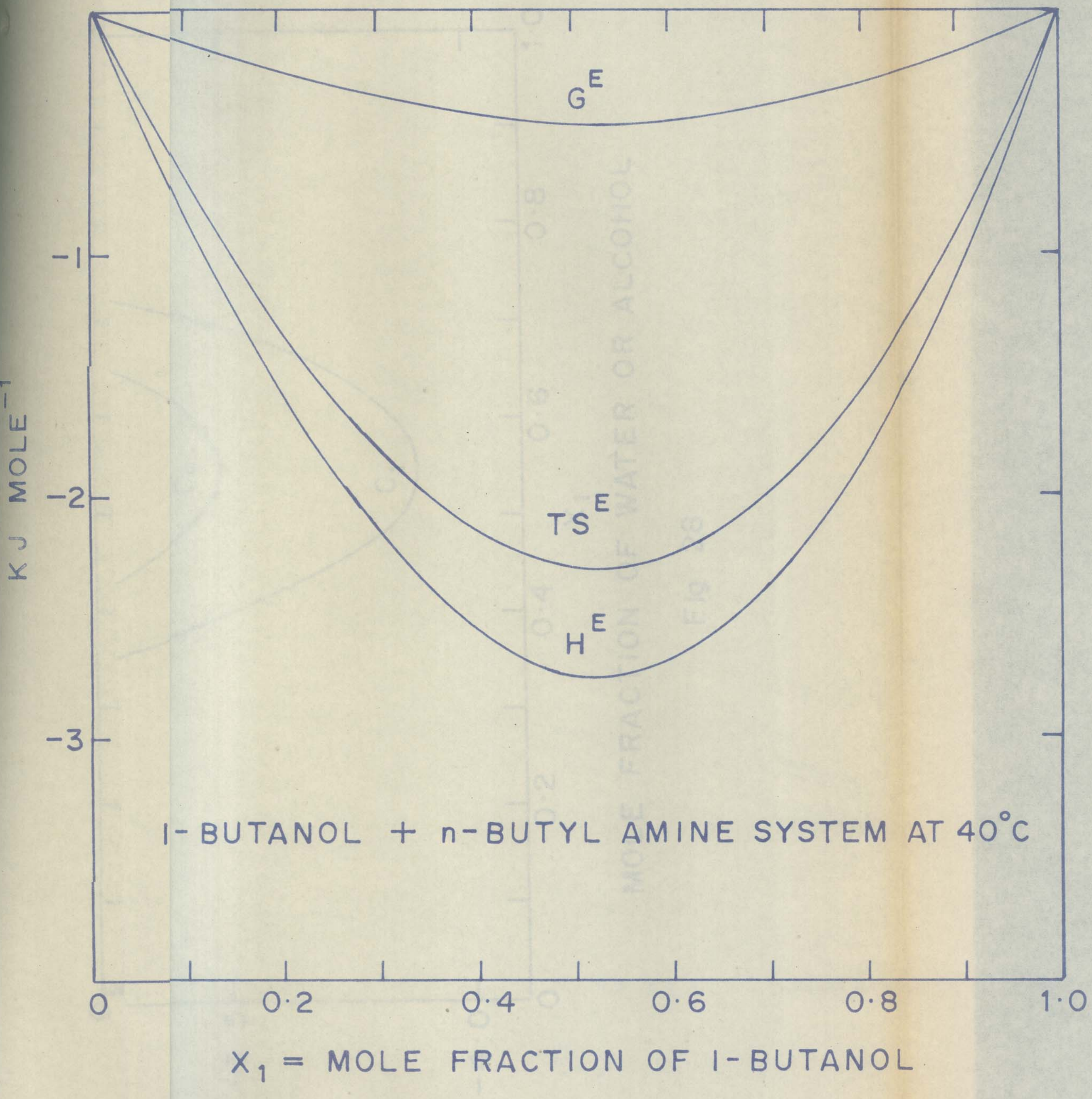

G^E
TS^E
H^E
-1
-2
-3
K J MOLE^-1
1-BUTANOL + n-BUTYL AMINE SYSTEM AT 40°C
0
0·2
0·4
0·6
0·8
1·0
X_1 = MOLE FRACTION OF 1-BUTANOL

Fig. 27

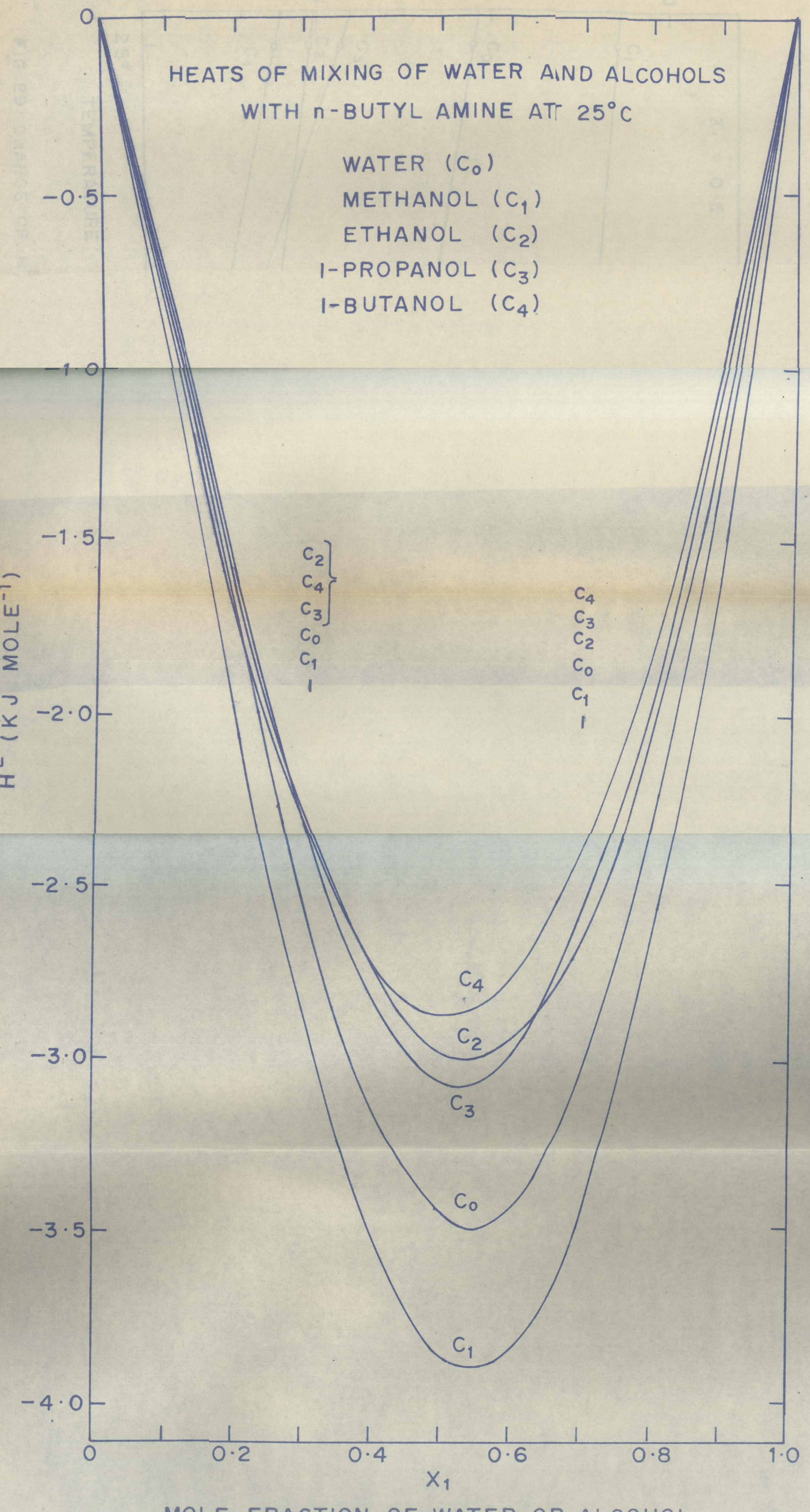

HEATS OF MIXING OF WATER AND ALCOHOLS
WITH n-BUTYL AMINE AT 25°C
WATER (C_0)
METHANOL (C_1)
ETHANOL (C_2)
1-PROPANOL (C_3)
1-BUTANOL (C_4)
C_2
C_4
C_3
C_0
C_1
1
C_4
C_3
C_2
C_0
C_1
1
C_4
C_2
C_3
C_0
C_1
0
-0·5
-1·0
-1·5
-2·0
-2·5
-3·0
-3·5
-4·0
H^E (KJ MOLE^{-1})
0
0·2
0·4
0·6
0·8
1·0
X_1
MOLE FRACTION OF WATER OR ALCOHOL

Fig 28

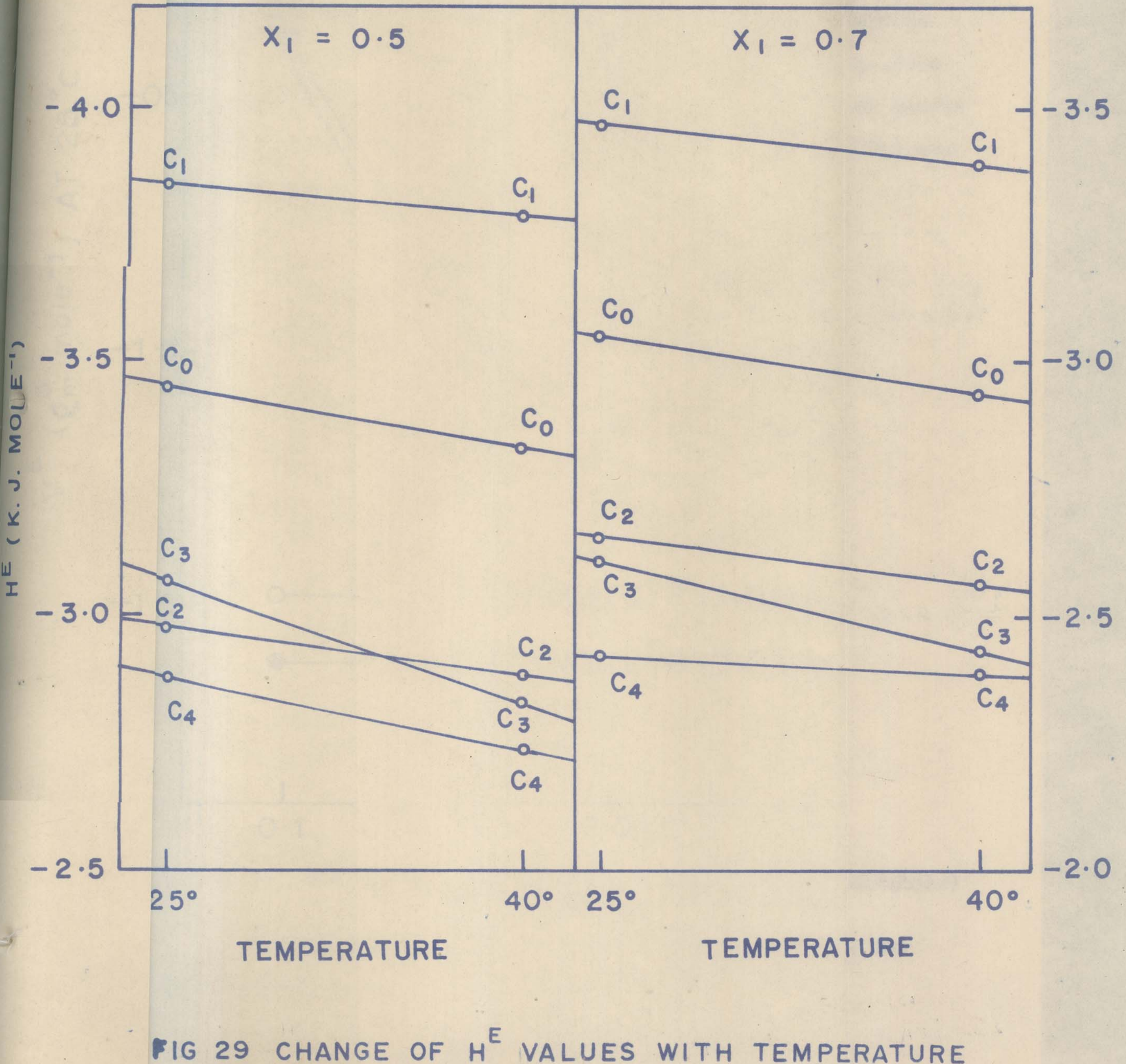
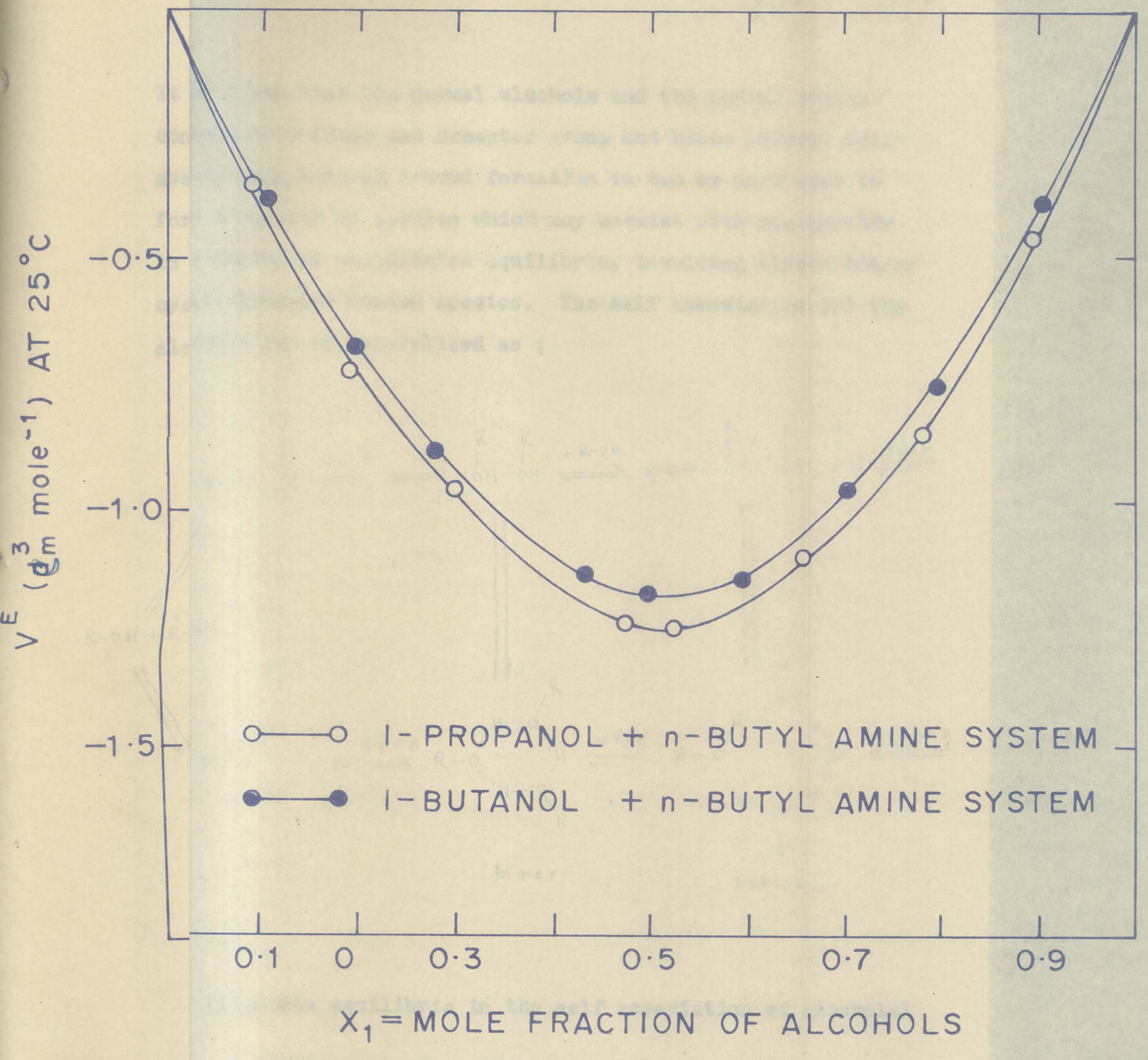


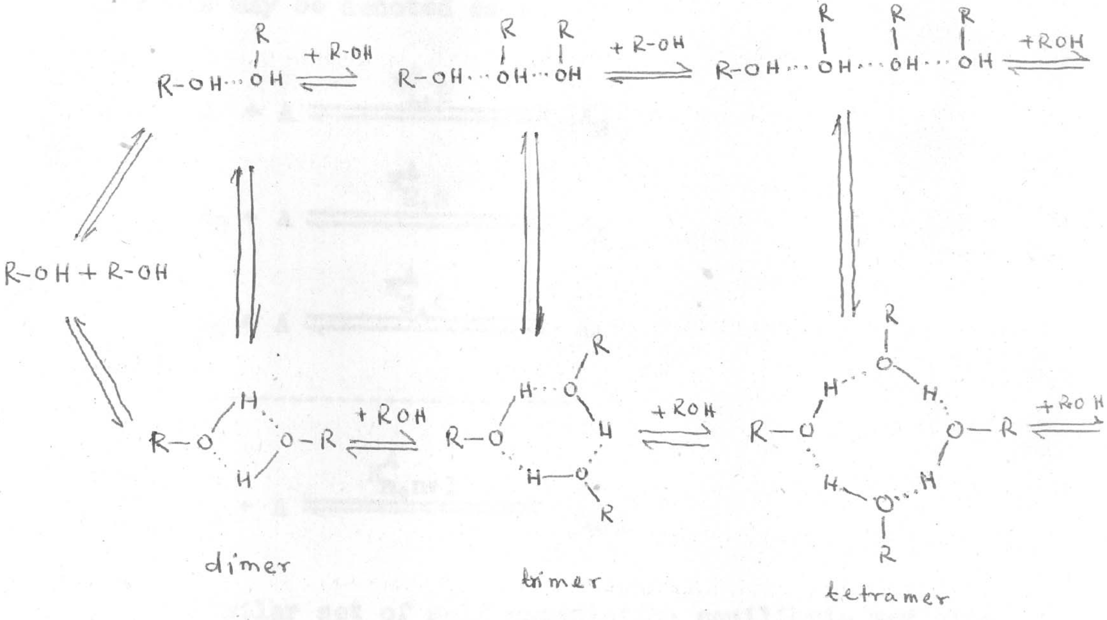
FIG 29 CHANGE OF H^E VALUES WITH TEMPERATURE



−0·5
−1·0
−1·5
V^E (dm^3 mole^{-1}) AT 25°C
0·1
0
0·3
0·5
0·7
0·9
X_1 = MOLE FRACTION OF ALCOHOLS
○—○ 1-PROPANOL + n-BUTYL AMINE SYSTEM
●—● 1-BUTANOL + n-BUTYL AMINE SYSTEM

Fig. 30

It is known that the normal alcohols and the normal amines contain both donar and acceptor group and hence undergo self-association through H-bond formation in two or more ways to form a variety of species which may coexist with one another in a series of complicated equilibria, involving linear and/or cyclic hydrogen bonded species. The self association for the alcohols may be generalised as :



(Possible equilibria in the self association of alcohols)

A similar set of equilibria can also be written for primary amines, such as n-butylamine.

One way to explain the behaviour of binary mixtures of n-alcohols with n-butyl amine is to attribute the deviation from the ideal behaviour primarily on account of the presence of the self associated species of the alcohols and the n-butyl amine, as well as the presence of mixed associates of alcohol molecules with n-butyl amine and to express the excess free energy as a function of the constants describing the various equilibria$^{9-12}$. The possible self association equilibria in alcohols may be denoted as :

$$A + A \xrightleftharpoons{K^A_{1,2}} A_2$$

$$A_2 + A \xrightleftharpoons{K^A_{2,3}} A_3$$

$$A_3 + A \xrightleftharpoons{K^A_{3,4}} A_4$$

$$A_n + A \xrightleftharpoons{K^A_{n,n+1}} A_{n+1}$$

Similar set of self association equilibria may also be written for n-butylamine.

$$B + B \xrightleftharpoons{K^{B}_{1,2}} B_2$$

$$B_2 + B \xrightleftharpoons{K^{B}_{2,3}} B_3$$

$$B_3 + B \xrightleftharpoons{K^{B}_{3,4}} B_4$$

$$B_n + B \xrightleftharpoons{K^{B}_{n,n+1}} B_{n+1}$$

The interaction of alcohol with n-butyl amine may be represented by the following equilibria.

$$A + B \xrightleftharpoons{K^{AB}} AB$$

$$AB + B \xrightleftharpoons{K^{AB_2}} AB_2$$

$$AB + A \xrightleftharpoons{K^{A_2B}} A_2B$$

The above set of equilibria will get more complicated if we consider the formation of linear as well as cyclic species. The analysis of the excess free energy in terms of the various equilibria describing self-association and mutual association of the amine and alcohols though possible in principle gets quite complicated. It has not been possible for us to reduce the relationship to a tractable form by assuming a reasonable relationship between the various equilibrium constants.

The literature on self association of alcohols in non-polar solvents presents a rather confusing picture and the problem of the composition of the associated species is far from being resolved. Venthiel et al.'s[13] infrared spectroscopic studies on liquid methanol indicated the presence of dimer, trimer, tetramer and higher polymers. Saunders and Hyne[14] from the shift of OH frequency with the concentration in the n.m.r. studies of alcohols showed that methanol is present predominantly as a tetramer and ethanol as a dimer. Fletcher and Heller[15,16] from their infrared spectroscopic studies showed that the only important species for ethanol in decane is the tetramer. Aveyard et al.[17] have shown that their infrared absorption data in respect of solutions of octanol in n-octane at 25°C can be explained both by a monomer-tetramer model of Fletcher and Heller[15,16] and by a monomer-dimer-tetramer model. On the other hand, Tuckner et al.[18] suggest that in dilute solutions of methanol in hexadecane (0.25 mol. dm^{-3}), the trimers and the octamers constitute the major portion of the associated species. The mode of self association of n-alcohols has been found to change not only with the concentration of the alcohols in a particular solvent but also with the change of the solvent.

All evidences seem~~s~~ to indicate that the primary and secondary amines are only slightly associated in non-polar solvents. Lambert and Strong[19] measured the second virial coefficients of a series of amines and showed that the normal amines are present as dimers. Feeney and Stucliffe[20] from their n.m.r. studies showed that the primary amines exist predominantly as tetramers in carbon tetrachloride solution. Wolff et al.[21] have analysed the vapour pressure data on solutions of methyl amine, ethyl amine and n-propyl amine in hydrocarbon solvents (n-hexane and n-heptane) in terms of Prigogine's theory of ideal associated solution to indicate the presence of monomer, dimer, trimer and tetramer species. Their calculations indicate a decreasing association of the primary amines with an increase in the chain length of the amines and also with an increase of the temperature. Schug and Chang[22] studied the proton magnetic resonance spectra upon dilution in cyclohexane of four isomeric butyl amines : n-butyl amine, iso-butyl amine, sec-butyl amine and tertiary-butyl amine. They interpreted their data both by simple monomer—n-mer equilibrium model and in terms of the quasi-chemical approximation[23-26]. A comparison of the two sets of results lead them to the correlation that the best self association model for all the four isomeric butylamines is the formation of non-cyclic trimer. This finding is however in disagreement with the work of Feeney and Stucliffe[20,27] who showed that iso-butyl amine forms tetramers in CCl_4. It will therefore be clear that the question of the composition of the associated species of n-butyl amine in solution is still debatable as is for the n-alcohols.

Despite the difficulties in formulating a specific model for the structure of the binary mixture of n-alcohols and n-butylamine, it will still be useful to approach the problem of alcohol-amine interaction from a purely thermodynamic standpoint without invoking beforehand any specific model for the structure of the binary liquid mixtures. The non-specific interaction of the binary mixtures of n-butyl amine with (C_1-C_4) n-alcohols are expected to be very similar and small as compared to the strength and the number of hydrogen bonds formed in these mixtures. The pronounced exothermic effect accompanying the mixing of n-butyl amine with water and the n-alcohols (C_1-C_4) observed in our experiments may be considered to arise mainly as a net result of the following three heat effects:

(1) Endothermic effect, $\Sigma n_i \Delta H_i$ accompanying the breaking of alcohol-alcohol bonds on dilution of the alcohols which undergo self association in pure state where n_i is the number of alcohol-alcohol bonds broken and ΔH_i is the heat associated with the breaking of each such bond.

(2) Endothermic effect, $\Sigma n_j \Delta H_j$, accompanying the breaking of amine-amine bonds on dilution of n-butyl amine which is self associated in its pure state, where n_j is the number of amine-amine bonds broken and ΔH_j is the heat associated with the breaking of such a bond.

(3) Exothermic effect associated with the formation of alcohol-amine bond viz. $\Sigma n_{ij} \Delta H_{ij}$, where n_{ij} is the number of

number of alcohol-amine bonds and ΔH_{ij} is the heat associated with the formation of each such bond in $A_i\ B_j$ complexes. Hence

$$-H^E = +\sum n_i \Delta H_i + \sum n_j \Delta H_j - \sum n_{ij} \Delta H_{ij} \quad \ldots\ldots \quad (3)$$

In order to estimate the hydrogen bond energy associated with the interaction of butyl amine with an alcohol we have made use of the thermochemical cycle shown in Fig. 31.

The Thermochemical Cycle

The system contains one mole of alcohol (A), x mole of amine (B) and y moles of n-hexane (H) such that

$$1 \ll x \ll y\ .$$

State I : One mole of alcohol and x moles of amine both kept separately.

State II : One mole of alcohol at infinite dilution in n-hexane and x moles of amine at infinite dilution in n-hexane both kept separately.

State III : One mole of alcohol-amine complex A-B in (x-1) moles of amine medium. Each A-B complex is separated from another A-B complex on account of its large dilution in the amine medium ($x \gg 1$).

State IV : One mole of A-B complex and (x-1) moles of amine both at infinite dilution in n-hexane medium.

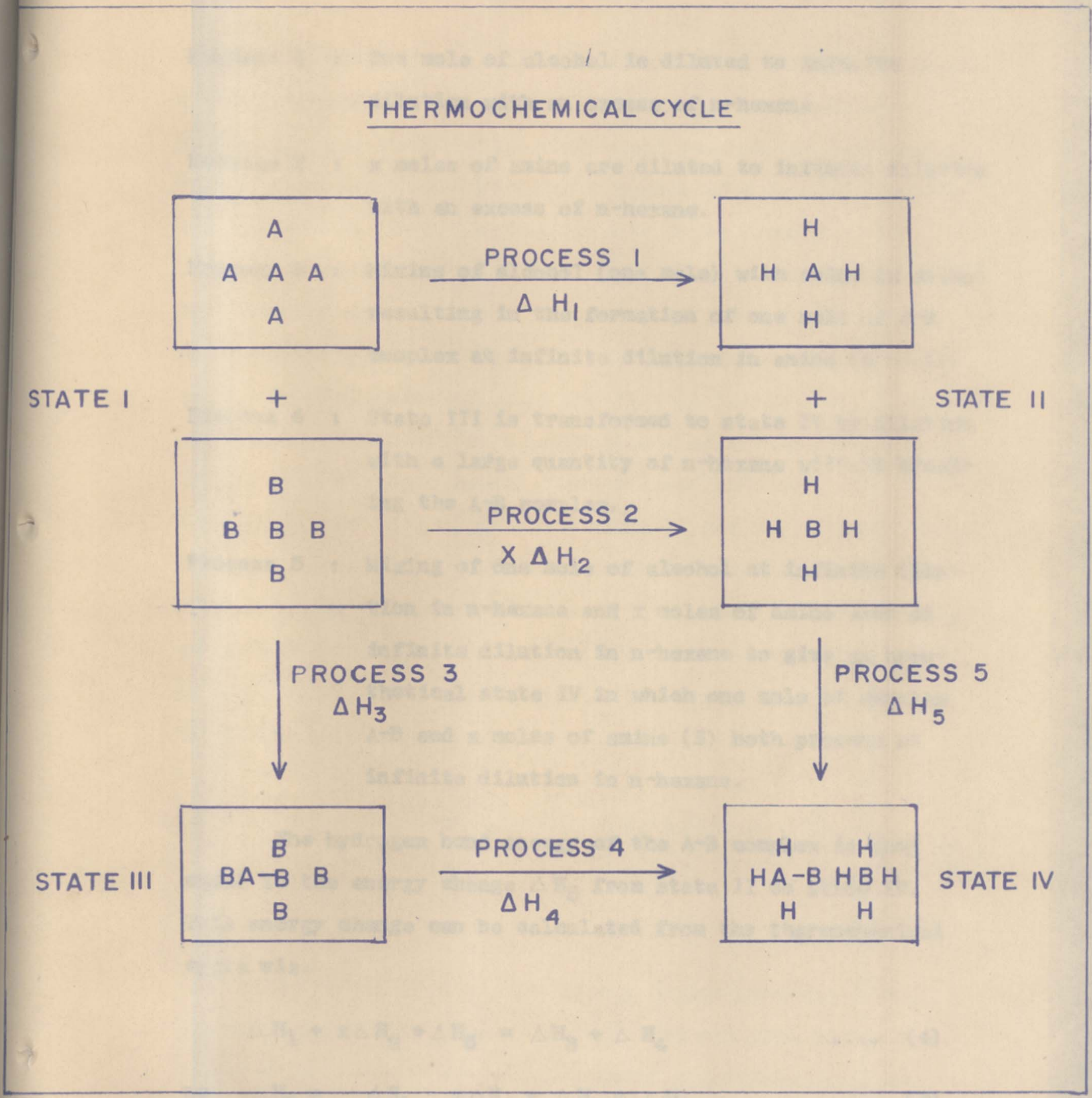

THERMOCHEMICAL CYCLE
STATE I
A
A A A
A
+
B
B B B
B
PROCESS 1
ΔH1
PROCESS 2
X ΔH2
STATE II
H
H A H
H
+
H
H B H
H
PROCESS 3
ΔH3
PROCESS 5
ΔH5
STATE III
B
BA-B B
B
PROCESS 4
ΔH4
STATE IV
H H
HA-B HBH
H H

FIG. 31.

Process 1 : One mole of alcohol is diluted to infinite dilution with an excess of n-hexane.

Process 2 : x moles of amine are diluted to infinite dilution with an excess of n-hexane.

Process 3 : Mixing of alcohol (one mole) with amine (x moles) resulting in the formation of one mole of A-B complex at infinite dilution in amine ($x \gg 1$).

Process 4 : State III is transformed to state IV by dilution with a large quantity of n-hexane without breaking the A-B complex.

Process 5 : Mixing of one mole of alcohol at infinite dilution in n-hexane and x moles of amine also at infinite dilution in n-hexane to give an hypothetical state IV in which one mole of complex A-B and x moles of amine (B) both present at infinite dilution in n-hexane.

The hydrogen bond energy of the A-B complex is then equal to the energy change $\triangle H_5$ from state II to state IV. This energy change can be calculated from the thermochemical cycle viz.

$$\triangle H_1 + x\triangle H_2 + \triangle H_5 = \triangle H_3 + \triangle H_4 \qquad \ldots. \quad (4)$$

$$\text{or} \quad \triangle H_5 = -\triangle H_1 - x\triangle H_2 + \triangle H_3 + \triangle H_4 \qquad \ldots. \quad (5)$$

where ΔH_1 and ΔH_2 are the energy associated with the transfer of one mole of alcohol and one mole of amine respectively from their pure state to a state where each alcohol and each amine molecule is surrounded by a large number of n-hexane molecules and a state in which they can be said to be present in the monomeric state. ΔH_3 is the energy change associated with the transfer of one mole of alcohol from pure alcohol state to a state where each alcohol molecule forms hydrogen bond with a n-butyl amine molecule and the alcohol—n-butyl amine complex is surrounded by a large number of n-butyl amine molecules. Two separate energy changes contribute to ΔH_4.

(a) ΔH_4^{BH}, the heat of dilution of (x-1) moles of n-butyl amine by a large quantity of n-hexane which is equal to $(x-1)\Delta H_2$ and

(b) ΔH_4^d, the difference in the dipolar stabilisation enthalpy of an A-B complex dipole arising from the reaction field of n-butyl amine and n-hexane media. The above equation (5) may therefore be rewritten as :

$$\Delta H_5 = -\Delta H_1 - x\Delta H_2 + \Delta H_3 + (x-1)\Delta H_2 + \Delta H_4^d$$

$$\text{or } \Delta H_5 = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4^d \qquad \text{.... (6)}$$

The value of ΔH_1, the energy change associated with the transfer of one mole of alcohol from its pure state to a state at infinite dilution in an inert hydrocarbon solvent can be determined by plotting the values of the heats of mixing per mole of alcohol H^E/x_1 in mixtures of alcohol+hydrocarbon <u>vs</u> the mole fraction x_1 of the alcohol and extrapolating to infinite dilution ($x_1 \longrightarrow 0$). The above information can also be obtained from plots of H^E/x_1x_2 versus x_1 and extrapolating the curve to $x_1 \longrightarrow 0$. Heats of mixing of the n-alcohols with normal aliphatic hydrocarbons have been determined by several workers[28,29-33]. Brown, Fock and Smith[33] have reported the values of heats of mixing of ethanol, 1-propanol, 1-butanol with n-hexane at 25°, 35° and 45°C and that of methanol with n-hexane at 45°C. Van Ness and coworkers have determined the heats of mixing of methanol and n-hexane at four temperatures in the interval 25°-50° and methanol + n-heptane system at 30°, 45° and 60°C(Ref.30) ;of ethanol + n-hexane and ethanol + n-nonane at 30° and 45°C(Ref.31) ; of ethanol + heptane at 10°, 30°, 45°, 60° and 75°C(Ref.32) ; of 1-propanol + n-heptane at 30° and 45°C of 1-butanol + n-heptane at 30° and 45°C(Ref.31). Elbe[29] has given the values of the heats of mixing of methanol and ethanol with n-hexane at 30°. Pahlke, Wolf and Wahage[28] have measured the heats of mixing of methanol, ethanol, 1-propanol and 1-butanol with n-hexane at 20°C. We have found that the data of Pahlke et al.[28] and Van Ness and coworkers[30-32] are most suitable for an extrapolation to the infinite dilution of alcohol since the measurement of these authors (unlike the work of Brown, Fock and Smith[33]) have been made also at very dilute concentrations of alcohols.

A perusal of the work of Van Ness and coworkers[32] on the heats of mixing of ethanol + n-heptane systems in the dilute concentration range of ethanol ($x_1 < 0.001$) indicates that a rise of temperature from 10° to 30°C is expected to bring about a decrease in the extrapolated value of the heat change $\Delta H_1 = \lim\limits_{x_1 \to 0} H^E/x_1x_2$ by about only 1%. Hence it is reasonable to take the value of $\lim\limits_{x_1 \to 0} H^E/x_1x_2$ at 20° or 30° equal to at 25°C. The work of Van Ness et al. further shows that the values of ΔH_1 determined from measurements at 30° on ethanol + n-hexane and ethanol + n-nonane are nearly equal (Fig. 3, Ref. 31). Therefore, it will not be unreasonable to ignore any possible effect of the change of a hydrocarbon solvent from hexane to heptane on the value of $\Delta H_1 = \lim\limits_{x_1 \to 0} H^E/x_1x_2$. Figures 32 to 35 show the plots of H^E/x_1x_2 versus x_1 for the systems, methanol + n-hexane at 20° and 25°C; ethanol + n-hexane at 20° and 30°C and ethanol + n-heptane at 30°C; 1-propanol + n-hexane at 20° and 1-propanol + n-heptane at 30°C; and of 1-butanol + n-hexane at 20° and 1-butanol + n-heptane at 30°C respectively. The nature of the curves shows that the self association of the alcohols is quite significant even at a very dilute concentrations. By the extrapolation of the curves to infinite dilution ($x_1 \to 0$) for each system we obtain the heats of mixing per mole of component 1 at infinite dilution. These are summarised in Table 25. It may be noted that the value of $\Delta H_1 = \lim\limits_{x_1 \to 0} H^E/x_1x_2$ obtained for ethanol from the work of

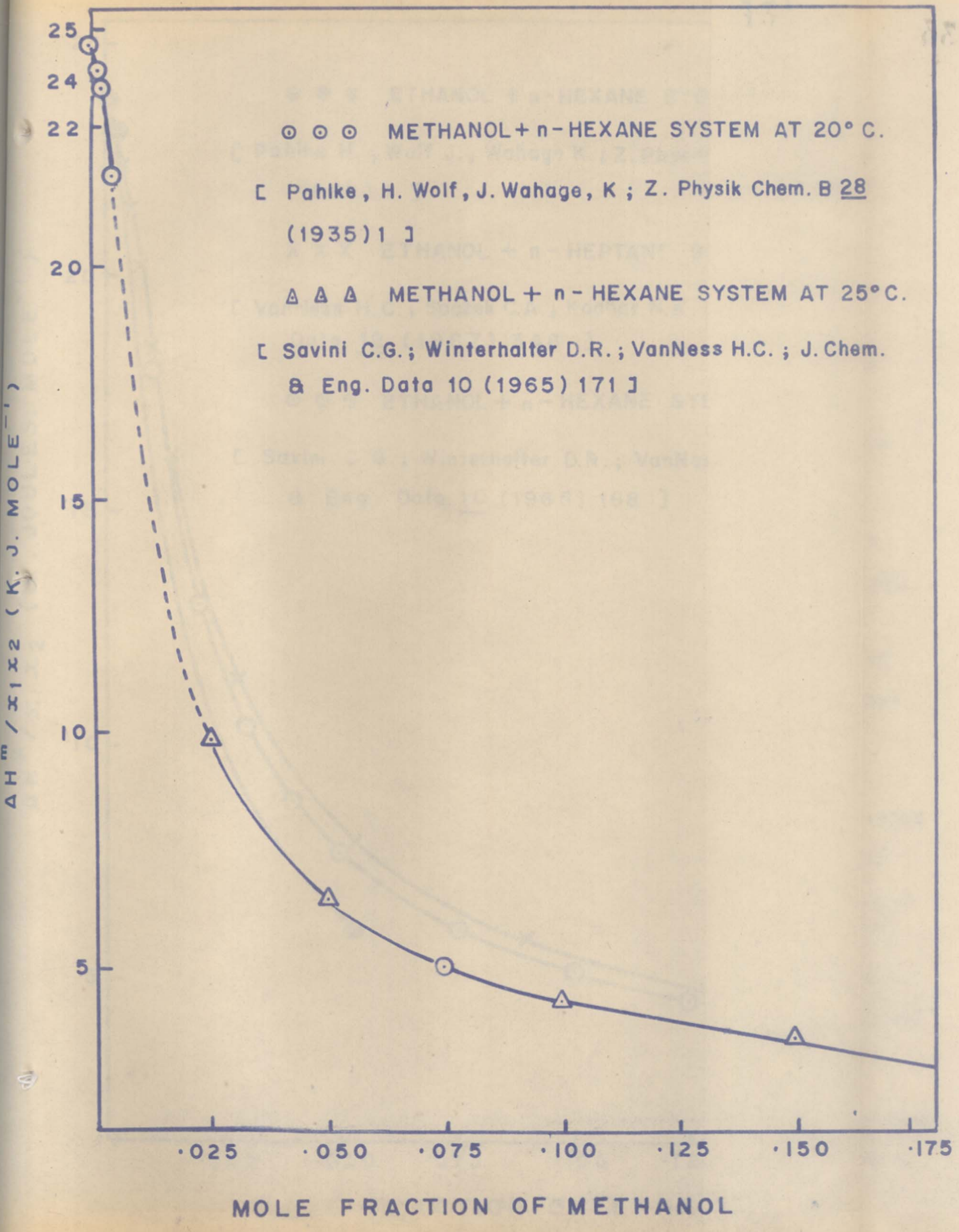

⊙ ⊙ ⊙ METHANOL + n-HEXANE SYSTEM AT 20° C.
[Pahlke, H. Wolf, J. Wahage, K ; Z. Physik Chem. B 28 (1935) 1]
Δ Δ Δ METHANOL + n-HEXANE SYSTEM AT 25° C.
[Savini C.G. ; Winterhalter D.R. ; VanNess H.C. ; J. Chem. & Eng. Data 10 (1965) 171]
$\Delta H^m / x_1 x_2$ (K. J. MOLE^{-1})
25
24
22
20
15
10
5
·025
·050
·075
·100
·125
·150
·175
MOLE FRACTION OF METHANOL

Fig 32

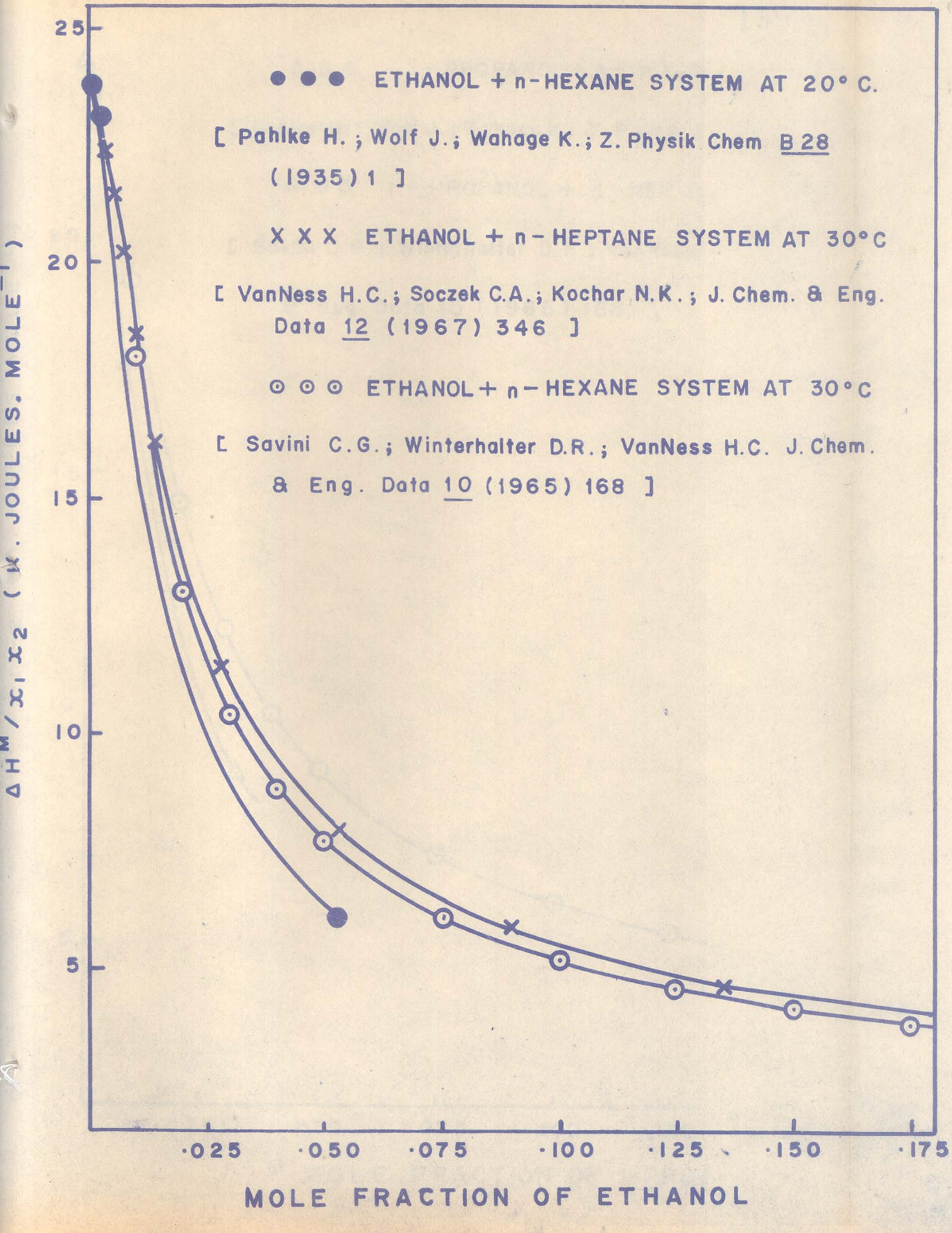

● ● ● ETHANOL + n-HEXANE SYSTEM AT 20° C.
[Pahlke H. ; Wolf J. ; Wahage K. ; Z. Physik Chem B 28 (1935) 1]
X X X ETHANOL + n-HEPTANE SYSTEM AT 30°C
[VanNess H.C. ; Soczek C.A. ; Kochar N.K. ; J. Chem. & Eng. Data 12 (1967) 346]
⊙ ⊙ ⊙ ETHANOL + n-HEXANE SYSTEM AT 30°C
[Savini C.G. ; Winterhalter D.R. ; VanNess H.C. J. Chem. & Eng. Data 10 (1965) 168]
$\Delta H^M / x_1 x_2$ (K. JOULES. MOLE^{-1})
25
20
15
10
5
·025
·050
·075
·100
·125
·150
·175
MOLE FRACTION OF ETHANOL

Fig. 33

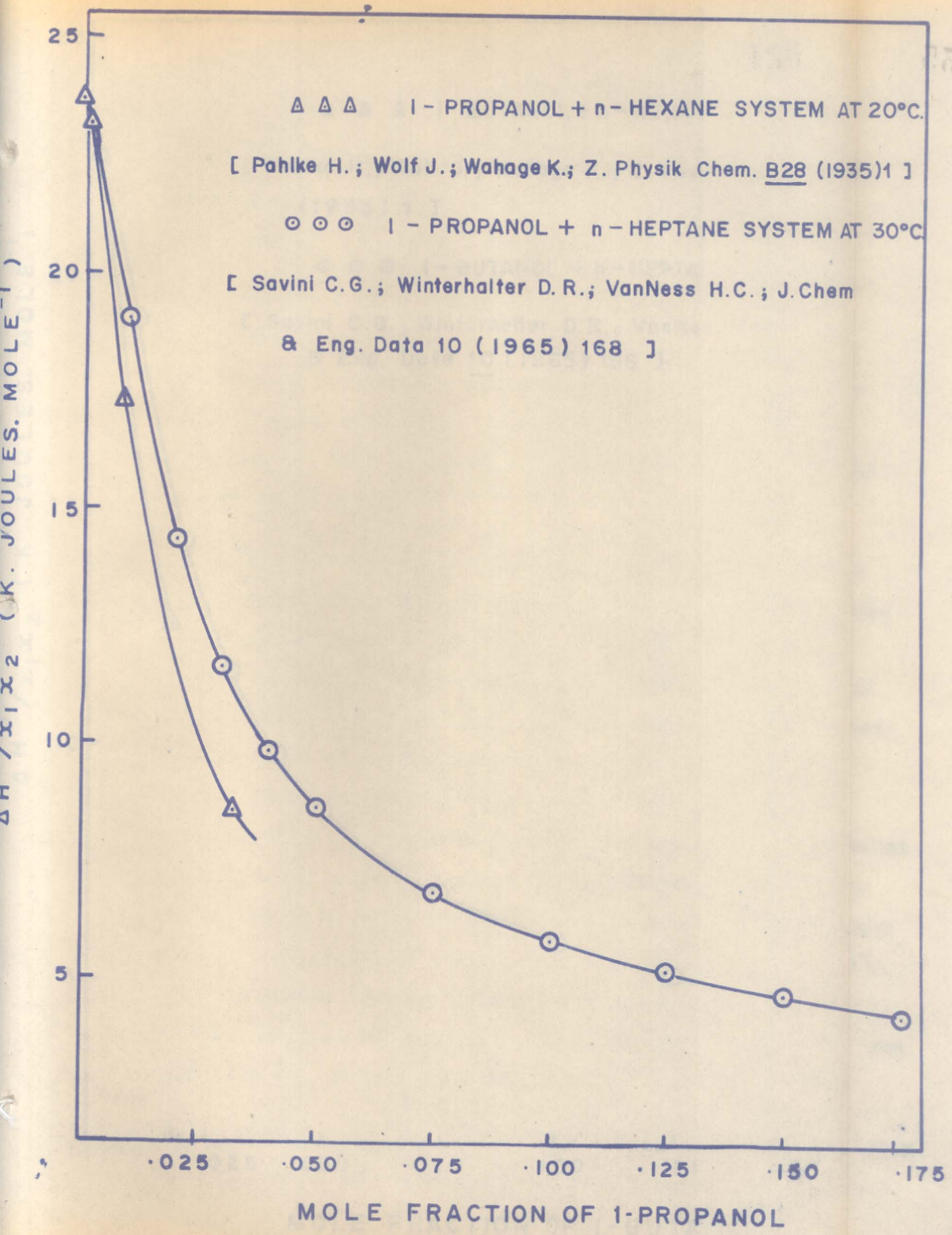

△ △ △ 1 - PROPANOL + n - HEXANE SYSTEM AT 20°C.
[Pahlke H.; Wolf J.; Wahage K.; Z. Physik Chem. B28 (1935)1]
⊙ ⊙ ⊙ 1 - PROPANOL + n - HEPTANE SYSTEM AT 30°C
[Savini C.G.; Winterhalter D.R.; VanNess H.C.; J. Chem & Eng. Data 10 (1965) 168]
25
20
15
10
5
ΔH^M / x1 x2 (K. JOULES. MOLE^-1)
·025
·050
·075
·100
·125
·150
·175
MOLE FRACTION OF 1-PROPANOL

Fig.34

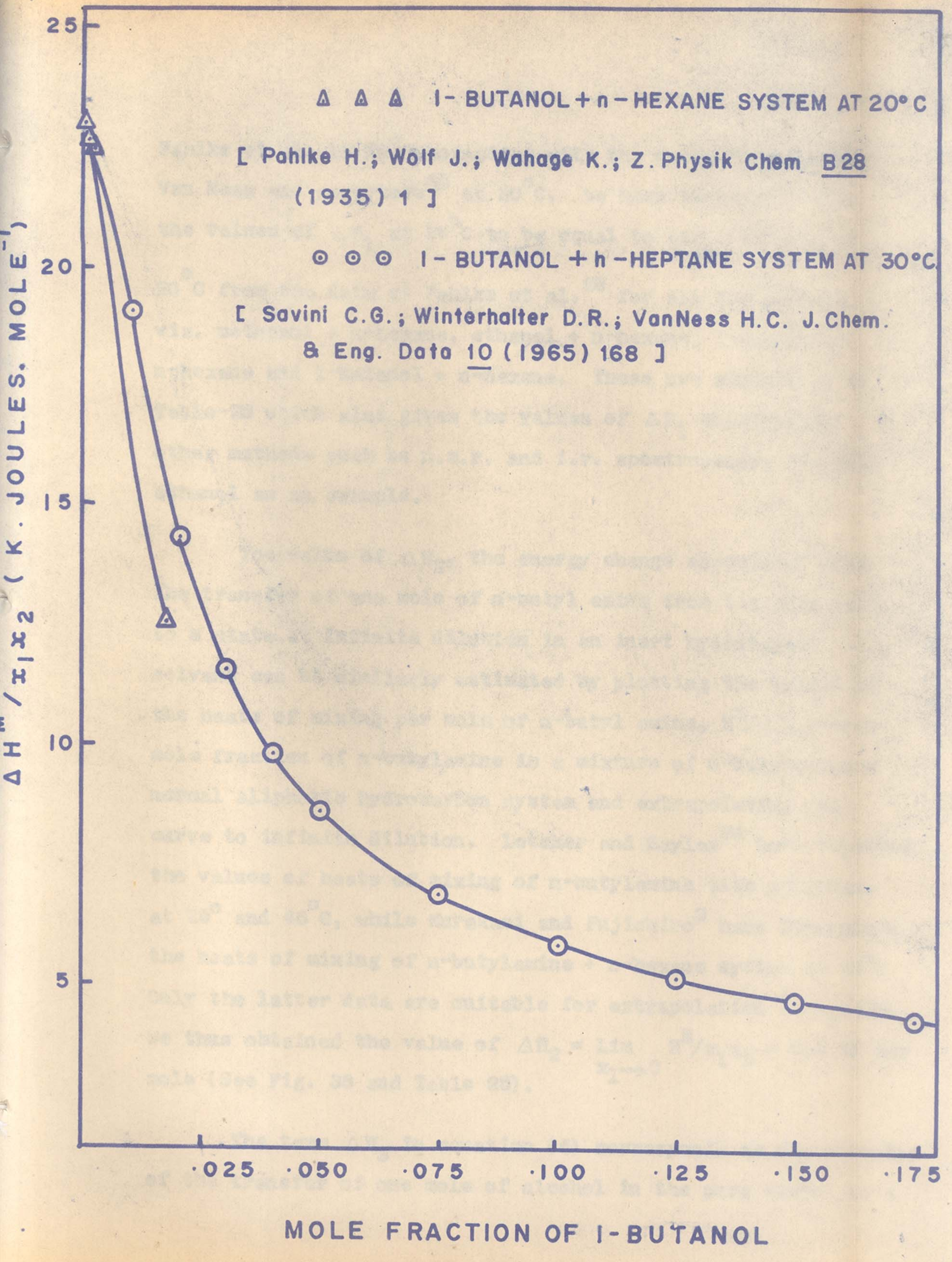
25
20
15
10
5
ΔH^M / x_1 x_2 (K. JOULES. MOLE^-1)
·025
·050
·075
·100
·125
·150
·175
MOLE FRACTION OF 1-BUTANOL
Δ Δ Δ 1-BUTANOL + n-HEXANE SYSTEM AT 20°C
[Pahlke H.; Wolf J.; Wahage K.; Z. Physik Chem B28 (1935) 1]
⊙ ⊙ ⊙ 1-BUTANOL + h-HEPTANE SYSTEM AT 30°C
[Savini C.G.; Winterhalter D.R.; VanNess H.C. J. Chem. & Eng. Data 10 (1965) 168]

Fig. 35

Pahlke et al. at 20°C coincides with the value reported by Van Ness and coworkers[32] at 30°C. We have therefore taken the values of ΔH_1 at 25°C to be equal to $\lim_{x_1 \to 0} H^E/x_1x_2$ at 20°C from the data of Pahlke et al.[28] for all the systems viz. methanol + n-hexane, ethanol + n-hexane, 1-propanol + n-hexane and 1-butanol + n-hexane. These are summarized in Table-25 which also gives the values of ΔH_1 obtained by other methods such as n.m.r. and i.r. spectroscopy, for only ethanol as an example.

The value of ΔH_2, the energy change associated with the transfer of one mole of n-butyl amine from its pure state to a state at infinite dilution in an inert hydrocarbon solvent can be similarly estimated by plotting the values of the heats of mixing per mole of n-butyl amine, H^E/x_1x_2 versus mole fraction of n-butylamine in a mixture of n-butylamine + normal aliphatic hydrocarbon system and extrapolating the curve to infinite dilution. Letcher and Bayles[34] have reported the values of heats of mixing of n-butylamine with n-heptane at 25° and 45°C, while Murakami and Fujishiro[3] have determined the heats of mixing of n-butylamine + n-hexane system at 25°C. Only the latter data are suitable for extrapolation to $x_1 \to 0$. We thus obtained the value of $\Delta H_2 = \lim_{x_1 \to 0} H^E/x_1x_2 = 5.3$ KJ per mole (See Fig. 36 and Table 25).

The term ΔH_3 in equation (6) corresponds to the enthalpy of the transfer of one mole of alcohol in the pure state to a

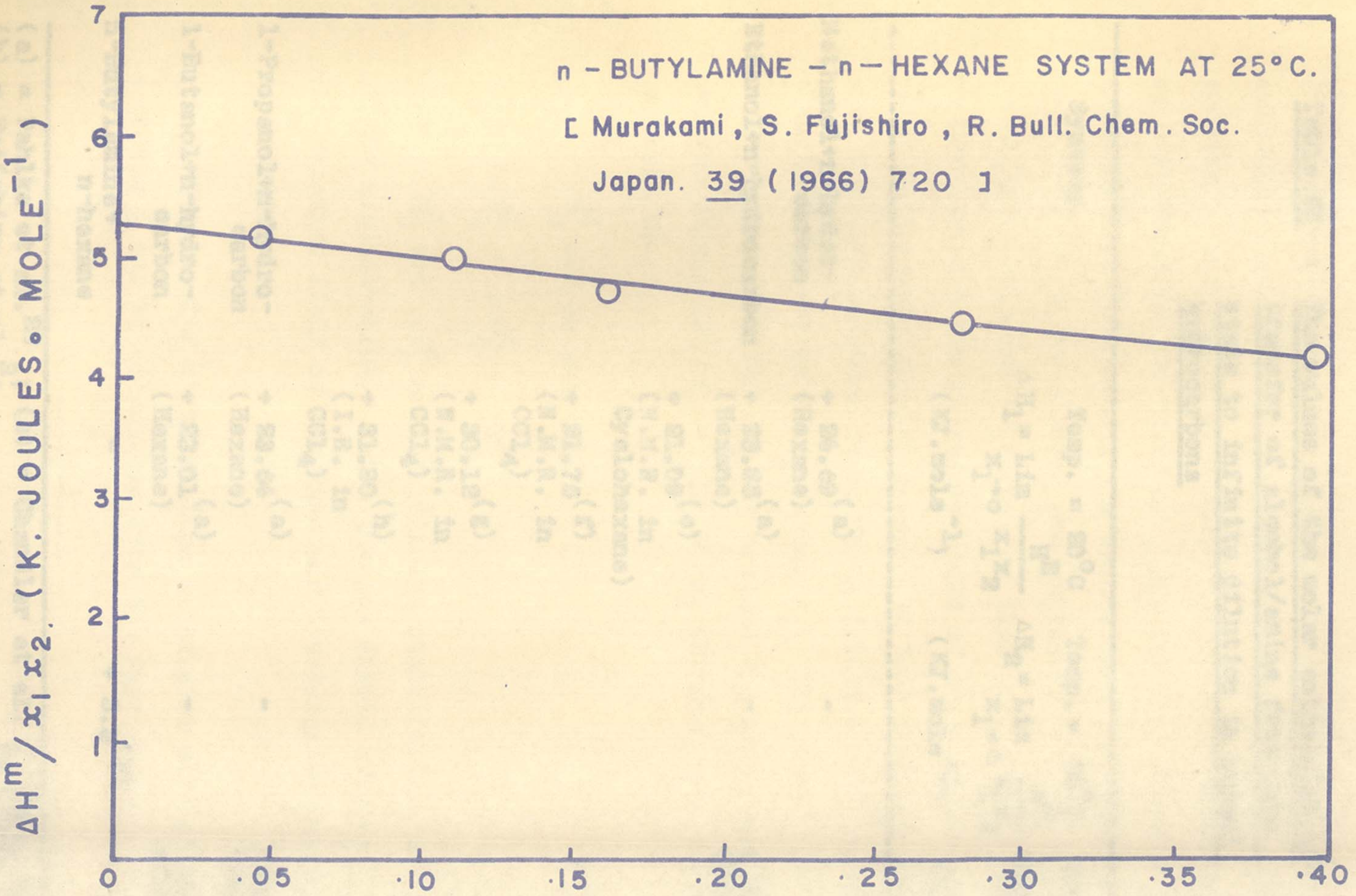
n - BUTYLAMINE - n - HEXANE SYSTEM AT 25°C.
[Murakami , S. Fujishiro , R. Bull. Chem. Soc. Japan. 39 (1966) 720]
$\Delta H^m / x_1 x_2$ (K. JOULES • MOLE^{-1})
7
6
5
4
3
2
1
0
·05
·10
·15
·20
·25
·30
·35
·40
MOLE FRACTION OF n-BUTYL AMINE

Fig. 36

Table 25 : The values of the molar enthalpies of transfer of alcohol/amine from pure state to infinite dilution in normal hydrocarbons

Systems	Temp. = 20°C $\Delta H_1 = \lim\limits_{x_1 \to 0} \frac{H^E}{x_1 x_2}$ (KJ.mole^{-1})	Temp. = 25°C $\Delta H_2 = \lim\limits_{x_1 \to 0} \frac{H^E}{x_1 x_2}$ (KJ.mole^{-1})	Temp. = 30°C $\Delta H_1 = \lim\limits_{x_1 \to 0} \frac{H^E}{x_1 x_2}$ (KJ.mole^{-1})
Methanol+n-hydrocarbon	+ 24.69$^{(a)}$ (Hexane)	-	-
Ethanol+n-hydrocarbon	+ 23.85$^{(a)}$ (Hexane) + 21.09$^{(e)}$ (N.M.R. in Cyclohexane) + 21.76$^{(f)}$ (N.M.R. in CCl_4) + 30.12$^{(g)}$ (N.M.R. in CCl_4) + 31.80$^{(h)}$ (I.R. in CCl_4)	-	+ 23.6$^{(c)}$ (Heptane)
1-Propanol+n-hydrocarbon	+ 23.64$^{(a)}$ (Hexane)	-	+23.1±0.5$^{(d)}$ (Heptane)
1-Butanol+n-hydrocarbon	+ 23.01$^{(a)}$ (Hexane)	-	22.8±0.5$^{(d)}$ (Heptane)
n-Butylamine + n-hexane	-	+ 5.3$^{(b)}$	-

(a) = Pahlke et al.[28] ; (e) = Chandler et al. J. Phys. Chem., 73 (1969) 1596.
(b) = Fujishiro et al.[3] ;
(c) = VanNess et al.[32] ; (f) = VanNess et al. J. Phys. Chem., 71 (1967) 1483.
(d) = VanNess et al.[31] ; (g) = Huggins et al. 60 (1956) 1311.
(h) = Liddel & Becker. Spectrochim Acta, 10 (1957) 70.

state where each alcohol molecule forms a complex with one molecule of n-butylamine and this alcohol—n-butylamine complex is surrounded by a large number of amine molecules. We have obtained the value of $\triangle H_3$, for the alcohol— n-butyl amine systems by plotting the values of H^E/x_1 versus the mole fraction x_1 of alcohol and extrapolating the curve to infinite dilution ($x_1 \rightarrow 0$), so that $\triangle H_3 = \lim_{x_1 \rightarrow 0} H^E/x_1$. We have avoided the customary plots of H^E/x_1x_2 versus x_1 since data showed greater scatter in this form and hence made the extrapolation to infinite dilution more uncertain than in the plots of H^E/x_1 versus x_1. The plots of H^E/x_1 versus x_1 at 25°C for all the systems are shown in Fig. 37 and the values of $\triangle H_3 = \lim_{x_1 \rightarrow 0} H^E/x_1$ obtained are summàrized in Table 26.

$\triangle H_4^d$ may be written as,

$$\triangle H_4^d = \triangle H_H^d - \triangle H_B^d \qquad \ldots. \quad (7)$$

where $\triangle H_H^d$ and $\triangle H_B^d$ are the dipolar stabilization enthalpies of the alcohol—n-butyl amine complex dipole arising from the reaction field of n-hexane and n-butylamine media respectively.

The dipolar stabilization enthalpies of a dipole in a medium i can be calculated from the expression

$$\triangle H_i^d = \frac{\delta(\triangle G_i/T)}{\delta(1/T)} \qquad \ldots. \quad (8)$$

where $\triangle G_i$ is the dipolar stabilization free energy of a

Table 26 : Values of $\Delta H_3 = \lim_{x_1 \rightarrow 0} \frac{H^E}{x_1}$ at 25°C

Systems	Values of ΔH_3 in KJ.mole^{-1}
Water + n-Butyl amine	- 10.4
Methanol + n-Butyl amine	- 11.2
Ethanol + n-Butyl amine	- 9.5
1-Propanol + n-Butyl amine	- 9.0
1-Butanol + n-Butyl amine	- 9.7

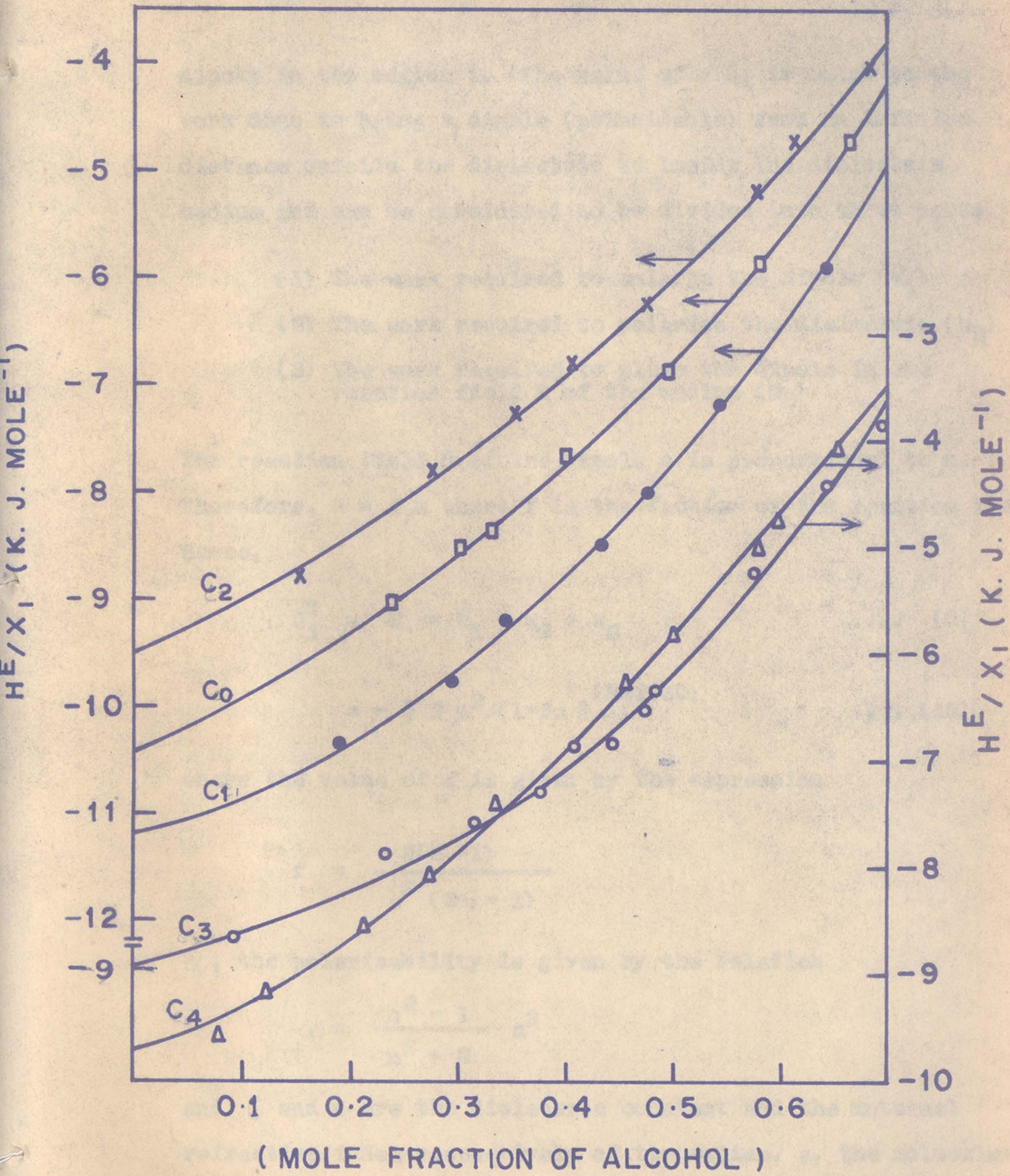


FIG. 37 HEATS OF MIXING OF n-ALCOHOLS WITH n-BUTYLAMINE

dipole in the medium i. The value of ΔG_i is equal to the work done to bring a dipole (polarisable) from an infinite distance outside the dielectric to inside the dielectric medium and can be considered to be divided into three parts.

(1) The work required to enlarge the dipole (W_1)

(2) The work required to polarise the dielectric (W_2)

(3) The work required to place the dipole in the reaction field R of the medium (W_3)

The reaction field R of the dipole μ is proportional to μ. Therefore, $R = f\mu$ where f is the fact~~ion~~or of the reaction field. Hence,

$$\Delta G_i^d = W = W_1 + W_2 + W_3 \qquad \ldots\ldots (9)$$

$$= -\tfrac{1}{2} f\mu^2/(1-f\alpha)^{(\text{Ref.35})} \qquad \ldots\ldots (10)$$

where the value of f is given by the expression

$$f = \frac{2(\epsilon - 1)}{a^3\,(2\epsilon + 1)}$$

α, the polarisability is given by the relation

$$\alpha = \frac{n^2 - 1}{n^2 + 2}\,a^3$$

and ϵ and n are the dielectric constant and the internal refractive index respectively of the medium, a, the molecular radius of the dipole can be calculated by the expression

$$a^3 = \frac{3M}{4N\pi d}$$

M = molecular weight, N = Avagadro's number, d = density.

The data necessary for the calculation of $\triangle G_1$ and hence of $\triangle H_H^d$ and $\triangle H_B^d$ are summarized in Table 27. The values of the densities, the refractive indices and the dielectric constants are those given by Timmermans[36], Landolf Bornstein[37] or Fujishiro et al.[3] or derived from these values by interpolation.

The dipole moments of(C_1-C_4) n-alcohols are known to be almost equal[38] and within the range 1.62-1.69 Debye. Huysken[39]et al. have given the value of the dipole moment of 1-butyl amine + 1-butanol 1:1 complex equal to 2.31×10^{-18} e.s.u. It has been therefore assumed that all the 1:1 n-butyl amine — (C_1-C_4) n-alcohol complexes have the same value of the dipole moment and the value does not change significantly between 15^o - 25^oC. The molecular radii and the polarisability of the amine-alcohol complexes have been assumed to be equal to the sum of the corresponding values of the component molecules of the complex.

The values of $\triangle G_1$ are summarised in Table 28 and those of $\triangle H_H^d$, $\triangle H_B^d$ in the Table 29 for all the n-butylamine — (C_1-C_4) n-alcohol complex dipoles. The values of $\triangle H_4^d = \triangle H_H^d - \triangle H_B^d$ thus having been derived, we can calculate the value of $\triangle H_5$ from equation (6) and these values are given in Table 29.

Table 27 : Values of the constants used for the calculation of the dipolar stabilisation energy of the alcohol—n-butylamine complexes.

Substances	Temperature °C	Density[40]	a^3 $\times 10^{23}$	Refractive index[40,41]	α $(\times 10^{23})$
Methanol	15	0.79609	1.593	1.3305	0.3254
	20	0.79131	1.602	1.3287	0.3257
	25	0.78653	1.612	1.3269	0.3261
Ethanol	15	0.7939	2.296	1.3633	0.5109
	20	0.7894	2.309	1.3613	0.5112
	25	0.7850	2.322	1.3593	0.5115
1-Propanol	15	0.8073	2.946	1.3878	0.6950
	20	0.8035	2.960	1.3854	0.6943
	25	0.7996	2.974	1.3830	0.6938
1-Butanol	15	0.8133	3.607	1.4014	0.8771
	20	0.8097	3.623	1.3991	0.8766
	25	0.8060	3.639	1.3968	0.8760
n-Butylamine	15	0.7484	3.868	-	0.9538
	20	0.7440	3.890	-	0.9516
	25	0.7395	3.914	-	0.9494

continued.....

Table 27 (continued)

Dielectric constants at different temperatures

Substance	15°C	20°C	25°C
n-Butyl amine(3)	5.52	5.34	5.16
n-Hexane(3)	1.897	1.890	1.883

Table 28 : Dipolar stabilisation free energy of Alcohol—n-Butylamine complexes

Complex dipole	Temperature ^{o}C	$\Delta G/T$	
		Amine medium	n-Hexane medium
Methanol + n-Butylamine	15	- 9.315	- 4.194
	20	- 8.975	- 4.074
	25	- 8.644	- 3.956
Ethanol + n-Butylamine	15	- 8.261	- 3.714
	20	- 7.979	- 3.614
	25	- 7.679	- 3.512
1-Propanol + n-Butylamine	15	- 7.517	- 3.373
	20	- 7.239	- 3.275
	25	- 6.982	- 3.184
1-Butanol + n-Butylamine	15	- 6.819	- 3.057
	20	- 6.597	- 2.978
	25	- 6.376	- 2.905

Table 29 : Dipolar Stabilisation Enthalpies

Complex dipoles	Dipole moment (Debye)	ΔH_H^d KJ/mole	ΔH_B^d KJ/mole	$\Delta H_4^d = \Delta H_H^d - \Delta H_B^d$ KJ/mole
Methanol + n-Butylamine	-	- 2.033	- 5.733	+ 3.700
Ethanol + n-Butylamine	-	- 1.748	- 5.017	+ 3.269
1-Propanol + n-Butylamine	-	- 1.667	- 4.667	+ 3.000
1-Butanol + n-Butylamine	2.31	- 1.290	- 3.821	+ 2.531

The values of the energy of the hydrogen bonds formed in the 1:1 complexes of n-butyl amine with methanol, ethanol, 1-propanol and 1-butanol thus calculated are summarized in Table 30. It may be observed that an increase in the chain length of the n-alcohols from C_1 to C_4 has practically no effect on the energy of the hydrogen bond which can be considered to have a constant value of -35.5 ± 1 KJ $mole^{-1}$ for C_2-C_4 n-alcohols. The only exception is the methanol + n-butyl amine bond for which the hydrogen bond energy is -37.5 ± 1 KJ $mole^{-1}$.

It may be pointed out that we have not been able to determine the strength of the water—n-butylamine bond by the same procedure for want of accurate values of the enthalpies of the water-water bond. The solubility of water in inert solvents like hydrocarbons or CCl_4 is too small to be of use for calorimetric measurements. There does not appear to be any agreement between the energy of water-water bond determined by different experimental techniques. For example, Walrafen[40] quotes a value of 2.55 Kcal./mole for the enthalpy of breakage of one hydrogen bond in water from the studies of the temperature dependence of intermolecular Raman vibrations of solutions of D_2O in H_2O. On the other hand, the infrared studies of solutions of H_2O and HDO in 1,2 dichloroethane, Jolicoeur and Cabana[41] estimate the energy of the hydrogen bond in water as 5.3 Kcal/mole.

Table 30 : Enthalpy of Hydrogen Bonding between n-butylamine– n-alcohols, rounded to the nearest 0.1 KJ/mole from equation $\Delta H_5 = -\Delta H_1 - \Delta H_2 + \Delta H_3 + \Delta H_4^d$ along with other published values.

Systems	Enthalpy of hydrogen bonding at 25°C (KJ/mole)	Reference
Methanol + n-Butylamine	-37.5 ± 1	Present work
Ethanol + n-Butylamine	-35.4 ± 1	Present work
	-30.2	Calorimetry[~~38~~ 42] 25°C
1-Propanol + n-Butylamine	-35.0 ± 1	Present work
1-Butanol + n-Butylamine	-35.5 ± 1	Present work
	-33.5	Calorimetry[3] 25°C
	-31.3	Calorimetry[~~38~~ 42] 25°C
	-37.24	Vapour density[~~39~~ 43] (70°-100°C)

The only results available in the literature on the heats of hydrogen bond formation between n-butyl amine and n-alcohols are those of Lambert and Huyskens[42] on n-butyl amine + 1-butanol and n-butyl amine + ethanol and of Cracco and Huyskens[43] and Murakami and Fujishiro[3] on n-butyl amine + 1-butanol system. The values of the enthalpy of hydrogen bond reported by these authors are also given in Table 30 for ready comparison. It may be observed that there is good agreement between our results and those of Murakami and Fujishiro[3], while the agreement with the other published work is fair. Cracco and Huyskens's[43] value of -37.5 KJ mole^{-1} for the hydrogen bond between n-butyl amine and 1-butanol is for the vapour phase in the temperature range 70°- 100°C. It has been observed that the value of the bond formed[44,45] in the vapour phase is usually higher in magnitude than that formed in the liquid phase.

We have noted earlier (Table 25) that the strength of the hydrogen bond formed on the self association of (C_2-C_4) alcohols may be considered to have a constant value of 23.5 ± 0.5 KJ mole^{-1}. In the case of methanol, the energy of the hydrogen bond has a slightly higher value of 24.7 KJ mole^{-1}. We have also found that the strength of the hydrogen bond formed between n-butyl amine and (C_2-C_4) n-alcohols is independent of the chain length of the alcohols and has a constant value of -35.5 ± 1 KJ mole^{-1}, with a slightly higher value of -37.5 ± 1 KJ mole^{-1} for the energy of the intermolecular hydrogen bond between n-butylamine and methanol.

In spite of these results, we observed significant differences in the heats of mixing H^E of n-butyl amine with (C_1-C_4) n-alcohols, as discussed earlier on page 113 (see Table 20 and Figures 28 and 38). For example, the magnitude of the exothermic heats of mixing at 25° for an equimolar mixture of n-butyl amine with (C_1-C_4) n-alcohols has the following decreasing order :

$$C_1 > C_3 > C_2 > C_4 \qquad \ldots\ldots \quad (f)$$

This order not only changes with the temperature (page 113) but also with the concentration at a fixed temperature of 25°C. It may be noted from Fig. 28 and Table 20 that the order of $|H^E|$ changes to

$$C_1 > C_2 > C_3 > C_4 \quad \text{at 0.7 mole fraction of n-alcohols} \qquad \ldots\ldots \quad (g)$$

and to

$$C_1 > C_3 \simeq C_4 > C_2 \quad \text{at 0.3 mole fraction of n-alcohols} \qquad \ldots\ldots \quad (h)$$

A qualitative explanation for this change in the order of $|H^E|$ may be provided by a consideration of equation (3) which relates the value of H^E in terms of the number n_i and strength ΔH_i of alcohol-alcohol and the number n_j and the strength ΔH_j of amine-amine bonds broken and the number n_{ij} and the strength ΔH_{ij} of the alcohol-amine bonds formed. As an approximation we may consider that the value of $\sum n_j \Delta H_j$ makes an almost equal contribution to H^E at equivalent mole fractions of alcohols for the mixtures of n-butyl amine with

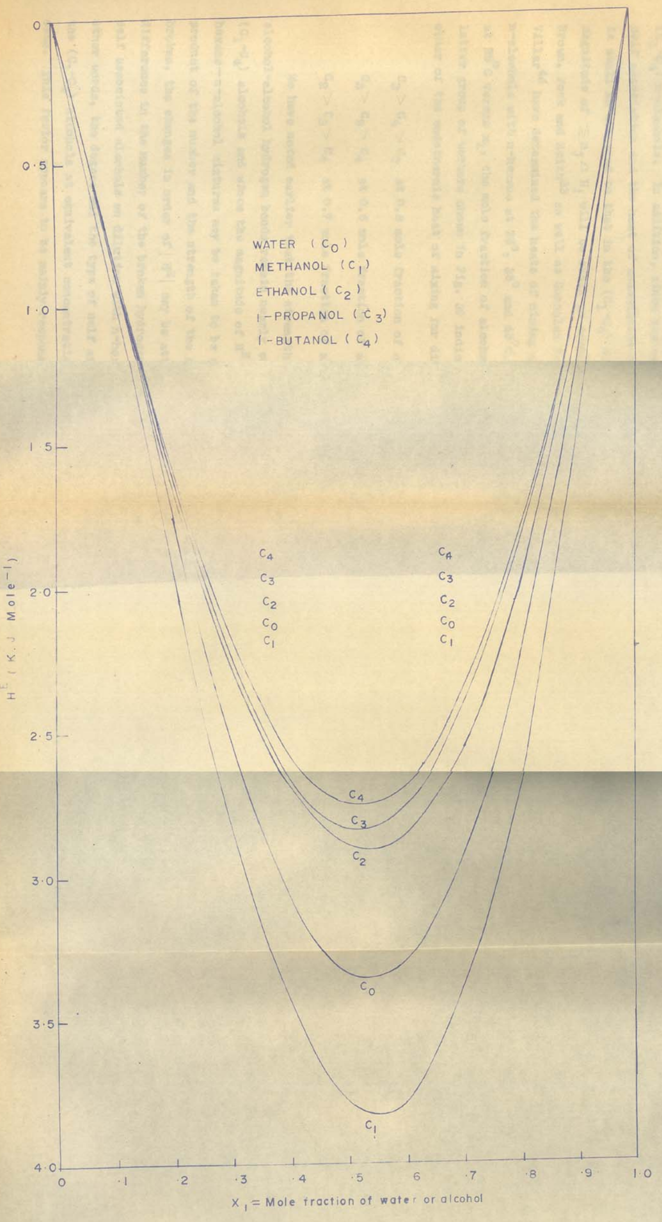


FIG 38. HEATS OF MIXING OF WATER AND ALCOHOLS WITH n-BUTYLAMINE AT 40°C

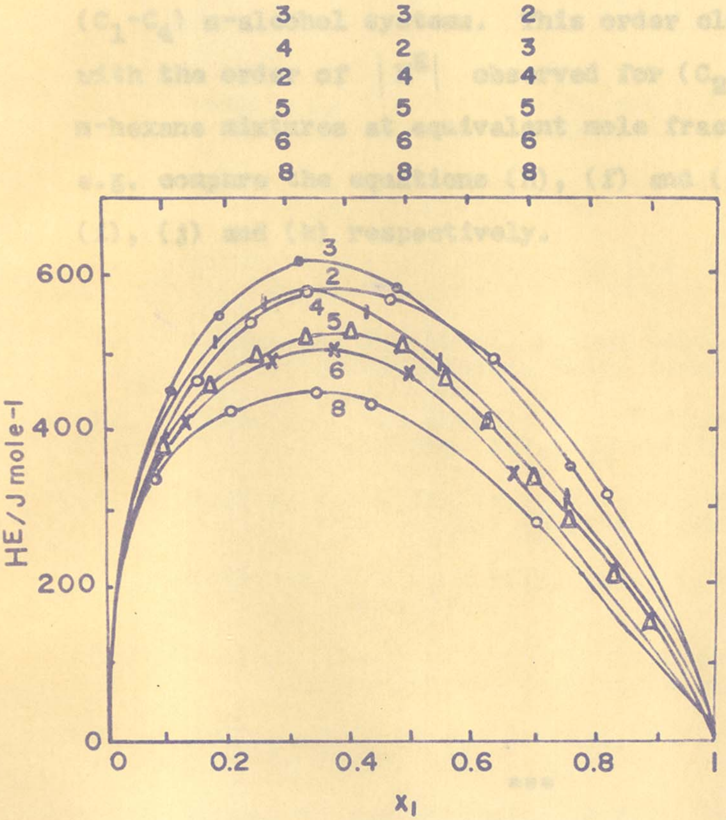
(C_1-C_4) n-alcohols. In addition, since the extent of the self association and the heat of association of n-butyl amine is small as compared to that in the (C_1-C_4) alcohols, the magnitude of $\sum n_j \Delta H_j$ will be small as compared to $\sum n_i \Delta H_i$. Brown, Fock and Smith[33] as well as Gonzalez Posa, Nunez and Villar[46] have determined the heats of mixing of several n-alcohols with n-hexane at 25°, 35° and 45°C. The plots of H^E at 25°C versus x_1, the mole fraction of alcohols, given by the latter group of workers shown in Fig. 39 indicate the following order of the endothermic heat of mixing for different alcohols:

$C_3 > C_4 > C_2$ at 0.3 mole fraction of alcohols .... (i)

$C_3 > C_2 > C_4$ at 0.5 mole fraction of alcohols .... (j)

$C_2 > C_3 > C_4$ at 0.7 mole fraction of alcohols .... (k)

We have noted earlier that the strength of the alcohol-alcohol hydrogen bonds remain nearly constant in the (C_1-C_4) alcohols and since the magnitude of H^E for the hexane—n-alcohol mixtures may be taken to be equal to the product of the number and the strength of the hydrogen bonds broken, the changes in order of $|H^E|$ may be attributed to the difference in the number of the broken hydrogen bonds in the self associated alcohols on dilution with n-hexane; or in other words, the degree and the type of self association of the (C_1-C_4) alcohols at equivalent concentration are not the same. This factor appears to be mainly responsible for the



Enthalpy of mixing H^E of 1-alkanol + n-hexane at 25°C, x_1 being the mole fraction of the 1-alkanol.

2, 1-ethanol + n-hexane; 3, 1-propanol + n-hexane; 4, 1-butanol + n-hexane; 5, 1-pentanol + n-hexane; 6, 1-hexanol + n-hexane; 8, 1-octanol + n-hexane.

FIG. 39

observed changes in the order of $|H^E|$ for the n-butyl amine + (C_1-C_4) n-alcohol systems. This order closely corresponds with the order of $|H^E|$ observed for (C_2-C_4) n-alcohols + n-hexane mixtures at equivalent mole fractions of the alcohols e.g. compare the equations (h), (f) and (g) with the equations (i), (j) and (k) respectively.

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SUMMARY

SUMMARY

This study concerns investigations on the thermodynamic excess properties of binary mixtures of n-butylamine with normal aliphatic alcohols-methyl, ethyl, 1-propyl and 1-butyl, and water.

The excess free energies of mixing, G^E have been determined from the vapour liquid equilibrium data for the binary mixtures at 40°C. A modified Jones-Colburn recirculating still has been used for the study of the vapour liquid equilibria. A twin-type mixing calorimeter has been used for the measurement of the heats of mixing $\triangle H^m$ of the binary mixtures at 25° and 40°C.

The heats of mixing $\triangle H^m$ (or H^E) for all these systems are highly negative throughout the entire concentration range. Plots of H^E versus the mole fractions of water or alcohols give nearly symmetrical parabolic curves. The magnitudes of the heats of mixing are largest in case of methanol (denoted by C_1-alcohol) + n-butylamine system followed by water + n-butylamine system for both the temperatures. But for mixtures of n-butylamine with other alcohols (C_2-C_4), the order of the magnitudes of the heats of mixing change with concentration as well as with temperature. The increase in temperature

is accompanied by a decrease in the magnitude of the heats of mixing, indicating positive values of the excess heat capacities, C_p^E for these systems. The values of G^E for the systems studied are also negative throughout the entire ranges of concentrations and their values when plotted against the mole fractions of n-butylamine also give nearly symmetrical parabolic curves. The values of TS^E for these systems obtained from H^E and G^E values at 40°C are also found to be negative. Their values when plotted against the mole fractions of alcohols also give nearly symmetrical parabolic curves. The excess volumes of mixing, V^E when plotted versus mole fractions of alcohols also lie on nearly symmetrical parabolic curves. All the above data strongly indicate the formation of a predominantly 1:1 complex in the binary mixtures of n-butylamine with n-alcohols through hydrogen bonding. The observed negative values of the heats of mixing at any concentration can be considered to be a net result of the (a) endothermic effect due to the breaking of the alcohol-alcohol bonds, (b) the endothermic effect arising out of the breaking of the amine-amine bonds and (c) the exothermic effect corresponding to the formation of alcohol-amine hydrogen bonded complexe species.

It has been realised that both the (C_1-C_4) alcohols, (a) and n-butylamine, (b) exist in pure state as associated liquids a_i and b_j and hence the formation of a_i b_j hydrogen bonded species cannot be ruled out completely at a finite concentration.

It can however be reasonably assumed that at infinite dilution those liquids exist essentially as monomers. Hence the heat of mixing at infinite dilution can be taken as a measure of the strength of the bond between a dimer species. The hydrogen bond energies associated with the formation of 1:1 amine-alcohol complex have been calculated for the systems at 25°C with the help of a thermochemical cycle and using (i) heats of mixing per mole of alcohol at infinite dilution of alcohol for alcohol + n-hexane system; (ii) heats of mixing per mole of n-butylamine at infinite dilution of amine for n-butylamine + n-hexane system; (iii) heats of mixing per mole of alcohol at infinite dilution of alcohol for alcohol + n-butylamine systems and (iv) differences in the dipolar stabilisation enthalpies of alcohol-amine complexes in n-butylamine medium and n-hexane medium.

It has been observed that the increase in chainlength of n-alcohols from C_1 to C_4 has practically no effect on the strength of the hydrogen bond formed between n-butylamine and one of the alcohols which has a constant value of - 35.5 ± 1 K.J.mole^{-1} for binary mixtures of n-butylamine with C_2-C_4 n-alcohols and a slightly higher value of -37.5 ± 1 K.J.mole^{-1} with methanol.

In spite of almost equal hydrogen bond strength for 1:1 amine-alcohol complex species for (C_1-C_4) n-alcohols, the magnitude of the exothermic heats of mixing at 25°C for an equimolar mixtures of n-butyl amine with (C_1-C_4) n-alcohols has the following order :

$$C_1 > C_3 > C_2 > C_4$$

This order not only changes with temperature but also with the concentration at a fixed temperature at 25°C. The changes observed in the order of magnitude of heats of mixing of the systems studied by us have been attributed to the difference in the relative number of hydrogen bond broken in the self associated alcohols on dilution.

-xXx-