GROUP CONTRIBUTION THEORIES AND EXCESS THERMODYNAMIC PROPERTIES OF n-ALCOHOL-n-PARAFFIN SOLUTIONS

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PREFACE

Solutions of molecular mixtures have been treated as solutions of the constituent groups of the component molecules. Based on the concept of group interaction contributions, models were developed. The models were then used for representation of excess thermodynamic properties of alcohol-n-paraffin binary systems. The well-known quasi-lattice theory was also tested for its ability to represent the excess properties of alcohol-n-paraffin systems.

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CHAPTER I

INTRODUCTION

One of the important applications of thermodynamics is in the area of development and design of processes for the recovery and purification of organic compounds. Since the need for accurate descriptions of the thermodynamic properties of solutions in this area is frequently great and the systems are complex, description of the thermodynamic properties of solutions relies primarily upon direct experimental measurements. However, experimental measurements are frequently difficult, tedious, and costly. These factors provide incentive to develop means to calculate the thermodynamic properties of solutions by reducing and generalizing the limited experimental data at hand. Toward this end, many sound theories, thermodynamic relations, and empirical relations have been developed for making such calculations.

In the past, theories and relations were developed in terms of component molecules, and molecular theories have been used to predict thermodynamic properties of solutions. Interactions among molecules have been visualized as the source of thermodynamic interaction, and thermodynamic properties are characterized by molecular interactions in solutions.

Recently, there has been new interest in solutions of groups; that is, breaking down a molecule into constituent groups and considering interactions among the groups. Suitable combinations of the interactions among the groups can be used to characterize the solution properties. Models which consider solutions to be made up of the constituent groups of the molecules in the solution rather than being made up of the molecules themselves have certain advantages:

1. Relatively few interaction parameters are required.
2. Mixture properties are related to the pure fluid properties.
3. Extension to multicomponent mixtures is easily facilitated.
4. Predictions are possible on mixtures for which no data are available.

Specifically, a large number of molecular solutions can be made up of a very few groups. By knowing the nature of interactions among these groups, a large number of solutions may be characterized. However, for molecular theories, information on interactions between the molecular pairs is needed, and each new molecule brought into the solution requires new information on interactions between that molecule and every other molecule in the solutions. Thus, group solution theory facilitates a considerable reduction of the information required to characterize solutions. For example, there is a large number of binary mixtures of n-paraffins and n-alcohols. If they are characterized thermodynamically by characterizing the interactions between molecular pairs, then a number of characteristic parameters for each binary mixture would be necessary. If group solution theory is used, only three groups, which have six different types of interaction (CH_3-CH_3, CH_3-CH_2, CH_2-CH_2, CH_3-OH, CH_2-OH, and OH-OH), need be considered. In this way, six types of interactions might characterize a large number of alcohol-paraffin mixtures. Thus, the measurement of the thermodynamic properties of a single alcohol-paraffin binary system could, in principle, be used to estimate the thermodynamic properties for any alcohol-paraffin system. Complicated multicomponent mixtures become amenable to calculations as they are reduced to systems containing only a few groups.

In dealing with mixtures of molecules in terms of their constituent groups, account must be taken of the interactions of the various groups in solutions, the restrictions imposed upon these interactions by the organization of the groups into molecules, and the organization of the molecules in the solution. Detailed theories of mixtures take these effects into account in terms of some models. But even for mixtures of simple molecules, the effects are so complicated that completely satisfactory models have yet to be developed.

It is the purpose of this study to develop theories based on constituent group contribution in liquid mixtures for calculating the excess thermodynamic properties of polar mixtures.

Previous development of theories and correlations for liquid solutions containing polar substances was hampered by a lack of experimental data. Recent contributions by Van Ness and co-workers (48, 56, 57) are notable for their systematic measurement of heat of mixing of alcohol-n-paraffin mixture systems. Their data on binary mixtures of alcohols and paraffins are used in the development and testing of the present theories.

CHAPTER II

REVIEW OF EARLIER GROUP CONTRIBUTION THEORIES

Because of the attractive advantages of group solution theory, investigations of solutions of groups have been of interest since the pioneering work of Langmuir (36). As a result, there exists considerable literature on the subject (14). This chapter makes no pretense of encompassing all previous contributions. However, a selected fraction of these contributions are presented to illustrate the present status of group solution theory as it applies to this study.

A. Langmuir Model

The most significant early description of simple mixtures in terms of groups was given by Langmuir (36) in 1925. He proposed that certain characteristics of solutions could be expressed in terms of the constituent groups or radicals on the molecules in the solution. He suggested that interaction forces among molecules were dependent on the exposed surface area of the groups in the molecules and that the force field around a group or radical is largely independent of the nature of the rest of the molecule. This forms the so-called "principle of independent surface action." As a first approximation, Langmuir neglected any local orientation and segregation of molecules in a liquid and considered instead the various interfacial energies he might expect for a molecule in a liquid mixture. By summing these interfacial energies of the pairs of groups in contact, weighted according to surface fraction in a binary mixture, he derived expressions for the partial pressures of the components. He dealt explicitly only with molecules of the kind R-X in which a nonpolar R group is considered a single group and X is a polar group. He applied this theory primarily to two-phase relations, such as surface tension, film adsorption and vapor pressures.

He indicated that the model could fit experimental data for binary systems with moderate deviations. Reasonable mutual solubility predictions could be made for a few systems with large deviations from Raoult's law.

B. Limiting Activity Coefficient Model

Group contribution theory has been extensively developed to describe the activity coefficient of a solute at infinite dilution in a solvent. The infinite dilution activity coefficient is directly related to the parameters in semi-empirical expressions for excess free energy. In fact, the two terminal activity coefficients in a binary system suffice to determine both equation parameters in any two-parameter excess free energy expression.

The work of Butler, et al. (8, 9) is a second early work which is basically a group approach. They considered the infinitely dilute solution of a series of solutes in a given solvent as the simplest case for study instead of the more conventional study of concentration effects within a single system of components. They systematically measured Henry's law constants for a wide range of solutes within a given family. Through these they observed a simple relation between solute carbon number and its activity coefficient. They noted that the partial molal excess free energies of solution increase by roughly constant increments through the homologous series. They also indicated that this roughly constant increment depends upon the nature of the polar group.

Pierotti and co-workers (41, 42) have made a more extensive, systematic study of homologous series. They experimentally measured activity coefficients at high dilution for homologous series of solutes in fixed solvent and fixed solute in homologous series of solvents and inspected the dependence of the limiting activity coefficient upon the carbon numbers of solute and solvent.

If a mono-functional molecule of the type RX, where R stands for an alkyl group and X the "functional" group which might be OH, CHO, or COOH (X might also stand for a nonpolar group such as phenyl or naphthyl group) is considered, and when a RX molecule is in solution at infinite dilution in a solvent of R'X' molecules, the RX molecules are completely surrounded by R'X' molecules. The significant contribution to the interaction energy involving RX molecules are visualized to be as shown in Figure 1. If it is assumed that $\ln\gamma_i^{o}$ ($= \bar{G}_i^{E}/RT$) of RX in R'X' is made up of group interaction contributions and these contributions do not mutually interact, then this concept may be expressed by

$$\ln\gamma_i^{o} = I_a + I_b + I_c + I_d + I_e + I_f \qquad (2\text{-}1)$$

where γ_i^{o} is the activity coefficient of RX at infinite dilution in R'X', and I's are the interaction contributions as shown in Figure 1.

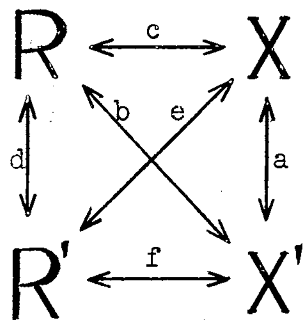


Figure 1. Group Interaction Between Two Mono-Functional Molecules

Pierotti, et al. (41, 42) empirically developed expressions for the I's in terms of the carbon numbers of solute and solvent based on their experimental results and re-expressed Equation (2-1) as a function of the carbon numbers.

$$\log \gamma_{RX}{}^{o} = C_1 + C_2 \frac{n_R}{n_{R'}} + C_3/n_R + C_4(n_R - n_{R'})^2 + C_5 \frac{n_{R'}}{n_R} + C_6/n_{R'} \quad (2\text{-}2)$$

where n_R, $n_{R'}$ = number of carbon atoms in hydrocarbon radicals R and R', respectively.

C_1 = coefficient which depends on nature of solute and solvent functional groups, X and X'.

C_2 = coefficient which depends only on nature of solvent functional group, X'.

C_3 = coefficient which depends only on solute functional group, X.

C_4 = coefficient independent of both X and X' depends on temperature, which was taken from the results of study of paraffin mixtures by Bronsted and Koefied (7).

C_5 = coefficient which depends only on nature of solute functional group, X.

C_6 = coefficient which essentially depends only on nature of the solvent functional group, X'.

Numerical values of C's are given for a large number of homologous series including acids, primary, secondary, and tertiary alcohols, aldehydes, ketones, acetals, ethers, nitriles, esters, water, hydrocarbons, etc. In spite of its coverage of an extremely broad range of limiting activity coefficients, this empirical correlation agrees quite well with the experimental data. For 44 sets of systems (350 individual cases), the overall average deviation in γ^o about 8%.

C. Quasi-Lattice Theory

Langmuir (36) indicated that two phase relations of a solution such as vapor pressures would be strongly influenced by the preferential orientation of the molecules at phase interfaces. In addition, increasing experimental evidence showed that the liquid state has many features, such as a large number of first neighbors and local order, in common with crystals. For this reason, several investigators (2, 3, 10, 11, 18, 24, 25, 26, 53, 54) have attempted, based on the theory of liquid solutions on a lattice model, to account for such orientation effects by applying statistics to a quasi-lattice arrangement of the molecules, in which a molecule is free to rotate about a fixed lattice point and different groups are subjected to contact with surrounding molecules.

Guggenheim (24, 25, 26) credited Chang (10, 11) with being the first to propose this theory based on the idea that the change on mixing of all relevant thermodynamic properties may be expressed in terms of the lattice partition function. The energies which appear in this partition function are those of the groups at rest in their equilibrium positions in the lattice. The evaluation of the combinatorial factor for polymer solutions by Flory (18) and Huggins (32) was a major success of this model.

Barker (2, 3) extended Guggenheim's theory to allow one molecule to have different kinds of segments. Barker's results are in terms of grand partition functions. Basically, the quasi-lattice theory considers each molecule in solution to be composed of given numbers of segments placed on a well-defined lattice. Each type of segment possesses a specified number of contact points where it may interact with adjacent segments. The interaction energy of the solution is the sum of contributions from interactions between pairs of adjacent sites. Barker and his associates (4, 5) have successfully applied such a model to several systems involving associated liquids. This theory has also been shown to apply well to paraffin-aromatic (34), alcohol-aromatic (2, 21, 22), alcohol-ester (53), and alcohol-n-paraffin (35) systems.

D. Corresponding States Theory of r-mers

Prigogine (43) developed, based on his average potential model (44), a corresponding states theory of r-mers which is basically a group approach. The average potential model which was developed based on statistical mechanics with average interaction energy for a pair of molecules combines the basic ideas underlying the theory of conformal solutions with those of the cell model of solutions.

The corresponding states theory of r-mers assumes that the number of degrees of freedom of a molecule may be divided into the internal degrees of freedom, which are controlled almost entirely by the valence forces of the molecule and are only slightly influenced by the molecular environment, and the external degrees of freedom, which are unaffected by the valence forces and are dependent on the environment of the molecule. The number of external degrees of freedom alone enters into the configurational partition function and gives rise to structure-dependent contributions to the excess functions.

This theory considers all of the molecules to be composed of groups or segments which may be thought of as point centers. Two molecules interact when one or more groups of one molecule interact with one or more groups of the second molecule. Pairwise additivity is assumed and hence the total potential energy of the liquid is given by summing the pairwise interactions over all two-group interactions in the system.

In this model the molecules are imagined to be arranged on a quasi-crystalline lattice with each group corresponding to a lattice point, and the cell method is applied in a straightforward manner to obtain the partition function.

This theory permits correlation of the thermodynamic properties of polymers and demonstration of how their size and structure determines these thermodynamic properties. However, the theory is restricted to systems where all segments of a molecular chain are identical.

Hermsen and Prausnitz (27, 28) extended the theory to the case where the segments of a molecule chain may be primary, secondary, or tertiary, or may have double bonds. They permitted the cell partition function to be a function of both reduced volume and reduced temperature. At the same time they included (in a semi-empirical manner) the effect of lattice irregularities on the configurational energy. The modified theory gives a satisfactory fit of the configurational properties of 35 hydrocarbons ranging from C_1 to C_{20} from the triple point to slightly above the normal boiling point.

E. Group Interaction Model

Redlich, Derr, and Pierotti (45) developed a group interaction model which calculates the heats of mixing of liquid solutions as the sum of contributions from pairs of interacting groups. The contribution of each pair of groups is assumed to be independent of the nature of the molecules involved and dependent on the group concentration, "group cross section" characteristic of each kind of group and interaction energy characteristic of each group pair.

This model has been tested by Papadopoulos and Derr (40) on binary solutions of hydrocarbons with a deviation within the experimental errors of the limiting heat data. Specially noteworthy features of the model include:

1. The energy of interaction of molecules is considered to be the sum of contributions due to contacts between groups (or radicals) in the molecules. The contribution of each contact is dependent on the two groups in question but is

independent of other groups either on the same molecule or on other molecules in the mixture.

2. The relative frequency of interaction among groups is assumed to depend on the cross section of the groups. Empirical rules are established to relate liquid molal volume of hydrocarbons to group volumes. The cross section of a group is then related to the 2/3 power of its group volume.

F. Solution of Groups Model

Wilson and Deal (59) have proposed a solution of groups model which describes the partial excess free energy as the sum of structural contributions and group contributions as

$$\log \gamma_i = \log \gamma_i^S + \log \gamma_i^G \qquad (2\text{-}3)$$

The first term on the right hand side of Equation (2-3) is a structural contribution due to structure of the molecule as a whole. The second term on the right hand side of the equation is a group contribution due to the interaction of the functional groups.

The structural contribution or the size contribution, which represents the only distinction between environments of the same group constitution and different molecular constitutions, is evaluated by a Flory-Huggins relation expressed in terms of the number of groups in the respective molecules of the mixture:

$$\log \gamma_i^S = \log \frac{\Sigma_v n'_{vi}}{\Sigma_j \Sigma_v x_j n'_{vj}} + 0.4343 \left(1.0 - \frac{\Sigma_v n'_{vi}}{\Sigma_j \Sigma_v x_j n'_{vj}}\right) \qquad (2\text{-}4)$$

where n'_{vi} is the number of atoms of type v in molecular component i. The contribution from interactions of groups is the sum of the individual contributions of each group taken as the difference between contributions in solution and molecular standard state.

$$\log \gamma_i^G = \Sigma_v n_v^i (\log \Gamma_v - \log \Gamma_v^*) \qquad (2\text{-}5)$$

where Γ_v is the activity coefficient of group v in a group solution and Γ_v^* is that in a standard group solution. The individual group contribution (Γ_v) is taken as a single function of the group concentrations of environment for both solution and standard state:

$$\Gamma_v = F(Y_1, Y_2, \ldots) \qquad (2\text{-}6)$$

where Y's are group concentrations in terms of fraction.

This model, with its assumptions that in some way both the enthalpic and entropic contributions to the partial molal excess free energy are simply additive (Equation 2-5) and that the concentration dependency of these contributions may be characterized from a base case (Equation 2-6), is most useful. Wilson applied this model to two fairly extreme cases, mixtures containing paraffin (CH_3, CH_2) and hydroxyl (OH) groups and mixtures containing paraffin and nitril (CN) groups; no distinction was made between methyl and methylene groups. In the -OH case, he used the single hexane-methanol binary as base to obtain Γ curves and estimated the ethanol-heptane binary. The results show satisfactory agreement with experimental data over a wide range of activity coefficient values.

Recently, Scheller (50) presented a correlation of a broad range of mixtures based on the solution of groups model. By the use of mixture data containing water, he has defined Γ_{OH} and Γ_{CH_2} curves over the entire range of CH_2-OH mixtures and calculated the log γ^s term with molar volumes instead of the group numbers. This correlation represents the experimental data of eight binary systems quite satisfactorily.

There are several models, which are basically group approaches, that have reached some success in representing thermodynamic properties of solutions, such as models by Flory (19), Hijmans (29), Irmann (33), Meyer and Wagner (38).

In summary, the preceding review of the literature on group contribution models serves to indicate the current state of progress in the field. The review demonstrates that the intuitively reasonable approach of treating mixtures in terms of their constituent groups to estimate the thermodynamic properties can be of considerable practical use. However, the approaches to handling mixtures in terms of groups remain essentially empirical in nature. Although some more theoretical approaches have been presented, more detailed and sufficiently quantitative theories to meet technological needs are needed.

CHAPTER III

THE LOCAL SURFACE GROUP CONTRIBUTION THEORY

A group contribution theory for liquid solutions containing polar substances is developed in this chapter in a manner similar to the group interaction theory of heat of mixing advanced by Redlich, Derr, and Pierotti (45); in this work, however, the probability of interaction between two groups is considered to depend both on the magnitude of the interaction energy between the groups and on the free surface areas of the groups. Thus, the local ordering or preferential interaction between groups due to interaction energy differences is considered in this study.

There is certainly oversimplification in the group interaction theory of Redlich, et al., for no account is taken of some generally recognized factors, such as (1) chemical effect of neighboring groups on the energy of an interacting pair of groups, (2) effect of variation of distance of separation of the groups in different mixtures, and (3) preferential interaction between groups due to either spatial or energy conditions. The effect of these factors can be expected to vary depending on the mixture.

In particular, the postulate concerning the relative frequency of group interaction appears to be adequate for hydrocarbon solutions in which the interaction energies are of comparable order of magnitude. For these interactions, the relative frequencies might reasonably be expected to be governed by a purely geometrical property such as the group cross section. However, interaction energies in solutions containing polar substances can be of very different magnitude and strongly attracted pairs interact preferentially. Thus, the relative frequency of interaction is governed by the energy properties of the groups as well as by their geometrical properties.

The objectives of the present study are (1) to develop quantitative expressions for relative frequency of interaction of groups in solutions containing polar substances, (2) to develop the necessary energy parameters to describe group interactions in solutions of alcohols and n-paraffins, and (3) to make comparisons with experimental data.

A. Heat of Mixing

1. Surface Area as a Measure of Frequency

Consider a pure liquid in which each molecule to be composed of characteristic groups, or radicals. These groups may be (1) CH_3, (2) CH_2, (3) OH, etc. Let the number of groups of type v per molecule be n_v and the free surface area per group be s_v. That is, a molecule may consist of n_v groups v with s_v free surface area per group, n_u groups u with s_u free surface area per group, etc. The total free surface area of v groups in a molecule is then

$$A_v = n_v s_v \tag{3-1}$$

The total surface of one molecule is

$$A_t = \Sigma_v A_v \tag{3-2}$$

where the summation is taken over all the kinds of groups in the molecule. The fractional area of the free surface belonging to group u is

$$f_u = A_u/\Sigma_v A_v \tag{3-3}$$

For the moment, if preferential interactions due to energy differences are ignored, the probability of interaction of the groups would be determined entirely by the surface fractions and is taken proportional to the free surface fraction in the liquid. Now consider a central group v being surrounded by all kinds of groups in the pure liquid. The fraction of the surface of group v interacting with group u in the liquid is the same as the fraction of the overall surface belonging to group u, that is f_u.

Let λ_{uv} denote the energy of interaction between group u and group v per unit surface area of contact. The energy of interaction between the v groups in a specified molecule and the u groups in the liquid is

$$A_v(A_u/\Sigma_w A_w)\lambda_{uv} \tag{3-4}$$

The energy of all interactions in which the v groups of a molecule participate is

$$A_v\Sigma_u(A_u/\Sigma_w A_w)\lambda_{uv} \tag{3-5}$$

By summing the above expression over all groups and dividing by two to avoid counting each interaction twice, the total energy of interaction of all the groups of a molecule is

$$\tfrac{1}{2}\,\Sigma_v A_v \Sigma_u (A_u/\Sigma_w A_w)\lambda_{uv} \qquad (3\text{-}6)$$

where all the v-v interactions must be counted twice. The sum extends over all groups present in the molecule. For example, for a molecule containing two types of groups of u and v, the total interaction energy is

$$\frac{A_u{}^2\lambda_{uu}}{(A_u + A_v)} + \frac{A_u A_v \lambda_{uv}}{(A_u + A_v)} + \frac{A_v{}^2\lambda_{vv}}{(A_u + A_v)} \qquad (3\text{-}6a)$$

The total energy of interactions in one mole of liquid is obtained simply by multiplying the total interaction energy of a molecule by Avogadro's number, N, and this energy is identified with the energy of vaporization into vacuum:

$$-\Delta U^v = \frac{N}{2}\,\Sigma_u\Sigma_v(A_u A_v/\Sigma_w A_w)\lambda_{uv} \qquad (3\text{-}7)$$

The concepts are extended to mixtures. The free surface area and the surface area fraction of groups in solution may be found in a similar way. The free surface area of group u in solution is given by

$$\Sigma_j x_j A_{uj} \qquad (3\text{-}8)$$

where x stands for mole fraction. The first subscript in a doubly subscripted quantity identifies a group; the second subscript a molecule. The fraction of the surface area of all molecules in solution that belong to group u is found to be

$$f_u = \Sigma_j x_j A_{uj}/\Sigma_w \Sigma_i x_i A_{wi} \qquad (3\text{-}9)$$

For one mole of mixture, the energy of vaporization into vacuum is

$$-\Delta U^{vM} = \frac{N}{2} \Sigma_j \Sigma_k \Sigma_u \Sigma_v (x_j x_k A_{uj} A_{vk} / \Sigma_w \Sigma_i x_i A_{wi}) \lambda_{uv} \qquad (3\text{-}10)$$

To evaluate the enthalpy of mixing, the following mixing processes are considered:

1. The components are mixed in the liquid state and the mixture is vaporized into vacuum.
2. Each pure component with an amount equal to its mole fraction in the mixture is vaporized at the same condition into vacuum, and the vapors are then mixed.

In the first case, the total energy change involves energy of vaporization and energy of mixing. In the second process, the total energy change is the energy of vaporization only, since there is no energy of mixing of ideal gases. Thus, the difference of the total energy changes between the two mixing processes is the energy of mixing of the liquid solution. If any minor differences between internal energy of mixing, ΔU^M, and heat of mixing, ΔH^M, for liquid solutions are ignored, then the enthalpy of mixing is related to the energies of vaporization into vacuum by

$$\Delta H^M \approx \Delta U^M = \Sigma_i x_i (\Delta U^v)_i - \Delta U^{vM} \qquad (3\text{-}11)$$

The surface areas of the groups and of the molecules are calculated from Van der Waals radii and covalent radii of atoms. Figure 2 shows the geometrical construction.

The atomic radii for carbon, hydrogen, and oxygen atoms are taken from Gould (23) and are given in Table I. The surface areas of groups thus computed are given in Table II. The detailed method of computation is given in everywhere (6, 51).

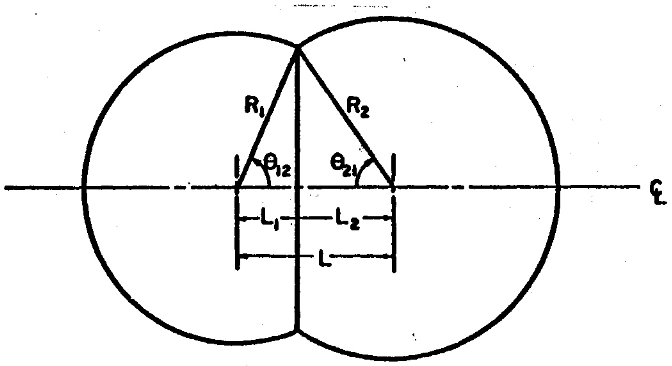


Figure 2. Geometry of Bonded Atoms

TABLE I

ATOMIC RADII (23)

Atom	R, Van der Waal's radius, Å.	L, Covalent radius, Å.
C	1.70	0.77
H	1.20	0.28
O	1.40	0.74

TABLE II

FREE SURFACE AREAS OF GROUPS

Group	Bonded to	s x 10^{-9}, sq. cm./mole/group
CH_2	Two carbons	1.35
CH_2	One carbon, one oxygen	1.54
CH_3	Carbon	2.13
CH_3	Oxygen	2.32
OH	Carbon	1.30

The use of atomic surfaces is a departure from the cross section of Redlich, et al. Atomic surfaces appear to be more natural choices for the development of a molecular model, since group cross sections cannot be evaluated for the hydroxyl group and most other polar groups as their group volumes are negative when evaluated from molal liquid volumes.

2. Local Concentration Due to Energy Differences

The foregoing treatment probably is suitable to account for the frequency of group interaction either in mixtures in which all the interaction energies are of comparable magnitude or at such high temperatures that the thermal energy of motion suffices to upset any preferential energy conditions. However, when the interaction energies between various group pairs are widely different, and the differences are large compared with the thermal energy of motion, one would expect the high energy group pairs to interact preferentially. The deciding factor for preferential interaction is the relative magnitude of the interaction and thermal energies.

To incorporate the preferential interaction due to interaction energy differences, a pure liquid is first considered. Prigogine (43) suggested that the external degree of freedom of a chain molecule of r-mers is 2r + 1. The average external degree of freedom per chain link is (1/r)(2r + 1), which is approximately equal to 2. The principle of equi-partition of energy states that the average energy associated with each degree of freedom is $\frac{1}{2}kT$. The thermal energy of each chain link or group is approximately kT.

As before, the interaction energy between group u and group v per unit area of contact is denoted by λ_{uv}. The thermal energy of u group per unit area is kT/s_u; and that of v group is kT/s_v. The total thermal energy associated with the interaction energy, λ_{uv}, is then

$$kT\left(\frac{1}{s_u} + \frac{1}{s_v}\right) = \left(\frac{s_u + s_v}{s_u \times s_v}\right)kT \qquad (3\text{-}12)$$

The probability of a v group interacting with a u group is then assumed to depend on the ratio of this interaction energy to its associated thermal energy.

The probability of interaction is taken to be proportional to the total surface of u groups weighted statistically by the Boltzmann factor $\exp[-(\frac{s_u s_v}{s_u + s_v})\frac{\lambda_{uv}}{kT}]$, that is

$$A_u \exp\left[-\left(\frac{s_u s_v}{s_u + s_v}\right)\frac{\lambda_{uv}}{kT}\right] \qquad (3\text{-}13)$$

This quantity when normalized leads to the expression of fractional probability as

$$A_u \exp\left[-\left(\frac{s_u s_v}{s_u + s_v}\right)\frac{\lambda_{uv}}{kT}\right]\Big/\Sigma_w A_w \exp\left[-\left(\frac{s_w s_v}{s_w + s_v}\right)\frac{\lambda_{wv}}{kT}\right] \qquad (3\text{-}14)$$

The energy of interaction of the v groups of a molecule with all other groups is given by

$$A_v \Sigma_u \left[A_u \exp(-s_{uv}\lambda_{uv}/kT)\Big/\Sigma_w A_w \exp(-s_{wv}\lambda_{wv}/kT)\right]\lambda_{uv} \qquad (3\text{-}15)$$

where by definition

$$s_{uv} = \frac{s_u s_v}{s_u + s_v}$$

s_{uv} is then a half of the harmonic mean of s_u and s_v.

The energy of all the interactions in one mole of pure liquid is identified with the molal energy of vaporization into vacuum:

$$-\Delta U^v = \frac{N}{2}\sum_u \sum_v \left[A_u A_v \exp(-s_{uv}\lambda_{uv}/kT)\Big/\Sigma_w A_w \exp(-s_{wv}\lambda_{wv}/kT)\right]\lambda_{uv} \qquad (3\text{-}16)$$

Equation (3-16) reduces to Equation (3-7) when all $s\lambda$'s are of comparable magnitude or when kT is large compared with $s\lambda$.

The same concepts are extended to mixtures. The fractional probability of interaction of a central v group with a u group is given by

$$\Sigma_j x_j A_{uj} \exp(-s_{uv}\lambda_{uv}/kT)\Big/\Sigma_w \Sigma_i x_i A_{wi} \exp(-s_{wv}\lambda_{wv}/kT) \qquad (3\text{-}17)$$

The total energy of all the interactions in one mole of mixture is identified with the molal energy of vaporization into vacuum:

$$-U^{vM} = \frac{N}{2}\sum_j\sum_k\sum_u\sum_v\left[\frac{x_j x_k A_{uj} A_{vk} \exp(-s_{uv}\lambda_{uv}/kT)}{\Sigma_w \Sigma_i x_i A_{wi} \exp(-s_{wv}\lambda_{wv}/kT)}\right]\lambda_{uv} \qquad (3\text{-}18)$$

The enthalpy of mixing is related to the energies of vaporization into vacuum by Equation (3-11) in the same way as before.

B. Excess Entropy and Excess Free Energy

Consider a liquid mixture containing n_u, n_v, . . . groups and ignore for the moment the preferential interactions due to energy differences and focus attention on a central group v in the solution, the probability of interaction of groups u and v would be equal to the fraction of the surface area of all molecules in the solution that belong to group u as given by Equation (3-9).

$$f_u = \Sigma_j x_j A_{uj} / \Sigma_w \Sigma_i x_i A_{wi} \qquad (3\text{-}9)$$

The number of groups u required to cover this fraction of v's surface is given by

$$n_{uv}{}^{o} = f_u s_v / s_u \qquad (3\text{-}19)$$

Thus, the group fraction of u about v is given by

$$\begin{aligned} Y_u{}^{o} &= n_{uv}{}^{o} / \Sigma_w n_{wv}{}^{o} \\ &= \left(\frac{\Sigma_j x_j A_{uj}}{\Sigma_w \Sigma_i x_i A_{wi}} \frac{s_v}{s_u}\right) \Bigg/ \Sigma_m \left(\frac{\Sigma_j x_j A_{mj}}{\Sigma_w \Sigma_i x_i A_{wi}} \frac{s_v}{s_m}\right) \\ &= \frac{\Sigma_j x_j n_u}{\Sigma_w \Sigma_j x_j n_w} \end{aligned} \qquad (3\text{-}20)$$

This is a bulk group fraction of u about v. The superscript o denotes the bulk quantity. Similarly, the group fraction of v is

$$Y_v^{\,o} = \left(\frac{\Sigma_j x_j A_{vj}}{\Sigma_w \Sigma_j x_j A_{wj}} \frac{s_v}{s_v}\right) \Big/ \sum_u \left(\frac{\Sigma_j x_j A_{uj}}{\Sigma_w \Sigma_j x_j A_{wj}} \frac{s_v}{s_u}\right) = \frac{\Sigma_j x_j n_v}{\Sigma_w \Sigma_j x_j n_w} \qquad (3\text{-}21)$$

If the preferential interactions due to energy differences are taken into account, the local group fractions Y_1, Y_2, . . . which differ from the bulk fractions due to the specific interaction of v with other groups can be evaluated in the same way.

The fraction of v's surface covered by u is given by Equation (3-17) as

$$\frac{\Sigma_j x_j A_{uj} \exp(-s_{uv}\lambda_{uv}/kT)}{\Sigma_w \Sigma_i x_i A_{wi} \exp(-s_{wv}\lambda_{wv}/kT)} \qquad (3\text{-}17)$$

The number of groups u required to cover this fraction of surface is

$$n_{uv} = \frac{s_v}{s_u} \frac{\Sigma_j x_j A_{uj} \exp(-s_{uv}\lambda_{uv}/kT)}{\Sigma_w \Sigma_i x_i A_{wi} \exp(-s_{wv}\lambda_{wv}/kT)} \qquad (3\text{-}22)$$

The number of group v is

$$n_{vv} = \frac{s_v}{s_v} \frac{\Sigma_j x_j A_{vj} \exp(-s_{vv}\lambda_{vv}/kT)}{\Sigma_w \Sigma_j x_j A_{wj} \exp(-s_{wv}\lambda_{wv}/kT)} \qquad (3\text{-}23)$$

and the total number of groups required to cover the surface of the central group v is

$$n_{Tv} = \Sigma_u n_{uv} \qquad (3\text{-}24)$$

Thus, the local group fraction of v is

$$Y_v = n_{vv}/\Sigma_w n_{wv} = \frac{\Sigma_j x_j A_{vj} \exp(-s_{vv}\lambda_{vv}/kT)/s_v}{\Sigma_w \Sigma_j x_j A_{wj} \exp(-s_{wv}\lambda_{wv}/kT)/s_w} \qquad (3\text{-}25)$$

From thermodynamics, the molal entropy of mixing of an ideal solution is

$$S^{Mo} = -R\Sigma_j x_j \ln(x_j) \tag{3-26}$$

and the partial molal entropy of mixing of i is

$$\bar{S}_i^{Mo} = -R\ln(x_i) \tag{3-27}$$

The same concept is extended to solution of groups. The partial group entropy of mixing of v of an ideal group solution is given by

$$\bar{S}_v^{Mo} = -R\ln(Y_v^o) \tag{3-28}$$

and that of group solution is

$$\bar{S}_v^{M} = -R\ln(Y_v) \tag{3-29}$$

A partial group excess entropy is defined to be the difference of Equation (3-29) and Equation (3-28).

$$\bar{S}_v^{E} = -R\ln(Y_v/Y_v^o) \tag{3-30}$$

Thus, the excess entropy of a mixture is the difference of the sum of contributions to the mixture and to the pure components from partial group excess entropies of groups in the solution.

$$S^E = (\Sigma_v \Sigma_j x_j n_v^j \bar{S}_v^E)_M - \Sigma_i x_i (\Sigma_v \Sigma_j x_j n_v^j \bar{S}_v^E)_i \tag{3-31}$$

Having known ΔH^M and S^E, the excess free energy of the solution can be calculated from the following thermodynamic relation:

$$G^E = \Delta H^M - TS^E \qquad (3\text{-}32)$$

C. Application of Theory to Alcohol-Paraffin Systems

The proposed model was tested by using experimental data on heats of mixing in n-alcohol-n-paraffin binary systems. These systems were chosen for initial study because they possess only a few groups (CH_2, CH_3, and OH) and because excellent data are available from the systematic study of Savini, Winterhalter, and Van Ness (48) and Van Ness, et al. (56, 57). The data are comprised of seven binary mixtures which include three paraffins and five alcohols.

To predict the heats of mixing from Equation (3-18), values for the surface areas of CH_2, CH_3, and OH groups are required, as are values of the interaction energies for CH_2-CH_2, CH_2-CH_3, CH_3-CH_3, CH_2-OH, CH_3-OH, and OH-OH group interactions. The surface areas were calculated from the geometric model of the molecules involved as discussed in the previous section and are listed in Table II.

The hydrocarbon interaction energy parameters (CH_2-CH_2, CH_2-CH_3, and CH_3-CH_3) were determined independently of the heat of mixing data by applying Equation (3-16) to experimental data on the energies of vaporization at 30°C of the pure n-paraffins propane through decane.

Heats of vaporization from API Project 44 tables (1) were converted to ΔU^V values by use of the generalized charts of Lyderson, et al. (37) to account for compressibility factor and effect of pressure on enthalpy. A nonlinear regression was performed to determine the values of the three energy parameters which would give the least-mean-squares fit of Equation (3-16) to the energies of vaporization.

Values of the resultant parameters are given in Table IIIa, and a comparison of the calculated and experimental energies of vaporization is shown in Table IV. The agreement is very good (maximum error of 0.1%). However, this is not an exacting test of the model, since numerous three-parameter models represent paraffin heats of vaporization accurately.

The remaining three energy parameters, CH_2-OH, CH_3-OH, and OH-OH, were determined directly from heat of mixing data on the seven binary mixtures. Nonlinear regression was used to determine the parameter values. The previously determined hydrocarbon interaction energy parameters from Table IIIa were used as fixed input to this calculation. Nine experimental points, spaced at 0.1 mole fraction intervals from each of the seven binary mixtures, were used. The resultant parameters are shown in Table IIIb. The predicted heats of mixing, based on these parameters, are compared with the experimental data in Table V and in Figures 3 through 9. Also shown in these Figures (dashed lines) are results of a modified version of the theory which is discussed later.

The energy parameter values in Table III were employed to calculate excess free energies and entropies by Equation (3-31) and Equation (3-32) for three alcohol-n-paraffin binary systems where experimental data are available at the same temperature. The excess free energy data of ethanol-n-hexane solution at 30°C were obtained from extrapolation of Smith's (52) data at 25°C, using Wilson's equation (54). Since the Wilson equation has a built-in temperature dependence and the range of extrapolation is small, the data obtained from the extrapolation should be adequate for the present study.

Results of the free energy and entropy predictions are given in Table VI and in Figures 10, 11, and 12.

TABLE III

GROUP INTERACTION ENERGY PARAMETERS

Groups	Interaction Energy $-\lambda \times 10^9$, cal./sq. cm.
a. Based on energies of vaporization	
CH_2-CH_2	1,731
CH_2-CH_3	1,406
CH_3-CH_3	911
b. Based on heats of mixing	
CH_2-OH	2,174
CH_3-OH	1,340
OH-OH	4,751

TABLE IV

HYDROCARBON INTERNAL ENERGIES OF VAPORIZATION AT 30°C

Hydrocarbon	Energy of Vaporization, ΔU^V cal./g.-mole Experimental*	 This Work**
Propane	3,265	3,263
n-butane	4,497	4,501
n-pentane	5,704	5,708
n-hexane	6,905	6,901
n-heptane	8,090	8,085
n-octane	9,262	9,265
n-nonane	10,441	10,441
n-decane	11,615	11,616

* Based on heats of vaporization from Reference 1

** Based on energy parameters from Table IIIa

TABLE V

COMPARISON OF CALCULATED AND EXPERIMENTAL HEATS OF MIXING AT 30°C

System	Mole Fraction Alcohol	ΔH^M @ 30°C, cal./g.-mole		Deviation	
		Expt'l. (48)	Calc'd.	cal./g.-mole	%
Ethanol-n-hexane	0.1	112.93	105.46	-7.47	-6.6
	0.2	138.85	156.21	17.36	12.5
	0.3	149.42	173.61	24.19	16.2
	0.4	151.15	169.83	18.68	12.4
	0.5	144.83	152.40	7.57	5.2
	0.6	133.27	126.37	-6.90	-5.2
	0.7	114.59	95.41	-19.18	-16.7
	0.8	88.46	62.40	-26.06	-29.5
	0.9	52.57	29.81	-22.76	-43.3
Ethanol-n-nonane	0.1	130.67	108.27	-22.40	-17.1
	0.2	161.15	172.29	11.14	6.9
	0.3	175.67	202.75	27.08	15.4
	0.4	179.42	207.75	28.33	15.7
	0.5	175.48	193.06	17.58	10.0
	0.6	164.42	164.25	-0.17	-0.1
	0.7	145.89	125.75	-20.14	-13.8
	0.8	118.08	82.04	-36.04	-30.5
	0.9	74.86	38.05	-36.81	-49.2
Propanol-n-heptane	0.1	127.21	103.96	-23.25	-18.3
	0.2	157.31	158.35	1.04	0.7
	0.3	170.12	180.55	10.43	6.1
	0.4	170.19	181.05	10.86	6.4
	0.5	160.07	166.67	6.60	4.1
	0.6	141.92	142.10	0.18	0.1
	0.7	116.61	110.74	-5.87	-5.0
	0.8	85.00	75.22	-9.78	-11.5
	0.9	46.73	37.69	-9.04	-19.3
Butanol-n-heptane	0.1	123.75	99.70	-24.05	-19.4
	0.2	151.92	151.11	-0.81	-0.5
	0.3	165.07	171.98	6.91	4.2
	0.4	165.00	172.61	7.61	4.6
	0.5	154.50	159.46	4.96	3.2
	0.6	134.42	136.79	2.37	1.8
	0.7	107.52	107.59	0.07	0.1
	0.8	75.38	74.01	-1.37	-1.8
	0.9	39.16	37.73	-1.43	-3.6

TABLE V (Continued)

System	Mole Fraction Alcohol	ΔH^M @ 30°C, cal./g.-mole		Deviation	
		Expt'l. (48)	Calc'd.	cal./g.-mole	%
	0.1	109.69	91.93	-17.76	-16.2
	0.2	132.31	133.99	1.68	1.3
	0.3	141.85	148.23	6.38	4.5
Pentanol-n-hexane	0.4	140.77	145.71	4.94	3.5
	0.5	129.81	132.57	2.76	2.1
	0.6	110.19	112.50	2.31	2.1
	0.7	85.82	87.87	2.05	2.4
	0.8	58.46	60.24	1.78	3.0
	0.9	29.42	30.71	1.29	4.4
	0.1	106.44	80.44	-26.00	-24.4
	0.2	123.08	118.10	-4.98	-4.0
	0.3	129.23	131.59	2.36	1.8
Octanol-n-heptane	0.4	127.50	130.30	2.80	2.2
	0.5	118.99	119.46	0.47	0.4
	0.6	103.85	102.20	-1.65	-1.6
	0.7	82.28	80.52	-1.76	-2.1
	0.8	56.92	55.72	-1.20	-2.1
	0.9	28.56	28.68	0.12	0.4
	0.1	121.59	84.91	-36.68	-30.2
	0.2	142.31	131.08	-11.23	-7.9
	0.3	149.93	151.75	1.82	1.2
Octanol-n-nonane	0.4	149.42	154.83	5.41	3.6
	0.5	141.23	145.40	4.17	2.9
	0.6	122.88	126.87	3.99	3.2
	0.7	99.45	101.58	2.13	2.1
	0.8	70.00	71.24	1.24	1.8
	0.9	36.13	37.08	0.95	2.6

TABLE VI

COMPARISON OF PREDICTED AND EXPERIMENTAL EXCESS FREE ENERGIES AND EXCESS ENTROPIES AT 30°C

System	Mole Fraction Alcohol	G^E, cal./g.-mole			TS^E, cal./g.-mole		
		Expt'l.	Calc'd.	Dev.	Expt'l.	Calc'd.	Dev.
Ethanol-n-hexane (52)	0.1	152.80	192.44	39.64		-86.97	
	0.2	244.80	304.41	59.61		-148.19	
	0.3	300.99	361.69	60.70		-188.07	
	0.4	329.74	379.16	49.42		-209.33	
	0.5	334.70	366.08	31.38		-213.70	
	0.6	317.35	328.58	11.23		-202.23	
	0.7	277.69	270.85	-6.84		-175.47	
	0.8	214.30	195.83	-18.47		-133.47	
	0.9	123.92	105.37	-18.55		-75.60	
	1.0	0.00	0.00	0.00		0.00	
Ethanol-n-heptane (56)	0.1	159.44	185.35	25.91	-38.78	-78.65	-39.87
	0.2	251.99	299.36	47.37	-104.89	-136.72	-31.83
	0.3	309.99	361.06	51.07	-150.37	-176.30	-25.93
	0.4	340.56	382.56	42.00	-178.70	-198.75	-20.05
	0.5	347.38	372.00	24.62	-190.72	-204.97	-14.25
	0.6	330.88	335.15	4.27	-185.89	-195.46	-9.57
	0.7	290.75	276.32	-14.43	-164.30	-170.41	-6.11
	0.8	226.64	198.92	-27.72	-126.79	-129.76	-2.97
	0.9	132.82	105.90	-26.92	-72.20	-73.19	-0.99
	1.0	0.00	0.00	0.00	0.00	0.00	0.00
Propanol-n-heptane (57)	0.1	147.40	178.86	31.46	-20.78	-74.92	-54.14
	0.2	230.17	285.94	55.77	-73.59	-127.61	-54.02
	0.3	279.76	342.04	62.28	-110.20	-161.53	-51.33
	0.4	304.35	359.98	55.63	-134.68	-178.96	-44.28
	0.5	307.38	348.15	40.77	-147.99	-181.51	-33.52
	0.6	289.79	312.35	22.56	-148.54	-170.30	-21.76
	0.7	251.61	256.80	5.19	-135.30	-146.11	-10.81
	0.8	191.64	184.63	-7.01	-106.85	-109.47	-2.62
	0.9	108.67	98.35	-10.32	-62.17	-60.72	+1.45
	1.0	0.00	0.00	0.00	0.00	0.00	0.00

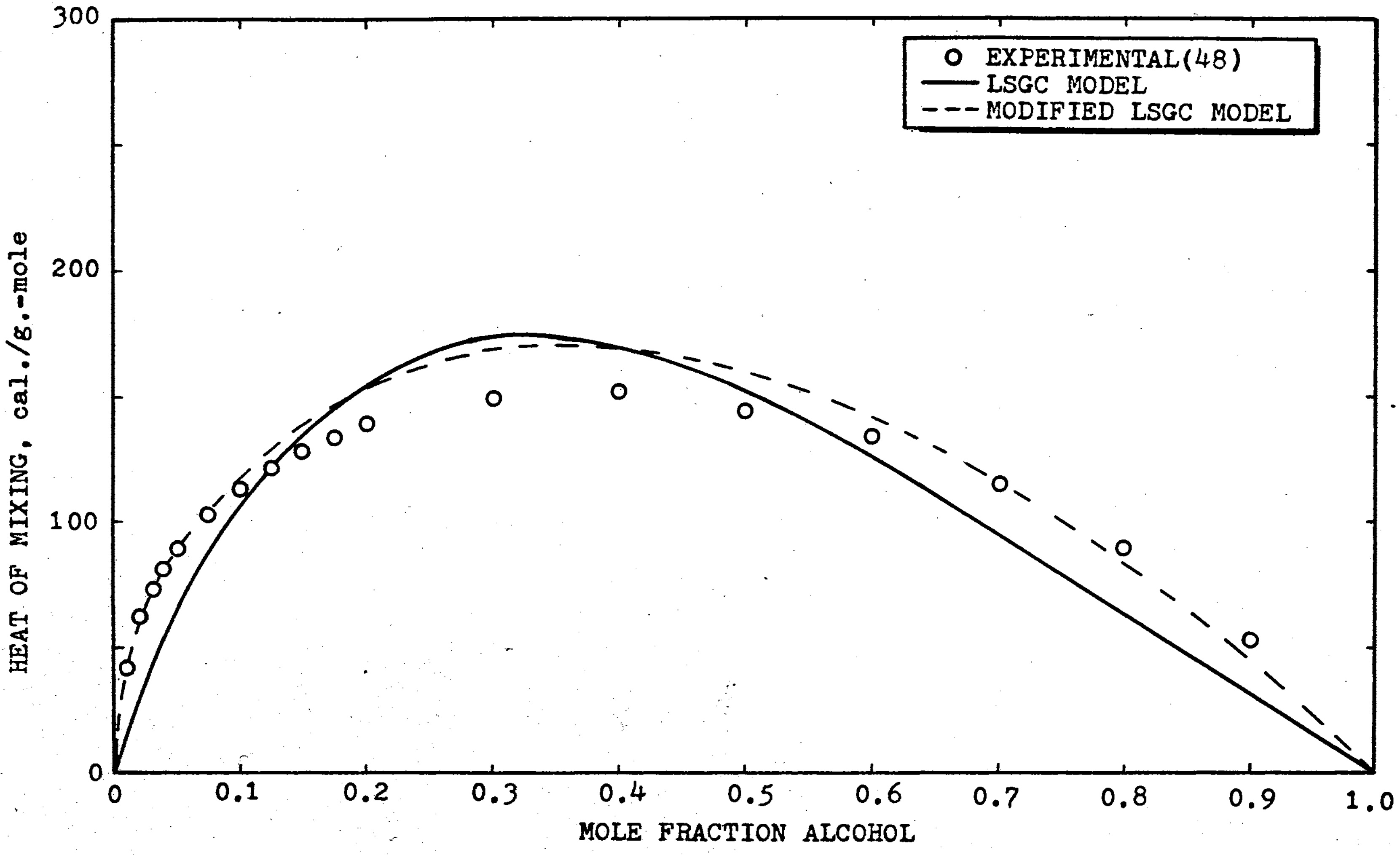


Figure 3. Heat of Mixing in the Ethanol-n-Hexane System at 30°C by the Local Surface Model

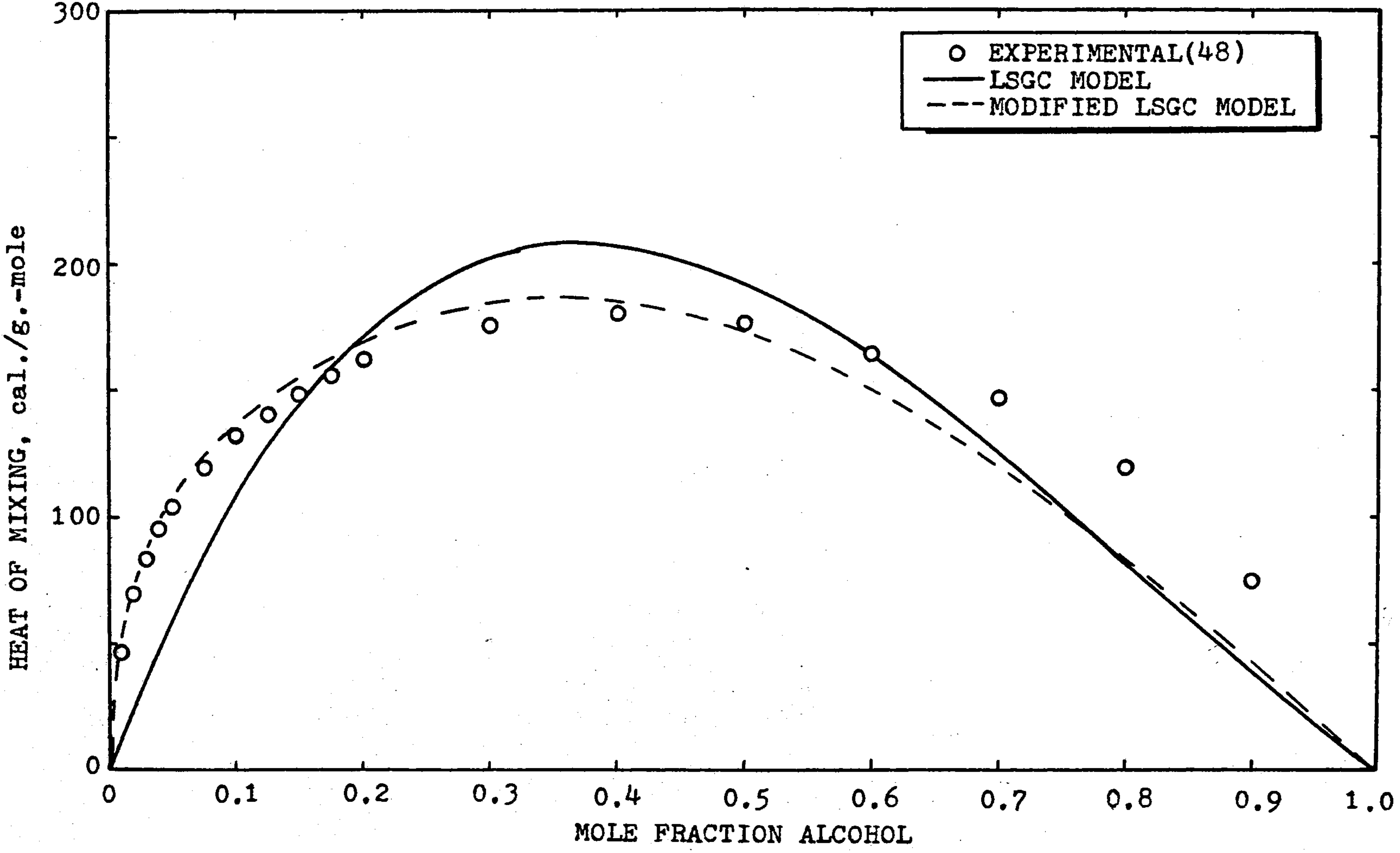


Figure 4. Heat of Mixing in the Ethanol-n-Nonane System at 30°C by the Local Surface Model

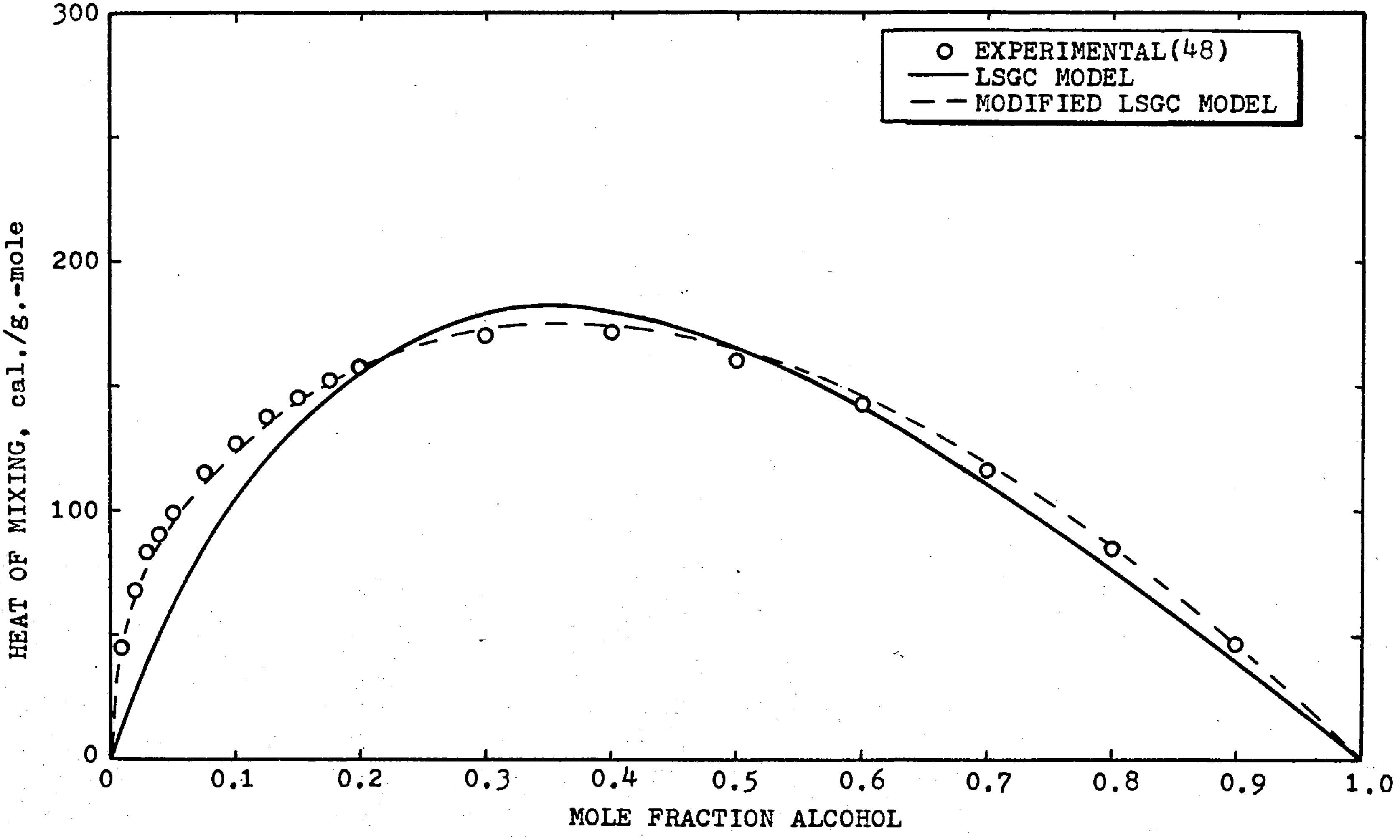


Figure 5. Heat of Mixing in the Propanol-n-Heptane System at 30°C by the Local Surface Model

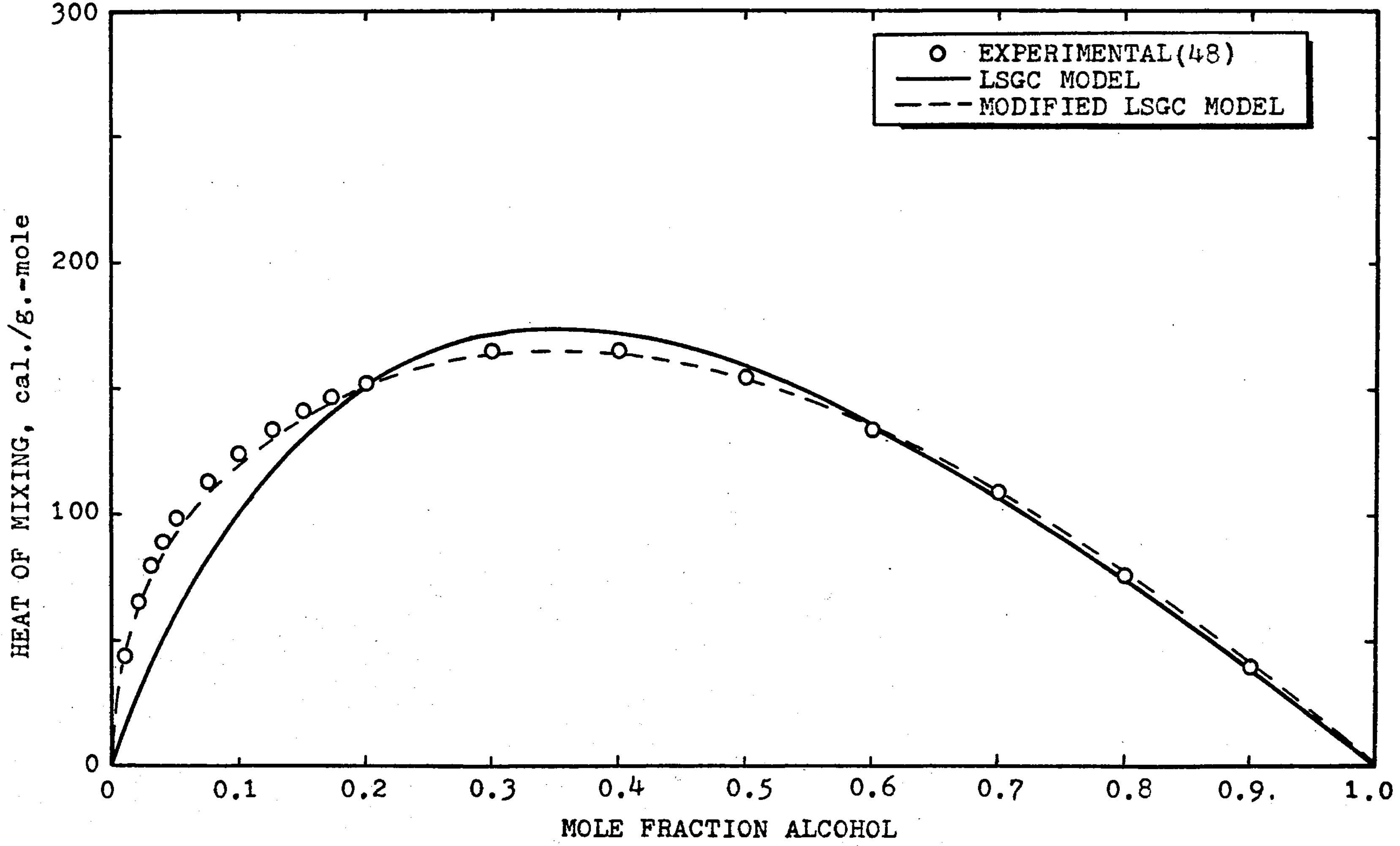


Figure 6. Heat of Mixing in the Butanol-n-Heptane System at 30°C by the Local Surface Model

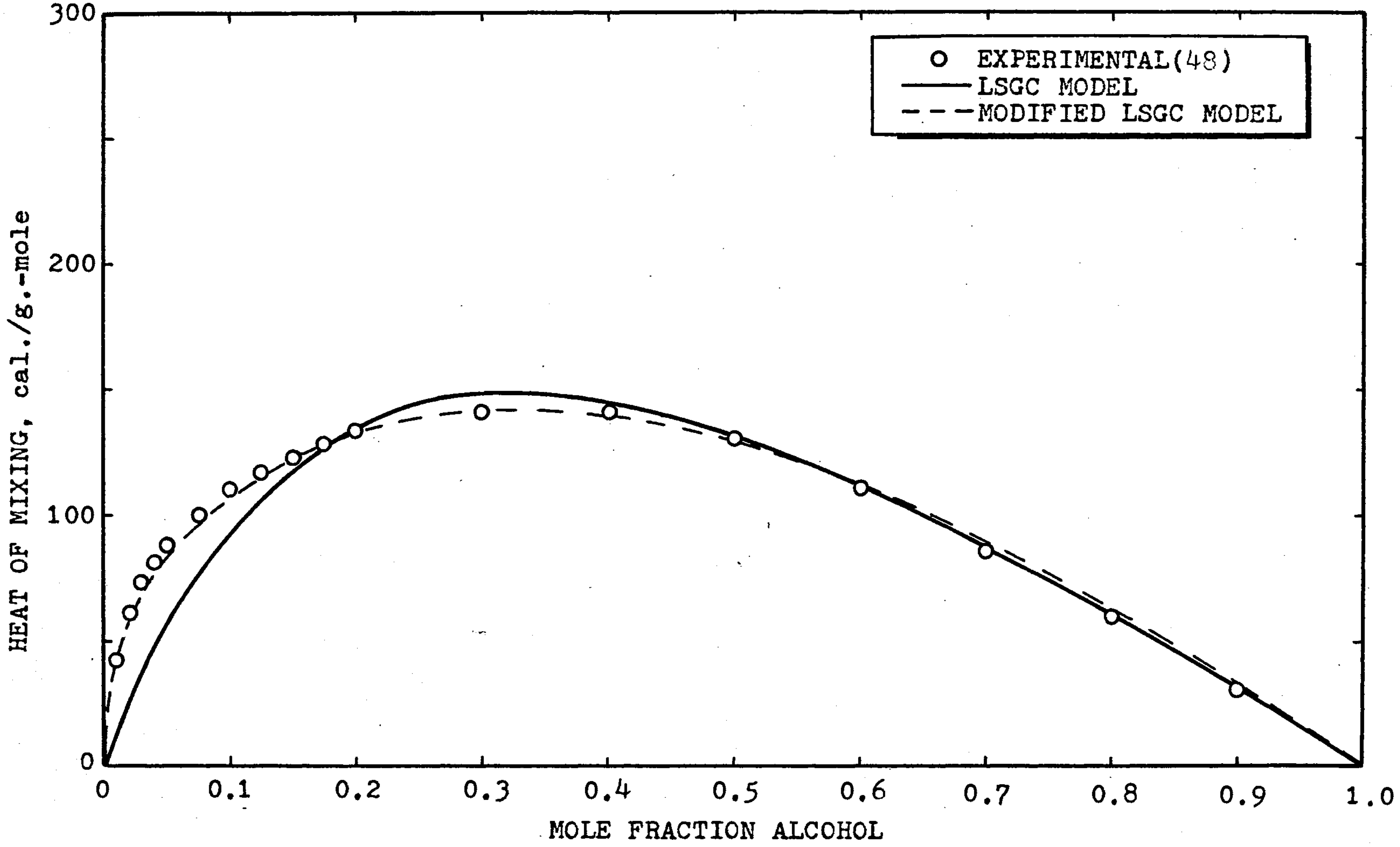


Figure 7. Heat of Mixing in the Pentanol-n-Hexane System at 30°C by the Local Surface Model

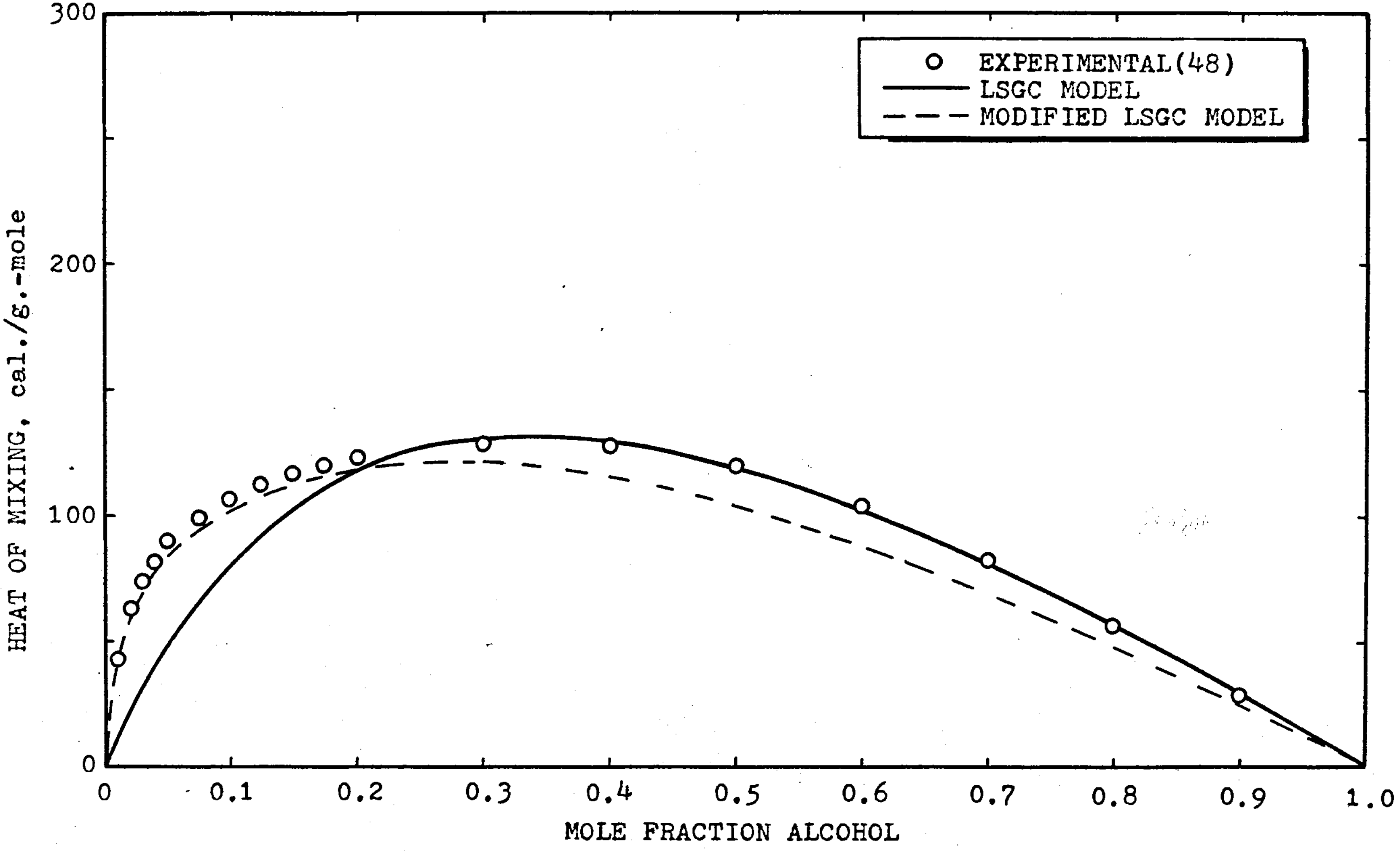


Figure 8. Heat of Mixing in the Octanol-n-Heptane System at 30°C by the Local Surface Model

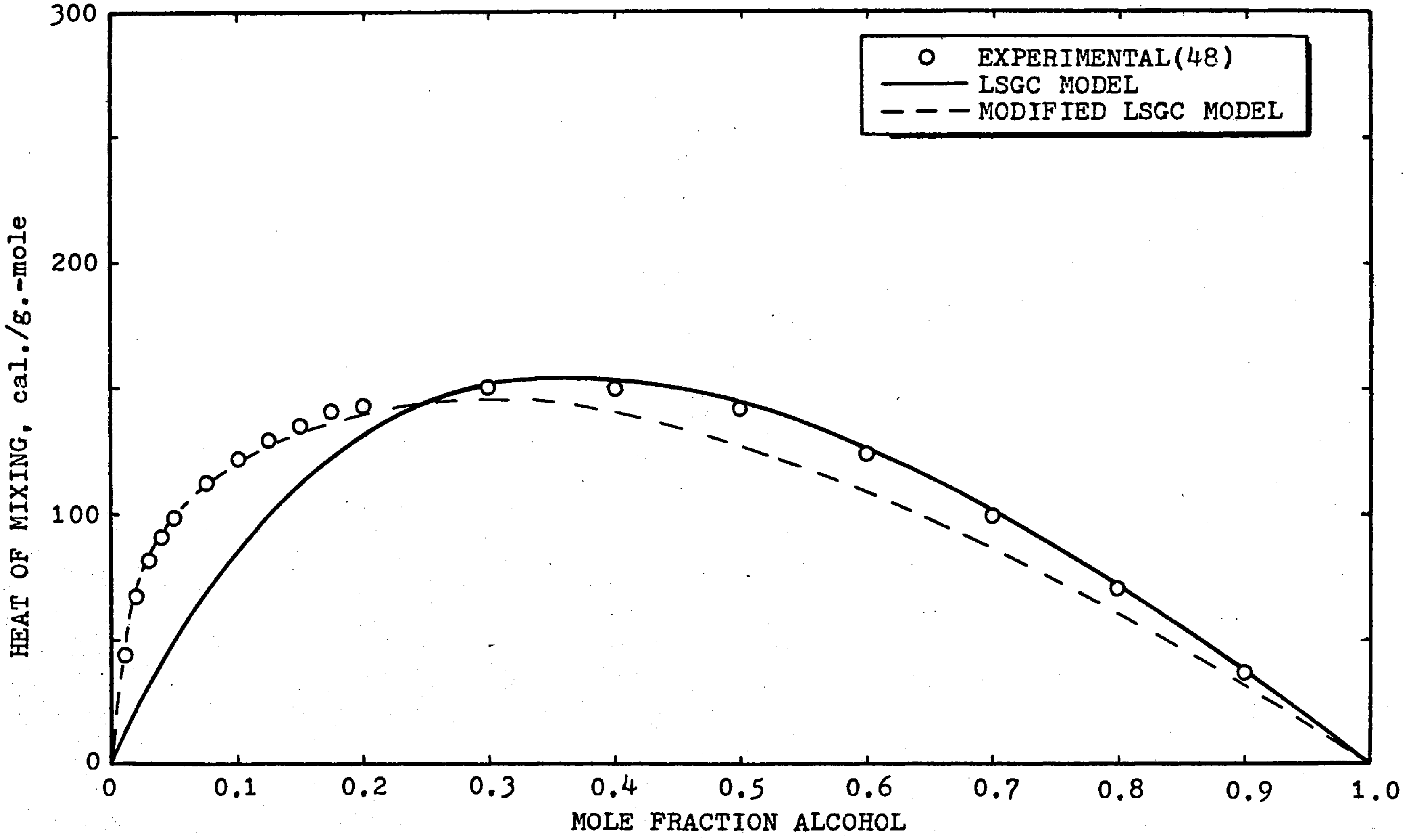


Figure 9. Heat of Mixing in the Octanol-n-Nonane System at 30°C by the Local Surface Model

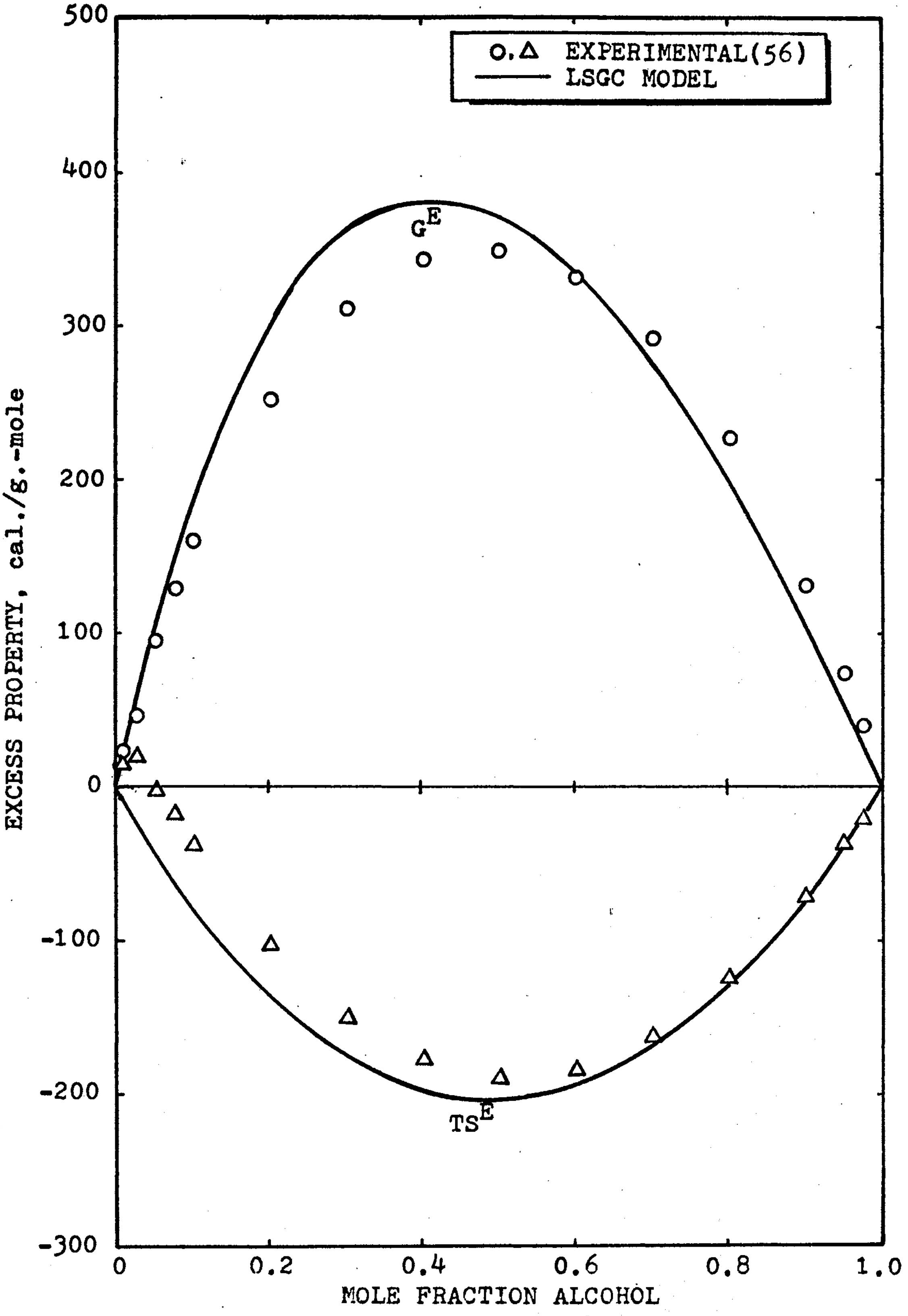


Figure 10. Excess Free Energy and Entropy for Ethanol-n-Heptane System at 30°C by the Local Surface Model

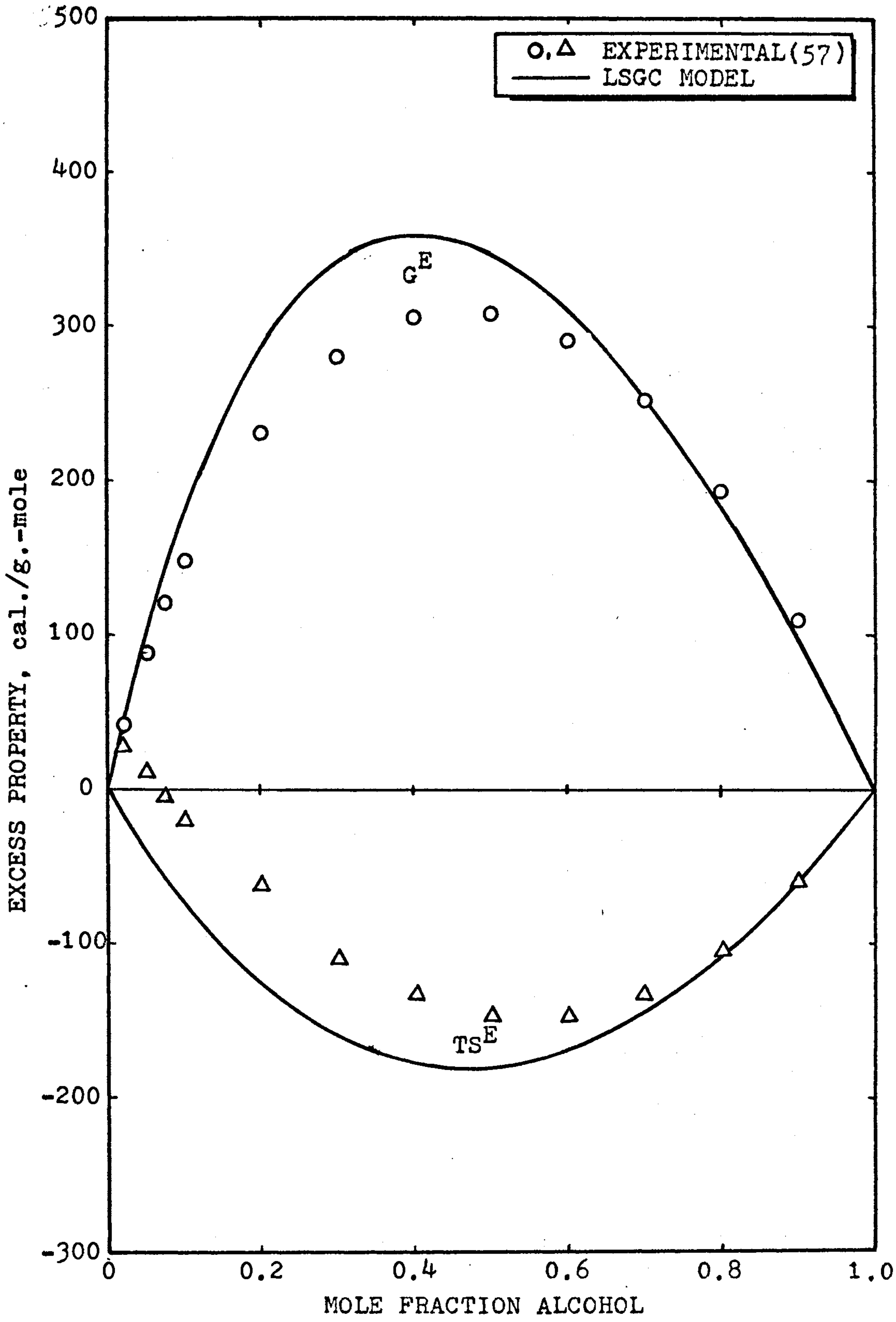


Figure 11. Excess Free Energy and Entropy for Propanol-n-Heptane System at 30°C by the Local Surface Model

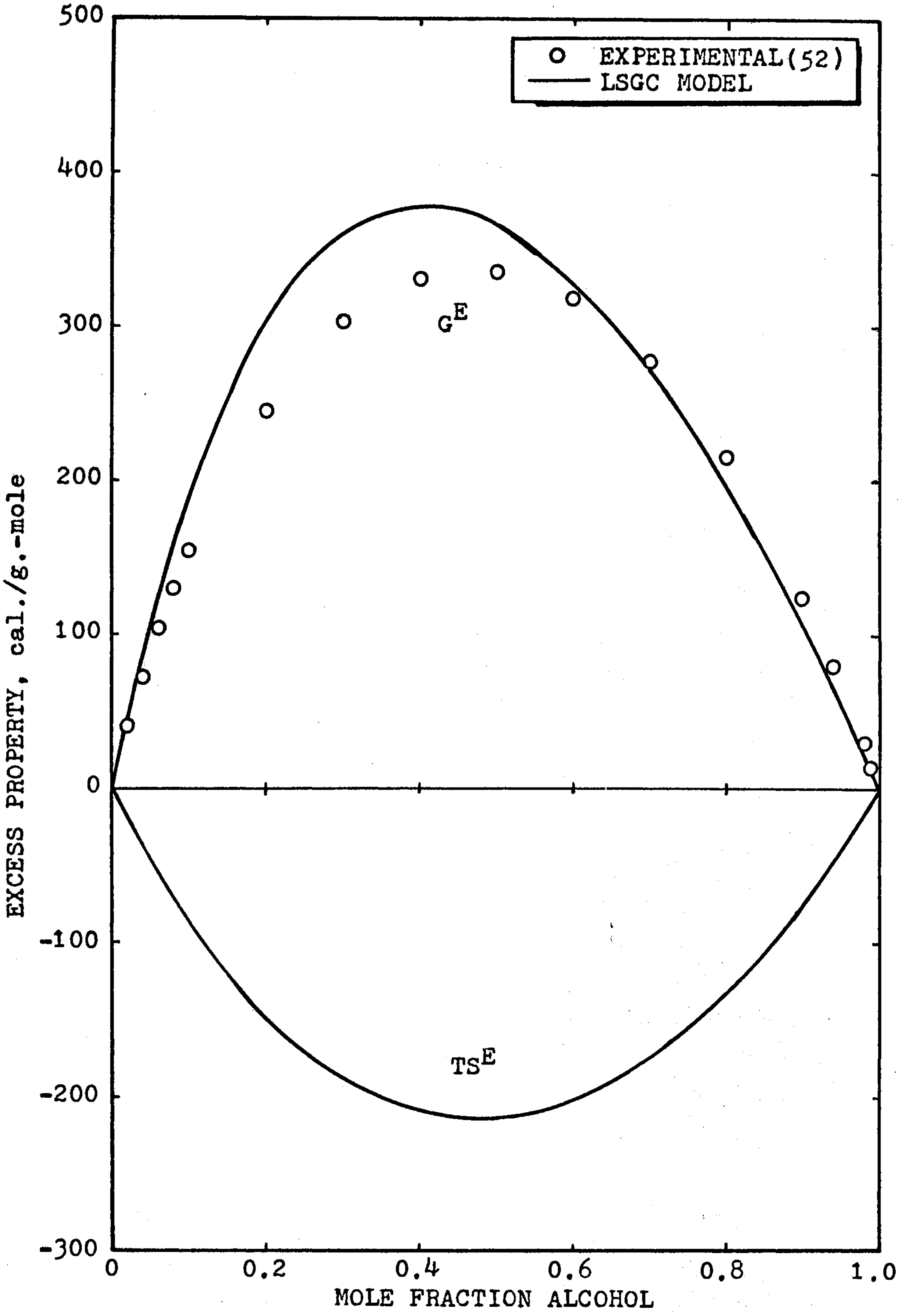


Figure 12. Excess Free Energy and Entropy for Ethanol-n-Hexane System at 30°C by the Local Surface Model

D. Discussion

1. Representation of Excess Properties

Figure 3 through Figure 9 show that by using three parameters based on the data of heats of mixing, reasonable agreement between theory and data is obtained for the seven binary systems. The asymmetry of the heat of mixing curves is correctly reflected by the model. The maximum values of ΔH^M seems to be well represented by the theory except for ethanol mixtures. Best agreement occurs for the mixtures of higher molecular weight components in the region of high alcohol concentrations. Least satisfactory agreement is found at low alcohol concentrations, where the model predicts consistently low values of ΔH^M.

Figures 10 through 12 show that the excess free energies and the excess entropies calculated from the set of energy parameters determined from energies of vaporization of n-paraffins and the heats of mixing data give a qualitative representation of the experimental excess entropies and free energies. The model fails to reflect the positive values of excess entropy at low alcohol concentrations. The positive TS^E values shown at low concentrations are due to the breaking of hydrogen bonds and the resulting gain in orientational freedom of the alcohol molecules. Since this breaking of hydrogen bonds is purely due to a dilution effect, it is significant at low alcohol concentrations.

2. Surface Energies of Group Pairs

The values of the interaction energy parameters of Table III are shown graphically in Figure 13. As expected the OH-OH interaction, where hydrogen bonding may occur, is by far the strongest interaction in the solution. However, when an OH group interacts with a hydrocarbon group, it behaves very similarly to a CH_2 group. The energies of CH_2-CH_2 and CH_3-CH_3 interactions appear in Figure 13 to be quite different. However, the values shown are in terms of energy per unit surface area. The energies per group pair may be obtained from these values by multiplying by the surface area per group and are as follows:

	cal./mole/group
CH_3-CH_3	1,940
CH_2-CH_2	2,337

In contrast, the value for OH-OH is 6,176 cal./mole/group.

Since the model has a built-in temperature dependence, these energy parameters could be considered, to a good approximation, to be independent of temperature over a small interval, which means that parameters obtained from data at one temperature may be used with reasonable confidence to predict properties at some other temperature not too far away.

In principle, the three interaction energy parameters involving the hydroxyl group (or, in fact, all six parameters) could be determined from data on energies of vaporization of pure n-alcohols. However, this was not attempted for the reason that any inaccuracies in the parameters and defficiencies in the theory would be magnified into excessively large errors in heats of mixing when all the energy parameters were determined from energies of vaporization. Thus, the remaining three energy parameters, CH_2-OH, CH_3-OH, and OH-OH were

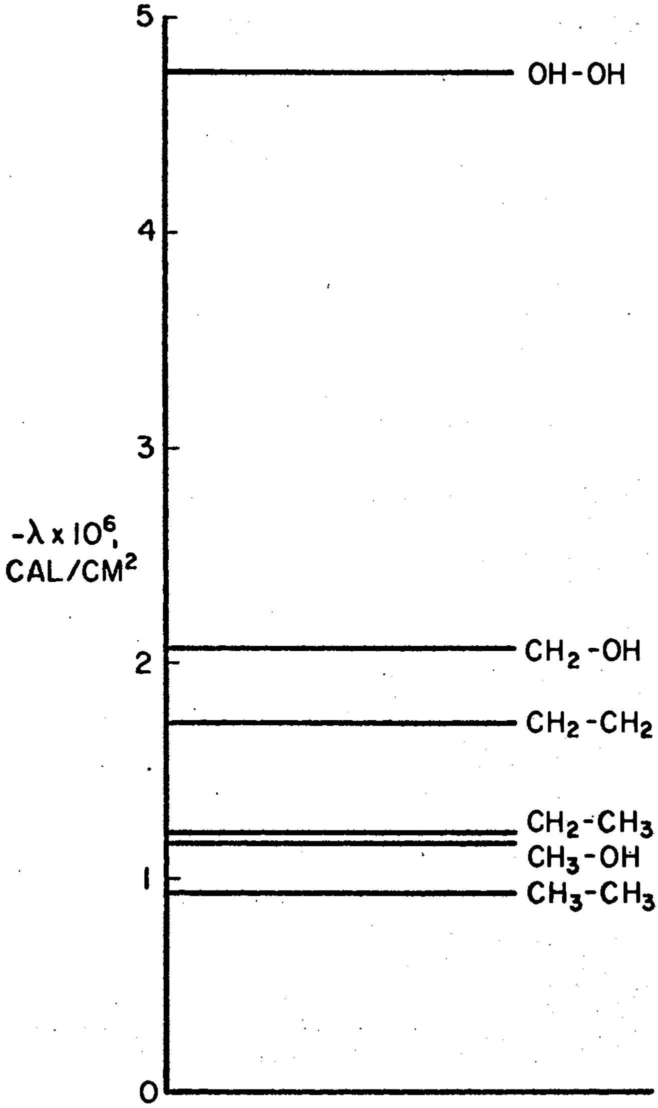


Figure 13. Surface Energies of Groups in Alcohol–Paraffin Systems

determined directly from the heat of mixing data.

3. Alcohol Internal Energies of Vaporization

In order to verify the attempt just mentioned, the previously determined energy parameters in Table III were used to predict the internal energies of vaporization of the normal alcohols and to compare with experimental data in Table VII. As expected, the agreement is poor.

TABLE VII

ALCOHOL INTERNAL ENERGIES OF VAPORIZATION AT 30°C
BASED ON ENERGY PARAMETERS IN TABLE III

	ΔU^v, cal./g.-mole		Deviation
Alcohol	Expt'l.*	Calc'd.	%
Methanol	8,233	4,195	-49.0
Ethanol	9,378	5,503	-41.3
Propanol	10,492	6,654	-36.6
Butanol	11,575	7,791	-32.7
Pentanol	12,672	8,923	-29.6

*Based on heats of vaporization from Reference 20.

The experimental internal energies of vaporization of n-alcohols at 30°C were converted from the heats of vaporization at 25°C given by Gjaldbaek and Niemann (20). They had collected the heats of vaporization data from several sources. The data reported at 25°C were converted to 30°C according to the following equation suggested by Hougen, Waston, and Ragatz (31).

$$\frac{H_2}{H_1} = \left(\frac{1.0 - T_{r2}}{1.0 - T_{r1}}\right)^{0.38} \qquad (3\text{-}33)$$

The heat of vaporization of butanol used by Gjaldbaek and Niemann seems to be small. The value used here was a smoothed value from a plot of internal energies of vaporization versus carbon number on the alcohol molecules as shown in Figure 14. The value of 11,575 cal./g.-mole for butanol used in this work is within the range of reported experimental values.

Values of the three energy parameters involving the hydroxyl group were also evaluated performing a nonlinear regression to obtain a least-mean-squares fit of Equation (3-16) to the energies of vaporization of alcohols. Values of the energy parameters so obtained are as follows:

λ_{CH_2-OH}	$-1{,}463 \times 10^{-9}$	cal./sq. cm.
λ_{CH_3-OH}	$-1{,}805 \times 10^{-9}$	cal./sq. cm.
λ_{OH-OH}	$-10{,}265 \times 10^{-9}$	cal./sq. cm.

A comparison of the calculated and experimental energies of vaporization is shown in Table VIII.

The agreement is very good, but the resultant energy parameters represent poorly the heats of mixing and excess properties. Thus, the possibility of determining properties of highly non-ideal mixtures from pure component properties is not achieved in the present work.

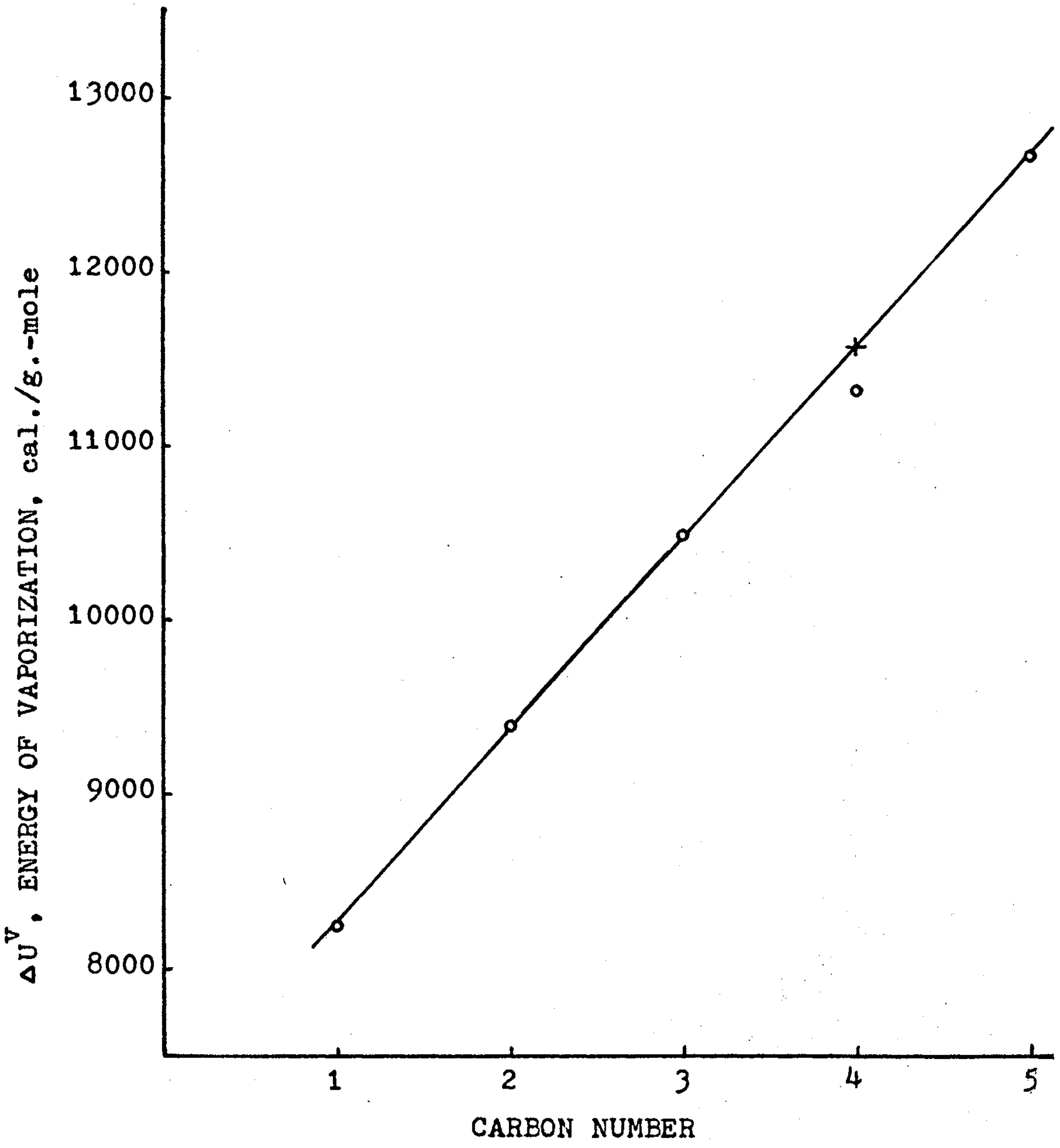


Figure 14. n-Alcohol Internal Energies of Vaporization Versus Number of Carbon Atoms in the Molecule

However, it is important to realize that this possibility is contained in the group solution theory. This possibility will continue to offer a worthwhile objective for further development of the theory in future investigations.

TABLE VIII

ALCOHOL INTERNAL ENERGIES OF VAPORIZATION AT 30°C: RESULTS OF FITTING EQUATION (3-16) TO THE DATA

	ΔU^V, cal./g.-mole		Deviation
Alcohol	Expt'l. (20)	Calc'd.	%
Methanol	8,233	8,288	0.67
Ethanol	9,378	9,366	-0.13
Propanol	10,492	10,460	-0.30
Butanol	11,575	11,581	0.05
Pentanol	12,672	12,717	0.35

4. Application to Partially Miscible Systems

Heats of mixing data for methanol-n-hexane and methanol-n-heptane mixtures at 30°C are available in literature from Savini, Winterhalter, and Van Ness (49). These systems show partial miscibility at 30°C. However, there is no way to test the applicability of the model to the partially miscible systems directly by heats of mixing data.

When a binary mixture is partially miscible, there exist two points with a common tangent on the plot of free energy of mixing versus mole fraction if the free energy of mixing is treated as a continuous function (47). The compositions of the two points represent the phase compositions in equilibrium.

To see whether the proposed model is applicable to the partially miscible systems, the free energies of mixing of methanol-n-hexane mixture are calculated from the following equation:

$$\Delta G^M = G^E + RT\Sigma_i x_i \ln(x_i) \tag{3-34}$$

by using the energy parameters in Table III. A plot of free energy versus mole fraction of the system is shown in Figure 15. Apparently there exists a common tangent. The predicted two phases in equilibrium have compositions of 0.02 and 0.745 mole fractions of methanol. The actual phase compositions in equilibrium at 30°C are 0.330 and 0.745 mole fractions of methanol. The proposed model predicts one phase composition exactly but fails to predict the other. Therefore, the application of the model to partially miscible systems is not recommended.

E. Modified Model--OH-OH Interaction as Function of OH Group Surface Concentration

The inability of the model to fit adequately the data at low alcohol concentrations led to further study in this region. Energy parameters for hydroxyl interactions were re-evaluated with only data below 0.4 mole fraction alcohol. The results were qualitatively similar to those in Figures 3 through 9; that is, the shape of the curve was not correctly reproduced. However, a study treating the

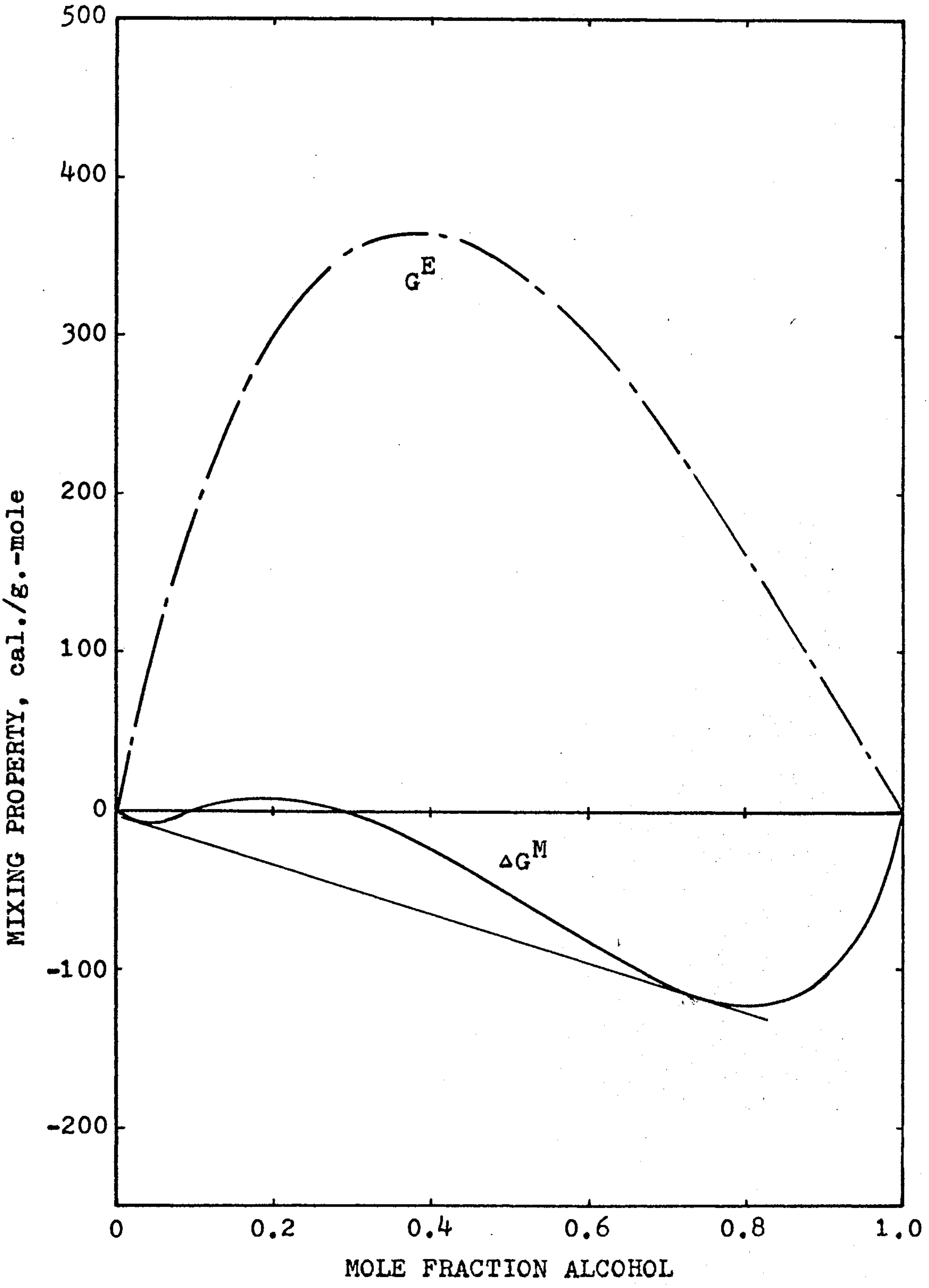


Figure 15. Free Energy of Mixing for Methanol-n-Hexane System at 30°C by the Local Surface Model

hydroxyl-hydroxyl interaction as a function of OH group surface concentration has made a substantial improvement of the model in representation of heats of mixing data at low alcohol concentrations.

If all the energy parameters in Table III except OH-OH interactions are used along with heat of mixing data, values of the OH-OH interaction energy for various concentrations can be calculated by Equations (3-11) and (3-18). Figure 16 shows a plot of the calculated OH-OH interaction energies versus OH group surface concentration on the semi-logarithmic scale. This figure shows that the OH-OH interaction energy may be represented empirically as a linear function of the logarithm of OH group surface concentration. This finding suggests the following form for OH-OH interaction energy.

$$\lambda_{OH-OH} = B_1 + B_2 \ln(f_{sOH}) \qquad (3\text{-}34)$$

Where f_{sOH} is OH group surface concentration as percent of total group surface area in solution.

The constants B_1 and B_2 in Equation (3-34) can be determined from the intercept and the slope of the plot in Figure 16. However, in order to have values for the two constants which provide an optimum fit of the model to the experimental heat of mixing data, a non-linear regression was performed to evaluate the two constants by fitting the model to heat of mixing data (48) on seven paraffin-alcohol binary systems at 30°C. The other two energy parameters involving OH group interaction, i.e., CH_2-OH and CH_3-OH, were re-determined at the same time. The hydrocarbon interaction energy parameters from Table IIIa were again used as fixed input to this calculation. The resultant values are shown in Table IX. The predicted heats of mixing are

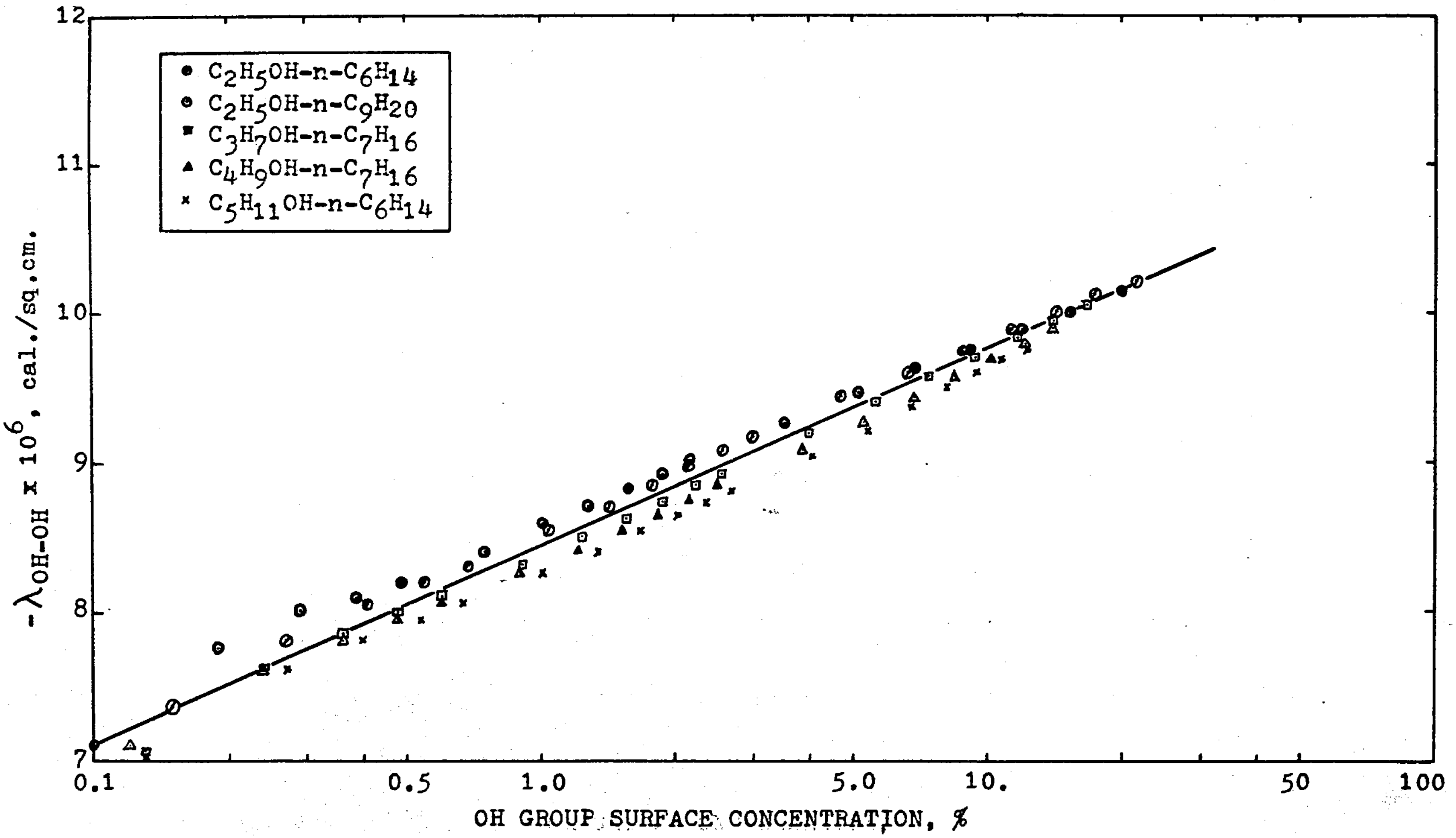


Figure 16. OH–OH Interaction Energy as a Function of OH Group Surface Concentration

compared with the data in Table X. The results are also shown in dashed line in Figures 3 through 9 to compare with experimental data and with the results based on energy parameters in Table III.

TABLE IX

GROUP INTERACTION ENERGY PARAMETERS INVOLVING OH GROUP INTERACTION DETERMINED FROM HEAT OF MIXING DATA WITH OH-OH INTERACTION AS A FUNCTION OF OH GROUP SURFACE CONCENTRATIONS

Groups	Interaction Energy, $-\lambda \times 10^9$, cal./sq.cm.
OH-OH	$8671 + 641 \ln (f_{sOH})$
$OH\text{-}CH_2$	2266
$OH\text{-}CH_3$	841

TABLE X

PREDICTED HEATS OF MIXING AT 30°C BASED ON ENERGY PARAMETERS IN TABLE IX

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l. (48)	Calc'd.	cal./g.-mole	%
Ethanol-n-hexane	.01	42.86	42.23	-0.63	-1.5
	.02	61.53	63.00	1.47	2.4
	.03	72.76	73.91	1.15	1.6
	.04	81.51	82.06	0.55	0.7
	.05	88.60	89.12	0.52	0.6
	.075	102.56	104.42	1.86	1.8
	.10	112.93	117.45	4.52	4.0
	.125	121.47	128.62	7.15	5.9
	.15	128.42	138.14	9.72	7.6
	.175	133.96	146.20	12.24	9.1
	.20	138.85	152.93	14.08	10.1
	.30	149.42	168.79	19.37	13.0
	.40	151.15	170.46	19.31	12.8
	.50	144.83	161.01	16.18	11.2
	.60	133.27	142.42	9.15	6.9
	.70	114.59	116.09	1.50	1.3
	.80	88.46	83.06	-5.40	-6.1
	.90	52.57	44.16	-8.41	
Ethanol-n-nonane	.01	46.57	46.87	0.30	0.6
	.02	70.01	75.24	5.23	7.5
	.03	84.01	91.30	7.29	8.7
	.04	94.71	101.66	6.95	7.3
	.05	103.56	109.43	5.87	5.7
	.075	119.74	124.38	4.64	3.9
	.10	130.67	136.51	5.84	4.5
	.125	140.14	146.92	6.78	4.8
	.15	148.34	155.88	7.54	5.1
	.175	155.48	163.53	8.05	5.2
	.20	161.15	169.94	8.79	5.4
	.30	175.67	184.78	9.11	5.2
	.40	179.42	184.97	5.55	3.1
	.50	175.48	173.11	-2.37	-1.4
	.60	164.42	151.13	-13.29	-8.1
	.70	145.89	120.73	-25.16	-17.2
	.80	118.08	83.70	-34.38	-29.1
	.90	74.86	42.34	-32.52	-43.4

TABLE X (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l. (48)	Calc'd.	cal./g.-mole	%
Propanol-n-heptane	.01	45.34	44.74	-0.60	-1.3
	.02	67.66	67.59	-0.07	-0.1
	.03	82.61	79.98	-2.63	-3.2
	.04	90.92	88.61	-2.31	-2.5
	.05	98.88	95.71	-3.17	-3.2
	.075	115.07	110.61	-4.46	-3.9
	.10	127.21	123.19	-4.02	-3.2
	.125	136.98	134.02	-2.96	-2.2
	.15	144.97	143.30	-1.67	-1.2
	.175	151.66	151.18	-0.48	-0.3
	.20	157.31	157.80	0.49	0.3
	.30	170.12	173.53	3.41	2.0
	.40	170.19	175.29	5.10	3.0
	.50	160.07	165.92	5.85	3.6
	.60	141.92	147.25	5.33	3.8
	.70	116.61	120.53	3.92	3.4
	.80	85.00	86.65	1.65	1.9
	.90	46.73	46.30	-0.43	-0.9
Butanol-n-heptane	.01	43.76	44.30	0.54	+1.2
	.02	65.77	66.80	1.03	1.6
	.03	79.60	78.86	-0.74	-0.9
	.04	89.72	87.16	-2.56	-2.8
	.05	97.74	93.92	-3.82	-3.9
	.075	112.40	107.96	-4.44	-4.0
	.10	123.75	119.69	-4.06	-3.3
	.125	132.77	129.68	-3.09	-2.3
	.15	140.37	138.16	-2.21	-1.6
	.175	146.80	145.29	-1.51	-1.0
	.20	151.92	151.20	-0.72	-0.5
	.30	165.07	164.55	-0.52	-0.3
	.40	165.00	164.74	-0.26	-0.2
	.50	154.50	154.67	0.17	0.1
	.60	134.42	136.20	1.78	1.3
	.70	107.52	110.63	3.11	2.9
	.80	75.38	78.93	3.55	4.7
	.90	39.16	41.85	2.69	6.9

TABLE X (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l. (48)	Calc'd.	cal./g.-mole	%
Pentanol-n-hexane	.01	42.57	41.90	-0.67	-1.6
	.02	61.77	60.59	-1.18	-1.9
	.03	73.10	70.47	-2.63	-3.6
	.04	81.42	77.58	-3.84	-4.7
	.05	87.92	83.56	-4.36	-5.0
	.075	100.39	96.15	-4.24	-4.2
	.10	109.69	106.53	-3.16	-2.9
	.125	117.00	115.16	-1.84	-1.6
	.15	123.21	122.28	-0.93	-0.8
	.175	128.06	128.09	0.03	0.0
	.20	132.31	132.73	0.42	0.3
	.30	141.85	141.85	0.00	0.0
	.40	140.77	139.46	-1.31	-0.9
	.50	129.81	128.67	-1.14	-0.9
	.60	110.19	111.43	1.24	1.1
	.70	85.82	89.07	3.25	3.8
	.80	58.46	62.58	4.12	7.0
	.90	29.42	32.70	3.28	11.1
Octanol-n-heptane	.01	42.43	42.03	-0.40	-0.9
	.02	62.33	62.59	0.26	0.4
	.03	73.66	72.87	-0.79	-1.1
	.04	81.23	79.39	-1.84	-2.3
	.05	87.12	84.35	-2.77	-3.2
	.075	98.39	93.93	-4.46	-4.5
	.10	106.44	101.34	-5.10	-4.8
	.125	112.53	107.24	-5.29	-4.7
	.15	117.08	111.88	-5.20	-4.4
	.175	120.43	115.45	-4.98	-4.1
	.20	123.08	118.06	-5.02	-4.1
	.30	129.23	121.08	-8.15	-6.3
	.40	127.50	115.41	-12.09	-9.5
	.50	118.99	103.82	-15.17	-12.7
	.60	103.85	87.99	-15.86	-15.3
	.70	82.28	69.03	-13.25	-16.1
	.80	56.92	47.71	-9.21	-16.2
	.90	28.56	24.56	-4.00	-14.0

TABLE X (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole Expt'l. (48)	ΔH^M, cal./g.-mole Calc'd.	Deviation cal./g.-mole	Deviation %
Octanol-n-nonane	.01	44.29	44.63	0.34	0.8
	.02	67.66	71.14	3.48	5.1
	.03	81.35	85.64	4.29	5.3
	.04	91.29	94.51	3.22	3.5
	.05	98.77	100.78	2.01	2.0
	.075	112.23	111.85	-0.38	-0.3
	.10	121.59	120.09	-1.50	-1.2
	.125	128.83	126.73	-2.10	-1.6
	.15	134.24	132.10	-2.14	-1.6
	.175	138.82	136.38	-2.44	-1.8
	.20	142.31	139.68	-2.63	-1.8
	.30	149.93	144.77	-5.16	-3.4
	.40	149.42	139.77	-9.65	-6.5
	.50	141.23	127.33	-13.90	-9.8
	.60	122.88	109.20	-13.68	-11.1
	.70	99.45	86.59	-12.86	-12.9
	.80	70.00	60.42	-9.58	-13.7
	.90	36.13	31.38	-4.75	-13.1

Both Table X and Figures 3 through 9 show that the agreement between theory and data has been substantially improved at lower alcohol concentrations with the modification that OH-OH interaction energy is a linear function of logarithmic surface concentration of OH group in solution. The shape of the heat of mixing curves is correctly reflected by the model with the use of energy parameters in Table IX.

Again energy parameters in Table IX were used to calculate the internal energies of vaporization of pure alcohols. The calculated internal energies of vaporization are compared with experimental data in Table XI. In view of the accuracy of pure alcohol heats of vaporization data, the agreement is encouraging.

However, energy parameters in Table IX fail to represent adequately the excess entropies and excess free energies.

TABLE XI

INTERNAL ENERGIES OF VAPORIZATION OF ALCOHOLS BASED ON ENERGY PARAMETERS IN TABLE IX

Alcohol	Energy of Vaporization, @ 30°C, ΔU^V cal./g.-mole		Deviation
	Experimental (20)	Calculated	%
Methanol	8,233	8,165	-0.8
Ethanol	9,378	9,595	2.3
Propanol	10,492	10,773	2.7
Butanol	11,575	11,929	3.1
Pentanol	12,672	13,077	3.2

F. Summary

A new group interaction theory is presented and applied to polar substances. The theory accounts, to a first approximation, for the effect of the strength of group interactions on the probability of interaction. The probability of interaction between two groups is considered to depend both on the magnitude of the interaction energy between the groups and on the free surface areas of the groups. The surface areas are calculated from a realistic geometric model of the molecules involved. The model is shown to provide satisfactory qualitative representation of excess properties of n-alcohol-n-paraffin systems with reasonable values used for group interaction energies. Unsatisfactory results from this and other models (22, 46) at low alcohol concentrations suggests the need for future study of the nature of dilute polar solutions.

A substantial improvement in predicting heats of mixing at low alcohol concentrations was obtained by the modified model which treats the OH-OH interaction energy as a function of OH group surface concentration in solution. However, this energy parameter modification is an empirical with no theoretical justification.

CHAPTER IV

THE QUASI-LATTICE THEORY

Previous investigators have applied group solution (13) and association-type (46, 58) models to the description of alcohol-paraffin systems. However, no similar results have appeared for the quasi-lattice theory (2, 25). The work in this chapter examines the quasi-lattice model in its ability to describe the excess enthalpy and free energy of alcohol-paraffin systems.

The quasi-lattice theory advanced by Guggenheim (25) and Barker (2), re-expressed in canonical partition function of group interactions, is used in the present study. The present equations serve as a convenient basis for further development and use in cell-theory calculations (12).

A. The Quasi-Lattice Theory

Basically, the quasi-lattice theory considers each molecule i in solution to be composed of a number (r_i) of segments (or groups) placed on well-defined lattice sites. Each type of segment v possesses a number (z_v) of contact points, where it interacts with adjacent segments. For example, a pentane molecule could be considered to consist of two methyl segments and three methylene segments. The configurational energy of the solution is the sum of contributions from interactions between pairs of adjacent segments.

Guggenheim (25) developed the quasi-lattice theory of molecules of different sizes and occupying different number of lattice sites. Segments of the same molecule interact in the same way. Barker (2) extended Guggenheim's theory to allow each molecule to have different kinds of segments. Barker's results are in terms of grand partition functions. In the following, Guggenheim's results are re-expressed, still allowing each molecule to have more than one kind of segment. The present results are in the canonical form and appear to be well suited for further development into the language of the cell-theories (12).

The configurational energy E of a lattice solution is completely determined by a set of numbers N_{uv} that represents the numbers of contacts between segments of types u and v. The canonical partition function is given by

$$Q = \sum_{N_{uv}} g \exp(-E/kT) \qquad (4-1)$$

where g denotes the degeneracy of the configuration described by the set of N_{uv}'s.

Let λ'_{uv} stand for the energy of interaction between an u segment and a v segment. Then,

$$E = \Sigma_u \Sigma_{v \geq u} N_{uv} \lambda'_{uv} \qquad (4-2)$$

The degeneracy g has so far not been evaluated rigorously for 3-dimensional lattices. However, several approximations have been developed. Following Guggenheim (25) and assuming that

1. $\ln(g)/\sum_i N^i$ is homogeneous of "degree zero" in the N^i's.

2. the free energy is a continuous function of E in the neighborhood of E = 0; that is, ln(g) reduces to ln(g*) when E = 0.
3. the conditions for maximizing Q with respect to N_{uv} are equivalent to conditions of a "quasi-chemical equilibrium."

the degeneracy g will have the following expression

$$\ln(g) = \ln(g^*) + \Sigma_u \ln\left(\frac{N^*_{uu}!}{N_{uu}!}\right) + \Sigma_u \Sigma_v \ln\left(\frac{N^*_{uv}!\ 2^{N_{uv}}}{N_{uv}!\ 2^{N^*_{uv}}}\right) \qquad (4\text{-}3)$$

The values of g and N_{uv} are related to the corresponding values (denoted by asterisks) in the athermal theories of Flory and Huggins (17). Thus,

$$N^*_{uv} = (\Sigma_i n^i_u N^i z_u)(\Sigma_i n^i_v N^i z_v)/\Sigma_w \Sigma_i (n^i_w N^i z_w) \qquad (4\text{-}4)$$

$$N^*_{uu} = \tfrac{1}{2}(\Sigma_i n^i_u N^i z_u)^2/\Sigma_w \Sigma_i (n^i_w N^i z_w) \qquad (4\text{-}5)$$

where n^i_u denotes the number of u groups in a molecule i.

As usual in statistical thermodynamics, the sum of Equation (4-1) is replaced by its maximum term. In order to pick the maximum, we differentiate with respect to N_{uv} and set the derivative equal to zero,

$$\frac{\partial}{\partial N_{uv}} [g \exp(-E/kT)] = 0 \qquad (4\text{-}6)$$

Upon performing the indicated operation, bearing in mind that all the asterisked quantities are independent of N_{uv}, the following expression is obtained,

$$\frac{N^2_{uv}}{N_{uu} N_{vv}} = 4 \exp(-2\Omega'_{uv}/kT) \qquad (4\text{-}7)$$

where the exchange energy Ω'_{uv} is defined by

$$\Omega'_{uv} = \lambda'_{uv} - \tfrac{1}{2}(\lambda'_{uu} + \lambda'_{vv}) \tag{4-8}$$

Equation (4-7) expresses the well-known quasi-chemical relation that is contained in the approximation of Equation (4-3).

In the evaluation of the N_{uv}'s, Equation (4-7) is combined with the following stoichiometric equations of contact points.

$$2\, N_{uu} + \Sigma_{v \neq u} N_{uv} = \Sigma_i N^i n^i_u z_u \tag{4-9}$$

In a solution containing n types of segments there are n(n-1)/2 equations like Equation (4-7), and n equations like Equation (4-9), making up a total system of n(n+1)/2 equations, corresponding to exactly the same number of N_{uv}'s. There are just as many equations as unknowns.

In the following applications of the theory, the exchange energies Ω'_{uv} are considered to be adjustable parameters. The geometric factors z and z_u are taken from previous results by other investigators. The N_{uv}'s are fixed by Equations (4-7) and (4-9) for specified values of N^i.

The excess enthalpy of the solution is expressed in terms of the N_{uv} by

$$H^E = - \Sigma_u \Sigma_{v>u} (\Sigma_i N^{oi}_{uv} - N_{uv}) \Omega'_{uv} \tag{4-10}$$

where the superscript oi denotes the assembly of N^i molecules of i (pure liquid).

Based on the thermodynamic relations, the entropy of solution is evaluated from the canonical partition function as follows:

$$S = kT\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} + k\ \ln(Q) \qquad (4\text{-}11)$$

$$= k\ \ln(g)$$

Similarly, the entropy of pure liquid i is

$$S_i = k\ \ln(g^{oi}) \qquad (4\text{-}12)$$

The entropy of mixing of the solution is then given by

$$S^M = k\ \ln(g) - k\ \Sigma_i \ln(g^{oi}) \qquad (4\text{-}13)$$

Combining Equation (4-3) and Equation (4-13), the entropy of mixing of the solution is expressed in terms of the N_{uv} by

$$\frac{S^M}{k} = \ln\left(\frac{g^*}{\prod_i g^{*oi}}\right) - \Sigma_u\Sigma_{v\neq u}\ \ln\left(\frac{N_{uu}!N_{uv}!}{N^*_{uu}!N^*_{uv}!}\prod_i \frac{N^{*\ oi}_{uu}!N^{*\ oi}_{uv}!}{N^{oi}_{uu}!\ N^{oi}_{uv}!}\right)$$

$$+ (\ln 2)\ \Sigma_u\Sigma_{v\neq u}[(N_{uv}-N^*_{uv}) - \Sigma_i(N^{oi}_{uv} - N^{*\ oi}_{uv})] \qquad (4\text{-}14)$$

For an ideal solution, the entropy of mixing is given by

$$S^{Mo} = -k\ \Sigma_i N_i \ln(x_i) \qquad (4\text{-}15)$$

Thus, the excess entropy of the solution is given by

$$\frac{S^E}{k} = \ln\left(\frac{g^*}{\prod_i g^{*oi}}\right) - \Sigma_u\Sigma_{v\neq u}\ln\left(\frac{N_{uu}!N_{uv}!}{N^*_{uu}!N^*_{uv}!}\prod_i \frac{N^{*\ oi}_{uu}!N^{*\ oi}_{uv}!}{N^{oi}_{uu}!\ N^{oi}_{uv}!}\right)$$

$$+ (\ln 2)\ \Sigma_u\Sigma_{v\neq u}[(N_{uv}-N^*_{uv}) - (N^{oi}_{uv} - N^{*\ oi}_{uv})]$$

$$+ \Sigma_i N_i \ln(x_i) \qquad (4\text{-}16)$$

The excess free energy is obtained upon combining Equations (4-10) and (4-16)

$$G^E = H^E - TS^E \tag{4-17}$$

For specified values of N^i, the N_{uv}'s are fixed by Equations (4-7) and (4-9). However, it is hard to solve the N_{uv}'s directly from the n(n+1)/2 simultaneous equations in the form of Equations (4-7) and (4-9). To make the solution easier, the following technique of change variables is employed.

If the substitutions

$$N_{uu} = NX_u^2 \tag{4-18a}$$

$$N_{uv} = 2NX_uX_v \exp(-\Omega'_{uv}/kT) \tag{4-18b}$$

are made, the quasi-chemical relation of Equation (4-7) are automatically satisfied, the the stoichiometric equations of Equation (4-9) become

$$X_u \Sigma_v X_v \exp(-\Omega'_{uv}/kT) = \frac{1}{2} \frac{\Sigma_i N^i n_u^i z_u}{N} \tag{4-19}$$

where X's are new variables to be solved from the n(n+1)/2 simultaneous equations. In the present study of alcohol-n-paraffin solutions, if the type of contact points is specified in the manner of Barker (2), Equation (4-19) becomes

$$X_H(X_H + X_O e^{-\Omega'_{OH}/kT} + X_I e^{-\Omega'_{HI}/kT} + X_S e^{-\Omega'_{HS}/kT}) = \frac{x_a}{2} n_H^a z_H$$

$$X_O(X_H e^{-\Omega'_{OH}/kT} + X_O + X_I e^{-\Omega'_{OI}/kT} + X_S e^{-\Omega'_{OS}/kT}) = \frac{x_a}{2} n_O^a z_O$$

$$X_I(X_H e^{-\Omega'_{HI}/kT} + X_O e^{-\Omega'_{OI}/kT} + X_I + X_S e^{-\Omega'_{IS}/kT}) = \frac{x_a}{2}\, n^a_I z_I$$

$$X_S(X_H e^{-\Omega'_{HS}/kT} + X_O e^{-\Omega'_{OS}/kT} + X_I e^{-\Omega'_{IS}/kT} + X_S) = \frac{x_p}{2}\, n^p_S z_S \qquad (4\text{-}20)$$

where x_a = mole fraction alcohol

x_p = mole fraction n-paraffin

H, O, I, S = hydroxyl hydrogen, hydroxyl oxygen, alkyl, and paraffin solvent groups respectively.

Combining Equations (4-10) and (4-18), the excess enthalpy of the solution is expressed in terms of new variables X's by

$$\begin{aligned} H^E = -2RT[& (X_H X_O - x_a X^1_H X^1_O)\ \exp(-\Omega'_{OH}/RT)(-\Omega'_{OH}/RT) \\ & + (X_H X_I - x_a X^1_H X^1_I)\ \exp(-\Omega'_{HI}/RT)(-\Omega'_{HI}/RT) \\ & + (X_O X_I - x_a X^1_O X^1_I)\ \exp(-\Omega'_{OI}/RT)(-\Omega'_{OI}/RT) \\ & + X_H X_S\ \exp(-\Omega'_{HS}/RT)(-\Omega'_{HS}/RT) \\ & + X_O X_S\ \exp(-\Omega'_{OS}/RT)(-\Omega'_{OS}/RT) \\ & + X_I X_S\ \exp(-\Omega'_{IS}/RT)(-\Omega'_{IS}/RT) \qquad (4\text{-}21) \end{aligned}$$

where X^1's in Equation (4-21) are found by solving Equation (4-20) for the special case of $x_i = 1.0$.

B. Application to Alcohol-Paraffin Systems

In the present work, the type and number of contact points were specified in the manner of Goates, et al. (21, 22). Each paraffin molecule was considered to contain only paraffin-type segments, S, with two contact points on each methylene group and three on each methyl group. The alcohols were divided into a hydroxyl hydrogen segment, H, a hydroxyl oxygen segment, O, and paraffin type segments, I. The H segments were specified to have a single contact point, O segments two and paraffin-type contacts specified as they were for the n-paraffins.

With the segments and contact points specified as in Table XII, the exchange energies, Ω', were evaluated by fitting the model to experimental data. In the present case, six exchange energies arise; O-H, O-I, O-S, H-I, H-S, and I-S. In past studies, certain exchange energies have been neglected by reasoning that their magnitudes (or the number of contacts) might be expected to be small. Results have been found to be sensitive to the choice of energy values retained as significant (21).

Five separate choices of energy parameters were evaluated in the present study. For each choice of parameters, a non-linear regression was performed to evaluate the parameter values which resulted in a least-squares fit to heat of mixing data (48) on eight paraffin-alcohol systems at 30°C. The five choices of energy parameter sets and their values are shown in Table XIII.

The considerations that led to these choices are as follows: Parameter set A, in which only the O-H and I-S energies were considered conforms to Goates, et al. (21) choice for describing cyclohexane-alcohol systems. Set B, which appears more reasonable on a physical basis, was previously evaluated for the cyclohexane-ethanol system with unsatisfactory results (21). Set C was tried as a possible improvement on B, although the I-S interaction energy was expected to be small. Set D is similar to that used by Goates, et al. (22) in aromatic-alcohol systems, where interactions of the O and H sites with paraffin segments on the alcohol were neglected. Set E placed no restrictions on the energy parameters, allowing all six parameters to be regressed. The ability of the energy parameter sets to represent the heat of mixing data improved from A to E. Set A was markedly inferior, set B and set C comparable and somewhat poorer than set D, which in turn was marginally inferior to E.

TABLE XII

NUMBER AND TYPE OF CONTACT POINTS, SITES AND COORDINATION NUMBERS

Component	$n_H z_H$	$n_O z_O$	$n_I z_I$	$n_S z_S$	z	r_1	r_2
Ethanol	1	2	5	-	4*	3	-
Propanol	1	2	7	-	4	4	-
Butanol	1	2	9	-	4	5	-
Pentanol	1	2	11	-	4	6	-
Octanol	1	2	17	-	4	9	-
n-hexane	-	-	-	14	4	-	6
n-heptane	-	-	-	16	4	-	7
n-nonane	-	-	-	20	4	-	9

* The coordination number, z, is given by $\Sigma_u n_u z_u = rz - (2r - 2)$

TABLE XIII

INTERACTION ENERGY PARAMETERS* AT 30°C

Set	Ω'_{O-H}	Ω'_{H-S}		Ω'_{H-I}	Ω'_{O-S}		Ω'_{O-I}	Ω'_{I-S}
A	-2,756	0		0	0		0	2
B	-3,173	(-224	=	-224)	(-284	=	-284)	0
C	-3,161	(-194	=	-194)	(-317	=	-317)	<1
D	-3,175	-91		0	216		0	<1
E	-3,748	-251		-253	-257		-465	<1

* cal./g.-mole

C. Discussion of Results

The results of fitting the quasi-lattice theory to the heat of mixing data by using the energy parameters set E in Table XIII are shown in Table XIV and for the purpose of ease in comparison, in Figures 17 through 24; these systems are the ones employed in least-squares regression to evaluate the energy parameters. Figures 17 through 24 show the degree to which the energy parameters of set E are capable of representing the data. Parameter set D produced results essentially identical to set E for heat of mixing. For comparison, results from set B and from the local surface group contribution model in previous chapters are shown in Figures 17 and 24. These figures show that reasonable agreement between the theory and the experimental heat of mixing data is obtained for the eight binary systems. The asymmetry of the heat of mixing curves is correctly reflected by the theory. The quasi-lattice theory predicts consistently low values of heat-of-mixing at low alcohol concentrations. Similar results have been reported for several other models (13, 22, 46) in representation of alcohol systems. Again, this inadequacy at low alcohol concentrations is felt to be a fault of the model and not of the interaction parameters used.

The energy parameter values in Table XIII were employed to represent the excess free energies and entropies for the systems in Figures 17 through 24 for which such data are available. Results are given in Figures 25 through 27. Results based on parameter set E are also given in Table XV to compare with experimental data. The predicted excess properties shown in these figures appear quite sensitive to selection of the energy parameter set. Parameter set E produces the best representation of the free energies and entropies.

Goates, et al. (21) obtained a value of -3,200 cal./g.-mole for the O-H exchange energy based on heat-of-mixing data for the cyclohexane-ethanol system. This is in general agreement with the O-H energy values obtained in the present work. No direct comparisons are available for the other energy parameters from this study.

TABLE XIV

HEATS OF MIXING OF ALCOHOL-PARAFFIN SOLUTIONS AT 30°C BASED ON QUASI-LATTICE THEORY ENERGY PARAMETER SET E

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l.	Calc'd.	cal./g.-mole	%
Ethanol-n-hexane (48)	.01	42.86	26.43	-16.43	-38.3
	.02	61.53	44.73	-16.80	-27.3
	.03	72.76	58.83	-13.93	-19.1
	.04	81.51	70.27	-11.24	-13.8
	.05	88.60	79.85	-8.75	-9.9
	.075	102.56	98.40	-4.16	-4.1
	.10	112.93	111.96	-0.97	-0.8
	.125	121.47	122.50	1.03	0.8
	.15	128.42	130.45	2.03	1.6
	.175	133.96	137.15	3.19	2.4
	.20	138.85	142.02	3.17	2.3
	.30	149.42	153.28	3.86	2.6
	.40	151.15	154.50	3.35	2.2
	.50	144.83	147.81	2.98	2.0
	.60	133.27	136.94	3.67	2.8
	.70	114.59	115.77	1.18	1.0
	.80	88.46	88.07	-0.39	-0.4
	.90	52.57	49.82	-2.75	-5.2
Ethanol-n-heptane (56)	.01	43.65	27.08	-16.57	-38.0
	.025	71.24	54.39	-16.85	-23.6
	.05	93.10	84.40	-8.70	-9.3
	.075	110.14	104.94	-5.20	-4.7
	.10	120.63	120.06	-0.57	-0.5
	.20	147.10	153.67	6.57	4.5
	.30	159.62	167.02	7.40	4.6
	.40	161.86	168.36	6.50	4.0
	.50	156.67	163.20	6.53	4.2
	.60	145.00	148.39	3.39	2.3
	.70	126.45	127.37	0.92	0.7
	.80	99.85	97.70	-2.15	-2.2
	.90	60.62	56.76	-3.86	-6.4
	.95	33.89	32.40	-1.49	-4.4
	.975	17.95	16.21	-1.74	-9.7

TABLE XIV (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l.	Calc'd.	cal./g.-mole	%
Ethanol-n-nonane (48)	.01	46.57	28.04	-18.53	-39.8
	.02	70.01	49.04	-20.97	-30.0
	.03	84.01	65.92	-18.09	-21.5
	.04	94.71	79.99	-14.72	-15.5
	.05	103.56	92.01	-11.55	-11.1
	.075	119.74	115.87	-3.87	-3.2
	.10	130.67	133.76	3.09	2.4
	.125	140.14	147.66	7.52	5.4
	.15	148.34	158.68	10.34	7.0
	.175	155.48	167.29	11.81	7.6
	.20	161.15	174.59	13.44	8.3
	.30	175.67	190.30	14.63	8.3
	.40	179.42	193.64	14.22	7.9
	.50	175.48	186.21	10.73	6.1
	.60	164.42	170.87	6.45	3.9
	.70	145.89	147.32	1.43	1.0
	.80	118.08	113.89	-4.19	-3.5
	.90	74.86	66.29	-8.57	-11.4
Propanol-n-heptane (48)	.01	45.34	26.80	-18.54	-40.9
	.02	67.66	45.91	-21.75	-32.1
	.03	82.61	60.81	-21.80	-26.4
	.04	90.92	72.96	-17.96	-19.8
	.05	98.88	83.22	-15.66	-15.8
	.075	115.07	103.29	-11.78	-10.2
	.10	127.21	118.00	-9.21	-7.2
	.125	136.98	129.08	-7.90	-5.8
	.15	144.97	137.83	-7.14	-4.9
	.175	151.66	144.74	-6.92	-4.6
	.20	157.31	150.44	-6.87	-4.4
	.30	170.12	161.65	-8.47	-5.0
	.40	170.19	161.69	-8.50	-5.0
	.50	160.07	153.70	-6.37	-4.0
	.60	141.92	138.39	-3.53	-2.5
	.70	116.61	116.34	-0.27	-0.2
	.80	85.00	86.48	1.48	1.7
	.90	46.73	48.48	1.75	3.7

TABLE XIV (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l.	Calc'd.	cal./g.-mole	%
Butanol-n-heptane (48)	.01	43.76	26.51	-17.25	-39.4
	.02	65.77	45.33	-20.44	-31.1
	.03	79.60	60.00	-19.60	-24.6
	.04	89.72	71.96	-17.76	-19.8
	.05	97.74	82.01	-15.73	-16.1
	.075	112.40	101.51	-10.89	-9.7
	.10	123.75	115.76	-7.99	-6.4
	.125	132.77	126.42	-6.35	-4.8
	.15	140.37	134.99	-5.38	-3.8
	.175	146.80	141.31	-5.49	-3.7
	.20	151.92	146.65	-5.27	-3.5
	.30	165.07	156.25	-8.82	-5.3
	.40	165.00	155.07	-9.93	-6.0
	.50	154.50	145.53	-8.97	-5.8
	.60	134.42	129.50	-4.92	-3.6
	.70	107.52	106.96	-0.56	-0.5
	.80	75.38	78.07	2.69	3.6
	.90	39.16	42.75	3.59	9.2
Pentanol-n-hexane (48)	.01	42.57	25.57	-17.00	-39.9
	.02	61.77	43.12	-18.65	-30.2
	.03	73.10	56.47	-16.63	-22.8
	.04	81.42	67.23	-14.19	-17.4
	.05	87.92	76.25	-11.67	-13.3
	.075	100.39	93.31	-7.08	-7.0
	.10	109.69	105.58	-4.11	-3.7
	.125	117.00	114.96	-2.04	-1.7
	.15	123.21	122.01	-1.20	-1.0
	.175	128.06	127.37	-0.69	-0.5
	.20	132.31	131.45	-0.86	-0.6
	.30	141.85	138.64	-3.21	-2.3
	.40	140.77	134.96	-5.81	-4.1
	.50	129.81	125.68	-4.13	-3.2
	.60	110.19	109.39	-0.80	-0.7
	.70	85.82	88.65	2.83	3.3
	.80	58.46	64.11	5.65	9.6
	.90	29.42	33.86	4.44	15.1

TABLE XIV (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole Expt'l.	ΔH^M, cal./g.-mole Calc'd.	Deviation cal./g.-mole	Deviation %
Octanol-n-heptane (48)	.01	42.43	25.40	-17.03	-40.1
	.02	62.33	43.17	-19.16	-30.7
	.03	73.66	56.80	-16.86	-22.9
	.04	81.23	67.83	-13.40	-16.5
	.05	87.12	77.07	-10.05	-11.5
	.075	98.39	94.51	-3.88	-3.9
	.10	106.44	107.12	0.68	0.6
	.125	112.53	116.36	3.83	3.4
	.15	117.08	123.07	5.99	5.1
	.175	120.43	128.52	8.09	6.7
	.20	123.08	131.94	8.86	7.2
	.30	129.23	137.12	7.89	6.1
	.40	127.50	132.87	5.37	4.2
	.50	118.99	121.10	2.11	1.8
	.60	103.85	104.30	0.45	0.4
	.70	82.28	83.14	0.86	1.0
	.80	56.92	58.82	1.90	3.3
	.90	28.56	31.45	2.89	10.1
Octanol-n-nonane (48)	.01	44.29	26.36	-17.93	-40.5
	.02	67.66	45.78	-21.88	-32.3
	.03	81.35	61.10	-20.25	-24.9
	.04	91.29	73.72	-17.57	-19.2
	.05	98.77	84.44	-14.33	-14.5
	.075	112.23	105.21	-7.02	-6.2
	.10	121.59	120.20	-1.39	-1.1
	.125	128.83	131.70	2.87	2.2
	.15	134.24	140.40	6.16	4.6
	.175	138.82	146.77	7.95	5.7
	.20	142.31	151.73	9.42	6.6
	.30	149.93	160.24	10.31	6.9
	.40	149.42	156.45	7.03	4.7
	.50	141.23	143.76	2.53	1.8
	.60	122.88	124.68	1.80	1.5
	.70	99.45	100.28	0.83	0.8
	.80	70.00	70.48	0.48	0.7
	.90	36.13	36.56	0.43	1.2

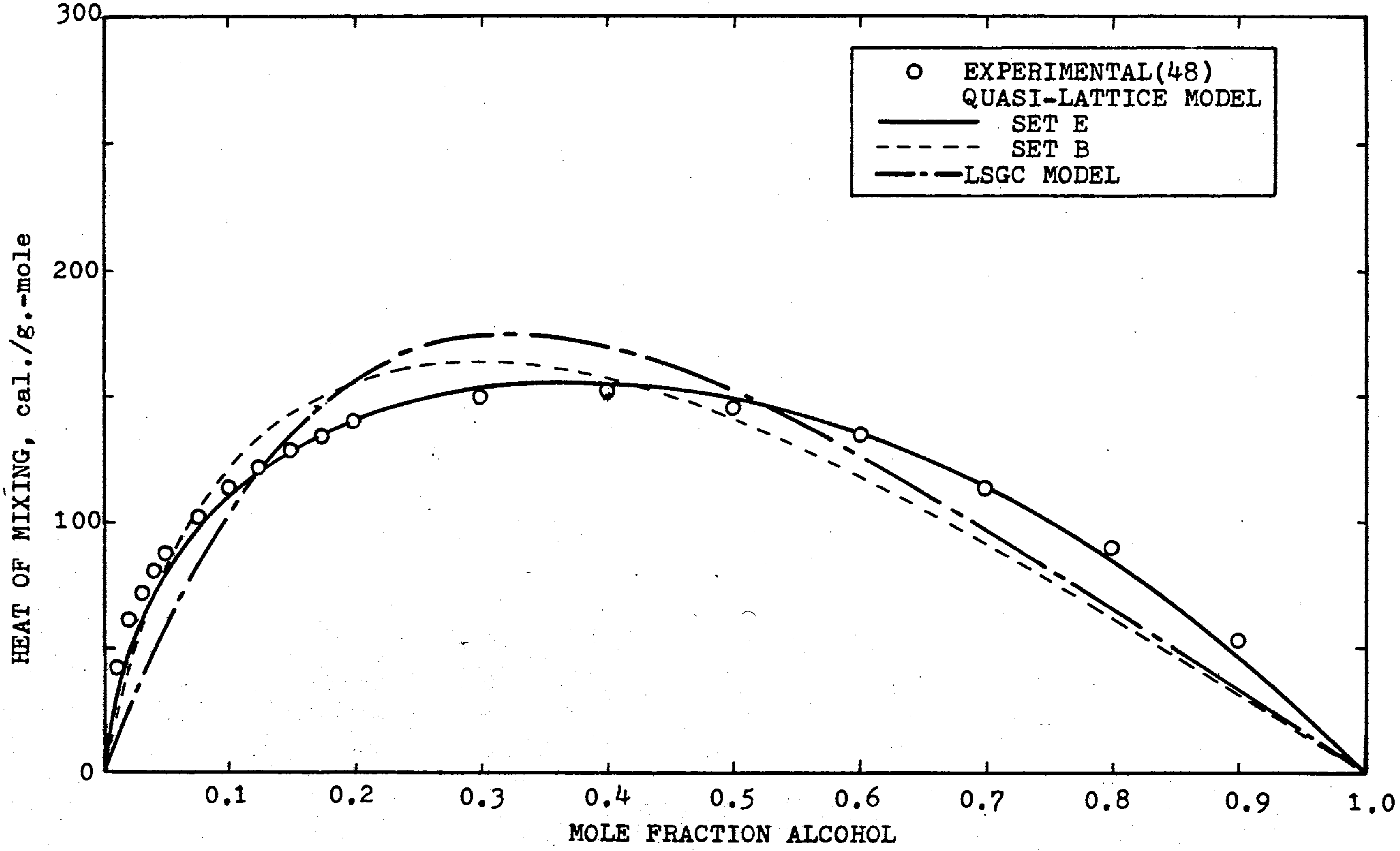


Figure 17. Heat of Mixing in the Ethanol-n-Hexane System at 30°C by the Quasi-Lattice Model

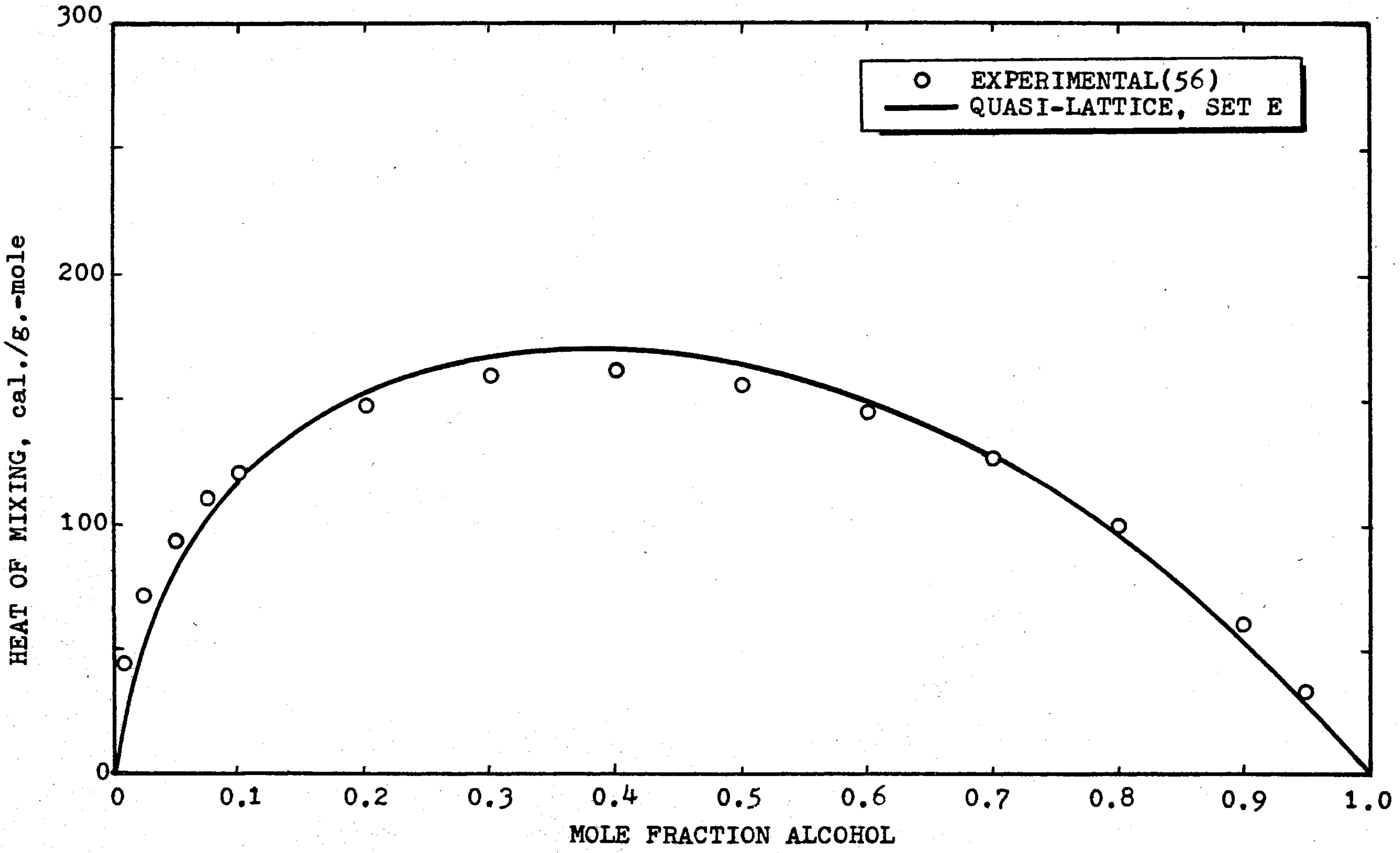


Figure 18. Heat of Mixing in the Ethanol-n-Heptane System at 30°C by the Quasi-Lattice Model

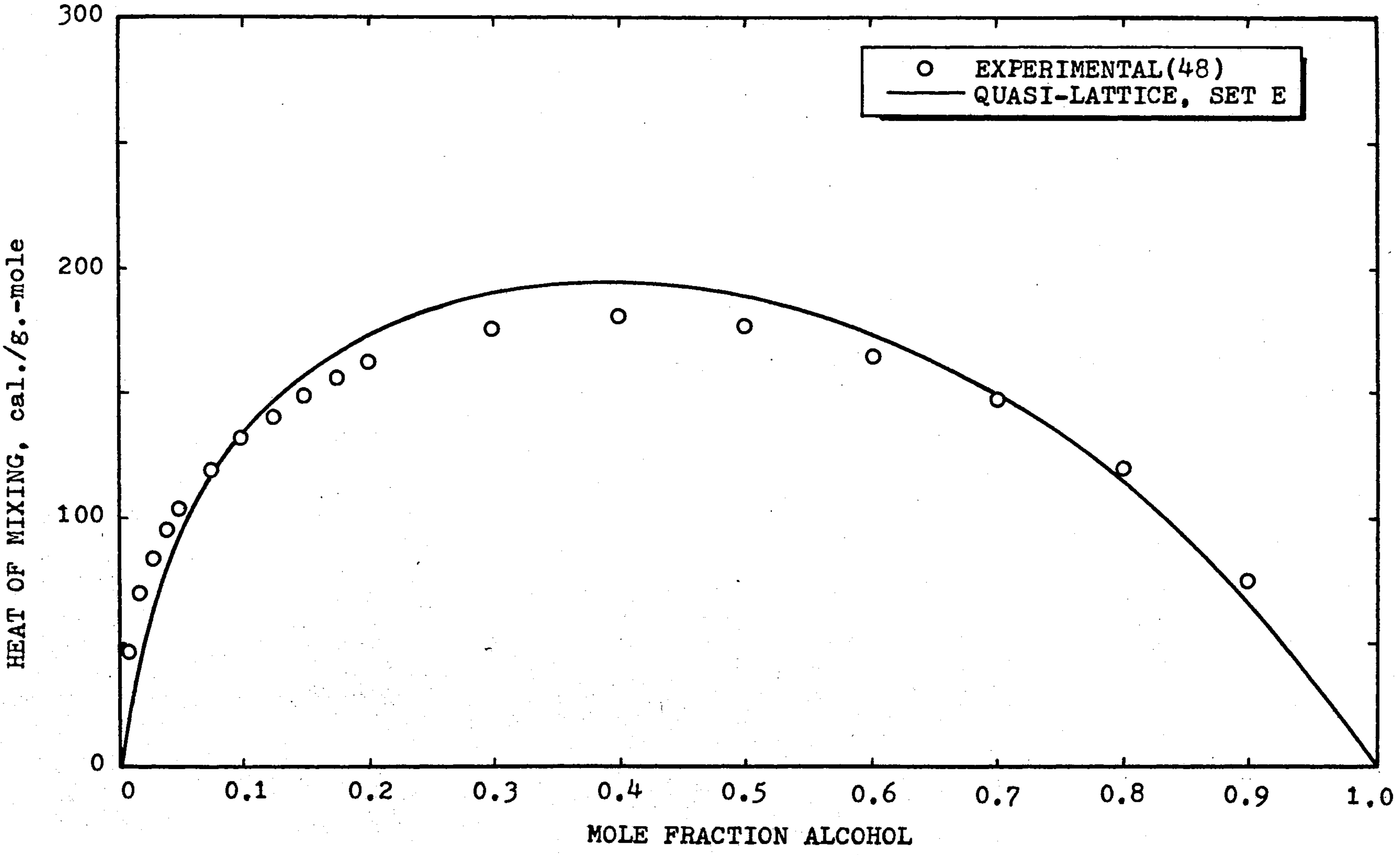


Figure 19. Heat of Mixing in the Ethanol-n-Nonane System at 30°C by the Quasi-Lattice Model

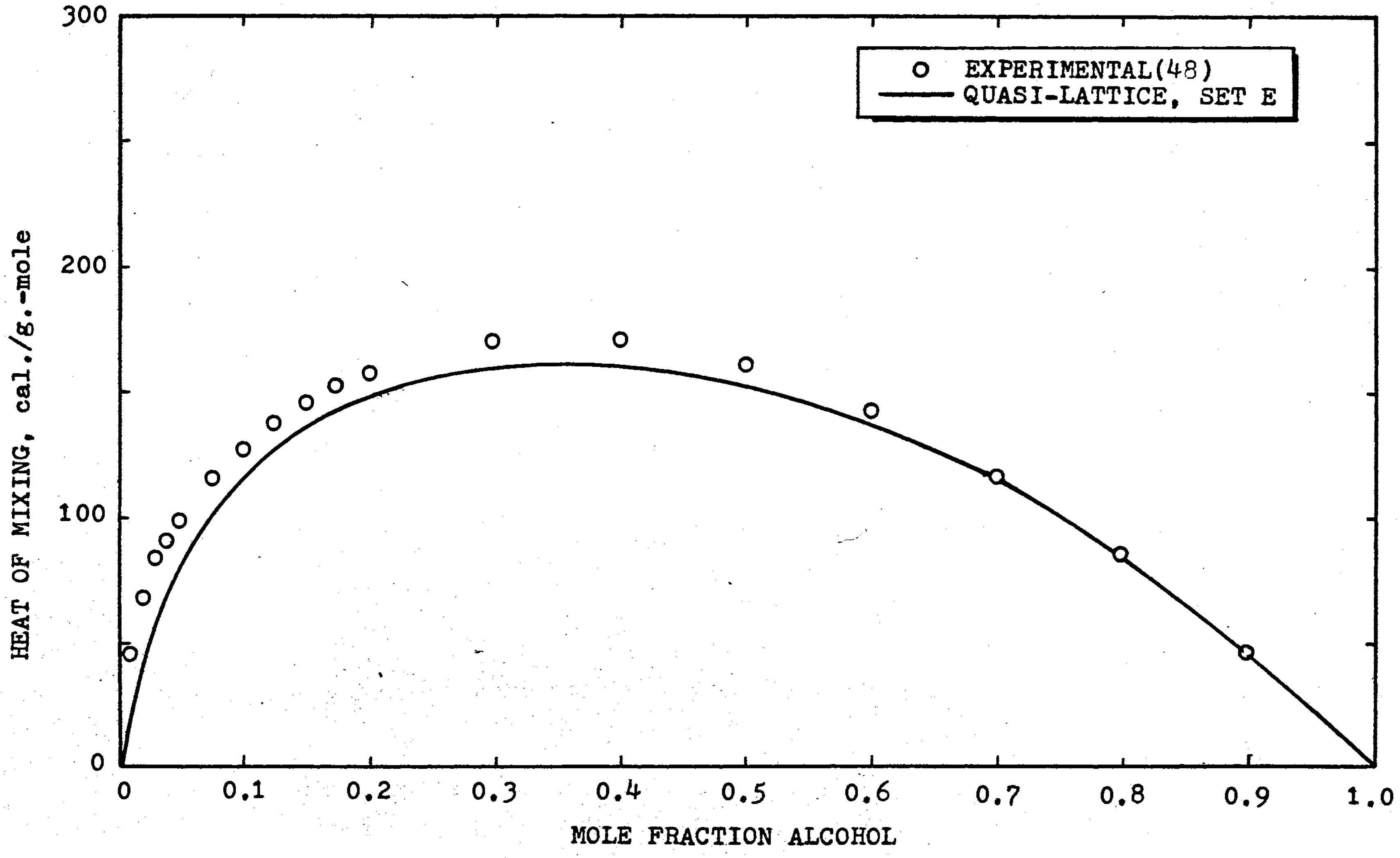


Figure 20. Heat of Mixing in the Propanol-n-Heptane System at 30°C by the Quasi-Lattice Model

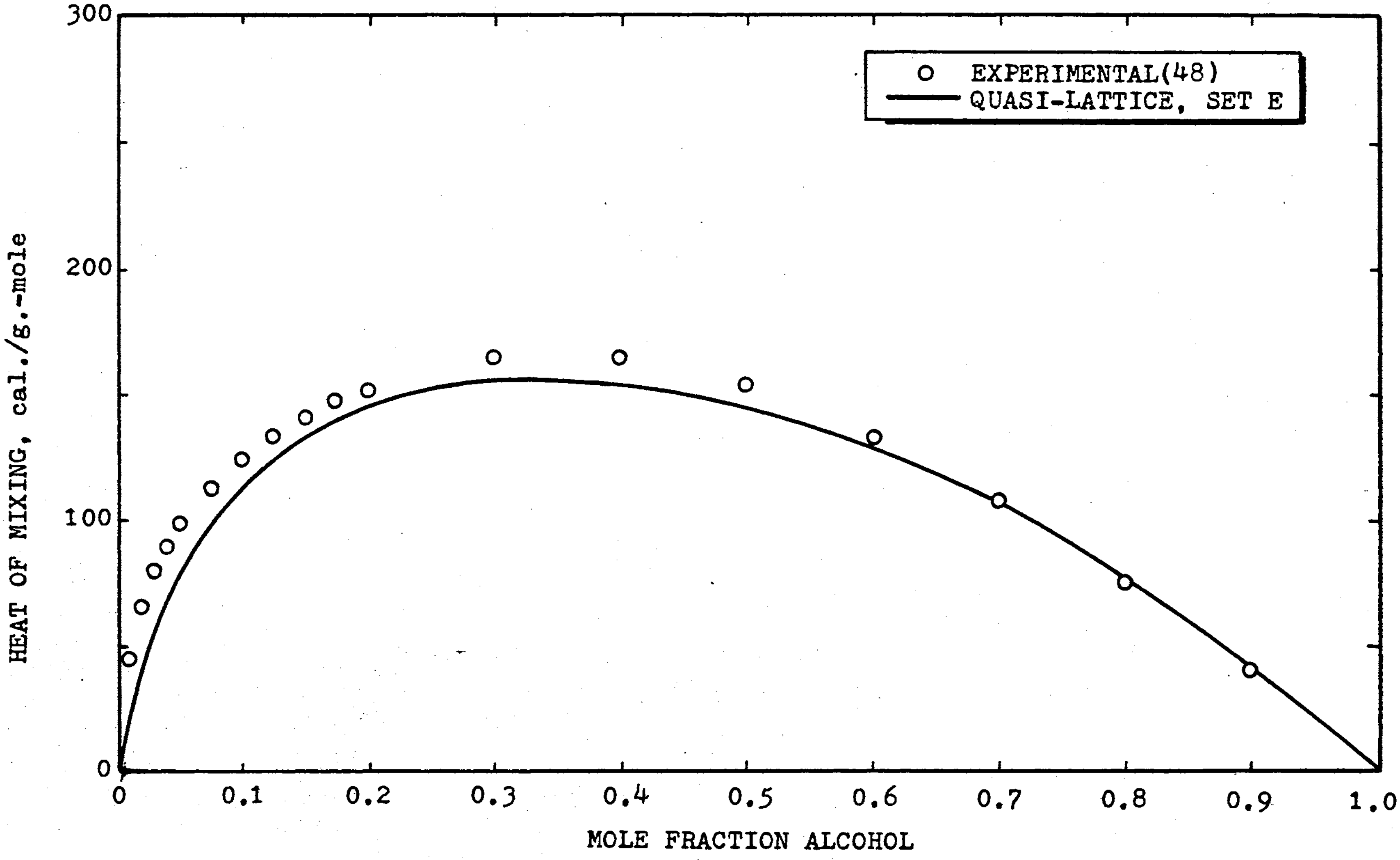


Figure 21. Heat of Mixing in the Butanol-n-Heptane System at 30°C by the Quasi-Lattice Model

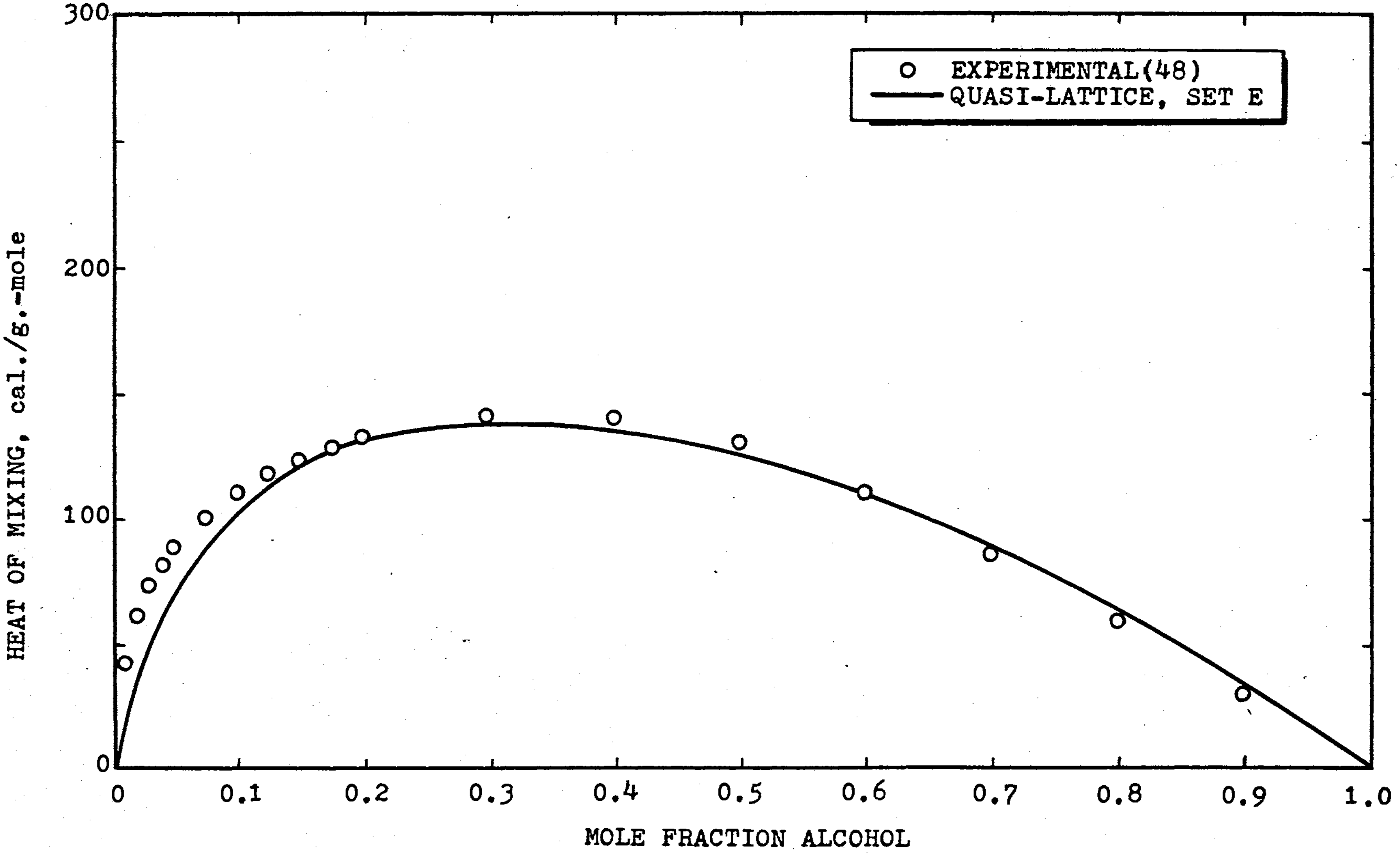


Figure 22. Heat of Mixing in the Pentanol-n-Hexane System at 30°C by the Quasi-Lattice Model

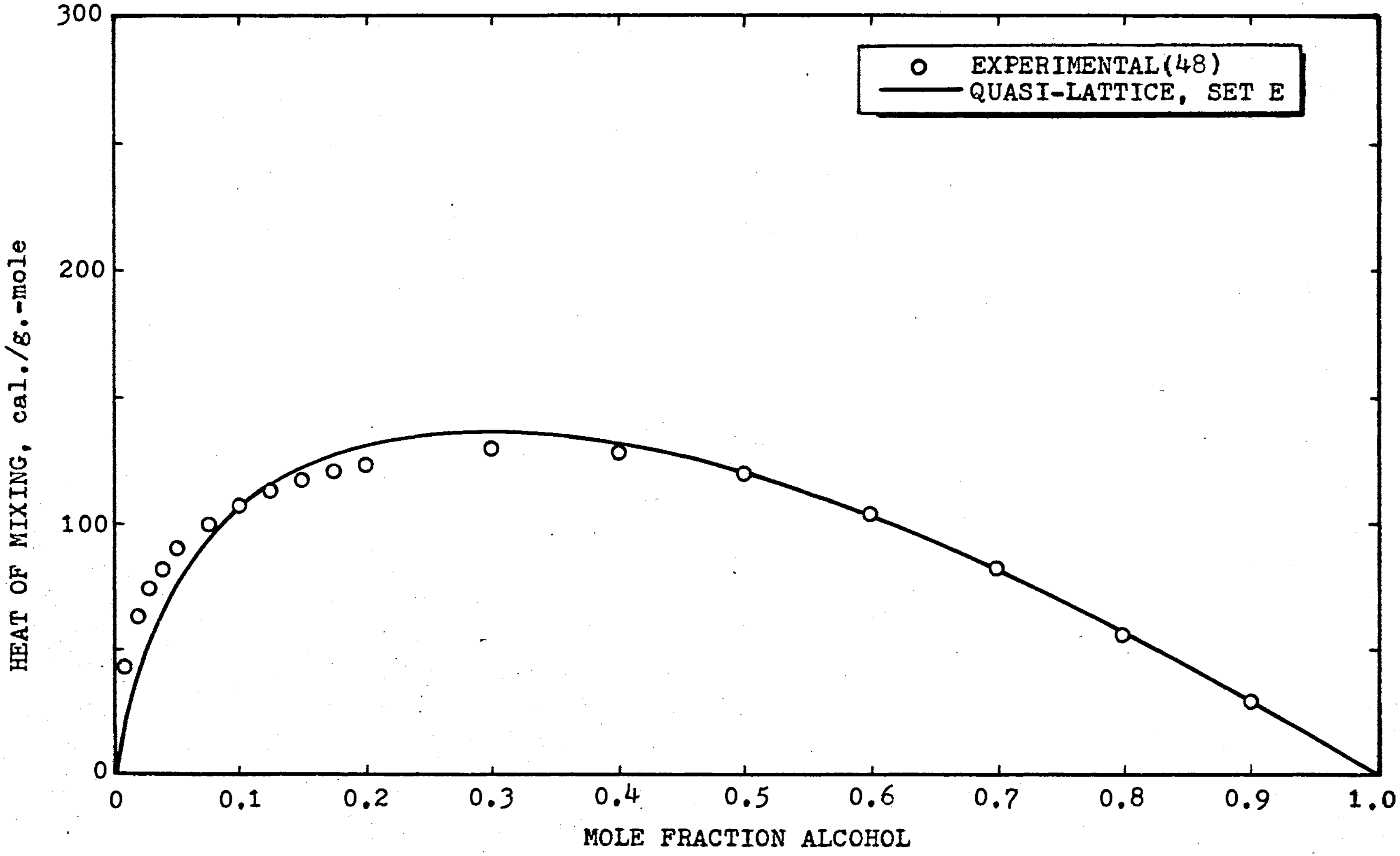


Figure 23. Heat of Mixing in the Octanol-n-Heptane System at 30°C by the Quasi-Lattice Model

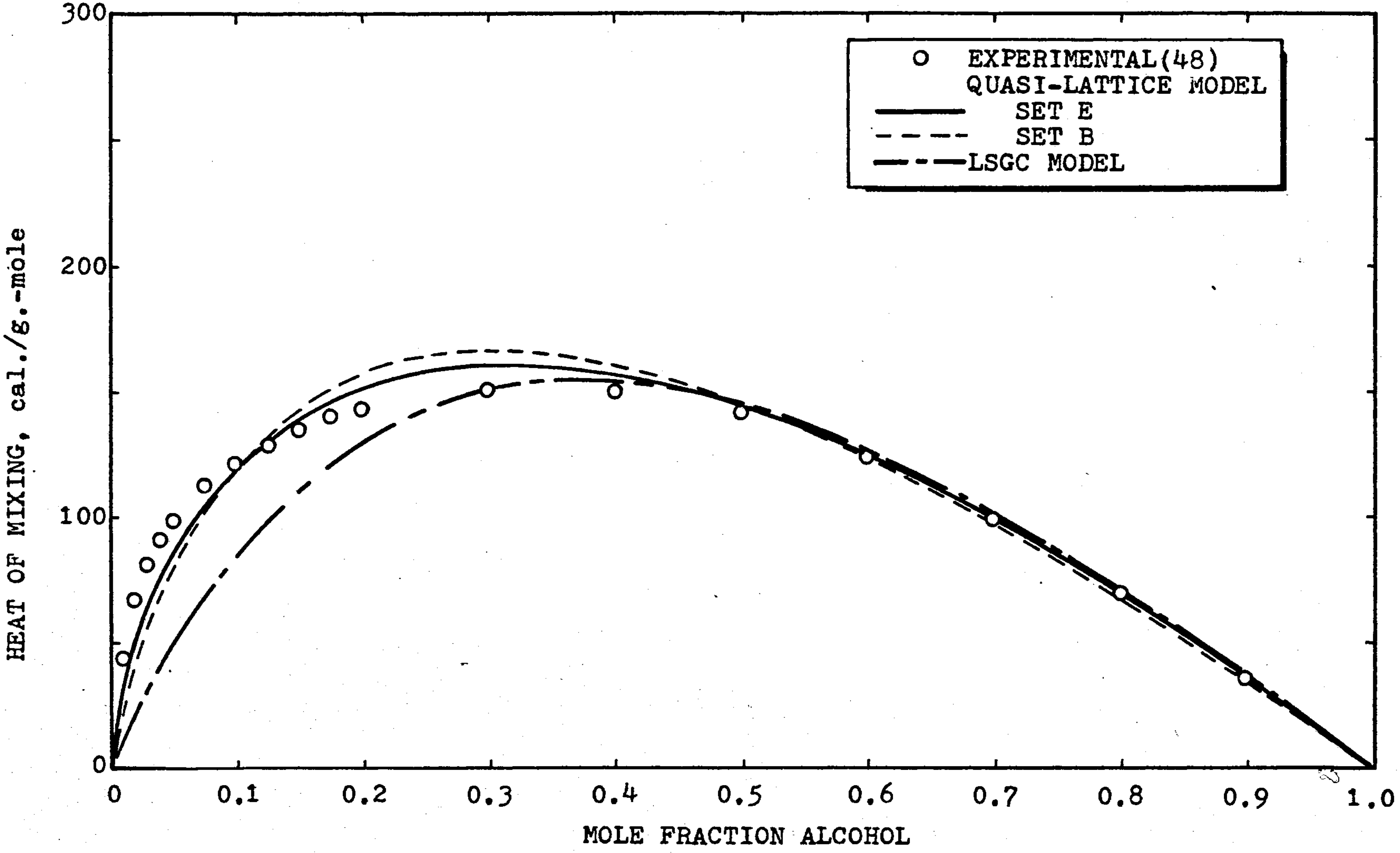


Figure 24. Heat of Mixing in the Octanol-n-Nonane System at 30°C by the Quasi-Lattice Model

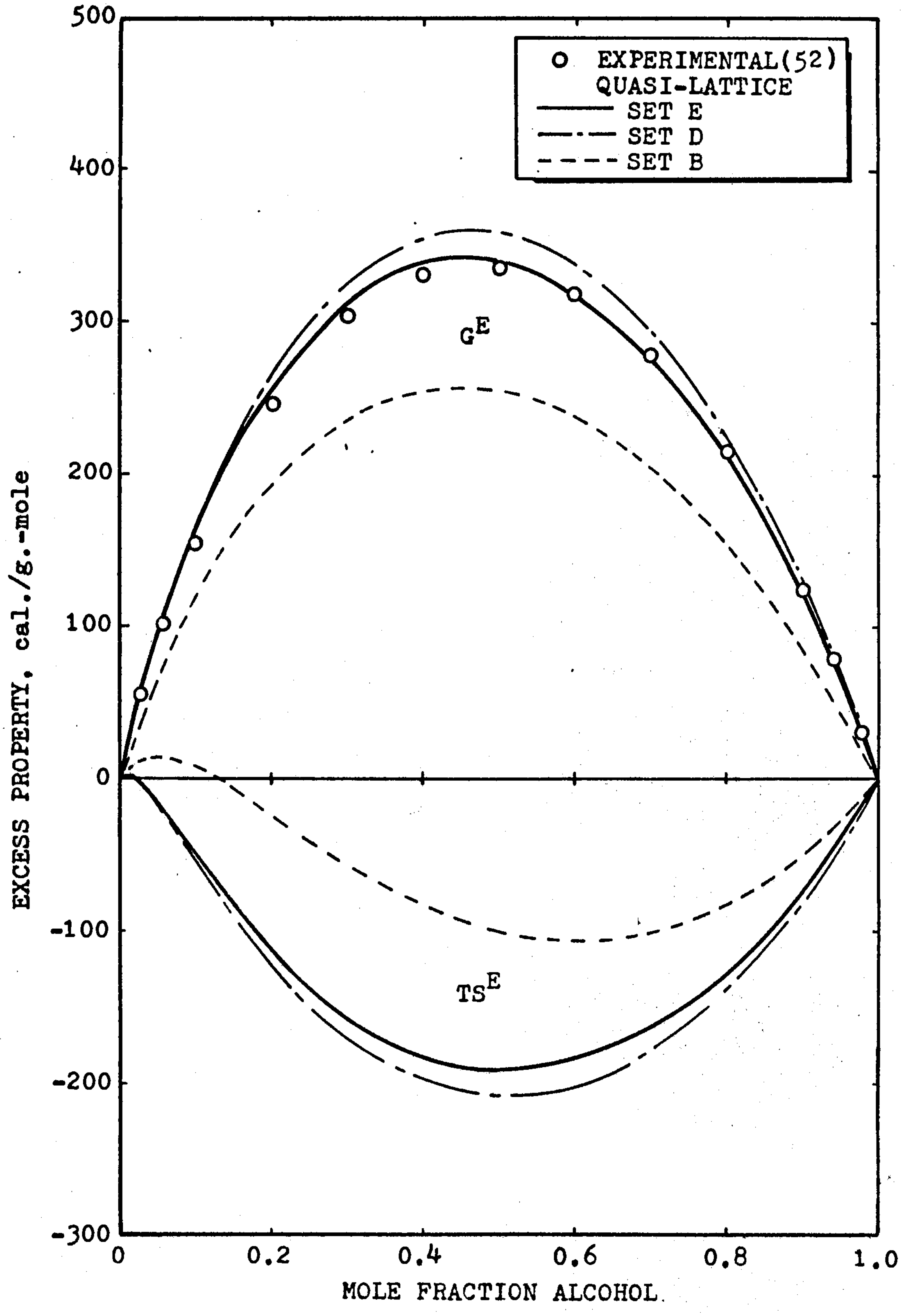


Figure 25. Excess Free Energy and Entropy for Ethanol-n-Hexane System at 30°C by the Quasi-Lattice Model

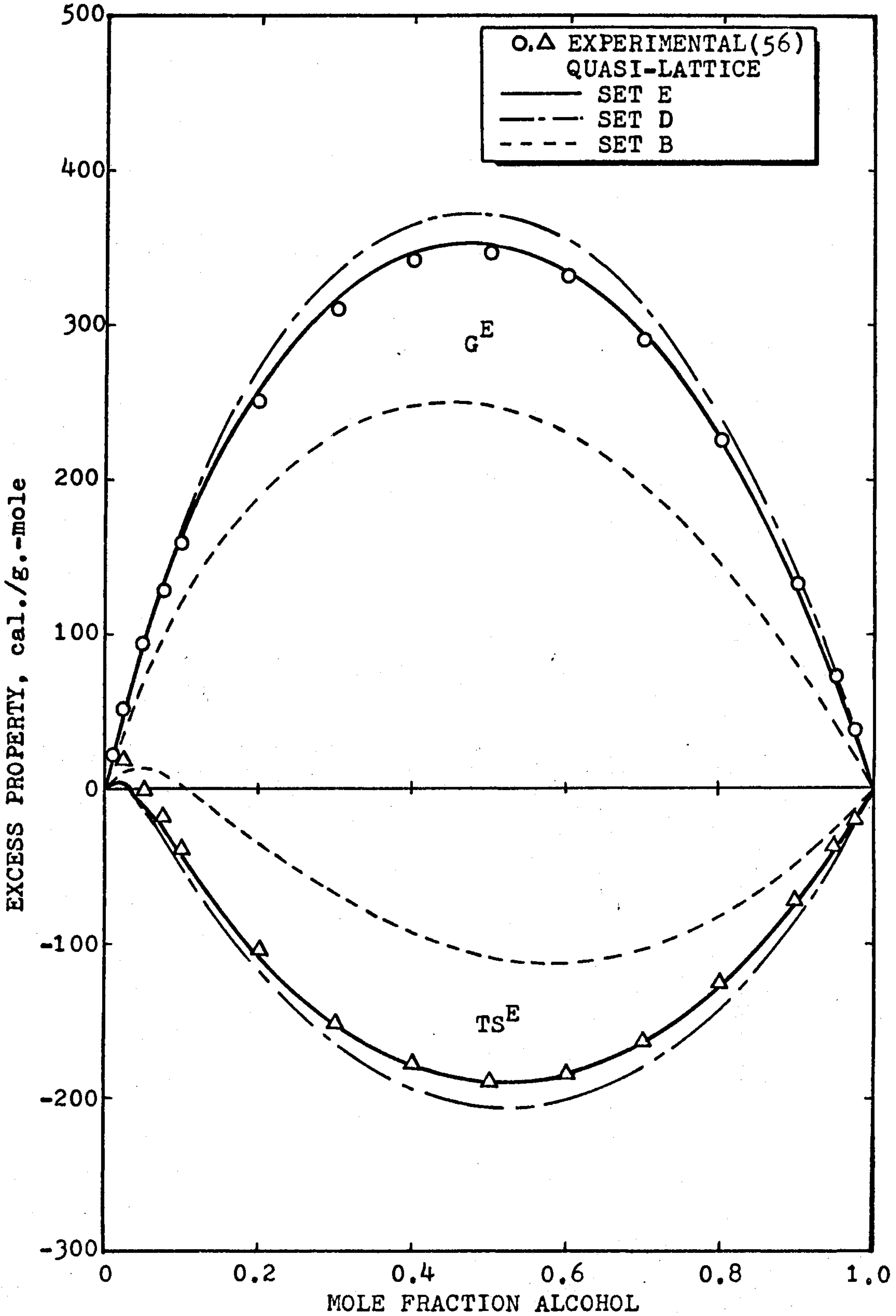


Figure 26. Excess Free Energy and Entropy for Ethanol-n-Heptane System at 30°C by the Quasi-Lattice Model

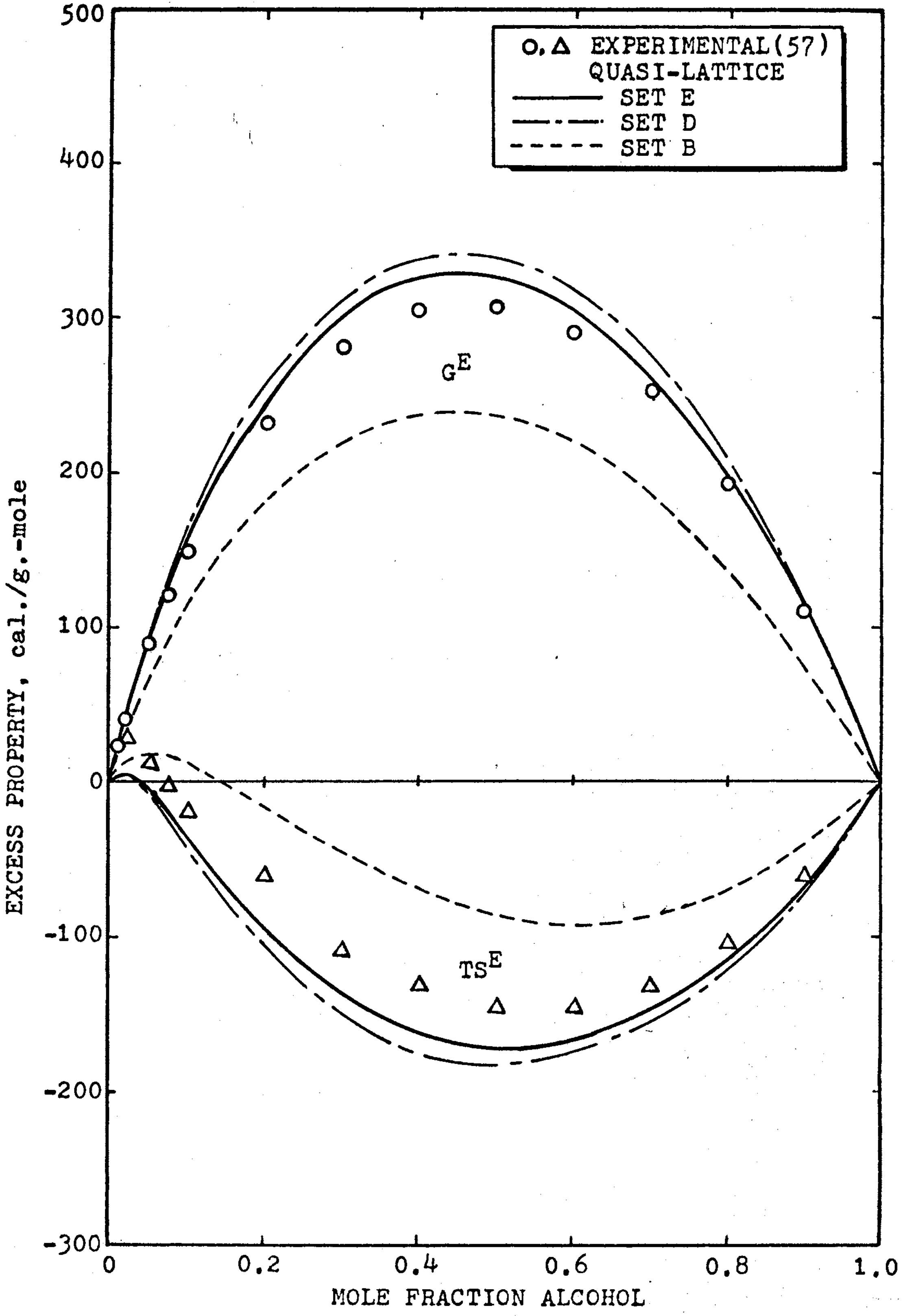


Figure 27. Excess Free Energy and Entropy for Propanol-n-Heptane System at 30°C by the Quasi-Lattice Model

TABLE XV

PREDICTED EXCESS FREE ENERGIES AND EXCESS ENTROPIES AT 30°C BASED ON QUASI-LATTICE THEORY ENERGY PARAMETER SET E

System	Mole Fraction Alcohol	G^E, cal./g.-mole			TS^E, cal./g.-mole		
		Expt'l.	Calc'd.	Dev.	Expt'l.	Calc'd.	Dev.
Ethanol-n-hexane (52)	.01	19.90	23.88	3.98		2.53	
	.02	38.41	43.84	5.43		0.88	
	.03	55.71	62.15	6.44		-3.32	
	.04	71.97	79.13	7.16		-8.87	
	.05	87.30	94.98	7.68		-15.14	
	.10	152.80	161.84	9.04		-49.88	
	.20	244.80	254.31	9.51		-112.30	
	.30	300.99	310.61	9.62		-157.35	
	.40	329.74	338.42	8.68		-183.95	
	.50	334.70	341.08	6.38		-193.30	
	.60	317.35	319.62	2.27		-182.72	
	.70	277.69	279.18	1.49		-163.45	
	.80	214.30	213.28	-1.02		-125.26	
	.90	123.92	121.43	-2.49		-71.68	
Ethanol-n-heptane (56)	.01	22.23	23.73	1.50	21.42	3.34	-18.08
	.025	52.16	52.98	0.82	19.08	1.41	-17.67
	.05	93.66	95.06	1.40	-0.56	-10.65	-10.09
	.075	128.76	127.96	-0.80	-18.62	-23.01	-4.39
	.10	159.44	159.77	0.33	-38.78	-39.72	-0.94
	.20	251.99	258.68	6.69	-104.89	-105.02	-0.13
	.30	309.99	315.15	5.16	-150.37	-148.12	2.25
	.40	340.56	348.71	8.15	-178.70	-180.35	-1.65
	.50	347.38	352.38	5.00	-190.72	-189.17	1.55
	.60	330.88	336.76	5.88	-185.88	-188.37	-2.49
	.70	290.75	294.49	3.74	-164.30	-167.11	-2.81
	.80	226.64	227.03	0.39	-126.79	-129.31	-2.52
	.90	132.82	130.33	-2.49	-72.20	-73.56	-1.36
	.95	72.75	69.22	-3.53	-38.87	-36.82	+2.05
	.975	38.09	36.40	-1.69	-20.14	-20.17	0.03

TABLE XV (Continued)

System	Mole Fraction Alcohol	G^E, cal./g.-mole			TS^E, cal./g.-mole		
		Expt'l.	Calc'd.	Dev.	Expt'l.	Calc'd.	Dev.
Propanol-n-heptane (57)	.01	21.28	19.75	-1.53	23.81	7.05	-16.76
	.02	40.24	39.04	-1.20	27.08	6.86	-20.22
	.05	87.21	91.94	+4.73	11.21	-8.72	-19.93
	.075	119.52	123.27	3.75	-4.99	-19.98	-14.99
	.10	147.40	153.53	6.13	-20.78	-35.53	-14.75
	.20	230.17	243.29	13.12	-73.59	-92.84	-19.25
	.30	279.76	299.13	19.37	-110.20	-137.48	-27.28
	.40	304.35	324.71	20.36	-134.68	-163.02	-28.34
	.50	307.38	326.36	18.98	-147.99	-172.65	-24.66
	.60	289.79	305.23	15.44	-148.54	-166.84	-18.30
	.70	251.61	262.72	11.11	-135.31	-146.39	-11.08
	.80	191.64	199.14	7.50	-106.85	-112.66	-5.81
	.90	108.67	112.03	3.36	-62.17	-63.55	-1.38

The magnitudes of the interaction energy parameters in Table XIII display two unexpected features. First, for set D, the O-S interaction energy is a positive number, contrary to the usual sign for such exchange energies. No physical explanation is offered for this occurrence. Second, the values of the O-S and O-I energies in set E differ by more than might be expected. It is possibly a reflection of the altered chemical nature of the methylene groups adjacent to a hydroxyl. It might be profitable in future work to consider the α-methylenes to be a separate group species. However, it has been found that the quasi-lattice theory does not require a unique set of parameters for representation of the heat-of-mixing data. Rather, it appears the response surface (in terms of sum-of-squares of deviations) is rather shallow, and a considerable range of parameter sets may produce essentially equivalent representation of the experimental data. This makes assigning physical significance to small differences in energies a tenuous proposition.

Previous models which have been applied to alcohol-paraffin systems include the local surface group contribution model (13), the association models of Renon and Prausnitz (46) and Wiehe and Bagley (58). The models are listed in order of their generality. The local surface group contribution model appears most general; it requires no information specific to a given binary molecular pair, only interaction energies between group pairs. In this regard, the group contribution model is more general in form than the quasi-lattice theory, which requires a priori specification of segments and contact points. The continuous linear association model studied by Renon and Prausnitz requires one parameter specific to each binary system, and the model of Wiehe and Bagley contains two such parameters.

In their ability to represent the excess properties of alcohol-paraffin systems, the continuous linear association model seems superior to the others. This might be expected in view of the presence of the adjustable parameter specific to each system. The Wiehe-Bagley model, while providing excellent fit to free energies for various systems, produces an inferior description of excess enthalpies (58). The quasi-lattice model predicts excess enthalpies with better accuracy than the local surface group contribution model developed in the previous chapter.

While the calculations of the present work are all at a single temperature, 30°C, the usefulness of the energy parameters reported here can be extended by means of the Helmholtz equation

$$\frac{(G^E/T)}{\partial T} = - \frac{H^E}{T^2} \qquad (4\text{-}22)$$

In this manner the excess free energy and phase equilibrium properties can be estimated at other temperatures if not far from the base value.

A possibility exists that representation of alcohol-paraffin excess properties by the quasi-lattice model could be improved by a choice of energy parameters other than those studied here. Also, the number of segments might be varied; such a modification was employed by Jones, et al. (34), to obtain an improved fit to heats-of-mixing in alkane-benzene systems. Using the segment, contact point, and exchange energies given herein, the quasi-lattice model appears to provide a less accurate description of the alcohol-paraffin systems than it does for the alcohol-aromatic, paraffin-aromatic, and alcohol-cycloparaffin systems studied in previous literature.

With the segments and contact points specified as in Table XII, the coordination number has a value of 4. This value seems to be small for liquids. For liquids, the coordination number varies in the neighborhood of from 8 to 12 (15). In order to test the effect of the value of coordination number to the application of the theory, a value of 10 was chosen for the coordination number and several choices of contact points were made as shown in Table XVI. In Table XVIa the number of contact points was specified in the same manner as that in Table XII. In Table XVIb the numbers of contact points of hydroxyl hydrogen and hydroxyl oxygen segments remain the same as before, but the contact points of paraffin-type segments were specified in the manner as that employed by Jones, et al. (34). In Table XVIc, the H segments were specified to have a single contact point O segments 8, and paraffin-type segments 8 on each methylene group and 9 on each methyl group. With these changes the results have not been affected in the application of the model to alcohol-paraffin systems; results were essentially identical to those obtained by using the values in Table XII. In this regard, the model seems to be insensitive to the choice of contact points and coordination number.

TABLE XVI

NUMBER AND TYPE OF CONTACT POINTS AND SITES WITH COORDINATION NUMBER EQUAL 10

Component	$n_H z_H$	$n_O z_O$	$n_I z_I$	$n_S z_S$	z	r
a. Contact Points Specified as Table XII						
Ethanol	1	2	5	-	10	.75
Propanol	1	2	7	-	10	1.00
Butanol	1	2	9	-	10	1.25
Pentanol	1	2	11	-	10	1.50
Octanol	1	2	17	-	10	2.25
n-Hexane	-	-	-	14	10	1.50
n-Heptane	-	-	-	16	10	1.75
n-Nonane	-	-	-	20	10	2.25
b. Contact Points Specified as that by Jones (31)						
Ethanol	1	2	10	-	10	1.375
Propanol	1	2	12	-	10	1.625
Butanol	1	2	14	-	10	1.875
Pentanol	1	2	16	-	10	2.125
Octanol	1	2	22	-	10	2.875
n-Hexane	-	-	-	19	10	2.125
n-Heptane	-	-	-	21	10	2.375
n-Nonane	-	-	-	25	10	2.875
c. Contact Points of Oxygen and Methylene = 8						
Ethanol	1	8	17	-	10	3
Propanol	1	8	25	-	10	4
Butanol	1	8	33	-	10	5
Pentanol	1	8	41	-	10	6
Octanol	1	8	65	-	10	9
n-Hexane	-	-	-	50	10	6
n-Heptane	-	-	-	58	10	7
n-Nonane	-	-	-	74	10	9

D. Summary

Reasonable representation of excess thermodynamic properties of alcohol-paraffin binary systems has been obtained using the quasi-lattice model. Results were found to be sensitive to the choice of exchange energies regarded as significant but not to the choice of coordination number and contact points. Description of excess properties by the quasi-lattice theory was superior to that of the local surface group solution model proposed in the previous chapter.

CHAPTER V

THE ONE DIMENSIONAL LATTICE MODEL

The thermodynamic properties of liquid mixtures containing polar substances show considerable complexity in their dependence on concentration. The local surface group contribution model which relates the heat of mixing of solutions of alcohol in n-paraffin solvents with the group interaction between two groups occurring in the solutions and the free surface area of the groups, predicts the heat of mixing of solutions of alcohol-paraffin binary systems with some success. However, the model is intuitive and difficult to extend to excess entropy and excess free energy of solutions.

In this chapter, the model has been restructured into a more formal framework. This facilitates the use of statistical mechanical methods in evaluating the complete expression for the canonical partition function of the system as determined by the interaction energies between group pairs in the solution and free surface area of the groups in the system. This leads to the development of the one-dimensional lattice model without using the quasi-lattice picture of the liquid.

A. Development of the Model

For the development, assumptions are made as follows:

1. The principle of "independent action of groups" advanced by

Langmuir (36) is valid.

2. The interaction energy between groups is a function only of the identity of the groups involved.
3. The interaction energy can be expressed in terms of a contact surface energy density.
4. The surface area of all like groups can be lumped.

Suppose a solution containing n types of groups has n_1 numbers of group 1 with surface area s_1, n_2 numbers of groups 2 with surface area s_2, and so on. The total lumped area of group 1 is $n_1 s_1$, of group 2 is $n_2 s_2$, and that of group u is $n_u s_u$. Let A_{uv} denote the total overlapping surface area of contact between group u and group v, and λ_{uv} be the corresponding interaction energy per unit area of overlap. Then, the sum of the overlapping surface area of group v is equal to the total lumped area of group v. This is expressed in equation as

$$2\,A_{vv} + \Sigma_{u \neq v} A_{uv} = n_v s_v \qquad (5\text{-}1)$$

There will be a total of n simultaneous equations of Equation (5-1) for a solution containing n types of groups.

The total interaction energy of the system is the sum of contributions from interactions between pairs of groups in the system.

$$E = \sum_{u} \sum_{u \geq v} A_{uv} \lambda_{uv} \qquad (5\text{-}2)$$

Define an interchange energy Ω_{uv} by

$$\Omega_{uv} = \lambda_{uv} - \tfrac{1}{2}(\lambda_{uu} + \lambda_{vv}) \qquad (5\text{-}3)$$

or

$$\lambda_{uv} = \Omega_{uv} + \tfrac{1}{2}(\lambda_{uu} + \lambda_{vv}) \qquad (5\text{-}4)$$

Substitution of Equation (5-4) into Equation (5-2) produced an expression in terms of Ω_{uv} for the energy of the system

$$E = E^{o} + \tfrac{1}{2}\Sigma_{u}\Sigma_{v}A_{uv}\Omega_{uv} \qquad (5\text{-}5)$$

where

$$E^{o} = \tfrac{1}{2}\Sigma_{v} n_{v} s_{v} \lambda_{vv} \qquad (5\text{-}6)$$

E^{o} is a constant for a system of specified molecular composition and is independent of A_{uv}.

Let $g(A_{uv})$ denote the number of ways of arrangement of lumped areas n_1s_1, n_2s_2, . . . n_ns_n corresponding to fixed values of overlapping areas between different types of groups, A_{12}, A_{13}, . . . $A_{n-1\ n}$. Then, the contribution of these configurations to the canonical partition function is

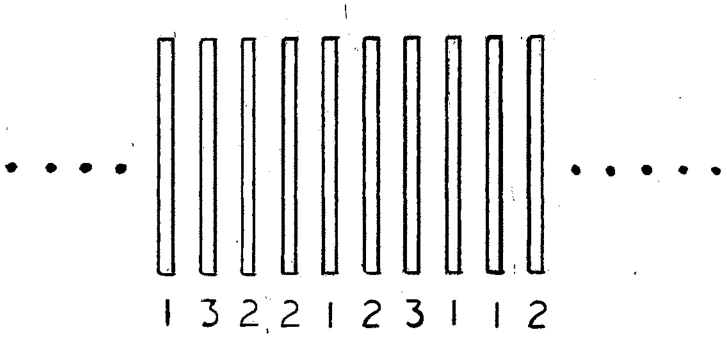
$$g(A_{uv}) \exp(-E/kT)$$

The canonical partition function of the system for given lumped areas is the sum of all possible ways of arrangement. This is expressed in equation as:

$$Q(n_1, n_2, \ldots n_n, T) = \exp(-E^{o}/kT)\Sigma_{A_{uv}} g(A_{uv}) \exp(-\tfrac{1}{2}\Sigma_{u}\Sigma_{v}A_{uv}\Omega_{uv}/kT) \qquad (5\text{-}7)$$

Since the only configurational contributions due to inter-group action are included in Q, the Q is a configurational partition function.

To evaluate $g(A_{uv})$, the lumped areas are divided into identical pieces (like poker chips) each with two sides and each side of unit area. Then there are $\tfrac{1}{2}n_1s_1$ pieces of type 1, and $\tfrac{1}{2}n_2s_2$ pieces of type 2, etc. The pieces are envisioned as being stacked together into a column as follows:



The number of contacts of the type 1-1 in this column is equal to A_{11}, and that of the type 1-2 in this column is equal to A_{12}. Similarly, the number of contacts of the type u-v in this column will be equal to A_{uv}.

By doing so, a one-dimensional adsorpted gas problem results which can be solved exactly in statistical mechanics. The number of possible arrangements of the column for specified values of n_1s_1, n_2s_2, . . . and A_{12}, A_{13}, . . . based on the one-dimensional lattice gas theory is given (16, 30) by

$$g(A_{uv}) = \prod_v \left\{ \frac{(n_v s_v/2)!}{(n_v s_v/2 - \frac{1}{2}\sum_{u \neq v} A_{uv})! \prod_{u \neq v} [(A_{uv}/2)!]} \right\} \tag{5-8}$$

For a system containing two types of groups, Equation (5-8) reduces to

$$g(A_{12}) = \frac{(n_1 s_1/2)!\ (n_2 s_2/2)!}{(n_1 s_1/2 - \frac{1}{2}A_{12})!\ (n_2 s_2/2 - \frac{1}{2}A_{12})!\ (\frac{1}{2}A_{12})!^2} \tag{5-8a}$$

For a system containing three types of groups, Equation (5-8) becomes

$$g(A_{12}, A_{13}, A_{23}) = \frac{(\frac{1}{2}n_1 s_1)!}{[\frac{1}{2}n_1 s_1 - (A_{12} + A_{13})/2]!\ (\frac{1}{2}A_{12})!\ (\frac{1}{2}A_{13})!}$$

$$\times \frac{(\frac{1}{2}n_2 s_2)!}{[\frac{1}{2}n_2 s_2 - (A_{12} + A_{23})/2]!\ (\frac{1}{2}A_{12})!\ (\frac{1}{2}A_{23})!}$$

$$\times \frac{(\frac{1}{2}n_3 s_3)!}{[\frac{1}{2}n_3 s_3 - (A_{13} + A_{23})/2)!\ (\frac{1}{2}A_{13})!\ (\frac{1}{2}A_{23})!} \qquad (5\text{-}8b)$$

Having a known g-function, evaluation of the canonical partition function, Q, can proceed, but the sum is difficult. In statistical mechanics, ln(Q) is of interest rather than Q itself, and the logarithm of a sum, as mentioned in previous chapter, is frequently approximated by logarithm of the largest term in the sum. Therefore, the partition function is evaluated with the maximum term in the sum found by setting the derivative of the logarithm of the partition function with respect to A_{uv} equal to zero.

$$\frac{\partial \ln Q(n_1, n_2, \ldots n_n, T)}{\partial A_{uv}} = 0 \qquad (5\text{-}9)$$

One obtains

$$\frac{A_{uu} A_{vv}}{(\frac{1}{2}A_{uv})^2} = \exp(2 s_{uv} \Omega_{uv}/kT) \qquad (5\text{-}10)$$

where $s_{uv} = s_u s_v/(s_u + s_v)$ is a factor empirically inserted into the above equation to maintain consistency of the thermal energy associated with the interchange energy Ω_{uv}. In a solution containing n types of groups, there are $\frac{1}{2}n(n - 1)$ simultaneous equations of Equation (5-10). Values of the A_{uv}'s evaluated from Equation (5-10) are the most probable values for system of specified values of

$n_1s_1, n_2s_2, \ldots n_ns_n$.

To evaluate the A_{uv}'s Equation (5-10) is combined with Equation (5-1) to make up a total of $\frac{1}{2}n(n+1)$ equations corresponding exactly to the number of the unknown A_{uv}'s.

Using the results of Equations (5-8) and (5-10), the thermodynamic functions for the solution may be calculated in terms of the most probable case of group interactions.

The enthalpy is given by

$$H \approx U = kT^2\left[\frac{\partial \ln Q(n_1, n_2, \ldots n_n, T)}{\partial T}\right]_{V,n}$$

$$= E^o + \tfrac{1}{2}\Sigma_u\Sigma_v A_{uv}\Omega_{uv} \qquad (5\text{-}11)$$

The entropy is given by

$$S = kT\left[\frac{\partial \ln Q(n_1, n_2, \ldots n_n, T)}{\partial T}\right]_{V,n}$$

$$+ k \ln Q(n_1, n_2, \ldots n_n, T)$$

$$= k \ln g(A_{uv}) \qquad (5\text{-}12)$$

and the free energy is given by

$$G \approx A = -kT\ln Q(n_1, n_2, \ldots n_n, T)$$

$$= -kT\ln g(A_{uv}) + E^o + \tfrac{1}{2}\Sigma_u\Sigma_v A_{uv}\Omega_{uv} \qquad (5\text{-}13)$$

The trivial differences between Gibbs free energy, G, and Helmholtz free energy, A, and between enthalpy, H, and internal energy, U, have been neglected.

By setting all components except one equal to zero, the thermodynamic functions for the pure components of the solution may be found. If an ideal solution of groups is defined as a mixture of groups with no interaction between groups, then the changes in the thermodynamic functions on mixing, and hence the changes in excess of those for an ideal solution may be calculated. Thus, the excess enthalpy of the solution is expressed in terms of the A_{uv} by

$$H^E = \sum_u \sum_{v>u} (A_{uv} - \Sigma_j A^{oi}_{uv})\Omega_{uv} \tag{5-14}$$

where the superscript oi denotes the quantity of pure component i.

The excess entropy is given by

$$\begin{aligned} S^E &= k[\ln \frac{g(A_{uv})}{\pi_i g(A_{uv})^{oi}} - \ln \frac{g(A_{uv})^*}{\pi_i g(A_{uv})^{*oi}}] \\ &= k\sum_i\sum_v \left[\ln \frac{(A_{vv} + \frac{1}{2}A_{uv})!\ (A^{*oi}_{vv} + \frac{1}{2}A^{*oi}_{uv})!}{(A^*_{vv} + \frac{1}{2}A^*_{uv})!\ (A^{oi}_{vv} + \frac{1}{2}A^{oi}_{uv})!} \right. \\ &\quad \left. - \ln \frac{A_{vv}!\ A^*_{vv}!}{A^{oi}_{vv}!\ A^{*oi}_{vv}!} - \sum_{u \neq v} \ln \frac{(\frac{1}{2}A_{uv})!\ (\frac{1}{2}A^*_{uv})!}{(\frac{1}{2}A^{oi}_{uv})!\ (\frac{1}{2}A^{*oi}_{uv})!} \right] \end{aligned} \tag{5-15}$$

where the quantities with * are ideal solution quantities.

The excess free energy is obtained upon combining Equations (4-14) and (-15).

$$G^E = H^E - TS^E \tag{5-16}$$

B. Application of the Model to Alcohol-Paraffin Systems

The proposed model was tested again by using excess properties of the n-alcohol-n-paraffin binary systems, mentioned previously. In prediction of the excess properties by this model, values for the surface areas of all groups and that for the interaction energies for all possible interactions between group pairs are required. The surface areas of the groups (calculated from geometric models of molecules) listed in Table II were used in this model. The interaction energies were evaluated by the same process used in the previous chapter to fit the model to experimental data; that is, the hydrocarbon interaction energy parameters (CH_2-CH_2, CH_2-CH_3, and CH_3-CH_3) were determined by application of the model to data on the energies of vaporization of the pure n-paraffins propane through decane, the remaining three energy parameters (CH_3-OH, CH_2-OH, and OH-OH) were determined from heat of mixing data on the eight binary mixtures. Non-linear regression was again used to determine the energy parameter values which would give the least-mean-squares fit of the model to the data.

Values of the resultant energy parameters for the hydrocarbon interactions are given in Table XVIIa, and a comparison of the calculated and experimental energies of vaporization is shown in Table XVIII. The agreement is very good with a maximum deviation of 0.05%.

TABLE XVII

GROUP INTERACTION ENERGIES FOR ONE-DIMENSIONAL LATTICE MODEL

Groups	Interaction Energy, $-\lambda \times 10^9$ cal./sq. cm.
	a. Based on energies of vaporization
CH_2-CH_2	1, 718
CH_2-CH_3	1,433
CH_3-CH_3	934
	b. Based on heats of mixing
CH_2-OH	2,894
CH_3-OH	3,231
OH-OH	8,283
	c. Based on heats of mixing
CH_2-OH	2,050.8
CH_3-OH	3,216.6
OH-OH	$9{,}525.2 + 253.2 \ln(f_{sOH})$

TABLE XVIII

HYDROCARBON INTERNAL ENERGIES OF VAPORIZATION AT 30°C CALCULATED FROM ONE-DIMENSIONAL LATTICE MODEL

Hydrocarbon	Energy of Vaporization ΔU^V, cal./g.-mole		
	Experimental*	Calculated**	Deviation %
Propane	3,265	3,264	-0.02
n-Butane	4,497	4,498	0.01
n-Pentane	5,704	5,707	0.05
n-Hexane	6,905	6,902	-0.05
n-Heptane	8,090	8,087	-0.04
n-Octane	9,262	9,266	0.05
n-Nonane	10,441	10,442	0.01
n-Decane	11,615	11,614	-0.01

* Based on heats of vaporization from Reference 1.
** Based on energy parameters from Table XVIIa.

The interaction energy parameters involving the OH group determined directly from heat of mixing data on the eight binary mixtures are given in Table XVIIb and Table XVIIc. The energy parameters in Table XVIIb are the resultant values from a nonlinear regression, treating the OH-OH interaction as constant. The parameters in Table XVIIc are that with treating the OH-OH interaction as a function of OH group surface concentration. In both regressions, the previously determined hydrocarbon interaction energy parameters from Table XVIIa were used as fixed input to the calculations. The predicted heats of mixing based on the parameters in Table XVIIb and Table XVIIc are compared with experimental data in Figures 28 through 35. The dashed lines in these figures are results from parameters in Table XVIIb.

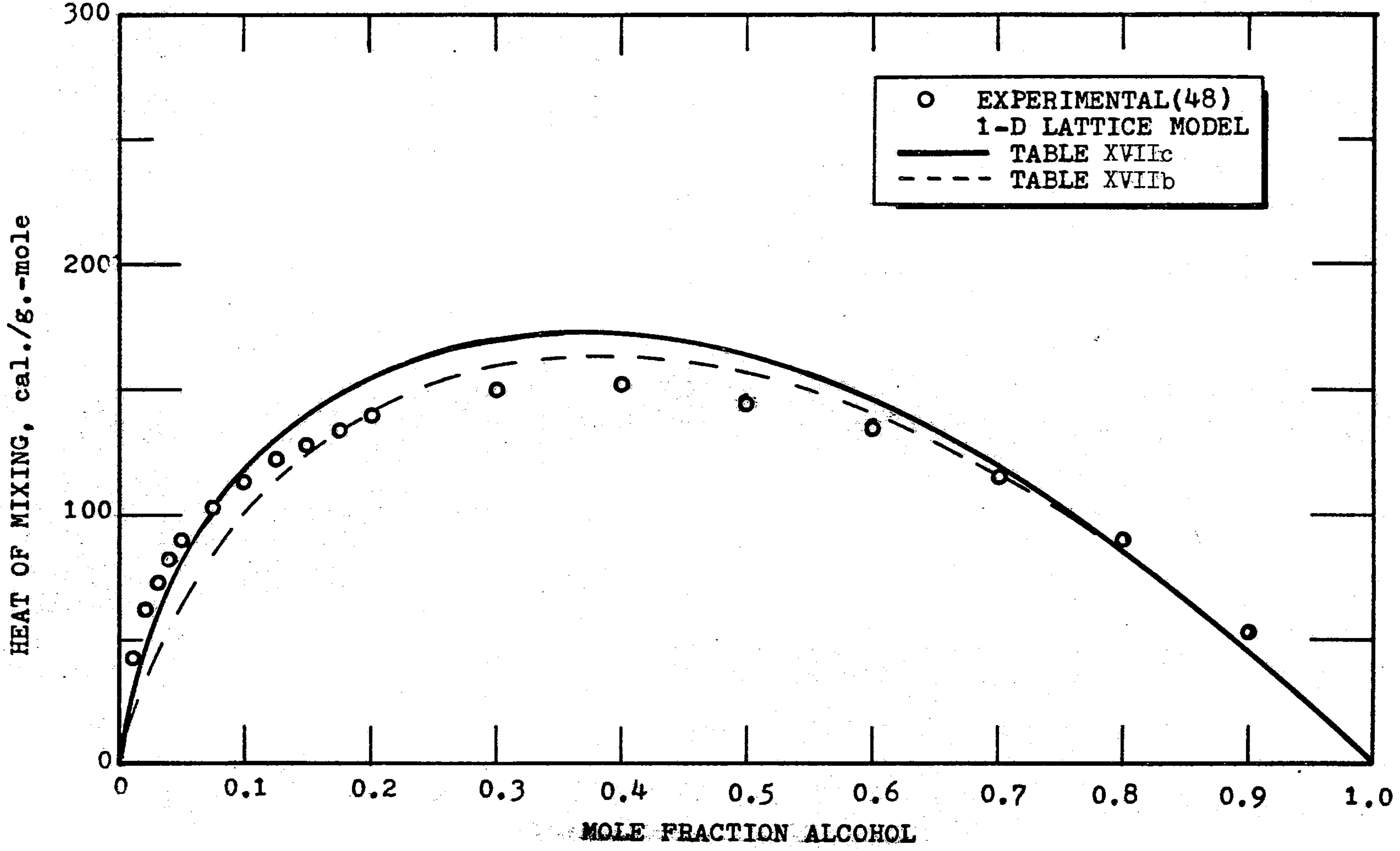


Figure 28. Heat of Mixing in the Ethanol-n-Hexane System at 30°C by the One-Dimensional Lattice Model

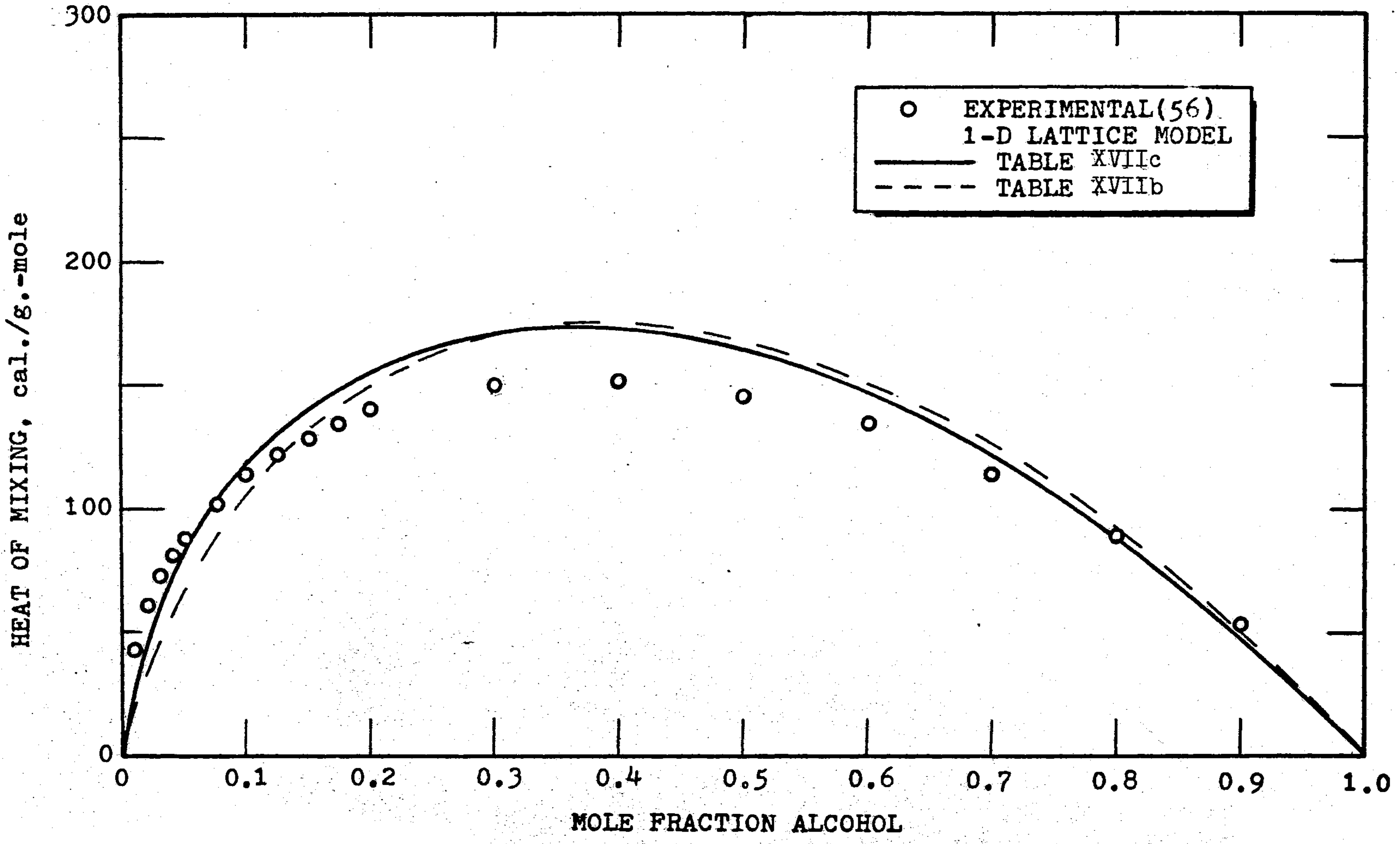


Figure 29. Heat of Mixing in the Ethanol-n-Heptane System at 30°C by the One-Dimensional Lattice Model

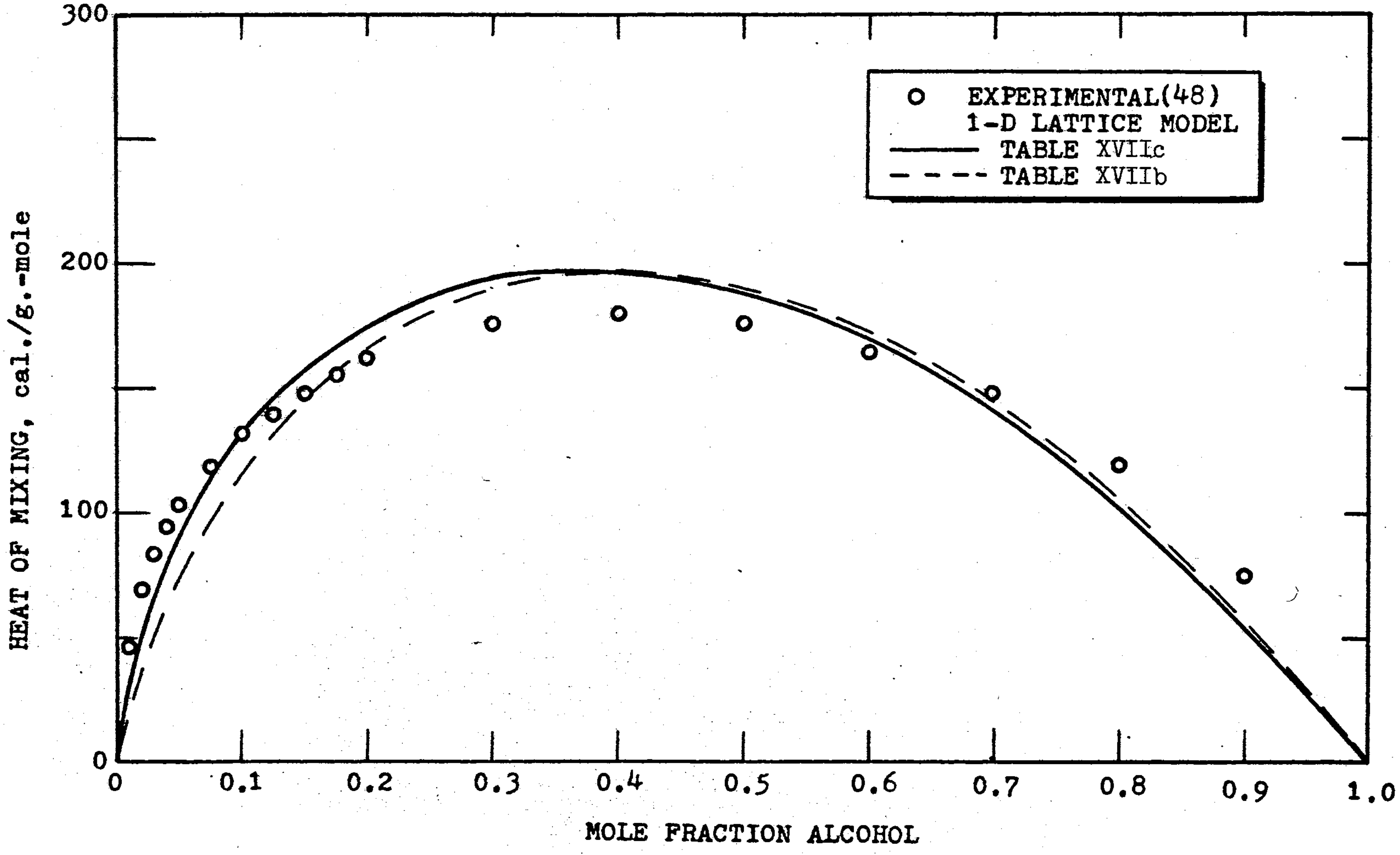


Figure 30. Heat of Mixing in the Ethanol-n-Nonane System at 30°C by the One-Dimensional Lattice Model

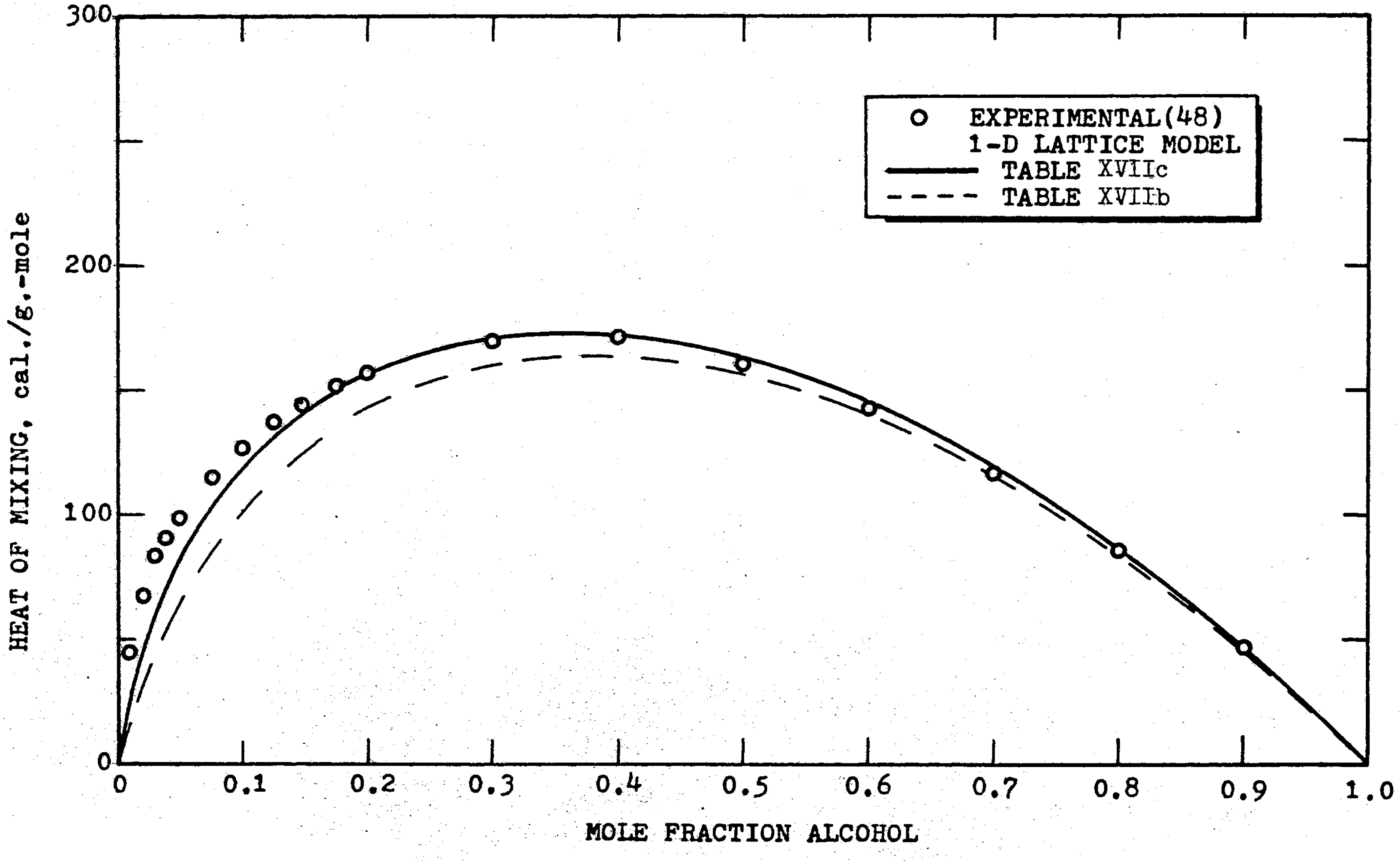


Figure 31. Heat of Mixing in the Propanol-n-Heptane System at 30°C by the One-Dimensional Lattice Model

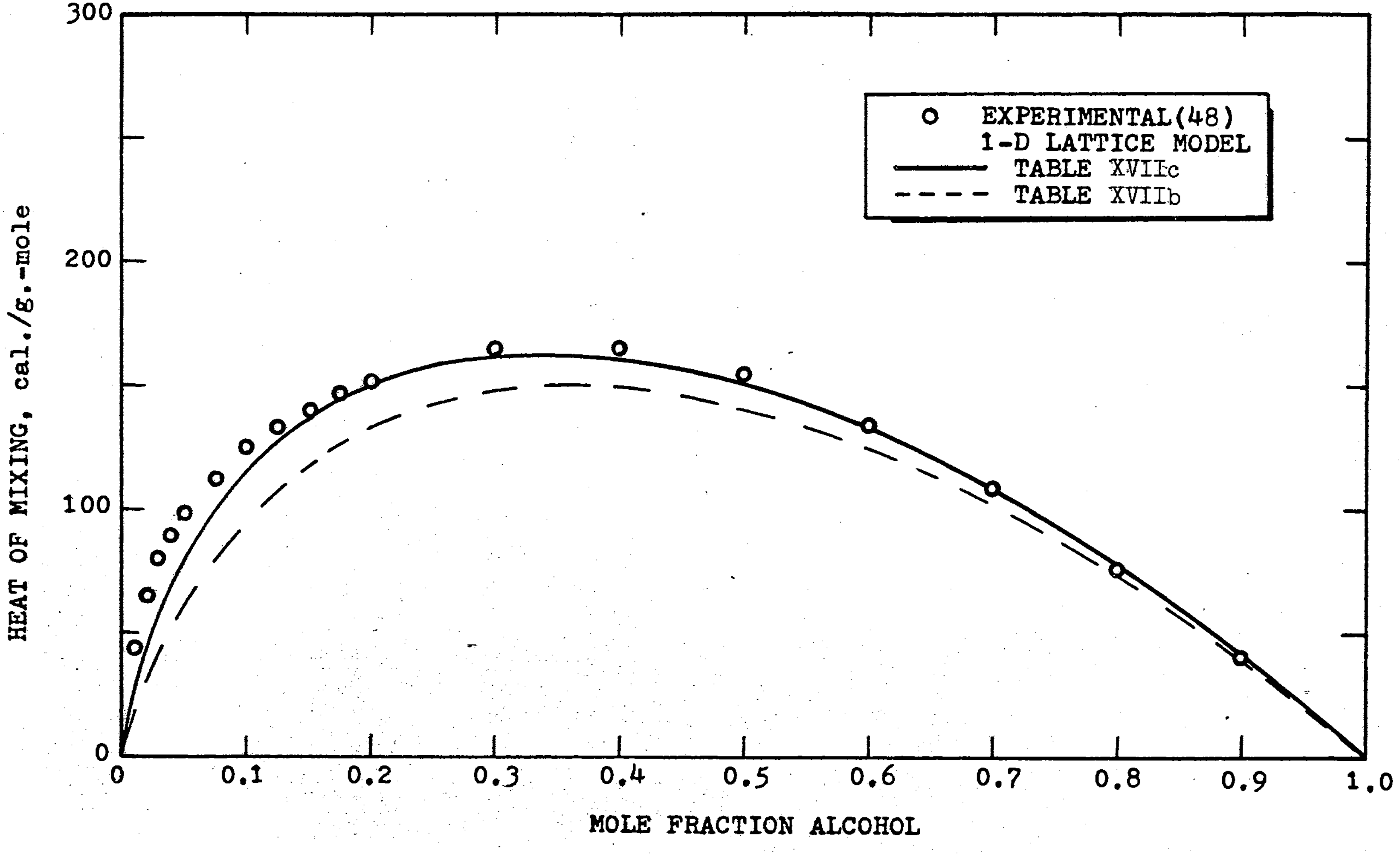


Figure 32. Heat of Mixing in the Butanol-n-Heptane System at 30°C by the One-Dimensional Lattice Model

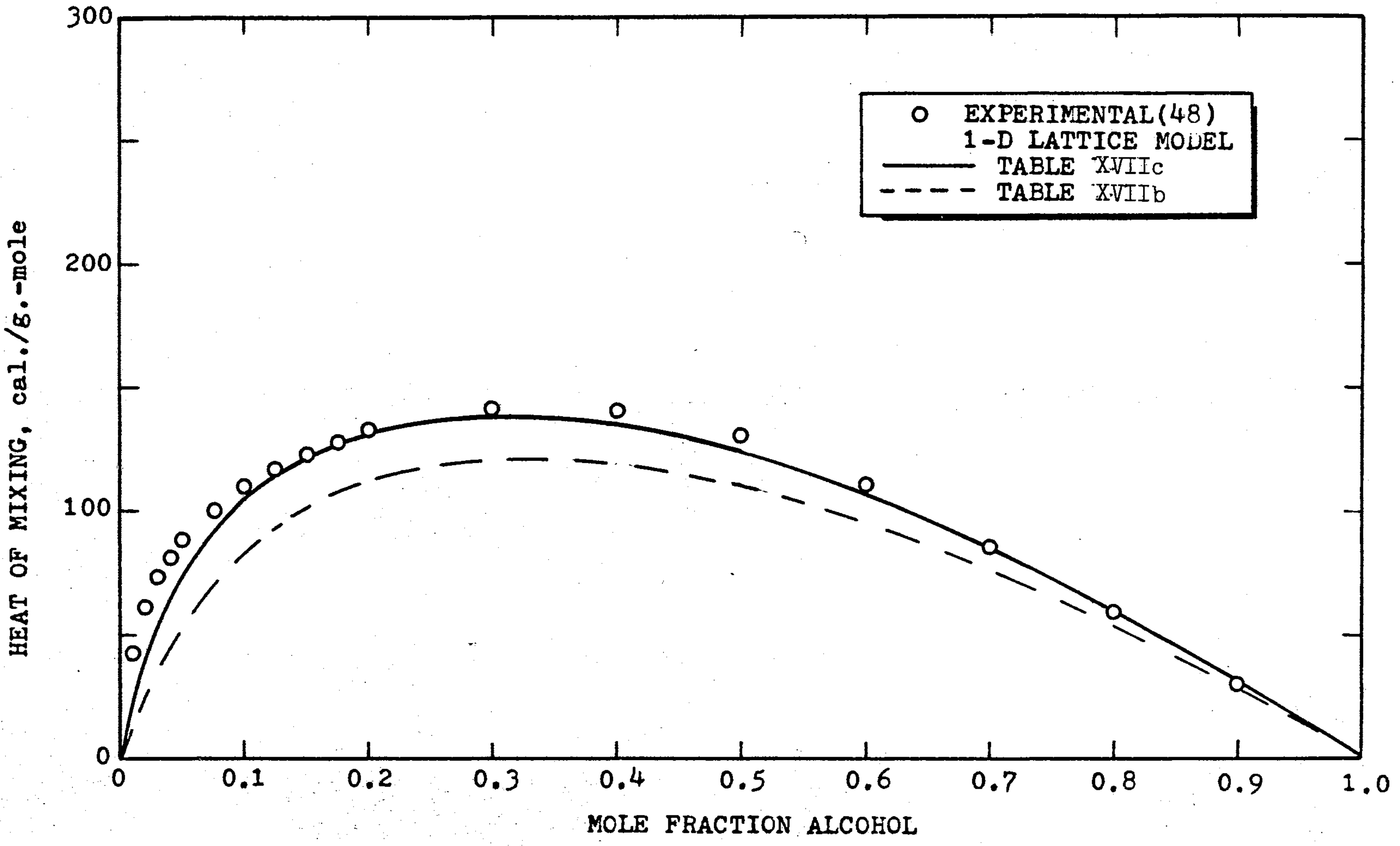


Figure 33. Heat of Mixing in the Pentanol-n-Hexane System at 30°C by the One-Dimensional Lattice Model

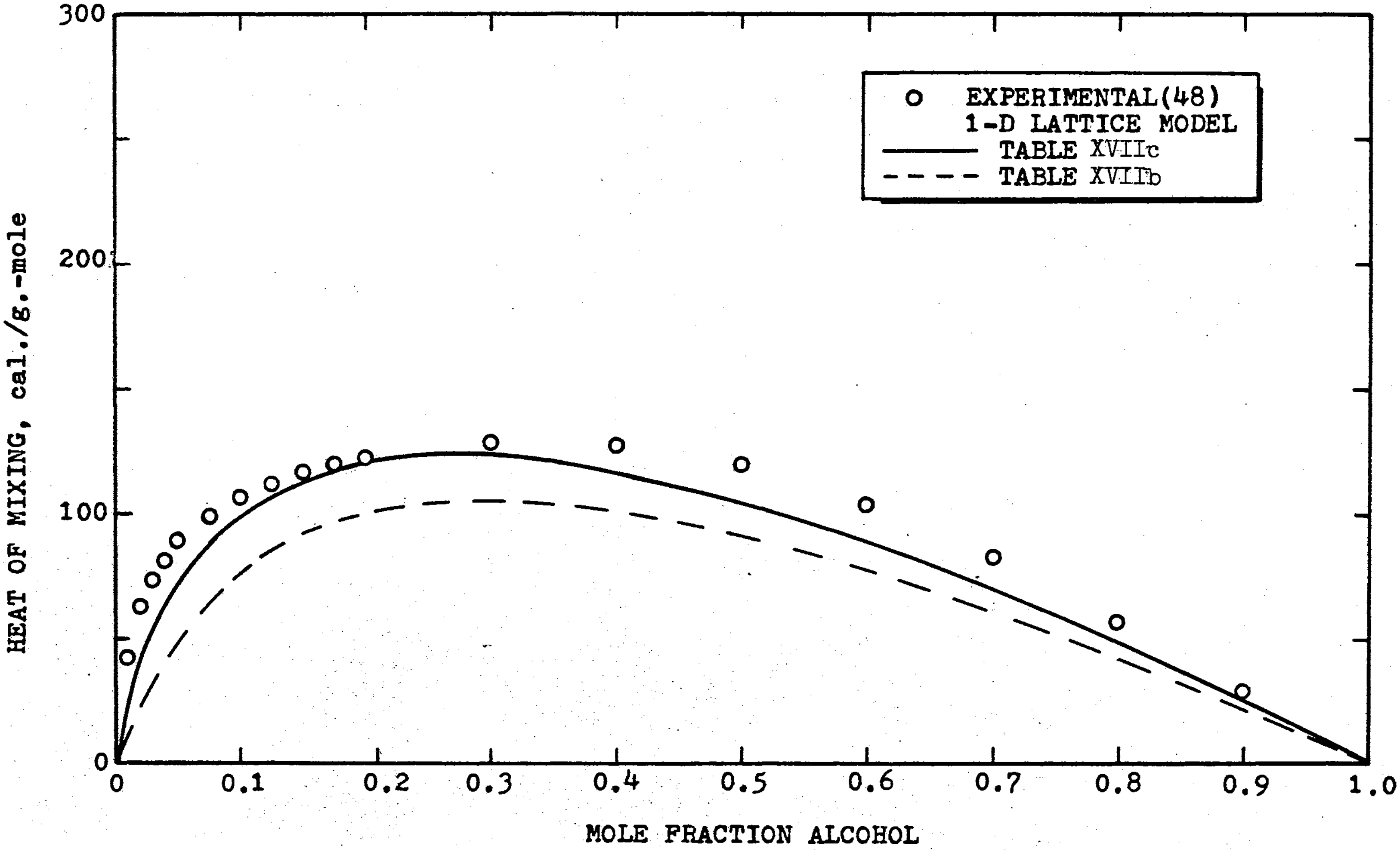


Figure 34. Heat of Mixing in the Octanol-n-Heptane System at 30°C by the One-Dimensional Lattice Model

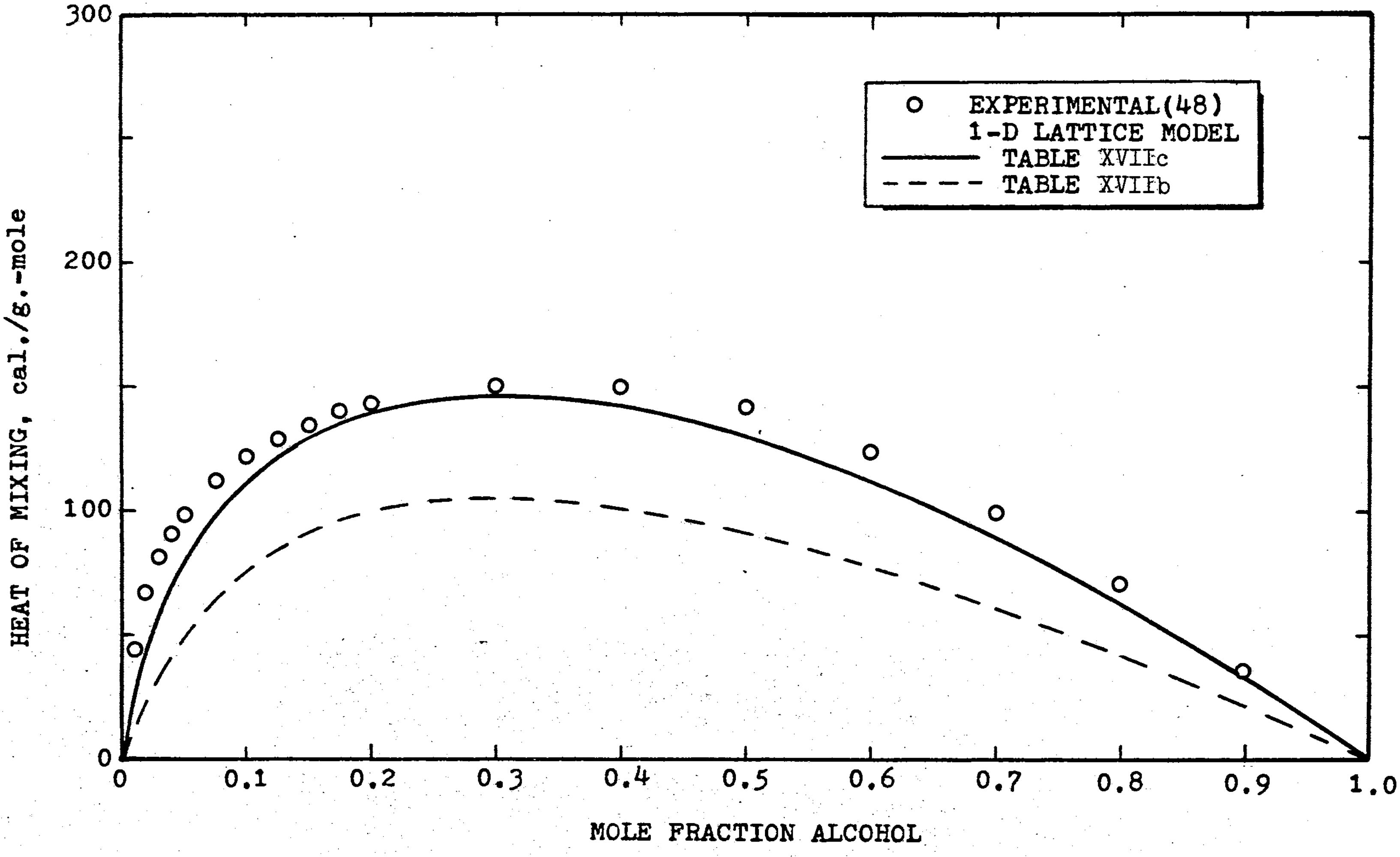


Figure 35. Heat of Mixing in the Octanol-n-Nonane System at 30°C by the One-Dimensional Lattice Model

The predicted heats of mixing from parameters in Table XVIIc are expressed as solid lines in these figures. Table XIX shows the comparison of results based on the parameters in Table XVIIc with experimental data.

The energy parameter values in Table XVII were employed to predict excess free energy and excess entropy for alcohol-paraffin systems where data are available at the same temperature. The predicted excess free energies and excess entropies for three binary systems from Equations (5-15) and (5-16) based on energy parameter values in Table XVIIa and Table XVIIc are compared with experimental data in Table XX. Comparison of the predicted results with data is also shown in Figures 36, 37, and 38 for ethanol-n-hexane, ethanol-n-heptane, and propanol-n-heptane systems, respectively (using energy parameters from Table XVIIc). The energy parameter values in Table XVIIb gave a qualitative representation of heat of mixing but were not able to represent the excess free energies and the excess entropies for the three systems.

From known excess free energies, the phase equilibrium properties of the system can be predicted. This can be done by several methods such as differentiation of the analytical G^E expression, graphical differentiation, or evaluation from parametric G^E expressions such as Wilson's equation (39) or Redlich and Kister's equation (31). The G^E expression developed in this chapter (Equation 5-16) is too complicated to perform the differentiation with respect to the number of moles of the components in solution to obtain the activity coefficient. In the present work Wilson's two parameter equation was employed.

TABLE XIX

HEATS OF MIXING OF ALCOHOL-PARAFFIN SOLUTIONS AT 30°C CALCULATED FROM ONE-DIMENSIONAL LATTICE MODEL WITH ENERGY PARAMETERS IN TABLE XVIIc

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l.	Calc'd.	cal./g.-mole	%
Ethanol-n-hexane (48)	.01	42.86	28.62	-14.24	-33.2
	.02	61.53	47.14	-14.39	-23.4
	.03	72.76	61.50	-11.26	-15.5
	.04	81.51	73.30	-8.21	-10.1
	.05	88.60	83.36	-5.24	-5.9
	.075	102.56	103.56	1.00	1.0
	.10	112.93	119.10	6.17	5.5
	.125	121.47	131.52	10.05	8.3
	.15	128.42	141.61	13.19	10.3
	.175	133.96	149.86	15.90	11.9
	.20	138.85	156.58	17.73	12.8
	.30	149.42	171.85	22.43	15.0
	.40	151.15	173.34	22.19	14.7
	.50	144.83	164.34	19.51	13.5
	.60	133.27	146.53	13.26	9.9
	.70	114.59	120.80	6.21	5.4
	.80	88.46	87.66	-0.80	-0.9
	.90	52.57	47.35	-5.22	-9.9
Ethanol-n-heptane (56)	.01	43.65	29.43	-14.22	-32.6
	.025	71.24	56.52	-14.72	-20.6
	.05	93.10	86.35	-6.75	-7.2
	.075	110.14	107.46	-2.68	-2.4
	.10	120.63	123.75	3.12	2.6
	.20	147.10	163.37	16.27	11.0
	.30	159.62	179.92	20.30	12.7
	.40	161.86	182.06	20.20	12.5
	.50	156.67	173.14	16.47	10.5
	.60	145.00	154.81	9.81	6.8
	.70	126.45	127.95	1.50	1.2
	.80	99.85	93.04	-6.81	-6.8
	.90	60.62	50.31	-10.31	-17.0
	.95	33.89	26.08	-7.81	-23.0
	.975	17.95	13.26	-4.69	-26.1

TABLE XIX (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l.	Calc'd.	cal./g.-mole	%
Ethanol-n-nonane (48)	.01	46.57	30.86	-15.71	-33.7
	.02	70.01	57.37	-12.64	-26.6
	.03	84.01	67.36	-16.65	-19.8
	.04	94.71	80.55	-14.16	-15.0
	.05	103.56	91.85	-11.71	-11.3
	.075	119.74	114.65	-5.09	-4.2
	.10	130.67	132.32	1.65	1.3
	.125	140.14	146.56	6.42	4.6
	.15	148.34	158.22	9.88	6.7
	.175	155.48	167.85	12.37	8.0
	.20	161.15	175.79	14.64	9.1
	.30	175.67	194.59	18.92	10.8
	.40	179.42	197.82	18.40	10.2
	.50	175.48	188.93	13.45	7.7
	.60	164.42	169.58	5.16	3.1
	.70	145.89	140.59	-5.30	-3.6
	.80	118.08	102.37	-15.71	-13.3
	.90	74.86	55.22	-19.64	-26.2
Propanol-n-heptane (48)	.01	45.34	29.06	-16.28	-35.9
	.02	67.66	47.91	-19.75	-29.2
	.03	82.61	62.48	-20.13	-24.4
	.04	90.92	74.42	-16.50	-18.1
	.05	98.88	84.58	-14.30	-14.5
	.075	115.07	104.89	-10.18	-8.8
	.10	127.21	120.42	-6.79	-5.3
	.125	136.98	132.77	-4.21	-3.1
	.15	144.97	142.75	-2.22	-1.5
	.175	151.66	150.86	-0.80	-0.5
	.20	157.31	157.42	0.11	0.1
	.30	170.12	171.98	1.86	1.1
	.40	170.19	172.79	2.60	1.5
	.50	160.07	163.26	3.19	2.0
	.60	141.92	145.11	3.19	2.2
	.70	116.61	119.32	2.71	2.3
	.80	85.00	86.40	1.40	1.6
	.90	46.73	46.61	-0.12	-0.2

TABLE XIX (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l.	Calc'd.	cal./g.-mole	%
Butanol-n-heptane (48)	.01	43.76	28.58	-15.18	-34.7
	.02	65.77	46.97	-18.80	-28.6
	.03	79.60	61.10	-18.50	-23.2
	.04	89.72	72.60	-17.12	-19.1
	.05	97.74	82.33	-15.41	-15.8
	.075	112.40	101.61	-10.79	-9.6
	.10	123.75	116.17	-7.58	-6.1
	.125	132.77	127.58	-5.19	-3.9
	.15	140.37	136.68	-3.69	-2.6
	.175	146.80	143.95	-2.85	-1.9
	.20	151.92	149.73	-2.19	-1.4
	.30	165.07	161.64	-3.43	-2.1
	.40	165.00	160.61	-4.39	-2.7
	.50	154.50	150.12	-4.38	-2.8
	.60	134.42	132.00	-2.42	-1.8
	.70	107.52	107.35	-0.17	-0.2
	.80	75.38	76.85	1.47	2.0
	.90	39.16	40.97	1.81	4.6
Pentanol-n-hexane (48)	.01	42.57	27.05	-15.52	-36.4
	.02	61.77	44.05	-17.72	-28.7
	.03	73.10	56.94	-16.16	-22.1
	.04	81.42	67.30	-14.12	-17.3
	.05	87.92	75.96	-11.96	-13.6
	.075	100.39	92.78	-7.61	-7.6
	.10	109.69	105.13	-4.56	-4.2
	.125	117.00	114.53	-2.47	-2.1
	.15	123.21	121.78	-1.43	-1.2
	.175	128.06	127.35	-0.71	-0.6
	.20	132.31	131.56	-0.75	-0.6
	.30	141.85	138.53	-3.32	-2.3
	.40	140.77	134.52	-6.25	-4.4
	.50	129.81	123.02	-6.79	-5.2
	.60	110.19	105.90	-4.29	-3.9
	.70	85.82	84.33	-1.49	-1.7
	.80	58.46	59.12	0.66	1.1
	.90	29.42	30.86	1.44	4.9

TABLE XIX (Continued)

System	Mole Fraction Alcohol	ΔH^M, cal./g.-mole		Deviation	
		Expt'l.	Calc'd.	cal./g.-mole	%
Octanol-n-heptane (48)	.01	42.43	26.63	-15.80	-37.2
	.02	62.33	43.14	-19.19	-30.8
	.03	73.66	55.44	-18.22	-24.7
	.04	81.23	65.18	-16.05	-19.8
	.05	87.12	73.19	-13.93	-16.0
	.075	98.39	88.38	-10.01	-10.2
	.10	106.44	99.12	-7.32	-6.9
	.125	112.53	106.98	-5.55	-4.9
	.15	117.08	112.77	-4.31	-3.7
	.175	120.43	116.98	-3.45	-2.9
	.20	123.08	119.93	-3.15	-2.6
	.30	129.23	122.87	-6.36	-4.9
	.40	127.50	116.51	-10.99	-8.6
	.50	118.99	104.31	-14.68	-12.3
	.60	103.85	88.07	-15.78	-15.2
	.70	82.28	68.89	-13.39	-16.3
	.80	56.92	47.51	-9.41	-16.5
	.90	28.56	24.43	-4.13	-14.5
Octanol-n-nonane (48)	.01	44.29	28.54	-15.75	-35.6
	.02	67.66	46.82	-20.84	-30.8
	.03	81.35	60.66	-20.69	-25.4
	.04	91.29	71.75	-19.54	-21.4
	.05	98.77	91.01	-17.76	-18.0
	.075	112.23	98.91	-13.32	-11.9
	.10	121.59	111.98	-9.61	-7.9
	.125	128.83	121.87	-6.96	-5.4
	.15	134.24	129.46	-4.78	-3.6
	.175	138.82	135.25	-3.57	-2.6
	.20	142.31	139.60	-2.71	-1.9
	.30	149.93	146.54	-3.39	-2.2
	.40	149.42	141.97	-7.45	-5.0
	.50	141.23	129.60	-11.63	-8.2
	.60	122.88	111.41	-11.47	-9.3
	.70	99.45	88.63	-10.82	-10.9
	.80	70.00	62.10	-7.90	-11.3
	.90	36.13	32.41	-3.72	-10.3

TABLE XX

EXCESS FREE ENERGIES AND ENTROPIES OF ALCOHOL-PARAFFIN AT 30°C PREDICTED FROM ONE-DIMENSIONAL LATTICE MODEL WITH ENERGY PARAMETERS IN TABLE XVIIa AND c

System	Mole Fraction Alcohol	G^E, cal./g.-mole			TS^E, cal./g.-mole		
		Expt'l.	Calc'd.	Dev.	Expt'l.	Calc'd.	Dev.
Ethanol-n-hexane (52)	.01	19.90	24.47	4.57		4.16	
	.02	38.41	42.74	4.33		4.40	
	.03	55.71	58.49	2.78		3.02	
	.04	71.97	72.57	0.60		0.73	
	.05	87.30	94.66	7.36		-11.30	
	.075	115.53	127.68	12.15		-27.71	
	.10	152.80	165.37	12.57		-46.26	
	.20	244.80	250.92	6.12		-94.34	
	.30	300.99	299.26	-1.73		-127.40	
	.40	329.74	320.63	-9.11		-147.28	
	.50	334.70	319.16	-15.54		-154.82	
	.60	317.35	296.78	-20.57		-150.25	
	.70	277.69	254.19	-23.50		-133.39	
	.80	214.30	191.25	-23.05		-103.59	
	.90	123.92	107.07	-16.85		-59.73	
Ethanol-n-heptane (56)	.01	22.23	25.94	3.71	21.42	3.50	-17.92
	.05	93.66	91.90	-1.76	-0.56	-5.55	-4.99
	.10	159.44	172.58	13.14	-38.78	-48.83	-10.05
	.20	251.99	264.21	12.22	-104.89	-100.85	+4.04
	.30	309.98	317.39	7.41	-150.37	-137.48	+12.89
	.40	340.56	342.44	1.88	-178.70	-160.38	+18.32
	.50	347.38	343.30	-4.08	-190.72	-170.16	+20.56
	.60	330.88	321.61	-9.27	-185.88	-166.80	+19.08
	.70	290.75	277.66	-13.09	-164.30	-149.71	+14.59
	.80	226.64	210.73	-15.91	-126.79	-117.70	+9.09
	.90	132.82	119.13	-13.69	-72.20	-68.82	+3.38
Propanol-n-heptane (57)	.01	21.28	24.57	3.29	23.81	4.49	-19.32
	.02	40.24	42.94	2.70	27.08	4.96	-22.12
	.05	87.21	85.32	-1.89	11.21	-0.74	-11.95
	.10	147.40	159.58	12.18	-20.78	-39.15	-18.37
	.20	230.17	239.85	9.68	-73.59	-82.43	-8.84
	.30	279.76	283.50	3.74	-110.20	-111.52	-1.32
	.40	304.35	301.22	-3.13	-134.68	-128.43	+6.25
	.50	307.38	297.41	-9.97	-147.99	-134.15	+13.84
	.60	289.79	274.27	-15.52	-148.54	-129.15	+19.39
	.70	251.61	232.88	-18.73	-135.31	-113.57	+21.74
	.80	191.64	173.61	-18.03	-106.85	-87.22	+19.63
	.90	108.67	96.24	-12.43	-62.17	-49.63	+12.54

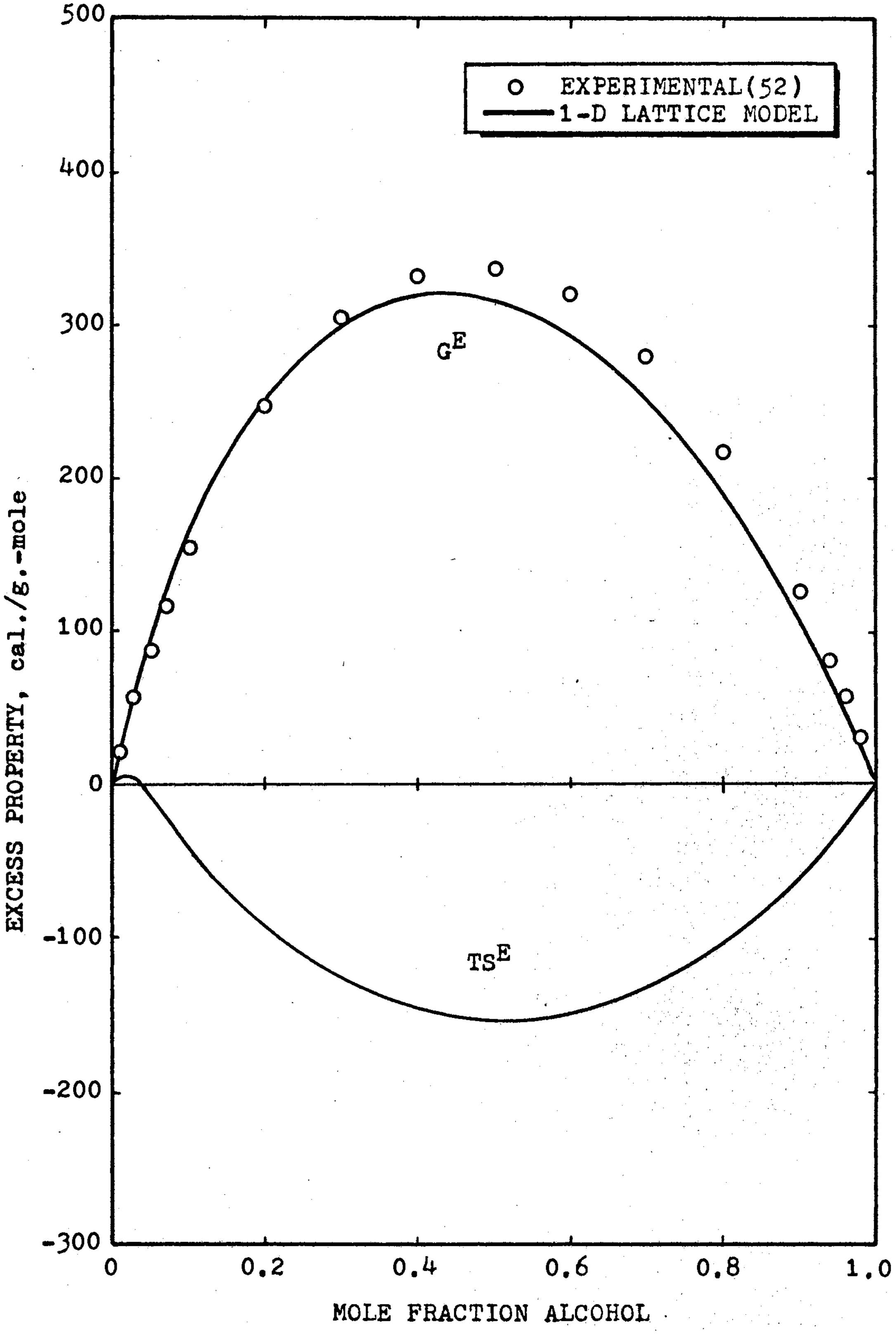


Figure 36. Excess Free Energy and Entropy for Ethanol-n-Hexane System at 30°C by the One-Dimensional Lattice Model

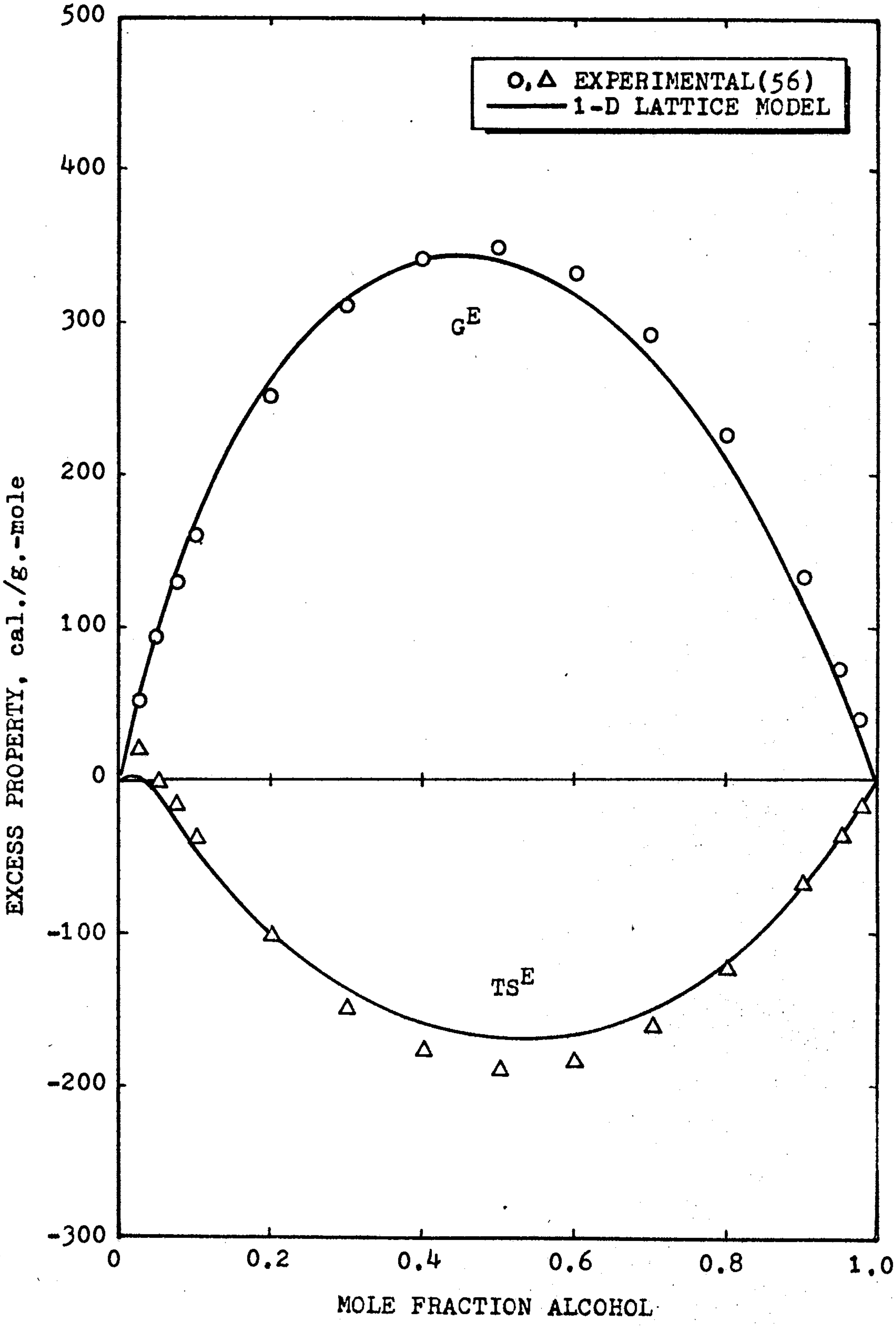


Figure 37. Excess Free Energy and Entropy for Ethanol-n-Heptane System at 30°C by the One-Dimensional Lattice Model

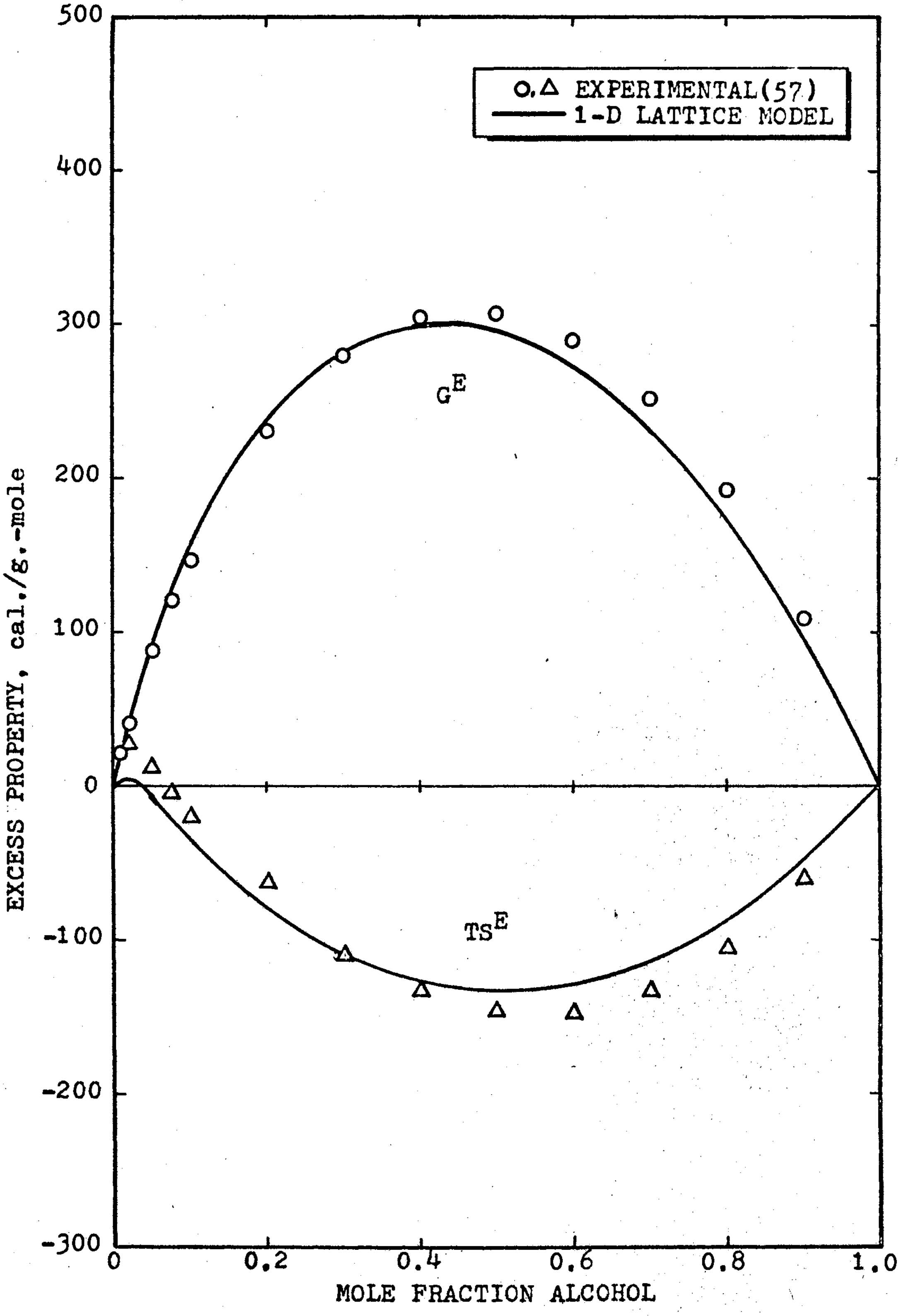


Figure 38. Excess Free Energy and Entropy for Propanol-n-Heptane System at 30°C by the One-Dimensional Lattice Model

The two parameters evaluated by fitting Wilson's equation

$$G^E = -RT[x_1 \ln(x_1 + \Lambda_{12}x_2) + x_2 \ln(\Lambda_{21}x_1 + x_2)] \qquad (5\text{-}17)$$

to the predicted excess free energies are shown in Table XXI. These parameters are defined as

$$\Lambda_{12} \equiv \frac{v_2^L}{v_1^L} \exp - [(\lambda'_{12} - \lambda'_{11})/RT] \qquad (5\text{-}18)$$

$$\Lambda_{21} \equiv \frac{v_1^L}{v_2^L} \exp - [(\lambda'_{12} - \lambda'_{22})/RT] \qquad (5\text{-}19)$$

where v_i^L = molar liquid volume of pure i.

λ'_{12}, λ'_{11} = interaction energies of type 1-2 and 1-1, respectively

In general $\Lambda_{12} \neq \Lambda_{21}$, whereas $\lambda'_{12} = \lambda'_{21}$.

TABLE XXI

WILSON PARAMETERS AT 30°C

System	Λ_{12}	Λ_{21}
Ethanol-n-Hexane	0.0261	0.3514
Ethanol-n-Heptane	0.0234	0.2558
Propanol-n-Heptane	0.0278	0.4479

The two parameters so obtained were used to calculate the activity coefficients according to the following equations

$$\ln \gamma_1 = -\ln(x_1 + \Lambda_{12}x_2) + x_2\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (5\text{-}20)$$

$$\ln \gamma_2 = -\ln(x_2 + \Lambda_{21}x_1) - x_1\left[\frac{\Lambda_{12}}{x_1 + \Lambda_{12}x_2} - \frac{\Lambda_{21}}{\Lambda_{21}x_1 + x_2}\right] \qquad (5\text{-}21)$$

Equations (5-20) and (5-21) are derived from Equation (5-17) by using the rigorous relation between activity coefficient and excess Gibbs energy.

From known activity coefficients the phase equilibrium compositions can be readily found from the equation of equilibrium.

$$\Phi_i y_i P = x_i P_i^o \nu_i^o \gamma_i \ \exp[v_i^L(P - P_i^o)/RT] \qquad (5\text{-}22)$$

where Φ_i = vapor phase fugacity coefficient of component i

ν_i^o = fugacity coefficient of pure i at system temperature and pressure P_i^o

v_i^L = molar liquid volume of component i at the system temperature

P = total vapor pressure of the system

P_i^o = vapor pressure of pure component i at system temperature

$\exp[v_i^L(P - P_i^o)/RT]$ = Poynting correction factor to the standard state fugacity of component i

The predicted phase compositions from Equation (5-22) are compared with experimental data in Table XXII and in Figures 39 through 41.

TABLE XXII

PREDICTED VAPOR COMPOSITIONS OF ALCOHOL AT 30°C

System	Liquid Mole Fraction Alcohol x	Vapor Mole Fraction Alcohol Expt'l.	Vapor Mole Fraction Alcohol Calc'd.
Ethanol-n-Hexane (52)	0.01	0.089	0.147
	0.02	0.139	0.188
	0.03	0.170	0.206
	0.04	0.190	0.215
	0.05	0.205	0.221
	0.10	0.239	0.232
	0.20	0.258	0.238
	0.30	0.265	0.243
	0.40	0.270	0.249
	0.50	0.275	0.258
	0.60	0.283	0.271
	0.70	0.297	0.293
	0.80	0.324	0.334
	0.90	0.398	0.437
	0.95	0.511	0.571
Ethanol-n-Heptane (56)	0.01	0.319	0.388
	0.05	0.471	0.500
	0.10	0.503	0.512
	0.20	0.531	0.518
	0.30	0.542	0.522
	0.40	0.547	0.527
	0.50	0.554	0.534
	0.60	0.555	0.545
	0.70	0.571	0.563
	0.80	0.597	0.596
	0.90	0.658	0.677
	0.95	0.741	0.771
	0.975	0.824	0.856

TABLE XXII (Continued)

System	Liquid Mole Fraction Alcohol x	Vapor Mole Fraction Alcohol Expt'l.	Calc'd.
Propanol-n-Heptane (57)	0.01	0.125	0.152
	0.02	0.166	0.197
	0.04	0.199	0.227
	0.10	0.238	0.247
	0.20	0.270	0.256
	0.30	0.281	0.264
	0.40	0.296	0.273
	0.50	0.308	0.287
	0.60	0.322	0.306
	0.70	0.343	0.337
	0.80	0.382	0.392
	0.90	0.482	0.516
	0.975	0.781	0.783

The energy parameter values in Table XVIIa and XVIIc were also employed to predict internal energies of vaporization of pure alcohol at 30°C. Results are compared with experimental data in Table XXIII.

C. Discussion of Results

Table XVIII shows that very good agreement is obtained between the model and experimental data on internal energies of vaporization at 30°C of the pure n-paraffins propane through decane.

Figures 28 through 38 show that reasonable agreement between theory and data is obtained for the alcohol-n-paraffin binary systems. The set of energy parameters in Table XVIIb, in which the OH-OH interaction is considered to be constant, gives only qualitative

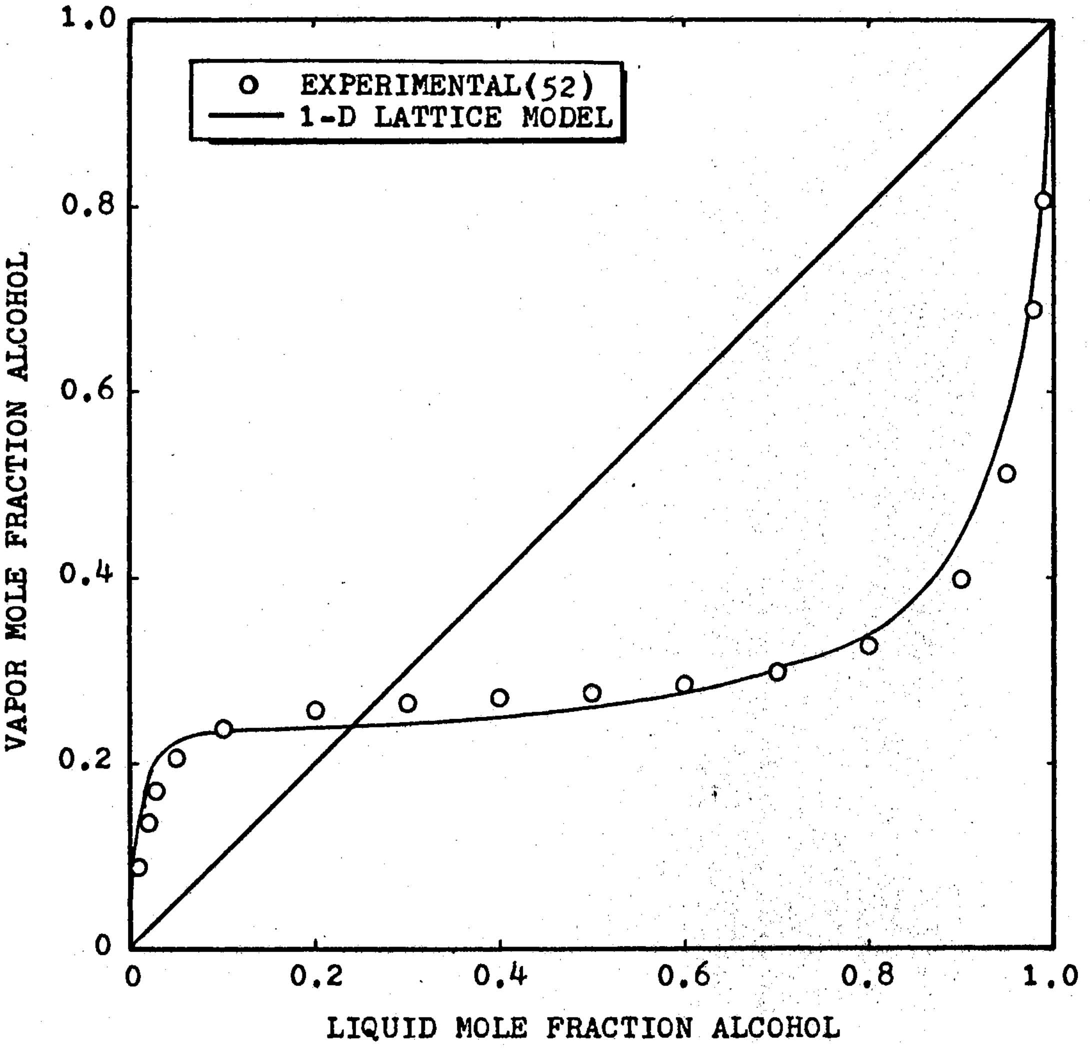


Figure 39. Predicted Phase Equilibrium Compositions for Ethanol-n-Hexane System at 30°C

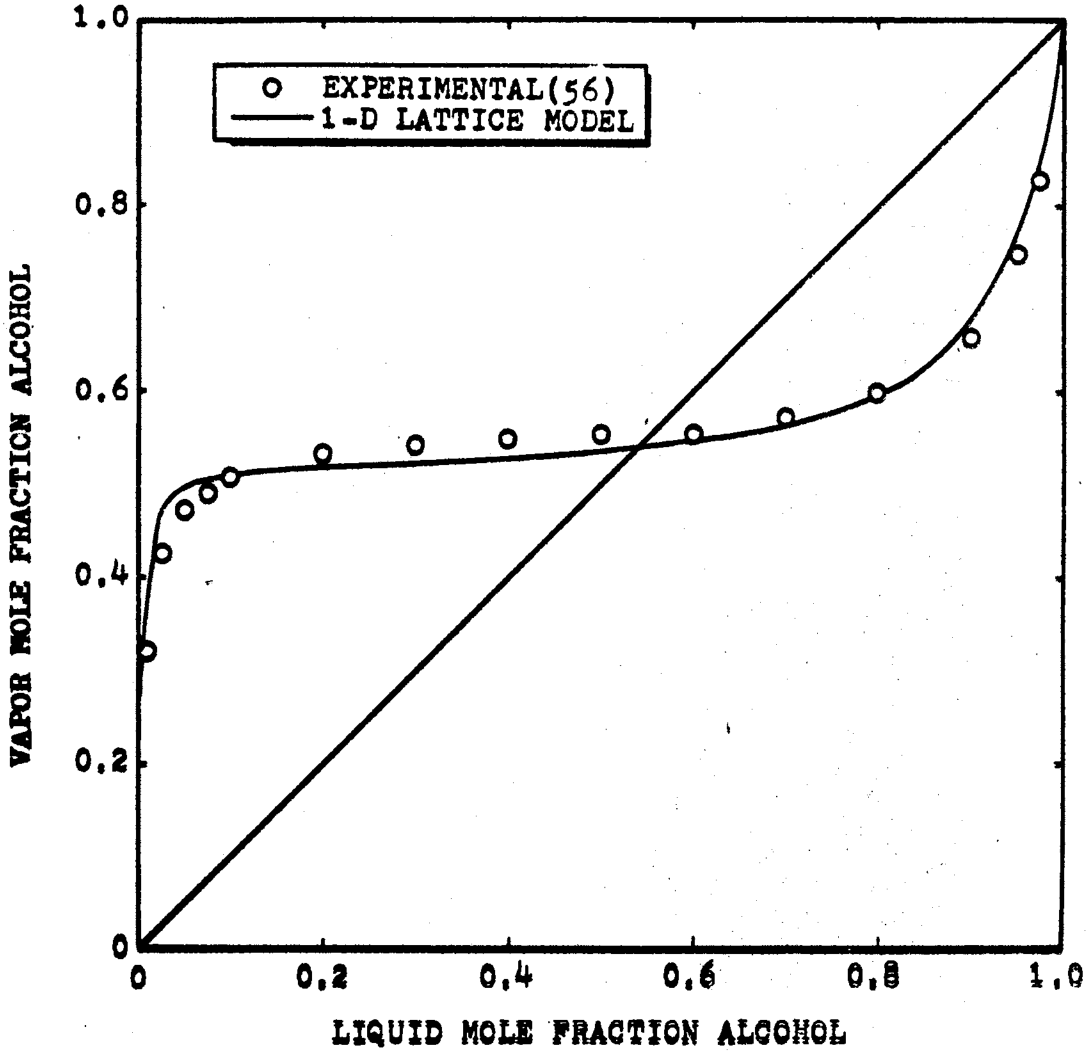


Figure 40. Predicted Phase Equilibrium Compositions for Ethanol-n-Heptane System at 30°C

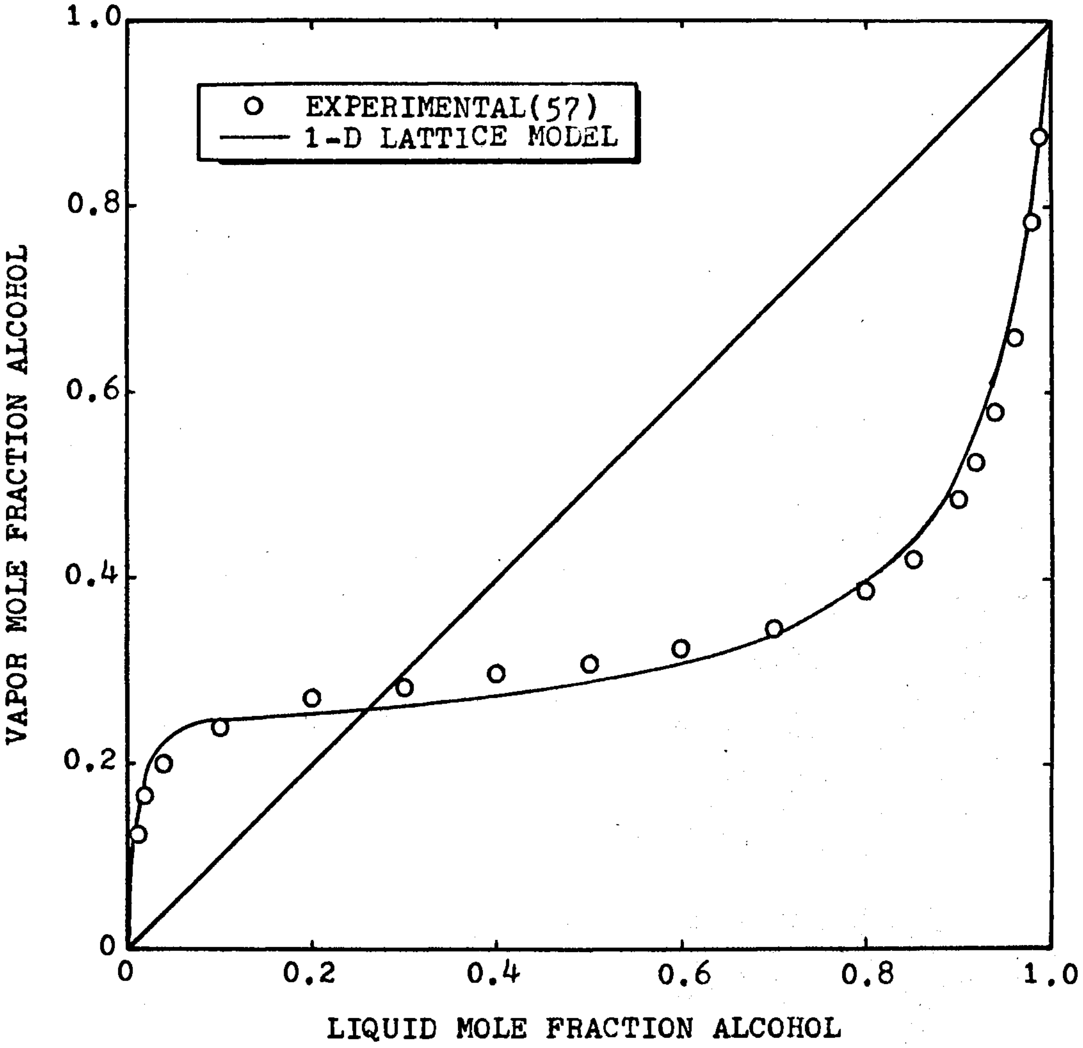


Figure 41. Predicted Phase Equilibrium Compositions for Propanol-n-Heptane System at 30°C

representation of heats of mixing and fails to represent the excess free energies and excess entropies. The asymmetry of the heat of mixing curves is reflected by the model with this set of energy parameters. However, the quantitative deviation between the model and data is significant, as shown by dashed lines in Figures 28 through 35.

TABLE XXIII

INTERNAL ENERGIES OF VAPORIZATION OF ALCOHOLS AT 30°C PREDICTED BY ONE-DIMENSIONAL LATTICE MODEL

Alcohol	Energy of Vaporization U^V, cal./g.-mole		
	Expt'l.*	Calc'd.**	Deviation %
Methanol	8,233	9,106	10.6
Ethanol	9,387	10,190	8.6
Propanol	10,492	11,315	7.8
Butanol	11,575	12,441	7.5
Pentanol	12,672	13,569	7.1

* Based on heats of vaporization from Reference 20.
** Based on energy parameters from Table XVIIa and c.

Reasonable agreement between the model and the experimental heat of mixing data is obtained for the eight binary systems with the use of energy parameters in Table XVIIc, in which the OH-OH interaction energy is considered to be a function of OH group surface concentration in the solution. As shown by solid lines in Figures 28 through 35, the asymmetry of the heat of mixing curves is correctly reflected by the model. However, the model predicts consistently low values of heat of mixing at low alcohol concentrations. Here again, this inadequacy at low alcohol concentrations is felt to be a fault of the model and not of the interaction parameters used.

The excess free energies and excess entropies predicted from this set of energy parameters are compared with data in Figures 36 through 38. These three figures show that reasonable agreement between the model and the experimental excess free energies is obtained for the three binary systems with the use of energy parameters in Table XVIIc.

The excess entropies of alcohol-n-paraffin binary mixtures exhibit positive values at low alcohol concentrations and negative values at higher alcohol concentrations. This behavior is reflected by the model. As mentioned in Chapter III, the positive excess entropies shown at low alcohol concentrations are due to the breaking of hydrogen bonds and the resulting gain in orientational freedom of the groups on alcohol molecules. The negative values of excess entropy at higher alcohol concentrations are due to the tendency of the alcohol molecules to cluster together (2). This behavior might be qualitatively reflected by the surface concentration dependent expression of the OH-OH group interaction energy, i.e., $\lambda_{OH-OH} = B_1 + B_2 \ln(f_{sOH})$. At lower alcohol concentrations, the absolute values of OH-OH interaction energy has a smaller value as can be seen in the surface concentration dependent expression. This results in the interactions between the OH groups and all groups other than OH being more probable; that is, more hydrogen bonds have been broken and the OH groups have gained more orientational freedom. At higher alcohol concentrations the OH-OH interaction has higher values, and that makes the OH groups cluster together. Thus, the more rapid breaking of hydrogen bonds at low alcohol concentration than is predicted by the basic model can be, in part, compensated by using $\lambda_{OH-OH} = F(s_{OH})$.

The three hydrocarbon energy parameters obtained in this model as shown in Table XVIIa are in agreement with the energy values obtained in the local surface group contribution model as shown in Table IIIa. However, the values of energy parameters involving OH group interaction for the two models are quite different.

As expected, the OH-OH interaction is by far the strongest interaction in the solution. Since a different means of breaking down molecules into constituent groups is used for quasi-lattice theory and this model, a comparison of energy parameters from these two studies is not feasible.

Like the local surface group contribution model, the one-dimensional lattice model developed in this chapter appears to be one of the most general of the models which have been applied to alcohol-paraffin systems, since it requires no information specific to a given binary molecular pair but only interaction energies between group pairs. In contrast, the quasi-lattice theory requires a priori specification of segments and contact points.

The quasi-lattice and the one-dimensional lattice model are comparable in predicting excess free energies. However, the quasi-lattice model predicts excess enthalpies with better accuracy than the one-dimensional lattice model and the local group contribution model. The one-dimensional lattice model represents the excess properties with better accuracy than the local surface group contribution model.

D. Summary

A group contribution model is developed with the use of statistical mechanical methods. The model is shown to provide satisfactory representation of excess properties in alcohol-n-paraffin systems. The one-dimensional lattice model predicts excess properties with better accuracy than that by the local surface group contribution model of Chapter III, but is marginally inferior to the quasi-lattice theory.

CHAPTER VI

CONCLUSIONS AND RECOMMENDATIONS

The present study consists of the development of liquid solution theories based on the group contribution concept and of the application of these theories to solutions containing polar substances. The major observations and conclusions drawn from the study are presented, along with recommendations for future study, in the following sections.

The first model developed based on group methods (the local surface group contribution model) takes into account the effects of both the strength of group interactions and the group free surface areas on the probability of interaction. This model was applied to alcohol-n-paraffin binary systems. Analysis of the results shows that the model provides satisfactory qualitative representation of excess thermodynamic properties in eight binary mixtures of alcohols and n-paraffins.

The second group contribution model, expressed in the framework of statistical mechanics, was developed by expressing the canonical partition function in terms of group interactions and free surface areas of groups. A one-dimensional lattice model resulted when the lumped surface areas of identical groups were divided into identical pieces. These pieces were envisioned as being arranged in a column and the configurational contributions to the canonical partition function were evaluated by summing all possible arrangements of this column. Analysis of the results shows that the one-dimensional lattice model is able to represent the excess thermodynamic properties of alcohol-n-paraffin binary mixtures provided the interaction energy between hydroxyl groups is considered to be a function of the hydroxyl group surface concentration.

The third model (the well-known quasi-lattice model) was re-expressed in terms of the canonical partition function of group interactions and applied to the data on the eight binary mixtures of alcohols and n-paraffins. Reasonable representation of excess thermodynamic properties of alcohol-n-paraffin binary systems was obtained. Results were found to be sensitive to the choice of exchange energies regarded as significant but not to the choice of coordination number and contact points.

In all three models, analysis of group interaction energy parameters reveals that the value of hydroxyl group interaction energy is far larger than the other interaction energies. This result is interpreted as an indication that the three models correctly reflect the existence of hydrogen bonds in the alcohol-n-paraffin solutions. However, the breaking of hydrogen bonds at low alcohol concentrations apparently occurs more rapidly than these models reflect. All three models predict consistently low values of heat-of-mixing and inadequately represent the excess free energies and entropies at low alcohol concentrations. Although this can be compensated, in part, by using the interaction energy between hydroxyl groups as a function of the hydroxyl group surface concentration, the conclusion is drawn that the inability of the models to adequately describe solution behavior at low alcohol concentrations is a fault of the models and not of the interaction parameters employed.

Of the three models, the local surface group contribution model and the one-dimensional lattice model are of equivalent generality and are more general in form than the quasi-lattice model; the former require only information on interaction energies between group pairs, while the quasi-lattice model requires additional a priori specification of contact points. However, in their ability to represent the excess properties of alcohol-n-paraffin systems, the quasi-lattice model predicts excess thermodynamic properties with a better accuracy than the other two models and is the recommended model for present applications. The one-dimensional lattice model is superior to the local surface group contribution model.

The developments of this study were directed at representation of the properties of solutions containing polar substances. This objective was achieved by applying the three models to the eight alcohol-n-paraffin binary mixtures. In this study, a maximum of six interaction energy parameters were used for each of the three models to represent the excess thermodynamic properties of these systems. In fact, the six energy parameters could be used to predict the excess properties of systems other than the eight on which the parameters are based. This is the power of the generality of group methods; once information on any pair interaction is determined, it is applicable to the same type of interaction in any other system.

The local surface group contribution model was applied to the partially miscible system methanol-n-hexane. The model predicts the existence of the two phases but it fails to predict the phase compositions correctly. Thus, application of the model to partially miscible systems is not recommended.

The complexity of group interactions in polar solutions is reflected by only semi-quantitative agreement of the models with experimental data. This suggested that more work is needed in developing group contribution models to represent excess thermodynamic properties of solutions containing polar substances. From this study, the following recommendations are made as guidelines for future work:

1. The inability of the models to fit adequately the data at low alcohol concentrations suggests the need for future study of the nature of dilute polar solutions. Future investigations into the theory should be directed at finding the fundamental criteria of group orientation and interactions.
2. A possible modification to improve the representation of excess properties of the three models would be to consider the α-methylene groups separately from other group species and/or to treat separately the groups on different molecules.
3. From the chemical similarity of methyl and methylene groups, a relation between their interaction energies should be evaluated, so that the required energy parameters could be reduced to half. This would considerably simplify calculations.
4. Two- or three-dimensional models should be developed, which could provide more realistic description of polar solutions.
5. The use of group surface areas instead of the number of contact points in the quasi-lattice model could possibly

improve the model for representation of the excess properties of polar solutions. The use of group surface areas would be more natural and realistic.

6. The possibility of determining properties of highly nonideal mixtures from pure component properties is not achieved in the present study. However, the possibility is contained in the group solution theory. Future investigations into the theory should be directed to this objective.
7. Experimental excess free energy and entropy data for the present interest are available for only three binary mixtures. For better analysis of the models, more data are needed. Data for multicomponent systems are also desirable to test the generality of the models.

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APPENDIX

COMPUTER PROGRAM

The non-linear regression computer program used in this study was written in FORTRAN IV by R. M. Baer at Chevron Research Corporation. It is a fully generalized program in that the only additional input required for its use in a particular problem are:

1. the particular equation to be fitted, and
2. data, including the assignment of program control variables.

The program is limited to a maximum of three hundred data points, twelve variables, and twenty parameters. The program consists of one main program and four subroutines. The brief description of the function of each of the five routines is presented in the following sections.

Main Program

DKNAME is an embedding program for subroutine GAUSS. Its function is to read in all input data required for the calculations. The major calculational subroutine GAUSS is called by this program after having read in all required data.

Subroutine GAUSS

GAUSS is the major calculational subroutine. Its function is to determine the optimum values of parameters for a least-sum-of-squares fit to the data and to print out the resultant parameters, the specified and calculated values of variables, the percent deviation for each data point, and average and maximum deviations. The dependent variable calculation subroutine, partial derivative, and matrix solution subroutines are called by this subroutine at the appropriate time during the iterative search for the parameter values.

Subroutine YCOMP

YCOMP is the only subroutine to be modified for each particular problem. YCOMP contains the correlating equation to which the data are to be fitted and calculates the value of the dependent variable for each data point using successive estimates of the parameters as determined in the GAUSS and partial derivative subroutines.

Subroutine DERIV

DERIV is employed to estimate the values of partial derivatives of the correlating equation by a difference method. The result is used to establish the parameter values for the succeeding iteration by GAUSS. It is called by GAUSS during the iterations of the search procedure.

Subroutine SOLV

SOLV is to solve a matrix formed by GAUSS for the determination of the parameter values for the next iteration. It is called by GAUSS during the interations of the search procedure.

Program Specifications

A listing of the non-linear regression computer program is presented at the end of Appendix A. The input data requirements and format are discussed in the following sections.

Input Data Cards

The input data cards required for the program are arranged in the following order:

CARD 1: Program Control Variables

This card contains the 12 general control variables, in 12I6 format, which control the operation of the program. Each variable and its allowable values are discussed below:

MM(1) = number of data points

MM(2) = total number of variables—dependent and independent variables

MM(3) = number of parameters

MM(4) = limit on number of iterations. A value of 15 is usually sufficient for convergence.

MM(5) = if negative, skips reading of Z(i,N) values from input (see below)

MM(6) = -1 give results of calculations for each iteration
= 0 give final results only
= 1 give results for only the first and last iterations

MM(7) = 0 to have a parabolic fit
= 1 to have a linear fit

MM(8) = 1 for input

MM(9) = 1 to print input data as part of output

= 0 to bypass this printing

MM(10) = -1 records each matrix

= 0 bypasses the recording of matrix

= 1 records first matrix only

MM(11) = number of problems in the run

MM(12) = if negative, prints the final solution only

CARD 2-5: Parameter Estimates

The second through fifth data cards are the initial estimates of parameter values in 6F12.0 format. The maximum number of parameters is twenty. The twenty-first through twenty-fourth fields are used as follows:

B(21) = tolerance on convergence (0.0001 is recommended)

B(22) = blank. It is used internally in DERIV subroutine

B(23) = limit on magnitude of iteration changes (1.0 is recommended)

B(24) = used to control entry point in YCOMP for multiple program runs or for other purposes.

The program reads 24 values regardless of the number of parameters actually used.

The remaining cards contain the independent and dependent variables of each data point read in by variable name Z(i,N) in a format specified in a card preceeding these data cards.

PROGRAM LISTING

```
//KUO1   JOB (10169,551-78-3878,3),'C. M. KUO',MSGLEVEL=1,CLASS=A
// EXEC FORTGCLG
//FORT.SYSIN DD *
C     EMBEDDING PROGRAM FOR GAUSS                                       DECK0010
       DIMENSION B(24), Z(12,300), MM(12)                               DECK0020
       DIMENSION FMT(18)
       COMMON NUMBER,B,Z                                                DECK0030
       COMMON /COMA/ MM                                                 DECK0040
       COMMON /COMB/ JJ                                                 DECK0050
    1 READ (5,2) (MM(J),J=1,12)                                         DECK0060
    2 FORMAT (12I6)                                                     DECK0070
      NUMBER=MM(1)                                                      DECK0080
      NSET=MM(2)                                                        DECK0090
      JJ=MM(3)                                                          DECK0100
      IF (NUMBER) 4,4,10                                                DECK0110
    4 WRITE (6,5)                                                       DECK0120
      CALL EXIT                                                         DECK0130
    5 FORMAT (40H0   GAUSS INPUT ZERO, PROGRAM STOP      /1H1)          DECK0140
   10  READ(5,11) (B(J),J=1,24)                                         DECK0150
   11 FORMAT(6F12.4)
      READ (5,100) (FMT(I),I=1,12)
  100 FORMAT (18A4)
      IF (MM(5)) 15,14,14                                               DECK0170
   13 FORMAT (4F12.12)                                                  DECK0175
   14 READ (5,FMT)((Z(J,N),J=1,NSET),N=1,NUMBER)                        DECK0180
   15 CALL GAUSS                                                        DECK0190
      IF (MM(8)-2) 30,20,30                                             DECK0200
   20 WRITE (6,21)                                                      DECK0201
   21 FORMAT (40H0  GAUSS CONVERGENCE                    //)            DECK0210
      MM(8)=1                                                           DECK0220
   30 MM(11)=MM(11)-1                                                   DECK0230
      IF (MM(11)) 1,1,14                                                DECK0240
      END                                                               DECK0250


       SUBROUTINE GAUSS                                                 GAUS0030
       DIMENSION A(20,21),B(24),BMIN(20),BSTART(20),C(20,1),X(20,1),    GAUS0040
     X Z(12,300),DEL(20),E(20),MM(12),RECORD(100),CY(300),FP(20,300)    GAUS0050
       COMMON NUMBER,B,Z                                                GAUS0060
       COMMON /COMA/ MM                                                 GAUS0061
       COMMON /COMB/ JJ                                                 GAUS0062
       COMMON /COMC/ CY                                                 GAUS0063
       COMMON /COMD/ FP                                                 GAUS0064
       COMMON /COME/ A,C,M                                              GAUS0065
       EQUIVALENCE  (A,X)                                               GAUS0070
       NUMBER = MM(1)                                                   GAUS0490
       NSET =   MM(2)                                                   GAUS0500
       JJ =     MM(3)                                                   GAUS0510
       LIMIT =  MM(4)                                                   GAUS0520
       NULL = MM(12)                                                    GAUS0530
       MM(12) = MM(12) + 1                                              GAUS0540
       IDNTFC = MM(12)                                                  GAUS0550
```

```
      TZERO = 1.0                                                       GAUS0570
      SCALE 1  = 0.2                                                    GAUS0580
      SCALE 2  = 1.5                                                    GAUS0590
      SCALE 3 = 1.0                                                     GAUS0600
      TOL1 = B(21)                                                      GAUS0610
      X NORM = 0.0                                                      GAUS0620
      MARK P = 0                                                        GAUS0640
      KKPATH = -1                                                       GAUS0650
      NDOWN = 0                                                         GAUS0660
      NN = 0                                                            GAUS0670
      NNPARA = 0                                                        GAUS0680
      NPATH = 1                                                         GAUS0690
      NTZERO = -1                                                       GAUS0700
      SUMSQ = 0.0                                                       GAUS0710
      T = 0.0                                                           GAUS0720
      X3 = 3.0                                                          GAUS0730
      X2 = 2.0                                                          GAUS0740
      Y2 = 2.0                                                          GAUS0750
      Y3 = 3.0                                                          GAUS0760
      IF (LIMIT - 100) 2,47,47                                          GAUS0780
   2  IF (TOL1) 420,420,1                                               GAUS0790
   1  DO 4 J=1,JJ                                                       GAUS0810
      BMIN(J) = B(J)                                                    GAUS0820
      BSTART(J) = B(J)                                                  GAUS0830
      X NORM = X NORM + B(J)**2                                         GAUS0840
      DEL(J) = 0.05*ABS (B(J))                                          GAUS0850
      IF (DEL(J)) 4,3,4                                                 GAUS0860
   3  DEL(J) = 0.05                                                     GAUS0870
   4  CONTINUE                                                          GAUS0880
      WRITE (6,5)                                                       GAUS0900
   5  FORMAT (51H1    GAUSSIAN PARAMETER SUBROUTINE       Z(12,300)   ) GAUS0910
      WRITE (6,412)            (MM(L), L=1,12)                          GAUS0930
      WRITE (6,108)            (B(J), J = 1,24)                         GAUS0940
      IF (MM(9)) 400,6,400                                              GAUS0960
   6  IF (MM(8) - 1) 7,80,7                                             GAUS0980
   7  IF (B(23)) 8,8,430                                                GAUS1000
   8  JPARA = -1                                                        GAUS1010
      MPATH = -1                                                        GAUS1020
      T = 0.0                                                           GAUS1030
      MM(8) = 2                                                         GAUS1040
      WRITE(6,59)                                                       GAUS1050
      DO 9  J=1,JJ                                                      GAUS1060
   9  BSTART(J) = B(J)                                                  GAUS1070
  10  SQLAST = SUMSQ                                                    GAUS1090
      SUMSQ = 0.0                                                       GAUS1100
      NTZERO = NTZERO + 1                                               GAUS1110
      NN = NN+1                                                         GAUS1120
      IF (NN - LIMIT) 12,12,11                                          GAUS1130
  11  MM(8) = -2                                                        GAUS1150
      GO TO 80                                                          GAUS1160
  12  CALL YCOMP                                                        GAUS1180
      DO 17 N= 1,NUMBER                                                 GAUS1181
      YC = CY(N)                                                        GAUS1190
      DELY = Z(NSET,N) - YC                                             GAUS1200
      SUMSQ = SUMSQ + DELY**2                                           GAUS1210
      IF (NULL) 17,13,13                                                GAUS1220
  13  IF (MM(6)) 14,17,14                                               GAUS1230
  14  IF (N-1)  16,15,16                                                GAUS1240
  15  WRITE (6,410)                                                     GAUS1250
  16  WRITE (6,18)             N,YC,Z(NSET,N),DELY                      GAUS1260
      MARK P = 1                                                        GAUS1270
  17  CONTINUE                                                          GAUS1280
      RECORD(NN) = SUMSQ                                                GAUS1290
```

```
18    FORMAT (I6,4E18.7)                                                GAUS1300
      GO TO 440                                                         GAUS1310
19    IF (NN - 1) 20,22,30                                              GAUS1330
20    IF (SUMSQ-SQMIN) 21,21,27                                         GAUS1360
21    NDOWN = 1                                                         GAUS1370
22    SQMIN = SUMSQ                                                     GAUS1380
      DO 24  J=1,JJ                                                     GAUS1390
24    BMIN(J) = B(J)                                                    GAUS1400
25    IF (MPATH) 301,200,38                                             GAUS1410
27    IF (NDOWN) 28,28,29                                               GAUS1430
28    NDOWN = -1                                                        GAUS1440
29    IF (MPATH) 301,200,36                                             GAUS1450
30    IF (MM(6)) 32,32,31                                               GAUS1470
31    MM(6) = 0                                                         GAUS1480
32    IF (MM(10)) 20,20,33                                              GAUS1490
33    MM(10) = 0                                                        GAUS1500
      GO TO 20                                                          GAUS1510
36    TZERO = TZERO*SCALE1                                              GAUS1530
      NTZERO = -1                                                       GAUS1540
38    DO 39  J=1,JJ                                                     GAUS1560
      B(J) = BMIN(J)                                                    GAUS1570
39    BSTART(J) = BMIN(J)                                               GAUS1580
      Y1 = SQMIN                                                        GAUS1600
      X1 = 0.0                                                          GAUS1610
      JPARA = -1                                                        GAUS1620
      MPATH = -1                                                        GAUS1630
      GO TO 301                                                         GAUS1640
40    SUM2 = SUM1                                                       GAUS1660
      SUM1 = SUMSQ                                                      GAUS1670
      NNPARA = 0                                                        GAUS1680
      IF (SUM1 - SUM2) 19,45,19                                         GAUS1690
45    TZERO = SCALE1*TZERO                                              GAUS1710
      NDOWN = 0                                                         GAUS1720
      T = 0.0                                                           GAUS1730
      GO TO 8                                                           GAUS1740
47    LIMIT = 99                                                        GAUS1760
      GO TO 2                                                           GAUS1770
49    T = -0.5*((X1*X1-X2*X2)*(Y1-Y3)-(X1*X1-X3*X3)*(Y1-Y2))/           GAUS1800
     X     ((X1-X3)*(Y1-Y2)-(X1-X2)*(Y1-Y3))                            GAUS1810
      MPATH = 1                                                         GAUS1830
      JPARA = -1                                                        GAUS1840
      NNPARA = 1                                                        GAUS1850
      NDOWN = 0                                                         GAUS1860
      GO TO 366                                                         GAUS1870
53    WRITE (6,54)                                                      GAUS1890
54    FORMAT (24H0 OVER-UNDERFLOW        //)                            GAUS1900
      MM(8) = -1                                                        GAUS1910
      MM(10) = -1                                                       GAUS1920
      GO TO 301                                                         GAUS1930
56    WRITE (6,57)                                                      GAUS1960
57    FORMAT (24H0 MATRIX IS SINGULAR    //)                            GAUS1970
      MM(8) = -1                                                        GAUS1980
      MM(10) = -1                                                       GAUS1990
      GO TO 301                                                         GAUS2000
59    FORMAT (114H0CYCLE     SUM OF SQUARES      ***********************GAUS2020
     X**************** PARAMETERS ********************************//)   GAUS2030
58    FORMAT (I6, F18.5, 5E18.6/(E42.6,4E18.6))                         GAUS2040
60    DO 66  J=1,JJ                                                     GAUS2090
      BTEST = B(J)-BSTART(J)-DEL(J)                                     GAUS2100
      IF (BTEST)  63,63,62                                              GAUS2110
62    B(J) = BSTART(J) + DEL(J)                                         GAUS2120
63    CONTINUE                                                          GAUS2130
      BTEST = B(J) - BSTART(J) + DEL(J)                                 GAUS2140
```

```
      IF (BTEST) 65,65,66                                               GAUS2150
  65  B(J) = BSTART(J)-DEL(J)                                           GAUS2160
  66  CONTINUE                                                          GAUS2170
      MPATH = -1                                                        GAUS2190
  67  DO 69  J=1,JJ                                                     GAUS2200
  69  BSTART(J) = B(J)                                                  GAUS2210
      GO TO 10                                                          GAUS2220
  80  IF (NULL) 1000,82,82                                              GAUS2260
  82  AV = 0.0                                                          GAUS2270
      AV1 = 0.0                                                         GAUS2280
      AV2 = 0.0                                                         GAUS2290
      YMAX = 0.0                                                        GAUS2300
      ZMAX = 0.0                                                        GAUS2310
      ZZMAX = 0.0                                                       GAUS2320
      DO 81  J=1,JJ                                                     GAUS2330
  81  B(J) = BMIN(J)                                                    GAUS2340
      N = 1                                                             GAUS2350
      DO 90  J=1,JJ                                                     GAUS2360
  90  WRITE (6,91)             J,B(J)                                   GAUS2370
  91  FORMAT (4H   B I2, E14.5)                                         GAUS2380
      WRITE (6,100)                                                     GAUS2390
  92  WRITE (6,93)                                                      GAUS2410
  93  FORMAT (82H0NUMBER           Y OBSERVED     Y CALCULATED          GAUS2420
     X DELTA Y      PCT DEVIATION ///)                                  GAUS2430
  94  CALL YCOMP                                                        GAUS2450
  98  YC = CY(N)                                                        GAUS2451
      DELY = YC - Z(NSET,N)                                             GAUS2460
      RATIO = 100.0 * (DELY / Z(NSET,N))                                GAUS2470
      ABSRAT = ABS (RATIO)                                              GAUS2480
      AV = AV + DELY                                                    GAUS2490
      AV1 = AV1 + RATIO                                                 GAUS2500
      AV2 = AV2 + ABSRAT                                                GAUS2510
      WRITE (6,95)           N,Z(NSET,N),YC,DELY,RATIO                  GAUS2520
  95  FORMAT (I5,E23.5,E17.5,2E19.5)                                    GAUS2530
      ABSVAL = ABS (DELY)                                               GAUS2540
      IF (YMAX - ABSVAL) 96,96,97                                       GAUS2550
  96  YMAX = ABSVAL                                                     GAUS2560
      YYMAX = DELY                                                      GAUS2570
      MARK = N                                                          GAUS2580
  97  IF (ZMAX-ABSRAT) 971,971,972                                      GAUS2590
 971  ZMAX = ABSRAT                                                     GAUS2600
      ZZMAX = RATIO                                                     GAUS2610
      MARK1 = N                                                         GAUS2620
 972  N = N+1                                                           GAUS2630
      IF (N - NUMBER) 98,98,99                                          GAUS2640
  99  D = NUMBER                                                        GAUS2660
      AV = AV/D                                                         GAUS2670
      AV1 = AV1/D                                                       GAUS2680
      AV2 = AV2/D                                                       GAUS2690
      RTMNSQ = SQRT (SUMSQ/D)                                           GAUS2700
      WRITE (6,100)                                                     GAUS2710
 100  FORMAT(118H0******************************************************GAUS2720
     X****************************************************************//GAUS2730
     X/)                                                                GAUS2740
      WRITE (6,101)           AV,AV1,AV2                                GAUS2750
 101  FORMAT (30H0  AVERAGE DEVIATION          E14.5,                   GAUS2760
     X        20H     AVERAGE PCT DEV          E14.5,                   GAUS2770
     X        20H     AVE ABS PCT DEV          E14.5)                   GAUS2780
      WRITE (6,103)           YYMAX,MARK                                GAUS2790
 103  FORMAT (30H0  MAXIMUM DEVIATION          E14.5,I6)                GAUS2800
      WRITE (6,104)             ZMAX,MARK1                              GAUS2810
 104  FORMAT (30H0  MAXIMUM   PCT DEV          E14.5,I6)                GAUS2820
      WRITE (6,105)           RTMNSQ                                    GAUS2830
```

```
 105  FORMAT (30H0  ROOT MEAN SQUARE DEVIATION E14.5)                   GAUS2840
 107  FORMAT ( 21H0       AT ITERATION I3,  24H, THE SUM OF SQUARES IS GAUS2860
     X    E16.7/ 22H0 FOR PARAMETER VALUES /1H0//(6E20.7))              GAUS2870
 108  FORMAT (5F20.5)                                                   GAUS2880
 109  FORMAT (//)                                                       GAUS2890
 110  FORMAT (I20, F20.8)                                               GAUS2900
      WRITE (6,5)                                                       GAUS2910
      IF (MM(8) + 2) 114,111,114                                        GAUS2920
 111  WRITE (6,112)                                                     GAUS2930
 112  FORMAT (30H0 EXCEEDED ITERATION LIMIT       //)                   GAUS2940
      GO TO 999                                                         GAUS2950
 114  IF (MM(8) - 1) 999,8,999                                          GAUS2970
 200  IF (NDOWN) 201,201,202                                            GAUS2990
 201  T = T*SCALE1                                                      GAUS3000
      GO TO 203                                                         GAUS3010
 202  T = T*SCALE2                                                      GAUS3020
 203  MPATH = 0                                                         GAUS3030
      JPARA = JPARA + 1                                                 GAUS3040
      GO TO 366                                                         GAUS3050
 301  MPATH = 0                                                         GAUS3070
      NDOWN = 0                                                         GAUS3080
      DO 305  M=1,JJ                                                    GAUS3090
      C(M,1) = 0.0                                                      GAUS3100
 302  DO 305 N=1,JJ                                                     GAUS3110
 305  A(M,N) = 0.0                                                      GAUS3120
      CALL DERIV                                                        GAUS3170
      CALL YCOMP                                                        GAUS3160
      DO 313 N = 1,NUMBER                                               GAUS3210
      DO 313 K = 1,JJ                                                   GAUS3220
      C(K,1) = C(K,1) + FP(K,N) * (Z(NSET,N) - CY(N))                   GAUS3230
      DO 313 J = K,JJ                                                   GAUS3240
 313  A(K,J) = A(K,J) + FP(K,N) * FP(J,N)                               GAUS3250
      IF (NTZERO) 318,318,317                                           GAUS3300
 317  TZERO = 1.0                                                       GAUS3310
 318  T = TZERO                                                         GAUS3320
      DO 316  I=2,JJ                                                    GAUS3340
      II=I-1                                                            GAUS3350
      DO 316 J=1,II                                                     GAUS3360
 316  A(I,J) = A(J,I)                                                   GAUS3370
      IF (MM(10)) 319,331,319                                           GAUS3390
 319  WRITE (6,320)          NN                                         GAUS3410
 320  FORMAT (19H0 MATRIX, ITERATION I3)                                GAUS3420
      MMPATH = 0                                                        GAUS3430
 322  DO 323  I=1,JJ                                                    GAUS3440
 323  WRITE (6,324)          (A(I,J), J=1,JJ)                           GAUS3450
 324  FORMAT (9E13.5)                                                   GAUS3460
      DO 328  I=1,JJ                                                    GAUS3480
 328  WRITE (6,324)          C(I,1)                                     GAUS3490
      IF (MMPATH) 350,331,350                                           GAUS3500
 331  DO 340  I=1,JJ                                                    GAUS3520
      DENOM = ABS (A(I,1))                                              GAUS3530
      DO 336  J=2,JJ                                                    GAUS3540
      IF (DENOM-ABS (A(I,J))) 335,336,336                               GAUS3550
 335  DENOM = ABS (A(I,J))                                              GAUS3560
 336  CONTINUE                                                          GAUS3570
      DO 338  K=1,JJ                                                    GAUS3580
 338  A(I,K) = A(I,K)/DENOM*SCALE3                                      GAUS3590
 340  C(I,1) = C(I,1)/DENOM*SCALE3                                      GAUS3600
      MMPATH = 1                                                        GAUS3620
      IF (MM(10)) 322,350,322                                           GAUS3630
 350  DD = 1.0                                                          GAUS3650
      IF (MM(8)) 999,354,354                                            GAUS3660
 354  CALL SOLV                                                         GAUS3670
```

```
      GO TO (351,53,56), M                                              GAUS3680
351   IF (MM(6)) 352,363,352                                            GAUS3690
352   WRITE (6,353)          (X(J,1), J=1,JJ)                           GAUS3700
353   FORMAT (13H0 DELTA B(J) /(9E13.5))                                GAUS3710
363   Y NORM = 0.0                                                      GAUS3730
      DO 364  J=1,JJ                                                    GAUS3740
364   Y NORM = Y NORM + X(J,1)**2                                       GAUS3750
      IF (Y NORM - X NORM)  366,366,365                                 GAUS3770
365   T = 0.5*SQRT (X NORM)/SQRT (Y NORM)                               GAUS3780
      X1 = T                                                            GAUS3790
366    DO 367  J=1,JJ                                                   GAUS3800
367     B(J) = BSTART(J) + T*X(J,1)                                     GAUS3810
371   DO 376  J=1,JJ                                                    GAUS3820
      IF (B(J)) 372,374,372                                             GAUS3830
372   XX = ABS ((B(J) - BSTART(J))/B(J))                                GAUS3840
      GO TO 375                                                         GAUS3850
374   XX = ABS (B(J) - BSTART(J))                                       GAUS3860
375   IF (XX-TOL1)  376,376,378                                         GAUS3870
376   CONTINUE                                                          GAUS3880
      MM(8) = 2                                                         GAUS3890
      GO TO 80                                                          GAUS3900
378   IF (MM(7)) 60,379,60                                              GAUS3920
379   IF (NDOWN) 10,10,380                                              GAUS3940
380   IF (JPARA) 10,10,49                                               GAUS3960
400   IF (NULL) 6,401,401                                               GAUS3980
401   WRITE (6,100)                                                     GAUS3990
      IF (MM(5)) 406,403,403                                            GAUS3991
403   WRITE (6,402)                                                     GAUS4000
402   FORMAT (15H   OBSERVATIONS//)                                     GAUS4010
      DO 404  N=1,NUMBER                                                GAUS4030
404   WRITE (6,405)          N, (Z(J,N), J=1,12)                        GAUS4040
405   FORMAT (I4,8E14.5/(E18.5,7E14.5))                                 GAUS4050
406   WRITE (6,5)           IDNTFC                                      GAUS4060
      GO TO 6                                                           GAUS4070
410   FORMAT ( 60H0 DATA       Y COMP             Y OBS            DIFFEGAUS4080
     XRENCE                            )                                GAUS4090
411   FORMAT (I6,F20.7)                                                 GAUS4100
412   FORMAT (12I6)                                                     GAUS4110
420   TOL1 = 0.0001                                                     GAUS4130
      GO TO 1                                                           GAUS4140
430   IF (B(23) - 1.0) 431,8,8                                          GAUS4160
431   T ZERO = B(23)                                                    GAUS4170
      WRITE (6,433)            TZERO                                    GAUS4180
433   FORMAT ( 30H0 VECTOR SCALE FACTOR = B(23),   E12.4//)             GAUS4190
      GO TO 8                                                           GAUS4200
440   IF (NULL) 446,441,441                                             GAUS4220
441   N SPIN = N SPIN + 1                                               GAUS4230
442   IF(MARK P) 444,443,444                                            GAUS4240
443   IF (N SPIN - 15) 445,444,444                                      GAUS4250
444   N SPIN = 0                                                        GAUS4260
      WRITE (6,59)                                                      GAUS4270
445   WRITE (6,58)           NN, SUMSQ, (B(J), J=1,JJ)                  GAUS4280
446   X3 = X2                                                           GAUS4290
      X2 = X1                                                           GAUS4300
      X1 = T                                                            GAUS4310
      Y3 = Y2                                                           GAUS4320
      Y2 = Y1                                                           GAUS4330
      Y1 = SUMSQ                                                        GAUS4340
      IF (NNPARA) 40,19,40                                              GAUS4350
999   WRITE (6,991)                                                     GAUS4360
      DO 990  J=1,NN                                                    GAUS4370
990   WRITE (6,405)           J, RECORD(J)                              GAUS4380
991   FORMAT ( 28H0  RECORD OF SUM OF SQUARES       //  )               GAUS4390
```

```
  993 FORMAT (24H0 MINIMIZING PARAMETERS     //)                          GAUS4400
      WRITE (6,993)                                                       GAUS4410
      WRITE (6,108)             (BMIN(J), J=1,JJ)                         GAUS4420
 1000 RETURN                                                              GAUS4450
      END                                                                 GAUS4460


      SUBROUTINE SOLV                                                     SOLV0010
      DIMENSION A(20,21), C(20,1),          LOC(20), CK(20)               SOLV0020
      COMMON /COMB/ JJ                                                    SOLV0030
      COMMON /COME/ A,C,M                                                 SOLV0040
      M = 1                                                               SOLV0050
      NP = JJ+ 1                                                          SOLV0060
      DO 11 I = 1,JJ                                                      SOLV0070
      CK(I) = 0.                                                          SOLV0080
   11 A(I,NP) = C(I,1)                                                    SOLV0090
      DO 50 I = 1,JJ                                                      SOLV0100
      IP = I + 1                                                          SOLV0110
C''''''FIND MAX ELEMENT IN I'TH COLUMN.                                   SOLV0120
      AMAX = 0.                                                           SOLV0130
      DO 2 K = 1,JJ                                                       SOLV0140
      IF (AMAX - ABS(A(K,I))) 3,2,2                                       SOLV0150
C''''''IS NEW MAX IN ROW PREVIOUSLY USED AS PIVOT                          SOLV0160
    3 IF (CK(K)) 4,4,2                                                    SOLV0170
    4 LOC(I) = K                                                          SOLV0180
      AMAX = ABS(A(K,I))                                                  SOLV0190
    2 CONTINUE                                                            SOLV0200
      IF (ABS(AMAX).LE.1.E-12)GO TO 99                                    SOLV0210
C''''''MAX ELEMENT IN I'TH COLUMN IS A(L,I)                                SOLV0220
    5 L = LOC(I)                                                          SOLV0230
      CK(L) = 1.                                                          SOLV0240
C''''''PERFORM ELIMINATION.  L IS PIVOT ROW, A(L,I) IS PIVOT ELEMENT.      SOLV0250
      DO 50 J = 1,JJ                                                      SOLV0260
      IF (L-J) 6,50,6                                                     SOLV0261
    6 F = -A(J,I) / A(L,I)                                                SOLV0262
      DO 40 K = IP,NP                                                     SOLV0270
   40 A(J,K) = A(J,K) + F * A(L,K)                                        SOLV0280
   50 CONTINUE                                                            SOLV0290
      DO 200 I = 1,JJ                                                     SOLV0300
      L = LOC(I)                                                          SOLV0310
  200 A(I,1) = A(L,NP) / A(L,I)                                           SOLV0320
      RETURN                                                              SOLV0330
   99 M = 3                                                               SOLV0340
      RETURN                                                              SOLV0350
      END                                                                 SOLV0360


      SUBROUTINE DERIV                                                    DERIV010
      DIMENSION B(24),Z(12,300),CY(300),FP(20,300),H(20),Y(300)           DERIV020
      COMMON NUMBER,B,Z                                                   DERIV030
      COMMON /COMB/ JJ                                                    DERIV040
      COMMON /COMC/ CY                                                    DERIV050
      COMMON /COMD/ FP                                                    DERIV060
      IF (B(22)) 20,1,20                                                  DERIV070
    1 B(22) = 1.                                                          DERIV080
      DO 7 J = 1,JJ                                                       DERIV090
      TEST = ABS(B(J))                                                    DERIV100
      IF (TEST - 0.001) 5,6,6                                             DERIV110
    5 H(J) = 0.001                                                        DERIV120
      GO TO 7                                                             DERIV130
    6 H(J) = 0.0001 * TEST                                                DERIV140
```

```
  7  CONTINUE                                                               DERIV150
 20  DO 22 J = 1,JJ                                                         DERIV160
     TEMP = B(J)                                                            DERIV170
     B(J) = TEMP + H(J)                                                     DERIV180
     CALL YCOMP                                                             DERIV190
     DO 21 N = 1,NUMBER                                                     DERIV200
 21  Y(N) = CY(N)                                                           DERIV210
     B(J) = TEMP - H(J)                                                     DERIV220
     CALL YCOMP                                                             DERIV230
     B(J) = TEMP                                                            DERIV240
     DO 22 N = 1,NUMBER                                                     DERIV250
 22  FP(J,N) = (Y(N) - CY(N))/(2. * H(J))                                   DERIV260
     RETURN                                                                 DERIV270
     END                                                                    DERIV280


      SUBROUTINE YCOMP
       DIMENSION B(24),Z(12,300),CY(300)
       COMMON /COMC/ CY
       COMMON NUM,B,Z
C     QUASI-LATTICE THEORY
      T=303.2
      R=1.987
      QH=1.
      QO=8.
      AH0=0.009
      AO0=0.3
      AI0=1.4
      ETOH=EXP(-B(1)/(R*T))
      ETHS=EXP(-B(2)/(R*T))
      ETOS=EXP(-B(3)/(R*T))
      ETIS=EXP(-B(4)/(R*T))
      ETHI=ETHS
      ETOI=ETOS
      DO 1 N=1,NUM
      IF(N.EQ.1.OR.N.EQ.19.OR.N.EQ.34.OR.N.EQ.52.OR.N.EQ.70.OR.N.EQ.88.
     1OR.N.EQ.106.OR.N.EQ.124) GO TO 5
    3 XA=Z(3,N)
      XB=1.-XA
      GO TO10
    5 XA=1.
      XB=0.
      QI=9. + 8.*Z(1,N)
      QS=18. + 8.*Z(2,N)
      AS1=(0.5*QS)**0.5
      AS0=AS1
   10 AH = 0.5*QH*XA/(AH0 + AO0*ETOH + AI0*ETHI + AS0*ETHS)
      AO = 0.5*QO*XA/(AH*ETOH + AO0 + AI0*ETOI + AS0*ETOS)
      AI = 0.5*QI*XA/(AH*ETHI + AO*ETOI + AI0 + AS0*ETIS)
      AS = 0.5*QS*XB/(AH*ETHS + AO*ETOS + AI*ETIS +AS0)
      AAH = ABS(AH-AH0)
      AAO = ABS(AO-AO0)
      AAI = ABS(AI-AI0)
      AAS = ABS(AS-AS0)
      IF(AAH.LT.0.0001 .AND. AAO.LT.0.0001 .AND. AAI.LT.0.001 .AND.
     1AAS.LT.0.001) GO TO 20
      AH0=AH
      AO0=AO
      AI0=AI
      AS0=AS
      GO TO 10
   20 IF(XA.NE.1.) GO TO 30
```

```
      AH1=AH
      AO1=AO
      AI1=AI
      AH0=0.005
      AO0=0.025
      AI0=0.09
      AS0=AS1-0.2
      GO TO 3
   30 HE = -2.*R*T*((AO*AH -XA*AO1*AH1)*ETOH*ALOG(ETOH) + (AH*AI - XA*
     1AH1*AI1)*ETHI*ALOG(ETHI) + (AO*AI - XA*AO1*AI1) *ETOI*ALOG(ETOI) +
     2 AO*AS*ETOS*ALOG(ETOS) + AH*AS*ETHS*ALOG(ETHS) + AI*AS*ETIS*
     3 ALOG(ETIS))
    1 CY(N)=HE
      RETURN
      END
//GO.SYSIN DD *
   141     6     4    15          -1           1     1    -1     1     1
-3049.      -526.       29.         1.2

                        0.0001                  1.
(6F12.3)
1.          4.          .01         1.54        2.13        42.86
 .
 .
 .
 .
 .
 .
141 DATA CARDS
//
```

NOMENCLATURE

A_v - total free surface area of groups of type v

A_{vj} - total free surface area of v groups in a component molecule j

A_{uv} - total overlapping surface area of contact between groups u and v

B_1, B_2 - constant in Equation (3-34)

C_k - coefficients in Equation (2-2), $k = 1, \ldots 6$

E - total interaction energy of solution

E^o - energy defined by Equation (5-6)

f_{sOH} - OH group surface concentration in solution, %

f_v - fractional free surface of group v in solution

G^E - excess free energy

$\bar{G}_i^E$ - partial excess free energy of component i

ΔG^M - free energy of mixing

ΔG^{Mo} - free energy of mixing of an ideal solution

g - degeneracy

H^E - excess enthalpy

ΔH^M - enthalpy of mixing

I_a, I_f - group interaction contribution defined in Figure 3

k - Boltzmann's constant

L - covalent radius

N - Avogadro's number

N^i - number of molecules of component i

N_{uv} - number of contact between segments u and v

N^{*}_{uv} - number of contact between segments u and v in athermal theory, defined by Equation (4-4)

N^{oi}_{uv} - number of contact between segments u and v in pure component i liquid

n_R - number of carbon atoms in hydrocarbon radical R

n_v - number of groups of type v

n^{i}_{v} - number of groups of type v in component molecule i

n'_{vj} - number of atoms of type v in component j

n_{uv} - number of group u required to cover the fractional surface of central group v that interacted with group u in solution

n^{o}_{uv} - number of group u required to cover the fractional surface of central group v that interacted with group u in an ideal solution

P - system pressure

P^{o}_{i} - vapor pressure of pure component i at system temperature

Q - canonical partition function defined by Equations (4-1) and (5-7)

R - universal gas law constant; alkyl group in RX molecule; or Van der Waal's radius

r_i - number of segments (groups) on a molecule i

S - entropy of solution

S^{E} - excess entropy

S^{M} - molal entropy of mixing

S^{Mo} - molal entropy of mixing of an ideal solution

$\bar{S}^{Mo}$ - partial molal entropy of mixing of an ideal solution

$\bar{S}^{E}_{v}$ - partial group excess entropy of v, defined by Equation (3-30)

$\bar{S}_v^M$ - partial group entropy of mixing of v, defined by Equation (3-29)

$\bar{S}_v^{Mo}$ - partial group entropy of mixing of v of an ideal solution, defined by Equation (3-28)

s_v - free surface area of group v

s_{uv} - $s_u \times s_v/(s_u + s_v)$, harmonic average of group surfaces of groups u and v

T - absolute temperature

T_r - reduce temperature

ΔU^M - energy of mixing

ΔU^{vM} - energy of vaporization of one mole mixture

V - total volume of solution

v_i^L - molar liquid volume of pure i

X - functional group in RX molecule

X_v - variable defined by Equation (4-18)

x_i - mole fraction of component i

Y_v - group fraction of group v

Y_v^o - group fraction of v in ideal solution

y_i - vapor phase mole fraction of component i

z - coordination number

z_v - number of contact points of group v

Greek Symbols

Γ_v - activity coefficient of group v in a group solution

Γ_v^* - activity coefficient of group v in a standard group solution

γ - activity coefficient

γ_i^o - activity coefficient of i at infinite dilution

γ^s - activity coefficient of structural contributions defined by Equation (2-4)

γ^G - activity coefficient of group contributions defined by Equation (2-5)

Λ - Wilson parameters defined by Equations (5-18) and (5-19)

λ_{uv} - interaction energy between groups u and v per unit surface area of contact, cal./sq. cm.

λ'_{uv} - interaction energy between groups u and v, cal./g-mole

ν_i^o - fugacity coefficient of pure i at system temperature and vapor pressure P_i^o

Φ_i - vapor phase fugacity coefficient of component i

Ω_{uv} - exchange energy defined by Equation (5-3), cal./sq. cm.

Ω'_{uv} - exchange energy defined by Equation (4-8), cal./g-mole

<u>Superscripts</u>

E - excess thermodynamic property

i - component i

L - liquid phase

M - thermodynamic mixing property

o - ideal solution property

oi - pure component i

s - structural contributions

G - group contributions to activity coefficient

v - vaporization

* - athermal property

Subscripts

a, b, c, d, e, f - types of interaction defined in Figure 1

a - alcohol

H - hydroxyl hydrogen segment

I - hydrocarbon segments in alcohol molecule

i, j, k - components i, j, k

O - hydroxyl oxygen segment

p - paraffins

R - radical R

S - paraffin solvent segments

u, v, w - types of group

VITA

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Doctor of Philosophy

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