Statistical Thermodynamics of Liquid Mixtures

by

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Chairman of Examining Committee

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Executive Officer

Supervisory Committee

The City University of New York

In memory of

My father and mother

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Abstract

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A parameter n, characteristic of the liquid, which appears in the cohesive energy-volume relation, $E=-A/V^n$, where A is a constant related to the interaction energy between molecules and V is the molar volume, is introduced to modify and expand Flory's theory, so that one would be able to predict the excess enthalpy from easily measurable excess volume. A partition function is developed for the description of polar and non-polar liquids. This partition leads to an equation of state, expressed in terms of reduced properties of the pure liquid; these depend on the parameter n and can be evaluated from the thermal expansion coefficient and thermal pressure coefficient.

The reduced properties, $\overline{V}$ and $\overline{T}$, and the characteristic properties, T^*, V^*, and P^*, as well as the external degrees

of freedom per molecule, C, which is equal to P^*V^*/RT^*, for molecules of various constituents were calculated at various values of n within appropriate ranges. They all show substantial change with n. This reveals the significance of the energy-volume surface curvature on the behavior of a liquid.

The parameter X_{12}, which characterizes the interaction energy between unlike molecules and is a function of n, is used to derive expressions for the characteristic pressure and characteristic temperature of binary mixtures in terms of the properties of the solution components. The excess enthalpy and volume of mixing are then expressed by the characteristic and reduced properties of the components and X_{12}. The reduced volume of a binary mixture, obtained from the experimental excess volume, is used to calculate X_{12}, and consequently, the excess enthalpy of mixing. The contact interaction contribution to the excess enthalpy, resulting from the interaction between unlike molecules, and the equation of state contribution to the excess enthalpy resulting from the difference in the reduced volumes between the mixture and its components, were discussed for various systems.

The refined theory has been applied to mixtures of various constituents, spherical and chain, polar and non-polar. The results have been found in most cases very good. A value

of n=1.29, independent of temperature and composition, was found for mixtures of n-paraffin hydrocarbons; a value of n=1.40 was found for mixtures composed of spherical or close-to-spherical molecules; a value of n=1.00 was obtained for mixtures of 1-alcohols; finally a value of n=0.92 was obtained for the 1-Alcohol—n-Hexane mixtures. The consistence in n, in fact, makes the prediction of the excess enthalpies at various temperatures and compositions possible, from just density measurements and one excess enthalpy measurement.

The geometric mean rule and the extent to which the different systems obey this rule is also discussed in this work.

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I. INTRODUCTION

The central problem in the statistical treatment of solutions is to calculate the properties of a given mixture from the intermolecular forces between the like and unlike molecules. The Lennard-Jones potential function is the most commonly applied relationship for this purpose. However, even for comparatively simple poly-atomic molecules, the acentric distribution of the polarizable electrons necessitates fairly drastic modification of this potential function (1). Kihara (2), Hamann and Lambert (3), and Pitzer (4, 5) have offered an improved intermolecular potential function for globular poly-atomic molecules.

The first attempts to give a description of the liquid state with the cell model were made by Eyring (6) and Eyring and Hirschfelder (7) in 1936. However, Lennard-Jones and Devonshire (8, 9) were the first to use the cell theory to express the thermodynamic properties in terms of intermolecular forces. The cell model assumes that the molecules are arranged in a perfect array, each being assigned to the center of its cell. The shortcomings of the model arise from the fact that it overestimates the local order in liquids.

Until 1950, of the various statistical theories existing, the most general were probably the theories of regular or strictly regular solutions by Fowler and Guggenheim (10), Rushbrooke (11), and Hildebrand and Scott (12). These theories assume that in a liquid mixture (a) the molecules are arranged in a regular lattice, (b) the individual liquid components have ordered structures of the same type and (c) the intermolecular potential energy is the sum of contributions arising solely from two neighboring molecules depending only on their chemical nature. The theory of regular solutions has been successful in describing mixtures of non-polar liquids; however, it cannot be regarded as satisfactory for the folowing reasons:

First, the assumption of a regular lattice is appropriate only to crystals, and possibly to liquids near their freezing points. It becomes less realistic as the critical temperature is approached, and breaks down completely for gases. Thus the theory of regular solutions overstresses the solid-liquid analogy, and takes no account of the observed continuity between the liquid and gaseous states.

Second, it is not reasonable to assume that the intermolecular energy is the sum of a number of fixed terms only, one for the interaction of each pair of neighbors. In reality, the intermolecular forces must vary continuously with distance,

and this variation is responsible mainly for the compressibility, thermal expansion, and other important thermodynamic properties of the system.

Third, it is not difficult to show that if the contact energy w_{12} (13), [which is equal to $\frac{1}{2}(\epsilon_{11}+\epsilon_{22}) - \epsilon_{12}$, where ϵ_{11}, ϵ_{22}, and ϵ_{12} are the interaction energies between two neighboring molecules of kind 1, two neighboring molecules of kind 2, and between two unlike molecules of kind 1 and 2, respectively], is regarded as temperature-independent, then the excess entropy of mixing of 1 with 2 must always be negative, which is in disagreement with experimental results. Although Guggenheim has shown that such discrepancies may be eliminated by allowing w_{12} to vary with temperature, the theory of regular solutions provides no clue as to the actual dependence of w_{12} on temperature.

The theorem of corresponding states (14) assumes that the potential energy of a pair of molecules, u(r), can be represented by a universal function, f, of two scale factors, ϵ and σ;

$$u(r) = \epsilon f(r/\sigma)$$

where ϵ is the energy parameter, σ is the length parameter, u is the intermolecular potential, and r is the distance between two molecules. The configuration partition function in terms

of the theorem of corresponding state can be written as

$$Q(N, T, V) = \sigma^{3N} q(\bar{T}, \bar{v})^N$$

$q(\bar{T}, \bar{v})$ is the partition function per molecule and N is Avogadro's number. The meaning of the reduced quantities is obvious from the relationships:

$$\bar{P} = P\sigma^3/\epsilon, \quad \bar{v} = V/N\sigma^3, \quad \bar{T} = kT/\epsilon$$

In 1951, Longuet-Higgins published the theory of comformal solution (15). The starting point of this theory is the theorem of corresponding states in its most modern form as developed by Pitzer (16), Guggenheim (17), de Boer, and other (18). Using a simple perturbation approach, Longuet-Higgins was able to show that, as long as one retains first-order perturbation terms only, the properties of a mixture can be directly deduced from assumptions about the intermolecular forces and the thermodynamic properties of the pure components, without any appeal to specific statistical model. The first-order theory was found reasonably successful in correlating the mixing properties of the nonpolar and slightly polar gas-liquid and liquid-liquid solutions which had been studied before 1950. All these solutions possess an important feature of the first-order theory, namely, that the thermodynamic excess mixing functions all have the same sign. This

occur in the case of the very simple mixtures such as CO—CH_4, CCl_4—$C(CH_3)_4$ for which the basic assumption of the theory of comformal solutions should be satisfied.

The importance of this theory lies in the fact that it showed for the first time the possibility of application of the theorem of corresponding states to multi-component systems.

Brown in 1957 derived an equation for the second-order perturbation free energy of a comformal solution by a vigorou Taylor-series expansion of the configuration integral in powers of the difference between the intermolecular energy and size parameter, about an ideal unperturbed reference solution. Unlike the first-order terms, those of the second order contain statistical functions of a reference solution which cannot, in general, be related to its thermodynamic properties.

Prigogine, Bellemans and Mathot (14) combined the main advantages of both the cell model and the theory of comformal solutions and made full use of the corresponding states to produce the average potential model (APM), in both crude and refined versions. Scott (20) independently developed a similar version with one liquid (crude version of Prigogine), two liquid (refined version of Prigogine), and three liquid models

based on the principle of corresponding states. The series expansions of Prigogine involved higher derivatives, whose values are rarely available in the literature, and when available, are generally not sufficiently accurate. The series expression of excess function converages very slowly, especially for the excess volume.

The average potential model was critically reviewed in an article by Bellemans, Mathot, and Simon (21), in which they presented a detailed and significant comparison of APM with experimental data available up to July, 1965, on simple mixtures. In their modified version, they used the full expressions instead of the expanded forms of the excess functions. Also, analytical expressions of the reduced properties based on the principle of corresponding states were used as basis for calculating excess functions. Quantitative discussions of the following five systems were given: CO—CH_4, Ar—Kr, N_2—CO, and CO—Ar. The results for the excess free energies and volumes obtained from the average potential model were compared with experimental data (23). The conclusion was that the APM was able to semi-quantitatively predict the excess properties of simple mixtures.

It has been observed that the older average potential, or the random mixing theory, grossly exaggerates the effects of difference in molecular size (24). It is now agreed (25,

26) that the prediction that a difference of molecular size should lead to very large positive contributions to the excess functions, G^E, H^E, and V^E, is incorrect. Recently Leland, Rowlinson, and Sather (25, 26) have shown that the van der Waals one-fluid-relations

$$a(x_1) = x_1^2 a_{11} + 2x_1x_2a_{12} + x_2^2a_{22} \qquad (A)$$

$$b(x_1) = x_1^2 b_{11} + 2x_1x_2b_{12} + x_2^2b_{22} \qquad (B)$$

[where x_1 and x_2 are the appropriate mole fractions, a_{ij} and b_{ij} the appropriate van der Waals constants, and $a(x_1)$ and $b(x_1)$ are the parameters in the van der Waals equation of state for a binary mixture of molecule 1 and 2:]

$$P = RT/[V-b(x_1)] - a(x_1)/V^2$$

lead to the expressions of various excess thermodynamic functions which show greatly improved agreement with experiment for mixtures of simple molecules.

Marsh et al. (27) have shown that the one-fluid-relations when combined with the various hard-sphere equations of state give values for the excess functions which agree about as well with experiment as those calculated by Leland, Rowlinson, and Sather. Leland, Rowlinson, Sather, and Watson (26) and Marsh et al. (27) have used the analogous van der Waals two-fluid-relations and obtained substantially better

agreement with the experimental results for simple systems than with the corresponding one-fluid theories.

Prigogine's corresponding states principle for polymeric liquids (14) was made possible by the concept of division of the degrees of freedom of a chain-molecule into internal and external categories. Flory and co-workers (28, 29, 30, 31) made full use of this concept to derive an equation of state, for mixtures as well as for pure liquids, by assuming that each molecule can be divided into a number of equal-size segments and that the excess thermodynamic properties result from the interactions among the segments.

Flory's theory made the calculation of one thermodynamic function from another possible. The calculated excess volumes from excess enthalpies are in fair agreement with the experimentally found excess volumes for polar and non-polar mixtures of various molecular size ratios. However, the reverse procedure, which would be more desirable, does not work. When excess enthalpies are calculated from the experimental excess volumes, the results based on Flory's formula fail to come even close to the experimental values. This is so because the excess enthalpy is a highly sensitive function of the reduced volumes. As for the estimation of the excess free energy and entropy from either the excess volume or the excess enthalpy, Flory's formula fails completely, since the

contributions to the excess free energies and entropies arising from the contact interactions are not included in the formula, and furthermore, the combinatorial partition function which accounts for the orientations and randomness are not included in the expression of S^E and G^E. This makes the contributions from the combinatorial partition function excluded from the calculations of S^E and G^E. Though an empirical method (32) has been suggested to amend the discrepancies between the estimated and experimental values of entropy, it offers no explanation whatsoever of the real physical nature of the solutions.

The significance of Flory's theory is that it enables one to estimate the interaction parameters between the unlike segments of molecules of mixtures and consequently the excess functions from the thermal expansion and thermal pressure coefficients of the two pure components without making any use of the combination rules. Nevertheless, the Berthelot's combination rule is discussed later in this work.

The principal objective of this work is to modify and to expand Flory's theory in such a way that it would be able to predict the more difficultly obtainable enthalpy of mixing from the more easily measurable excess volume. The refined theory has been applied to mixtures of various constituents, spherical and chain, polar and non-polar; the results are,

in most cases, very good. Part of Flory's theory is restated briefly in order to facilitate its modifications and its application.

II. REDUCED EQUATION OF STATE

1. Classical Partition Function:

Statistically an equation of state is defined as

$$P = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \tag{1}$$

where P, V, T, N, k, and Q are the pressure, volume, temperature, total number of particle, Botzmann's constant, and the partition function of the system. If the partition function is known the pressure of the system can be determined. Equations relating the other thermodynamic properties of a system to the partition function may be also derived from statistical thermodynamics.

The classical partition function can be written as

$$Q = \left(\frac{1}{h^{3N} N!}\right) \int_{6N} \exp\left(\frac{-H}{kT}\right) dq_1 dp_1 \cdots dq_{3N} dp_{3N} \tag{2}$$

where H is the Hamiltonian defined by

$$H = \frac{\sum_{i}^{3N} p_i^2}{2m} + E(q_1, q_2, \cdots, q_{3N}) \tag{3}$$

where $E(q_1, q_2, \cdots, q_{3N})$ is the intermolecular energy depending on the coordinates of the particles in the system, $1/h^{3N}$ is introduced as a proportionality constant, p and q are the momentum and the position coordinates of the N molecules, and m is the mass of a molecule.

The integration over the momentum space can be made easily and leads to

$$Q = \left(\frac{2\pi mkT}{h^2}\right)^{\frac{3N}{2}} Q_{conf} \tag{4}$$

where Q_{conf} is the configurational partition function and is defined as

$$Q_{conf} = \left(\frac{1}{N!}\right)\int_{3N} \exp\left(-\frac{E}{kT}\right) dq_1 \cdots dq_{3N} \tag{5}$$

For a system of non-interacting particles $E(q_1, q_2, \cdots, q_{3N}) = 0$, and eq.(5) takes the form

$$Q_{conf}^{id} = \frac{V^N}{N!} \tag{6a}$$

For systems in which N is a very large number, stirling approximation, $N! = N^N e^{-N}$, may be used,to express N!. Consequently eq. (6a) becomes

$$Q_{conf}^{id} = \left(\frac{eV}{N}\right)^N \tag{6b}$$

2. Partition Function of Systems of Interacting Molecules:

The evaluation of Q_{conf} for interacting particles is not an easy task. The following procedure has been used in this work.

Let us consider a collection of N indistinguishable hard-sphere particles, A_1, A_2, $\cdots$, A_N, of diameter a, whose centers are constrained to move along a straight line between two fixed boundaries a distance L apart. Let the position of particle A_k be x_k. The possible values of x_k are restricted both by the boundaries of the straight line and finite size of the other molecules present. Thus

$$\frac{a}{2} \leq x_k \leq L-\frac{a}{2} \qquad \text{and} \qquad x_i - x_j \geq a \tag{7}$$

which can be better seen from Fig. 1:

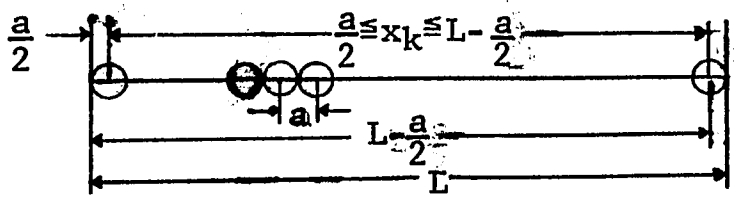

Fig. 1. Boundary Conditions of Particles

We shall number the molecules from 1 to N in the order they actually occur. The allowed positions of the particles are

$$\frac{a}{2} \leq x_1, \quad x_1 \leq x_2 - a, \quad x_2 \leq x_3 - a, \quad \cdots, \quad x_N \leq L - \frac{a}{2} \tag{8}$$

The minimum coordinate condition for each molecule is

$$\frac{a}{2} < x_1, \quad \frac{3a}{2} < x_2, \quad \frac{5a}{2} < x_3, \quad \cdots, \quad (2N-1)\frac{a}{2} < x_N \tag{9}$$

This is illustrated in the following Fig. 2:

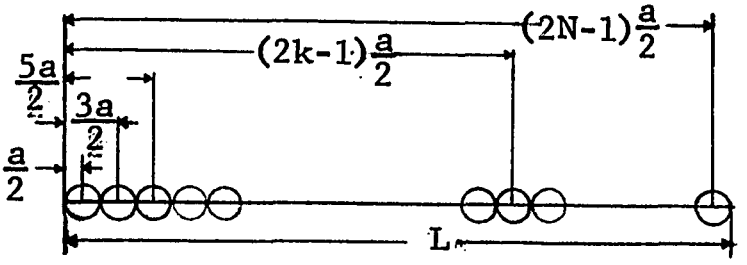

Fig. 2. Mininmun Coordinate Condition for each Particle

The maximum coordinate condition depends on the position of the next molecule to the right.

According to Tonk (33) the total number of point positions (all the possible ways of distributing the N particles along the length L) of such a system is

$$I = \int_{\frac{(2N-1)a}{2}}^{L-\frac{a}{2}} \cdots \int_{\frac{3a}{2}}^{x_3-a} \int_{\frac{a}{2}}^{x_2-a} \cdots dx_1 dx_2 \cdots dx_N \tag{10}$$

The integral (also called configurational space integral) can be evaluated and is equal to

$$I = \frac{(L-aN)^N}{N!} \tag{11}$$

If a certain way of distributing the N particles along the length L is called a given configuration of this N particle assembly, then the probability of any given configuration is equal to

$$P = \frac{N!}{(L-aN)^N} \tag{12}$$

which is proportional to $\exp(-\frac{E_i}{kT})$, or

$$P = \frac{N!}{(L-aN)^N} = (\frac{1}{Q'_{conf}})\exp(-\frac{E_i}{kT}) \tag{13}$$

where E_i is the energy of a given configuration and Q'_{conf} is the molar partition function

$$Q'_{conf} = \frac{(L-aN)^N}{N!}\exp(-\frac{E_i}{kT}) \tag{14}$$

Stirling approximation is used to express N!. Consequently eq. (14) becomes

$$Q'_{conf} = \left[(1-a)e\right]^{N} \exp\left(-\frac{E_i}{kT}\right) \qquad (15)$$

where $l = L/N$ is the average length accessible to each particle.

Using the same argument for a three dimensional system and assuming that there exits a geometric factor q which establishes the relationships $(qv^*)^{1/3} = a$ and $(qv)^{1/3} = 1$, where v^* is the actual volume of each molecule, and v is the volume available for each molecule, we obtain the configurational partition function for a three dimensional system

$$Q_{conf} = \left[qe^3(v^{\frac{1}{3}} - v^{*\frac{1}{3}})^3\right]^{N} \exp\left(-\frac{E_i}{kT}\right) \qquad (16)$$

3. Partition Function of Flory's Version:

According to Flory and his co-workers (30, 31), a non-spherical molecule can be considered as consisting of r homogeneous elements (or segments); consequently there are rN segments in all in the N molecules. The segments are arbitrarily chosen isometric portions of the molecule. The r elements can be treated as a collection of r point-centres, each of which is subjected to a system of central forces

exerted by the centers of the nearest neighbors (molecules).

Prigogine and co-workers (14, 34, 35, 36) made a significant contribution to the theory of chain molecules. According to these theories there are two types of degrees of freedom of molecular motion in liquids: the intramolecular (internal), and the intermolecular (external) degrees of freedom. The former are associated with the higher frequency motions such as bond stretching, which is unaffected by the environment. The latter are associated with the lower energy motions of molecules, such as rotation around a bond, and these interact with the surrounding. These external degrees of freedom are important when dealing with the configuration properties. Prigogine achieved remarkable success with this concept in the development of the principle of corresponding states for chain molecules.

Making use of the assumption made by Prigogine for polymer chain molecules that each segment has 3c external degrees of freedom, which are independent of the central force of the segment and depend only on the environment of the segment, and letting Q_{comb} be the combinatorial factor taking account of the number of ways of interspersing the rN elements among one another regardless of the precise location of each segment relative to its chosen neighbors, we can write eq. (16) as

$$Q_{conf} = Q_{comb}\exp(3N)\left[q(v^{\frac{1}{3}} - v^{*\frac{1}{3}})^3\right]^{rNc}\exp(-\frac{E_i}{kT}) \qquad (17)$$

4. Cohesive Energy:

Next we intend to approximate the intermolecular energy with the cohesive energy. The cohesive energy of liquids as a function of volume has been studied by many investigators (37-40) and the following form is often recommended over a small temperature range:

$$E = -\frac{A}{V^n} \qquad (18)$$

where E is the molar cohesive energy, V is the molar volume, and A and n are constants within a narrow temperature range; their values depend on the nature of the particular liquid only. It has been shown experimentally that, for a number of pure liquid substances, the exponent n has values ranging from one to two (37-42), For a uniformly expanded model, Benson (43) derived a value of n=2.0, but a value of 1.67 resulted in better agreement with experiment. In the normal liquid range, Scott found for perfect liquids and hydrocarbons a value of n equal to about 1.50 for non-isothermal conditions (along the vapor-liquid equilibrium curve). According to a

paper by V. Fried (39), n depends on the polarity of the molecule and for non-polar molecules a value of 1.40 has been found.

Recently, Lee (41) has assumed a constant value of n=1.15 as it appears in eq. (18) for n-alkanes in his derivation of a partition function which leads to the expression of the heat of vaporization, and found good agreement between the calculated and experimental values. Also, Fang (42) has calculated the values of n for 29 simple liquids over a wide temperature range, and found that the values of n vary between 0.81 and 1.66.

Complying with the above assumption of isometric segments of each molecule, and assuming that each segment has s intermolecular contact sites capable of interacting with the nearest sites of the other molecules, we can express eq. (18) in the following form:

$$E = - \frac{Nrs\eta'}{2V^n} \qquad (19a)$$

where η' represents a constant characterizing the energy between a pair of interacting sites for one mole of liquid substance, and factor of 2 in eq. (19a) corrects for double counting of pairs. If η is the energy constant responsible

for a pair of interacting sites only, then eq. (19a) becomes:

$$E = - \frac{Nrs\eta}{2V^n} \qquad (19b)$$

where v is the available volume per segment in accord with the terminology used above. In short, the dimension of or η has to be consistent with the volume to which it is applied. In eq. (19b) only the energy resulting from the interaction of a pair of nearest sites is included in the total cohesive energy; the energy resulting from the interaction with the more distant sites is fully ignored.

5. Reduced Equation of State:

Substituting eq. (19b) into eq. (17), we obtain for the partition function as follows:

$$Q_{conf} = Q_{comb} \exp(3N) \left[q(v^{\frac{1}{3}} - v^{*\frac{1}{3}})^3\right]^{rNc} \exp\left(\frac{Nrs\eta}{2V^n RT}\right) \qquad (20)$$

and its logarithm takes the form

$$\ln Q = \ln Q_{comb} + 3N + rNc \ln q + 3rNc \ln(v^{\frac{1}{3}} - v^{*\frac{1}{3}}) + \frac{Nrs\eta}{2V^n RT} \qquad (21)$$

Differentiation of eq. (21) with respect to v at constant temperature, yields

$$\left(\frac{\partial \ln Q}{\partial v}\right)_{T,N} = \frac{rNcv^{-2/3}}{v^{\frac{1}{3}} - v^{*\frac{1}{3}}} - \frac{nNrs\eta}{2v^{n+1}RT} \qquad (22)$$

The combinatorial factor Q_{comb} and the communal entropy factor, e^{3N}, (44, 45), along with q^N have disappeared in the process of differentiation. Thus, for the evaluation of the thermodynamic functions in which the derivative of the partition function appears, e^{3N}, q^N, and Q_{comb} are unimportant. Nevertheless, these functions are significant for the evaluation of the thermodynamic functions directly related to the partition function, such as entropy and Gibbs free energy.

Assuming that a constant, k', equivalent to Botzmann constant, k, for a molecule, can be found for a segment, we write $k = rk'$. Since $R = Nk$, it follows that $R = rNk'$. Therefore eq. (22) becomes

$$\left(\frac{\partial \ln Q}{\partial v}\right)_{T,N} = \frac{rNcv^{-2/3}}{v^{\frac{1}{3}} - v^{*\frac{1}{3}}} - \frac{ns\eta}{2v^{n+1}k'T} \qquad (23)$$

It follows from eq. (1) that $P = k'T(\partial \ln Q/\partial v)_{T,N}$ and consequently:

$$P = \frac{k'TrNcv^{-2/3}}{v^{\frac{1}{3}} - v^{*\frac{1}{3}}} - \frac{ns\eta}{2v^{n+1}} \tag{24a}$$

or

$$P = \frac{RTcv^{-2/3}}{v^{\frac{1}{3}} - v^{*\frac{1}{3}}} - \frac{ns\eta}{2v^{n+1}} \tag{24b}$$

Let us now use v, v^*, and η for the corresponding molar quantities (one mole of segments) and further let us define the characteristic pressure P^* and characteristic temperature T^* of the liquid system in the following way:

$$P^* = \frac{s\eta}{2v^{*n+1}} \tag{25}$$

$$T^* = \frac{s\eta}{2v^{*}ncR} \tag{26}$$

Consequently

$$P^* = \frac{cRT^*}{v^*} \tag{27a}$$

or

$$P^* = \frac{CRT^*}{V^*} \tag{27b}$$

where C = rc and V = rv. The reduced quantities per mole of segment are equal to

$$\overline{P} = \frac{P}{P^*} = \frac{2v^{*n+1}}{s\eta} \tag{28}$$

$$\overline{T} = \frac{T}{T^*} = \frac{2v^{*n}cRT}{s\eta} \tag{29}$$

$$\overline{V} = \frac{V}{V^*} = \frac{v}{v^*} \tag{30}$$

where V is the molar volume of the liquid and V^* is the corresponding hard core molar volume (since $V^* = rv^*$).

Substituting P, T, and v from eqs. (28), (29), and (30), respectively, into eq. (24), we obtain a reduced equation of state for liquids composed of non-spherical as well as spherical molecules

$$\frac{\overline{PV}}{\overline{T}} = \frac{\overline{V}^{\frac{1}{3}}}{\overline{V}^{\frac{1}{3}}-1} - \frac{n}{\overline{V}^{n}\overline{T}} \tag{31}$$

The reduced equation of state at low pressure ($P \cong 0$) can then be approximately represented by

$$\frac{\overline{V}^{\frac{1}{3}}-1}{\overline{V}^{n+\frac{1}{3}}} = \frac{\overline{T}}{n} \tag{32a}$$

As is obvious, at the same $\overline{V}$ and $\overline{T}$ all the systems must have the same n.

The reduced equation of state may be expressed alternatively as

$$\frac{\bar{P}}{\bar{d}^{n+1}} = \frac{\bar{T}}{\bar{d}^{n}(1-\bar{d})} - n \qquad (32b)$$

where $\bar{d} = 1/\bar{V}$ is the reduced density.

6. Comparison with the other existing Equations of State:

In general, the equation of state of a pure substance can be written approximately as

$$PV = RT\left[\frac{1+y+y^2+w_1y^2+w_2y^3}{(1-y)^3}\right] - \frac{a}{V} \qquad (33)$$

where $y = b/4V$ and a and b are van der Waals parameters.

The various equations of state can be written to a good approximation in a form similar to the above generalizied equation. For the van der Waals equation

$$PV = RT\left(\frac{1}{1-4y}\right) - \frac{a}{V} \qquad (34)$$

the term $1/(1-4y)$ can be expanded as

$$\frac{1}{1-4y} = \left[\frac{1}{(1-y)^3}\right]\left[\frac{(1-y)^3}{1-4y}\right]$$

$$= \left[\frac{1}{(1-y)^3}\right](1+y+y^2+6y^2+27y^3+\cdots)$$

Thus, by neglecting the higher order terms in the above equation, the van der Waals equation becomes

$$\text{(vdW)} \qquad PV = RT\left[\frac{1+y+y^2+6y^2+27y^3}{(1-y)^3}\right] - \frac{a}{V} \qquad (34b)$$

that is $w_1 = 6$, $w_2 = 27$

For Guggenheim's equation (46):

$$PV = RT\left[\frac{1}{(1-y)^4}\right] - \frac{a}{V} \qquad (35a)$$

the term $1/(1-y)^4$ can be written as

$$\frac{1}{(1-y)^4} = \left[\frac{1}{(1-y)^3}\right]\left(\frac{1}{1-y}\right)$$

$$= \left[\frac{1}{(1-y)^3}\right](1+y+y^2+y^3+\cdots)$$

Thus, by neglecting the higher order terms in the Guggenheim's equation, it assumes

$$\text{(G)} \qquad PV = RT\left[\frac{1+y+y^2+y^3}{(1-y)^3}\right] - \frac{a}{V} \qquad (35b)$$

that is $w_1 = 0$, $w_2 = 1$.

For the Longuet-Higgins and Widom equation (47):

$$\text{(LH,W)} \qquad PV = RT\left[\frac{1+y+y^2}{(1-y)^3}\right] - \frac{a}{V} \tag{36}$$

The two parameters in the generalized equation are $w_1 = 0$, $w_2 = 0$.

If we use the Percus-Yevick pressure equation of state for hard sphere (48, 49), we have

$$PV = RT\left[\frac{1+2y+3y^2}{(1-y)^2}\right] - \frac{a}{V} \tag{37a}$$

It can be rewritten as

$$\text{(PYP)} \qquad PV = RT\left[\frac{1+y+y^2-3y^3}{(1-y)^3}\right] - \frac{a}{V}$$

this corresponds to the generalized equation with $w_1 = 0$, $w_2 = -1$.

Finally, by using the Carnahan-Startling equation (50) for the hard sphere part, the equation of state can be expressed as

$$\text{(CS)} \qquad PV = RT\left[\frac{1+y+y^2-y^3}{(1-y)^3}\right] - \frac{a}{V} \tag{38}$$

which corresponds to the generalized equation with $w_1 = 0$, $w_2 = 0$.

Recently, Leland, Rowlinson, and Sather (25, 26) have used the Percus-Yevick approximation to support the argument that the prescriptions of eq. (A) and eq. (B) given in the introduction are the most appropriate to use in the one-fluid corresponding states treatment of mixtures. In order to apply the one-fluid principle of corresponding state, it is necessary to determine the pertinent set of constants a and b of the pure components for each set of w_1 and w_2. This can be done by solving the following equations for a and b without referring to any experimental values

$$\left(\frac{\partial P}{\partial y}\right)_{T_c} = 0 \qquad \text{and} \qquad \left(\frac{\partial^2 P}{\partial y^2}\right)_{T_c} = 0$$

where T_c is the critical temperature of the pure liquid.

For mixtures of simple globular molecules it has been shown that eq. (37b) and eq.(38) lead to results similar to those predicted by (G) and (LH,W).

Multiplying both sides of eq. (24b) by V (or rv), we obtain the following equation:

$$PV = RT\left(\frac{v^{\frac{1}{3}}}{v^{\frac{1}{3}} - v^{*\frac{1}{3}}}\right) - \frac{s\eta}{2v^{n+1}} \qquad (39a)$$

or

$$PV = RT\left[\frac{c}{1 - \left(\frac{V^*}{V}\right)^{\frac{1}{3}}}\right] - \frac{s\eta}{2V^{n+1}} \qquad (39b)$$

which in turn equal to

$$PV = RT\left(\frac{c}{1 - y^{\frac{1}{3}}}\right) - \frac{s\eta}{2V^{n+1}} \qquad (39c)$$

where $y = V^*/V$ (i.e. $b=4V^*$) and a is equivalent to $s\eta/2$. In fact, y is the reciprocal of the reduced volume, $\overline{V}$, since $y = b/4V = V^*/V = 1/\overline{V}$ which is usually smaller than one.

Apparently, eq. (39c) can not be reduced exactly to the general form of the equation of state, eq. (33), because of the appearance of the fraction power of y and the (n+1)th power of V. Besides, both c and y are functions of n too.

If the magnitudes of c and $s\eta/2$ in eq. (39c) are comparable with those of $1+y+y^2+w_1y^2+w_2y^3$ and a, respectively, in eq. (33), then the first term of eq. (39c) is always greater than that of eq. (33) because $y^{\frac{1}{3}} > y^3$. When $n>1$, $s\eta/(V^{n+1}) < a/V$, so that the value of PV calculated from eq. (39c) is always greater. When $n<1$, $s\eta/(V^{n+1}) > a/V$, and the value of PV is diminished by that of the second term. When $n=1$, the product of P and V from eq. (39c) is always greater than that from eq. (33).

However, I. Pollin* has calculated the product of P and V from eq. (39c) at various values of n and found that PV is independent of n.

7. The Reduced Properties and Characteristic Parameters of Pure Components:

Differentiating eq. (31) with respect to reduced temperature, $\overline{T}$, at constant reduced pressure, $\overline{P}$, and rearranging, we have

$$\left(\frac{\overline{T}}{\overline{V}}\right)\left(\frac{\partial \overline{V}}{\partial \overline{T}}\right)_{\overline{P}}(\overline{PV}^{n+1} + n^2) + \frac{\overline{PV}^{n+1} + n}{3(\overline{V}^3 - 1)} = \overline{PV}^{n+1} + n \qquad (40)$$

Differentiating eq. (31) with respect to reduced pressure, $\overline{P}$, at constant reduced temperature, $\overline{T}$, we have

$$-\left(\frac{\overline{P}}{\overline{V}}\right)\left(\frac{\partial \overline{V}}{\partial P}\right)_{\overline{T}}(\overline{V} - \frac{n^2}{\overline{P}}) + \frac{\overline{V}^{n+1} + \frac{n}{\overline{P}}}{3(\overline{V}^3 - 1)} = \overline{V}^{n+1} \qquad (41)$$

Differentiating eq. (31) with respect to reduced temperature, $\overline{T}$, at constant reduced volume, $\overline{V}$, we have

$$\overline{T}\left(\frac{\partial \overline{P}}{\partial \overline{T}}\right)_{\overline{V}} = \overline{P} + \frac{n}{\overline{V}^{n+1}} \qquad (42)$$

*I. Pollin just started to work for Prof. V. Fried on a similar topic.

From the definitions of the coefficient of thermal expansion, α, the coefficient of compressibility, β, and the thermal pressure coefficient, γ, and from eqs. (28), (29), and (30), the following expressions can be derived:

$$\alpha = \left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\bar{T}}{T\bar{V}}\right)\left(\frac{\partial \bar{V}}{\partial \bar{T}}\right)_{\bar{P}} \tag{43}$$

$$\beta = -\left(\frac{1}{V}\right)\left(\frac{\partial V}{\partial P}\right)_T = \left(\frac{\bar{P}}{P\bar{V}}\right)\left(\frac{\partial \bar{V}}{\partial \bar{P}}\right)_{\bar{T}} \tag{44}$$

$$\gamma = \frac{\alpha}{\beta} = \left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\bar{T}P}{T\bar{P}}\right)\left(\frac{\partial \bar{P}}{\partial \bar{T}}\right)_{\bar{V}} \tag{45}$$

To eliminate $(\partial\bar{V}/\partial\bar{T})_{\bar{P}}$, $(\partial\bar{V}/\partial\bar{P})_{\bar{T}}$, and $(\partial\bar{P}/\partial\bar{T})_{\bar{V}}$ from eqs. (40), (41), and (42), we solve eqs. (43), (44), (45) in terms of $(\partial\bar{V}/\partial\bar{T})_{\bar{P}}$, $(\partial\bar{V}/\partial\bar{P})_{\bar{T}}$, and $(\partial\bar{P}/\partial\bar{T})_{\bar{V}}$ and substitute these terms into eqs. (40), (41), (42), respectively, through which $\bar{T}$ is also eliminated. The substitution yields the following equations:

$$\frac{1}{\alpha T} = \frac{1}{3(\bar{V}^{\frac{1}{3}} - 1)} - \frac{n(n+1)}{\bar{P}\bar{V}^{n+1} + n} + 1 \tag{46a}$$

$$\frac{1}{\beta T} = \frac{1}{3(\bar{V}^{\frac{1}{3}} - 1)} - n\left(\frac{n}{\bar{P}\bar{V}^{n+1}} + 1\right) + n + 1 \tag{47}$$

and

$$\gamma = \left(\frac{P}{T}\right)\left(1 + \frac{n}{\bar{P}\bar{V}^{n+1}}\right) \tag{48}$$

Substitution of $P = \bar{P}P^*$ into eq. (47) results in

$$\frac{1}{\beta} = \frac{1}{3(\bar{V}^{\frac{1}{3}} - 1)} - n\left(\frac{1}{\bar{P}\bar{V}^{n+1}} + 1\right) + n+1 \tag{49a}$$

and

$$\gamma = \left(\frac{1}{T}\right)\left(P + \frac{nP^*}{\bar{V}^{n+1}}\right) \tag{50a}$$

respectively.

At low pressure, $\bar{P}$ is close to zero, and eqs. (46a), (49a), and (50) take the forms

$$\alpha T = \frac{3(\bar{V}^{\frac{1}{3}}-1)}{1 - 3n(\bar{V}^{\frac{1}{3}}-1)} \tag{46b}$$

$$\beta = \frac{\bar{T}\bar{V}^{n+1}}{nP^*} \tag{49b}$$

$$\gamma = \frac{nP^*}{\bar{V}^{n+1}T} \tag{50b}$$

respectively.

These equations furnish a simple way for evaluating the various characteristic and reduced parameters. Solving eq.

(46b) for $\overline{V}$, we have

$$\overline{V} = \left[\frac{T}{3(1+\alpha T)} + 1\right]^3 \tag{51}$$

Eq. (51) permits $\overline{V}$ to be computed from the coefficient of thermal expansion of liquids at low pressure. Thus, the characteristic volume, V^*, can therefore be calculated from V according to eq. (30). Substitution of $\overline{V}$ into eq. (32) yields T and hence T^* by eq. (29). The value of P^* may then be estimated from the limiting compressibility using eq. (49b). Alternatively, P^* may be obtained from the thermal pressure coefficient using eq. (50b).

Having evaluated these characteristic parameters V^*, T^*, and P^*, the primary parameters C and $s\eta$ are available from eq. (28) and (29):

$$s\eta = 2P^*V^{*n+1} = \frac{2\gamma TV^{n+1}}{n} \tag{52}$$

$$C = \frac{P^*V^*}{RT^*} \tag{53}$$

III. THERMODYNAMIC PROPERTIES OF BINARY MIXTURES

1. Basic Assumptions:

Flory's theory deals with liquids as composed of molecules with mutually interacting surface sites. According to this theory, the thermodynamic properties are related to the kinds of chemical segments of which the molecules are composed, the average contacting surface area per segment of each kind, and the average energy of segment-segment interaction per unit area for each type of contact. Let subscripts 1 and 2 represent the two components of a randomly mixed binary mixture and assume that molecules of the two components are divided into equal-sized segments so that $v_1^* = v_2^*$. The division of V^* into rv^* is for convenience only, and the size of a segment has no absolute significance. The corresponding number of contacting segments of components 1 and 2, r_1 and r_2 , shall be in the ratio of the respective molar hard core volume, V_1^* and V_2^*. In analogy, we take the number of contact sites $r_i s_i$ per molecule to be proportional to the surface area of a sphere of the same core volume. Thus

$$\frac{r_1}{r_2} = \frac{V_1^*}{V_2^*}$$

$$\frac{r_1 s_1}{r_2 s_2} = \left(\frac{V_1^*}{V_2^*}\right)^{-\frac{2}{3}}$$

$$\frac{s_1}{s_2} = \left(\frac{r_1}{r_2}\right)^{-\frac{1}{3}} = \left(\frac{V_1^*}{V_2^*}\right)^{-\frac{1}{3}}$$

2. Descriptions of Binary Mixtures by the Properties of its Components:

Consider a N-particle binary mixture in which N_1 is the number of molecules of component 1 and N_2 is that of component 2. As us obvious, $N = N_1 + N_2$. Let A_{11}, A_{12}, and A_{22} be the number of contact pairs between the respective species in one mole of substance, and let η_{11}/v^n, η_{12}/v^n, and η_{22}/v^n be the energies associated with each contact pair. The energy of the binary mixture is therefore

$$-E = (A_{11}\eta_{11} + A_{12}\eta_{12} + A_{22}\eta_{22})/v^n \qquad (54)$$

Since

$$2A_{11} + A_{12} = s_1 r_1 N_1 \qquad (55)$$

$$2A_{22} + A_{12} = s_2 r_2 N_2 \qquad (56)$$

eq. (54) can be written as

$$-E = (s_1 r_1 N_1 \eta_{11} + s_2 r_2 N_2 \eta_{22} - A_{12} \Delta\eta)/2v^n \quad (57)$$

where

$$\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12} \quad (58)$$

We next define the site fractions of the species of kind 1 and 2 for a binary mixture as:

$$\theta_2 = 1 - \theta_1 = \frac{s_2 r_2 N_2}{srN} \quad (59)$$

where

$$\bar{r} = \frac{r_1 N_1 + r_2 N_2}{N} \quad (60)$$

and

$$\bar{s} = \frac{s_1 r_1 N_1 + s_2 r_2 N_2}{rN} \quad (61)$$

Let us further assume that the probability of a species of kind 1 and 2 to be a neighbor of any given site is proportional to its site fraction θ_1 or θ_2; consequently,

$$A_{12} = s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1 \quad (62)$$

Combining eqs. (57), (59), (62), we

$$-\frac{E}{\bar{r}N} = \left(\frac{\bar{s}}{2v^n}\right)(\theta_1\eta_{11} + \theta_2\eta_{22} - \theta_1\theta_2\Delta\eta) \tag{63}$$

Substitution of eq. (58) into eq. (63) and rearrangement of the resulting equation yields

$$-\frac{E}{\bar{r}N} = \left(\frac{\bar{s}}{2v^n}\right)(\theta_1\eta_{11} + \theta_2\eta_{22} + 2\theta_1\theta_2\eta_{12}) \tag{64}$$

Let us introduce next the segment fractions φ_1 and φ_2 defined as

$$\varphi_1 = \frac{r_1N_1}{\bar{r}N} \tag{65}$$

$$\varphi_2 = 1 - \varphi_1 = \frac{r_2N_2}{\bar{r}N} \tag{66}$$

From this we may express $\bar{r}$, $\bar{s}$, θ_1, and θ_2 in terms of φ_1 and φ_2:

$$\frac{1}{\bar{r}} = \frac{\varphi_1}{r_1} + \frac{\varphi_2}{r_2} \tag{67}$$

$$\bar{s} = \varphi_1 s_1 + \varphi_2 s_2 \tag{68}$$

$$\theta_2 = \left(\frac{s_2}{\bar{s}}\right)\varphi_2 \qquad \text{and} \qquad \theta_1 = \left(\frac{s_1}{\bar{s}}\right)\varphi_1 \tag{69a}$$

Rearrangement of eq. (69a) gives

$$\varphi_2 = \left(\frac{\bar{s}}{s_2}\right)\theta_2 \qquad \text{and} \qquad \varphi_1 = \left(\frac{\bar{s}}{s_1}\right)\theta_1 \tag{69b}$$

By analogy to the characteristic pressure of the pure components [see eq. (25)], we define an interaction parameter, X_{12}, in the following way:

$$X_{12} = \frac{s_1 \Delta\eta}{2v^{*n+1}} \tag{70}$$

X_{12} has the dimension of pressure and can be expressed as energy per unit volume.

Applying eq. (19b) for a mixture, we have

$$-\frac{E}{\bar{r}N} = \frac{\bar{s}\,\eta}{2v^n} \tag{71a}$$

Making use of eq. (25) for binary mixtures and conbining it with eq. (71a), we obtain

$$-\frac{E}{\bar{r}N} = \frac{P^*v^*}{\tilde{v}^n} \qquad \text{or} \qquad E = -\frac{\bar{r}NP^*v^*}{\tilde{v}^n} \tag{71b}$$

Analogously, combination of eq. (26) and eq. (71a) yields

$$-\frac{E}{rN} = \frac{ckT^*}{\tilde{v}^n} \tag{71c}$$

where P^*, v^*, and T^* are the characteristic functions of the mixture, and c has the form of $c = \varphi_1 c_1 + \varphi_2 c_2$.

The characteristic pressure of the mixture, P^*, in terms of the characteristic pressure of the pure components, P_1^* and P_2^*, and the interaction parameter X_{12}, can be derived as follows:

Substitution of η_{11}, η_{22} from eq. (25) and $\Delta\eta$ from eq. (70) into eq. (63) results in

$$\left(\frac{\bar{s}}{\tilde{v}}\right)\left(\frac{\theta_1 P_1^* v_1^*}{s_1} + \frac{\theta_2 P_2^* v_2^*}{s_2} - \frac{\theta_1 \theta_2 X_{12}}{s_1}\right) = -\frac{E}{\tilde{r}N} \tag{72}$$

Then, upon substitution from eq. (69) and comparing with eq. (71b), we obtain for the characteristic pressure of a binary mixture as follows:

$$P^* = \varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1 \theta_2 X_{12} \tag{73}$$

From eqs. (71c) and (73) and from the formula that $c = \varphi_1 c_1 + \varphi_2 c_2$, the equation for the characteristic tempe-

rature of a mixture is derived in terms of X_{12}:

$$\frac{1}{T^*} = \frac{\frac{\varphi_1 P_1^*}{T_1^*} + \frac{\varphi_2 P_2^*}{T_2^*}}{\varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1 \theta_2 X_{12}} = \frac{\frac{\varphi_1 P_1^*}{T_1^*} + \frac{\varphi_2 P_2^*}{T_2^*}}{P^*} \tag{74a}$$

Consequently, the reduced temperature of the mixture, $\bar{T} = T/T^*$, is expressed as

$$\bar{T} = \frac{\bar{T}_1 \varphi_1 P_1^* + \bar{T}_2 \varphi_2 P_2^*}{\varphi_1 P_1^* + \varphi_2 P_2^* - \varphi_1 \theta_2 X_{12}} = \frac{\bar{T}_1 \varphi_1 P_1^* + \bar{T}_2 \varphi_2 P_2^*}{P^*} \tag{74b}$$

An expression relating the reduced volume of the mixturr to the reduced temperature and the characteristic pressure of the pure components is obtained from eq. (32) (when it is applied to a mixture) and eq. (74b):

$$\frac{n(\bar{v}^{\frac{1}{3}} - 1)}{\bar{V}^{n+\frac{1}{3}}} = \frac{\varphi_1 P_1^* \bar{T}_1 + \varphi_2 P_2^* \bar{T}_2}{\varphi_1 P_1 + \varphi_2 P_2 - \varphi_1 \theta_2 X_{12}}$$

$$= \frac{\varphi_1 P_1^* \bar{T}_1 + \varphi_2 P_2^* \bar{T}_2}{P^*} \tag{75}$$

Eqs. (74) and (75) provide a way to calculate the reduced properties of mixtures from the behavior of their

pure components if X_{12} is known. It can be evaluated from any measurable property of a solution.

It is evident from eq. (70) that, at constant temperature, X_{12} is only a function of the parameter n. To treat n as an adjustable parameter is just like to adjust X_{12} to its best representation of interaction.

3. Excess Enthalpy and Volume of Binary Mixtures:

(a). Excess Enthalpy of Mixing:

Excess functions are thermodynamic properties of solutions which are in excess of those of an ideal solution at the same conditions of temperature, pressure, and composition. For an ideal solution all excess functions are zero. The molar excess enthalpy of mixing of liquid solutions (essentially equal to the excess molar energy of mixing) is the difference between the enthalpy of one mole of solution and the sum of the molar enthalpies of its pure components; that is

$$H_{mixing} = H^E = H(mixture) - H(1) - H(2) \qquad (76)$$

Ignoring the difference between the energies and enthapies in condensed systems, we may write

$$H^E = E(\text{mixture}) - E(1) - E(2) \tag{77}$$

Combination of eqs. (65), (66), (71b), and (77) results in an equation expressing the excess enthalpy of mixing:

$$H^E = \overline{r}Nv^*\left(\frac{\varphi_1 P_1^*}{\tilde{V}_1^n} + \frac{\varphi_2 P_2^*}{\tilde{V}_2^n} - \frac{P^*}{\tilde{V}^n}\right) \tag{78}$$

Substitution for P^* from eq. (73) into eq. (78) yields

$$H^E = rNv^*\left[\varphi_1 P_1^*\left(\frac{1}{\tilde{V}_1^n} - \frac{1}{\tilde{V}^n}\right) + \varphi_2 P_2^*\left(\frac{1}{\tilde{V}_2^n} - \frac{1}{\tilde{V}^n}\right) + \frac{\varphi_1\theta_2 X_{12}}{\tilde{V}^n}\right] \tag{79}$$

This is an equation of general validity. In order to eliminate r, we substitute eqs. (65) and (66) into eq. (79) to obtain

$$H^E = N_1 P_1^* \nu_1^*\left(\frac{1}{\tilde{V}_1^n} - \frac{1}{\tilde{V}^n}\right) + N_2 P_2^* \nu_2^*\left(\frac{1}{\tilde{V}_2^n} - \frac{1}{\tilde{V}^n}\right) + \frac{N_1 V_1^* \theta_2 X_{12}}{\tilde{V}^n} \tag{80}$$

where $\nu_1^* = r_1 v_1^*$ and $\nu_2^* = r_2 v_2^*$, are the actual volumes of molecules 1 and 2, respectively.

Substituting $N_1 = x_1 N$ and $N_2 = x_2 N$ (x_1 and x_2 are mole fractions of components 1 and 2, and N is Avogadro's num-

ber, respectively) into eq. (80) and replacing $N\nu_1^*$ by the characteristic molar volume of component 1, V_1^*, and $N\nu_2^*$ by that of component 2, V_2^*, we obtain

$$H^E = x_1 P_1^* V_1^* \left(\frac{1}{\tilde{V}_1^n} - \frac{1}{\tilde{V}^n}\right) + x_2 P_2^* V_2^* \left(\frac{1}{\tilde{V}_2^n} - \frac{1}{\tilde{V}^n}\right) + \frac{x_1 V_1^* \theta_2 X_{12}}{\tilde{V}^n} \quad (81)$$

Substitution of eq. (60) and (68) into eq. (59) yields for the c ntact site fraction

$$\theta_2 = \frac{s_2 r_2 N_2}{(\varphi_1 s_1 + \varphi_2 s_2)(r_1 N_1 + r_2 N_2)} \quad (82a)$$

Dividing both the numerator and denominator of the right-hand side of eq. (82a) by $s_2 r_2 N$, we obtain

$$\theta_2 = \frac{x_2}{\varphi_1 \left(\frac{s_1}{s_2}\right) + \varphi_2 \left(\frac{r_1}{r_2}\right) x_1 + x_2} \quad (82b)$$

where

$$\frac{r_1}{r_2} = \frac{V_1^*}{V_2^*} \qquad \text{and} \qquad \frac{s_1}{s_2} = \left(\frac{V_1^*}{V_2^*}\right)^{-\frac{1}{3}}$$

The last term on the right hand side of eq. (81) represents the contribution from the contact interactions atrri-

butable to a difference in interacting energy between 1,2 pairs and the average of 1,1 and 2,2 contact pairs. It is the term similar to the contact energy, w_{12}, in the regular solution theory (13), and d_{12} in the theory of comformal solutions (15). As will be seen later in results and discussion, we designate the enthalpy resulting from this contact interaction as H^E_{cont}. The terms preceding it are referred to as the enthalpy resulting from the equation of state. The contribution from the equation of state depends on the reduced volume of the solution and the reduced volume of the pure components.

(b). Excess Volume of Mixing:

Likewise the way the reduced functions of pure components were defined, the excess reduced volume of solutions can be written as

$$V^E = \frac{V^E}{V^*} = \overline{V} - \overline{V}^o \qquad (83)$$

where V^E is the molar excess volume of mixing, V^E = V(mixture) - x_1V_1 - x_2V_2, $V^* = x_1V_1^* + x_2V_2^*$, and $\overline{V}^o$ = $(x_1V_1+x_2V_2)/(x_1V_1^*+x_2V_2^*)$ is the "ideal" reduced volume which is obtainable when additivity of volumes prevails. $\overline{V}^o$ can be expressed in terms of segment fraction φ_1 and φ_2 with

the assistance of the basic assumption that $(V_1^*/V_2^*)=(r_1/r_2)$ as follows:

$$\overline{V}^{o} = \frac{x_1\left(\frac{V_1}{V_2^*}\right)\left(\frac{V_1^*}{V_1^*}\right)+x_2\left(\frac{V_2}{V_2^*}\right)}{x_1\left(\frac{V_1^*}{V_2^*}\right)+x_2} = \frac{x_1\left(\frac{r_1}{r_2}\right)V_1+x_2V_2}{x_1\left(\frac{r_1}{r_2}\right)+x_2}$$

$$= \frac{N_1\left(\frac{r_1}{r_2}\right)\overline{V}_1+N_2\overline{V}_2}{N_1\left(\frac{r_1}{r_2}\right)+N_2} = \frac{r_1N_1\overline{V}_1+r_2N_2\overline{V}_2}{r_1N_1+r_2N_2}$$

$$= \varphi_1\overline{V}_1+\varphi_2\overline{V}_2 \qquad (84)$$

where the segment fraction φ_1 can be alternatively expressed as

$$\varphi_1 = \frac{N_1V_1^*}{N_1V_1^*+N_2V_2^*} = \frac{x_1V_1^*}{x_1V_1^*+x_2V_2^*}$$

4. Calculations of Excess Quantities:

These derived formulas enable one to calculate thermodynamic properties of a solution from other easily obtainable thermodynamic property. Either experimental excess volumes or excess enthalpies of mixing can be used for the evaluation

of the reduced volume of solutions and consequently X_{12}. The following procedure illustrates the calculations of H^E from the observed V^E and vice versa:

(a). Calculations of H^E from V^E:

Since measurements of V^E are experimentally easier to achieve, and also because these data are more available in the literature, it is more essential to find a way of estimating H^E or other excess thermodynamic properties from V^E of solutions. From eqs. (75) and (81), we have

$$H^E = \frac{x_1 P_1^* V_1^*}{\bar{V}_1^n} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2^n} - \frac{x_1 P_1^* V_1^* + x_2 P_2^* V_2^*}{\bar{V}^n} + \left(\frac{x_1 V_1^*}{\bar{V}^n}\right)\left[\frac{\varphi_1 P_1^* + \varphi_2 P_2^*}{\varphi_1} - \frac{\bar{V}^{n+\frac{1}{3}}(\varphi_1 P_1^* T_1^* + \varphi_2 P_2^* T_2^*)}{n\varphi_1(\bar{V}^{\frac{1}{3}} - 1)}\right] \qquad (85)$$

where $\bar{V}$ can be found from eq. (84).

Eq. (85) indicates that H^E is a function of n, $\bar{V}$ (or V^E), and the reduced and characteristic properties of the pure components. The parameters, P_i^*, V_i^*, $\bar{T}_i$, and $\bar{V}_i$ of the pure components for any given value of n can be evaluated by the method described previously. H^E calculated from eq. (85) for the various values of n are then compared with the value

of H^E of the mixture. The value of n for which H^E_{calc} agrees with H^E is then taken as the parameter characterizing the mixture under consideration. $\bar{V}$ evaluated from eq. (84) can also be adopted in the estimation of excess free energies and excess entropies. With the value of n fixed, the contact interaction contribution to the enthalpy of mixing can be evaluated from eq. (81).

(b). Calculation of V^E from H^E:

Solving eq. (75) for $\theta_2 X_{12}$ and substituting it into eq. (81), we obtain an equation which enables one to calculate $\bar{V}$ of binary mixtures from the observed value of H^E and from the properties of their respective pure components:

$$\left(\frac{n\varphi_1}{x_1 V_1^*}\right)\left[H^E - \frac{x_1 P_1^* V_1^*}{V_1^n} + \frac{x_2 P_2^* V_2^*}{V_2^n} + (\varphi_1 P_1^* \bar{T}_1 + \varphi_2 P_2^* \bar{T}_2)\right]\bar{V}^{n+\frac{1}{3}}$$

$$- \left(\frac{n\varphi_1}{x_1 V_1^*}\right)\left(H^E - \frac{x_1 P_1^* V_1^*}{\bar{V}_1^n} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2^n}\right)\bar{V}^n$$

$$- \left[n(\varphi_1 P_1^* + \varphi_2 P_2^*) - x_1 n\varphi_1 \frac{P_1^* V_1^* + P_2^* V_2^*}{x_1 V_1^*}\right]\bar{V}^{\frac{1}{3}}$$

$$- \left[\left(\frac{n\varphi_1}{x_1 V_1^*}\right)(x_1 P_1^* V_1^* + x_2 P_2^* V_2^*) - n(\varphi_1 P_1^* + \varphi_2 P_2^*)\right] = 0 \quad (86)$$

The value of $\bar{V}$ at any given value of n is found by a trial-and-error method. First a value of $\bar{V}$ which is expected to be smaller than the root of the equation is assigned for $\bar{V}$. The left-hand side of the equation is then calculated. $\bar{V}$ is then gradually increased by a small increment of 0.005 until the value of the left-hand side of eq. (86) changes its sign. One tenth of each previous increment is then repeatedly added to the last assigned value of $\bar{V}$-0.005 until the value of the left-hand side of eq. (86) falls within the range of ±0.0005 (any further change in $\bar{V}$ at this point does not have any significant change at all in the value of the left-hand side of the equation for four systems of various constituents tested for this purpose). The value of $\bar{V}$ so obtained is then employed to estimate V^E from eq. (84). All the calculations are done by a computer using a specially written program. The best-fit value of n is determined from comparison of V^E_{calc} with V^E.

The procedures described in (a) and (b) are applicable to any binary mixtures of any compositions.

IV. Results and Discussion

1. Application of the Modified Theory to the n-paraffin Hydrocarbons Mixtures:

The introduction of the adjustable parameter n makes the successful application of this modified Flory's theory to different types of molecules possible. The first group of mixtures used to test the proposed theory is the binary mixtures of normal paraffin hydrocarbons. Excess enthalpies and excess volumes of mixing for six normal paraffin hydrocarbon mixtures at various mole fractions and at several temperatures were examined. They are the following: $n\text{-}C_6H_{14}$—$n\text{-}C_{12}H_{26}$, $n\text{-}C_6H_{14}$—$n\text{-}C_{16}H_{34}$, $n\text{-}C_7H_{16}$—$n\text{-}C_{16}H_{34}$, $n\text{-}C_7H_{16}$—$n\text{-}C_{36}H_{74}$, $n\text{-}C_8H_{18}$—$n\text{-}C_{16}H_{34}$, and $n\text{-}C_8H_{18}$—$n\text{-}C_{24}H_{50}$.

(a). Physical Properties of the Pure n-paraffin Hydrocarbons:

Physical properties, such as density d, molar volume V, thermal expansion coefficient α, and thermal pressure coefficient γ, for the individual pure component at various temperature are shown in Table I. The values of d, α, and γ were calculated from the best-fit polynomial expressions based

Table I: Physical Properties of the Pure n-paraffin Hydrocarbons

Compound	T (°C)	d (g/ml)	V (ml/mole)	$\alpha \times 10^3$ (/deg)	γ (cal/ml·deg)
$n\text{-}C_6H_{14}$	20	0.65951	130.67	1.346	0.2012
	25	0.65530	131.51	1.391	0.1946
	30	0.65045	132.49	1.417	0.1882
	35	0.64585	133.43	1.441	0.1820
	40	0.64120	134.40	1.465	0.1760
	50	0.63175	136.41	1.513	0.1643
	51	0.63081	136.62	1.518	0.1632
$n\text{-}C_7H_{16}$	20	0.68354	146.60	1.243	0.2110
	25	0.67930	147.51	1.253	0.2040
	76	0.63483	157.85	1.429	0.1470
$n\text{-}C_8H_{18}$	20	0.70236	162.64	1.151	0.2185
	106	0.62919	181.55	1.426	0.1286
$n\text{-}C_{12}H_{26}$	20	0.74895	227.44	0.974	0.2440
$n\text{-}C_{16}H_{34}$	20	0.77330	292.83	0.878	0.2537
	25	0.76990	294.13	0.884	0.2468
	30	0.76650	295.43	0.890	0.2401
	35	0.76308	296.76	0.896	0.2337
	40	0.75966	298.09	0.903	0.2274
	50	0.75279	300.81	0.916	0.2155
	51	0.75210	301.09	0.917	0.2144
$n\text{-}C_{24}H_{50}$	106	0.74380	455.32	0.873	0.174
$n\text{-}C_{36}H_{74}$	76	0.78276	647.69	0.804	0.214

on the experimental temperature dependent data provided by Orwell and Flory (51). Molar volume were directly computed from their respective densities and molecular weights. γ of n-C_7H_{16} and n-$C_{12}H_{26}$, and d, α, and γ of n-$C_{24}H_{50}$; for which no accurate measurements are reported, were obtained by graphical interpolation from the behavior of their homologs as explained in reference (51).

(b). The Dependence of the Characteristic and Reduced Quantities of the Pure Components on the Exponent n:

Values of the characteristic quantities, V^*, P^*, T^* and the reduced quantity $\overline{V}$ of the pure components as a function of n (from n=0.90 to 1.50) at several temperatures are shown in Table II. The temperatures chosen are those at which both excess enthalpy and excess volume of mixing of a mixture have been investigated (52).

The variation of these parameters for n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}, and n-$C_{16}H_{34}$ with the value n at 20°C is graphically shown in Figs. 3, 4, 5, and 6, respectively. In these figures V^*, P^*, T^*, and $\overline{V}$ were plotted against the value n. These parameters all show substantial change with n at constant temperature. Following from this one may conclude that properties of pure liquids vary strongly with the value of n.

Table II: The Dependence of the Characteristic and Reduced Propertities of the Pure Components on n

1. Compound: $n\text{-}C_6H_{14}$

T (°C)	n	V^* (ml/mole)	T^* (°K)	P^* (cal/ml)	$\bar{V}$	$\bar{T}$	C
20	0.90	98.71	4697	112	1.3238	0.06241	1.18
	1.00	99.47	4430	102	1.3137	0.06618	1.15
	1.10	100.19	4213	93.7	1.3042	0.06959	1.12
	1.20	100.88	4033	86.8	1.2953	0.07269	1.09
	1.30	101.54	3882	81.0	1.2869	0.07552	1.07
	1.40	102.17	3753	76.0	1.2789	0.08048	1.04
	1.50	102.78	3643	71.7	1.2714	0.08048	1.02
25	0.90	98.63	4693	111	1.3334	0.06353	1.18
	1.00	99.42	4430	102	1.3227	0.06730	1.14
	1.10	100.18	4217	93.4	1.3127	0.07071	1.12
	1.20	100.91	4040	86.6	1.3033	0.07380	1.09
	1.30	101.60	3892	80.8	1.2944	0.07661	1.06
	1.40	102.26	3766	75.8	1.2860	0.07918	1.04
	1.50	102.90	3657	71.4	1.2781	0.08153	1.01
30	0.90	98.66	4692	111	1.3429	0.06461	1.17
	1.00	99.50	4434	101	1.3316	0.06837	1.14
	1.10	100.29	4224	93.1	1.3210	0.07177	1.11
	1.20	101.05	4050	86.3	1.3111	0.07485	1.08
	1.30	101.78	3904	80.5	1.3017	0.07764	1.06
	1.40	102.47	3780	75.5	1.2930	0.08019	1.03
	1.50	103.13	3674	71.1	1.2847	0.08252	1.01
35	0.90	98.69	4696	111	1.3520	0.06562	1.17
	1.00	99.57	4442	101	1.3401	0.06938	1.14
	1.10	100.40	4235	92.6	1.3290	0.07277	1.11
	1.20	101.19	4064	85.9	1.3186	0.07583	1.08
	1.30	101.95	3920	80.1	1.3088	0.07861	1.05
	1.40	102.67	3798	75.1	1.2996	0.08114	1.02
	1.50	103.36	3693	70.8	1.2909	0.08345	1.00
40	0.90	98.74	4702	110	1.3611	0.06660	1.16
	1.00	99.66	4451	100	1.3486	0.07036	1.13
	1.10	100.53	4247	92.2	1.3369	0.07374	1.10
	1.20	101.36	4078	85.4	1.3260	0.07678	1.06
	1.30	102.14	3937	79.7	1.3158	0.07954	1.04
	1.40	102.90	3817	74.7	1.3062	0.08205	1.01
	1.50	103.61	3713	70.4	1.2971	0.08434	0.99

(to be continued)

Table II (continued)

T (°C)	n	V* (ml/mole)	T* (°K)	P* (cal/ml)	$\overline{V}$	$\overline{T}$	C
50	0.90	98.89	4717	109	1.3794	0.06850	1.15
	1.00	99.89	4473	99.0	1.3656	0.07225	1.11
	1.10	100.83	4275	91.0	1.3528	0.07560	1.08
	1.20	101.73	4111	84.4	1.3409	0.07861	1.05
	1.30	102.59	3973	78.7	1.3297	0.08133	1.02
	1.40	103.40	3857	73.7	1.3192	0.08380	0.99
	1.50	104.18	3756	69.4	1.3094	0.08604	0.97
51	0.90	98.01	4719	109	1.3813	0.06869	1.15
	1.00	99.91	4475	98.9	1.3674	0.07243	1.11
	1.10	100.87	4278	90.9	1.3544	0.07578	1.07
	1.20	101.77	4114	84.3	1.3424	0.07879	1.05
	1.30	102.64	3977	78.6	1.3311	0.08151	1.02
	1.40	103.46	3861	73.7	1.3206	0.08620	0.97
	1.50	104.24	3760	69.4	1.3107	0.08620	0.97
2. Compound: $n\text{-}C_7H_{16}$							
20	0.90	112.75	4923	113	1.3003	0.05955	1.30
	1.00	113.51	4632	103	1.2916	0.06329	1.27
	1.10	114.23	4395	94.5	1.2833	0.06671	1.24
	1.20	114.93	4198	87.6	1.2756	0.06983	1.21
	1.30	115.60	4033	81.8	1.2682	0.07268	1.18
	1.40	116.24	3893	76.8	1.2612	0.07531	1.15
	1.50	116.85	3772	72.4	1.2546	0.07773	1.12
25	0.90	112.91	4943	112	1.3065	0.06032	1.28
	1.00	113.70	4654	102	1.2974	0.06417	1.25
	1.10	114.45	4418	93.7	1.2888	0.06749	1.22
	1.20	115.17	4223	86.9	1.2808	0.07060	1.19
	1.30	115.86	4059	81.1	1.2731	0.07345	1.17
	1.40	116.53	3920	76.1	1.2659	0.07607	1.14
	1.50	117.16	3799	71.8	1.2590	0.07848	1.11
76	0.90	112.75	4923	113	1.3003	0.05955	1.30
	1.00	113.51	4632	103	1.2916	0.06329	1.27
	1.10	114.23	4395	94.5	1.2833	0.06671	1.24
	1.20	114.93	4198	87.6	1.2756	0.06983	1.21
	1.30	115.60	4033	81.8	1.2682	0.07268	1.18
	1.40	116.24	3893	76.8	1.2612	0.07531	1.15
	1.50	116.85	3772	72.4	1.2546	0.07773	1.13

(to be continued)

Table II (continued)

T (°C)	n	V^* (ml/mole)	T^* (°K)	P^* (cal/ml)	$\overline{V}$	$\overline{T}$	C
3. Compound: n-C_8H_{18}							
20	0.90	126.88	5128	114	1.2818	0.05717	1.42
	1.00	127.65	4815	104	1.2741	0.06089	1.39
	1.10	128.38	4560	95.7	1.2668	0.06429	1.36
	1.20	129.09	4349	88.7	1.2599	0.06741	1.33
	1.30	129.76	4171	82.8	1.2534	0.07028	1.30
	1.40	130.41	4020	77.7	1.2471	0.07293	1.27
	1.50	131.04	3889	73.3	1.2412	0.07538	1.24
106	0.90	128.80	5307	104	1.4096	0.07145	1.27
	1.00	130.28	5045	94.7	1.3936	0.07515	1.23
	1.10	131.67	4833	87.0	1.3880	0.07845	1.19
	1.20	133.00	4658	80.6	1.3651	0.08139	1.16
	1.30	134.25	4512	75.1	1.3523	0.08404	1.12
	1.40	135.45	4387	70.4	1.3404	0.08643	1.09
	1.50	136.58	4280	66.2	1.3292	0.08859	1.06
4. Compound: n-$C_{12}H_{26}$							
20	0.90	182.71	5636	120	1.2448	0.05202	1.96
	1.00	183.57	5269	110	1.2390	0.05564	1.92
	1.10	184.40	4970	101	1.2334	0.05898	1.89
	1.20	185.20	4722	92.7	1.2281	0.06208	1.85
	1.30	185.97	4514	87.4	1.2230	0.06495	1.81
	1.40	186.71	4336	82.0	1.2182	0.06762	1.78
	1.50	187.42	4182	77.4	1.2135	0.07010	1.74
5. Compound: n-$C_{16}H_{34}$							
20	0.90	239.26	5999	121	1.2239	0.04887	2.43
	1.00	240.22	5595	111	1.2190	0.05240	2.39
	1.10	241.15	5265	102	1.2143	0.05568	2.34
	1.20	242.04	4991	94.2	1.2098	0.05874	2.30
	1.30	242.91	4760	87.9	1.2055	0.06159	2.26
	1.40	243.74	4563	82.5	1.2014	0.06424	2.22
	1.50	244.55	4393	77.8	1.1974	0.06673	2.18
25	0.90	239.42	6013	120	1.2285	0.04958	2.42

(to be continued)

Table II (continued)

T (°C)	n	V* (ml/mole)	T* (°K)	P* (cal/ml)	$\overline{V}$	$\overline{T}$	C
5. Compound: n-$C_{16}H_{34}$ (continued)							
25	1.00	240.41	5611	110	1.2234	0.05314	2.37
	1.10	241.37	5283	101	1.2186	0.05644	2.33
	1.20	242.30	5011	93.9	1.2139	0.05950	2.28
	1.30	243.20	4782	87.7	1.2094	0.06236	2.24
	1.40	244.06	4586	82.3	1.2052	0.06502	2.20
	1.50	244.90	4417	77.6	1.2010	0.06750	2.16
30	0.90	239.57	6028	102	1.2332	0.05029	2.41
	1.00	240.60	5628	110	1.2279	0.05387	2.36
	1.10	241.60	5302	101	1.2228	0.05718	2.31
	1.20	242.56	5031	93.6	1.2180	0.06026	2.27
	1.30	243.48	4803	87.4	1.2133	0.06312	2.23
	1.40	244.38	4609	82.0	1.2089	0.06578	2.19
	1.50	245.24	4441	77.3	1.2046	0.06827	2.15
35	0.90	239.74	6043	120	1.2379	0.05099	2.40
	1.00	240.81	5645	109	1.2324	0.05459	2.35
	1.10	241.84	5321	101	1.2271	0.05791	2.30
	1.20	242.84	5052	93.3	1.2221	0.06100	2.26
	1.30	243.80	4825	87.1	1.2173	0.06386	2.21
	1.40	244.72	4632	81.7	1.2126	0.06653	2.17
	1.50	245.62	4465	77.0	1.2082	0.06900	2.13
40	0.90	239.86	6055	120	1.2428	0.05172	2.38
	1.00	240.97	5659	109	1.2370	0.05533	2.33
	1.10	242.04	5337	100	1.2316	0.05867	2.29
	1.20	243.07	5070	93.0	1.2263	0.06177	2.24
	1.30	244.07	4845	86.8	1.2214	0.06464	2.20
	1.40	245.03	4653	81.4	1.2166	0.06830	2.16
	1.50	245.95	4487	76.8	1.2120	0.06979	2.12
50	0.90	240.18	6083	119	1.2524	0.05312	2.36
	1.00	241.38	5693	108	1.2462	0.05677	2.31
	1.10	242.52	5374	99.5	1.2403	0.06013	2.26
	1.20	243.63	5110	92.3	1.2347	0.06324	2.21
	1.30	244.69	4888	86.1	1.2294	0.06611	2.16
	1.40	245.72	4699	80.8	1.2242	0.06878	2.13
	1.50	246.70	4535	76.2	1.2193	0.07126	2.09

(to be continued)

Table II (continued)

T (°C)	n	V^* (ml/mole)	T^* (°K)	P^* (cal/ml)	$\bar{V}$	$\bar{T}$	C
5. Compound: n-$C_{16}H_{34}$ (continued)							
51	0.90	240.23	6087	119	1.2533	0.05325	2.36
	1.00	241.43	5697	108	1.2471	0.05690	2.31
	1.10	242.59	5379	99.5	1.2412	0.06026	2.26
	1.20	243.70	5115	92.2	1.2355	0.06337	2.21
	1.30	344.77	4893	86.1	1.2301	0.06625	2.17
	1.40	245.80	4704	80.8	1.2249	0.06891	2.12
	1.50	246.80	4540	76.2	1.2200	0.07139	2.08
6. Compound: n-$C_{24}H_{50}$							
106	0.90	356.46	6702	117	1.2773	0.05657	3.12
	1.00	358.56	6290	106	1.2699	0.6057	3.05
	1.10	360.56	5954	97.9	1.2628	0.06368	2.98
	1.20	362.48	5876	90.8	1.2561	0.06680	2.92
	1.30	364.33	5442	84.7	1.2497	0.06968	2.86
	1.40	366.11	5242	79.5	1.2437	0.07233	2.80
	1.50	367.82	5070	75.0	1.2379	0.07478	2.74
7. Compound: n-$C_{36}H_{74}$							
76	0.90	521.80	6780	125	1.2413	0.05150	4.85
	1.00	524.19	6336	114	1.2356	0.05511	4.75
	1.10	526.50	5975	105	1.2302	0.05844	4.65
	1.20	528.72	5675	97.3	1.2250	0.06153	4.56
	1.30	530.86	5422	90.8	1.2201	0.06440	4.47
	1.40	532.92	5206	85.2	1.2154	0.06707	4.39
	1.50	534.91	5020	80.4	1.2108	0.06955	4.31

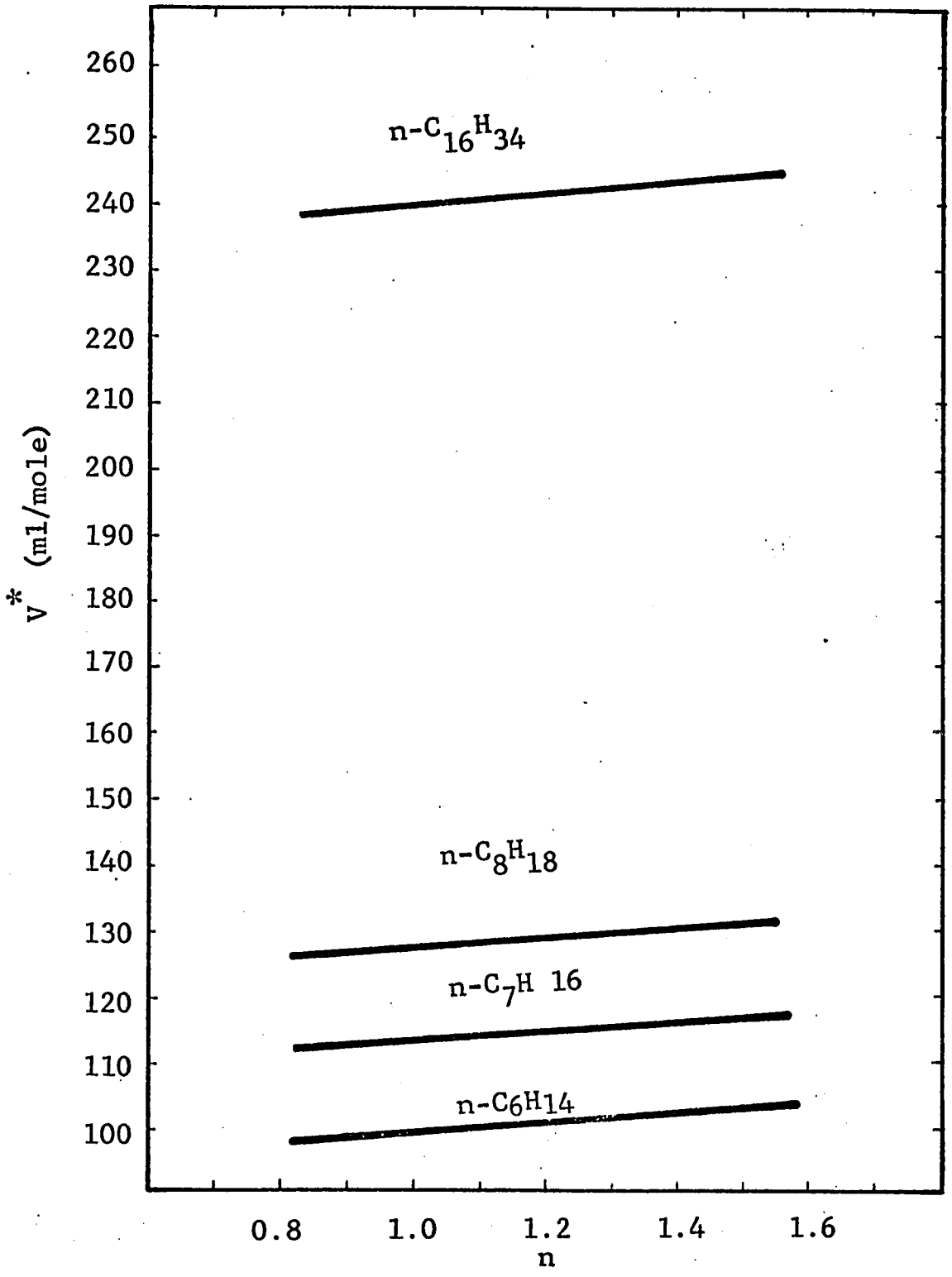

Fig. 3. The Change of the Characteristic Volume, V^*, with the Exponent n for the Pure Component, n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}, and n-$C_{16}H_{34}$ at 20°C.

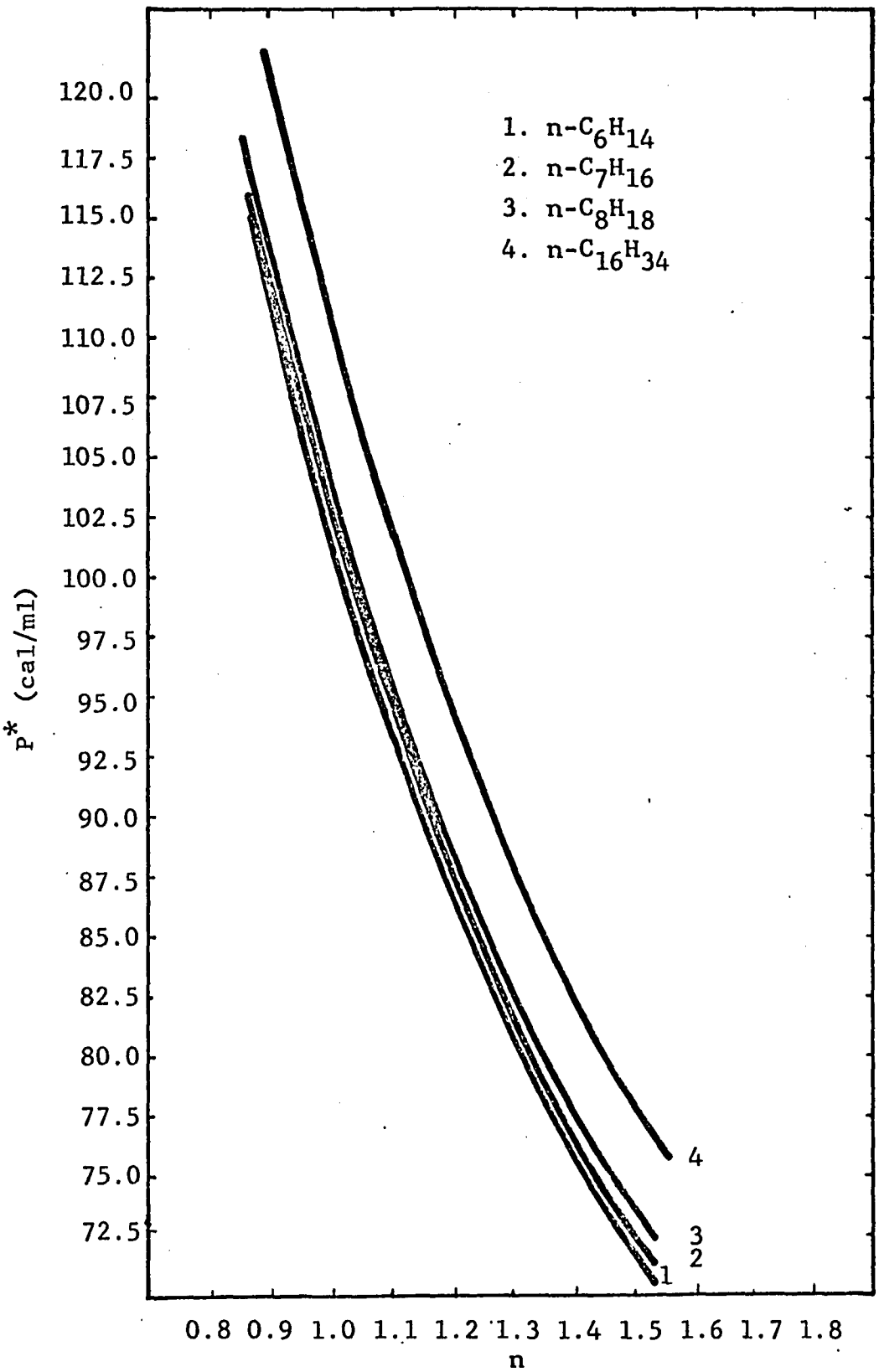

Fig. 4. The Change of the Characteristic Pressure, P^*, with the Exponent n for the Pure Components, n-C_6H_{14}, n-C_7H_{16}, n-C_8H_{18}, and n-$C_{16}H_{34}$ at 20°C.

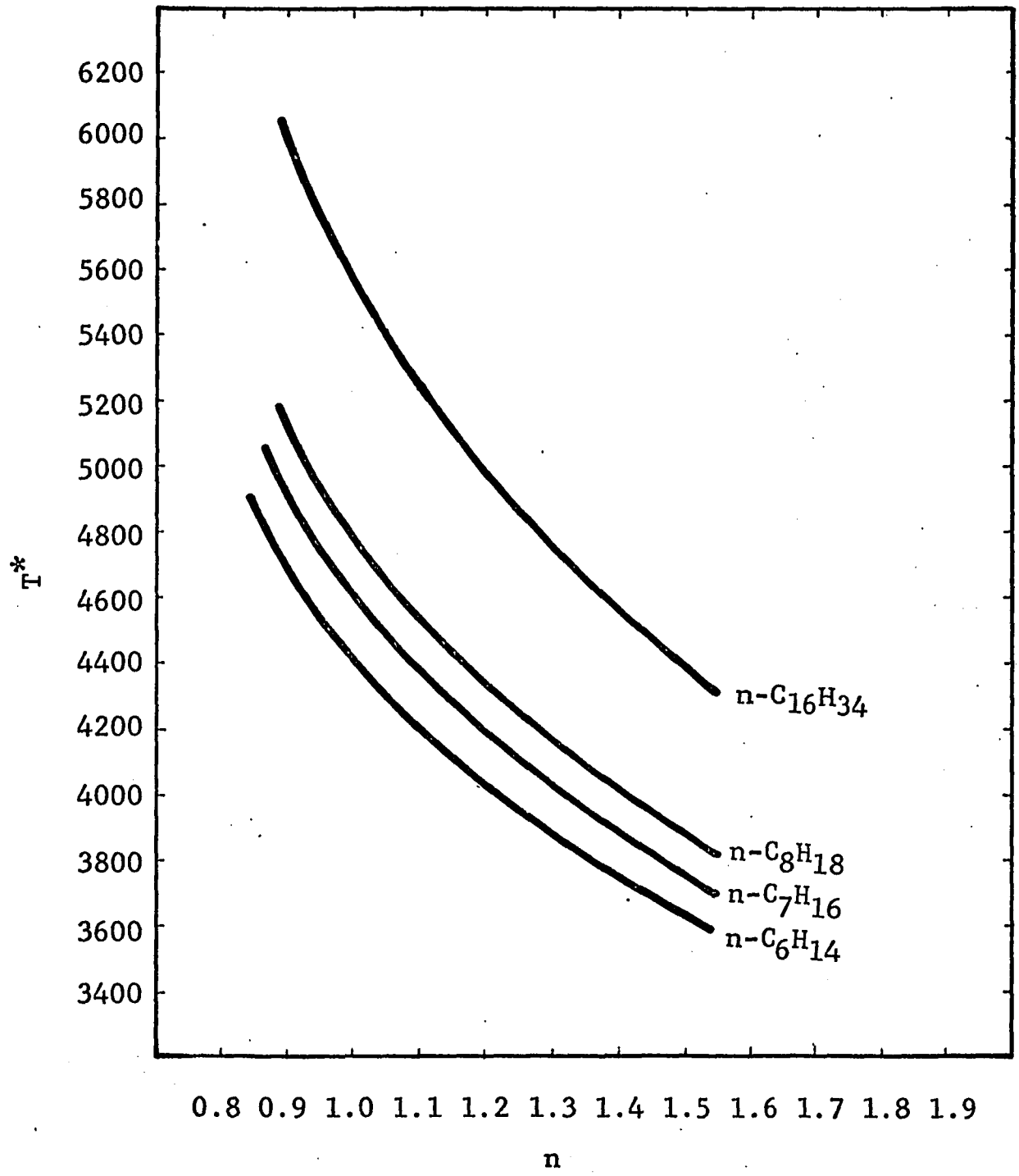

Fig. 5. The Change of the Characteristic Temperature, T^*, with the Exponent n for the Pure Components, n-C_6H_{14}, n-C_7H_{16}, and n-C_8H_{18}, and n-$C_{16}H_{34}$ at 20°C.

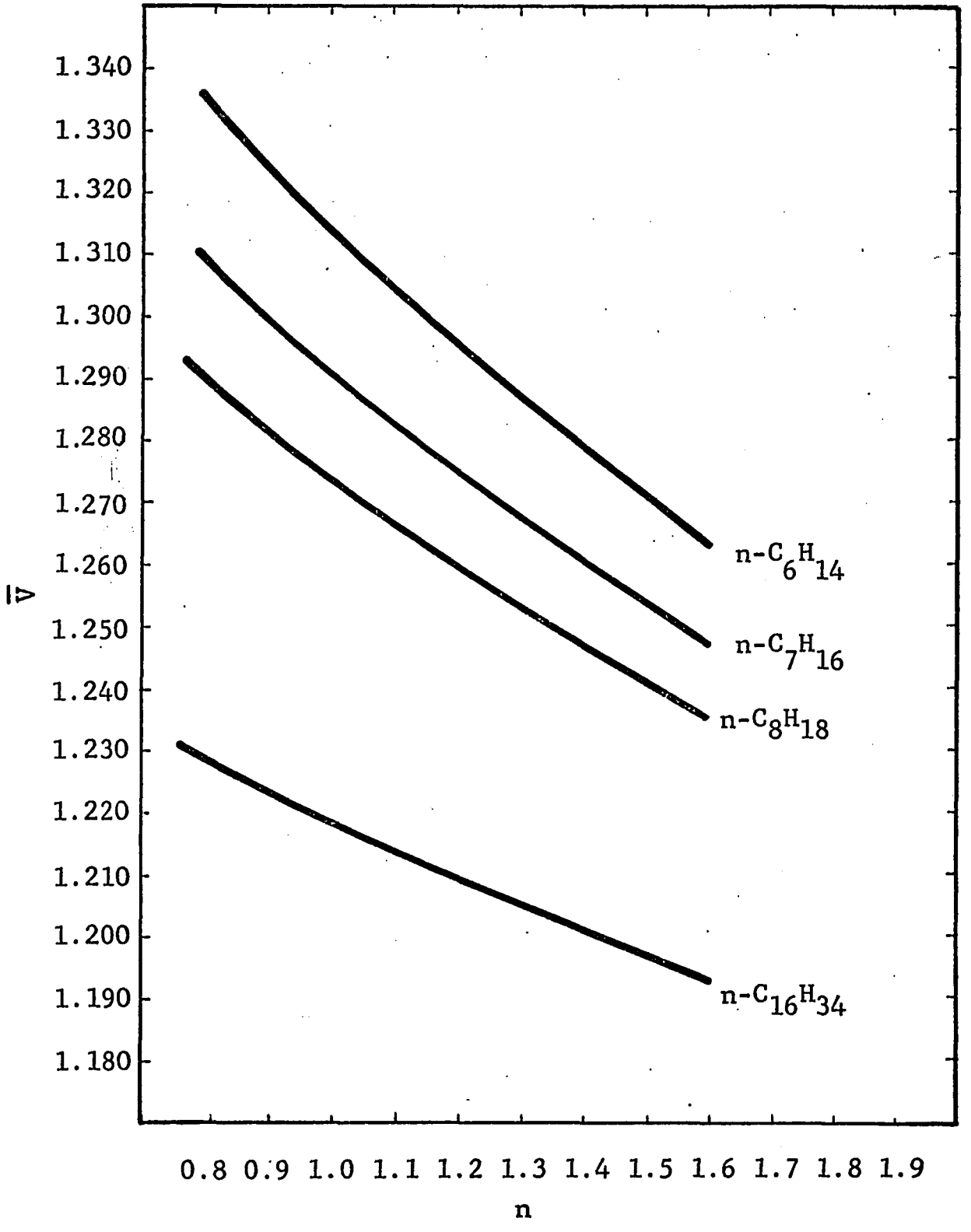

Fig. 6. The Change of the Reduced Volume, $\bar{V}$, with the Exponent n for the Pure Components, n-C_6H_{14}, n-C_7H_{16}, n-C_7H_{16}, and n-$C_{16}H_{34}$ at 20°C.

(c). The Dependence of the Characteristic and Reduced Quantities of the Pure Components on Temperature:

The characteristic and reduced quantities, V^*, P^*, T^*, and $\bar{V}$ at n = 1.29 [see section (d); the estimated value of n characterizing the mixtures of n-paraffin hydrocarbons] of n-C_6H_{14}, n-C_8H_{18}, and n-$C_{16}H_{34}$, the components of those binary mixtures whose excess enthalpies and volumes are available in the literature at more than on temperature, are shown in Table III. The effet of temperature on these quantities is clearly shown in Figs. 7, 8, 9, and 10, respectively. V^* shows very small increase with temperature. Since V increases faster with temperature than V^*, $\bar{V}$ shows a greater rate of increase with temperature. The small change of T^* with temperature is, however, significant. This affects directly the increase of V^* with T. In fact, eq. (17) and eq. (24) require that

$$d\ln T^*/dT = (1/\alpha T)(d\ln V^*/dT) \qquad (87)$$

Values of the parameter $C = P^*V^*/RT^*$, expressing the effective number of external degrees of freedom per molecule, are listed in the last column of Table II. They are of incidental interest for the purpose of this work.

Table III: The Change of the Characteristic and Reduced Properties with Temperature at n=1.29

Compound	T (°C)	V^* (ml/mole)	T^* (°K)	P^* (cal/ml)	$\overline{V}$	$\overline{T}$	C
$n\text{-}C_6H_{14}$	20	101.48	3896	81.6	1.2877	0.07525	1.07
	25	101.53	3906	81.3	1.2953	0.07634	1.06
	30	101.71	3918	81.0	1.3027	0.07738	1.06
	35	101.80	3947	81.0	1.3097	0.07834	1.05
	40	102.08	3950	80.2	1.3168	0.07928	1.04
	50	102.50	3986	79.2	1.3308	0.08107	1.02
	51	102.55	3990	79.1	1.3322	0.08125	1.02
$n\text{-}C_8H_{18}$	20	129.68	4188	83.4	1.2540	0.07001	1.30
	106	134.01	4539	76.1	1.3548	0.08353	1.13
$n\text{-}C_{16}H_{34}$	20	242.97	4793	88.4	1.2052	0.06116	2.25
	25	243.11	4803	88.3	1.2099	0.06208	2.25
	30	243.39	4825	87.9	1.2138	0.06284	2.23
	35	243.61	4868	88.2	1.2182	0.06359	2.22
	40	243.97	4866	87.3	1.2218	0.06434	2.20
	50	244.59	4908	86.7	1.2299	0.06583	2.17
	51	244.67	4913	86.7	1.2306	0.06597	2.17

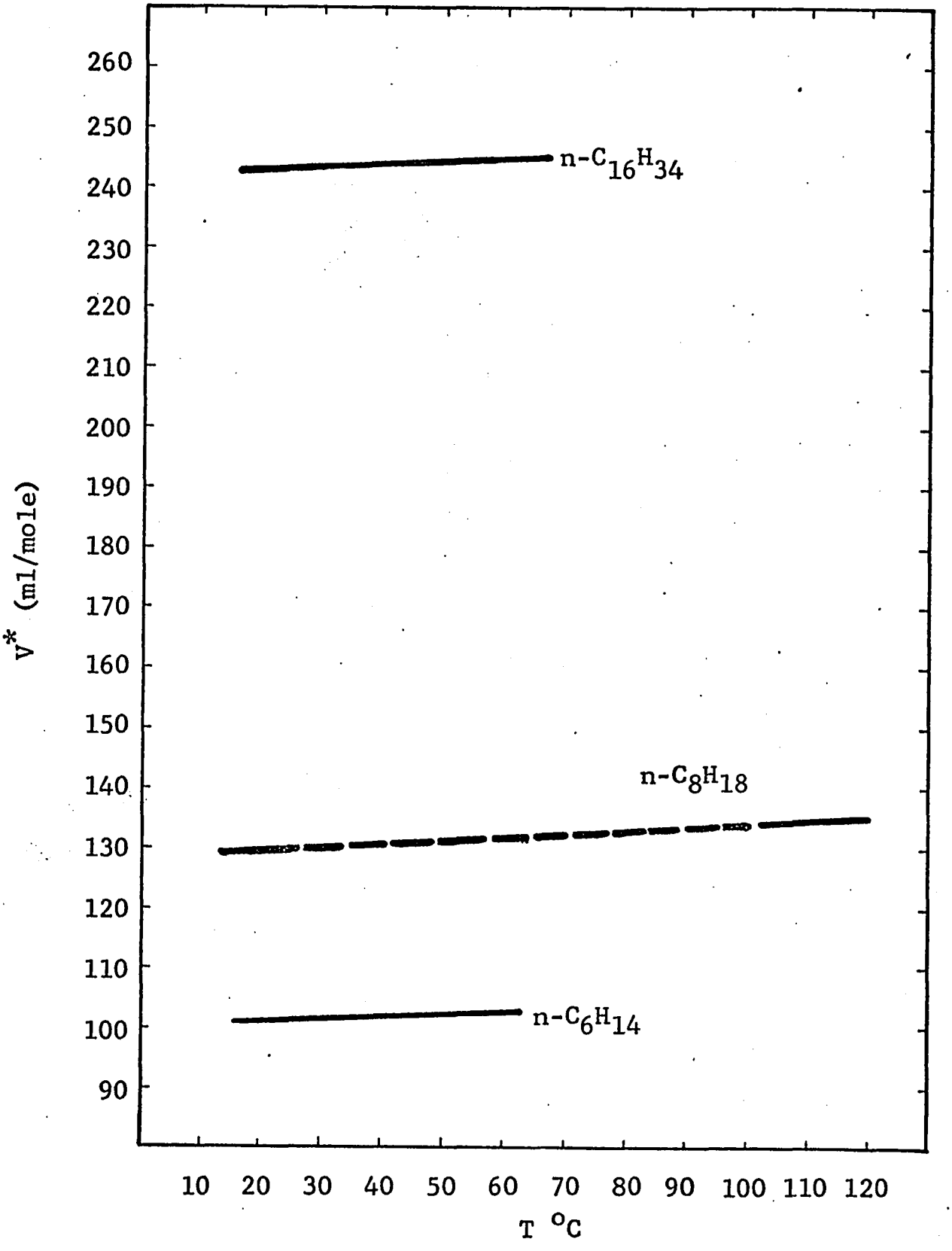

Fig. 7. The Dependence of the Characteristic Volume, V^*, of the Pure Components, n-C_6H_{14}, n-C_8H_{18}, and n-$C_{16}H_{34}$, on Temperature at n = 1.29.

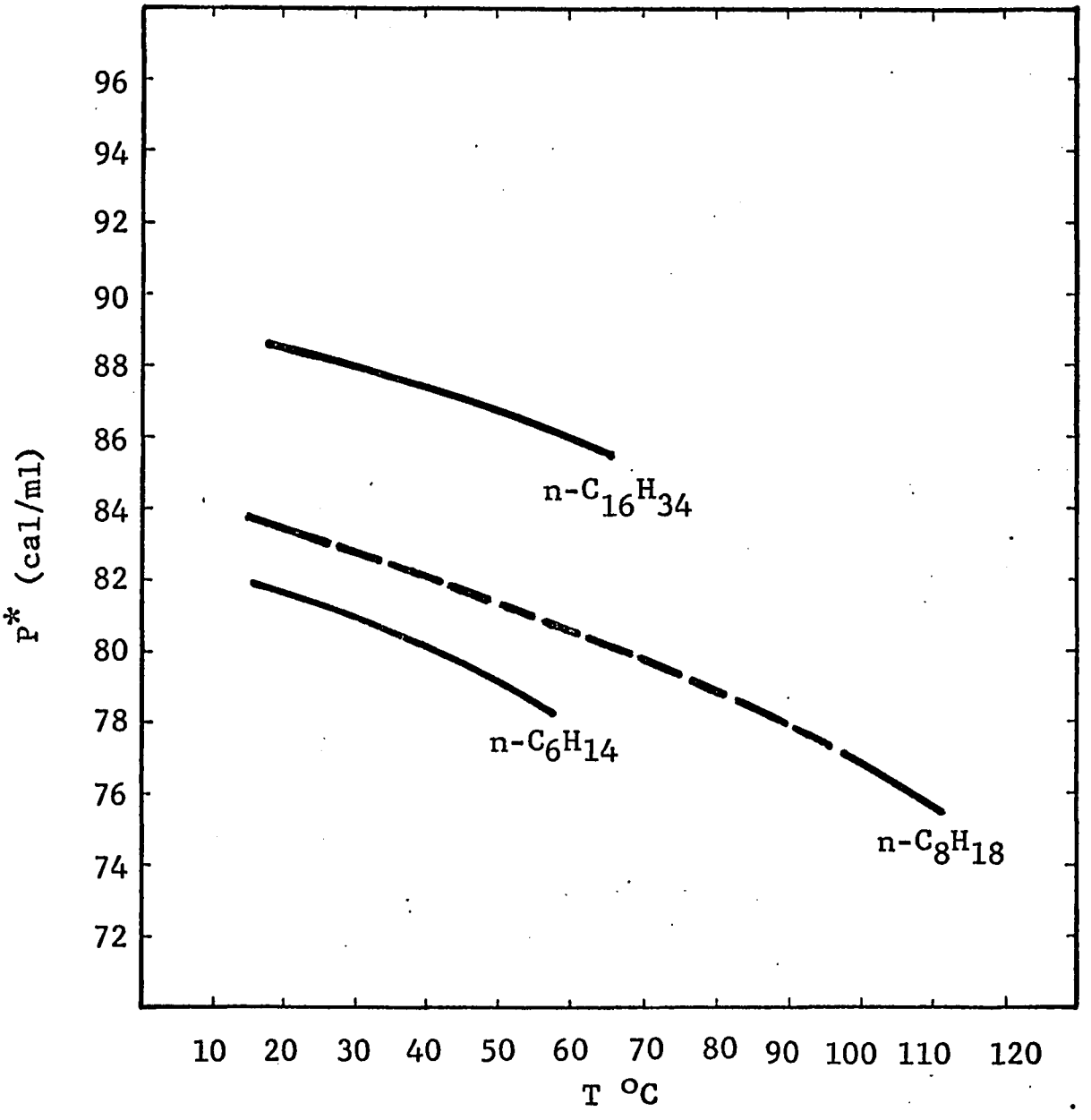

Fig. 8. The Dependence of the Characteristic Pressure, P^*, of the Pure Components, n-C_6H_{14}, n-C_8H_{18}, and n-$C_{16}H_{34}$, on Temperature at n = 1.29.

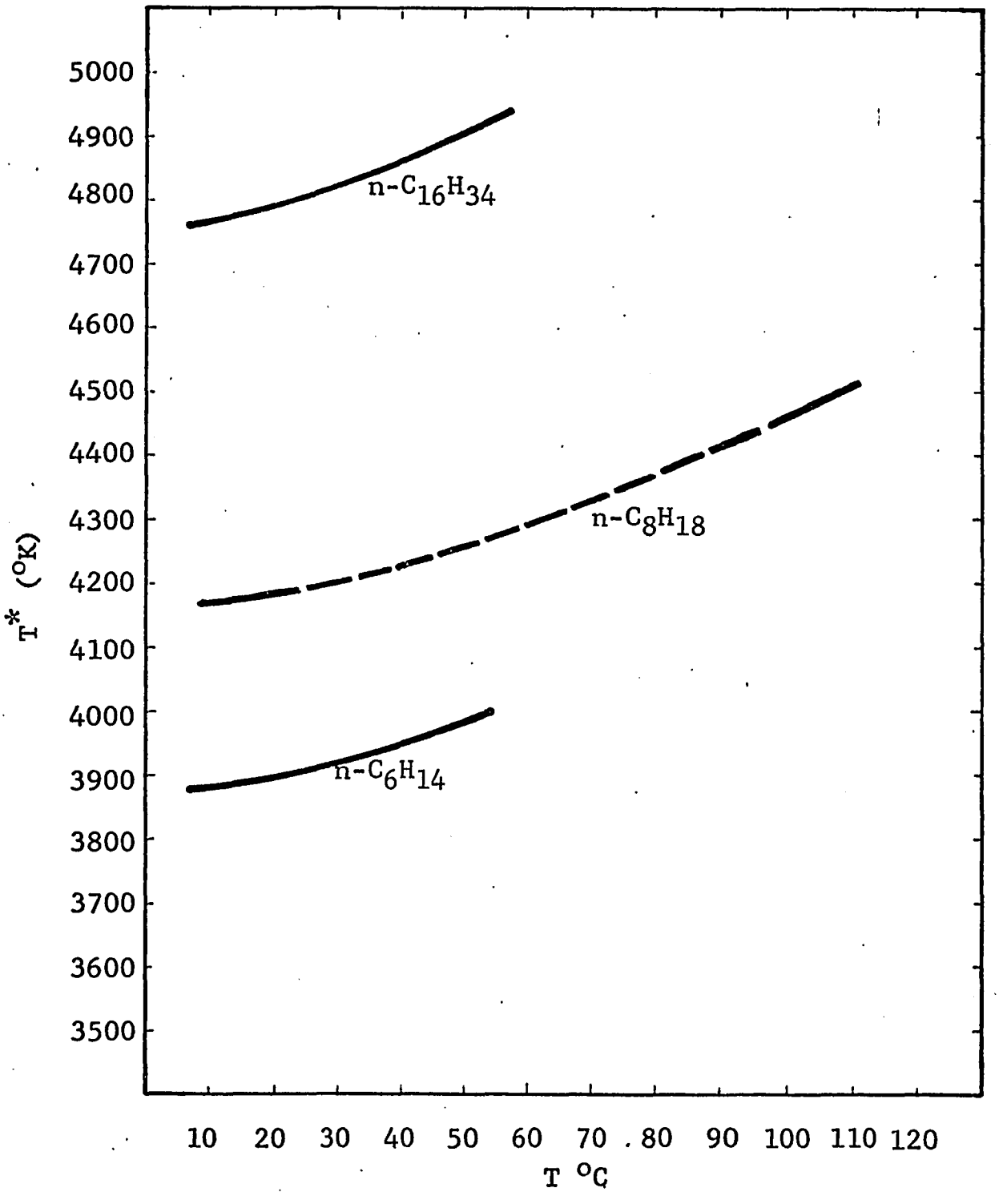

Fig. 9. The Dependence of the Characteristic Temperature, T , of the Pure Components, n-C_6H_{14}, n-C_8H_{18}, and n-$C_{16}H_{34}$, on Temperature at n = 1.29.

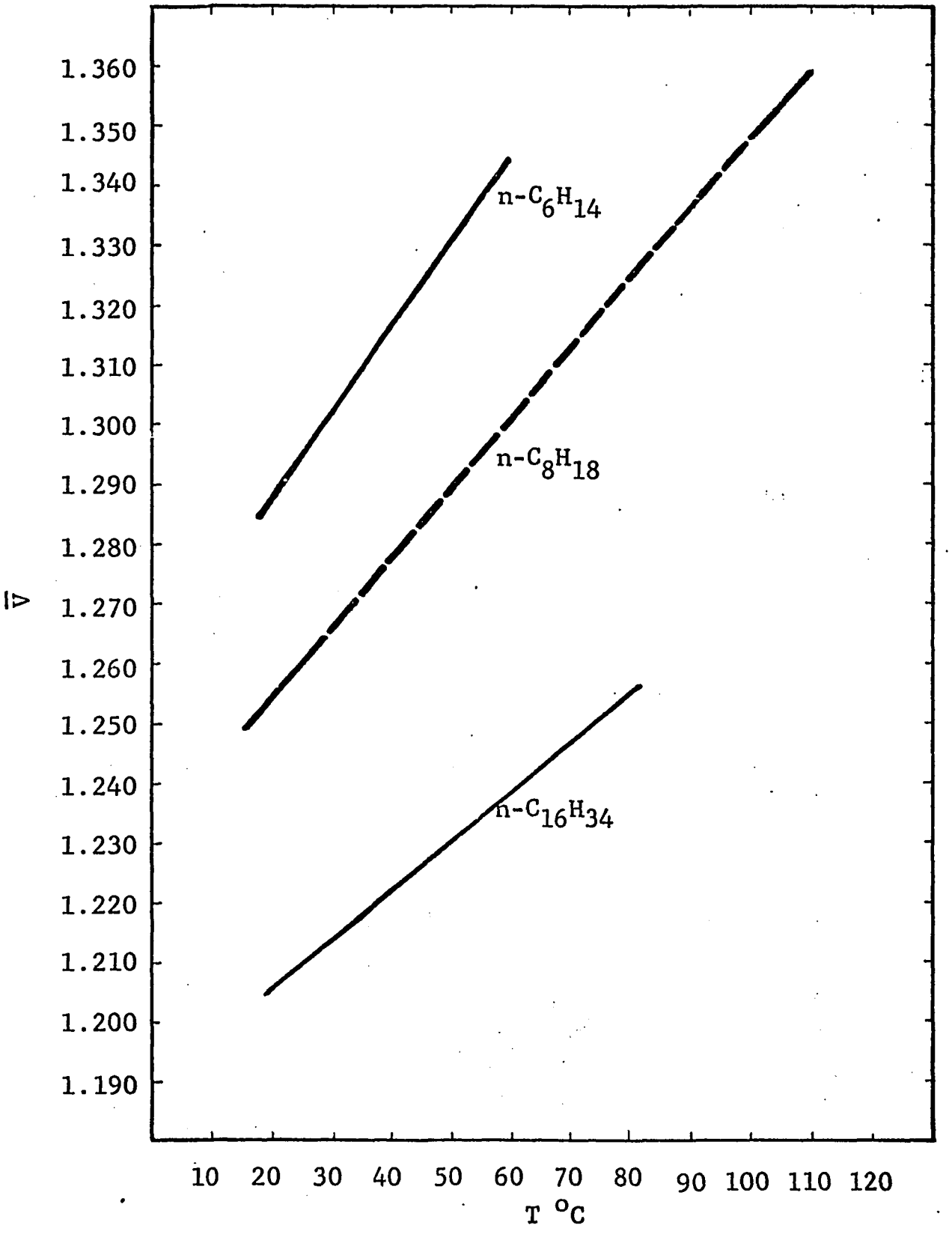

Fig. 10. The Dependence of the Reduced Volume, $\bar{V}$, of the Pure Components, n-C_6H_{14}, n-C_8H_{18}, and n-$C_{16}H_{34}$, on Temperature at n = 1.29.

(d). The Evaluation of the Value of the Exponent n for the Equal Molar Mixtures:

Table IV shows the enthalpy of mixing at equal molar concentration at each iterated value of n ranging between 0.90 and 1.60 for the afore-mentioned six systems at various temperatures. Also shown in Table IV are $\bar{V}$ calculated from eq. (85) and the contact interaction energy, H^E_{cont}, defined as $x_1V_1\theta_2X_{12}/\bar{V}^n$, in which subscript 1 refers to the component with fewer number of carbon atoms in the molecule, at their correponding values of n.

The change of $\bar{V}$ with n for the system n-C_6H_{14}—n-$C_{16}H_{34}$ at x_1=0.5 at several temperatures and for the systems n-C_6H_{14}—n-$C_{12}H_{26}$, n-C_6H_{14}—n-$C_{16}H_{34}$, n-C_7H_{16}—n-$C_{16}H_{34}$, and n-C_8H_{18}—n-$C_{16}H_{34}$, all at x_1= 0.5 at 20°C is graphically shown in Figs. 11 and 12, respectively. The dependence of $\bar{V}$ on both temperature and n, for these binary mixtures is of the same nature as for the pure components.

It is apparent from Table IV that H^E_{calc}, the enthalpy of mixing calculated, decreases sharply as the value of n increases. Since the change in H^E_{calc} corresponding to a change in n of 0.10 (see column 1 of Table IV) is large, values of H^E_{calc} corresponding to smaller increments in n are necessary in order to be able to evaluate the value of n for which $H^E_{calc} = H^E$. In practice, H^E_{calc} corresponding to con-

Table IV: The Dependence of the Excess Enthalpy of Mixing at $x_1 = 0.50$ On the Exponent n

n	$\overline{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
1. System: $n\text{-}C_6H_{14}$—$n\text{-}C_{12}H_{26}$, T = 20°C				
H^E = 11 cal/mole (53,54), V^E = -0.31 ml/mole				
0.90	1.2703	34.2	32.7	1.37
1.00	1.2630	26.6	26.2	1.11
1.10	1.2562	20.5	21.0	0.90
1.20	1.2496	15.3	16.7	0.72
1.30	1.2434	11.1	13.4	0.58
1.40	1.2375	7.4	10.5	0.46
1.50	1.2319	4.3	8.1	0.36
2. System: $n\text{-}C_6H_{14}$—$n\text{-}C_{16}H_{34}$, T = 20°C				
H^E = 30 cal/mole (56), V^E = -0.48 ml/mole (57)				
0.90	1.2502	66.4	63.4	2.44
1.00	1.2439	52.8	51.5	2.01
1.10	1.2378	41.4	41.9	1.65
1.20	1.2321	32.2	34.1	1.35
1.30	1.2267	25.5	27.7	1.11
1.40	1.2215	17.9	22.5	0.908
1.50	1.2165	12.2	18.0	0.733
T=25°C, H^E=27 cal/mole (58), V^E=-0.53 ml/mole (59)				
0.90	1.2560	66.6	64.2	2.48
1.00	1.2494	52.4	51.8	2.03
1.10	1.2431	40.8	41.9	1.66
1.20	1.2371	31.2	33.9	1.35
1.30	1.2314	23.2	27.4	1.10
1.40	1.2260	16.4	22.0	0.89
1.50	1.2208	10.6	16.4	0.71
T=30°C, H^E=23 cal/mole (60), V^E=-0.58 ml/mole (57)				
0.90	1.2618	64.7	63.3	2.46
1.00	1.2548	50.2	50.7	1.99
1.10	1.2482	38.3	40.6	1.61
1.20	1.2420	28.5	32.6	1.30
1.30	1.2360	20.4	26.0	1.05
1.40	1.2304	13.5	20.5	0.83
1.50	1.2250	7.5	15.8	0.65

(to be continued)

Table IV (continued)

n	$\overline{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
T=35°C, H^E=19 cal/mole (60), V^E=-0.62 ml/mole (59)				
0.90	1.2675	66.4	65.1	2.54
1.00	1.2602	51.3	52.1	2.05
1.10	1.2534	38.8	41.5	1.65
1.20	1.2468	28.6	33.1	1.33
1.30	1.2407	20.3	26.4	1.07
1.40	1.2348	13.0	20.7	0.85
1.50	1.2292	6.8	15.9	0.65
T=40°C, H^E=16 cal/mole (61), V^E=-0.69 ml/mole (57)				
0.90	1.2732	58.7	59.5	2.33
1.00	1.2656	43.7	46.7	1.85
1.10	1.2585	31.5	36.6	1.46
1.20	1.2517	21.4	28.4	1.14
1.30	1.2452	13.1	21.8	0.89
1.40	1.2391	5.9	16.2	0.66
1.50	1.2333	- 0.3	11.5	0.48
T=50°C, H^E= 8 cal/mole (60), V^E=-0.82 ml/mole (57)				
0.90	1.2846	51.9	55.3	2.18
1.00	1.2764	36.5	42.4	1.68
1.10	1.2686	23.8	32.0	1.29
1.20	1.2612	13.4	23.7	0.96
1.30	1.2543	4.8	17.0	0.70
1.40	1.2477	- 2.5	11.5	0.47
1.50	1.2414	- 8.8	6.8	0.28
T=51°C, H^E= 9 cal/mole (61), V^E=-0.82 ml/mole (61)				
0.90	1.2858	55.4	58.1	2.29
1.00	1.2775	39.4	44.7	1.78
1.10	1.2697	26.6	34.2	1.37
1.20	1.2622	15.9	25.6	1.04
1.30	1.2552	7.0	18.7	0.76
1.40	1.2486	- 0.5	13.0	0.53
1.50	1.2460	- 7.0	8.2	0.34

(to be continued)

Table IV (continued)

n	$\overline{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
3. System: $n\text{-}C_7H_{16}$—$n\text{-}C_{16}H_{34}$				
T=20 °C, H^E=26 cal/mole (62), V^E=-0.31 ml/mole (55)				
0.90	1.2466	57.5	52.9	1.84
1.00	1.2405	47.1	43.8	1.54
1.10	1.2348	38.5	36.2	1.29
1.20	1.2293	31.4	30.2	1.08
1.30	1.2240	25.5	25.3	0.92
1.40	1.2190	20.5	21.2	0.77
1.50	1.2142	16.1	17.6	0.65
T=25 °C, H^E=23 cal/mole (63), V^E=-0.34 ml/mole (55)				
0.90	1.2516	54.8	50.7	1.77
1.00	1.2453	44.3	41.5	1.46
1.10	1.2393	35.8	34.2	1.22
1.20	1.2335	28.7	28.2	1.01
1.30	1.2313	22.7	23.3	0.85
1.40	1.2229	17.7	19.2	0.70
1.50	1.2179	13.4	15.8	0.58
4. System: $n\text{-}C_7H_{16}$—$n\text{-}C_{36}H_{74}$				
T=76 °C, H^E=31 cal/mole (61), V^E=-1.56 ml/mole (61)				
0.90	1.2622	156.4	148.5	4.38
1.00	1.2551	116.4	114.4	3.40
1.10	1.2484	84.4	87.7	2.63
1.30	1.2361	35.6	28.5	1.48
1.40	1.2303	16.9	34.1	1.05
1.50	1.2243	1.2	22.3	0.69
5. System: $n\text{-}C_8H_{18}$—$n\text{-}C_{16}H_{34}$				
T=20 °C, H^E=21 cal/mole (62), V^E=-0.19 ml/mole (55)				
0.90	1.2429	43.5	39.4	1.25
1.00	1.2371	36.1	32.7	1.05
1.10	1.2315	30.1	27.5	0.89
1.20	1.2262	25.1	23.3	0.76
1.30	1.2212	20.9	19.6	0.65
1.40	1.2163	17.6	16.9	0.57
1.50	1.2117	14.5	14.3	0.49

(to be continued)

Table IV (continued)

n	$\bar{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
6. System: $n\text{-}C_8H_{18}$—$n\text{-}C_{24}H_{50}$				
T=106°C, H^E= -6 cal/mole (61), V^E=-1.33 ml/mole (61)				
0.90	1.3069	60.1	65.6	1.95
1.00	1.2974	38.3	47.8	1.44
1.10	1.2884	20.7	33.9	1.03
1.20	1.2800	6.1	22.6	0.69
1.30	1.2720	- 6.0	13.6	0.42
1.40	1.2645	-16.4	6.1	0.19
1.50	1.2574	-25.0	0.1	0.00

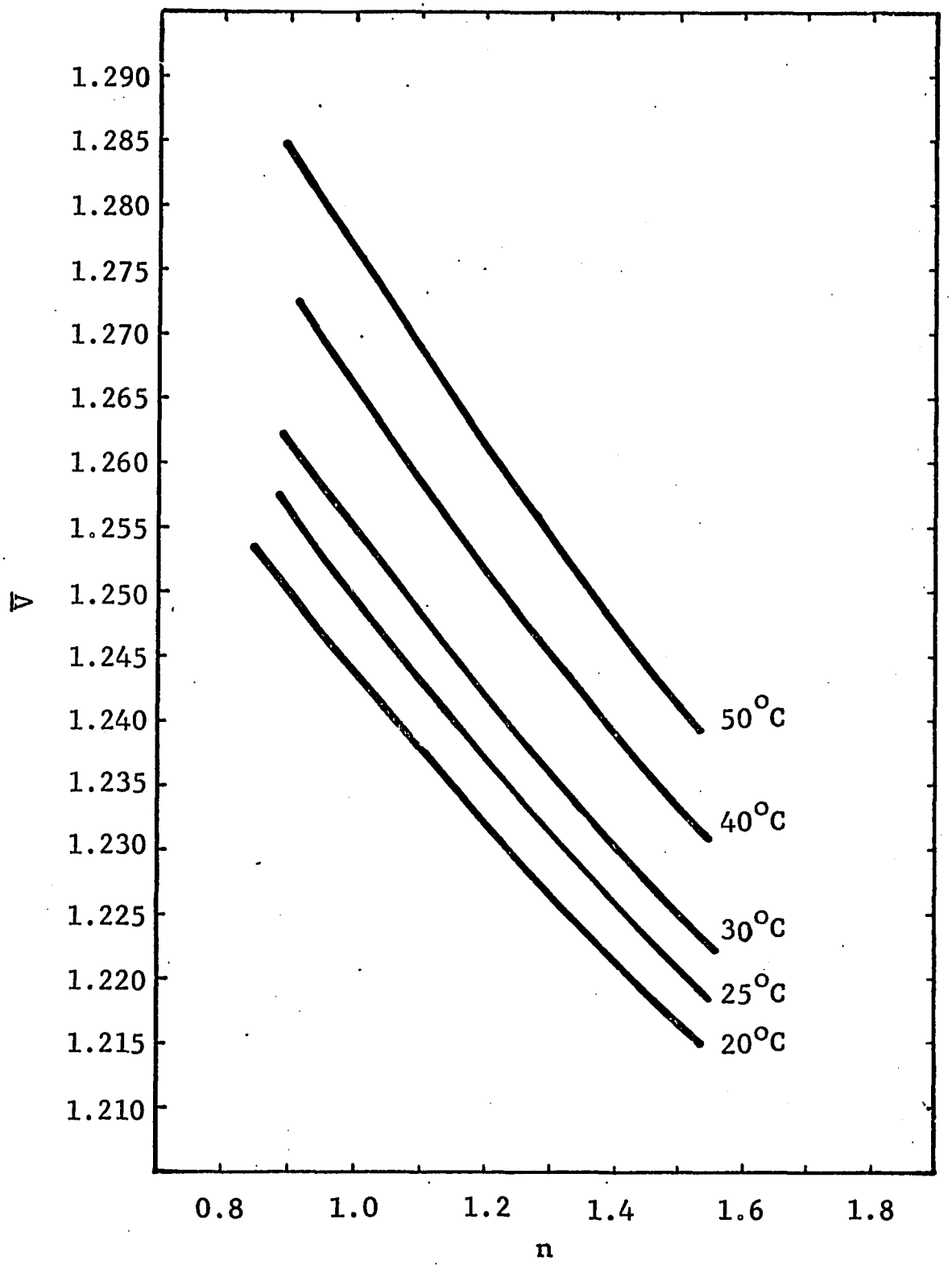

Fig. 11. The Dependence of the Reduced Volume, $\bar{V}$, of the System n-C_6H_{14}—n-$C_{16}H_{34}$ on the Exponent n at Various Temperatures.

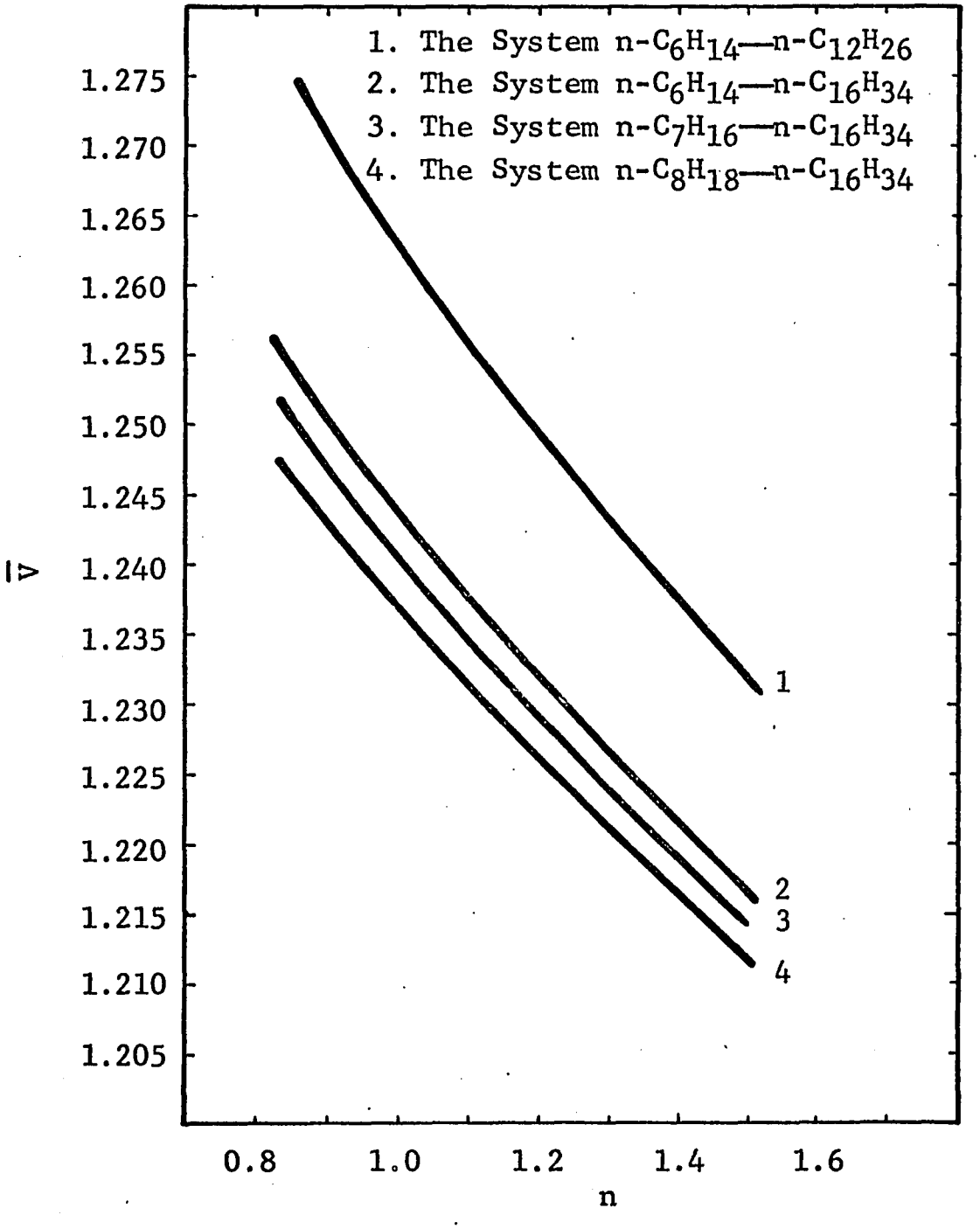

Fig. 12. The Dependence of the Reduced Volume, $\bar{V}$, of the Systems 1. n-C_6H_{14}—n-$C_{12}H_{26}$, 2. n-C_6H_{14}—n-$C_{16}H_{34}$, 3. n-C_7H_{16}—n-$C_{16}H_{34}$, and 4. n-C_8H_{18}—n-$C_{16}H_{34}$ on the Exponent n at 20°C.

tinuous n with an interval of 0.02, and if necessary, of 0.01 were calculated. The best-fit values of n so evaluated for the six above mentioned systems at their respective temperatures are listed in the third column of Table V. The uncertainty in n is expected to be less than 0.01. The value of n may also be evaluated graphically as shown in Fig. 13 for the systems n-C_6H_{14}—n-$C_{12}H_{26}$, n-C_6H_{14}—n-$C_{16}H_{34}$, n-C_7H_{16}—n-$C_{16}H_{34}$, and n-C_8H_{18}—n-$C_{16}H_{34}$ at 20°C.

It is of great interest to note that the value of n characterizing these six systems lie within the range of n=1.29± 0.03 regardless of temperature and the size ratio of molecules of the two components of the mixtures. The system n-C_6H_{14}—n-$C_{16}H_{34}$ at 20°C for which n=1.22 seems to be exceptional.

The error in n resulting from the possible maximun error in the measurement of V^E is seen in the last column of Table VI. The value of δV^E (see column 4) is the assumed possible maximun error in V^E. When the error in V^E is 0.005 ml/mole, the corresponding error in n, or δn, ranges from 0.05 for the system n-C_7H_{16}—n-$C_{16}H_{34}$ at 20°C to 0.01 for the system n-C_6H_{14}—n-$C_{16}H_{34}$ at 50°C. The error depends mainly on the magnitude of the value of V^E of the system. For the system n-C_7H_{16}—n-$C_{36}H_{74}$ which has the largest absolute value of V^E (-1.56 ml/mole), the relative uncertainty in n is quite small.

Table V: Results of the Estimation of the Exponent n from Comparison of H^E_{calc} with H^E at x_1=0.50

System	T (°C)	V^E (ml/mole)	H^E (cal/mole)	H^E_{calc} (cal/mole)	n	$H^E_{n=1.00}$ (cal/mole)
n-C_6H_{14}— n-$C_{12}H_{26}$	20	-0.31	11	11.1	1.30	26.6
n-C_6H_{14}— n-$C_{16}H_{34}$	20	-0.49	31	30.7	1.22	57.1
	25	-0.53	27	27.1	1.25	52.4
	30	-0.58	23	22.7	1.27	50.2
	35	-0.62	19	18.7	1.32	
	40	-0.69	16	16.3	1.26	43.7
	50	-0.82	8	8.1	1.26	36.5
	51	-0.82	9	8.7	1.28	39.4
n-C_7H_{16}— n-$C_{16}H_{34}$	20	-0.31	26	25.7	1.29	47.1
	25	-0.34	23	23.5	1.29	44.3
n-C_7H_{16}— n-$C_{36}H_{74}$	76	-1.56	31	31.8	1.32	116.4
n-C_8H_{18}— n-$C_{16}H_{34}$	20	-0.19	21	21.3	1.29	36.1
n-C_8H_{18}— n-$C_{24}H_{50}$	106	-1.33	-6	-6.0	1.30	38.3

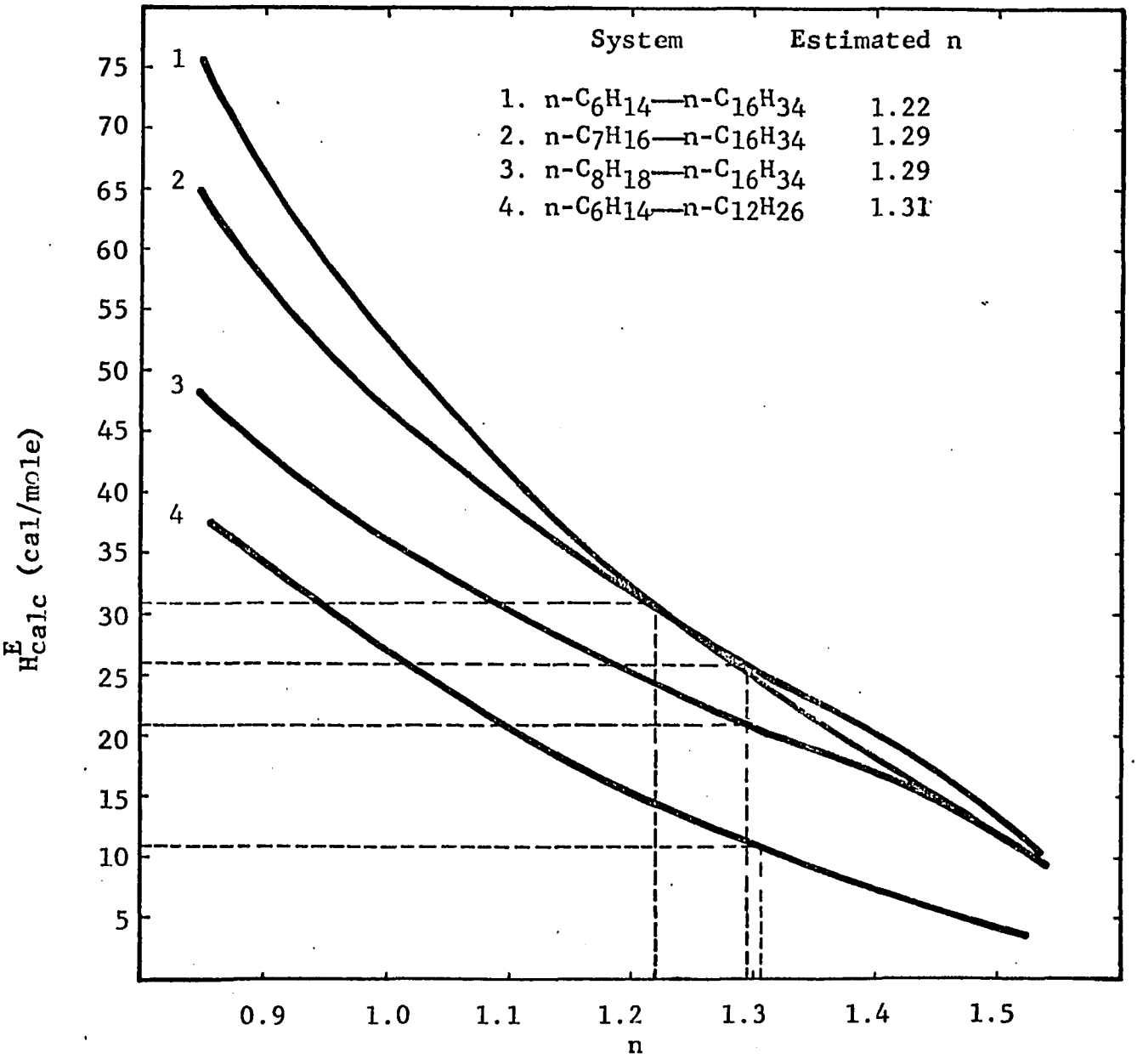

Fig. 13. The Evaluation of the Exponent n by a Graphical Method for the Systems 1. n-C_6H_{14}—n-$C_{12}H_{26}$, 2. n-C_6H_{14}—n-$C_{16}H_{34}$, 3. n-C_7H_{16}—n-$C_{16}H_{34}$, and 4. n-C_8H_{18}—n-$C_{16}H_{34}$ at 20 C.

Table VI: The Effect of the Error in V^E on the Exponent n

System	T (°C)	V^E (ml/mole)	δV^E (ml/mole)	H^E (cal/mole)	δH^E	n
$n\text{-}C_6H_{14}$— $n\text{-}C_{12}H_{26}$	20	0.31	±0.005	11	±1	1.30±0.03
			±0.01		±2	1.30±0.06
$n\text{-}C_6H_{14}$— $n\text{-}C_{16}H_{34}$	20	-0.48	±0.005	30	±1	1.22±0.02
			±0.01		±3	1.22±0.03
	25	-0.53	+0.005	30	0	1.25+0.00
			-0.005		-3	1.25-0.04
			+0.01		+1	1.25+0.01
			-0.01		-4	1.25-0.05
	30	-0.58	+0.005	23	+1	1.27+0.02
			-0.005		-1	1.27-0.02
			+0.01		+2	1.27+0.03
			-0.01		-3	1.27-0.04
	40	-0.69	+0.005	16	+1	1.26+0.01
			-0.005		-2	1.26-0.02
	50	-0.82	+0.005		+1	1.26+0.01
			-0.005		-1	1.26-0.01
			+0.01		+2	1.26+0.03
			-0.01		-2	1.26-0.03
$n\text{-}C_7H_{16}$— $n\text{-}C_{16}H_{34}$	20	-0.31	+0.005	26	+1	1.29+0.05
			-0.005		-1	1.29-0.04
			+0.01		+3	1.29+0.05
			-0.01		-3	1.29-0.05
	25	-0.34	+0.005	23	+2	1.29+0.03
			-0.005		-1	1.29-0.03
			+0.01		+3	1.29+0.05
			-0.01		-2	1.29-0.04
$n\text{-}C_7H_{16}$— $n\text{-}C_{36}H_{74}$	76	-1.56	+0.01	31	+3	1.32+0.02
			-0.01		-2	1.32-0.01
			+0.05		+13	1.32+0.07
			-0.05		-12	1.32-0.06
$n\text{-}C_8H_{18}$— $n\text{-}C_{16}H_{34}$	20	-0.19	+0.005	21	+2	1.29+0.04
			-0.005		-1	1.29-0.03
			+0.01		+4	1.29+0.08
			-0.01		-2	1.29-0.06

Column 6 of Table VI lists the values of H^E which cause a similar error in n. Table VII illustrates the error in n caused by a change in H^E of ±1 and ±2 cal/mole, respectively, should V^E remain constant. The error is moderate, ranging from 0.02 to 0.05 for an uncertainty in H^E of ±2 cal/mole. In measuring the density an error of only 10^{-4} g/ml, may lead to an error of about 0.01 ml/mole or 6% in V^E (this depends on systems). Taking into consideration the vapor space of a calorimeter, difference in the vapor pressure of the pure componets, and the maximum error in the temperature reading, we believe that the maximun error in H^E could amount to 1 cal/mole. The numerical values of V^E and H^E used in the calculation of n are given to one hundredth for the volume and to one unit for the enthalpy. Considering the possible maximum error in either, or both V^E and H^E , the best-fit value of n=1.29 ± 0.03 for this group of mixtures is considerablely very good.

(e). The Relative Change of H^E_{cont} and Equation of State Contribution to the Enthalpy of Mixing at x_1=0.5 with n:

H^E_{cont} (see column 4 of Table IV) can be identified through eq. (81) as the contact interaction contribution to the enthalpy of mixing. The difference between H^E_{calc} and H^E_{cont} represents the equation of state contribution to the enthalpy of mixing, as expressed by the other terms of eq. (81). The equation of state contribution depends not only on the reduced

Table VII: The Effect of the Error in H^E on the Exponent n

System	T (°C)	V^E (ml/mole)	H^E (cal/mole)	δH^E	n
$n\text{-}C_6H_{14}$—$n\text{-}C_{12}H_{26}$	20	-0.31	11	±1	1.30∓0.03
				±2	1.30∓0.05
$n\text{-}C_6H_{14}$—$n\text{-}C_{16}H_{34}$	20	-0.49	31	+1	1.22-0.01
				-1	1.22+0.02
				+2	1.22-0.02
				-2	1.22+0.03
	25	-0.53	27	±1	1.26∓0.01
				+2	1.26-0.02
				-2	1.26+0.03
	30	-0.58	23	+1	1.27-0.02
				-1	1.27+0.03
	40	-0.69	16	+1	1.26-0.02
				-1	1.26+0.01
				+2	1.26-0.03
				-2	1.26+0.02
	50	-0.82	8	±1	1.26∓0.01
				+2	1.26-0.02
				-2	1.26+0.03
$n\text{-}C_7H_{16}$—$n\text{-}C_{16}H_{34}$	20	-0.31	26	±1	1.29∓0.02
				±2	1.29∓0.04
	25	-0.34	23	+1	1.29-0.02
				-1	1.29+0.03
				+2	1.29-0.03
				-2	1.29+0.04
$n\text{-}C_8H_{18}$—$n\text{-}C_{16}H_{34}$	20	-0.19	21	+1	1.29-0.02
				-1	1.29+0.03
				+2	1.29-0.04
				-2	1.29+0.06
$n\text{-}C_7H_{16}$—$n\text{-}C_{36}H_{74}$	76	-1.56	31	+1	1.32-0.00
				-1	1.32+0.01
				+2	1.32-0.01
				-2	1.32+0.02
$n\text{-}C_8H_{18}$—$n\text{-}C_{24}H_{50}$	106	-1.33	-6	±1	1.30∓0.01
				±2	1.30∓0.02

volume of the mixture, and therefore on the excess volume, but also on the difference between the reduced volumes $\bar{V}_1$ and $\bar{V}_2$ of the pure components, respectively.

Like H^E_{calc}, H^E_{cont} also decreases sharply as n increases. The relatively slower decrease in H^E_{cont} (see Figs. 14 and 15) makes the equation of state contribution more significant at higher values of n. This contribution tends to be negative for mixtures of components with very different reduced volumes. Comparing the reduced volumes of the pair of components of any systems at various temperature in Table II, we conclude that, as temperature increases, the difference between $\bar{V}_1$ and $\bar{V}_2$ also increases, so that the equation of state contribution usually becomes negative, except at low temperatures. For n-paraffin hydrocarbon mixtures, the enthalpy of mixing decreases with increasing temperature. The equation of state contribution becomes more and more important and dominates the contact interaction term at high temperatures, rendering the enthalpy of mixing negative (29); this is the case of the system n-C_8H_{18}—n-$C_{24}H_{50}$ at 106°C. The contact interaction contribution dominates, however, the equation of state contribution for all the other systems at n=1.29 ± 0.03.

X_{12}, a parameter characterizing the interaction between unlike molecules, has the same dimension as pressure and ap-

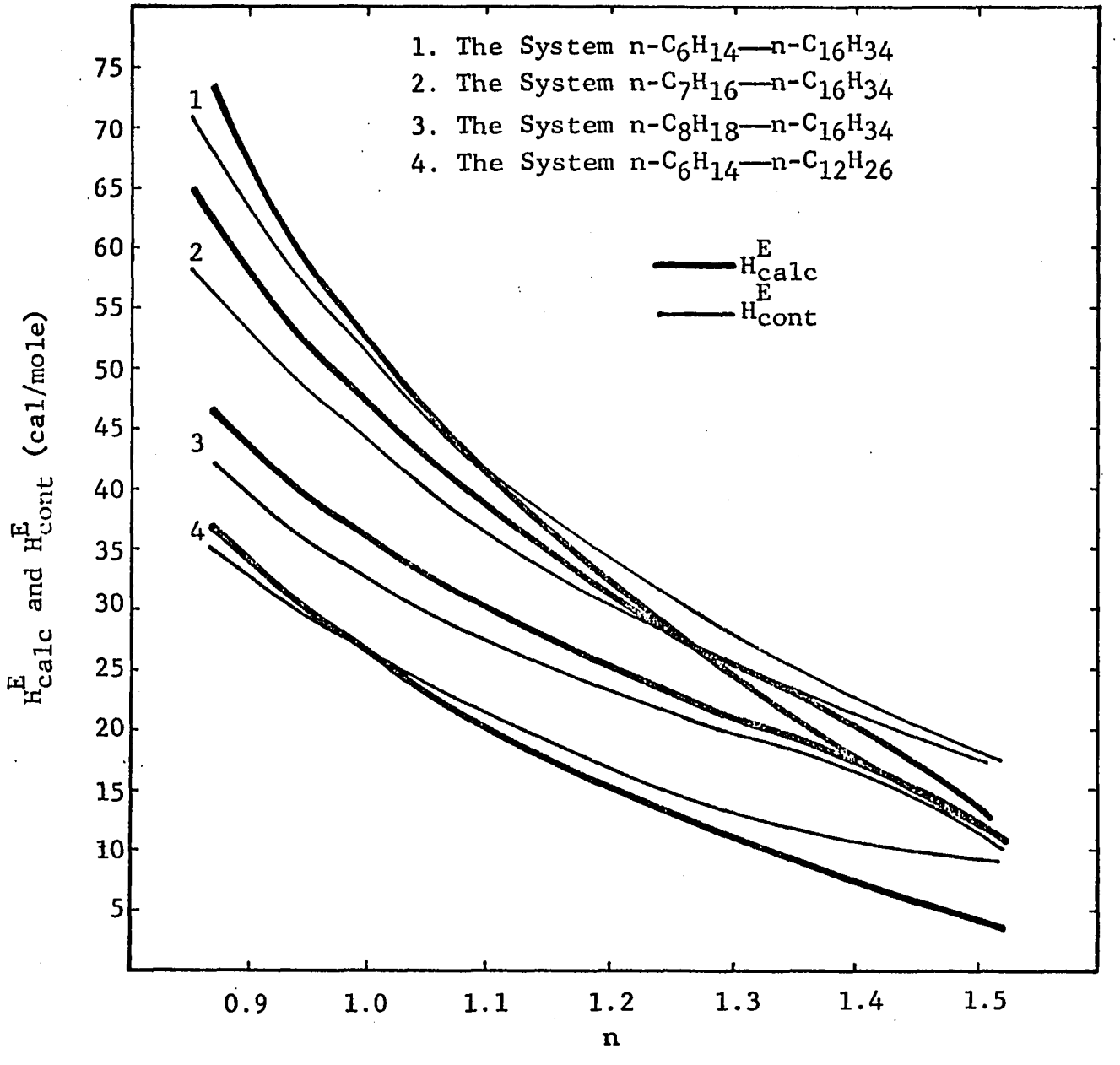

Fig. 14. The Change of H_{calc} and H_{cont} with the Exponent n for the Systems 1. n-C_6H_{14}—n-$C_{12}H_{26}$, 2. n-C_6H_{14}—n-$C_{16}H_{34}$, 3. n-C_7H_{16}—n-$C_{16}H_{34}$, and n-C_8H_{18}—n-$C_{16}H_{34}$ at 20°C.

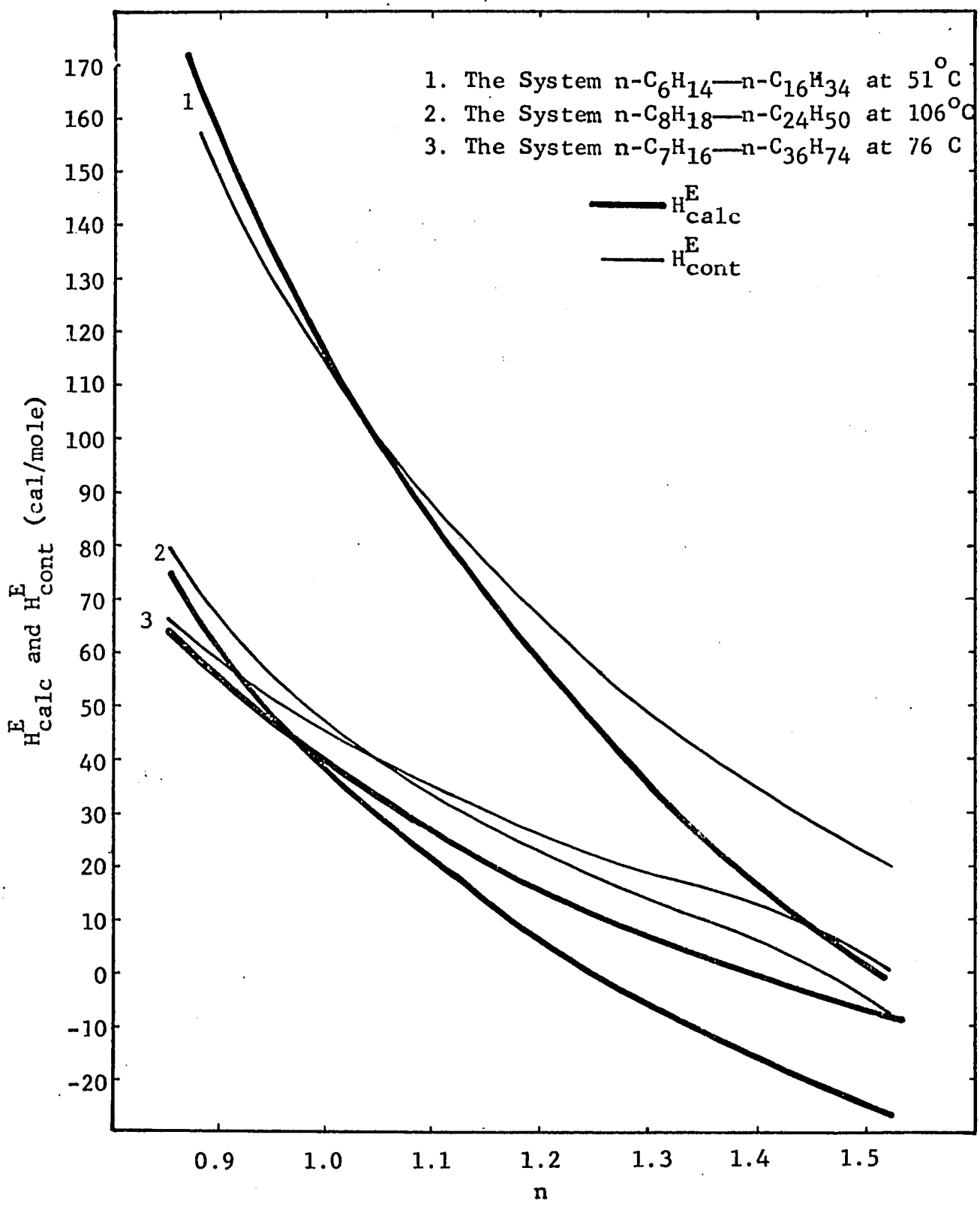

Fig. 15. The Change of H^E_{calc} and H^E_{cont} with the Exponent n of the Systems 1. $n\text{-}C_6H_{14}$—$n\text{-}C_{16}H_{34}$ at 51 C, 2. $n\text{-}C_8H_{18}$—$n\text{-}C_{24}H_{50}$ at 106 °C, and 3. $n\text{-}C_7H_{16}$—$n\text{-}C_{36}H_{74}$ at 76°C.

pears only in the contact interaction term. It is worth mentioning that at constant composition it depends on n, temperature, and also on the relative size of the two components of the mixture. Its temperature dependence for the system n-C_6H_{14}—n-$C_{16}H_{34}$ at x_1=0.5 is shown graphically in Fig. 16. Fig. 17 in which X_{12} is plotted against the segment ratio r_1/r_2 (equal to the hard core volume ratio, V_1^*/V_2^*) for the equal molar mixtures n-C_6H_{14}—n-$C_{12}H_{26}$, n-C_6H_{12}—n-$C_{16}H_{34}$, n-C_7H_{16}—n-$C_{16}H_{34}$, and n-C_8H_{18}—n-$C_{16}H_{34}$ at 20°C, shows that X_{12} is inversely proportional to V_1^*/V_2^*.

(f). Dependence of the Excess Enthlpy of Mixing at Various Compositions of the Binary Mixtures on the Exponent n:

V^E and H^E for the systems n-C_6H_{14}—n-$C_{16}H_{34}$, n-C_7H_{16}—n-$C_{16}H_{34}$, and n-C_8H_{18}—n-$C_{16}H_{34}$ at several compositions are summarized in Table VIII where the corresponding values of $\overline{V}$, H^E_{calc}, H^E_{cont}, and X_{12} are also given. The value of n at each mole fraction estimated from the best-fit between H^E_{calc} and H^E, as described in section (d) is given in column 8. It is clear that in general the value of n at each composition agrees very well with that obtained at x_1=0.5 for the same mixture. The system n-C_6H_{14}—n-$C_{16}H_{34}$ require, throughout the whole concentration range, a value of n=1.22 ± 0.01 which is somewhat lower than the average value of n=1.29 ± 0.03

Data used for Fig. 16

T °C	X_{12} (cal/ml)
20	1.22
25	1.10
40	0.89
50	0.70

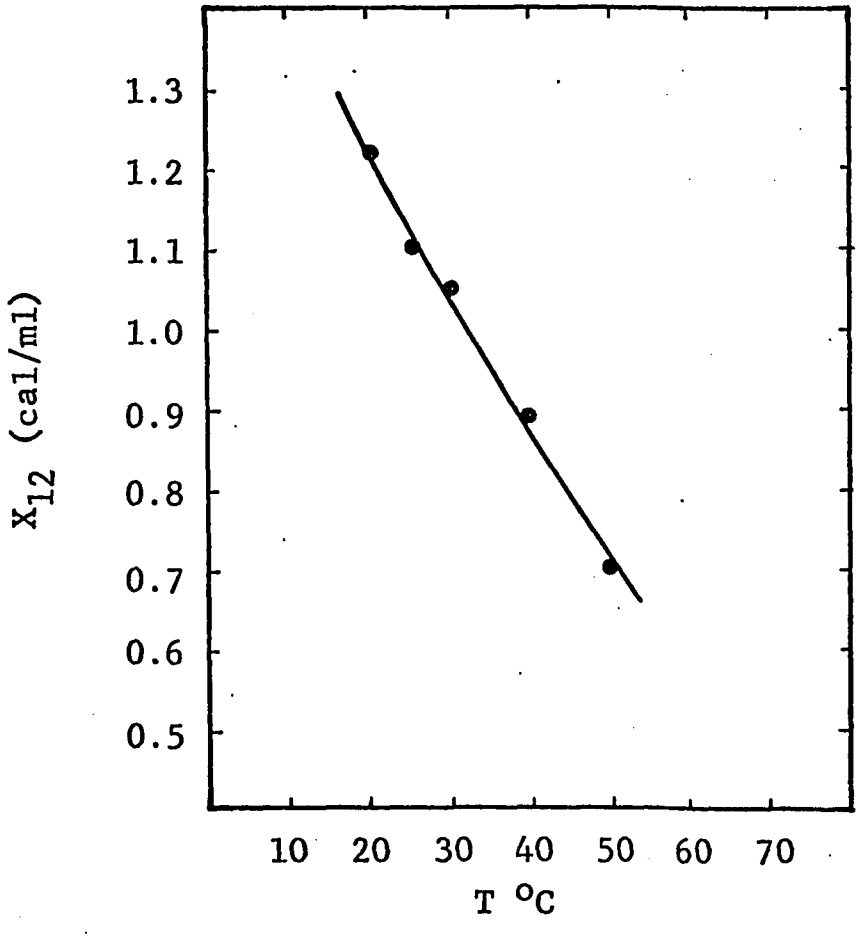

Fig. 16. The Dependence of X_{12} on Temperature for the System n-C_6H_{14} —n-$C_{16}H_{34}$.

Data used for Fig. 17:

System	X_{12} (cal/ml)	V_1^*/V_2^*
$n\text{-}C_6H_{14}$—$n\text{-}C_{12}H_{26}$	0.58	0.546
$n\text{-}C_8H_{18}$—$n\text{-}C_{16}H_{34}$	0.66	0.534
$n\text{-}C_7H_{16}$—$n\text{-}C_{16}H_{34}$	0.93	0.476
$n\text{-}C_6H_{14}$—$n\text{-}C_{16}H_{34}$	1.28	0.417

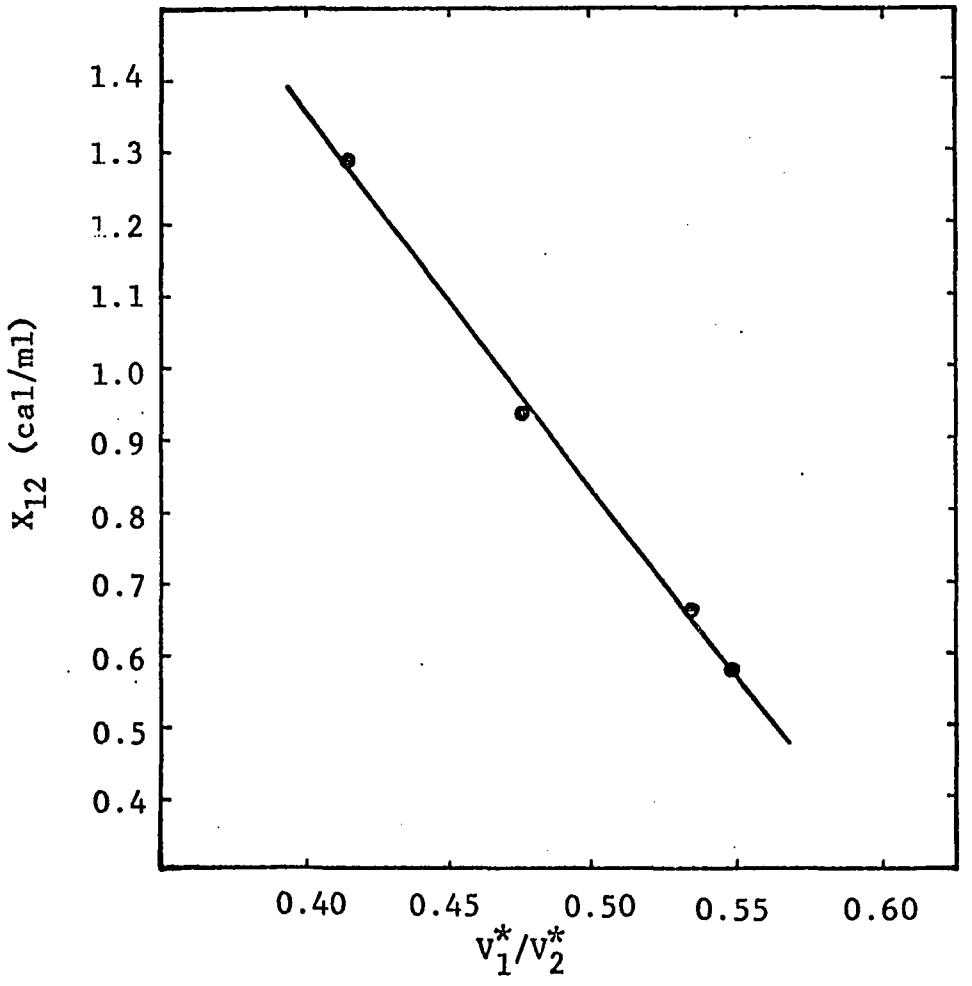

Fig. 17. The Change of X_{12} with the Ratio of the Hard Core Volumes of the Two Components of n-paraffin Hydrocarbon Systems at 20°C.

Table VIII: The Exponent n Evaluated for three n-paraffin Hydrocarbon Mixtures at Various Compositions

System	T (°C)	x_1	V^E (ml/mole)	$\bar{V}$	H^E (cal/mole)	H^E_{calc} (cal/mole)	n	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
$n\text{-}C_6H_{14}$—	20	0.3117	-0.344	1.2211	27.2	27.0	1.21	27.6	1.40
$n\text{-}C_{16}H_{34}$		0.3355	-0.367	1.2218	27.2	27.1	1.22	28.1	1.36
		0.4070	-0.427	1.2255	29.1	29.2	1.22	30.8	1.33
		0.4873	-0.481	1.2302	30.9	30.5	1.22	32.6	1.31
		0.4988	-0.487	1.2309	30.8	30.7	1.22	32.9	1.31
		0.5527	-0.510	1.2335	31.0	30.9	1.22	33.3	1.30
		0.5941	-0.521	1.2371	30.0	29.7	1.23	32.3	1.27
		0.6151	-0.524	1.2394	30.1	30.2	1.22	32.8	1.30
		0.6365	-0.526	1.2412	29.2	29.5	1.22	32.2	1.30
		0.6559	-0.527	1.2435	29.7	29.4	1.21	32.1	1.30
		0.6977	-0.520	1.2475	27.5	27.6	1.21	30.5	1.29
		0.7127	-0.515	1.2483	26.0	26.0	1.22	29.1	1.26
		0.7861	-0.268	1.2559	21.1	21.1	1.23	24.4	1.24
$n\text{-}C_7H_{16}$—	20	0.4008	-0.282	1.2266	25.8	25.6	1.22	25.2	0.98
$n\text{-}C_{16}H_{34}$		0.5571	-0.332	1.2297	26.7	26.6	1.25	26.6	0.95
		0.5762	-0.332	1.2303	26.2	26.1	1.26	26.2	0.93
		0.6180	-0.335	1.2324	24.9	25.1	1.27	24.9	0.91
$n\text{-}C_8H_{18}$—	20	0.4654	-0.183	1.2197	20.8	21.0	1.30	19.6	0.66
$n\text{-}C_{16}H_{34}$		0.5735	-0.195	1.2234	20.3	20.7	1.32	19.5	0.65
		0.5944	-0.195	1.2244	20.5	20.8	1.32	19.5	0.65

found for the other mixtures in the group. This is probably due to the discrepancies in the measurements of V^E and/or H^E.

The effect of composition on X_{12} is given in Table VIII. It shows very small change with composition.

(g). The Dependence of n on Temperature:

It is interesting to note from Table V that, like being independent of composition, n is also independent of temperature for the six systems tested. The constant value of n throughout the concentration and temperature ranges enables one to predict the excess enthalpy from excess volume at any mole fraction and at any temperature, provided that one pair of V^E and H^E at any one temperature and composition of the binary mixture is experimentally available.

(h). Prediction of Enthalpy of Mixing:

Taking n=1.29 as a constant characterizing the n-paraffin hydrocarbon mixtures in the expression of the mean intermolecular energy, $E=-A/V^{1.29}$, we are ready to compute the corresponding characteristic and reduced parameters, and consequently H^E_{calc} from V^E. H^E_{calc} computed for the average n=1.29 is labeled as $H^E_{n=1.29}$ in Table IX. It is reasonable to say that $H^E_{n=1.29}$ and H^E agree remarkably well considering the possible maximum error in the experimental data used in the computation. The third column of Table IX shows the value of n

Table IX: Comparison of the Enthalpy of Mixing predicted at n=1.29, $H^E_{n=1.29}$ with H^E

System	T (°C)	n	$H^E_{n=1.29}$ (cal/mole)	$H^E_{n=1.00}$ (cal/mole)	H^E (cal/mole)
$n\text{-}C_6H_{14}$— $n\text{-}C_{12}H_{26}$	20	1.30	11.4	26.6	11
$n\text{-}C_6H_{14}$— $n\text{-}C_{16}H_{34}$	20	1.22	28.6	57.1	31
	25	1.25	24.0	52.4	27
	30	1.27	21.2	50.2	23
	35	1.32	21.0		19
	40	1.26	13.8	26.6	16
	50	1.26	5.6	36.5	8
	51	1.28	7.9	39.4	9
$n\text{-}C_7H_{16}$— $n\text{-}C_{16}H_{34}$	20	1.29	26.1	47.1	26
	25	1.29	23.3	44.3	23
$n\text{-}C_7H_{16}$— $n\text{-}C_{36}H_{74}$	76	1.32	37.7	116.4	31
$n\text{-}C_8H_{18}$— $n\text{-}C_{16}H_{34}$	20	1.29	21.3	36.1	21
$n\text{-}C_8H_{18}$— $n\text{-}C_{24}H_{50}$	106	1.30	-4.9	38.3	-6

at which H^E_{calc} best reproduces H^E.

H^E_{calc} for n=1.00 from Flory's formula is shown in column 5 of Table V. It is obvious that these values are nowhere even close to H^E, even though Flory (31) has shown that for mixtures comprising pairs of small globular molecules, except those containing benzene as one of the components, the volume of mixing calculated from H^E appears to agree within the limit of error. Because of extreme sensitivity of the change of H^E_{calc} with the value of the exponent n in $E=-A/V^n$, it is inappropriate to use Flory's equations to predict enthalpy of mixing of binary mixtures from experimental volume of mixing.

2. Application of the Modified Theory to Binary Mixtures Comprising small Globular Molecules:

The binary mixtures CCl_4—c-C_6H_{12}, CCl_4—$C(CH_3)_4$, CCl_4—$SiCl_4$, $SiCl_4$—$SnCl_4$, c-C_6H_{12}—n-C_6H_{14}, and c-C_6H_{12}—n-C_7H_{16} at various temperatures are considered here. They comprise pairs of molecules which (a) are rather small, (b) do not differ significantly in size, (c) are approximately spherical, and (d) are non-polar. Deviations of those solutions from ideality or from regularity is generally small. This fact places grater demands on the experimentally accuracy of the data and at the same time provides, in some respects, a stricter test of the theory. Such systems require very reliable equation of state parameters for the pure components such as V^*, T^*, and P^*. We estimate them from molar volume V, thermal expansion coefficient α, and isothermal compressibility β, or thermal pressure coefficient γ, which is equal to $(\partial P/\partial T)$ or α/β.

(a). Physical Properties of the Pure Components:

Experimental values of the physical properties V, α, and γ, for the components of the above mentioned binary mixtures are given in Table X at several temperatures. All data refer to ordinary pressure and may be used at lower pressure. Sources of reference are indicated in the Table.

Table X: Physical Properties of the Pure Components

Compound	(°C)	V (ml/mole)	$\alpha x10^3$ (1/deg)	γ (cal/ml·deg)
CCl_4	0	94.21 (64)	1.191 (65)	0.321 (66,67)
	20	96.49 (65)	1.219 (65)	0.277 (68)
	25	97.08 (65)	1.229 (65)	0.273 (69)
	40	98.91 (65)	1.265 (65)	0.248 (69)
$c\text{-}C_6H_{12}$	20	108.10 (65)	1.202 (65)	0.264 (70)
	25	108.75 (65)	1.217 (65)	0.255 (69)
	40	110.79 (65)	1.265 (65)	0.234 (69)
$C(CH_3)_4$	0	118.03 (64)	1.811 (71)	0.185 (66,67)
$n\text{-}C_6H_{14}$	20	130.67	1.346	0.2012
$n\text{-}C_7H_{16}$	20	146.60	1.243	0.2110
$SiCl_4$	20	114.64 (72)	1.415 (72)	0.214 (68)
	25	115.47 (72)	1.442 (72)	0.208 (68)
$SnCl_4$	20	116.92 (72)	1.171 (72)	0.271 (68)

(b). The Dependence of the Characteristic and Reduced Quantities on the Exponent n:

$\bar{V}$, V^*, T^*, P^*, and C for the non-polar, spherical components, all computed as functions of the exponent n in the range of n = 0.90 to 1.50, are found in Table XI. The trend is similar to that of n-paraffin hydrocarbons.

(c). The Evaluation of n for the Equal-Molar Mixtures:

Table XII lists H^E_{calc}, H^E_{cont}, X_{12} and $\bar{V}$ for various values of n (range between n = 1.00 and 1.60) at the indicated temperatures. Included in the table is also $\bar{V}^o$ of the mixture, which was calculated directly from the pure components using the relation $\bar{V}^o = \varphi_1\bar{V}_1+\varphi_2\bar{V}_2$. The dependence of X_{12} on n is shown in Fig. 18. The variation of H^E_{calc} and H^E_{cont} with n for these mixtures is seen in Fig. 18, in which the thick curves represent the change of H^E_{calc} with n while the thin curves represent that of H^E_{cont} with n. Both H^E_{calc} and H^E_{cont} show moderate decrease with n except for the system CCl_4—$C(CH_3)_4$ at 0°C in which the decrease is rapid. For the system CCl_4—c-C_6H_{12}, the difference between H^E_{calc} and H^E_{cont}, $(H^E_{calc}-H^E_{cont})$, is the same for all n values, indicating that the corresponding equation of state contributions to H^E_{calc} of this system at x_1=0.5 are the same regardless of the exponent n. For the other systems, the equation of state contributions show a

Table XI: The Dependence of the Characteristic and Reduced Properties of the Pure Components on n

T (°C)	n	V* (ml/mole)	T* (°K)	P* (cal/ml)	$\overline{V}$	$\overline{T}$	C
1. Compound: CCl_4							
0	1.00	74.41	4572	141	1.2661	0.05974	1.15
	1.10	74.82	4527	129	1.2592	0.06313	1.13
	1.20	75.21	4123	120	1.2527	0.06625	1.10
	1.30	75.58	3951	112	1.2465	0.06913	1.08
	1.40	75.94	3805	105	1.2406	0.07179	1.06
	1.50	76.29	3679	99.1	1.2350	0.07424	1.03
	1.60	76.62	3570	93.8	1.2296	0.07652	1.01
20	1.00	74.97	4677	135	1.2871	0.06268	1.09
	1.10	75.44	4435	124	1.2799	0.06610	1.06
	1.20	75.88	4235	115	1.2715	0.06922	1.04
	1.30	76.31	4067	107	1.2644	0.07208	1.01
	1.40	76.73	3924	101	1.2576	0.07271	0.99
	1.50	77.12	3801	94.8	1.2512	0.07714	0.97
	1.60	77.50	3693	89.7	1.2450	0.07938	0.95
25	1.00	75.09	4698	136	1.2929	0.06347	1.09
	1.10	75.57	4458	125	1.2846	0.06688	1.07
	1.20	76.03	4259	116	1.2767	0.07000	1.04
	1.30	76.48	4092	108	1.2703	0.07286	1.02
	1.40	76.91	3950	102	1.2623	0.07548	0.99
	1.50	77.32	3828	95.9	1.2556	0.07790	0.97
	1.60	77.71	3721	90.7	1.2492	0.08012	0.95
40	1.00	75.42	4753	134	1.3114	0.06589	1.07
	1.10	75.96	4519	123	1.3021	0.06930	1.04
	1.20	76.48	4325	114	1.2933	0.07240	1.01
	1.30	76.98	4162	106	1.2849	0.07524	0.99
	1.40	77.45	4024	99.8	1.2771	0.07783	0.97
	1.50	78.34	3801	94.0	1.2696	0.08020	0.94
	1.60	78.34	3801	89.0	1.2616	0.08239	0.92
2. Compound: $C(CH_3)4$							
0	1.00	86.23	3763	94.7	1.3688	0.07259	1.09
	1.10	87.06	3597	87.1	1.3558	0.07593	1.06
	1.20	87.84	3460	80.7	1.3436	0.07894	1.03
	1.30	88.59	3345	75.2	1.3323	0.08165	1.00

(to be continued)

Table XI (continued)

(°C)		V* (ml/mole)	T* (°K)	P* (cal/ml)	$\tilde{V}$	$\tilde{T}$	C
2. Compound: $C(CH_3)_4$ (continued)							
0	1.40	89.30	3248	70.5	1.3217	0.08411	0.98
	1.50	89.98	3164	66.4	1.3117	0.08634	0.95
	1.60	90.63	3091	62.8	1.3023	0.08837	0.93
3. Compound: $c\text{-}C_6H_{12}$							
20	1.00	84.20	4710	128	1.2838	0.06224	1.15
	1.10	84.72	4465	117	1.2760	0.06565	1.12
	1.20	85.21	4262	109	1.2687	0.06878	1.10
	1.30	85.68	4092	102	1.2617	0.07164	1.07
	1.40	86.13	3947	95.4	1.2550	0.07428	1.05
	1.50	86.57	3822	89.9	1.2487	0.07671	1.02
	1.60	86.99	3713	85.1	1.2427	0.07896	1.00
25	1.00	84.26	4721	127	1.2906	0.06316	1.14
	1.10	84.80	4479	117	1.2824	0.06658	1.11
	1.20	85.32	4278	108	1.2747	0.06969	1.08
	1.30	85.81	4110	101	1.2674	0.07255	1.06
	1.40	86.28	3966	94.6	1.2604	0.07518	1.04
	1.50	86.72	3842	89.2	1.2539	0.07760	1.01
	1.60	87.17	3735	84.5	1.2476	0.07983	0.99
40	1.00	84.49	4755	126	1.3112	0.06586	1.13
	1.10	85.10	4520	116	1.3019	0.06928	1.10
	1.20	85.68	4327	107	1.2931	0.07238	1.07
	1.30	86.23	4164	100	1.2848	0.07521	1.05
	1.40	86.76	4025	94.1	1.2769	0.07780	1.02
	1.50	87.27	4906	88.1	1.2695	0.08018	1.00
	1.60	87.76	3802	83.9	1.2625	0.08237	0.98
4. Compound: $SiCl_4$							
20	1.00	86.67	4356	110	1.3228	0.06731	1.10
	1.10	87.33	4146	101	1.3127	0.07071	1.07
	1.20	87.96	3972	93.6	1.3033	0.07380	1.04
	1.30	88.56	3826	87.4	1.2944	0.07661	1.02
	1.40	89.14	3702	82.0	1.2860	0.07918	0.99
	1.50	89.69	3596	77.2	1.2781	0.08153	0.97
	1.60	90.22	3503	73.1	1.2700	0.08369	0.95
25	1.00	86.70	4359	110	1.3318	0.06840	1.10
	1.10	87.40	4153	101	1.3212	0.07180	1.07
	1.20	87.40	4153	93.8	1.3113	0.07487	1.04
	1.30	88.69	3839	87.5	1.3019	0.07767	1.02

(to be continued)

Table XI (continued)

T (°C)	n	V^* (ml/mole)	T^* (°K)	P^* (cal/ml)	$\overline{V}$	$\overline{T}$	C
4. Compound: $SiCl_4$							
25	1.40	89.30	3717	82.1	1.2931	0.08022	0.99
	1.50	89.87	3612	77.4	1.2848	0.08255	0.97
	1.60	90.43	3521	73.2	1.2770	0.08468	0.95
5. Compound: $SnCl_4$							
20	1.00	91.49	4773	130	1.2780	0.06143	1.25
	1.10	92.03	4522	119	1.2705	0.06483	1.22
	1.20	92.55	4314	111	1.2634	0.06780	1.20
	1.30	93.04	4139	103	1.2566	0.07083	1.17
	1.40	93.52	3990	97.0	1.2502	0.07347	1.14
	1.50	93.98	3862	91.4	1.2442	0.07591	1.12
	1.60	94.42	3750	86.6	1.2384	0.07817	1.10
6. $n\text{-}C_6H_{14}$ (see Table II)							
7. $n\text{-}C_7H_{16}$ (see Table II)							

Table XII: The Dependence of the Excess Enthlpy of Mixing at $x_1 = 0.50$ on the Exponent n

n	$\bar{V}$	$\bar{V}^o$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
1. System: CCl_4—c-C_6H_{12}, T = 25°C					
H^E = 35 cal/mole (73), V^E = 0.16 ml/mole (65,74,75)					
1.00	1.2937	1.2917	45.9	33.6	2.23
1.10	1.2854	1.2834	42.8	30.5	2.05
1.20	1.2776	1.2756	40.3	28.0	1.90
1.30	1.2703	1.2683	38.1	25.8	1.77
1.40	1.2633	1.2613	36.8	24.0	1.67
1.50	1.2566	1.2547	34.7	22.4	1.57
1.60	1.2503	1.2484	33.4	21.0	1.49
T=40°C, H^E=34 cal/mole (73), V^E=0.16 ml/mole (65)					
1.00	1.3133	1.3113	42.2	30.2	2.03
1.10	1.3040	1.3020	39.3	27.3	1.86
1.20	1.2951	1.2932	37.1	25.1	1.73
1.30	1.2868	1.2849	35.1	23.1	1.61
1.40	1.2789	1.2770	33.5	21.5	1.51
1.50	1.2715	1.2696	32.1	20.1	1.43
1.60	1.2644	1.2625	30.8	18.8	1.35
2. System: CCl_4—$C(CH_3)_4$, T = 0°C					
H^E = 75 cal/mole (76), V^E=-0.50 ml/mole (76,64)					
1.00	1.3150	1.3212	135.1	103.5	6.97
1.10	1.3050	1.3112	114.7	86.4	5.90
1.20	1.2956	1.3017	97.7	72.6	5.01
1.30	1.2867	1.2928	83.6	61.4	4.28
1.40	1.2784	1.2844	71.6	52.0	3.67
1.50	1.2705	1.2765	61.3	44.2	3.15
1.60	1.2630	1.2690	52.5	37.7	2.71
3. CCl_4—$SiCl_4$, T = 20°C					
H^E = 42 cal/mole (77), V^E = 0.05 ml/mole (72)					
1.00	1.3068	1.3062	58.3	43.0	2.86
1.10	1.2978	1.2971	52.4	37.6	2.53
1.20	1.2892	1.2971	47.5	33.3	2.27
1.30	1.2944	1.2886	43.4	29.7	2.05

(to be continued)

Table XII (continued)

n	$\overline{V}$	$\overline{V}^{o}$	H_{calc} (cal/mole)	H_{cont} (cal/mole)	X_{12} (cal/ml)
3. System: CCl_4—$SiCl_4$, T = 20°C (continued)					
1.40	1.2735	1.2805	39.9	26.7	1.86
1.50	1.2663	1.2729	36.9	24.1	1.69
1.60	1.2594	1.2588	34.3	21.9	1.56
T=25°C, H^E=36 cal/mole (77,78), V^E=0.02 ml/mole (68,72)					
1.00	1.3140	1.3137	56.1	41.2	2.75
1.10	1.3045	1.3042	50.0	35.8	2.42
1.20	1.2955	1.2953	45.1	31.5	2.16
1.30	1.2871	1.2868	40.8	27.9	1.93
1.40	1.2791	1.2791	37.3	24.9	1.74
1.50	1.2715	1.2713	34.2	22.3	1.58
1.60	1.2644	1.2642	31.6	20.1	1.44
4. System: $SiCl_4$—$SnCl_4$, T = 20°C H^E = 64 cal/mole (77), V^E = 0.13 ml/mole (72)					
1.00	1.3012	1.2998	91.2	67.8	4.00
1.10	1.2925	1.2911	82.6	59.8	3.57
1.20	1.2843	1.2828	75.5	53.4	3.23
1.30	1.2765	1.2751	69.5	48.0	2.93
1.40	1.2691	1.2677	64.3	43.4	2.68
1.50	1.2622	1.2607	59.9	39.5	2.46
1.60	1.2555	1.2541	56.2	36.3	2.28
5. System: c-C_6H_{12}—n-C_6H_{14}, T = 20°C H^E = 51 cal/mole (79,80), V^E = 0.15 ml/mole (79,81,82)					
1.00	1.2999	1.2983	76.6	56.2	3.28
1.10	1.2913	1.2897	69.7	49.8	2.95
1.20	1.2832	1.2815	64.0	44.6	2.67
1.30	1.2755	1.2739	59.2	40.2	2.44
1.40	1.2682	1.2666	55.1	36.5	2.24
1.50	1.2613	1.2597	51.6	33.4	2.07
1.60	1.2547	1.2531	48.5	30.7	1.92
1.70	1.2485	1.2469	45.8	28.3	1.79

(to be continued)

Table XII (continued)

n	$\overline{V}$	$\overline{V}^{o}$	H^{E}_{calc} (cal/mole)	H^{E}_{cont} (cal/mole)	X_{12} (cal/ml)
6. System: $c\text{-}C_6H_{12}$—$n\text{-}C_7H_{16}$, T = 20°C					
H^{E} = 64 cal/mole (83,84,85), V^{E} = 0.30 ml/mole (79,86)					
1.00	1.2913	1.2883	87.6	64.4	3.59
1.10	1.2832	1.2802	81.3	58.1	3.29
1.20	1.2756	1.2726	76.0	52.9	3.03
1.30	1.2684	1.2654	71.5	48.6	2.81
1.40	1.2615	1.2586	67.6	44.8	2.62
1.50	1.2550	1.2521	64.3	41.6	2.46
1.60	1.2488	1.2459	61.4	38.9	2.32
1.70	1.2430	1.2400	58.9	36.4	2.19

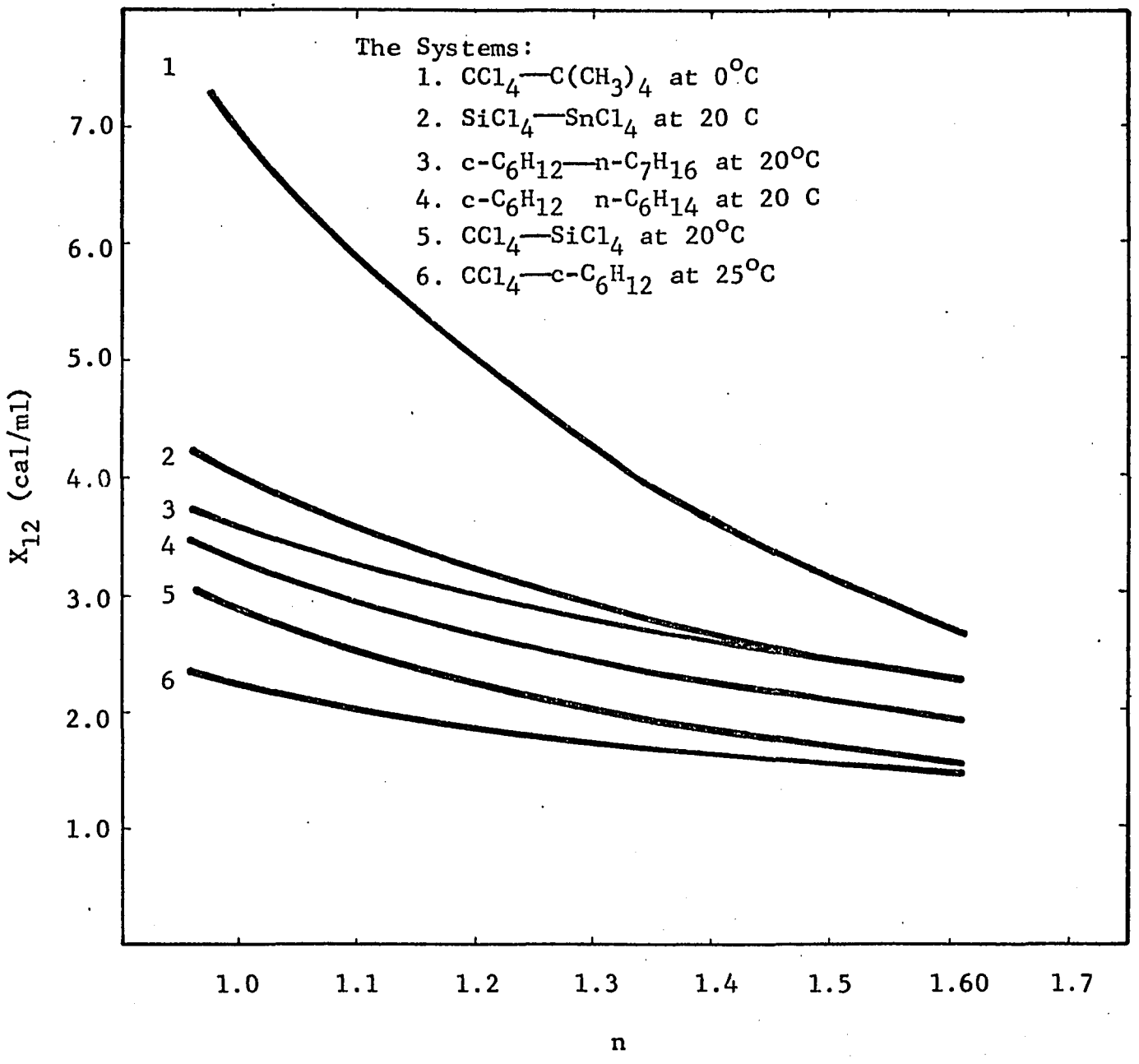

Fig. 18. The Dependence of X_{12} on the Exponent n for the second Group of Mixtures.

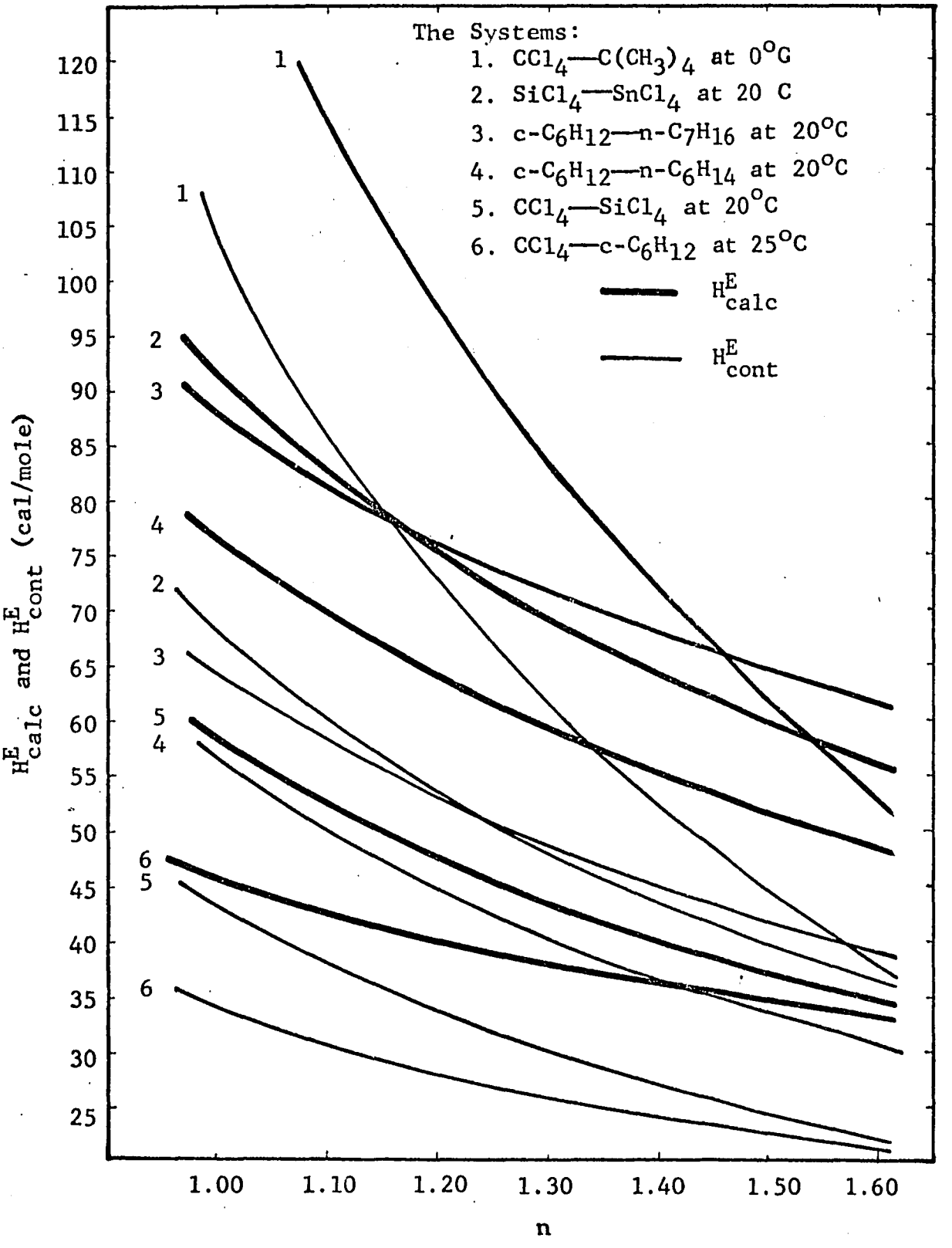

Fig. 19. The Relative Change of H^E_{calc} and H^E_{cont} with the Exponent n for the second Group of Mixtures.

rather slight decline with n except for the system CCl_4—$C(CH_3)_4$ at 0°C, in which the decline with n is more rapid.

The values of n which best repropduce H^E are shown in Table XIII. These systems show a rather constant range of n at which H^E_{calc} reproduces H^E. The average is n = 1.40 ± 0.05. If we exclude the systems c-C_6H_{12}—n-C_6H_{14} and c-C_6H_{12}—n-C_7H_{16}, which are not as spherical as the others, the average value of n is equal to 1.39 ± 0.03. Considering the large error in n resulting from the possible maximun experimental errors, the value of n = 1.40 ± 0.05 is expected to be within experimental error. For instance, an error of ±0.01 ml/mole in the excess volume alone causes an uncertainty of as much as 0.13 in n for the system CCl_4—c-C_6H_{12}, 0.06 for the system CCl_4—$SiCl_4$, and 0.07 for both the systems c-C_6H_{12}—n-C_6H_{14} and c-C_6H_{12}—n-C_7H_{16}. Column 6 of Table XIV shows the change in H_{calc} caused by a possible error in V^E, should n remain constant.

As n = 1.29 ± 0.02 characterized the binary mixtures of the n-paraffin hydrocarbons, n = 1.40 ± 0.05 characterizes the excess enthalpy of mixing of mixtures of non-polar and spherical molecules. The excess enthalpies of mixing calculated from eq. (85) for n = 1.40 for each of these systems are also given in Table XV and are denoted as $H^E_{n=1.40}$. The predicted enthalpies of mixing agree well with the experimental

Table XIII: The Values of the Exponent n at which H^E_{calc} reproduces H^E at $x_1=0.5$

System	T (°C)	V^E (ml/mole)	H^E (cal/mole)	$\overline{V}$	n
CCl_4—c-C_6H_{12}	25	0.16	35	1.2306	1.44
	40	0.16	34	1.2813	1.37
CCl_4— $C(CH_3)_4$	0	-0.50	75	1.2825	1.37
CCl_4— $SiCl_4$	20	0.50	42	1.2780	1.34
	25	0.02	36	1.2760	1.44
$SiCl_4$— $SnCl_4$	20	0.13	64	1.2691	1.40
c-C_6H_{12}— n-C_6H_{14}	20	0.15	51	1.2743	1.50
c-C_6H_{12}— n-C_7H_{16}	20	0.30	64	1.2645	1.50

Table XIV: The Effect of the Error in V^E on the Exponent n

System	T (°C)	V^E (ml/mole)	δV^E (ml/mole)	H^E (cal/mole)	δH^E	n
CCl_4—c-C_6H_{12}	25	0.16	+0.005	35	+2	1.44+0.08
			-0.005		-2	1.44-0.04
			+0.01		+3	1.44+0.11
			-0.01		-2	1.44-0.11
	40	0.16	+0.005	34	+1	1.37+0.06
			-0.005		-1	1.37-0.06
			+0.01		+2	1.37+0.13
			-0.01		-2	1.37-0.13
CCl_4—$C(CH_3)_4$	0	-0.50	+0.005	75	0	1.37+0.01
			-0.005		-2	1.37-0.02
			+0.01		+1	1.37+0.02
			-0.01		-3	1.37-0.03
CCl_4—$SiCl_4$	25	0.02	+0.005	36	+1	1.44+0.03
			-0.005		-1	1.44-0.03
			+0.01		+2	1.44+0.06
			-0.01		-2	1.44-0.06
$SiCl_4$—$SnCl_4$	20	0.12	+0.005	64	+0.4	1.42+0.01
			-0.005		-1.6	1.42-0.03
			+0.01		+1.4	1.42+0.03
			-0.01		-2.6	1.42-0.06
c-C_6H_{12}— n-C_6H_{14}	20	0.15	+0.005	51	+1.5	1.50+0.04
			-0.005		-0.4	1.50-0.01
			+0.01		+2.4	1.50+0.07
			-0.01		-1.3	1.50-0.03
c-C_6H_{12}— n-C_7H_{16}	20	0.30	+0.005	64	+1.3	1.50+0.04
			-0.005		-0.6	1.50-0.02
			+0.01		+2.2	1.50+0.07
			-0.01		-1.6	1.50-0.05

Table XV: Comparison of H^E predicted at n=1.40, and at n=1.00, with the Experimental Value

System	T (°C)	V^E (ml/mole)	n	$H^E_{n=1.40}$ (cal/mole)	$H^E_{n=1.00}$ (cal/mole)	H^E (cal/mole)	$H^E - H^E_{n=1.40}$
CCl_4— $c\text{-}C_6H_{12}$	25	0.16	1.44	36.3	45.9	35	-1.3
	40	0.16	1.37	33.5	42.2	34	+0.5
CCl_4— $C(CH_3)_4$	0	-0.50	1.37	71.6	135.1	75	+3.4
CCl_4— $SiCl_4$	20	0.50	1.34	39.9	58.3	42	+2.1
$SiCl_4$— $SnCl_4$	20	0.13	1.40	64.3	91.2	64	-0.3
$c\text{-}C_6H_{12}$— $n\text{-}C_6H_{14}$	20	0.15	1.50	55.0	66.4	51	-4.0
$c\text{-}C_6H_{12}$— $n\text{-}C_7H_{16}$	20	0.30	1.50	67.6	81.0	64	-3.6

data. Enthalpies of mixing calculated at n = 1.00, or $H^E_{n=1.00}$, which correspond to the version of Flory's original theory, are in very poor agreement with the experimental values.

(d). Dependence of the Excess Enthalpy of Mixing at Various Compositions of Binary Mixtures on the Exponent n:

The values of n = 1.40 ± 0.05 applies to the solutions of equal molar concentration. If we assume that the same value of n can be used also for the solutions of other concentrations, the parameters of the pure components can easily be calculated at this value of n. The excess enthalpy of mixing calculated, H^E_{calc}, depends on the parameters of the pure components and the reduced volume $\bar{V}$ of the solution. The reduced volume in turn depends on the excess volume of mixing, V^E, at a particular mole fraction, and therefore H^E_{calc} can be expressed as a function of x_1, provided that the equation of V^E as a function of x_1 is given.

V^E for the system CCl_4—c-C_6H_{12} at 25°C and 40°C is experimentally expressed by the formulas (65):

$$V^E = 0.633x_1(1-x_1) \text{ ml/mole} \quad \text{at } 25^oC \qquad (a)$$

and

$$V^E = 0.0015 + 0.633x_1(1-x_1) \text{ ml/mole at } 40^oC \qquad (b)$$

Substituting from eq. (a) or eq. (b) into eq. (83) for $\bar{V}$ of the system, and combining the resulting equation with eq. (85), we arrive at the expression for the enthalpy of mixing in terms of x_1 only. H^E_{calc} and H^E_{cont} and X_{12} of the system CCl_4—c-C_6H_{12} at different mole fractions are given in Table XVI. The values of H^E at the corresponding mole fractions which are also shown in the table were obtained from the following experimental data (73):

$$H^E = (1/4.18)\left[571.6x_1(1-x_1)\right] \text{ cal/mole} \qquad \text{at } 25^oC$$

$$H^E = (1/4.18)\left[562.2x_1(1-x_1)\right] \text{ cal/mole} \qquad \text{at } 40^oC$$

H^E_{calc}, H^E, and H^E_{cont} are plotted against x_1 in Fig. 20. Note that the agreement between H^E_{calc} and H^E is excellent within the entire composition range. It is reasonable to assert that the value of n = 1.40 characterizes the solutions over the whole composition range very well.

Analyzing eq. (85), it is observed that the equation can be written as sum of two terms:

$$H^E = Ax_1 + Bx_2 \tag{88}$$

where

$$A = \frac{P_1^* V_1^*}{\bar{V}_1^n} - \frac{P_1^* V_1^*}{\bar{V}^n} + \left(\frac{V_1^*}{\bar{V}^n}\right)\left[\frac{\varphi_1 P_1^* + \varphi_2 P_2^*}{\varphi_1} - \left(\bar{V}^{n+\frac{1}{3}}\right)\left(\frac{\varphi_1 P_1^* \bar{T}_1 + \varphi_2 P_2^* \bar{T}_2}{n\varphi_1(\bar{V}^{\frac{1}{3}} - 1)}\right)\right] \tag{89a}$$

Table XVI: Comparison of the Calculated and Experimental Enthalpy of Mixing for the System CCl_4—c-C_6H_{12} over the whole Composition Range

n	x_1	V^E (ml/ mole)	H^E (cal/ mole)	H^E_{calc} (cal/ mole)	H^E_{cont} (cal/ mole)	X_{12} (cal/ ml)	A (cal/ mole)	B (cal/ mole)
T = 25°C								
1.42	0.10	0.0570	12.7	12.5	8.3	1.64	76.3	5.43
	0.20	0.1013	22.6	22.4	14.3	1.64	71.8	10.0
	0.30	0.1339	29.7	29.5	19.4	1.63	66.5	13.5
	0.40	0.1519	33.9	34.0	22.3	1.63	60.2	16.5
	0.50	0.1582	35.3	35.6	23.4	1.63	52.9	18.3
	0.60	0.1529	33.9	34.3	22.5	1.62	44.5	19.1
	0.70	0.1329	29.7	30.3	19.9	1.62	35.1	18.9
	0.80	0.1013	22.6	23.2	25.3	1.62	24.6	17.7
	0.90	0.0570	12.7	13.1	8.6	1.62	12.9	15.3
T = 40°C								
1.40	0.10	0.0585	12.1	12.1	12.0	1.54	79.9	4.40
	0.20	0.1028	21.5	21.1	13.6	1.53	74.5	7.86
	0.30	0.1344	28.2	27.8	17.9	1.52	68.5	10.4
	0.40	0.1534	32.2	32.0	20.5	1.52	61.8	12.1
	0.50	0.1597	33.6	33.4	21.4	1.51	54.1	12.8
	0.60	0.1534	32.2	32.3	20.7	1.50	45.5	12.5
	0.70	0.1344	28.2	28.5	18.3	1.51	35.9	11.3
	0.80	0.1028	21.5	21.9	14.1	1.51	25.2	8.97
	0.90	0.0585	12.1	12.6	8.1	1.53	13.3	5.60

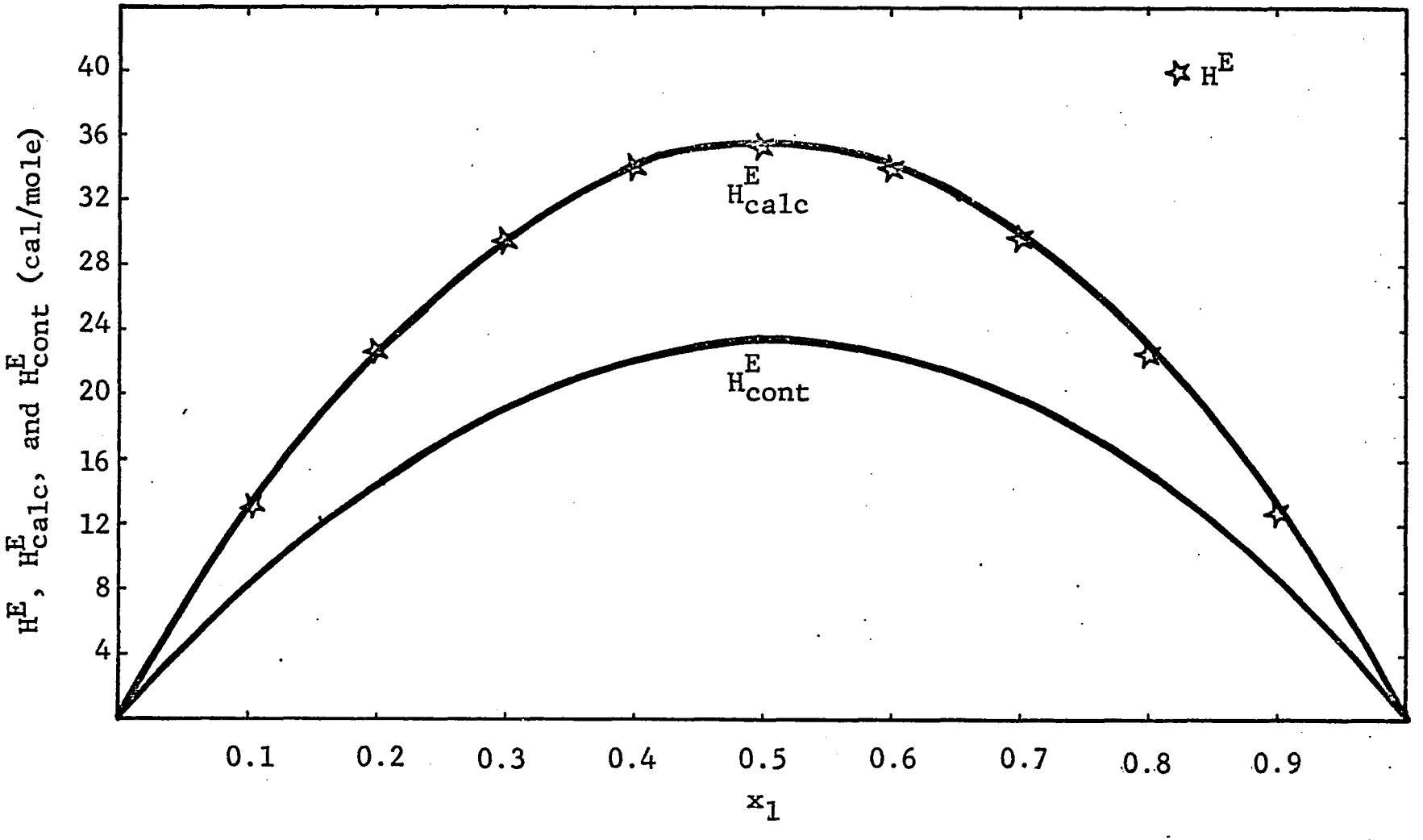

Fig. 20. H^E, H^E_{calc}, and H^E_{cont} of the System CCl_4—c-C_6H_{12} at 25°C of Function of the Mole Fraction of CCl_4, x_1.

and

$$B = P_2^* V_2^* \left(\frac{1}{\bar{V}_2^n} - \frac{1}{\bar{V}^n}\right) \tag{90}$$

A and B depend on the behavior of the pure components and on the reduced volume, $\bar{V}$, (change with concentration), of the mixture and are easily obtainable.

When $x_1 = 0.0$, $\bar{V} = \bar{V}_2$ and B of eq. (90) vanishes, as does H^E of solutions. When $x_1 = 1.0$, $\bar{V} = \bar{V}_1$, $\varphi_1 = 1.00$, $\varphi_2 = 0.0$, and eq. (89) becomes

$$A = \left(\frac{V_1^*}{\bar{V}_1^n}\right)\left[P_1^* - \bar{V}^{n+\frac{1}{3}} \frac{P_1^* \bar{T}_1}{n(\bar{V}_1^{\frac{1}{3}} - 1)}\right] \tag{89b}$$

The second term in the bracket of eq, (89b) is simply equal to P_1^* by substitution of eq. (32). This makes H^E in eq. (88) as well as A equal to zero. The thermodynamic boundary conditions of excess enthalpy of mixing are therefore satisfied. by eq. (88).

Values of A and B from $x_1 = 0.10$ to o.90 for the system CCl_4—c-C_6H_{12} at 25°C and 40°C are also given in Table XVI. Both are positive over the whole molae fraction range. They are plotted against x_1 and extrapolated to $x_1 = 0$ and 1, respectively in Fig. 21.

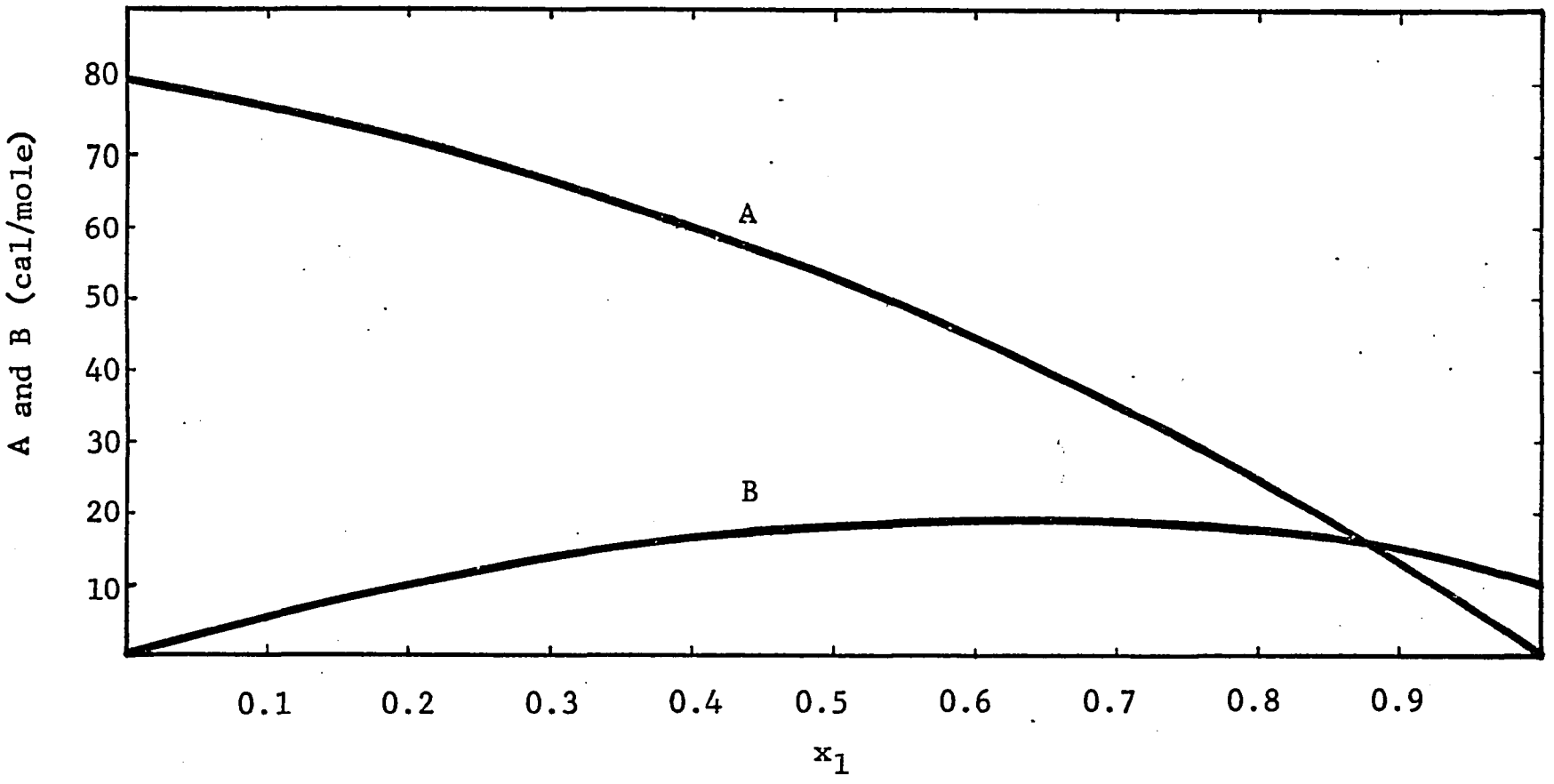

Fig. 21. The Values of A and B for the System CCl_4—c-C_6H_{14} at 25°C as Functions of the Mole Fraction of CCl_4, x_1.

3. Application of the Modified Theory to the Binary 1-Alcohol—1-Alchol Mixtures:

So far, this refined theory has been useful in interpreting the excess properties of a number of binary mixtures composed of molecular species different in size and shape. In Flory's original theory (87-89), compounds whose molecules are forming hydrogen bonds and exhibiting strong dipolar interactions were specifically excluded. The assumption that a molecule can be divided into isometric segments and that each segment has equal opportunity to interact with the other segments may no longer be applicable to such systems. However, we have found that the application of the modified theory to the binary normal alcohol systems provides a reasonable good correlation between the excess enthalpies and excess volumes of mixing.

(a). The Dependence of the Excess Enthalpy of Mixing at $x_1 = 0.50$ on the Exponent n:

Enthalpies of mixing calculated from volumes of mixing for 21 binary 1-Alcohol—1-Alcohol systems are shown in Table XVII. Values of V, α, β, and γ for the pure components at 25°C are given in Table XVIII,, and the characteristic and reduced volumes, temperatures, and pressures at n=1.00 (n=1.00 seems to best fit this group of systems) are given in Table XIX. For all the 21 systems, H^E_{cont} appears to be dominant over the

*Table XVII: The Dependence of the Excess Enthalpy of Mixing at $x_1 = 0.50$ on the Exponent n

n	$\overline{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
T = 25 °C				
1. System: Methanol—Ethanol H^E = 1.07 cal/mole, V^E = 0.0085 ml/mole				
0.70	1.2970	1.82	1.61	0.221
0.80	1.2885	1.74	1.51	0.210
0.90	1.2804	1.62	1.34	0.194
1.00	1.2728	1.56	1.30	0.186
1.10	1.2656	1.27	1.19	0.172
2. System: Methanol—1-Propanol H^E = 19.60 cal/mole, V^E = 0.0503 ml/mole				
0.70	1.2805	20.83	17.71	2.23
0.80	1.2729	18.74	15.67	2.00
0.90	1.2657	17.08	13.95	1.81
1.00	1.2589	15.74	12.59	1.65
1.10	1.2524	14.64	11.48	1.52
3. System: Methanol—1-Butanol H^E = 34.01 cal/mole, V^E = 0.0738 ml/mole				
0.70	1.2712	39.97	34.04	4.05
0.80	1.2641	35.58	29.70	3.58
0.90	1.2573	32.14	26.29	3.21
1.00	1.2509	29.40	23.59	2.91
1.10	1.2448	27.11	21.32	2.67
4. System: Methanol—1-Hexanol H^E = 56.39 cal/mole, V^E = 0.116 ml/mole				
0.70	1.2519	73.60	63.73	6.98
0.80	1.2457	65.32	55.55	6.16
0.90	1.2398	58.86	49.19	5.51
1.00	1.2343	53.65	44.06	4.99
1.10	1.2289	49.46	39.94	4.58

(to be continued)

Table XVII (continued)

n	$\bar{\bar{V}}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
5. System: Methanol—1-Octanol				
H^E = 80.64 cal/mole, V^E = 0.1563 ml/mole				
0.70	1.2420	111.65	96.88	10.06
0.80	1.2364	98.70	84.14	8.84
0.90	1.2309	88.74	74.35	7.90
1.00	1.2258	80.69	66.47	7.13
1.10	1.2208	74.09	60.00	6.51
6. System: Methanol—1-Decanol				
H^E = 94.92 cal/mole, V^E = 0.178 ml/mole				
0.70	1.2366	157.84	136.70	13.68
0.80	1.2312	138.84	118.09	11.95
0.90	1.2260	124.17	103.78	10.61
1.00	1.2210	112.37	92.30	9.54
1.10	1.2163	102.78	83.01	8.66
1.18	1.2126	96.19	76.63	8.06
7. System: Ethanol—1-Propanol				
H^E = 4.59 cal/mole, V^E = 0.0084 ml/mole				
0.70	1.2736	6.16	5.28	0.504
0.80	1.2664	5.43	4.57	0.442
0.90	1.2595	4.87	4.02	0.395
1.00	1.2529	4.38	3.55	0.352
1.10	1.2567	4.02	3.20	0.321
8. System: Ethanol—1-Butanol				
H^E = 11.49 cal/mole, V^E = 0.0121 ml/mole				
0.70	1.2659	15.94	13.60	1.216
0.80	1.2590	13.82	11.65	1.055
0.90	1.2525	12.23	10.13	0.930
1.00	1.2463	11.01	8.97	0.833
1.10	1.2404	9.97	7.98	0.750

(to be continued)

Table XVII (continued)

n	$\overline{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
9. System: Ethanol—1-Hexanol				
H^E = 30.19 cal/mole, V^E = 0.0363 ml/mole				
0.70	1.2493	42.65	37.15	3.02
0.80	1.2432	37.42	32.06	2.64
0.90	1.2374	33.18	27.97	2.33
1.00	1.2319	29.92	24.84	2.09
1.10	1.2267	27.25	22.28	1.90
10. System: Ethanol—1-Octanol				
H^E = 51.95 cal/mole, V^E = 0.0599 ml/mole				
0.70	1.2405	73.14	63.69	4.87
0.80	1.2348	63.99	54.80	4.24
0.90	1.2295	56.80	47.86	3.75
1.00	1.2243	51.18	42.45	3.36
1.10	1.2194	46.57	38.04	3.05
11. system: Ethanol—1-Decanol				
H^E = 71.89 cal/mole, V^E = 0.0885 ml/mole				
0.70	1.2357	121.93	105.58	7.73
0.80	1.2303	106.39	90.50	6.70
0.90	1.2251	94.27	78.81	5.90
1.00	1.2202	84.68	69.62	5.27
1.10	1.2154	76.76	62.06	4.75
1.18	1.2118	71.49	57.06	4.41
12. System: 1-Propanol—1-Butanol				
H^E = 1.29 cal/mole, V^E = -0.0019 ml/mole				
0.70	1.2571	1.39	1.21	0.089
0.80	1.2507	1.23	1.06	0.079
0.90	1.2445	0.99	0.83	0.063
1.00	1.2387	0.84	0.70	0.053
1.10	1.2332	0.77	0.63	0.049

(to be continued)

Table XVII (continued)

n	$\overline{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
13. System: 1-Propanol—1-Hexanol H^E = 14.70 cal/mole, V^E = 0.0187 ml/mole				
0.70	1.2434	20.60	17.88	1.189
0.80	1.2376	18.11	15.45	1.042
0.90	1.2321	16.14	13.55	0.925
1.00	1.2269	14.48	11.95	0.825
1.10	1.2218	13.28	10.81	0.755
14. System: 1-Propanol—1-Octanol H^E = 36.67 cal/mole, V^E = 0.0513 ml/mole				
0.70	1.2362	50.21	43.46	2.70
0.80	1.2308	44.06	37.46	2.36
0.90	1.2256	39.34	32.85	2.10
1.00	1.2206	35.47	29.12	1.88
1.10	1.2159	32.36	26.13	1.71
15. System: 1-Propanol—1-Decanol H^E = 60.21 cal/mole, V^E = 0.0890 ml/mole				
0.70	1.2324	96.22	82.86	4.91
0.80	1.2271	84.38	71.32	4.28
0.90	1.2221	75.05	62.26	3.78
1.00	1.2173	67.60	55.08	3.39
1.10	1.2127	61.65	49.37	3.07
16. System: 1-Butanol—1-Hexanol H^E = 6.45 cal/mole, V^E = 0.0115 ml/mole				
0.70	1.2404	8.34	7.31	0.418
0.80	1.2348	7.43	6.41	0.371
0.90	1.2294	6.63	5.64	0.331
1.00	1.2243	5.99	5.00	0.297
1.10	1.2194	5.63	4.65	0.279

(to be continued)

Table XVII (continued)

n	$\overline{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
17. System: 1-Butanol—1-Octanol				
H^E = 24.79 cal/mole, V^E = 0.0413 ml/mole				
0.70	1.2341	32.02	27.74	1.475
0.80	1.2288	28.23	24.03	1.294
0.90	1.2237	25.34	21.19	1.155
1.00	1.2188	23.06	18.96	1.046
1.10	1.2141	21.04	17.00	0.949
18. System: 1-Butanol—1-Decanol				
H^E = 48.08 cal/mole, V^E = 0.0778 ml/mole				
0.70	1.2307	73.00	62.84	3.172
0.80	1.2256	64.16	54.19	2.770
0.90	1.2206	57.22	47.43	2.455
1.00	1.2159	51.76	42.14	2.207
1.10	1.2114	47.28	37.82	2.003
19. System: 1-Hexanol—1-Octanol				
H^E= 6.21 cal/mole, V^E = 0.0098 ml/mole				
0.70	1.2269	7.37	6.34	0.266
0.80	1.2219	6.61	5.59	0.238
0.90	1.2171	5.93	4.91	0.212
1.00	1.2125	5.23	4.23	0.184
1.10	1.2081	4.88	3.90	0.172
20. System: 1-Hexanol—1-Decanol				
H^E = 22.80 cal/mole, V^E = 0.0375 ml/mole				
0.70	1.2246	32.24	27.64	1.095
0.80	1.2197	28.28	23.77	0.954
0.90	1.2150	25.30	20.84	0.847
1.00	1.2105	23.01	18.63	0.766
1.10	1.2062	21.00	16.68	0.694

(to be continued)

Table XVII (continued)

n	$\bar{V}$	H^E_{calc} (cal/mole)	H^E_{cont} (cal/mole)	X_{12} (cal/ml)
21. System: 1-Octanol—1-Decanol				
H^E = 5.35 cal/mole, V^E = 0.0075 ml/mole				
0.70	1.2213	6.80	5.81	0.194
0.80	1.2165	6.09	5.21	0.173
0.90	1.2119	5.24	4.29	01147
1.00	1.2075	4.98	4.04	0.140
1.10	1.2033	4.41	3.49	0.122

* All the excess enthalpies and volumes of mixing data were taken from ref. (90) and ref. (91), respectively.

*Table XVIII: Physical Properties of the pure Alcohols at 25°C

Compound	V (ml/mole)	$\alpha \times 10^3$ (1/deg)	$\beta \times 10^6$ (1/atm)	γ (cal/ml·deg)
Methanol	40.73	1.185	126.4	0.227
Ethanol	58.68	1.083	116.5	0.225
1-Propanol	75.16	0.981	102.5	0.232
1-Butanol	91.96	0.936	94.5	0.240
1-Hexanol	125.26	0.852	84.3	0.245
1-Octanol	158.42	0.818	78.9	0.251
1-Decanol	191.43	0.804	73.9	0.263

* All the physical prpperties data were taken from ref. (90).

Table XIX: Characteristic and Reduced Properties of 1-Alcohols at n=1.00 at 25°C

Compound	V^* (ml/mole)	T^* (°K)	P^* (cal/ml)	$\overline{V}$	$\overline{T}$	C
Methanol	31.71	4784	112	1.2845	0.06233	0.373
Ethanol	46.41	5011	107	1.2645	0.05950	0.500
1-Propanol	60.43	5287	107	1.2438	0.05639	0.615
1-Butanol	74.48	5425	109	1.2337	0.05496	0.754
1-Hexanol	102.96	5735	108	1.2166	0.05990	0.977
1-Octanol	131.02	5877	109	1.2092	0.05074	1.228
1-Decanol	158.72	5939	114	1.2061	0.05021	1.534

equation of state contribution to the enthalpy of mixing. The effect of n on H^E_{calc} and H^E_{cont} are shown graphically in Fig. 22. As seen from this figure the equation of state contributions are almost independent of the value of n for the 21 systems.

Table XVII shows that X_{12} varies moderately with n. For systems with large differences in molecular size, X_{12} is much larger than for system with a small difference in size. For instance, the value of X_{12} for the system Methanol—1-Decanol, which has the largest difference in size from all the Alcohol—Alcohol systems, is 9.54 cal/ml. Table XX and Fig. 23 show the effect of the ratio of molar core volumes, V_1^*/V_2^*, on X_{12} for mixtures of methanol, ethanol, 1-propanol, and 1-butanol.

The values of n at which $H^E_{calc}=H^E$, or n_{calc}, for these 21 systems of equal molar concentrations are shown in column 3 of Table XVII. The values of n_{calc} vary about 1.00. Systems of constituents with large molecular size differences show deviations from $n_{calc}=1.00$.

Because of the large uncertainty in n (see column 6 of Table XXI) resulting from a small change in V^E (see column 4), the effect of n on H^E_{calc} for systems with larger molecular size ratio is smaller. This allows accepatable values of n for these systems to have greater range and still be within

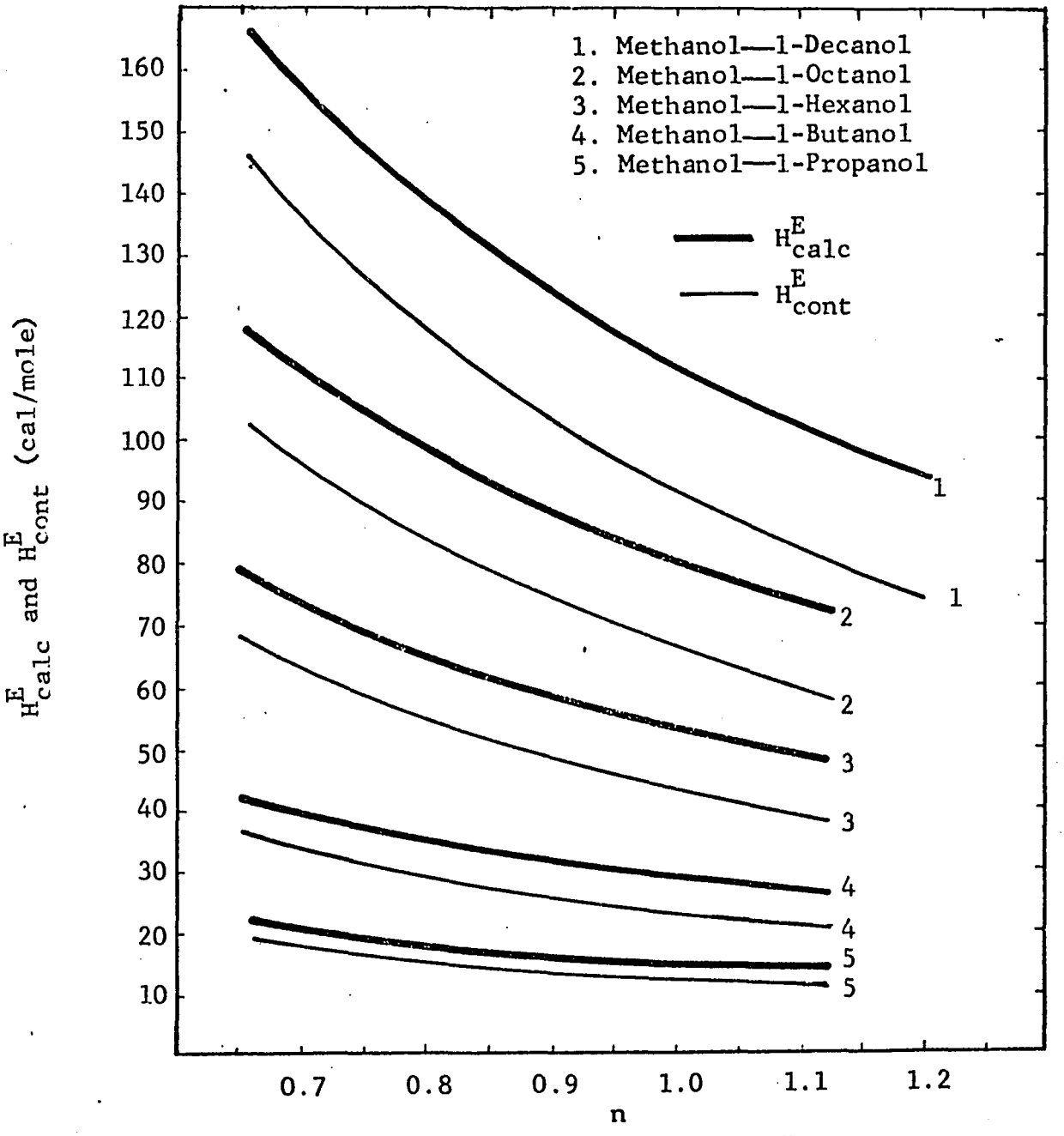

Fig. 22a. The Dependence of H^E_{calc} and H^E_{cont} on the Exponent n for the Alcohol—Alcohol Systems at 25°C.

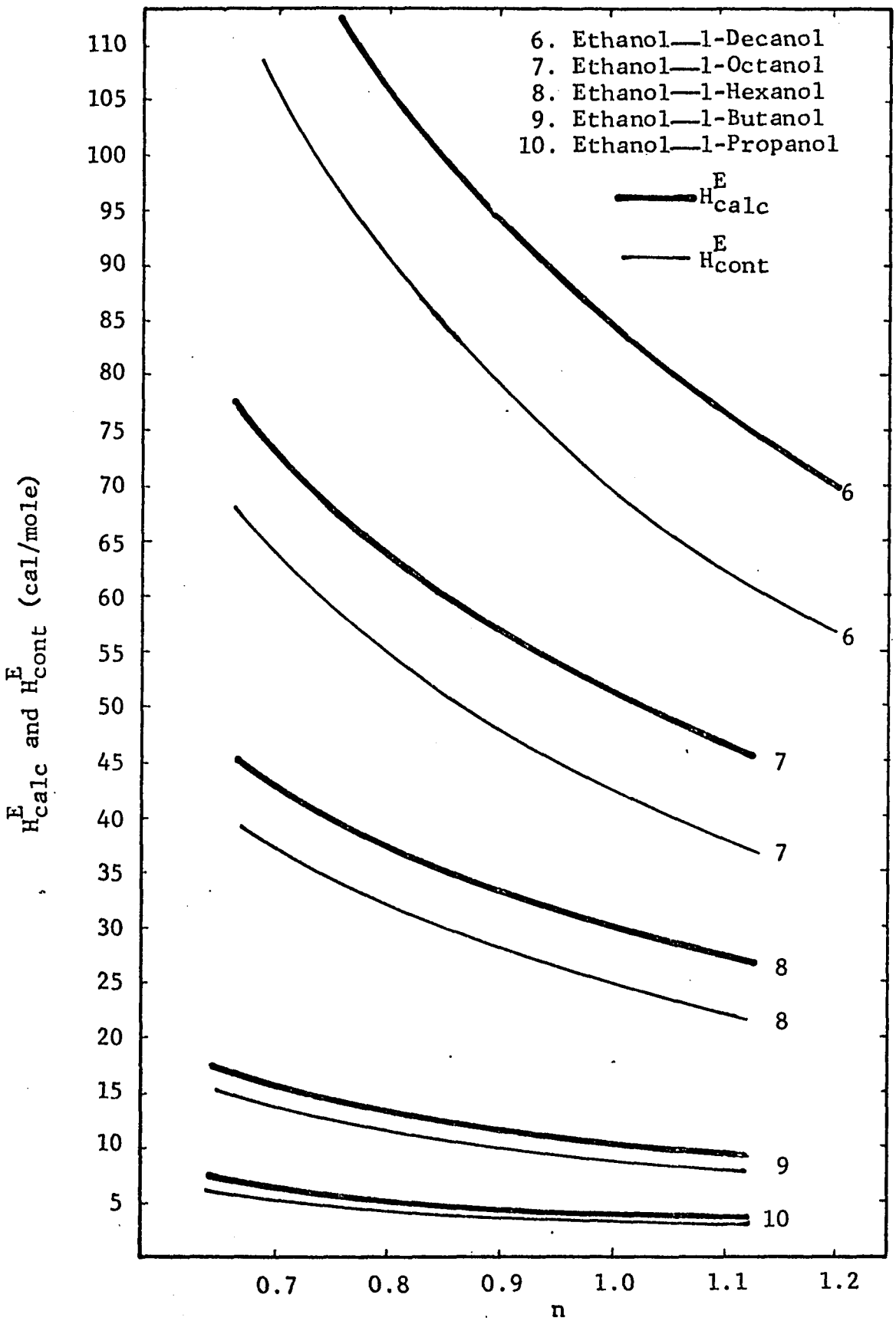

Fig. 22b. The Dependence of H^E_{calc} and H^E_{cont} on the Exponent n for the Alcohol—Alcohol Systems at 25°C.

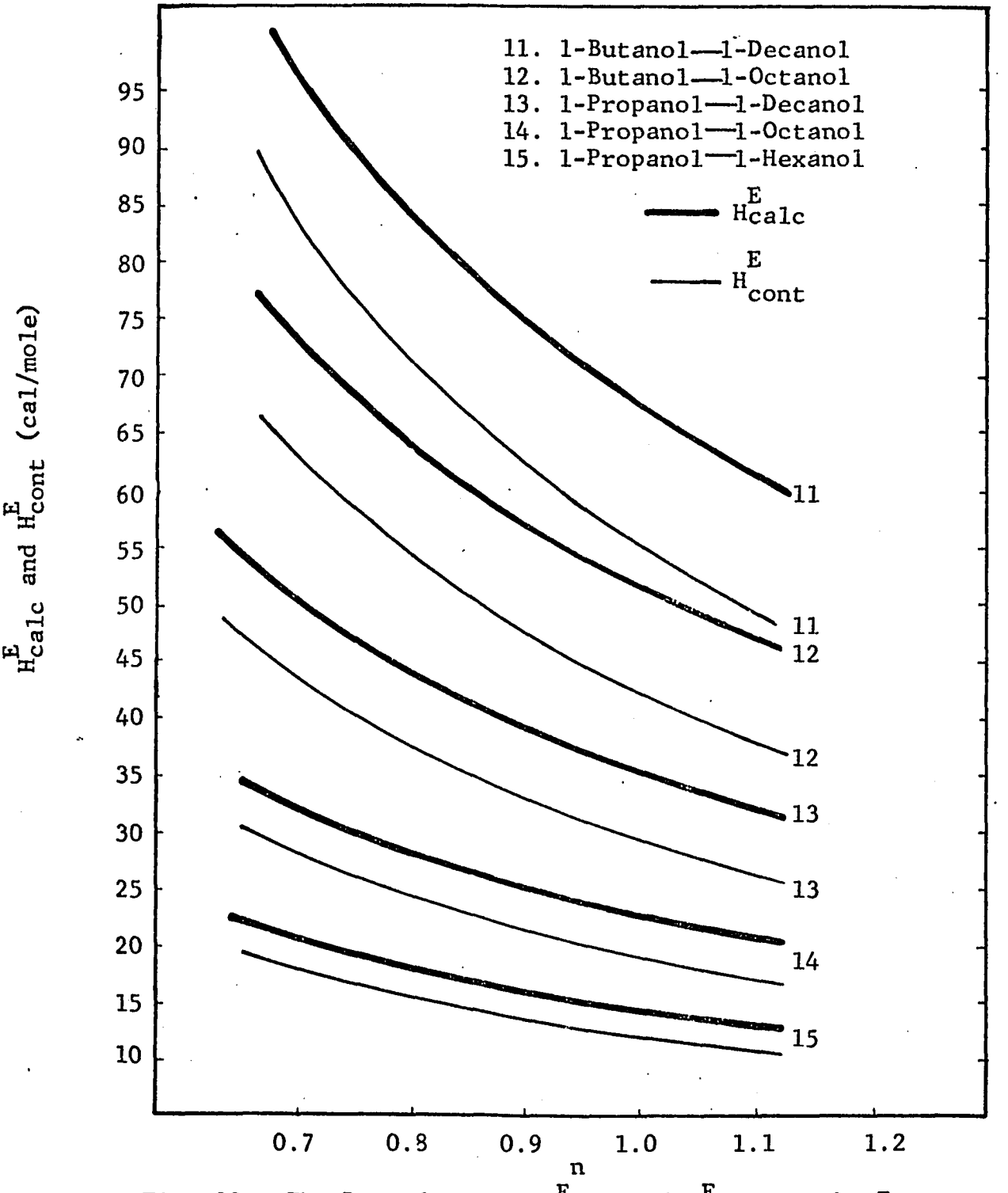

Fig. 22c. The Dependence of H^E_{calc} and H^E_{cont} on the Exponent n for the Alcohol—Alcohol Systems at 25 °C.

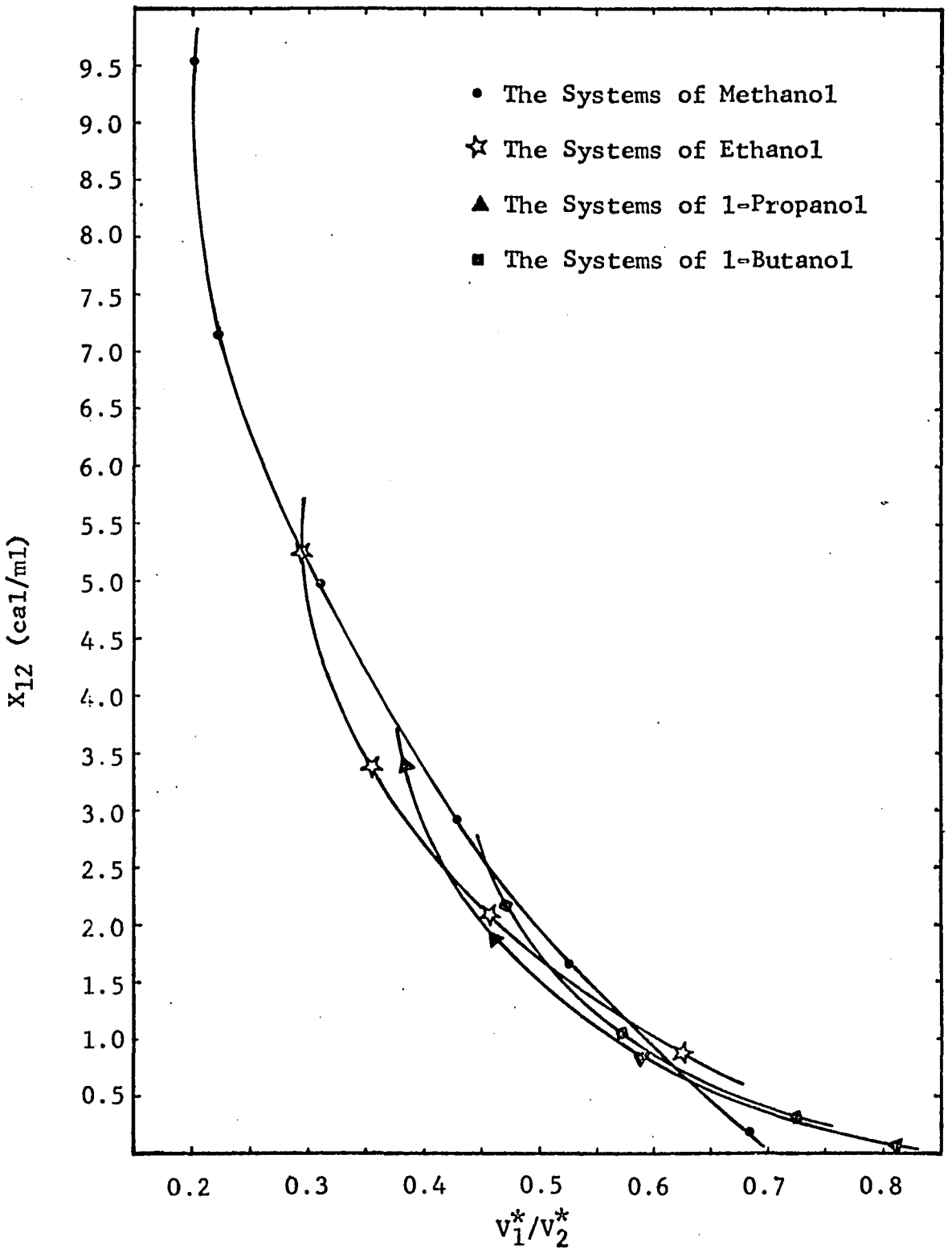

Fig. 23. The Change of X_{12} of the Alcohol—Alcohol Systems with the Ratio of their Respective Molar Core Volume at 25°C.

Table XX: The Effect of the Ratio of the Molar Core Volume, V_1^*/V_2^*, on X_{12} of the Alcohol—Alcohol Systems

System	V_1^*/V_2^*	X_{12} (cal/ml)
Methanol—Ethanol	0.683	0.186
Methanol—1-Propanol	0.525	1.65
Methanol—1-Butanol	0.426	2.91
Methanol—1-Hexanol	0.308	4.99
Methanol—1-Octanol	0.242	7.13
Methanol—1-Decanol	0.200	9.45
Ethanol—1-Propanol	0.768	0.352
Ethanol—1-Butanol	0.623	0.833
Ethanol—1-Hexanol	0.451	2.09
Ethanol—1-Octanol	0.354	3.36
Ethanol—1-Decanol	0.292	5.27
1-Propanol—1-Butanol	0.811	0.053
1-Propanol—1-Hexanol	0.587	0.825
1-Propanol—1-Octanol	0.461	1.88
1-Propanol—1-Decanol	0.381	3.39
1-Butanol—1-Hexanol	0.723	0.297
1-Butanol—1-Octanol	0.568	1.05
1-Butanol—1-Decanol	0.469	2.21
1-Hexanol—1-Octanol	0.786	0.184
1-Hexanol—1-Decanol	0.649	0.766
1-Octanol—1-Decanol	0.825	0.140

Table XXI: The Effect of the Error in V^E on the Exponent n

System	V^E (ml/mole)	H^E (cal/mole)	δV^E (ml/mole)	δH^E (cal/mole)	n
T = 25°C					
Methanol— 1-Propanol	0.0503	19.6	+0.005	+0.7	0.76+0.08
			-0.005	-1.8	0.76-0.09
			+0.01	+3.5	0.76+0.17
			-0.01	-3.6	0.76-0.19
Methanol— 1-Butanol	0.0738	34.01	+0.005	+1.9	0.84+0.05
			-0.005	-1.6	0.84-0.05
			+0.01	+3.6	0.84+0.10
			-0.01	-3.4	0.84-0.09
Methanol— 1-Hexanol	0.1160	56.39	+0.005	+2.2	0.94+0.04
			-0.005	-1.5	0.94-0.04
			+0.01	+3.6	0.94+0.07
			-0.01	-3.2	0.94-0.06
Methanol— 1-Octanol	0.1563	80.64	+0.005	+1.7	1.00+0.03
			-0.005	-1.7	1.00-0.02
			+0.01	+3.5	1.00+0.05
			-0.01	-3.4	1.00-0.05
Methanol— 1-Decanol	0.1780	94.92	+0.005	+1.5	1.19+0.03
			-0.005	-1.0	1.19-0.02
			+0.01	+3.8	1.19+0.04
			-0.01	-2.7	1.19-0.03
Ethanol— 1-Propanol	0.0084	4.59	+0.005	+1.5	0.96+0.31
			-0.005	-1.5	0.96-0.31
			+0.01	+3.0	0.96+0.52
			-0.01	-3.0	0.96-0.68
Ethanol— 1-Butanol	0.0121	11.49	+0.005	+1.6	0.96+0.13
			-0.005	-1.6	0.96-0.12
			+0.01	+3.2	0.96+0.24
			-0.01	-3.2	0.96-0.25
Ethanol— 1-Hexanol	0.0363	30.19	+0.005	+1.7	0.99+0.05
			-0.005	-1.6	0.99-0.05
			+0.01	+3.4	0.99+0.11
			-0.01	-3.3	0.99-0.11
Ethanol— 1-Octanol	0.0599	51.95	+0.005	+1.5	0.99+0.03
			-0.005	-2.0	0.99-0.03
			+0.01	+3.2	0.99+0.06
			-0.01	-3.8	0.99-0.07
Ethanol— 1-Decanol	0.0885	71.89	+0.005	+1.8	1.17+0.03
			-0.005	-1.4	1.17-0.02

(to be continued)

Table XXI (continued)

System	V^E (ml/mole)	H^E (cal/mole)	δV^E (ml/mole)	δH^E (cal/mole)	n
Ethanol— 1-Decanol	0.0885	71.89	+0.01	+3.4	1.17+0.05
			-0.01	-3.0	1.17-0.04
1-Propanol— 1-Butanol	-0.0019	11.29	+0.005	+1.8	0.80+0.40
			-0.005	-2.0	0.80-0.40
			+0.01	+3.8	
			-0.01	-4.8	
1-Praopanol— 1-Hexanol	0.0187	14.70	+0.005	+1.7	0.98+0.12
			-0.005	-1.6	0.98-0.10
			+0.01	+3.6	0.98+0.23
			-0.01	-3.3	0.98-0.22
1-Propanol— 1-Octanol	0.0514	36.67	+0.005	+1.7	0.97-0.05
			-0.005	-2.0	0.97-0.05
			+0.01	+3.5	0.97+0.10
			-0.01	-3.8	0.97-0.10
1-Propanol— 1-Decanol	0.0890	60.21	+0.005	+2.1	1.12+0.04
			-0.005	-1.3	1.12-0.04
			+0.01	+3.8	1.12+0.07
			-0.01	-3.0	1.12-0.06
1-Butanol— 1-Hexanol	0.0115	6.45	+0.005	+1.9	0.92+0.32
			-0.005	-1.8	0.92-0.31
			+0.01	+3.7	0.92+0.49
			-0.01	-3.7	0.92-0.41
1-Butnaol— 1-Octanol	0.0413	24.79	+0.005	+1.8	0.93+0.07
			-0.005	-2.1	0.93-0.09
			+0.01	+3.7	0.93+0.15
			-0.01	-4.0	0.93-0.16
1-Butnaol— 1-Decanol	0.0778	48.08	+0.005	+1.9	1.08+0.05
			-0.005	-1.8	1.08-0.04
			+0.01	+3.6	1.08+0.08
			-0.01	-3.6	1.08-0.08
1-Hexanol— 1-Octanol	0.0098	6.21	+0.005	+2.9	0.88+0.30
			-0.005	-2.3	0.88-0.29
			+0.01	+4.9	0.88+0.42
			-0.01	-4.3	0.88-0.41
1-Hexanol— 1-Decanol	0.0375	22.80	+0.005	+1.7	1.02+0.08
			-0.005	-2.4	1.02-0.10
			+0.01	+3.6	1.02+0.16
			-0.01	-4.0	1.02-0.19
1-Octanol— 1-Decanol	0.0075	5.35	+0.005	+2.0	0.92+0.32
			-0.005	-2.5	0.92-0.30

the experimental error.

The value of n to give the best fit between H^E_{calc} and H^E is about 1.00. The enthalpy of mixing calculated at n = 1.00 for these 21 systems is shown in Table XXII along with the error, $H^E - H^E_{n=1.00}$. The agreement between H^E_{calc} and H^E is satisfactory. Although the absolute errors for the systems with larger molecular size differences, such as the systems Methanol—1-Decanol and Ethanol—1-Decanol are higher, the percent relative errors are about the same since these systems tend to have larger enthalpies of mixing.

Unlike the two previous groups of mixtures, n_{calc} ahows a slow increase with the molar core ratio, V_1^*/V_2^*. Though a constant value of n was just demonstrated to be applicable, the range actually varies from 0.75 for the system Methanol—1-Propanol to 1.19 for the system Methanol—1-Decanol.

(b). Dependence of the Excess Enthalpy of Mixing at Various Compositions on the Exponent n:

The Redlich-Kister equations obtained experimentally through the method of least squares by Benson and Pflug (91) for the volumes of mixing, V^E, and the enthalpies of mixing, H^E, for the systems 1-Propanol—1-Hexanol, 1-Propanol—1-Decanol, and 1-Hexanol—1-Decanol at 25°C are as follows:

Table XXII: Comparison of $H^E_{n=1.00}$ with the Experimentally found Value of H^E

System	V^E (ml/mole)	n_{calc}	$H^E_{n=1.00}$ (cal/mole)	H^E (cal/mole)	Error $H^E - H^E_{n=1.00}$
Methanol—Ethanol	0.0085		1.56	1.07	- 0.49
Methanol—1-Propanol	0.0503	0.76	15.74	19.60	+ 3.86
Methanol—1-Butanol	0.0738	0.84	29.40	34.01	+ 4.61
Methanol—1-Hexanol	0.1160	0.94	53.65	56.39	+ 2.74
Methanol—1-Octanol	0.1563	1.00	80.70	80.64	- 0.06
Methanol—1-Decanol	0.1780	1.19	112.37	94.92	-17.45
Ethanol—1-Propanol	0.0084	0.96	4.37	4.59	+ 0.22
Ethanol—1-Butanol	0.0121	0.96	11.01	11.49	+ 0.48
Ethanol—1-Hexanol	0.0363	0.99	29.92	30.19	+ 0.27
Ethanol—1-Octanol	0.0599	0.99	51.18	51.95	+ 0.77
Ethanol—1-Decanol	0.0885	1.17	84.68	71.89	-12.79
1-Propanol—1-Butanol	-0.0019	0.80	0.84	1.29	+ 0.45
1-Propanol—1-Hexanol	0.0187	0.98	14.47	14.70	+ 0.23
1-Propanol—1-Octanol	0.0513	0.97	35.47	36.67	+ 1.20
1-Propanol—1-Decanol	0.0890	1.12	67.60	60.21	- 7.39
1-Butnaol—1-Hexanol	0.0115	0.92	5.99	6.45	+ 0.46
1-Butanol—1-Octanol	0.0413	0.93	23.05	24.79	+ 1.74
1-Butanol—1-Decanol	0.0778	1.08	51.76	48.08	+ 3.68
1-Hexanol—1-Octanol	0.0098	0.88	5.22	6.21	+ 0.99
1-Hexanol—1-Decanol	0.0375	1.02	23.01	22.80	- 0.21
1-Octanol—1-Decanol	0.0075	0.92	4.97	5.35	+ 0.38

For the system 1-Propanol—1-Hexanol:

$$V^E = x_1(1-x_1)\left[0.0749 - 0.0249(1-2x_1) + 0.0058(1-2x_1)^2 - 0.0049(1-2x_1)^3 + 0.019(1-2x_1)^4\right] \quad \text{(ml/mole)}$$

$$H = \left(\frac{1}{4.18}\right)x_1(1-x_1)\left[245.89 - 43.34(1-2x_1) + 26.86(1-2x_1)^2 - 14.60(1-2x_1)^3\right] \quad \text{(cal/mole)}$$

For the system 1-Propanol—1-Decanol:

$$V^E = x_1(1-x_1)\left[0.3559 - 0.0791(1-2x_1) + 0.0571(1-2x_1)^2 - 0.0260(1-2x_1)^3 + 0.072(1-2x_1)^4\right] \quad \text{(ml/mole)}$$

$$H^E = \left(\frac{1}{4.18}\right)x_1(1-x_1)\left[1008.21 - 221.65(1-2x_1) + 108.21(1-2x_1)^2 + 11.98(1-2x_1)^3 + 99.50(1-2x_1)^4 - 128.23(1-2x_1)^5\right] \quad \text{(cal/mole)}$$

For the system 1-Hexanol—1-Decanol:

$$V^E = x_1(1-x_1)\left[0.01500 + 0.0028(1-2x_1) + 0.0148(1-2x_1)^2\right] \quad \text{(ml/mole)}$$

$$H^E = \left(\frac{1}{4.18}\right)x_1(1-x_1)\left[382.34 - 27.72(1-2x_1) + 17.38(1-2x_1)^2 - 14.04(1-2x_1)^3\right] \quad \text{(cal/mole)}$$

V^E and H^E calculated from these equations for the above three systems along with their corresponding H^E_{calc}, H^E_{cont}, X_{12}, A, and B, computed accordingly at various mole fractions from x_1=0.10 to 0.90 at their corresponding n obtained in (a) (see column 3 of Table XXII) for the equal molar solutions, are shown in Table XXIII. H^E, H^E_{calc}, and H^E_{cont} of these systems are plotted against x_1 in Figs. 24, 25, 26, respectively. H^E and H^E_{calc} show excellent agreement. This proves that a constant value of n can be applied to the binary mixtures of 1-alcohols over the whole concentration range. X_{12}, and A and B are plotted against x_1 in Fig. 27 and Fig. 28, respectively. As is seen, X_{12} changes very little with composition. A tends to be negative and B increase sharply with x_1.

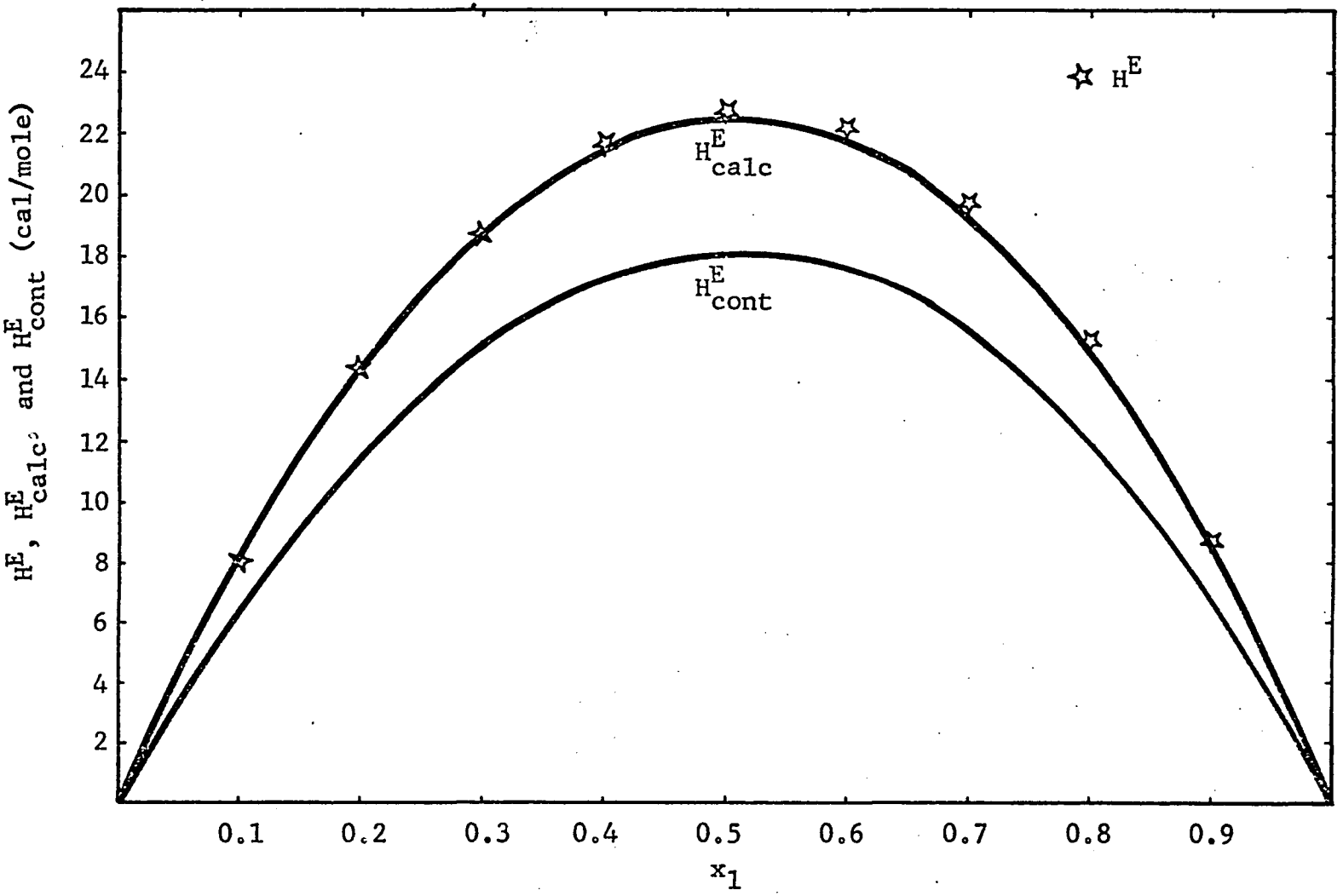

Fig. 24. H^E, H^E_{calc}, and H^E_{cont} of the System 1-Hexanol—1-Decanol at 25°C as Functions of the Molar Fraction of 1-Hexanol, x_1.

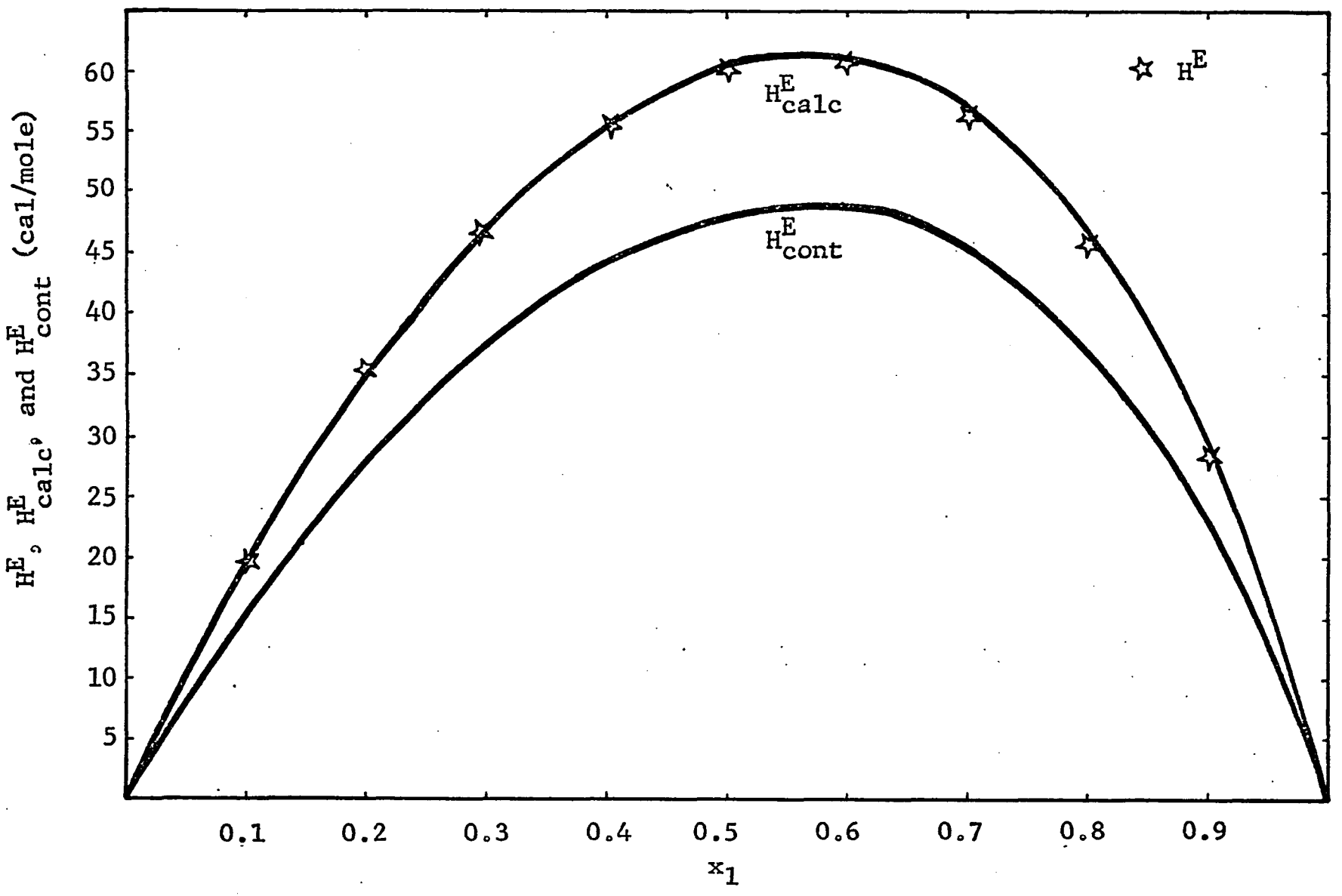

Fig. 25. H^E, H^E_{calc}, and H^E_{cont} of the System 1-Propanol—1-Decanol at 25°C as Functions of the Mole Fraction of 1-Propanol, x_1.

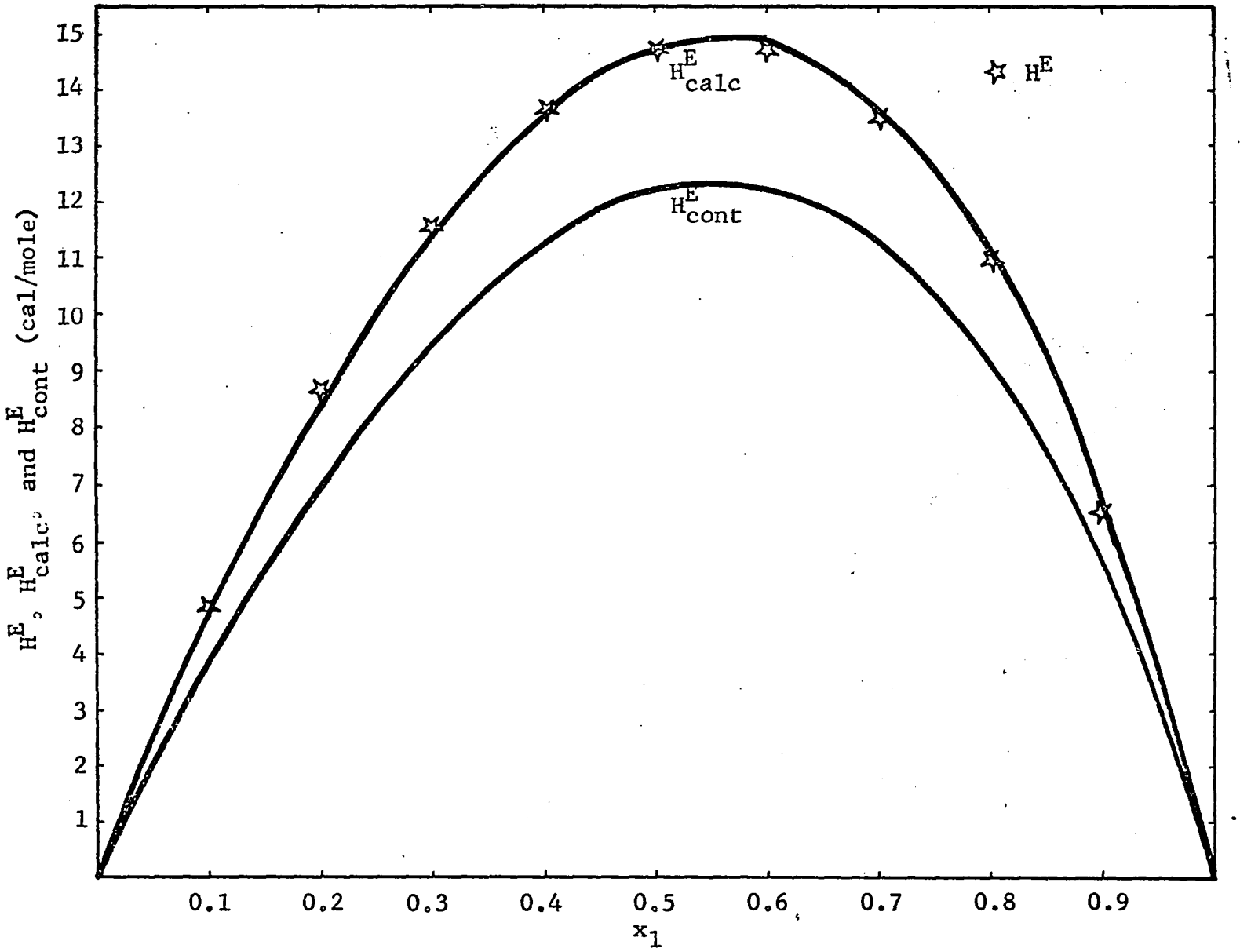

Fig. 26. H^E, H^E_{calc}, and H^E_{cont} of the System 1-Propanol—1-Hexanol at 25°C as Functions of the Mole Fraction of 1-Propanol, x_1.

Table XXIII: Comparison of the Calculated and Experimental Enthalpy of Mixing for three Alcohol—Alcohol Systems over the whole Composition Range

	x_1	V^E (ml/ mole)	H^E (cal/ mole)	H^E_{calc} (cal/ mole)	H^E_{cont} (cal/ mole)	X_{12} (cal/ ml)	A (cal/ mole)	B (cal/ mole)
1. System: 1-Propanol—1-Hexanol, T = 25°C								
0.98	0.10	0.0058	4.8	4.8	4.0	0.86	-70.0	13.1
	0.20	0.0102	8.7	8.4	7.0	0.83	-66.5	27.1
	0.30	0.0139	11.6	11.4	9.5	0.83	-61.0	42.5
	0.40	0.0168	13.7	13.6	11.3	0.84	-54.6	59.2
	0.50	0.0187	14.7	14.8	12.3	0.85	-47.8	77.5
	0.60	0.0192	14.7	14.9	12.3	0.85	-40.2	97.5
	0.70	0.0182	13.5	13.7	11.3	0.87	-31.7	119.7
	0.80	0.0153	10.9	11.1	9.1	0.89	-22.2	144.3
	0.90	0.0098	6.6	6.7	5.5	0.92	-11.6	171.6
2. System: 1-Hexanol—1-Decanol, T = 25°C								
1.02	0.10	0.0146	8.1	8.3	6.7	0.85	-6.07	9.9
	0.20	0.0252	14.3	14.4	11.6	0.81	-8.30	20.1
	0.30	0.0322	18.8	18.8	15.2	0.79	-9.21	30.8
	0.40	0.0363	21.7	21.5	17.4	0.77	-9.45	42.2
	0.50	0.0375	22.8	22.5	18.1	0.75	-9.24	54.2
	0.60	0.0363	22.3	21.8	17.6	0.73	-8.32	67.0
	0.70	0.0318	19.8	19.3	15.5	0.72	-7.00	80.7
	0.80	0.0246	15.4	14.9	12.0	0.71	-5.18	95.3
	0.90	0.0142	8.8	8.5	6.8	0.69	-2.92	111.1
3. System: 1-Propanol—1-Decanol, T = 25°C								
1.12	0.10	0.0311	19.5	19.8	15.9	3.42	11.7	20.7
	0.20	0.0532	35.2	35.2	28.0	3.21	0.49	43.5
	0.30	0.0701	47.1	46.9	37.6	3.12	-4.95	69.2
	0.40	0.0821	55.6	55.7	44.6	3.06	-8.46	98.4
	0.50	0.0890	60.2	60.6	48.4	3.01	-11.0	132.2
	0.60	0.0898	60.6	61.3	48.8	2.98	-12.2	171.7
	0.70	0.0840	56.1	57.1	45.3	2.96	-12.2	218.6
	0.80	0.0702	45.9	46.9	37.0	2.96	-10.3	275.4
	0.90	0.0449	28.6	29.0	22.8	3.01	-6.20	345.4

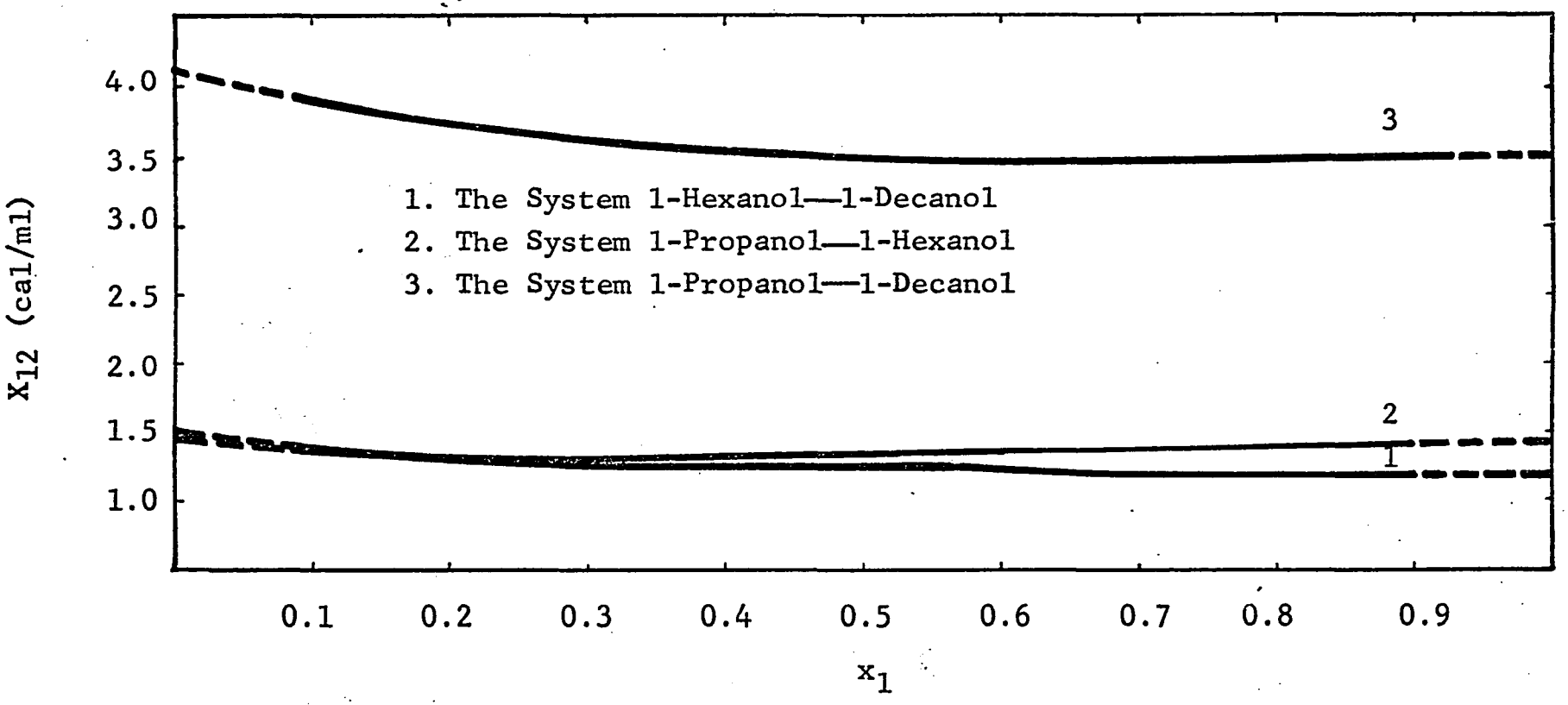

Fig. 27. The Change of X_{12} of the Systems 1. 1-Hexanol—1-Decanol, 2. 1-Propanol —1-Hexanol, and 3. 1-Propanol—1-Decanol at 25°C with the Mole Fraction, x_1.

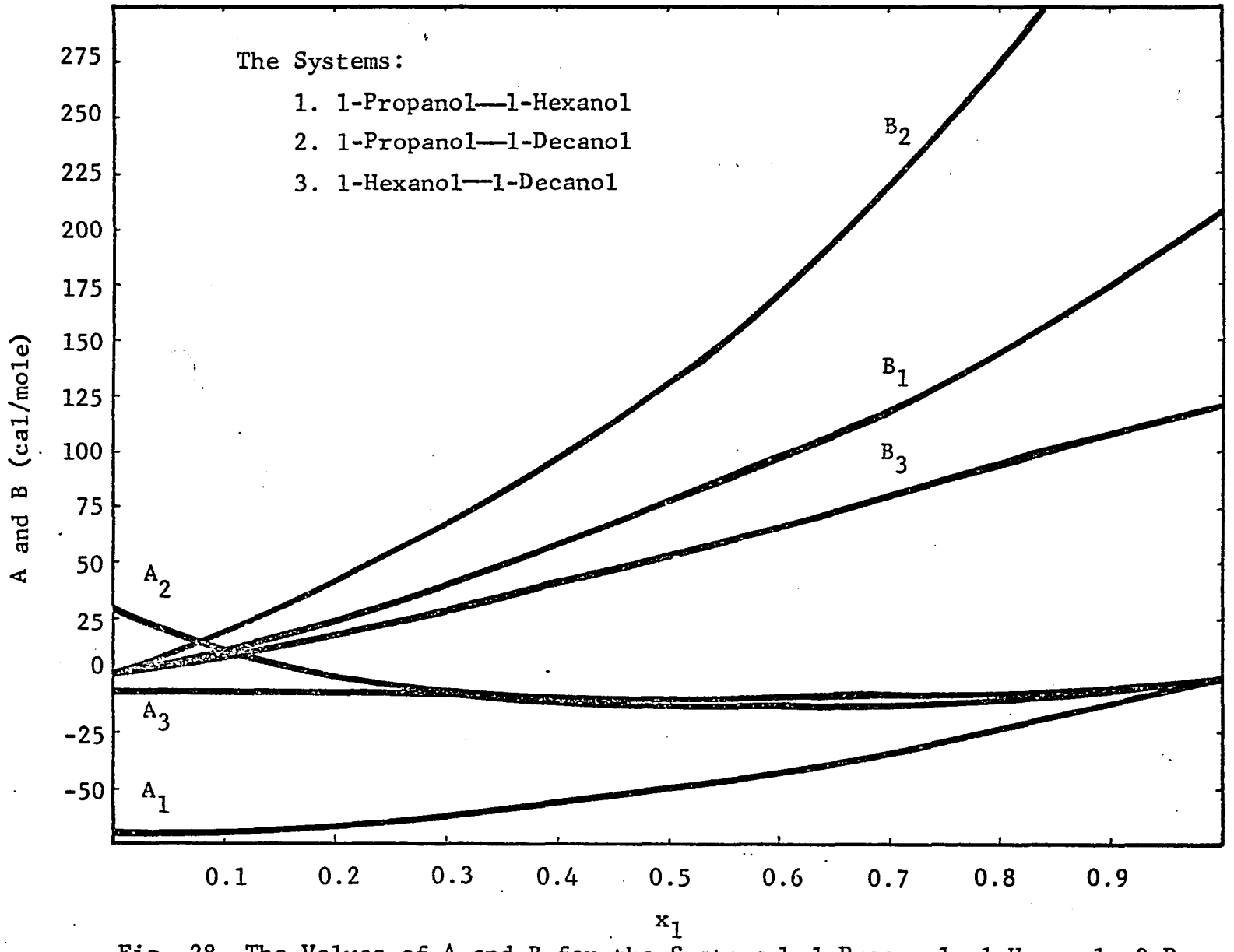

Fig. 28. The Values of A and B for the Systems 1. 1-Propanol—1-Hexanol, 2. Propanol—1-Decanol, and 3. 1-Hexanol—1-Decanol at 25°C as functions of x_1.

4. Application of the Modified Theory to the Binary 1-Alcohol—n-Hexane Mixtures:

The fourth group of mixtures to be tested here is the group of the 1-Alcohol—n-Hexane systems. They are the following: Ethanol—n-Hexane, 1-Propanol—n-Hexane, 1-Butanol—n-Hexane, 1-Hexanol—n-Hexane, and 1-Octanol—n-Hexane at 25°C. n-Hexane is the common component; its physical properties were already included in Table I.

Table XXV shows the changes of H_{calc}, H_{cont}, $\overline{V}$, and X_{12} of these systems with the value of n (from 0.70 to 1.00). Like the 1-Alcohol—1-Alcohol systems, the difference between H_{calc} and H_{cont} decreases slowly with n. The degree of decreasing gradually declines from the system Ethanol—n-Hexane to the system 1-Octanol—n-Hexane. The values of n at which H^E_{calc} best reproduce H^E are listed in Table XXVI as n_{calc} along with H^E predicated at n = 0.92 (see note on the next page of this section), $H_{n=0.92}$, which is the average value of n_{calc}(see column 3 of Table XXVI). The characteristic and reduced properties of the pure components at n = 0.92 are found in Table XXIV.

It is to be noted that, like for the 1-Alcohol—1-Alcohol systems, n_{calc} increases gradually as the molecular size ratio increases. But unlike the former systems, the error in n (see the last column of Table XXVII) due to

Table XXIV: Characteristic and Reduced Properties of the Pure Components at n=0.92 at 25°C

Compound	V^* (ml/mole)	T^* (^oK)	P^* (cal/ml)	$\overline{V}$	$\overline{\overline{V}}$	C
Ethanol	46.20	5270	115	1.2702	0.05657	0.509
1-Propanol	60.19	5572	115	1.2486	0.05351	0.636
1-Butanol	74.21	5723	117	1.2391	0.05210	0.766
1-Hexanol	102.64	6060	116	1.2204	0.04920	0.992
1-Octanol	130.63	6216	118	1.2127	0.04797	1.25
n-Hexane	98.79	4636	109	1.3312	0.06432	1.17

*Table XXV: The Dependence of the Excess Enthalpy of Mixing at $x_1 = 0.50$ on the Exponent n

n	$\overline{V}$	H_{calc} (cal/mole)	H_{cont} (cal/mole)	X_{12} (cal/ml)
1. System: Ethanol—n-Hexane, H^E=133 cal/mole), V^E=0.41 ml/mole				
0.70	1.3405	155.5	124.0	10.72
0.80	1.3296	138.5	107.3	9.42
0.90	1.3194	135.2	94.4	8.41
1.00	1.3098	114.6	84.1	7.60
2. System: 1-Propanol—n-Hexane, H^E=135 cal/mole, V^E=0.180ml/mole				
0.70	1.2336	135.2	111.6	7.86
0.80	1.3135	118.6	95.6	6.48
0.90	1.3040	105.6	83.3	6.05
1.00	1.2952	95.3	73.5	5.41
3. System: 1-Butabol—n-Hexane, H^E=122 cal/mole, V^E=0.080 ml/mole				
0.70	1.3129	154.6	129.7	7.83
0.80	1.3033	134.0	110.2	6.75
0.90	1.2944	118.1	95.2	5.92
1.00	1.2859	105.3	83.3	5.25
4. System: 1-Hexanol—n-Hexane, H^E=111 cal/mole, V^E=-0.16 ml/mole				
0.70	1.2912	159.0	139.5	6.67
0.80	1.2827	135.0	117.0	5.67
0.90	1.2747	116.7	99.8	4.91
1.00	1.2671	101.3	86.0	4.29
5. System: 1-Octanol—n-Hexane, H^E=99.1 cal/mole, V^E=-0.35 ml/mole				
0.70	1.2774	170.4	153.0	6.21
0.80	1.2695	141.9	126.6	5.21
0.90	1.2621	119.7	106.4	4.43
1.00	1.2551	102.1	90.5	3.82
1.10	1.2485	87.7	77.7	3.32

* All the enthalpies and volumes of mixing data were taken from ref. (92).

Table XXVI: Comparison of the Enthalpy of Mixing predicted at n=0.92 with Experimentally found H^E

System	V^E (ml/mole)	n	$H^E_{n=0.92}$ (cal/mole)	H^E (cal/mole)	$H^E - H^E_{n=0.92}$
Ethanol— n-Hexane	0.41	0.84	123	133	+10
1-Propanol— n-Hexane	0.18	0.70	104	135	+31
1-Butanol— n-Hexane	0.08	0.87	115	122	+ 7
1-Hexanol— n-Hexane	-0.16	0.93	113	111	- 2
1-Octanol— n-Hexane	-0.35	1.02	116	99	-17

Table XXVII: The Effect of the Error in V^E on the value of n

System	V^E (ml/mole)	H^E (cal/mole)	δV^E (ml/mole)	δH^E (cal/mole)	n
T = 25°C					
Ethanol —n-Hexane	0.41	133	+0.005	+1.0	0.84+0.01
			-0.005	-1.5	0.84-0.01
			+0.01	+2.2	0.84+0.02
			-0.01	-2.6	0.84-0.02
1-Propanol —n-Hexane	0.18	135	+0.005	+1.5	0.70+0.01
			-0.005	-1.4	0.70-0.01
			+0.01	+3.0	0.70+0.02
			-0.01	+3.0	0.70-0.02
1-Butanol —n-Hexane	0.08	122	+0.005	+1.8	0.87+0.01
			-0.005	-1.8	0.87-0.01
			+0.01	+3.2	0.87+0.02
			-0.01	-2.1	0.87-0.02
1-Hexanol —n-Hexane	-0.16	111	+0.005	+1.9	0.93+0.01
			-0.005	-0.9	0.83-0.01
			+0.01	+3.3	0.93+0.02
			-0.01	-2.3	0.93-0.02
1-Octanol —n-Hexane	-0.35	99	+0.005	+1.3	1.02+0.01
			-0.005	-1.6	1.02-0.01
			+0.01	+2.7	1.02+0.02
			-0.01	-2.9	1.02-0.02

the possible maximun error in V^E (see column 4) is relatively small. This makes the error in $H^E_{n=0.92}$ more sensitive to n. Therefore, if one is to apply one value of n to all these systems, the ones whose n_{calc} deviate more from the average value of n are expected to have large errors in H^E calculated at the assigned value of n (see the last column of Table XXIV for the system 1-Octanol—n-Hexane). One way to amend this shortcoming is to obtain an emperical formula for n as a function of the molecular size ratio and allow n to vary as the molecular size ratio of the two components of a system varies.

The values of X_{12} and V_1^*/V_2^* at their corresponding n_{calc} are listed in Table XXVIII and graphically illustrated in Fig. 29. Their non-linear relationship is different from that of n-paraffin hydrocarbon mixtures.

Note;

We would like to point out here that the experimental enthalpy of mixing of the system 1-Propanol—n-Hexane seems to be inconsistent with the other four systems. This could be the reason for the low value of n_{calc} and of the particular large error in $H^E_{n=0.92}$ for this system. Therefore we excluded the value of n_{calc} for this system in averaging n. The average value of n would have been equal to 0.88 if we included n_{calc} of this system. This would make the overall

Table XXVIII: The Dependence of X_{12} on the Ratio of the Hard Core Molar Volumes of the two Components for the 1-Alcohol—n-Hexane Systems at 25°C

System	n_{calc}	X_{12} (cal/ml)	V_1^*/V_2^*
Ethanol—n-Hexane	0.84	9.02	0.468
1-Propanol—n-Hexane	0.70	7.86	0.610
1-Butanol—n-Hexane	0.87	6.17	0.753
1-Hexanol—n-Hexane	0.93	4.72	1.040
1-Ocatnol—n-Hexane	1.02	3.72	1.324

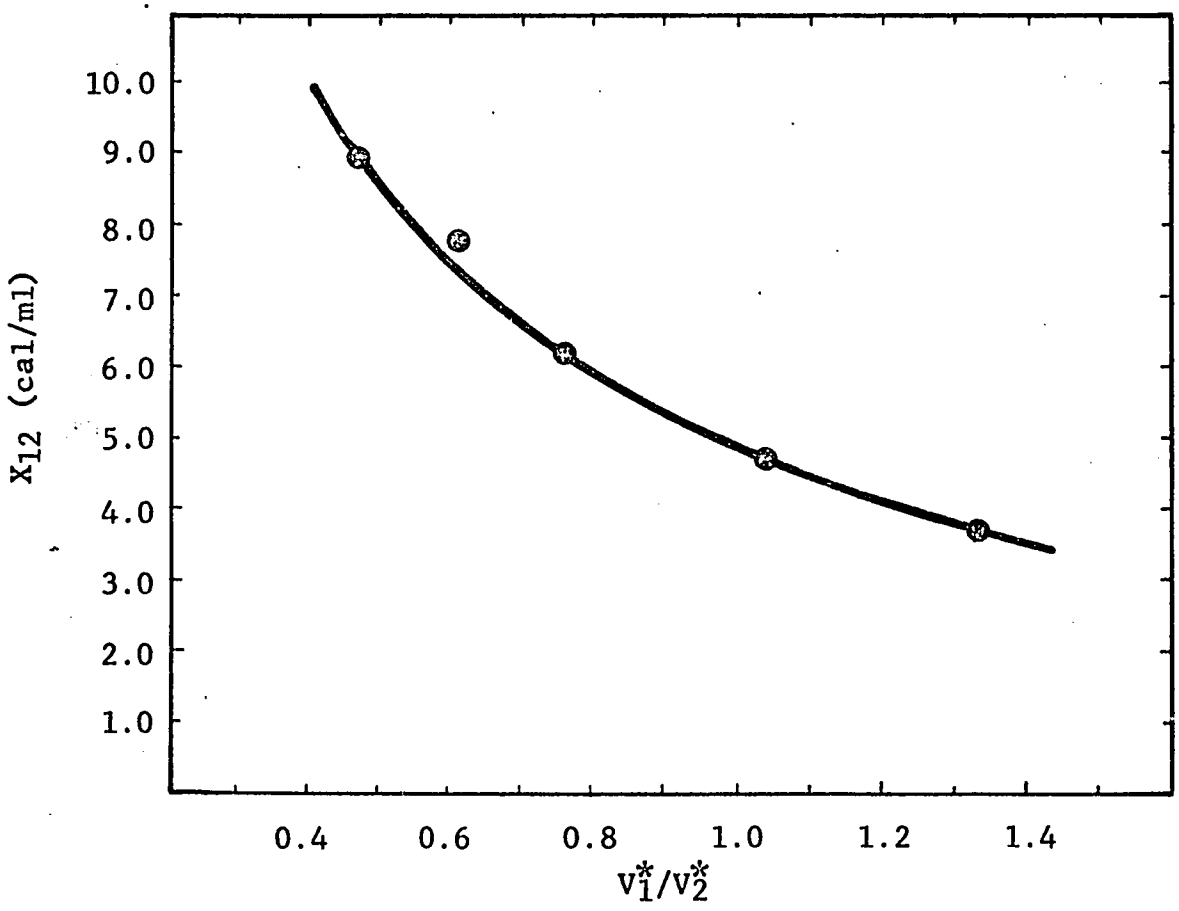

Fig. 29. The Change of X_{12} with the Ratio of the Hard Core Molar Volumes of the two Components for the 1-Alcohol—n-Hexane Systems at 25°C.

deviation of H^E predicted at n=0.88 from H^E (excluding the system 1-Propanol—n-Hexane) greater.

5. Uncertainties in the Characteristic Properties of the Pure Components:

The properties of the pure components refer to atmospheric pressure and therefore be considered to hold for zero pressure without an appreciable error. V^* and T^* depend only on the density d and the thermal expansion coefficient α, both of which are known to high accuracy, in general to about 1%. Thermal pressure coefficients are subject to large errors. Values reported by different investigators for the same liquid frequently differ by more than the acknowledged limits of error. Values of γ, calculated from the best-fit polynomial expressions formulated by Orwoll and Flory for n-paraffin hydrocarbons are said to be fairly reliable, with limits of error ranging from 1% to 3%. Mixtures of these liquids can therefore be treated with assurance that the parameters for the pure components are both accurate and mutually consistent. In general, the error in γ is between 2% and 5%. The values of γ calculated from the adiabatic compressibilities obtained from sonic measurements are usually of greater error. Since P^* is principally determined by γ, it could be subject to a large error. An uncertainty of 5% in γ could cause the same percentage error in P^* and consequently a 5% error in H^E_{calc} when X_{12} is small.

6. Significance of the Reduced Temperature of Mixtures:

Dividing both the numerator and denominator of eq. (74) by $\varphi_1 P_1^* + \varphi_2 P_2^*$, we obtain

$$\overline{T} = \frac{\dfrac{\varphi_1 P_1 \overline{T}_1 + \varphi_2 P_2 \overline{T}_2}{\varphi_1 P_1^* + \varphi_2 P_2^*}}{1 - \dfrac{\varphi_1 \theta_2 X_{12}}{\varphi_1 P_1^* + \varphi_2 P_2^*}} \qquad (91)$$

eq. (91) presents a clue to the factors affecting V^E and H^E. If the characteristic temperature for the pure components are equal, $T_1^* = T_2^*$, which is approximately true for the system CCl_4—c-C_6H_{12}, then eq. (91) becomes

$$\overline{T} = \frac{\overline{T}_1}{1 - \dfrac{\varphi_1 \theta_2 X_{12}}{\varphi_1 P_1^* + \varphi_2 P_2^*}} = \frac{\overline{T}_2}{1 - \dfrac{\varphi_1 \theta_2 X_{12}}{\varphi_1 P_1^* + \varphi_2 P_2^*}} \qquad (92)$$

If also $X_{12} = 0$, then $\overline{T} = \overline{T}_1 = \overline{T}_2$. This also indicates through eq. (32) that $\overline{V} = \overline{V}_1 = \overline{V}_2$, and through eq. (84) that $\overline{V} = \overline{V}_1 = \overline{V}_2 = \overline{V}^o$, and consequently $V^E = 0$, and $H^E = 0$, as follows from eqs. (84) and (81), respectively. The mixture is then ideal under these conditions.

A positive value of X_{12} increases $\overline{T}$ for mixtures, therefore $\overline{T} > \overline{T}_1 = \overline{T}_2$. As is seen from Table II, $\overline{V}$ increases as $\overline{T}$

increases at constant $\tilde{n}$ so that $\bar{V} > \bar{V}_1 = \bar{V}_2$ which makes $\bar{V}$ $> \varphi_1\bar{V}_1+\varphi_2\bar{V}_2 = \bar{V}^o$; hence $V^E > 0$ from eq. (84) and its magnitude depending exclusively on the ratio of $\varphi_1\theta_2X_{12}/(\varphi_1P_1^*+\varphi_2P_2^*)$, and a more positive value of H^E is to be expected.

If the characteristic temperature of the pure components T_1^* and T_2^* differ considerable but $P_1^* = P_2^*$ and $X_{12} = 0$, then eq. (74) becomes $\bar{T} = \varphi_1\bar{T}_1+\varphi_2\bar{T}_2$; $\bar{T}$ is then linear in the segment fractions. This reveals the same character as $\bar{V}$ of eq. (82). Due to the pronounced upward curvature of $\bar{V}$ with $\bar{T}$, the reduced volume $\bar{V}$ of a mixture having the linearly interpolated $\bar{T}$ must fall below $\bar{V}^o$ given by eq. (83). As a result of this, the negative terms involving $\bar{V}$ appearing in the equation of state contribution to H^E increase; This results in a negative effect in H^E, and accordingly, V^E and $\bar{V}^E$ are negative with magnitudes increasing rapidly with the difference between T_1^* and T_2^*. Examples closely following this description are the mixtures of n-paraffin hydrocarbons treated in this work. In these instances the negative excess volume is somewhat diminished by a small, positive interaction parameter X_{12}.

7. Test of Geometric Mean Rule (Berthelot Relationship):

None of the combination rules of energy has been used in the derivation of the equation for H^E, therefore the interaction parameter, X_{12}, we have obtsined for the four different groups of mixtures of various constituents may provide a way to test the validity of the combination rule. The geometric mean rule for ϵ_{12} is

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{\frac{1}{2}} \tag{93}$$

where ϵ_{11}, ϵ_{12}, and ϵ_{22} are appropriate energy parameters. Eq. (93) gives acceptable results for simple spherical or nearly spherical molecules (93). For mixtures of spherical as well as non-spherical molecules, an empirical coefficient has been introduced to take into account any deviation from the geometric mean rule; we accordingly write

$$\epsilon_{12} = \xi(\epsilon_{11}\epsilon_{22})^{\frac{1}{2}} \tag{94}$$

The factor ξ is experimentally accessible. For the van der Waals approximation, eq. (94) can be written as

$$\frac{a_{12}}{b_{12}} = \xi\left(\frac{a_{11}a_{22}}{b_{11}b_{22}}\right)^{\frac{1}{2}} \tag{95}$$

where ratios of a_{ij}/b_{ij} correspond to interaction energies ϵ_{ij}. The values of a_{ij} and b_{ij} can be obtained from the critical data of the mixture.

We apply next the geometric mean rule for this modified Flory's theory to the interaction energies per unit molecular volume and write

$$\eta_{12} = \xi (\eta_{11}\eta_{22})^{\frac{1}{2}} \tag{96}$$

From eq. (96) and eq. (58) it follows that

$$\Delta\eta = \eta_{11} + \eta_{22} - 2\xi(\eta_{11}\eta_{22})^{\frac{1}{2}} \tag{97}$$

Combining eq. (97) with eq. (70) yields

$$X_{12} = \left(\frac{\bar{s}}{2v^{*n+1}}\right)\left[\eta_{11} + \eta_{22} - 2\xi(\eta_{11}\eta_{22})^{\frac{1}{2}}\right] \tag{98}$$

By inserting η_{11} and η_{22} from eq. (25) into the above equation, X_{12}/P_1^* takes the form

$$\frac{X_{12}}{P_1^*} = 1 - 2\xi\left(\frac{\frac{P_2^*}{s_2}}{\frac{P_1^*}{s_1}}\right) + \left(\frac{\frac{P_2^*}{s_2}}{\frac{P_1^*}{s_1}}\right) \tag{99}$$

or

$$\frac{X_{12}}{P_1^*} = 2\left(\frac{\frac{P_2^*}{s_2}}{\frac{P_1^*}{s_1}}\right)(1-\xi) + \left(1-\frac{\frac{P_2^*}{s_2}}{\frac{P_1^*}{s_1}}\right)^2 \qquad (100)$$

X_{12} is equal to zero for systems of which the geometric mean rule can be applied and of which P_2^*/P_1^* and s_2/s_1 are equatl to one. In case when $\xi = 1$, the X_{12}/P_1^* ratio is given only by the second term of the right-hand side of eq. (99).

Solving eq. (99) for ξ, we obtain

$$\xi = \frac{1}{2}\left[1 + \left(\frac{\frac{P_1^*}{s_1}}{\frac{P_2^*}{s_2}}\right)\left(1 - \frac{X_{12}}{P_1^*}\right)\right] \qquad (101)$$

The parameter P_i^* correspond to a molecular interaction energy per unit volume, and s_i to a molecule surface/volume ratio. Thus P_i^*/s_i corresponds to an energy/surface ratio. In fact ξ depends on two main factors, one is s_1/s_2 which relates to the molecular size ratio of the two components, the other is X_{12} which relates to the polarity or the interaction between unlike molecules. As is seen from eqs. (100) and (101), when ξ is known one can find X_{12} from the properties of the

pure components.

Next we use X_{12} and the properties of the pure components to evaluate ξ. Table XXIX shows the results of ξ calculated from eq. (101) and the corresponding parameters for the afore-tested four groups of mixtures at their appropriate values of n. As is seen from Table XXIX for the more spherical systems (the second group of mixtures), ξ is closer to unity. This means that these systems follow much closer the Berthelot's relationship than do the other groups of less spherical systems. In the same group of mixtures, those systems whose components are closer in molecular size usually have closer-to-unity values for ξ, like the systems Ethanol—1-Propanol, 1-Hexanol—1-Octanol, and 1-Octanol—1-Decanol in the third group, and 1-Hexanol—n-Hexane in the fourth group of mixtures.

It has been shown theoretically (94) that the enthalpy of mixing is very sensitive to the deviation from the geometric mean rule. There is increasing evidence that ξ is often, if not always, slightly less than one (25, 95). The uncertainty of ξ within a group of systems is mainly due to the errors in P_1^* and P_2^* (result from inaccuracies in γ_1 and γ_2) and perhaps also due to the error in the evaluation of the ratio of s_1/s_2. The calculated value of ξ is obviously very sensitive to $s_2P_1^*/s_1P_2^*$, especially when ξ is near unity, and

discrepancies are significant.

Table XXIX: Test of the Geometric Mean Rule for All the Systems Studied

System	T (°C)	P_1^* (cal/ml)	P_2^* (cal/ml)	X_{12} (cal/ml)	s_1/s_2	$10^2 X_{12}/P_1^*$	ξ
1. Mixtures of n-paraffin Hydrocarbons, n = 1.29							
$n\text{-}C_6H_{14}$— $n\text{-}C_{12}H_{26}$	20	81.6	88.0	0.595	1.224	0.729	0.877
$n\text{-}C_6H_{14}$— $n\text{-}C_{16}H_{34}$	20	81.6	88.4	1.238	1.338	1.515	0.840
	25	81.3	88.3	1.226	1.338	1.508	0.839
	30	81.0	87.9	1.073	1.337	1.325	0.840
	35	80.7	87.7	1.093	1.337	1.354	0.839
	40	80.3	87.4	0.909	1.337	1.132	0.840
	50	79.2	86.7	0.719	1.336	0.908	0.839
	51	79.1	86.7	0.790	1.336	0.999	0.838
$n\text{-}C_7H_{16}$— $n\text{-}C_{16}H_{34}$	20	82.3	88.5	0.932	1.281	1.132	0.859
	25	81.7	88.3	0.892	1.281	1.092	0.857
$n\text{-}C_8H_{18}$— $n\text{-}C_{16}H_{34}$	20	83.4	88.5	0.663	1.233	0.795	0.879
$n\text{-}C_7H_{16}$— $n\text{-}C_{36}H_{74}$	76	77.2	91.4	1.529	1.650	1.981	0.751
$n\text{-}C_8H_{18}$— $n\text{-}C_{24}H_{50}$	106	75.6	85.3	0.445	1.395	0.589	0.816
2. Mixtures composed of nearly spherical molecules, n = 1.40							
CCl_4— $c\text{-}C_6H_{12}$	25	102	94.6	1.67	1.039	1.637	1.010
	40	99.8	94.1	1.51	1.039	1.513	1.003
CCl_4— $C(CH_3)_4$	0	105	70.5	3.67	1.056	3.495	1.180

Table XXIX (continued)

System	(°C)	P_1^* (cal/ml)	P_2^* (cal/ml)	X_{12} (cal/ml)	s_1/s_2	$10^2X_{12}/P_{11}^*$	ξ
CCl_4— $SiCl_4$	20	101	82.0	1.86	1.051	1.841	1.075
	25	102	82.1	1.74	1.051	1.706	1.081
c-C_6H_{12}— n-C_6H_{14}	20	92.5	75.7	1.95	1.058	2.108	1.065
c-C_6H_{12} n-C_7H_{16}	20	92.5	77.1	2.44	1.104	2.638	1.029
$SiCl_4$— $SnCl_4$	20	82.0	97.0	2.68	1.016	3.27	0.903
3. Mixtures of 1-Alcohols, T = 25°C, and n = 1.00							
Methanol— 1-Propanol		109	108	1.91	1.239	1.752	0.900
Methanol— 1-Butanol		109	108	3.09	1.329	2.835	0.869
Methanol— 1-Hexanol		109	108	5.33	1.480	4.890	0.824
Methanol— 1-Octanol		109	110	7.78	1.604	7.138	0.787
Ethanol— 1-Butanol		109	108	0.288	1.091	0.264	0.961
Ethanol— 1-Hexanol		109	108	1.80	1.304	1.651	0.907
Ethanol— 1Octanol		109	110	3.17	1.413	1.908	0.840
1-Butanol— 1-Decanol		108	113	2.13	1.287	1.97	0.864
1-Hexanol— 1-Octanol		108	110	0.207	1.084	0.192	0.952
1-Octanol— 1-Decanol		110	113	0.121	1.066	0.110	0.956

Table XXIX (continued)

System	P_1^* (cal/ml)	P_2^* (cal/ml)	X_{12} (cal/ml)	s_1/s_2	$10^2 X_{12}/P_1^*$	ξ
4. 1-Alcohol—n-Hexane Mixtures, T = 25°C, n = 0.92						
Ethanol—n-Hexane	109	102	7.94	1.289	1.18	0.884
1-Propanol—n-Hexane	108	102	5.50	1.181	5.09	0.925
1-Butanol—n-Hexane	106	102	4.69	1.101	4.42	0.951
1-Hexanol—n-Hexane	108	102	4.29	0.988	3.97	1.008
1-Octanol—n-Hexane	110	102	4.26	0.912	3.69	1.019

V. CONCLUDING REMARKS

The use of interaction between segments instead of between molecules takes into account the difference in structure among the various contacting segments. Although there are two different kinds of segments in a n-paraffin hydrocarbon molecule, say, $-CH_3$ on both ends of the chain and $-CH_2-$ in between, their ability of interacting with any other segments may be regarded comparable since they both are composed of carbon and hydrogen atoms. For mixtures composed of spherical symmetric molecules, the assumption of only one type of segment is always valid. It is therefore expected that the refined theory will give good results for these two groups of mixtures. As for a 1-alcohol molecule, there are two types of segments, the -OH and the $-CH_2-$ or $-CH_3$. The small but consistent deviation of n from the average value from system to system for the 1-Alcohol—1-Alcohol and 1-Alcohol—n-Hexane mixtures reveals the necessity of assigning two types of segments if a more constant n is to be obtained. However, for systems in which the number of $-CH_2-$ segments of both component molecules outnumber the -OH segments, the difference in the interaction with other segments will be lessened, and a more constant n is to be expected.

There is little theoretical evidence to assume that a constant n would be applicable over the whole composition range for solutions whose components are very different in molecule structure. A linear trend for the $n\text{-}x_1$ relation is, however, expected for such solutions. If this is the case then the value of n for a solution of any composition can be obtained from linear combination of the n's of the solution components.

Summary: The modified theory is able to predict the enthalpy of mixing for a group of similar systems from density measurements and one calorimeteic measurement for any one of the systems from within the group. It is expected that if correct values of n for the pure components will become more available, then, even the only calorimetric measurement, could be eliminated. The value of n for any mixture at any composition can be obtained from the linear combination of the n's of the pure solution constituents. More calculations are, however, required before such a final conclution can be made.

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