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IN THEORIES OF FLUIDS AND FLUID MIXTURES

by

Arlene G. Pollin

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

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Abstract

THE SIGNIFICANCE OF THE ENERGY-VOLUME RELATIONSHIP

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IN THEORIES OF FLUIDS AND FLUID MIXTURES

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Arlene G. Pollin

Adviser: Professor Vojtech Fried

A theory of liquid mixtures is developed which is able to predict the excess enthalpy of binary liquid mixtures accurately from volumetric data. The treatment is a modification of the methodology developed by Flory and coworkers, in which the van der Waals energy-volume relationship is replaced by the more general expression $E = -a/V^m$. The exponent m in this expression is postulated to be a fundamental property of each liquid component and the value of m for a binary liquid mixture assumed to be a volume fraction averaged function of the values for the individual components. The mixture is treated as composed of two pseudo-components whose properties are not quite the same as those of the pure components from which they are derived.

The theory is successfully applied to fifty binary mixtures of seventeen non-polar and weakly polar liquids and to ten binary mixtures of four polar liquids. The calculated excess enthalpy is found to be sensitive to values of the excess volume and to pure

component values of the thermal expansion and thermal pressure coefficients. The composition dependence of the excess enthalpy predictions is used in a semi-empirical procedure to calculate the excess free energy.

To my husband

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I. INTRODUCTION

The purpose of this thesis is to develop a theory of liquid mixtures which is able to predict accurately the excess enthalpy of binary solutions of nonelectrolytes. An attempt is made to extend these predictions to the excess free energy. The proposed theory stresses the importance of the exponent m in the liquid cohesive energy - volume relation in the behavior of fluids and fluid mixtures.

The thesis is divided into three major parts. The first part (Chapter II) surveys the methods by which liquid mixtures can be treated and presents the theoretical foundations for the current treatment. The theory is described and developed in the second part (Chapters III, IV and V), and is successfully applied in the last part (Chapters VI and VII) to fifty binary mixtures of non-polar and weakly polar liquids and ten binary mixtures containing polar liquids.

II. THEORETICAL FOUNDATIONS

Interest in predicting the properties of liquid mixtures from the properties of their constituents dates from the turn of the century. Many of the theories and methods on which such predictions are based relate to the van der Waals equation of state (1),

$$(P + a/V^2)(V - b) = RT \tag{1}$$

to the energy-volume relationship associated with it,

$$E = -a/V \tag{2}$$

and to the assumption of zero volume change on mixing.

II-1: Treatment of van Laar and Lorenz

The van der Waals equation of state can be applied to gaseous and liquid mixtures (2) by considering the mixture as a simple equivalent fluid in which the mixture constants a and b are composition dependent averages related to the pure component constants by

$$a = a_1x_1^2 + 2x_1x_2a_{12} + a_2x_2^2 \tag{3}$$

and

$$b = b_1x_1^2 + 2x_1x_2b_{12} + b_2x_2^2 \tag{4}$$

In Equation (3), a_{12} is a measure of the interactions between molecules 1 and 2 in the mixture (1-2 interactions), a_1 the interactions between molecules of type 1 (1-1 interactions), and a_2 the interactions of molecules of type 2 (2-2 interactions). The interactions between like molecules in the mixture are identical with similar interactions in the respective pure liquids. If the Lorentz combination rule (3) is used to represent b_{12},

$$b_{12} = (b_1 + b_2)/2 \tag{5}$$

Equation (4) becomes

$$b = x_1b_1 + x_2b_2 \tag{6}$$

Use of this combination rule is therefore equivalent to assuming that the volume actually occupied by a mole of type 1 or type 2 molecules, b_1 or b_2, is the same in the mixture as in the pure components.

Based on the van der Waals equation of state and the mixture rules given in Equations (3) and (6), van Laar developed (4,5,6) a relation for the molar enthalpy of mixing, ΔH^M, of binary mixtures of unexpanded liquids,

$$\Delta H^M = \frac{x_1a_1}{b_1} + \frac{x_2a_2}{b_2} - \frac{a}{b} \tag{7}$$

Using the Berthelot (7) combination rule,

$$a_{12} = (a_1 a_2)^{1/2} \tag{8}$$

to estimate the magnitude of the 1-2 interaction in the mixture, Equation (7) becomes

$$\Delta H^M = \frac{x_1 x_2 b_1 b_2}{x_1 b_1 + x_2 b_2}\left[\frac{a_1^{1/2}}{b_1} - \frac{a_2^{1/2}}{b_2}\right]^2 \tag{9}$$

where x_1 and x_2 are the mole fractions of components 1 and 2 respectively. Although Equation (9) expresses the enthalpy of mixing in terms of pure component properties only, it permits ΔH^M to be zero if and only if

$$\frac{a_1^{1/2}}{b_1} = \frac{a_2^{1/2}}{b_2} \tag{10}$$

Since according to the van der Waals equation of state, a/b^2 is proportional to the critical pressure, only liquids that have the same critical pressure should mix with no change in enthalpy. By replacing b_1 and b_2 by the molar volumes of components 1 and 2, van Laar and Lorenz (8) were able to predict zero enthalpies of mixing of liquids for which the critical pressures are not the same. Van Laar insisted (9) that all mixing effects were due only to differences in van der Waals forces.

II-2: Solubility Theory

In 1931, Scatchard (10) introduced the concept of excess properties for the differences between the behavior of real and ideal solutions. Since ideal solutions are formed without volume or enthalpy changes, the molar excess volume, V^E, and molar excess enthalpy, H^E, are respectively identical to the molar volume of mixing and molar enthalpy of mixing. The molar excess Gibbs free energy, G^E, is the molar free energy of mixing, ΔG^M, less the free energy of mixing of an ideal solution,

$$G^E = \Delta G^M - (RTx_1 \ln x_1 + RTx_2 \ln x_2) \qquad (11)$$

In addition to originating the terminology used to describe liquid mixtures, Scatchard developed (10,11,12,13) a simple and widely applied theoretical treatment, called solubility parameter theory. The treatment incorporates some of Hildebrand's ideas (14) on the importance of the energy of vaporization per unit volume, which Hildebrand called the cohesive energy density.

Scatchard assumed that the energy of two molecules in a liquid is a function only of their relative orientation and intermolecular distance, that the molecules are randomly distributed in the solution, and that there is no volume change on mixing. He expressed the molar cohesive energy, E_m, of a mixture as

$$E_m = - \frac{c_{11}V_1^2x_1^2 + 2c_{12}V_1V_2x_1x_2 + c_{22}V_2^2x_2^2}{x_1V_1 + x_2V_2} \qquad (12)$$

The molar cohesive energies, E_1 and E_2, of the pure components are

$$E_1 = - c_{11}V_1 \qquad (13)$$

and

$$E_2 = - c_{22}V_2 \qquad (14)$$

Scatchard assumed that the vapors of each component behave ideally and equated E_1 and E_2 with the negative of the respective pure component energies of vaporization; c_{11} and c_{22} are then the cohesive energy densities. Equation (12) is structurally analogous to the van Laar-Lorenz equation,

$$E = - \frac{a_1x_1^2 + 2a_{12}x_1x_2 + a_2x_2^2}{x_1V_1 + x_2V_2} \qquad (15)$$

although unlike the constants in Equation (15), the constants in Equation (12) are not related to the van der Waals equation of state.

The excess energy, E^E, given by

$$E^E = E_m - x_1E_1 - x_2E_2 \qquad (16)$$

then becomes

$$E^E = (x_1V_1 + x_2V_2)(c_{11} + c_{22} - 2c_{12})\,\phi_1'\phi_2' \qquad (17)$$

where ϕ_1' and ϕ_2' are ideal volume fractions,

$$\phi_1' = \frac{x_1V_1}{x_1V_1 + x_2V_2} \qquad (18)$$

and

$$\phi_2' = \frac{x_2V_2}{x_1V_1 + x_2V_2} \qquad (19)$$

If the Berthelot geometric mean is introduced for c_{12}, Equation (17) can be written as

$$E^E = (x_1V_1 + x_2V_2)(\delta_1 - \delta_2)^2\,\phi_1'\phi_2' \qquad (20)$$

where δ, the solubility parameter, has been introduced for the square root of the cohesive energy density,

$$\delta = \left(\frac{\Delta E_i^V}{V_i}\right)^{1/2} \qquad (21)$$

and ΔE_i^V is the energy of vaporization to the ideal gas state. Like the van Laar - Lorenz modification of Equation (9), Equation

(20) permits only positive or zero values for the excess energy.

Hildebrand and Wood (15) simultaneously and independently obtained Equation (20) by assuming superimposable mixture and pure component potential functions and integrating the intermolecular pair potential energies using a spherically symmetrical radial distribution function. Their derivation, called regular solution theory, utilizes Hildebrand's (16) definition of a regular solution--one in which there is "no entropy change when a small amount of one of its components is transferred from an ideal solution of the same composition, the total volume remaining unchanged."

Since the excess entropy of a regular solution is zero by definition, its excess enthalpy and excess free energy are equal. This equality is rarely observed experimentally and the predictions of solubility and regular solution theories usually agree more closely with experimental values of the excess free energy than with experimental values of the excess enthalpy. Mixtures containing non-polar components which are neither too alike nor too dissimilar, so that $\delta_1 - \delta_2$ is neither small nor large, most closely conform to solubility theory predictions.

While the difference between the excess enthalpy and excess energy both measured at constant volume or both measured at constant pressure is small, the difference between one of these functions at constant volume and the other at constant pressure is frequently as large as either of the functions themselves. Since real liquids seldom actually mix without volume change at constant pressure ($V^E \neq 0$), it is realistic to compare the predictions of solubility theory with thermodynamic properties constrained to constant volume. For suitably matched components, solubility theory has been found (17) to predict the qualitative composition dependence of the excess energy at constant volume, E_V^E, correctly locating the maximum value of E_V^E near high concentrations of the lighter component.

In spite of its limitations, the general simplicity and straightforward application of the solubility parameter concept have supported sustained interest in it. Recently, several researchers have re-examined ways of evaluating solubility parameters. Konstam and Feairheller (18) investigated the relationship between δ and chemical structure, Fedors (19,20) proposed a group method, and Barton, Holland and McCormick (21) a self-consistent method to evaluate δ. Bagley _et al_. (22) suggested a way to include in δ the effect of changes in the effective number of external degrees of freedom accompanying increased rotational hindrance in the liquid state. Wheeler and Smith (23) derived the Scatchard - Hildebrand equation by considering probability weighting functions for clusters of molecular pairs in the liquid. Thomsen (24) has shown that deviations from the geometric mean rule change the excess property predictions of solubility theory by 170 joules/mole. Many treatments (24,25,26, 27,28), therefore, have concentrated on ways by which the restriction to the geometric mean rule can be relaxed. Some have also included corrections for non-zero excess volumes. Reed (27) proposed use of partial molar volumes and a new approximate combination rule, and Thomsen (24,25,26) proposed incorporating experimental values of the excess volume into the expression for the excess enthalpy through use of volume fractions defined by

$$\phi_i'' = \frac{x_i V_i}{x_i V_i + x_j V_j + V^E} \tag{22}$$

Using a correlative method based on the analysis of gaseous mixtures to obtain geometric mean rule corrections, Thomsen was able to predict excess enthalpies which agree well with experiment for mixtures which do not contain aromatic molecules.

II-3: Statistical Mechanical Basis for Liquid Mixture Theories

Statistical mechanical models of the liquid state and of liquid mixtures were first introduced in the mid 1930's. These models are based on the canonical partition function, Z,

$$Z = \sum_r \exp(-E_r / kT) \tag{23}$$

and on the relationship of the partition function to macroscopic thermodynamic properties,

$$A = -kT \ln Z \tag{24}$$

and

$$E = kT^2 \left(\frac{\partial \ln Z}{\partial T}\right)_V \tag{25}$$

If the energy of each quantum state can be expressed as the sum of contributions due to different degrees of freedom, the partition function may be factored into the product of several terms. For discussions of the thermodynamic properties of mixtures, it is usually sufficient to separate Z into the product of two terms,

$$Z = Z_{int} \cdot Z_{trans} \tag{26}$$

Z_{int} represents contributions from rotations and vibrations; Z_{trans} represents contributions due to the relative positions of the molecules and the relative motion of their centers of mass. Equation (26) is usually valid for spherical, non-polar molecules; it is inapplicable to polar molecules and to molecules with strong orientational forces, since the rotation of a dipole is influenced by the position of its neighbors.

If the translational partition function can be expressed in the classical approximation as

$$Z_{trans} = \frac{1}{N!h^{3N}} \int \cdots \int \exp\left(\frac{-\mathcal{H}}{kT}\right) dp_1 \cdots dp_N dr_1 \cdots dr_N \tag{27}$$

and the Hamiltonian for the motion of the molecules written as

$$\mathcal{H} = \frac{1}{2m} \sum_{i=1}^{N} (p_i)^2 + U(r_1 \cdots r_N) \tag{28}$$

where p_i is the momentum of the i^{th} molecule, N is the number of molecules and U(r) is the potential energy of the system, then Z_{trans} is resolved into two terms. The first term is due to the kinetic energy of the molecules; the second is due to their mutual potential energy. The kinetic energy term is $[(2\pi mkT)^{1/2}/h]^{3N}$ and is usually incorporated into the internal partitior$^{1/2}/h]^{3N}$ion. The term due to the configurational potential energy of the molecules,

$$Q = \frac{1}{N!} \int \cdots \int \exp(-U/kT)\, dr_1 \cdots dr_N \tag{29}$$

is called the configuational partition function. Since virtually all theories of liquid mixtures assume that the internal partition function is invarient on mixing, the task of liquid mixture theorists involves finding a reasonable approximation for the configurational energy of the molecules and a less complex form for the configurational partition function.

II-4: Lattice Theories

The first group of theories which relies on the configurational partition function consists of the lattice theories. The most complete of these were introduced and extended by Guggenheim (29,30). In the simple lattice theory model, molecular motion in the liquid is regarded as oscillations of the molecules about equilibrium positions on a regular array. The partition function is divided into internal and translational terms; the internal part is assumed independent of volume. The configurational part of the translational term is in turn subdivided into two independent factors,

$$Q = Q_{latt} \cdot Q_{vib} \tag{30}$$

Q_{latt} corresponds to contributions due to the rest energy of the molecules in their equilibrium positions and Q_{vib} corresponds to contributions due to oscillations of the molecules about these equilibrium positions. Q_{latt} depends on the composition of the system while Q_{vib} is independent of composition. The lattice is rigid, undergoes no volume change on mixing, and has a negligible coefficient of thermal expansion. Each molecule occupies one lattice position. Guggenheim called mixtures which can be described by these approximations strictly regular.

If a mixture consists of N_1 molecules of 1 and N_2 molecules of 2, each molecule with z nearest neighbors, all situated on lattice sites, the total numbers of 1-1, 1-2 and 2-2 closest pairs are related by

$$zN_1 = 2N_{11} + N_{12} \tag{31}$$

and

$$zN_2 = 2N_{22} + N_{12} \tag{32}$$

The energy of the lattice can be written,

$$E_{latt} = N_{11}\mu_{11} + N_{12}\mu_{12} + N_{22}\mu_{22} \tag{33}$$

where μ_{11}, μ_{22} and μ_{12} are the interaction energies of nearest neighbor 1-1, 2-2 and 1-2 pairs respectively, and are a function only of the distance between the ij pair. By combining Equations (31), (32) and (33), the expression for the lattice energy becomes

$$E_{latt} = \tfrac{1}{2}zN_1\mu_{11} + \tfrac{1}{2}zN_2\mu_{22} + N_{12}(\mu_{12} - \tfrac{1}{2}\mu_{11} - \tfrac{1}{2}\mu_{22}) \tag{34}$$

Since the intermolecular distance in the pure and mixed liquids is assumed to be identical, and since μ_{ij} is a function only of this distance, the first and second terms in Equation (34) are the lattice energies of pure components 1 and 2. If w is defined as the lattice energy gained on creation of a 1-2 pair,

$$w = \mu_{12} - \tfrac{1}{2}(\mu_{11} + \mu_{22}) \tag{35}$$

then Equation (26) becomes

$$E_{latt} = E_{11} + E_{22} + N_{12}w \tag{36}$$

The lattice partition function for the mixture can consequently be written as

$$Q_{latt} = \sum_{N_{12}} g(N_1,N_2,N_{12}) \exp[-(E_{11} + E_{22} + N_{12}w)/kT] \quad (37)$$

or

$$Q_{latt} = \exp[-(E_{11} + E_{22})/kT] \sum_{N_{12}} g(N_1,N_2,N_{12}) \exp(-N_{12}w/kT) \quad (38)$$

where the combinatory part of the partition function, $g(N_1,N_2,N_{12})$, is the number of combinations of molecules resulting in N_{12} 1-2 pairs. A major difficulty in this and other treatments is the explicit evaluation of $g(N_1,N_2,N_{12})$.

Applying the statistical mechanical relation between the partition function and the Helmholtz free energy to the mixture and to each pure component, the Helmholtz free energy of mixing, ΔA^M, is,

$$\Delta A^M = -kT \ln[\sum_{N_{12}} g(N_1,N_2,N_{12}) \exp(-N_{12}w/kT)] \quad (39)$$

If the exchange energy, w, is zero, the exponential term is unity, and the combinatorial term sum reduces to the classical permutation expression,

$$\sum_{N_{12}} g(N_1, N_2, N_{12}) = \frac{(N_1 + N_2)!}{N_1! N_2!} \tag{40}$$

The free energy of mixing is then equal to that of an ideal solution,

$$\Delta A^M = -kT \ln \frac{N!}{N_1! N_2!} \tag{41}$$

and the excess free energy is zero. If the somewhat contradictory approximation that random mixing occurs in spite of a non-zero interchange energy is made (Guggenheim's zeroth approximation), the sum in Equation (39) is replaced by a single term, so that,

$$\Delta A^M = -kT \ln \frac{N!}{N_1! N_2!} + N_{12}^{*} w \tag{42}$$

where N_{12}^{*} is the number of 1-2 pairs formed in random mixing. N_{12}^{*} can be evaluated from probability theory in terms of the numbers of molecules of components 1 and 2,

$$N_{12}^{*} = \frac{zN_1N_2}{N_1 + N_2} \tag{43}$$

so that the molar excess enthalpy is

$$H^E = \frac{zwx_1x_2}{x_1 + x_2} \tag{44}$$

For non-zero values of w, some amount of preferential ordering must occur in the molecular distribution. Fowler and Guggenheim (31,32) attempted to take this ordering into account by first considering the value of $g(N_1, N_2, N_{12})$ for non-interacting pairs and then introducing a correction factor to reduce the high value for $g(N_1, N_2, N_{12})$ caused by the assumption of non-interaction. They evaluated this correction factor by a normalization process involving the random distribution. The relationship they derived is of the same form as that obtained if one imagines a simple chemical equilibrium among the types of pairs present,

$$1\text{-}1 \ + \ 2\text{-}2 \ \rightleftharpoons \ 2(1\text{-}2) \qquad (45)$$

having an equilibrium constant expression,

$$\frac{N_{12}^2}{N_{11} N_{22}} = 4 \exp(-2w/kT) \qquad (46)$$

The exchange energy replaces the free energy change used in the equilibrium expression for an actual reaction; from the similarity, however, the method is called the quasi-chemical approximation. The quasi-chemical treatment outlined above tends to give too few configurations for ordered mixtures. An alternate method, which yields closer agreement with exact treatments of two dimensional lattices (33) was developed by Prigogine, Sarolea and Van Hove (34). Other treatments of the order-disorder problem for quasi-lattices have been developed by Rushbrooke (35) and by Kirkwood (36).

A number of investigators (37,38,39,40,41,42) have extended the lattice method to chain molecules, called r-mers, by assuming that a molecule containing r segments occupies r lattice sites. Chang (37) investigated the configurational free energy in mixtures of monomers ($r=1$) and dimers ($r=2$) and Miller (40,41) investigated the configurational free energy first in mixtures of monomers and trimers and then in mixtures of monomers and open r-mers.

The fraction of lattice sites occupied by r-mers, ϕ_r, given by

$$\phi_r = \frac{rN_r}{N_1 + rN_r} \tag{47}$$

where N_r is the number of r-mers in the mixed lattice, is frequently used instead of mole fractions in theoretical treatments of chain molecules. Even with simple alkanes, however, the choice of elements to use as lattice points is ambiguous. Van der Waals and Hermans (43) have suggested choosing a mixture of CH_3 and CH_2-CH_2 elements while Tompa (44) has suggested using a mixture of CH_3-CH_2 and CH_2-CH_2 elements.

R-mers may be treated by analogies of the zeroth and first order approximations discussed for monomers. Guggenheim (45) found that the first order expressions reduce to the zeroth order expressions both when only the leading terms are retained in an appropriate Taylor series expansion and when the lattice coordination number approaches infinity.

In 1942, Huggins (39) derived an expression for the free energy of mixing of polymers which contains a complex correction factor for the possible back-coiling of the r-mers on themselves. If this correction is neglected and the coordination number of the lattice approaches infinity, the entropy part of this expression reduces to an expression independently derived by Flory (38) for the molar entropy of mixing of polymers,

$$\Delta S^M = - R(x_1 \ln \phi_1 + x_2 \ln \phi_2) \tag{48}$$

where ϕ_1 and ϕ_2 are the r-mer fractions defined by Equation (47). The Flory-Huggins expression, Equation (48), is said (46) to give an upper limit and the ideal expression a lower limit for the combinatorial entropy. In a recent treatment of the combinatorial entropy problem, Huggins (47) used a stepwise procedure to obtain expressions for the combinatorial entropy of mixing. He first derived a relation for the combinatorial entropy of rigid, randomly distributed molecules, and then introduced successive additive terms to account for molecular flexibility and preferential ordering. Evaluation of the latter two contributions involves four parameters obtained from excess enthalpy and excess volume data. Lichtenthaler, Abrams and Prausnitz (48) derived a form for the combinatorial entropy intermediate between the ideal and the polymeric, applicable to mixtures in which the molecules have significant differences in size and shape. Their expression contains the Flory-Huggins expression as the leading term and includes a correction for molecular bulkiness which is evaluated from bond length and bond angle data. Donohue and Prausnitz (49) have proposed a different modification of the Flory-Huggins lattice treatment, which also requires bond length and bond angle data to evaluate the necessary parameters and yields intermediate results.

Refinements of excess enthalpy calculations from the basic lattice theory have also been numerous. Guggenheim (50) has suggested using the quasi-chemical equilibrium expression to define the exchange energy, so that w then becomes a function of temperature, as well as a function of the number of 1-1, 1-2 and 2-2 pairs. Guggenheim and McGlashan (51) included consideration of next nearest neighbors in a quasi-chemical treatment, concluding that the effect on measurable physical quantities is negligible. Much earlier Lennard-Jones and Ingles (52) found that all non-nearest interactions contribute no more than 20% to the total attractive potential energy in liquids. Further modifications of lattice theory were suggested by Matsen and Watsen (53), Matsen and Walkey (54) and Frankel (55).

II-5: Conformal Solution Theory

The most general criticism of lattice theories is that they are based on an unrealistic picture of long range order in the liquid state. In 1951, Longuet-Higgins (56) published a theory of solutions not associated with any particular model. The treatment is called conformal solution theory and is a perturbation approach based on the theorem of corresponding states (57). The basic assumptions of conformal solution theory are similar to those of corresponding states theory. The internal energies of the molecules are assumed independent of environment, so that the internal partition function can be factored out of the total partition function; the translational partition function is expressed in its classical form. The total intermolecular energy, U, is approximated as the sum of all possible pairwise interactions, each a function only of distance,

$$U = \sum_{i<j} u_{ij}(r) \qquad (49)$$

where r is the distance between molecules i and j in a given configuration. Rigorous application of the assumptions limit the treatment to mixtures of spherical, non-polar molecules for which quantum effects are unimportant.

The mutual potential energy of two molecules i and j separated by a distance r is given in conformal theory by

$$u_{ij}(r) = f_{ij} u_{oo}(r g_{ij}) \qquad (50)$$

In Equation (50), $u_{oo}(r)$ is the mutual potential energy of two molecules of a reference species separated by distance r; f_{ij} and g_{ij} are constants dependent on the nature of molecules i and j and are related to the energy and distance parameters, u_{oo} and σ_{oo}, of the reference species by

$$f_{ij} = u_{ij}/u_{oo} \tag{51}$$

and

$$g_{ij} = \sigma_{ij}/\sigma_{oo} \tag{52}$$

Equation (50) is closely related to the corresponding states expression,

$$\epsilon(r) = \epsilon^* \phi(r/r^*) \tag{53}$$

where ϕ is universal function used in conjuction with characteristic reducing parameters, ϵ^* and r^*, for energy and distance respectively. The reference species in conformal theory must be chosen such that f_{ij} and g_{ij} are close to unity, so that $(f - 1)$ and $(g - 1)$ will be small. This requirement limits the treatment to mixtures of very similar molecules, for which one of the pure components can serve as the reference. The theory has been modified for application to mixtures of less similar molecules (58) by using composition dependent references, such that $u_{oo} \longrightarrow u_{ii}$ and $\sigma_{oo} \longrightarrow \sigma_{ii}$ when $x_i \longrightarrow 1$, and $u_{oo} \longrightarrow u_{jj}$ and $\sigma_{oo} \longrightarrow \sigma_{jj}$ when $x_j \longrightarrow 1$.

The configurational partition functions, Q and Q_o, of a liquid and reference liquid are related (57) by the expression,

$$Q(T,V) = g^{-3N} Q_o(T/f,\ g^3 V) \qquad (54)$$

The relationship between the Helmholtz free energies of the two liquids, obtained by applying Equation (24) to Equation (54), is

$$A(T,V) = A_o(T/f,\ g^3 V) + RT \ln g \qquad (55)$$

$A(T,V)$ can be expanded in a Taylor series in powers of $(f-1)$ and $(g-1)$ to give, after appropriate substitution,

$$A(T,V) - A_o(T,V) = E_o(f-1) + 3(RT - P_o V)(g-1) \qquad (56)$$

The corresponding expression for a mixture of molecules i and j is

$$A(T,V) - A_o(T,V) = \sum_{i,j} x_i x_j [E_o(f_{ij}-1) + 3(RT - P_o V)(g_{ij}-1)] \qquad (57)$$

The excess Gibbs free energy, obtained by applying Equations (57) and (56) to the mixture and pure components and relating the Helmholtz and Gibbs free energies is then,

$$G^E = \sum_{i,j} x_i x_j [E_o(2f_{ij} - f_{ii} - f_{jj}) + 3(RT - PV_o)(2g_{ij} - g_{ii} - g_{jj})] \tag{58}$$

If the Lorentz combination rule is used to approximate g_{ij}, the three excess functions, G^E, H^E and V^E are

$$G^E = E_o \sum_{i<j} x_i x_j d_{ij} \tag{59}$$

$$H^E = (E_o - T\frac{\partial E_o}{\partial T}) \sum_{i<j} x_i x_j d_{ij} \tag{60}$$

$$V^E = \frac{\partial E_o}{\partial P} \sum_{i<j} x_i x_j d_{ij} \tag{61}$$

where

$$d_{ij} = 2f_{ij} - f_{ii} - f_{jj} \tag{62}$$

The configurational energy, E_o, of the reference fluid is usually approximated by the latent energy of vaporization to the ideal gas state. Experimental data for one excess function are used to evaluate d_{ij} and the other excess functions functions are calculated from this value. Longuet-Higgins (56) found, however, that values of d_{ij} computed for the same mixture from different excess funtions differ by as much as a factor of two. For the same mixtures, Waelbroeck (59) calculated still other values for d_{ij} from virial coefficient measurements.

In this first order approximation, all the excess functions must have the same sign and be mutually proportional. Brown and Longuet-Higgins (60) have shown that retention of second order terms in the expansion permits the excess functions to have opposite signs but requires recourse to a more specific statistical model of the liquid state. The proportionality of the excess functions resulting from the first order approximation, however, suggests that no theory which includes only the equivalent of first order terms can accurately predict the magnitude and sign of all the excess functions. In spite of this limitation, Kreglewski (58) has recently applied conformal solution theory to the calculation of several types of mixture properties for an extensive number of dissimilar systems. Perhaps the major importance of conformal solution theory is that it has served as an impetus to the formulation of other theories based on the theorem of corresponding states and to perturbation treatments of collections of hard spheres (61,62)

II-6: Cell Theories

A physical model of the liquid state is a central feature in the cell theory first proposed by Eyring and Hirschfelder (63,64) and applied to the interpretation of liquid properties through intermolecular forces by Lennard-Jones and

and Devonshire (65). The cell in which each molecule is imagined confined is a spherical cage composed of its nearest neighbors.

In the mean potential cell theory model, the force acting on a molecule in its cage is approximated by a mean field of spherical symmetry; the field is a function only of the distance of the molecule from the center of its cell. The cell partition function, q, for a molecule with mean interaction energy $\mu(r)$ is given by

$$q = 4\pi \int_{cell} \exp\{-[\mu(r) - \mu(0)]/kT\} r^2 dr \tag{63}$$

and the configurational partition function for N molecules is given by

$$Q = q^N \exp[-N\mu(0)/kT] \tag{64}$$

$N\mu(0)/kT$ is the energy of the liquid when all molecules are at their cell centers and $\mu(0)$ is the mean interaction energy of each molecule at its cell center.

For hard spheres, the cage has a radius $(a-d)$ where a is the average distance between the center molecule and its nearest neighbors and d is the molecular diameter. The accesible or free volume per molecule, v_f, can be written,

$$v_f = \frac{4}{3}\pi\lambda(v^{1/3} - v_o^{1/3})^3 \tag{65}$$

where v, the total volume per molecule, and v_0, the volume per molecule in an unexpanded liquid, have replaced a and d, and where λ is a geometric constant dependent on the nearest neighbor arrangement. Because the mean potential for hard spheres is either zero or infinite, the exponential expression in Equation (63) is unity, and the hard sphere cell partition function becomes identical with the expression for the free volume. The configurational partition function is then

$$Q = \left[\frac{4}{3}\pi\lambda(v^{1/3} - v_0^{1/3})^3 \right]^N \tag{66}$$

If the molecules are point particles, the free volume is equal to the total volume, so that the configurational partition function becomes

$$Q = v_f^N \tag{67}$$

The difference between Equation (67) and the partition function for an ideal gas,

$$Q = (ev)^N \tag{68}$$

is called the communal entropy difference (63,64) and is attributed to the artificial confinement of each molecule to a given region in the liquid. Communal entropy can be formally included in cell theory treatments by considering empty and multiply occupied cells (66,67,68).

Use of a more realistic potential function than that associated with hard spheres, such as the Lennard-Jones 6-12 potential (69), leads (65) to a complex expression for $\mu(r)$ which strongly depends on the volume per molecule. Approximate numerical methods must be used to evaluate the integral in Equation (63) and the thermodyamic functions derived from it.

Prigogine and Mathot (70) developed a major simplification of the mean potential model, called the smoothed potential cell model, by representing the potential as a well with infinite walls and a flat floor. The cell partition function then has the same form as obtained for a collection of hard spheres, and only the value of the constant potential within the cell is additionally needed to specify the configurational partition function.

Several investigators (70,71,72,73,74) have extended the different forms of cell theory to mixtures. The extensions begin by considering separate mean potentials, $\mu_1(r)$ and $\mu_2(r)$, acting on type 1 and type 2 molecules in the mixture, each with corresponding effective cell partition functions, q_1 and q_2. Assuming a random mixing combinatorial term, the mixture configurational partition function is

$$Q = \frac{(N_1 + N_2)!}{N_1!N_2!} q_1^{N_1} q_2^{N_2} \exp\{-[N_1\mu_1(0) + N_2\mu_2(0)]/kT\} \qquad (69)$$

Cell partition functions, q_{11} and q_{22}, and mean potentials, $\mu_{11}(r)$ and $\mu_{22}(r)$, are used to express the configurational partition functions of pure unmixed components 1 and 2. The
$_{11}(r)$ and $\mu_{22}(r)$, are used to express the configurational
treatment explicitly distinguishes between the mean potentials experienced by each type of molecule in the mixed and unmixed environments. The excess free energy,

$$A^E = x_1 \{\tfrac{1}{2}[\mu_1(0) - \mu_{11}(0)] - kT\,\ell n\,(q_1/q_{11})\} + x_2 \{\tfrac{1}{2}[\mu_2(0) - \mu_{22}(0)] - kT\,\ell n\,(q_2/q_{22})\} \tag{70}$$

and excess energy,

$$E^E = x_1 \{\tfrac{1}{2}[\mu_1(0) - \mu_{11}(0)] - kT^2 \frac{\partial\, \ell n(q_1/q_{11})}{\partial T}\} + x_2 \{\tfrac{1}{2}[\mu_2(0) - \mu_{22}(0)] - kT^2 \frac{\partial\, \ell n(q_2/q_{22})}{\partial T}\} \tag{71}$$

follow from the straightforward application of Equations (24) and (25) to the three configurational partition functions involved. Additional information and approximations are needed to obtain numerical values for these excess properties.

Prigogine and Mathot (70) applied cell theory to mixtures of equal sized molecules, using an average mixture characteristic energy, $<\epsilon^*>$, defined in terms of the average characteristic energies, $<\epsilon_1^*>$ and $<\epsilon_2^*>$, for molecules 1 and

2 in the mixture,

$$\langle \epsilon^* \rangle = x_1 \langle \epsilon_1^* \rangle + x_2 \langle \epsilon_2^* \rangle \tag{72}$$

They related the average characteristic energy of each molecule in the mixture to characteristic energies associated with distinct interactions between like and unlike molecules,

$$\langle \epsilon_1^* \rangle = x_1 \epsilon_{11}^* + x_2 \epsilon_{12}^* \tag{73}$$

and

$$\langle \epsilon_2^* \rangle = x_2 \epsilon_{22}^* + x_1 \epsilon_{12}^* \tag{74}$$

Interactions between like molecules in the mixture are assumed characterized by the same interaction constants as they are in each pure liquid. With these definitions, Equation (72) becomes

$$\langle \epsilon^* \rangle = x_1^2 \epsilon_{11}^* + 2x_1 x_2 \epsilon_{12}^* + x_2^2 \epsilon_{22}^* \tag{75}$$

Although Equation (75) looks similar to the van der Waals averaging expression, Equation (3), the dimension of the quantity averaged in Equation (75) is energy, while the dimension of the quantity averaged in Equation (3) is energy · volume. In spite of the dimensional difference, both averages enable the mixture to be treated as a single effective fluid acting with an effective characteristic energy.

The mean potentials $\mu_1(r)$ and $\mu_2(r)$ in the mixture, like the mean potentials $\mu_{11}(r)$ and $\mu_{22}(r)$ in the pure components, can be expressed using the Lennard-Jones 6-12 potential, and the necessary integrals numerically evaluated in terms of the average characteristic energies. The excess functions can then be obtained by systematic application of the appropriate statistical mechanical relations to mixed and unmixed components.

Salsberg and Kirkwood (72,73) applied the mean potential model to several mixtures of polyatomic molecules of unequal size, including in their calculations an order-disorder correction to random mixing. In spite of the complexity of the calculations, simultaneous agreement of the excess functions is poor, and the agreement of the excess entropy with experiment is not improved even if the mixture energy and distance constants are calculated from excess enthalpy and volume data. The mixing properties were found to be extremely sensitive to the numerical values of the Lennard-Jones parameters chosen for the pure components.

Simpler expressions for the excess properties as functions of the characteristic energy parameters have been obtained (75) by applying the smoothed potential cell model to mixtures of molecules having the same characteristic volume, V^*. The expressions are

$$\frac{V^E}{V^*} = 2.03\frac{kT}{z}\ \frac{1}{<\epsilon^*>} - \frac{x_1}{\epsilon^*_{11}} - \frac{x_2}{\epsilon^*_{22}} \qquad (76)$$

$$A^E = G^E = -1.44x_1x_2[\epsilon^*_{12} - \tfrac{1}{2}(\epsilon^*_{11} + \epsilon^*_{22})] - 5.3kT\frac{V^E}{V^*} \qquad (77)$$

$$E^E = H^E = -1.44x_1x_2[\epsilon^*_{12} - \tfrac{1}{2}(\epsilon^*_{11} + \epsilon^*_{22})] + 5.3kT\frac{V^E}{V^*} \qquad (78)$$

While the parameters in Equations (76) - (78) can be evaluated for specific gases and gaseous mixtures from virial coefficient data, the restriction to molecules of the same size makes the set of equations more valuable in comparative studies on the effect of characteristic interaction energy differences on the excess properties.

II-7: The Average Potential Model

Prigogine, Bellemans and Englert-Chwoles (76) formulated the average potential model (APM) from cell and conformal solution theories; the model has been widely applied in the study of mixtures of simple molecules. In the crude version of the APM, it is assumed that the average interaction energy in the mixture, $<\epsilon(r)>$, can be expressed by an equation having the same form as is used to express the average characteristic energy constant in cell theory, so that

$$<\epsilon(r)> = x_1^2\epsilon_{11}(r) + 2x_1x_2\epsilon_{12}(r) + x_2^2\epsilon_{22}(r) \qquad (79)$$

$\epsilon_{11}(r)$, $\epsilon_{22}(r)$ and $\epsilon_{12}(r)$ are the interaction energies associated with the interaction of the different types of molecules present in the mixture. As in Equation (75), the quantity averaged in Equation (79) has the dimensions of energy. In the refined version of the APM, the averaging process is applied separately to each type of molecule present in the mixture using the form associated with the mixture-influenced characteristic energies of each molecule in cell theory, so that

$$\langle \epsilon_1(r) \rangle = x_1 \epsilon_{11}(r) + 2x_1 x_2 \epsilon_{12}(r) \tag{80}$$

and

$$\langle \epsilon_2(r) \rangle = x_2 \epsilon_{22}(r) + 2x_1 x_2 \epsilon_{12}(r) \tag{81}$$

Scott (77) suggested parallel averaging techniques and introduced the nomenclature, one-fluid theory, for treatments which, like the crude version of the APM, consider the mixture as a single equivalent fluid and two-fluid theory for treatments which, like the refined version of the APM, consider the mixture composed of two pseudofluids with independent interaction constants. Scott was among the first to advocate that empirical equations of state based on pure component properties be applied to mixtures and that characteristic reducing parameters be obtained from pure component cohesive energies and liquid molar volumes.

In the average potential model, the corresponding states relation, Equation (53), is applied separately to each of the terms in Equation (79) or in Equations (80) and (81). In the crude version, the resulting expression is

$$<\epsilon^*>\phi\left(\frac{r}{<r^*>}\right) = x_1^2\epsilon_{11}^*\phi\left(\frac{r}{r_{11}^*}\right) + 2x_1x_2\epsilon_{12}^*\phi\left(\frac{r}{r_{12}^*}\right) + x_2^2\epsilon_{22}^*\phi\left(\frac{r}{r_{22}^*}\right) \qquad (82)$$

If the molecules are of the same size, so that $\phi(\bar{r})$ is the same in each term of Equation (82), the average characteristic energy in the APM, $<\epsilon^*>$, becomes identical to the average characteristic energy used in cell theory. If the molecules are of different sizes, ϕ must first be expressed by an appropriate two parameter inverse potential function and then substituted for each term in Equation (82). For an $(m-n)$ potential, the identifications,

$$<\epsilon^*> = \left[\sum_A\sum_B x_A x_B \epsilon_{AB}^* r_{AB}^{*m}\right]^{\left(\frac{m}{n-m}\right)} \left[\sum_A\sum_B x_A x_B \epsilon_{AB}^* r_{AB}^{*}\right]^{\left(\frac{-m}{n-m}\right)} \qquad (83)$$

and

$$<r^*> = \left[\sum_A\sum_B x_A x_B \epsilon_{AB}^* r_{AB}^{*m}\right]^{\left(\frac{-1}{n-m}\right)} \left[\sum_A\sum_B \epsilon_{AB}^* r_{AB}^{*n}\right]^{\left(\frac{1}{n-m}\right)} \qquad (84)$$

can eventually be made. Equations (83) and (84) were later named the one-fluid random mixture approximations. The relationship of the unlike (1-2) characteristic constants for energy and volume to the like (1-1 and 2-2) characteristic constants must be approximated by an appropriate combination rule or obtained empirically from mixture data.

Using the appropriate characteristic constants, the corresponding states configurational partition function,

$$Q = [r^{*3}q(\overline{T},\overline{V})]^N \quad (85)$$

is then applied to each pure component, and the extension of Equation (85) for a mixture in which the molecules are randomly distributed,

$$Q = \frac{(N_1 + N_2)!}{N_1!N_2!}\left[<r^*>^3 q(<\overline{T}>,<\overline{V}>)\right]^{N_1+N_2} \quad (86)$$

is applied to the mixture in the crude version. The reduced variables for the mixture, $<\overline{T}>$ and $<\overline{V}>$, are defined by

$$<\overline{T}> = \frac{kT}{<\epsilon^*>} \quad (87)$$

and

$$<\overline{V}> = \frac{V}{<r^*>^3} \quad (88)$$

with analogous definitions for the reduced variables of each pure component.

The configurational thermodynamic properties of all three fluids (the mixture equivalent fluid and each pure component) are obtained in terms of universal functions of their reduced variables by application of the appropriate statistical mechanical relations to Equations (85) and (86). The excess properties can then be expressed in terms of the differences of the reduced variables of the mixture and the constituent pure components, and evaluated explicitly by comparison with a reference for which the thermodynamic properties as functions of reduced variables are known. This comparison may be made graphically or by formal expansion of the thermodynamic functions of the three fluids in powers of the appropriate reduced variable about the reduced functions of the reference. The first order expressions resulting from application of either the crude or the refined version of the APM are equivalent to those obtained from conformal solution theory. The average potential model has been applied with moderate success to many mixtures of simple molecules (75,78,79).

The two-fluid version of the APM differs from the one-fluid version in that the two-fluid version relates the excess thermodynamic properties to changes in the reduced variables of each pure component resulting from the transition from the environment of the pure state to the new environment of the mixture. In general, when pure component 1 becomes pseudocomponent 1, its molecular properties are altered by the new environment, acquiring some of the characteristics of component 2. Upon becoming pseudocomponent 2, pure component 2 similarly aquires some of the characteristics of pure component 1.

II-8: Excess Properties and Characteristic Constants

The pure component characteristic energy and volume parameters necessary in the theories discussed above to obtain numerical values for the excess properties can be deduced from a variety of experimental data. Types of data which are of use include second virial coefficients, gas phase viscosities, critical constants, enthalpies of vaporization and volume changes as functions of temperature. For very light molecules, the methods are quite accurate; for heavier molecules, many of them are far less so.

Salsberg and Kirkwood (73) have shown that the excess functions are very sensitive to the numerical values chosen for the pure component energy interaction constants; the excess functions are even more sensitive to the values of the unlike interaction constants, which, until recently, were invariably calculated from the Berthelot and the Lorentz combination rules. Even though the geometric mean rule is qualitatively correct, small deviations from it result in large differences in the excess functions. As noted earlier, Thomsen (24) has demonstrated that large errors are introduced into solubility theory calculations by geometric mean rule deviations. Singer and Singer (80) have studied the effect of both geometric and arithmetic mean rule deviations on the excess properties of model Lennard-Jones fluids. Representative calculations show that a decrease in the unlike energy interaction parameter of about 1% causes increases in G^E and H^E of about 30 and 50 joules per mole and a decrease in V^E of about 0.06 cm^3 per mole. G^E is also sensitive to changes in the unlike distance parameter, although H^E is relatively insensitive to this parameter.

Analysis of gaseous mixture virial coefficients and liquid mixture excess functions shows that the characteristic energy parameter for unlike interactions, ϵ_{12}^*, is always lower than predicted by the geometric mean rule (81,82,83,84). The difference ranges from about 1% for argon-krypton interactions to 3-5% for the interactions between different non-polar polyatomic molecules. Because of the pattern of deviation, Kreglewski (85) has suggested equating ϵ_{12}^* and ϵ_{11}^* when ϵ_{11}^* is much less than ϵ_{22}^*. Prausnitz and Gunn (86) have suggested an empirical combination rule based on pure component critical volumes, and Eckert, Renon and Prausnitz (87) a combination rule based on mixture virial coefficients.

Because of the sensitivity of mixture properties to the unlike interaction constants, Rowlinson (88) has concluded that 1-2 forces determined from the average of 1-1 and 2-2 forces are inadequate for the detailed description of simple mixtures and for the crude description of complex mixtures, and has suggested that such forces be determined from observed mixture properties.

II-9: Van der Waals Combination Rules

In the middle of the 1960's, there was a renewal of interest in theories of mixtures based on the van der Waals equation of state and later generalizations. The impetus was a publication by Leland, Rowlinson and Sather (89). Using as their justification several studies on pure liquids (90,91, 92,93) which indicated that the pair distribution function is primarily determined by repulsive forces, these investigators adapted the Percus-Yevick (94) integral equation for mixtures of hard spheres and using a perturbation method, applied it to mixtures of real molecules having conformal potentials. They introduced combination rules to obtain characteristic energy, ϵ^*, and volume, $V^* = r^{*3}$, parameters for mixtures which resemble the quadratic forms originally suggested by van der Waals for a and b,

$$\epsilon^* = \left[\sum_A \sum_B x_A x_B \epsilon^*_{AB} V^*_{AB}\right]\left[\sum_A \sum_B x_A x_B V^*_{AB}\right]^{-1} \tag{89}$$

and

$$V^* = \sum_A \sum_B x_A x_B V^*_{AB} \tag{90}$$

Unlike Equation (75), Equation (89) quadratically averages terms with the dimension energy·volume, the same dimension as in Equation (3). These averaging rules for the characteristic parameters differ substantially from those which result from the application of a (m - n) potential to the average potential model [Equations (83) and (84)]; the latter tend to overestimate positive contributions to the excess functions caused by molecular size differences. Equations (89) and (90) are called the one-fluid van der Waals combination rules. Leland <u>et. al</u>. (95) extended their perturbation technique to a two-fluid treatment, defining two-fluid van der Waals characteristic parameters for pseudocomponent 1 by

$$\epsilon_1^* = \left[\sum_B x_B \epsilon_{1B} V_{1B}^*\right] \left[\sum_B x_B V_{1B}^*\right]^{-1} \tag{91}$$

and

$$V_1^* = \sum_B x_B V_{1B}^* \tag{92}$$

with similar relations for the characteristic parameters of pseudocomponent 2. The one- and two-fluid mixture rules are similar if the molecules are approximately equal in size. These two papers are among the first major theoretical treatments in which the magnitude of the unlike energy interaction parameter is routinely evaluated from one of the excess functions as well as from the geometric mean rule, although the Lorentz arithmetic mean rule is retained for the 1-2 volume parameter. Both the one- and two-fluid versions of the Leland, Rowlinson and Sather model yield better agreement for the remaining excess functions if ϵ_{12}^* is empirically determined from G^E; the results of the two-fluid version are slightly more accurate. Modification of the procedure by the introduction of shape factors for molecules that are not conformal with the reference species did not further improve the results.

The introduction of the van der Waals combination rules generated renewed interest in the original van der Waals equation of state and in generalizations of the form,

$$P/\rho RT \;=\; f(\rho) \;-\; a\rho/RT \tag{93}$$

The repulsive term in Equation (93), $f(\rho)$, can either be a function of density, as in the van der Waals equation of state, or can be an approximation to the repulsive term in the equation of state of a collection of hard spheres. The attractive term in generalized van der Waals equations of state is always inversely proportional to volume.

Many investigators have applied the one- and two-fluid van der Waals combination rules, in conjunction with the original and generalized van der Waals equations of state to various types of liquid mixtures. McGlashan (96) applied the original van der Waals equation of state to binary mixtures of simple molecules using the one-fluid approximation. He found that use of values of a and b for the pure components calculated from critical data, values of b_{12} calculated from the Lorentz approximation, and values of a_{12} calculated from excess enthalpy data, gave results for the other excess properties close to those calculated by Leland, Rowlinson and Sather (85) by their more elaborate method. McGlashan's treatment differs from that of van Laar and Lorenz (8) both by the use of excess enthalpy data and by the calculation of the volume of the mixture directly from the equation of state using the mixture values of a and b. Scott and Konynenberg (97) directly applied Equation (1) to mixtures of chain hydrocarbons. They approximated van der Waals a for pure liquid paraffins by the product of the molar volume and energy of vaporization and expressed the results analytically as a function of carbon number; they calculated b for each pure liquid directly from the equation of state and similarly expressed the results as a function of carbon number. The mixture parameters were then determined by application of the principle of congruence, which relates the properties of liquid paraffinic mixtures to an effective carbon number, defined by the mole fraction average of the carbon numbers of the pure components. The form of H^E obtained in this treatment is identical to that obtained by van Laar and Lorenz with a and b expressed in terms of carbon number. The H^E predictions support earlier conclusions (98,99) that when used in association with heats of vaporization, the principle of congruence tends to yield low values for excess enthalpies.

Using the van der Waals combination rules, Marsh, McGlashan and Warr (100) calculated the excess properties of mixtures of simple molecules from several different equations of state. They found that even if G^E was used to determine the characteristic energy of the unlike interactions, none of the equations of state yielded quantitative predictions for V^E. Use of the two-fluid combination rules gave better agreement than did the one-fluid combination rules and each of the equations of state tested predicted the excess properties more accurately than did the original van der Waals equation of state. Marsh (101) and Despande and Patterson (102) applied several generalized van der Waals equations to mixtures of large, bulky molecules. They found that moderate adjustments to the geometric mean rule were insufficient to bring theory and experiment into better accord for these mixtures and that both one- and two-fluid van der Waals mixture prescriptions predicted very large volume contractions for octamethylcyclotetrasiloxane mixtures, although no such contractions are experimentally observed. Monte Carlo calculations suggest (80, 103) that this false contraction is due to a tendency of the van der Waals combination rules to overestimate negative contributions to V^E due to size differences. Kreglewski (104,105) proposed using an empirical adjustment factor to calculate the excess properties of mixtures of simple, globular and chain molecules when the components differ greatly in size. He combined a hard sphere equation of state with a temperature-dependent van der Waals attractive term, calculated size parameters from molar volumes and used mixture critical constants as the basis for mixed interaction combination rules. Williamson and Scott (106) compared the van der Waals treatment of n-alkane mixtures to lattice treatments and Boublik and Benson (107) examined the effect of use of a square well potential on the excess properties of mixtures of non-polar molecules.

II-10: Mixture Theories Based on Modifications of the Cell Partition Function

In addition to its use in perturbation approaches, the van der Waals attractive potential has been used extensively with many of the modifications of Eyring and Hirschfelder's (64) original cell partition function, which can be written for Avogodro's number of molecules, N_o, as

$$Q = [\lambda(v^{1/3} - v^{*1/3})^3]^{N_o} \exp(\Delta E^V/RT) \tag{94}$$

where ΔE^V is the molar energy of vaporization.

Tonks (108) derived a partition function of essentially the same form as that in Equation (94) without reference to the cell formalism. He first obtained the partition function of a one-dimensional fluid of incompressible molecules and then extended the partition function to three-dimensional molecules. Although the one-dimensional treatment is exact, the extension to three dimensions is not. Tonks' derivation is additionally important since it introduces naturally the factor $1/N!$ which appears in Equation (29) and becomes the exponential e, in contrast to the simple cell theory treatment in which this factor does not initially appear.

Prigogine, Trappeniers and Mathot (109,110) applied the cell method to the treatment of homogeneous r-mers by dividing the degrees of freedom of each r-mer into internal and external categories; only the external degrees of freedom depend on the intermolecular forces and enter the configurational partition function, which is written as

$$Q = Q_{comb}[q_s(T,\nu)]^{3CN}\exp(-E_o/kT) \tag{95}$$

The segment partition function in Equation (95), $q_s(T,\nu)$, is related to the cell partition function, $q(T,\nu)$, by

$$q(T,\nu) = [q_s(T,\nu)]^{3C} \tag{96}$$

where 3C is the number of external degrees of freedom per molecule. Q_{comb} is the combinatory partition function. Instead of employing the smoothed potential or mean potential models, Prigogine, Bellemans and Colin-naar (111) instead introduced a three-parameter corresponding states approach which can be extended to solutions through adaptation of the average potential model.

Their reduced partition function for a collection of N r-mers has the form,

$$Q = Q_{comb}[r^{*3}\,\phi(\bar{T},\bar{\nu})^{C}]^{N} \tag{97}$$

where ϕ is a universal potential function and $\bar{\nu}$ is the reduced volume per element. If $\phi(\bar{T},\bar{\nu})$ is expressed by the Lennard-Jones (6-12) potential, the characteristic constants of the pseudocomponents in the mixture can be obtained from the Lennard-Jones parameters of the pure components and appropriate approximations for the unlike interaction parameters by application of combination rules similar to those obtained in the average potential model. Expressions for the thermodynamic functions are then obtained directly from the partition function. Janini and Matire (112) have recently derived analytical expressions for the excess functions of chain molecules by extension and simplification of Prigogine's original equations. Their method requires accurate data for the enthalpy and volume derivatives of the pure components. The effective number of external degrees of freedom per molecule in the mixture is treated as an adjustable parameter and is determined empirically from activity coefficients at infinite dilution obtained from gas-liquid chromotagraphy.

Perhaps the most widely applied modification of Prigogine's work is the method developed by Flory and coworkers (113,114,115,116,117), who combined the van der Waals attractive energy and Prigogine's concepts of external degrees of freedom and contact between neighboring segments with the Eyring and Hirschfelder - Tonks partition function. We will later discuss several aspects of this theory in conjunction with our proposed modifications.

The formalism involves dividing the molecules into homogeneous segments of equal size, although a special treatment limited to n-alkanes (113,116,117) involves heterogeneous segments. The total configurational energy is assumed to arise only from the pairwise contacts of the segments. The characteristic parameters of the pure components are obtained from liquid molar volumes, thermal expansion coefficients and thermal pressure coefficients.

The theory is applied to mixtures through an empirically determined contact interaction parameter, X_{12}, somewhat analogous to Guggenheim's exchange interaction parameter, w, but with the dimensions of energy density. There are almost as many methods of computing X_{12} as there are investigators correlating their data in terms of Flory's treatment. X_{12} should be independent of concentration; while it is nearly concentration independent for some mixtures, it is strongly composition dependent for others. It is usually (118) calculated either from the equimolar value of one excess function or by minimizing the integral,

$$\sigma^2(X_{12}) = \int_0^1 \left[X^E_{\text{observed}} - X^E(X_{12})_{\text{calculated}} \right]^2 dx_1 \qquad (98)$$

where X^E is one of the excess properties.

Theoretically, the choice of the excess function from which X_{12} is evaluated should be unimportant; this is not the case. An additional empirical parameter, Q_{12} is usually needed to correlate Second Law excess functions (117). Enthalpy is more sensitive to the numerical value of X_{12} than is volume, so that the agreement of predicted excess enthalpy with experiment using an excess volume-based X_{12} is far poorer than the excess volume prediction based on excess enthalpy data. Excess volume, however, is the experimentally more accessible function, and excess enthalpy (and excess free energy) predictions pragmatically most important. The treatment confined to mixtures of n-alkanes uses a composite value of X_{12} related to the strength of the interactions between different types of segments.

The theory produces, somewhat as an artifact, temperature dependent characteristic parameters. Patterson and Bardin (119) explored possible causes of the variation of these characteristic parameters with temperature for chain liquids. They found that the three parameter corresponding states principle is obeyed and concluded that the temperature dependence is due not to the failure of the principle of corresponding states, but to the inadequacy of theoretical equations of state based on cell-like partition functions.

Patterson and Bardin (119) also examined the special treatment confined to n-alkanes in which both the pure components and their mixtures are considered to be mixtures of end and middle segments. They found that in order to obtain reasonable values for H^E, an unusually weak methyl-methylene interaction must be postulated. With a stronger methyl-methylene interaction, the theory predicts negative rather than positive values for H^E. They interpret their own extensive results on the enthalpy of mixing of normal and highly branched alkanes (120,121,122) in terms of Borthorel's correlation of molecular orientations treatment (123) which attributes the origin of the excess enthalpy to changes in orientational order and free volume on mixing. The relationship of Flory's n-alkane theory to other simple segment theories has been examined by Cruickshank and Hicks (124).

Fisher and Leland (125) developed a treatment of liquids explicitly based on temperature dependent characteristic parameters; other investigators have tried to eliminate the temperature dependence of Flory's characteristic parameters and at the same time assure strict adherence to the principle of corresponding states. One such method (126) involves using n-octane as a reference liquid. The characteristic parameters of n-octane are computed as suggested by Flory; the characteristic parameters of all other alkanes are then determined from semi-empirical relationships to the reference (127). Fang and Wiehe (128) have suggested that temperature independent characteristic volumes be obtained by relating the critical volumes of various liquids to the critical volume of argon. Bhatnagar and Sharma (129) used an empirical method and critical constants data to obtain temperature independent values for all the characteristic parameters, which they then used in a cell-type partition function which incorporates heat capacity data to represent intermolecular energy changes.

An earlier approach which builds on the ideas of Prigogine and Flory and also uses heat capacity data was introduced by Renon, Eckert and Prausnitz (130). Modifying a proposal by

Wertheim (131) that the configurational partition function be factored into two terms, one a function of temperature and volume and the other a function of temperature only, they suggested instead using the functional form,

$$Q = [v^{*1/3} f_1(\overline{V}) f_2(\overline{T})]^{3CN} \exp(U^* \overline{E}(\overline{V})/kT) \quad (99)$$

where U^* is a characteristic energy. If $C = 1$, $f_1(\overline{V}) = (\overline{V}^{1/3} - 1)$ and $f_2(\overline{T}) = 0$, Equation (99) reduces to the partition function of Eyring and Hirschfelder; if $f_1(\overline{V}) = (\overline{V}^{1/3} - 1)$ and $f_2(\overline{T}) = 0$, it reduces to partition function used by Prigogine, and if in addition, the energy-volume dependence is of the van der Waals form, $\overline{E}(\overline{V}) = -\text{constant}/\overline{V}$, Equation (99) becomes Flory's partition function. Since the configurational heat capacity at constant volume must be zero if $f_2(\overline{T}) = 0$, Renon, Eckert and Prausnitz assumed the functional forms,

$$f_1(\overline{V}) = (\overline{V}^{1/3} - 1) \quad (100)$$

$$f_2(\overline{T}) = \exp(a/3\overline{T}^2) \quad (101)$$

and

$$\overline{E}(\overline{V}) = -1/\overline{V} \quad (102)$$

for the terms in Equation (99). The magnitude of the constant a was approximated from experimental heat capacity data as 0.4.

The characteristic parameters are obtained from temperature, volume and energy of vaporization data under conditions when $(\partial \ell nV/\partial \ell nT) = 0.4$. Eckert, Renon and Prausnitz (87) applied this partition function to binary mixtures of simple liquids using Scott's two-fluid approximation. They found that the calculated excess properties are very sensitive to the magnitude of the energy parameter for interactions between the unlike molecules and therefore investigated the effect of arbitrary combinations of molecular parameters on the excess properties of model liquid mixtures.

Winnick and Prausnitz (132) used a semi-empirical modification of the above partition function in order to extend it to larger and more complex molecules. They include in $f_2(\overline{T})$ all temperature effects not already taken into account, and determined $f_2(\overline{T})$ empirically for each substance by equating gas and liquid free energy expressions; the equation of state obtained from Equation (99) is itself independent of the form of $f_2(\overline{T})$. The modification was extended to mixtures (133) using an empirical constant for the energy parameter associated with the interaction of unlike molecules and an adaptation of the mixing rules proposed by Eckert, Renon and Prausnitz (87). While the results are reasonably good for simple mixtures, they are only fair for more complex ones. Winnick (134) applied this partition function to polar molecules by adding to the van der Waals attractive term a reduced dipolar energy related to the canonically averaged energy of a pair of dipoles. In extending this latter treatment to mixtures (135) he assumed that the unlike dipole and induced dipole interactions outweigh geometric mean rule deviations. One empirical mixture parameter is needed for each mixture; if an excess enthalpy measurement is used to determine this parameter, the predicted excess enthalpy and excess volume composition curves qualitatively agree with experiment.

II-11: Volume Dependence of the Liquid Cohesive Energy

Patterson, Bhattacharyya and Picker (136) compared the form of the characteristic parameters resulting from the Lennard-Jones (m - n) liquid configurational energy dependence used by Prigogine,

$$\bar{E} = \frac{1}{(m-n)}\left[-n\bar{V}^{-m/3} + m\bar{V}^{-n/3}\right] \qquad (103)$$

with the (3 - ∞) van der Waals form used by Flory. Applying the principle of corresponding states, Patterson and Bardin (119) found that experimental n-alkane data could be more readily shifted onto the reduced property curves produced by a (3 - ∞) potential than onto those produced by (6 - ∞) or (6 - 12) potentials.

The first experimental investigations on the best way to represent the volume dependence of the average configurational energy in liquids over a moderate temperature interval were conducted by Hildebrand and his colleagues (137,138,139,140), although some of the conclusions in these early papers were amended in the later monographs (141,142,143).

The expression for the internal pressure, $P_i = (\partial E/\partial V)_T$, is called the thermodynamic equation of state, and can be obtained straightforwardly from the combined first and second laws and the appropriate Euler's identity,

$$(\partial E/\partial V)_T = T(\partial P/\partial T)_V - P \qquad (104)$$

Equation (104) relates the internal pressure to a simple experimental quantity, the thermal pressure coefficient, $(\partial P/\partial T)_V$. The contribution of the external pressure to $(\partial E/\partial V)_T$ is usually negligible at low pressure.

If the volume dependence of the configurational energy can be represented by the van der Waals expression, then

$$(\partial E/\partial V)_T = a/V^2 \qquad (105)$$

and the product $V^2(\partial E/\partial V)_T$ should be constant over a reasonable temperature inteval. If the average configurational energy should be represented more generally as

$$E = - a/V^m \qquad (106)$$

then the product $V^{m+1}(\partial E/\partial V)_T$ should instead be constant. Early investigations showed that m is equal to or greater than one for non-polar liquids.

Equation (106) can be differentiated and rearranged to yield

$$(\partial E/\partial V)_T = - mE/V \qquad (107)$$

If the liquid is sufficiently expanded so that the effect of the repulsive forces is unimportant, the average configurational energy can be approximated by the negative of the energy needed to overcome all attractive forces and vaporize the fluid to the ideal gas, so that

$$(\partial E/\partial V)_T = m\Delta E^V/V \qquad (108)$$

where ΔE^V is the latent energy of vaporization. One way to establish values of m, then, is from the ratio of the internal pressure to the cohesive energy density. Applying this method to Hildebrand's original data (140) results in values of 1.10, 1.08 and 1.05 for the energy-volume exponents in carbon tetrachloride, heptane and benzene.

Eyring and Hirschfelder (64) used Equation (106) initially in their cell partition function, but later introduced the simplication $m = 1$. They derived expressions for α, the thermal expansion coeficient, and β, the isothermal compressibility, in terms of m and the energy of vaporization. They noted that although the thermal pressure coefficient, $\gamma = (\partial P/\partial T)_V$, is thermodynamically equivalent to α/β, values of m determined from experimental measurements of α and β differ from those determined from the direct measurment of $(\partial P/\partial T)_V$ due to the sensitivity of m to small uncertainties in the experimental quantities.

Several attempts have been made to estimate m theoretically. Benson (144) applied the smoothed potential model of the liquid state, assumed isotropic expansion of the liquid with temperature, and found that the configurational energy reduced to a function only of density. If the intermolecular forces can be represented by a polynomial, then this function is

$$E = -B_1\rho^2 - B_2\rho^{8/3} - B_3\rho^{-10/3} + B_4\rho^4 \tag{109}$$

where ρ is the density of the fluid and the B_i's are constants. If Equation (109) is approximated by

$$E = -A\rho^{x/3} \tag{110}$$

then the energy of vaporization can be written

$$\Delta E^V = A(\rho^{x/3}_{liquid} - \rho^{x/3}_{gas}) \tag{111}$$

Since Benson found that only values of x between 5 and 6 led to constant values for A, values of the exponent in Equation (110) should range from 5/3 to 2. Snider (145) applied a varient of the hard core model of liquids and examined the values of m in the finite attractive outer potential which must be added to a perfectly repulsive inner core. He found that the potential energy per molecule is dominated by a term which is a function of density only and concluded that m should be close to or equal to unity.

Experimental measurements of $(\partial P/\partial T)_V$ in the 1950's and 1960's confirmed the implication of earlier data that $m > 1$ for non-polar liquids. Benninga and Scott (146) measured the thermal pressure coefficient of CCl_4 over a wide temperature interval and used the data to compute the internal pressure. They expressed both the internal pressure and the cohesive energy density analytically as functions of temperature and found that their ratio has the temperature independent value $m = 1.09$. Smith and Hildebrand (147) similarly measured $(\partial P/\partial T)_V$ for n-heptane and several fluorinated hydrocarbons. They found that the internal pressure is a function only of volume and that the value of the exponent in the energy-volume relation increases with molecular size and fluorine content. Ross and Hildebrand (148) found that values of m obtained from $[\partial \ln(\partial E/\partial V)_T / \partial \ln V]$ are considerably higher than those obtained from the ratio of the internal pressure to cohesive energy density. This effect was also observed by Dunlap and Scott (149) who attributed it to small deviations of $(\partial^2 P/\partial T^2)_V$ from zero. The theoretical study of Fried and Schneier (150) of the cohesive energy of n-alkanes and other non-polar molecules as a function of temperature demonstrated that m is relatively constant in the reduced temperature range 0.6 - 0.7. The average value of m that they obtained for n-alkanes by considering the differential form of the logarithm of Equation (106) agrees with the higher value for n-hexane found by

Dunlap and Scott (149) by their graphical method.

Bianchi, Agabio and Tuturro (151) studied the internal pressure as a function of temperature under both constant volume and constant pressure conditions. The small negative values found for $(\partial \ln P_i/\partial T)_V$ indicate that the liquid intermolecular energy is not strictly a function of volume only; examination of their values for $(\partial \ln P_i/\partial T)_P$, which is related to m by

$$(\partial \ln P_i/\partial T)_P = -(m-1)\alpha \tag{112}$$

indicates that m for the three liquids studied is slightly greater than one.

Recent reviews (152,153) have stressed the importance of the internal pressure and the cohesive energy density in solution phenomena. Dack (153) obtained expressions for the internal pressure,

$$P_i = -\frac{2\pi}{3}\rho^2 kT\int_0^\infty r^3[\partial u(r)/\partial r][\partial g(r)/\partial T]\,dr \tag{113}$$

and the cohesive energy,

$$E = 2\pi\rho N\int_0^\infty r^3 u(r)g(r)\,dr \tag{114}$$

in terms of the pair potential function, u(r), and the radial distribution function, g(r). The internal pressure is associated with those intermolecular forces which do not vary rapidly with distance while the cohesive energy is associated with all the intermolecular forces in the liquid state; the internal pressure approaches the cohesive energy when repulsive and dispersive forces are dominant and is significantly lower than the cohesive energy density when strong orientational forces are present.

Bagley, Nelson and Scigliano (154) derived expressions for the excess volume and excess enthalpy solely in terms of internal pressure differences,

$$V^E = RT\left(\frac{1}{P_{im}} - \frac{x_1}{P_{i1}} - \frac{x_2}{P_{i2}} \right) \tag{115}$$

and

$$H_p^E = -\left(P_{im}V_m - x_1P_{i1} - x_2P_{i2} \right) \tag{116}$$

Agreement with experiment is poor, since the results are very sensitive to small errors in the internal pressure data. Better agreement was obtained for the excess enthalpy if experimental mixture volumetric data is used in Equation (116) along with experimental mixture internal pressure data or if the excess volume is used to compute the mixture internal pressure from Equation (115) and these two quantities used together in Equation (116).

II-12: Theories Based on $1/V^m$ Relationships

Kreglewski (155) studied the effect of molecular size and size differences on the configurational properties of liquid mixtures by analyzing Hildebrand's values (141,142,143) for the internal pressure-cohesive energy density ratio. He found that the relationship between m and liquid molar volume could be approximated by the expression,

$$m = 0.262(V - V_o)^{1/3} \tag{117}$$

where V_o equals 30 cm^3/mole or the approximate size of a methyl group and V is the molar volume at a reduced temperature $T/T_c = 0.6$. For molecules which approach the size of a methyl group $m \longrightarrow 0$ and the configurational energy and corresponding reduction parameters become independent both of volume and of molecular size. For very large molecules, Equation (117) becomes approximately

$$m = \frac{1}{4} V^{1/3} \tag{118}$$

so that the configurational energy is

$$E = -\frac{3}{4} E^V V^{1/3} + \text{constant} \tag{119}$$

and the energy reduction parameters should be volume dependent. This analysis has caused Kreglewski to conclude that there should be an abrupt change in the properties of liquids and their mixtures when the size of one of the components passes through

V_o and that the reductions parameters for mixtures of small molecules should be more sensitive to size differences than those for mixtures of large molecules.

Fang and Wiehe (156) constructed a semi-empirical partition function, similar to those used in conjunction with a van der Waals attractive term, but with the energy-volume relationship in Equation (106) instead, which they applied to monomeric and polymeric liquids. Its form is given by

$$Q = Q_{comb}[bf(\overline{V})]^{3CN} v^{*N} \exp(Ns\epsilon/kT\overline{V}^{m}) \qquad (120)$$

The characteristic volume, v^*, of each liquid is determined from its critical volume and the critical volume of argon; the four other molecular constants, b, C, m and $s\epsilon$ are calculated so as to give best simultaneous agreement with experiment of expressions for the liquid molar volume, thermal pressure coefficient, vapor pressure and heat of vaporization. The values of m obtained from this procedure range from 0.76 for neopentane to 1.67 for acetylene. Attempts to extend the application of the partition function to mixtures proved unsuccessful.

A more successful approach that included non-integral powers of volume in the attractive energy term is based on the group interaction method (157,158,159). Group interaction methods assume that the interactions energy between molecules can be represented as the sum of contributions from pairs of interacting groups, each pair acting independently of all others present.

The magnitude of each contribution is assumed to depend only on the group concentration, the group cross section and the group interaction coefficient. The partition function developed by Lee, Greenkorn and Chao (160) for polar and non-polar molecules combines cell and quasi-lattice theories and looks like Flory's partition function expressed in terms of groups,

$$Q = Q_{comb}\left(\prod_i (\lambda_i^3 \nu_i^*)^{r_i c_i N}\right)(\tilde{V}^{1/3} - 1)^{3rcN} \exp \frac{-\Sigma \epsilon_{ij} N_{ij}}{kT} \qquad (121)$$

where r_i, c_i, ν_i^* and λ_i are the number of groups of type i per molecule, the number of external degrees of freedom per group, group characteristic volume and group geometric constant respectively. The interaction energy, ϵ_{ij}, between groups i and j is written as

$$\epsilon_{ij} = -\eta_{ij}/\nu_B^{1.15} \qquad (122)$$

where η_{ij} is an energy interaction constant for groups i and j and ν_B is the volume of a base group. The exponent $m = 1.15$ was chosen for Equation (122) because of the large number of normal and branched alkanes with internal pressure-cohesive energy density ratios near this value (161). The energy of a hydrogen bond was represented by adding an additional attractive term,

$$\epsilon_{HB} = -\eta_{HB}/\nu_B^{1.15} - \sigma_{HB} \qquad (123)$$

to the interaction energy. The number of interactions, N_{ij}, between the different groups is determined from Guggenheim's quasi-chemical relation. The core volumes, energy interaction parameters and number of external degrees of freedom for methyl and methylene groups are determined from molar volumes, enthalpies of vaporization and thermal expansion coefficients of pure n-alkanes; the interaction properties of hydroxyl groups are then obtained from similar data for n-alkanols. No distinction is made between the interaction energies of methyl and methylene groups, although the two groups are assigned different coordination numbers. The treatment was extended to branched alkanes (162) using a Taylor series expansion and to mixtures of n-alcohols and mixtures of n-alkanes with n-alcohols (163) by including an empirical orientation factor calculated from excess enthalpy data. The last paper in the series (164) treated pure ketones and mixtures of ketones and alkanes.

Brontow and Lu (165) obtained characteristic parameters for normal alcohols by dividing the molecules into segments, relating the segments to graph points and counting what they term interesting walks on graphs. Using Equation (106) to express the configurational energy, they derived expressions for the excess properties in terms of interacting pairs of walks. They stressed the need for very accurate pure component data since the configurational energies involved are much larger than the excess energy.

II-13: Semi-empirical Correlation Methods

None of the molecular approaches discussed so far gives a totally satisfactory account of the excess properties of liquid mixtures even if some data on the mixture itself is incorporated. Empirical functions, such as the Redlich-Kister expression (166), can be used to represent the concentration dependence of one excess property, but the least squares constants for one type of data are unrelated to the constants for other types of data, so that one excess function cannot be predicted from another. The Wilson equation (167), a two-parameter semi-empirical equation based on the concept of local mole fractions, is particularly useful for the correlation of vapor-liquid equilibrium and excess free energy data. Although expressions for the excess enthalpy can be obtained from the temperature dependence of the Wilson parameters, the agreement with experiment is poor (168). The Wilson equation has been used to provide an analytical form for the calculation of group excess enthalpies (169) and in a correlation scheme based on a modification of the conformal solution formalism (170,171).

Fried and Liebermann (172,173) have recently modified the Wilson equation by introducing a molecular size contribution term and a method for estimating the temperature dependence of the parameters. This new equation permits the calculation of the excess free energy from isothermal excess enthalpy data with improved accuracy and so provides a way to avoid specification of the combinatory term in partition functions which predict First Law properties accurately.

III. PURE FLUID RELATIONS

The treatment of liquid mixtures we propose differs in several important ways from the methodology developed by Flory and coworkers (113-117). Initially, we assume the necessity of replacing the van der Waals energy-volume relationship by the more general expression as given by Equation (106). We postulate that the exponent m in this expression is a fundamental property of each liquid component and that the value of m for a binary liquid mixture is a suitably averaged function of the values for the individual components.

The present treatment is an extension of work initially undertaken by Hsu (174), who associated a single common value of m with all members of a group of similar liquids and their mixtures. While Hsu's treatment gives good agreement between experimental excess enthalpies and excess enthalpies calculated from excess volume data for certain groups of liquid mixtures, the method ultimately implies that the same value of m should be associated with all liquids of all groups.

III-1: The Configurational Partition Function and Equation of State

We begin by employing the Prigogine formalism, in which each molecule is considered divided into r homogeneous segments, each with 3c external degrees of freedom. It is assumed that only the external degrees of freedom are affected by the environment; interactions with other molecules leave the internal degrees of freedom unchanged. The segments interact with each other through contact sites distributed over the molecular surface; there are s such contact sites per segment. No distinction is made between the interaction of segments belonging to the same molecule and the interaction of segments located on different molecules.

The Prigogine modification of the Eyring and Hirschfelder - Tonks configurational partition function for N molecules can be written as

$$Q = Q_{comb}(\lambda \nu^*)^{rNc}(\bar{\nu}^{1/3} - 1)^{3rNc} \exp(-E_o/kT) \qquad (124)$$

Q_{comb} is the combinatory part of the partition function and need not be specified for treatments of either the PVT properties or energy relations of fluids. Tonks' geometric constant, λ, similarly need not be specified. The reduced volume, $\bar{\nu}$, is defined by

$$\bar{\nu} = \nu/\nu^* \qquad (125)$$

where ν is the total fluid volume per segment and ν^* is the core or occupied volume per segment. The total fluid volume per molecule, v, and core volume per molecule, v^*, are related to the respective quantities per segment by

$$v = \nu r \qquad (126)$$

and

$$v^* = r\nu^* \tag{127}$$

The molar and core molar volumes, V and V^*, can be expressed by

$$V = N_o v \tag{128}$$

and

$$V^* = N_o v^* \tag{129}$$

where N_o is Avogodro's number of molecules. Expressions for the reduced volume analogous to Equation (125) can be written using molecular and molar volumes. All three expressions,

$$\bar{\nu} = \bar{v} = \bar{V} \tag{130}$$

are equivalent and can be used interchangeably.

The average configurational energy of the system, E_o, is expressed in terms of the interaction of pairs of neighboring contact sites. Using Equation (106) as the model for the form of the energy-volume relation, the attractive energy of interaction of two such sites is η/ν^m, of two segments is $s\eta/\nu^m$ and of two molecules is $rs\eta/\nu^m$, so that the average configurational energy of the N molecules is

$$E_o = -Nrs\eta/2\nu^m \tag{131}$$

where the factor 2 corrects for the duplicate counting of the contribution from each pair. If $N = N_o$, Equation (131) represents the molar interaction energy of the liquid. If $m = 1$, these relations reduce to forms ressembling the van der Waals attractive energy. Although Flory briefly considered values of $m \neq 1$, he felt that they produced no improvement in the representation of the PVT properties of pure fluids and so chose attractive energies of the van der Waals form instead. Expressing the average configurational energy by Equation (131), the partition function for N molecules becomes

$$Q \;=\; Q_{comb}(\lambda\, v^{*})^{rNc}(\bar{V}^{1/3} - 1)^{3rNc}\exp(Nrs\eta / 2v^{m}kT) \qquad (132)$$

In order to obtain the equation of state, the natural logarithm of the partition function is differentiated with respect to the total volume, $V_N = Nrv$, of the N molecules. The combinatorial term and the core volume per segment are assumed independent of volume, so that Equation (132) becomes

$$(\partial\, \ell n\, Q/\partial V_N)_T \;=\; \frac{rNc\bar{V}^{-2/3}}{(\bar{V}^{1/3} - 1)}(\partial \bar{V}/\partial V_N)_T \;-\; \frac{mNrs\eta}{2kTv^{m+1}}(\partial v/\partial V_N)_T \qquad (132)$$

Since, from the chain rule and the definition of reduced volume,

$$(\partial v/\partial V_N)_T \;=\; 1/Nr \qquad (133)$$

and

$$(\partial \overline{V}/\partial V_N)_T = 1/Nr\nu^* \tag{134}$$

Equation (132) becomes

$$(\partial \ln Q/\partial V_N)_T = \frac{c\overline{V}^{-2/3}}{(\overline{V}^{1/3} - 1)\nu^*} - \frac{ms\eta}{2\nu^{m+1}kT} \tag{135}$$

Applying the statistical mechanical relationship between pressure and the partition function,

$$P = kT(\partial \ln Q/\partial V_N)_T \tag{136}$$

the equation of state is

$$P = \frac{kTc\overline{V}^{-2/3}}{(\overline{V}^{1/3} - 1)\nu^*} - \frac{ms\eta}{2\nu^{m+1}} \tag{137}$$

Equation (137) is expressed in terms of the properties of explicit segments; it can be put into reduced form by defining the characteristic pressure, P^*, and characteristic pressure, T^*, by

$$P^* = s\eta/2\nu^{*m+1} \tag{138}$$

and

$$T^* = s\eta/2\nu^{*m}ck \tag{139}$$

and using the reduced variables, $\overline{P}$,

$$\overline{P} = P/P^{*} \tag{140}$$

and $\overline{T}$,

$$\overline{T} = T/T^{*} \tag{141}$$

The characteristic parameters are interrelated by

$$P^{*}v^{*} = ckT^{*} \tag{142}$$

III-2: Temperature Dependence of the Characteristic Parameters

When evaluated from pure component data and the reduced equation of state at zero pressure, the characteristic parameters show a small but definite dependence on temperature. Differentiating Equation (104) with respect to temperature,

$$[\partial(\partial E/\partial V)_T/\partial T]_V = (\partial^2 P/\partial T^2)_V \tag{143}$$

shows that the internal pressure, and therefore perhaps the configurational energy, is purely a function of volume only if $(\partial^2 P/\partial T^2)_V = 0$. Since thermal pressure coefficients generally decrease with temperature, the temperature dependence of the characteristic parameters might be due to the lack of an explicit temperature dependence in the expression for the configurational energy.

Berthelot (261) formulated an equation of state, given by

$$(P + a/TV^2)(V - b) = RT \tag{144}$$

which ressembles the van der Waals equation of state but which implies an energy-volume relationship explicitly involving temperature,

$$E = - a/VT \tag{145}$$

We therefore explored whether the temperature dependence of the characteristic parameters could be eliminated by expressing the interaction energy of two sites as $\eta/v^m T^n$ for some value of $n \neq 0$.

Using an expression for the average configurational energy based on site interactions of this form, the configurational partition function becomes

$$Q = Q_{comb}(\lambda v^*)^{rNc}(\bar{V}^{1/3} - 1)^{3rNc} \exp(Nrs\eta / 2v^m T^{n+1} k) \tag{146}$$

and leads to the equation of state,

$$P = \frac{kTc\bar{V}^{-2/3}}{(\bar{V}^{1/3} - 1)v^*} - \frac{ms\eta}{2v^{m+1}T^n} \tag{147}$$

In order to preserve the correct dimensionality, P^* and T^* must be defined as

$$P^* = s\eta / 2v^{*m+1}\, T^{*n} \tag{148}$$

and

$$T^* = (s\eta / 2v^{*m} ck)^{1/n+1} \tag{149}$$

with the restriction that $n \neq -1$. Substituting expressions for pressure and temperature from the definitions of the reduced properties into Equation (147) and using Equations (148) and (149) to simplify the results, leads to the reduced equation of state,

$$\frac{\bar{P}\,\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{(\bar{V}^{1/3} - 1)} - \frac{m}{\bar{T}^{\,n+1}\bar{V}^{m}} \tag{150}$$

In the limit of zero pressure and without appreciable error at atmospheric pressure, Equation (150) becomes

$$\bar{T}^{\,n+1} = \frac{m(\bar{V}^{1/3} - 1)}{\bar{V}^{\,m+1/3}} \tag{151}$$

If $n = 0$, Equations (150) and (151) reduce to

$$\frac{\bar{P}\,\bar{V}}{\bar{T}} = \frac{\bar{V}^{1/3}}{(\bar{V}^{1/3} - 1)} - \frac{m}{\bar{T}\,\bar{V}^{m}} \tag{152}$$

and

$$\overline{T} = \frac{m(\overline{V}^{1/3} - 1)}{\overline{V}^{m+1/3}} \qquad (153)$$

Expressions for the thermal expansion coefficient, $\alpha = [\frac{1}{V}(\partial V/\partial T)_P]$, and the thermal pressure coefficient, $\gamma = (\partial P/\partial T)_V$, can be obtained from the reduced equations of state; experimental values of these properties and the molar volume of the liquid can then be used to evaluate the characteristic parameters as functions of m and n.

The product αT is related to the reduced variables $\overline{P}$, $\overline{V}$ and $\overline{T}$ by

$$\alpha T = \frac{\overline{T}}{\overline{V}}\left(\frac{\partial \overline{V}}{\partial \overline{T}}\right)_{\overline{P}} \qquad (154)$$

In order to evaluate $\overline{V}$, the reduced equation of state at zero pressure is implicitly differentiated and the result rearranged to yield,

$$\frac{\overline{T}}{\overline{V}}\left(\frac{\partial \overline{V}}{\partial \overline{T}}\right)_{\overline{P}}\left[\frac{\overline{V}^{-2/3}}{3(\overline{V}^{1/3} - 1)^2} - \frac{m}{\overline{T}^{n+1}\,\overline{V}^{m+1}}\right] = \frac{m(n+1)}{\overline{T}^{n+1}\,\overline{V}^{m+1}} \qquad (155)$$

Equation (155) can be solved for the reduced volume at temperature T in terms of α, m and n,

$$\overline{V} = \left[\frac{\alpha T}{3(1 + n + m\alpha T)} + 1\right]^3 \tag{156}$$

by substituting from Equations (151) and (154). V^*, the characteristic volume of a mole of molecules, is then calculated from $\overline{V}$ and the experimental molar volume using the definition of reduced volume. The reduced temperature, $\overline{T}$, is obtained from $\overline{V}$ through the reduced equation of state at zero pressure; values for the characteristic temperature, T^*, are then calacaulated from Equation (141).

An expression relating the remaining characteristic parameter, P^*, to experimental data is obtained by first expressing γ in terms of reduced variables,

$$\gamma = \frac{P}{\overline{P}}\frac{\overline{T}}{T}\left(\frac{\partial \overline{P}}{\partial \overline{T}}\right)_{\overline{V}} \tag{157}$$

and then differentiating Equation (150) at constant $\overline{V}$. At low pressures, the resulting expression is

$$P^* = \frac{\gamma \overline{V}^{m+1}\,\overline{T}^{n}\,T}{m(n+1)} \tag{158}$$

Equations (151) and (158) show that any artificial variation of V^* with temperature will cause related variations of T^* and P^* with temperature. For $m=1$, $n=0$, $\overline{V}$ increases with temperature too slowly, so that V^* and therefore T^* both increase slightly with increasing temperature. The effect is magnified in P^*, which decreases with temperature.

Equation (156) indicates that positive values of n will accelerate the increase of $\overline{V}$ with temperature at a given value of m. As $n \longrightarrow \infty$, $\overline{V} \longrightarrow 1$, so that even for infinite values of n, the expansion of the characteristic volume with temperature will parallel the expansion of the molar volume. The values of $m > 1$ experimentally associated with the cohesive energy of relatively non-polar liquids somewhat accentuate the expansion of the core volume with temperature. While positive values of n will markedly change the magnitude of the characteristic pressure, the variation with temperature will remain relatively unaffected.

We must conclude that the temperature dependence of the characteristic parameters cannot be attributed to the absence of a simple but explicit temperature dependence in the configurational energy expression, and so for simplicity, set $n = 0$. The effect of characteristic parameter temperature variation on excess property calculations can be minimized by using experimental values of α and γ at the temperature of interest.

With $n = 0$, the equation of state is given by Equation (137), the characteristic parameters P^* and T^* are defined by Equations (138) and (139) and the reduced equation of state and reduced equation of state near $P = 0$ are given by Equation (152) and (153). The expressions for the evaluation of $\overline{V}$ and P^* become

$$\overline{V} = \left[\frac{\alpha T}{3(1 + m\alpha T)} + 1\right]^3 \qquad (159)$$

and

$$P^* = \frac{\gamma \overline{V}^{m+1} T}{m} \tag{160}$$

III-3: Molar Properties of Pure Fluids

Although the reduced equation of state depends explicitly on m, Equation (152) cannot be used to determine m analytically from the PVT properties of pure fluids. The indeterminate nature of m from PVT properties arises from the zero pressure approximations needed to evaluate the characteristic parameters and from the determination of values of T^* and P^* consistent with V^* at a given m. If $\overline{P}$, $\overline{V}$ and $\overline{T}$ could be independently determined, Equation (152) could in principle be used to calculate m; with interdependent values of the reduced variables, mutually consistent at any value of m, Equation (152) cannot be so used.

Numerical values of the characteristic pressure and volume may be used to calculate the molar interaction energy as a function of m. By dividing the defining equation for characteristic pressure by ν^m, and rearranging the result, the attractive interaction energy per segment is seen to be

$$s\eta / 2\nu^m = P^* \nu^* / \overline{V}^m \tag{161}$$

The interaction energy per molecule is

$$rs\eta / 2\nu^m = P^* \nu^* / \overline{V}^m \tag{162}$$

and for Avogadro's number of molecules, the molar interaction energy is

$$N_o rs\eta / 2v^m = P^* V^* / \bar{V}^m \tag{163}$$

Although we have formally divided the molecules into segments, we need never actually specify either the physical number of segments per molecule or the relative size of the segments in order to calculate the excess enthalpy of binary mixtures, and so are primarily concerned only with the molar core volume, V^*, and the corresponding molar interaction energy, given in Equation (163). Numerical values of the core volume per segment, v^*, and the number of external degrees of freedom per segment, 3c, both depend upon the somewhat arbitrary identification of segments. The value of 3C, number of external degrees of freedom per molecule, related to 3c by $C = rc$, depends only on the molar characteristic parameters and can be calculated from the expression

$$C = P^* V^* / R T^* \tag{164}$$

which is obtained from Equation (142) by multiplying by rN_o.

IV. FIRST LAW EXCESS FUNCTIONS

The ultimate goal of this research has been the prediction of excess properties of binary liquid mixtures. As shown in Section II-8, this goal cannot be realized quantitatively using pure component data alone; therefore, a reliable procedure for calculating H^E and G^E from excess volume data was sought. Volumetric data was chosen as the source of information on the mixture itself since it is generally the easiest excess property to measure experimentally. The development of the present theory was designed to extract the maximum benefit from this information source.

IV-1: Basic Equation for H^E

The definition of the excess enthalpy of a binary mixture of components 1 and 2 is

$$H^E = H - H_1 - H_2 \tag{165}$$

where H_1 and H_2 are the enthalpies of the pure components and H is the enthalpy of the mixture. We have assumed that the internal part of the partition function is unaffacted by the mixing process, so that only that part of the enthalpy which arises from the configurational partition function contributes to the excess enthalpy. Each quantity in Equation (165) was therefore replaced, without changing notation, by its configurational component.

At constant pressure, Equation (165) is identical to

$$H^E = E - E_1 - E_2 + P\Delta V_p \qquad (166)$$

where ΔV_p is the volume change on mixing at constant pressure and E, E_1 and E_2 are the configurational erergies of the mixture and respective pure components. At atmospheric pressure, $P\Delta V_p$ does not exceed a few tenths of a joule/mole, even for mixtures for which V^E is as large as 1 cm^3/mole, so that the contribution of the last term in Equation (166) is completely negligible and Equation (166) becomes

$$H^E = E - E_1 - E_2 \qquad (167)$$

Expressions for each of the configurational energy terms in Equation (181) were obtained by application of the statistical mechanical relation, Equation (25), to the partition functions of the pure components and to the partition function of the equivalent fluid associated with the mixed components. This procedure produced expressions for each term identical to the average interaction energies of Equation (131), since only the exponential term in Equation (132) is a function of temperature at constant volume. We associated the exponent m_1 with the energy-volume relation of pure unmixed component 1, the exponent m_2 with pure unmixed component 2 and defined m of the mixture as a composition dependent average of the exponents of the pure components,

$$m = \frac{x_1 V_1 m_1 + x_2 V_2 m_2}{V} \qquad (168)$$

where V is the actual molar volume of the mixture. The volumetric average was chosen to take full advantage of mixture input data. Equation (168) is valid over the entire concentration range; m reduces to the appropriate pure component value when the mole fraction of that component approaches one.

From these considerations, the excess enthalpy of a mixture of N molecules, N_1 of component 1 and N_2 of component 2, was found to be

$$H^E = -\frac{Nrs\eta}{2v^m} + \frac{N_1 r_1 s_1 \eta_1}{2v_1^{m_1}} + \frac{N_2 r_2 s_2 \eta_2}{2v_2^{m_2}} \qquad (169)$$

where the subscript 1 refers to properties of pure component 1, subscript 2 to properties of pure component 2 and where the properties of the effective mixture have been left unsubscripted. By applying the definition of the characteristic pressure to the effective fluid formed by the mixed components and to the unmixed pure components, Equation (169) becomes

$$H^E = -\frac{NrP^* v^*}{\overline{V}^m} + \frac{N_1 r_1 P_1^* v_1^*}{\overline{V}_1^{m_1}} + \frac{N_2 r_2 P_2^* v_2^*}{\overline{V}_2^{m_2}} \qquad (170)$$

Multiplying by N_o/N and appropriately substituting from Equation

(129) results in an expression for the molar excess enthalpy, H^E, as a function of molar and reduced characteristic parameters,

$$H^E = -\frac{P^* V^*}{\bar{V}^{m}} + \frac{x_1 P_1^* V_1^*}{\bar{V}_1^{m_1}} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2^{m_2}} \qquad (171)$$

Each of the characteristic parameters in the second and third terms of the right side of Equation (171) is readily identified from the discussion of pure fluids in Chapter III. The characteristic and reduced parameters of a binary mixture and the relationship of these parameters to the parameters of the individual components is discussed in the following section.

IV-2: Pseudo-2-fluid and Simple-1-fluid Theories

We have examined two theories of binary liquid mixtures. In the simple-1-fluid treatment, the components of the mixture retain the same characteristic parameters in the mixture as in the unmixed state; in the pseudo-2-fluid treatment, the values of the characteristic parameters of the mixed components are altered by the new environment from their values in the unmixed state.

In the simple-1-fluid model, if the interaction energy of two sites in pure i is $\eta_{ii}/\nu_i^{m_i}$, then the interaction energy of the same two sites in the mixture is η_{ii}/ν^{m}. The energy constant η_{ii} is the same in the mixed and unmixed states and is unaffected by the presence of a second component; it is unaltered by the different potential fields which must exist in the solution and in the separate pure component. The only difference between an i-i interaction in the mixture and in the pure component in the simple-1-fluid formulation relates to the volume in which the interaction takes place.

In the pseudo-2-fluid model, molecules of component 1 experience a potential field which has been altered by the presence of molecules of component 2, and which causes their properties to undergo subtle change. Pure component 1 of the isolated state becomes pseudocomponent 1 of the mixture. Molecules of component 2 experience similar changes in their characteristic properties, so that pure component 2 becomes pseudocomponent 2 in the mixture. The energy of an i-i interaction in the mixture, η_{iim}/v^m, reflects the alteration in these characteristic properties; η_{ii} for an i-i interaction in the absence of a second component is not quite the same as η_{iim} for the interaction of similar sites in the presence of a second component.

In both the simple-1-fluid and the pseudo-2-fluid treatments, the number and strength of the 1-2 interactions are implicit in the magnitude of P^* for the mixture. The number and strength of such interactions are interdependent; we will show in Section IV-4 that explicit calculations related to the magnitude of the unlike interactions reflect artifical assumptions about the number of such interactions and about the relative size of the segments.

The pseudo-2-fluid treatment, which we feel more accurately reflects the nature of liquid mixtures, combines aspects of both one- and two-fluid mixture theories. It resembles formal two-fluid models since the mixture is treated as composed of two distinct pseudocomponents whose properties are not quite the same as those of the pure components from which they are derived. It also resembles one-fluid models, however, since the average interaction energy in the mixture is initially formulated in terms of the properties of a single equivalent fluid. We have related the properties of the equivalent fluid in the pseudo-2-fluid model to composition dependent averages of the properties of the two pseudocomponents. In the strictly one-fluid approach of the simple-1-fluid model, the properties of the equivalent fluid are instead directly related to the properties of the two pure components.

IV-3: Mixture Characteristic Properties

In most two-fluid treatments of mixtures, the characteristic properties of each pseudocomponent are defined by suitable averages of the pure component properties, augmented by terms related to the interactions of unlike molecules. The additional flexibility attributed to two-fluid treatments can be incorporated into the present treatment in a unique way. We calculate the characteristic parameters, V^*_{im}, P^*_{im} and T^*_{im}, of each pseudocomponent i from α_i, γ_i, and V_i of pure i, but substitute the composition dependent mixture m for the m_i from which the characteristic parameters of the pure component are calculated. The result is a subtle but definite change, reflecting the new energy-volume relationship in the mixture, in each of the characteristic parameters as the pure component becomes increasingly diluted.

Since V_i^* becomes V_{im}^* as $m_i \longrightarrow m$, the characteristic volume of a molecule, v_i^*, must become v_{im}^* as the pure component becomes the pseudocomponent. The pseudo-2-fluid model, therefore, implies that a certain degree of flexibility exists in the molecular cores so that they can expand or contract according to the external environment. Since the number of segments per molecule, r_i, must be the same for both pure component and pseudocomponent, the characteristic volume of a segment must also expand or contract according to the environment. No such flexibility is implied by the simple-1-fluid model, since the characteristic properties of the pure components are then unaltered on mixing.

We have defined the effective molar core volume of the mixture in the pseudo-2-fluid theory by the mole fraction average of the molar core volumes of the two pseudocomponents,

$$V^* = x_1 V_{1m}^* + x_2 V_{2m}^* \qquad (172)$$

The reduced volume of the mixture, $\overline{V}$, is the ratio of the molar volume of the mixture to its characteristic volume, V^*, defined by Equation (172). The effective molecular core volume of the mixture is

$$v^* = x_1 v_{1m}^* + x_2 v_{2m}^* \qquad (173)$$

In the simple-1-fluid form, Equations (172) and (173) become mole fraction averages of the core volumes of the pure components rather than of the pseudocomponents.

It is convenient to define a segment fraction, ϕ_i, in terms of the number of segments of type i in the mixture, r_iN_i, and the total number of segments in the mixture, $rN = \sum_i r_iN_i$,

$$\phi_i = r_iN_i / rN \tag{174}$$

The core volume of the mixture per segment is then

$$\nu^* = \phi_1\nu^*_{1m} + \phi_2\nu^*_{2m} \tag{175}$$

Although the concept of molecular segments is an integral part of the preceding discussions, we have needed to make no assumptions about the size, ν^*_1 and ν^*_2, of these segments, about the number of segments per molecule, r_1 and r_2, or about the number of interaction sites per segment, s_1 and s_2. Although Flory does not specify the size of an individual segment, he divides the molecules of both components and of the mixture effective fluid into equal sized segments,

$$\nu^*_1 = \nu^*_2 = \nu^* \tag{176}$$

Because of the core size flexibility built into the pseudo-2-fluid treatment, the segments of the pure components, the pseudocomponents and the mixture equivalent fluid can all be the same size only if $m_1 = m_2$ and $V^E = 0$.

IV-4: Relationship of P^* to Mixture Interactions

We have derived expressions which relate the characteristic pressure of the mixture, P^*, to the number and type of the different interactions present in the mixture. Numerical evaluation of the expressions, however, necessitates the introduction of information and assumptions which are not necessary to calculate P^* and H^E from mixture volumetric data; the magnitude of the contact interaction energy, X_{12}, calculated from these expressions depends upon the specific assumptions introduced. The expressions divide the excess enthalpy into equation of state and contact interaction contributions.

The configurational energy of the mixture, E, may be expressed in terms of the number and type of the different interactions in the mixture,

$$-E = \frac{A_{11}\eta_{11m} + A_{22}\eta_{22m} + A_{12}\eta_{12m}}{v^m} \qquad (177)$$

A_{11} and A_{22} are the number of interactions between like sites of types 1 and 2 in the mixture and A_{12} is the number of interactions between unlike sites. The quantities η_{11m}/v^m, η_{22m}/v^m and η_{12m}/v^m are mixture interaction energies of pairs of the appropriate types of sites. In the simple-1-fluid model, η_{iim} is replaced by η_{ii}, and η_{ijm} refers to the interaction of the pure components in the mixture rather than the interaction of the different pseudocomponents. For nearest neighbor interactions, the equations

$$2A_{11} + A_{12} = s_1 r_1 N_1 \tag{178}$$

and

$$2A_{22} + A_{12} = s_2 r_2 N_2 \tag{179}$$

relate the number of interactions involving component i to the total number of type i sites. Equations (178) and (179) are similar to Equations (31) and (32) of lattice theory. Using these relations, Equation (177) may be rewritten

$$-E = \frac{s_1 r_1 N_1 \eta_{11m} + s_2 r_2 N_2 \eta_{22m} - A_{12} \Delta\eta}{2v^m} \tag{180}$$

where

$$\Delta\eta = 2\eta_{12m} - \eta_{11m} - \eta_{22m} \tag{181}$$

If the molecules are randomly distributed, the number of 1-2 interactions may be expressed as the product of the total number of type 1 sites, $s_1 r_1 N_1$, and the site fraction, θ_2, of type 2 sites,

$$A_{12} = (s_1 r_1 N_1) \cdot \theta_2 \tag{182}$$

where

$$\theta_i = s_i r_i N_i / srN \tag{183}$$

and srN represents the total number of sites,

$$srN = \sum_i s_i r_i N_i \tag{184}$$

The expression for the number of 1-2 interactions is symmetrical, $A_{12} = A_{21}$.

Substituting Equation (182), (183) and (184) into Equation (180) and rearranging the result leads to an expression for the average mixture interaction per segment,

$$-\frac{E}{rN} = \frac{s}{2\nu^{m}}(\theta_1\eta_{11m} + \theta_2\eta_{22m} - \theta_1\theta_2\Delta\eta) \tag{185}$$

By analogy with the expression for η_{iim} for the environment-influenced interaction of like sites in the mixture,

$$\eta_{iim} = 2P^{*}_{im}\nu^{*\,m+1}_{im}/s_i \tag{186}$$

we constructed a similar expression for $\Delta\eta$,

$$\Delta\eta = 2X_{12}\nu^{*\,m+1}/s_1 \tag{187}$$

Equation (186) is not symmetrical, since it involves s_1.

The mixture contact interaction term, X_{12}, has the dimensions of pressure, and like both Guggenheim's exchange energy, w, and $\Delta\eta$ itself, is related to the difference between the energy of like and unlike interactions. In the simple-1-fluid treatment, the energy-volume exponent in Equation (186) would be m_i, while that in Equation (187) would remain m.

Since the magnitude of η_{iim} of the i^{th} pseudocomponent is a function of composition, varying as m varies, X_{12} should be a function of composition in the pseudo-2-component treatment. X_{12} should also be a function of composition in the simple-1-fluid treatment, since η_{12m} and therefore $\Delta\eta$ is associated with the composition-dependent m. If, however, the van der Waals approximation, $m = 1$, or any other constant value of m is used throughout the concentration range, X_{12} should be independent of concentration, since η_{ijm} and $\eta_{iim} = \eta_{ii}$ are then concentration independent.

The energy of the mixture can be expressed in terms of X_{12} by substituting Equation (187) and equations of the form of Equation (186) into Equation (185),

$$\frac{-E}{rN} = \frac{s}{2\nu^m}\left[\frac{2\theta_1 P^*_{1m}\nu^{*\,m+1}_{1m}}{s_1} + \frac{2\theta_2 P^*_{2m}\nu^{*\,m+1}_{2m}}{s_2} - \frac{2\theta_1\theta_2 X_{12}\nu^{*\,m+1}}{s_1}\right] \qquad (188)$$

Using Equations (174), (183) and (184), Equation (188) becomes

$$\frac{-E}{rN} = \frac{\phi_1 P^*_{1m}\nu^{*\,m+1}_{1m} + \phi_2 P_{2m}\nu^{*\,m+1}_{2m} - \phi_1\theta_2 X_{12}\nu^{*m+1}}{\nu^m} \qquad (189)$$

Rewriting the expression for the configurational energy per segment of a pure or equivalent fluid as

$$\frac{-E}{rN} = \frac{P^{*}\nu^{*\,m+1}}{\nu^{m}} \tag{190}$$

shows that P^{*} and X_{12} are interrelated in the pseudo-2-fluid model by

$$P^{*}\nu^{*\,m+1} = \phi_1 P^{*}_{1m}\nu^{*\,m+1}_{1m} + \phi_2 P^{*}_{2m}\nu^{*\,m+1}_{2m} - \phi_1\theta_2 X_{12}\nu^{*\,m+1} \tag{191}$$

The equivalent expression in the simple-1-fluid model is

$$P^{*}\nu^{*\,m+1} = \phi_1 P^{*}_{1}\nu^{*\,m_1+1}_{1} + \phi_2 P^{*}_{2}\nu^{*\,m_2+1}_{2} - \phi_1\theta_2 X_{12}\nu^{*\,m+1} \tag{192}$$

Equation (192) differs from Equation (191) in that the contributions of the first two terms in the former are identical to similar contributions from the unmixed components, while in the latter these contributions are identified with the pseudocomponents and are not identical with pure component contributions. If the same energy-volume exponent is identified with all species and if, as Flory assumed, the segments of both components have the same characteristic volume, then Equation (192) reduces to

$$P^{*} = \phi_1 P^{*}_{1} + \phi_2 P^{*}_{2} - \phi_1\theta_2 X_{12} \tag{193}$$

Explicit calculation of X_{12} from Equation (191), (192) or (193) through P^* necessitates numerical specification of the site and segment fractions in the mixture. Although the ratios r_1/r_2 and s_1/s_2, rather than r_1, r_2, s_1 and s_2 individually, are sufficient to calculate the segment and site fractions, separate values of r_1 and r_2 are needed to calculate the characteristic volumes per segment needed to evaluate X_{12} from Equations (191) or (192). The magnitude calculated for X_{12}, therefore, depends upon the numerical values chosen for these parameters.

The magnitude of X_{12} depends not only on the values chosen for the site and segment ratios, but also on the assumptions used to estimate the number of interactions between unlike sites. If a quasi-chemical equilibrium of the form,

$$A_{11} + A_{22} \rightleftharpoons 2A_{12} \tag{194}$$

is substituted for the random mixing approximation used above, then the number of 1-2 interactions is instead expressed as

$$A_{12} = (A_{11}A_{22})^{1/2}\exp[-(2\eta_{12} - \eta_{11} - \eta_{22})/\nu kT] \tag{195}$$

where an energy-volume relationship of the van der Waals form has been used for simplicity. Use of Equation (195) leads, even for segments assumed to have equal characteristic volumes, to a complex relationship between P^* and X_{12},

$$P^* = 2\theta_1\phi_1P_1^* + 2\theta_2\phi_2P_2^* + e^{\Delta\eta/\nu kT}[\phi_1\theta_2P_1^* + \phi_2\theta_1P_2^* + \theta_1\theta_2X_{12}] \tag{196}$$

With the same values for the site and segment ratios, the magnitude of X_{12} implicit in Equation (196) is very different from the magnitude of X_{12} in Equation (193).

As will be shown in Section IV-5, mixture volumetric data yields direct values for P^* rather than for X_{12}, so that specification of the additional information needed to explicitly calculate X_{12} is not necessary, and values of X_{12} are themselves somewhat arbitrary. Formal expressions, however, for the excess enthalpy as a function of X_{12} have been obtained by substituting Equations (191), (192) and (193) into the appropriate form of Equation (171). These are

$$H^E = \frac{x_1 P_1^* V_1^*}{\bar{V}_1^{m_1}} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2^{m_2}} - \frac{V^*}{\bar{V}^m}\left[\frac{\phi_1 P_{1m}^* \nu_{1m}^{*\,m+1}}{\nu^{*\,m+1}} + \frac{\phi_2 P_{2m}^* \nu_{2m}^{*\,m+1}}{\nu^{*\,m+1}} - \phi_1 \theta_2 X_{12}\right] \quad (197)$$

$$H^E = \frac{x_1 P_1^* V_1^*}{\bar{V}_1^{m_1}} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2^{m_2}} - \frac{V^*}{\bar{V}^m}\left[\frac{\phi_1 P_1^* \nu_1^{*\,m_1+1}}{\nu^{*\,m+1}} + \frac{\phi_2 P_2^* \nu_2^{*\,m_2+1}}{\nu^{*\,m+1}} - \phi_1 \theta_2 X_{12}\right] \quad (198)$$

and

$$H^E = \frac{x_1 P_1^* V_1^*}{\bar{V}_1} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2} - \frac{V^*}{\bar{V}}\left[\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12}\right] \quad (199)$$

Equation (197) refers to the pseudo-2-fluid treatment, Equation (198) to the simple-1-fluid treatment and Equation (199) is the result of using Flory's van der Waals and equal segment size assumptions. The terms in Equation (199) not explicitly containing X_{12}

are called equation of state contributions to the excess enthalpy; the term involving X_{12} is called the contact interaction contribution. The relative magnitude of the two contributions depends on the values of ϕ_i and θ_i. Similar labels are not strictly appropriate in the pseudo-2-fluid model since the entire mixture contribution is influenced by the presence of the second component.

IV-5: Calculation of H^E from V^E

By relating P^* of the mixture to mixture volumetric data, we have developed expressions from which the molar excess enthalpy can be directly evaluated. The procedure involves applying the relations developed for pure fluids to the mixture equivalent fluid and to the two pseudocomponents.

The effective molar characteristic volume of the mixture was defined in Equation (172) as a mole fraction average of the characteristic molar volumes of the pseudocomponents. We assumed that the effective number of external degrees of freedom of the mixture equivalent fluid could be similarly expressed as a mole fraction average of the number of external degrees of freedom of the two pseudocomponents,

$$C = x_1 C_{1m} + x_2 C_{2m} \tag{200}$$

In terms of segments, Equation (200) can be written

$$c = \phi_1 c_{1m} + \phi_2 c_{2m} \tag{201}$$

although only Equation (200) is of interest numerically.

By applying Equation (164) to the mixture equivalent fluid and using Equation (200) to express the results, P^* of the mixture can be written as

$$P^* = \frac{RT^*}{V^*}\left[x_1 C_{1m} + x_2 C_{2m}\right] \tag{202}$$

By applying Equation (164) again, this time to each pseudocomponent separately, P^* can be expressed in terms of more directly evaluated characteristic parameters,

$$P^* = \frac{T^*}{V^*}\left[\frac{x_1 P^*_{1m} V^*_{1m}}{T^*_{1m}} + \frac{x_2 P^*_{2m} V^*_{2m}}{T^*_{2m}}\right] \tag{203}$$

The characteristic temperature of the mixture, T^*, is related to the reduced temperature of the mixture, $\overline{T}$, by Equation (141) and the reduced temperature of the mixture is related to the reduced volume of the mixture by Equation (153), so that Equation (203) becomes

$$P^* = \frac{T(\overline{V}^{\,m+1/3})}{mV^*(\overline{V}^{\,1/3} - 1)}\left[\frac{x_1 P^*_{1m} V^*_{1m}}{T^*_{1m}} + \frac{x_2 P^*_{2m} V^*_{2m}}{T^*_{2m}}\right] \tag{204}$$

Equation (204) shows that the characteristic pressure of the mixture in the pseudo-2-fluid model is the product of the environment influenced pseudocomponent PVT characteristic parameters and terms related to the volume of the solution. In the simple-

1-fluid model, P^* is a product of the pure component characteristic parameters and terms related to the solution volume,

$$P^* = \frac{T(\bar{V}^{m+1/3})}{mV^*(\bar{V}^{1/3}-1)}\left[\frac{x_1P_1^*V_1^*}{T_1^*} + \frac{x_2P_2^*V_2^*}{T_2^*}\right] \tag{205}$$

An expression for P^* based on the van der Waals energy-volume relationship can be obtained from Equation (205) by setting $m=1$ explicitly and evaluating all characteristic parameters at $m=1$. P^* remains a function of the original pure component characteristic parameters and of the solution volume.

Equations (204) and (205) can be evaluated directly from mixture volumetric data and information on the physical properties of the pure components. X_{12} can be evaluated from the van der Waals form of Equation (205) combined with Equation (174) if the assumption of equal sized segment cores is introduced and the site ratio approximated. X_{12} can be evaluated in the pseudo-2-fluid treatment by combining Equations (204) and (172), and in the simple-1-fluid treatment by combining Equations (205) and (173) under the restrictions mentioned in Section IV-4. Since such values would be related to arbitrary values of the number of segments per molecule, we will leave X_{12} defined implicitly.

The final expression relating the molar excess enthalpy to mixture volumetric data, obtained by substituting Equation (204) into Equation (171), is

$$H^E = \frac{x_1 P_1^* V_1^*}{\bar{V}_1^{m_1}} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2^{m_2}} - \frac{T\bar{V}^{1/3}}{m(\bar{V}^{1/3} - 1)}\left[\frac{x_1 P_{1m}^* V_{1m}^*}{T_{1m}^*} + \frac{x_2 P_{2m}^* V_{2m}^*}{T_{2m}^*}\right] \quad (206)$$

Equation (206) expresses the excess enthalpy in terms of the characteristic parameters of the pure components and pseudocomponents and of the volumetric properties of the effective fluid. It does not require that H^E be zero when V^E is zero, and permits H^E and V^E to have opposite signs. As the physical properties, V_i, α_i, γ_i and m_i of the pure components collectively become more similar, H^E approaches zero and is zero exactly for "mixtures" composed of identical species.

In the simple-1-fluid treatment, the equivalent of Equation (206) is

$$H^E = \frac{x_1 P_1^* V_1^*}{\bar{V}_1^{m_1}} + \frac{x_2 P_2^* V_2^*}{\bar{V}_2^{m_2}} - \frac{T\bar{V}^{1/3}}{m(\bar{V}^{1/3} - 1)}\left[\frac{x_1 P_1^* V_1^*}{T_1^*} + \frac{x_2 P_2^* V_2^*}{T_2^*}\right] \quad (207)$$

The molar excess enthalpy arises from the modification, by the new volumetric conditions and new value of m, of the pure components' contributions to the mixture. In Equation (206), the contribution of each pure component is first modified by the presence of the other, and then their sum is further modified by these new volumetric conditions.

Since m appears explicitly in the mixture's contribution to the excess enthalpy, the excess enthalpy should be very sensitive to the value of m for the solution in both pseudo-2-fluid and simple-1-fluid treatments of mixtures. We will show in Chapter VI that the excess enthalpy predictions of the two models generally approach each other when the energy-volume exponents of the pure components are similar and diverge most when the energy-volume exponents of the pure components are dissimilar.

IV-6: Calculations using Flory's Model

Section IV-5 showed how mixture volumetric data can be used to calculate H^E in the pseudo-2-fluid and simple-1-fluid treatments of mixtures. We now describe how similar data has been used to calculate H^E in Flory's model and how excess enthalpy data has been used to calculate V^E in the same model. We will describe excess volume calculations from excess enthalpy data in the present models in Section IV-7.

As discussed in Section II-10, Flory's model results in more accurate predictions for excess volume than for excess enthalpy, although calculation of H^E from V^E is more straightforward than is calculation of V^E from H^E. In order to obtain H^E, mixture volumetric data is used to calculate $\overline{V}$; through $\overline{V}$, first $\overline{T}$, then T^* and finally P^* are obtained. The segment ratio, r_1/r_2, is fixed at V_1^*/V_2^* by the assumption that all segments have the same characteristic volume; the number of sites per molecule ratio, r_1s_1/r_2s_2, is approximated by assuming that the number of sites per molecule is proportional to surface area of a sphere whose volume is equal to V^*. These assumptions allow X_{12} to be calculated from P^*. $\overline{V}$ and X_{12} are then used, along with the site and segment ratios, to calculate H^E from Equation (199). Values of X_{12} calculated from P^*, however, frequently vary substantially with composition for a given mixture. As mentioned in Section IV-4, X_{12} in the van der Waals model should be concentration invarient; we suggest that the observed concentration dependence might partially be due to use of artificial site and segment ratios and to the constraint to segments of equal core size. Both concentration-dependent values of X_{12} and the single value of X_{12} which minimizes Equation (98) with respect to excess volume have variously been used to calculate H^E. While the predictions are frequently more accurate than those of other theories, there is often considerable disagreement with experimental values.

Better agreement with experiment is usually obtained with the reverse procedure, the calculation of excess volume from excess enthalpy data, although this calculation is both less direct and of less practical importance. Since X_{12} and $\bar{V}$ cannot both be obtained from Equation (199) alone, a second expression is obtained by substituting into Equation (164) the appropriate $m=1$ expressions for P^*, C and T^* from Equations (193), (200), (141) and (153),

$$(\phi_1 P_1^* + \phi_2 P_2^* - \phi_1 \theta_2 X_{12})\, V^* = (x_1 C_1 + x_2 C_2)\, RT \left[\frac{(\bar{V}^{1/3} - 1)}{\bar{V}^{4/3}}\right] \quad (208)$$

Using experimental H^E data, Equations (199) and (208) are numerically solved simultaneously at each concentration for X_{12}

and $\bar{V}$ and this value of $\bar{V}$ is then used to compute the excess volume. The values of X_{12} obtained by this procedure also vary with concentration, and Equation (98) is sometimes used to find the single value of X_{12} which best represents the excess enthalpy over the entire concentration range.

If the intermediate calculation of X_{12} and the associated site and segment ratio specification is eliminated, evaluation of V^E from H^E in the van der Waals approximation is considerably simplified, since Equation (207) with $m_1 = m_2 = m$ can then be solved directly for $\bar{V}$ using experimental H^E data.

IV-7: Calculation of V^E from H^E

In the pseudo-2-fluid and simple-1-fluid treatments of mixtures, Equations (206) and (207) permit direct calculation of H^E from V^E provided that m_1 and m_2 of the pure components are known. Developing a procedure that would permit such direct calculation was the goal of this research. The reverse procedure, with which we are only incidently concerned, is less direct than such a calculation would be if m were constant from $x_1 = 0$ to $x_1 = 1$. Since m is itself a function of total solution volume, V^E cannot be calculated analytically from H^E. The calculation can, however, be performed iteratively by successively improving trial values of V^E until the calculated and experimental values of H^E agree.

V. SECOND LAW EXCESS FUNCTIONS

The calculation of the excess entropy of a mixture from the excess volume of the mixture requires more drastic approximations than does the calculation of excess enthalpy from excess volume. The primary difficulty is the combinatory term in the partition function; while the combinatory term vanishes upon taking the derivatives of Equation (132) needed to obtain the equation of state and configurational energy, the entire configurational partition function, including the combinatory part, appears explicitly in the configurational entropy expression.

V-1: Partition Function Based Excess Entropy Expressions

Direct application of the statistical mechanical relation

$$S = kT(\partial \ln Q/\partial T)_V + k \ln Q \qquad (209)$$

to the configurational partition function in Equation (132), leads, after simplification, to an expression for the configurational entropy,

$$S = 3rNck \ln(\tilde{V}^{1/3} - 1) + rNck \ln(\lambda \nu^*) + k \ln Q_{comb} \qquad (210)$$

The entropy of mixing, ΔS^M, was obtained by applying Equation (210) to the mixture equivalent fluid and to each separate pure component individually,

$$\Delta S^M = 3rNck\,\ell n(\bar{V}^{1/3} - 1) - \sum_{i=1}^{2} 3r_iN_ic_ik\,\ell n(\bar{V}_i^{1/3} - 1)$$

$$+ \; rNck\,\ell n(\lambda\nu^*) - \sum_{i=1}^{2} r_iN_ic_ik\,\ell n(\lambda\nu_i^*) \qquad (211)$$

$$+ \; k\,\ell n\left[Q_{comb}/(Q_{comb_1}\cdot Q_{comb_2})\right]$$

The expression for the molar excess entropy, obtained from Equation (211) by multiplying by N_o/N, subtracting the ideal molar entropy of mixing, and using relations defined in Chapters III and IV is

$$S^E = 3RC\,\ell n(\bar{V}^{1/3} - 1) - \sum_{i=1}^{2} 3Rx_iC_i\,\ell n(\bar{V}_i^{1/3} - 1)$$

$$+ \; RC\,\ell n(\lambda\nu^*) - \sum_{i=1}^{2} Rx_iC_i\,\ell n(\lambda\nu_i^*) \qquad (212)$$

$$+ \; \frac{R}{N}\,\ell n\left[Q_{comb}/(Q_{comb_1}\cdot Q_{comb_2})\right] - \Delta S^M_{ideal}$$

Unlike the expression for the excess enthalpy, Equation (212) does not contain any terms in which m appears explicitly and none of the terms originate from that part of the partition function directly associated with the energy-volume relationship. The excess entropy should therefore be less sensitive than the excess enthalpy to alterations in the value of m associated with the mixture and pure components. Under equivalent sets of approximations, the magnitude of the excess entropy calculated from the pseudo-2-fluid and simple-1-fluid models should differ little from that calculated using the van der Waals approximation.

Apart from any deficiencies inherent in the partition function itself, Equation (212) is exact. In order to evaluate the excess entropy, however, the terms involving $\ell n(\lambda\nu^*)$ and the combinatory ratio must be approximated or eliminated. Since the combinatory ratio is by far the largest contributor to the entropy of mixing, the resulting expression is not expected to be accurate.

Flory assumed that all segments have the same characteristic volume, so that the net contribution from the fourth, fifth and sixth terms of the expanded form of Equation (212) is zero. For liquids having similar molar volumes, he approximated the combinatory ratio term by ΔS^M_{ideal}, so that the molar excess entropy expression reduces to

$$S^E = 3RC\,\ell n(\bar{V}^{1/3} - 1) - 3Rx_1C_1\,\ell n(\bar{V}_1^{1/3} - 1) - 3Rx_2C_2\,\ell n(\bar{V}_2^{1/3} - 1) \qquad (213)$$

Experimental values of the excess entropy at equimolar concentration range from about 0.1 - 4.0 joules/K; since ΔS^M_{ideal} at $x_1 = 0.5$ is about 6 joules/K, the error introduced by approximating the combinatory entropy by the ideal entropy, even if the approximation is accurate to 10%, is very large. If the molar volumes of the two components are very different, the combinatory entropy of mixing is sometimes approximated by $\Delta S^{M}_{polymeric}$; the magnitude of the error introduced by the latter approximation is about the same as for the former. Neither of these approximations leads to a good representation of the excess entropy; a separate constant, Q_{12}, must be introduced in addition to X_{12} in order to correlate excess entropy data.

In order to obtain for the two new treatments an expression equivalent to Equation (213) but not requiring that all segments have the same characteristic volume, the fourth through seventh terms of the expanded form of Equation (212) were collectively equated with ΔS^{M}_{ideal}, and all other contributions evaluated as discussed in Chapters III and IV. This approximation is no more realistic than the first approximations described, and produces (as will be shown in Section VI-5) excess entropy predictions which are similar to those above and which are almost independent of m_i. A second alternative is to again equate only the contribution of of the combinatory term with ΔS^{M}_{ideal}. If the geometric constant, λ, is to be eliminated from the excess entropy expression, then $[x_1(C_{1m} - C_1) + x_2(C_{2m} - C_2)]$ must be approximated as zero in the pseudo-2-fluid model. S^E then becomes

$$S^E = 3RC\,\ell n(\bar{V}^{1/3} - 1) - 3Rx_1C_1\,\ell n(\bar{V}_1^{1/3} - 1) - 3Rx_2C_2\,\ell n(\bar{V}^{1/3} - 1)$$
$$+ RC\,\ell n(\nu^*) - Rx_1C_1\,\ell n(\nu_1^*) - Rx_2C_2\,\ell n(\nu_2^*) \qquad (214)$$

The excess entropy in Equation (214) is a function of the size of the various segments and so depends on the actual physical division of the molecules into segments. The values obtained if the molecules are assumed to consist of single segments are very different from those obtained if the molecules are divided into chemical groups. Any physical division of the molecules into actual segments, however, is artificial and cannot result in accurate second law property predictions. The artificiality is compounded by the necessity to approximate the combinatory entropy contribution.

V-2: Semi-empirical Determination of the Excess Entropy

The excess entropy can be evaluated, however, without specifying the combinatorial entropy by a semi-empirical method which does not involve the partition function in Equation (132) and does not require the introduction of any new information. The method is the modification of the Wilson treatment proposed by Liebermann and Fried (172,173); the modifcation permits the prediction of the excess Gibbs free energy from single temperature values of the experimental enthalpy of mixing. We have employed this method to predict the excess entropy of binary liquid mixtures from experimental volumetric data using excess enthalpy predictions obtained from the pseudo-2-fluid treatment of mixtures. The results will be presented in Section VI-5.

In the Fried-Liebermann modification of the Wilson equation, the excess Gibbs free energy is represented as

$$G^E = - RT \frac{x_1 x_2 \ln(D_{12} D_{21})}{(x_1 + x_2 D_{12})(x_2 + x_1 D_{21})}$$

$$- RT[x_1 \ln(x_1 + x_2 V_2/V_1) + x_2 \ln(x_2 + x_1 V_1/V_2)] \qquad (215)$$

The first term arises from contributions to non-ideality due to intermolecular forces and is abbreviated G^*; the second term arises from molecular size differences and is abbreviated $RT f(V)$,

$$G^E = G^* - RT f(V) \qquad (216)$$

D_{12} and D_{21} are constants characteristic of the mixture. The excess enthalpy is thermodynamically related to the excess free energy by

$$H^E = - T^2 \left[\frac{\partial(G^E/T)}{\partial T}\right]_{P,x} \qquad (217)$$

Neglecting $\{\partial[f(V)/T]/\partial T\}_{P,x}$ for mixtures in which the components have similar thermal expansion coefficients, Equation (217) becomes

$$\frac{H^E}{G^*} = T\left(\frac{\partial D_{12}}{\partial T}\right)\left[\frac{x_2}{x_1 + x_2 D_{12}} - \frac{1}{D_{12} \ln(D_{12} \cdot D_{21})}\right]$$

$$+ T\left(\frac{\partial D_{21}}{\partial T}\right)\left[\frac{x_1}{x_2 + x_1 D_{21}} - \frac{1}{D_{21} \ln(D_{12} \cdot D_{21})}\right] \qquad (218)$$

Equation (218) is solved for the temperature dependence of D_{12} and D_{21} by using the approximations

$$\lim_{x_1 \to 0} \frac{H^E}{G^*} = \lim_{x_2 \to 0} \frac{H^E}{G^*} = 2 \tag{219}$$

The temperature derivatives of D_{12} and D_{21} are then

$$(\partial D_{12}/\partial T) = (D_{12}/T)\left(\frac{2\,\ln(D_{12}\cdot D_{21})}{\ln(D_{12}\cdot D_{21}) - 2}\right) \tag{220}$$

and

$$(\partial D_{21}/\partial T) = (D_{21}/T)\left(\frac{2\,\ln(D_{12}\cdot D_{21})}{\ln(D_{12}\cdot D_{21}) - 2}\right) \tag{221}$$

By substituting Equations (220) and (221) into Equation (218), an expression is obtained which relates the constants D_{12} and D_{21} to the excess enthalpy of the mixture,

$$H^E = \left[\frac{2RTx_1x_2[\ln(D_{12}\cdot D_{21})]^2}{(x_1 + x_2D_{12})(x_2 + x_1D_{21})[2 - \ln(D_{12}\cdot D_{21})]}\right] \times \left[\frac{x_2D_{12}}{x_1 + x_2D_{12}} + \frac{x_1D_{21}}{x_2 + x_1D_{21}} - \frac{2}{\ln(D_{12}\cdot D_{21})}\right] \tag{222}$$

Equation (222) was solved by an iterative process for D_{12} and D_{21} using the concentration dependence of the excess enthalpy predicted from volumetric data. The numerical values of D_{12} and D_{21} were used in turn to compute the excess free energy. The results of these calculations are presented in Section VI-5.

VI. APPLICATION TO NON-POLAR AND WEAKLY POLAR LIQUIDS

We have successfully applied the theory described in the previous chapters to fifty mixtures of binary combinations of seventeen non-polar and weakly polar liquids. These liquids are listed in Table I, grouped according to their chemical class. The fifty mixtures studied comprise more than one-third of the 136 possible binary combinations and represent those systems for which reliable experimental excess volume and excess enthalpy data are both available.

VI-1: Pure Components

Physical properties of the pure components are listed the Table II. Molar volumes, thermal expansion coefficients and thermal pressure coefficients were used to compute the characteristic parameters of the pure liquids and of the pseudocomponents in the pseudo-2-fluid model. Enthalpies of vaporization to the ideal gas state, although not directly related to the calculation of characteristic parameters, were used to estimate the value of m for each liquid in the cohesive energy-volume relation by the ratio method described in Section II-11. Energies of vaporization were calculated assuming ideal vapor phase behavior by subtracting RT from the corresponding enthalpies of vaporization and were used to approximate the negative of the cohesive energies. The value of m for each liquid was then computed from the ratio of the internal pressure, $(\gamma T - P)$, to the cohesive energy density. These "ratio method" values of m are listed in the first column of Table III.

Table I

Non-polar and Weakly Polar Liquids Investigated

Chemical class	Compounds
normal alkanes	n-hexane n-heptane n-octane n-hexadecane
branched alkanes	2,3-dimethylbutane 2,2,4-trimethylpentane
cycloalkanes	c-pentane c-hexane c-heptane c-octane
aromatics	benzene toluene o-xylene m-xylene p-xylene
halogen containing	CCl_4
organometallic	octamethylcyclotetrasiloxane

Table II

Physical Properties of Non-polar and Weakly Polar Liquids†

Liquid	$V/cm^3\ mol^{-1}$		$\alpha \times 10^3/K^{-1}$		$\gamma/J\ cm^{-3}\ K^{-1}$		$\Delta H^v/J\ mol^{-1}$	
n-hexane	131.56	(175)	1.386	(116)	0.814	(116)	31550	(198)
n-heptane	147.51	(176)	1.253	(176)	0.854	(137)	36560	(183)
n-octane	163.59	(116)	1.159	(116)	0.880	(116)	41480	(183)
n-hexadecane	294.20	(116)	0.901	(116)	1.033	(116)	81090	(198)
2,3-dimethylbutane	131.17	(177)	1.409	(177)	0.783	(177)	29130	(183)
2,2,4-trimethylpentane	166.05	(178)	1.197	(179)	0.749[a]	(180)	35150	(198)
c-pentane	94.71	(181)	1.347	(182)	1.010	(182)	28530	(198)
c-hexane	108.77	(182)	1.215	(182)	1.075	(182)	33040	(198)
c-heptane	121.73	(182)	1.095	(183)	1.154	(184)	38530	(183)
c-octane	134.87	(182)	0.979	(182)	1.222	(182)	43350	(183)
benzene	89.43	(185)	1.223	(186)	1.263	(187)	33850	(198)
toluene	106.84	(185)	1.071	(183)	1.142[a]	(188)	37990	(198)
o-xylene	121.21	(189)	0.952	(190)	1.161[a]	(191,192)	43430	(198)
m-xylene	123.47	(189)	0.981	(193)	1.121[a]	(194)	42660	(198)
p-xylene	123.92	(189)	1.003	(190)	1.104[a]	(195)	42380	(198)
CCl_4	97.09	(196)	1.229	(178)	1.142	(187)	32430	(199)
octamethylcyclotetrasiloxane	312.12[b]	(181)	1.216	(199)	0.798	(197)	56050	(200)

[a] calculated from α and β
[b] calculated from β and γ

† at 298 K

Table III

Values of m for Non-polar and Weakly Polar Liquids

Liquid	m(ratio method)	m(mixture method)
n-hexane	1.098	1.115
n-heptane	1.101	1.140
n-octane	1.097	1.165
n-hexadecane	1.152	1.195
2,3-dimethylbutane	1.148	1.150
2,2,4-trimethylpentane	1.134	1.170
c-pentane	1.094	1.087
c-hexane	1.140	1.140
c-heptane	1.160	1.150
c-octane	1.202	1.192
benzene	1.073	1.020
toluene	1.024	1.070
o-xylene	1.024	1.095
m-xylene	1.026	1.080
p-xylene	1.022	1.095
CCl_4	1.103	1.080
octamethylcyclotetrasiloxane	1.386	1.190

Correction for gas-phase imperfections would alter these values by several tenths of a percent. Also listed in Table III are the values of m obtained from experimental mixture data by the method described in Section VI-2.

Table IV lists the characteristic parameters of the pure components calculated from the molar analogy of Equation (125) and Equations (141), (151), (159), (160) and (164) at three different values of m for each liquid. These values correspond to the $m = 1$ van der Waals approximation used by Flory, to the ratio method approximation and to the values we derived as the most representative of the liquid state and best suited for computations of liquid mixture behavior. The total range of these m values for all the non-polar and weakly polar liquids investigated in this thesis extends only from 1.000 to 1.380. Even within this very limited range of m, significant changes were found for the characteristic properties of the individual liquids. As m increases, V^* increases slightly and T^* and P^* both decrease substantially; C decreases, indicating more restricted molecular motion within the liquid.

The characteristic parameters in Table IV have been used to compute the molar interaction energy for each pure liquid from Equation (163). Table V compares the molar interaction energy calculated at each of the above values of m with the energy of vaporization. Comparison is made for the energy rather than for the enthalpy of vaporization because while the difference between the energy and enthalpy of mixing

Table IV

Characteristic Parameters of Non-polar and Weakly Polar Liquids

Liquid	m	$V^*/cm^3\ mol^{-1}$	T^*/K	$P^*/J\ cm^{-3}$	C
n-hexane	1.000	99.53	4437.5	424.2	1.144
	1.098	100.27	4227.3	390.9	1.115
	1.115	100.40	4194.7	385.7	1.110
n-heptane	1.000	113.70	4653.5	428.4	1.259
	1.101	114.46	4415.9	393.9	1.228
	1.140	114.73	4335.9	382.1	1.216
n-octane	1.000	127.86	4837.6	432.4	1.375
	1.097	128.60	4591.1	398.9	1.344
	1.165	129.10	4443.4	379.5	1.326
n-hexadecane	1.000	239.77	5549.7	463.7	2.409
	1.152	241.26	5082.8	409.7	2.339
	1.195	241.66	4972.6	396.9	2.320
2,3-dimethylbutane	1.000	98.98	4404.5	410.4	1.109
	1.148	100.05	4106.0	363.8	1.066
	1.150	100.07	4102.5	363.3	1.066
2,2,4-trimethylpentane	1.000	129.07	5040.4	542.3	1.205
	1.134	130.13	4442.1	331.3	1.167
	1.190	130.41	4369.0	322.4	1.158
c-pentane	1.000	72.23	4496.2	520.5	1.006
	1.087	72.69	4302.6	483.9	0.983
	1.094	72.73	4288.3	481.2	0.982

(continued)

Table IV (continued)

Liquid	m	$V^*/cm^3\ mol^{-1}$	T^*/K	$P^*/J\ cm^{-3}$	C
c-hexane	1.000	84.31	4724.3	533.5	1.145
	1.140	85.05	4397.3	476.0	1.107
c-heptane	1.000	96.09	4981.8	552.2	1.281
	1.150	96.87	4598.5	488.9	1.239
	1.160	96.92	4576.5	485.3	1.236
c-octane	1.000	108.47	5293.0	563.3	1.338
	1.192	109.42	4766.9	483.4	1.334
	1.202	109.47	4744.3	479.9	1.332
benzene	1.000	69.23	4709.1	628.3	1.111
	1.020	69.32	4657.0	617.5	1.106
	1.073	69.56	4528.7	590.8	1.091
toluene	1.000	84.65	5040.4	542.3	1.096
	1.024	84.76	4969.9	531.2	1.090
	1.070	84.97	4843.7	511.2	1.079
o-xylene	1.000	97.93	5376.7	530.3	1.162
	1.024	98.03	5297.9	519.4	1.156
	1.095	98.34	5085.2	489.9	1.139
m-xylene	1.000	99.27	5287.0	517.1	1.168
	1.026	99.39	5204.3	505.6	1.161
	1.080	99.62	5059.0	485.4	1.150
p-xylene	1.000	99.27	5222.5	512.9	1.173
	1.022	99.38	5153.6	503.2	1.167
	1.095	99.73	4945.1	473.8	1.149

(continued)

Table IV (continued)

Liquid	m	$V^*/cm^3\ mol^{-1}$	T^*/K	$P^*/J\ cm^{-3}$	C
CCl_4	1.000	75.10	4437.5	424.2	1.094
	1.080	75.49	4502.3	531.7	1.072
	1.103	75.60	4451.5	522.5	1.067
octamethylcyclotetra-siloxane	1.000	242.10	4734.0	395.5	2.432
	1.180	244.80	4326.6	342.4	2.330
	1.380	247.58	4002.3	299.2	2.226

Table V

Molar Interaction Energies of Non-polar and Weakly Polar Liquids

Liquid	ΔE^V/J mol^{-1}	Interaction energy/J mol^{-1}		
		m = 1	ratio method	mixture method
n-hexane	28970	32111	29089	28647
n-heptane	33980	37546	34101	32929
n-octane	38900	43212	39393	37178
n-hexadecane	78510	90610	78656	75825
2,3-dimethylbutane	26550	30625	26674	26629
2,2,4-trimethylpentane	32570	39084	32699	31541
c-pentane	25950	28596	26273	26308
c-hexane	30460	34865	30581	30581
c-heptane	35950	41885	36106	36420
c-octane	40770	49138	40880	41222
benzene	31270	33672	31385	33014
toluene	35410	36374	35524	33998
o-xylene	40850	41961	40672	38316
m-xylene	40080	41267	40221	38401
p-xylene	39800	40789	39913	37252
CCl_4	29850	33060	29972	30584
octamethylcyclotetra-siloxane	53570	74267	53813	62933

at constant pressure is small, the difference between the energy and enthalpy of vaporization of the individual fluids is large. It is reasonable to expect the molar interaction energy not to exceed in general the total liquid cohesive energy, which is approximated here by the energy of vaporization. As seen in Table V, molar interaction energies computed from the van der Waals approximation are consistently higher than the experimental energies of vaporization. This implies that the molecules can be separated and the fluid vaporized with less energy than needed to overcome the mutual attaction between the molecules. The ratio method values result in interaction energies approximately equal to the energies of vaporization and, with the exception of benzene, our suggested values of m result in interaction energies somewhat lower than those required for vaporization. The ability of the theory to yield interaction energies of the same order of magnitude as the energies of vaporization supports the validity of approximating the liquid configurational energy by an attractive term.

VI-2: Excess Enthalpy Calculations

The sources and equimolar values of the experimental V^E and H^E data used in the computations are listed in Table VI. For many of the mixtures studied, experimental data from different sources differ by more than the combined acknowledged limits of error.

Using the pseudo-2-fluid and simple-1-fluid models described in Chapter IV, we first attempted to compute the excess enthalpy with pure component values of m estimated by the ratio

Table VI

Excess Properties[†] of Binary Mixtures of Non-polar and Weakly Polar Liquids at $x_1 = 0.5$

Mixture	$V^E/cm^3\ mol^{-1}$		$H^E/J\ mol^{-1}$		$G^E/J\ mol^{-1}$	
n-hexane + c-hexane	0.143	(201)	216	(202)	71[e]	(255)
n-heptane + c-hexane	0.27	(203)	240	(204)		
n-hexadecane + c-hexane	0.62	(205)	498	(204)	-177	(254)
n-hexane + n-hexadecane	-0.529	(206)	114	(207)	- 68	(252)
	-0.532	(208)				
n-heptane + n-hexadecane	-0.34	(209)	96	(204)	- 55[e]	(253)
224TMP[a] + n-hexadecane	-0.50	(209)	232	(204)	7	(253)
CCl_4 + n-hexane	0.044	(210)	317	(210)	149	(247)
CCl_4 + n-heptane	0.213	(210)	339	(210)	134	(248)
CCl_4 + n-octane	0.32	(211)	364	(212)	95	(249)
CCl_4 + n-hexadecane	0.62	(213)	578	(214)	-116	(250)
CCl_4 + c-hexane	0.159	(215)	166	(216)	70	(251)
CCl_4 + 224TMP[a]	0.216	(217)	405	(214)	158[f]	(217)
benzene + n-hexane	0.414	(218)	897	(219)	385	(243)
benzene + n-heptane	0.591	(220)	919	(221)	354	(243)
					430	(245)
benzene + n-octane	0.710	(222)	969	(223)	331	(245)
					364	(243)
benzene + n-hexadecane	1.05	(213)	1209	(223)	91	(245)
			1255	(204)		
benzene + 224TMP[a]	0.502	(224)	992	(204)	400	(243)

(continued)

Table VI (continued)

Mixture	$V^E/cm^3\ mol^{-1}$		$H^E/J\ mol^{-1}$		$G^E/J\ mol^{-1}$	
toluene + n-hexane	-0.032	(225)	512[d]	(243)	332	(243)
toluene + n-heptane	0.137	(225)	552	(204)	201	(243)
toluene + 224TMP[a]	0.087	(224)	657	(226)	354	(243)
OMCTS[b] + CCl_4	-0.252	(227)	163	(227)	-133	(246)
OMCTS[b] + benzene	-0.009	(227)	793	(227)	116	(246)
c-pentane + 23DMB[c]	-0.297	(228)	- 2	(228)	13	(228)
c-hexane + 23DMB[c]	-0.113	(177)	156	(177)	87	(177)
c-heptane + 23DMB[c]	-0.440	(229)	163	(229)	135	(229)
c-octane + 23DMB[c]	-0.701	(230)	176	(230)	184	(230)
c-pentane + c-hexane	0.041	(231)	28	(216)	- 4	(182)
c-pentane + c-heptane	-0.113	(182)	- 4	(182)	- 5	(182)
c-pentane + c-octane	-0.283	(232)	- 41	(233)	- 2	(182)
c-hexane + c-heptane	-0.031	(234)	6	(234)	9	(234)
c-hexane + c-octane	-0.107	(182)	1	(182)	26	(182)
c-heptane + c-octane	-0.025	(234)	4	(234)	5	(234)
benzene + c-pentane	0.344	(235)	630	(236)	291	(243)
benzene + c-hexane	0.650	(237)	799	(238)	331	(243)
benzene + c-heptane	0.666	(236)	758	(236)		
benzene + c-octane	0.581	(236)	797	(236)	286	(244)
toluene + c-pentane	0.076	(236)	365	(236)		
toluene + c-hexane	0.570	(236)	603	(236)	332	(243)
toluene + c-heptane	0.527	(236)	544	(236)		
toluene + c-octane	0.513	(236)	610	(236)	296	(244)

(continued)

Table VI (continued)

Mixture	V^E/cm^3 mol^{-1}		H^E/J mol^{-1}		G^E/J mol^{-1}
benzene + toluene	0.088	(239)	68	(239)	-
benzene + o-xylene	0.249	(240)	216	(240)	-
benzene + m-xylene	0.293	(240)	223	(240)	-
benzene + p-xylene	0.206	(240)	164	(240)	-
toluene + o-xylene	0.042	(239)	97	(239)	-
toluene + m-xylene	0.051	(239)	43	(239)	-
toluene + p-xylene	0.017	(239)	19	(239)	-
o-xylene + m-xylene	0.0015	(241)	11	(242)	-
o-xylene + p-xylene	-0.0079	(242)	6	(242)	-
m-xylene + p-xylene	-0.0106	(242)	- 8	(242)	-

[a]224TMP = 2,2,4-trimethylpentane

[b]OMCTS = octamethylcyclotetrasiloxane

[c]23DMB = 2,3-dimethylbutane

[d]estimated from the temperature dependence of G^E

[e]at 293 K

[f]extrapolated from data at higher temperatures

†at 298 K

method. The results of these calculations are compared at $x_1 = 0.5$ with experimental excess enthalpy values in Table VII. In general, the predictions of the two models tend to merge as the values of m of the pure components approach each other and to diverge as the difference between the pure component values of m increases. Using ratio method values of m, neither model yields quantitatively accurate results. Agreement is worst for mixtures containing benzene or toluene and best for mixtures of cycloalkanes and cycloalkanes with 2,3-dimethylbutane. Replacing the volume fraction averaged value of m for the mixture by a mole fraction averaged value altered the magnitude of the individual excess enthalpy predictions, but did not produce improved agreement with experiment.

The accuracy of values of m computed from the ratio of the internal pressure to the cohesive energy density has been estimated to be 5% (161). This error estimate and the very much higher values of m computed by the slope method led us to explore the effect on the excess functions of small changes in m about their ratio method values.

We expected that adjusted individual values of m_1 and m_2 for each pure component near but not equal to their ratio method values, would successfully reproduce the excess enthalpy for each binary mixture. Instead of unique pairs, we found sets of pairs of such m_1 and m_2 values for each binary mixture; the m_1/m_2 ratio of these sets was nearly constant. Excess enthalpy predictions, using the pseudo-2-fluid model and combinations of pure component values of m near their ratio method values, are shown for represen-

Table VII

Comparison of the Pseudo-2-fluid and Simple-1-fluid
Treatments of Mixtures using
Ratio Method Values of m

Mixture	H^E/J mol^{-1}		
	experiment	pseudo-2-fluid	simple-1-fluid
n-hexane + c-hexane	216	196	216
n-heptane + c-hexane	240	173	190
n-hexadecane + c-hexane	498	468	467
n-hexane + n-hexadecane	114	156	188
n-heptane + n-hexadecane	96	323	300
224TMP + n-hexadecane	233	261	277
CCl_4 + n-hexane	317	205	208
CCl_4 + n-heptane	339	179	180
CCl_4 + n-octane	364	153	156
CCl_4 + n-hexadecane	578	404	388
CCl_4 + c-hexane	166	153	149
CCl_4 + 224TMP	405	185	161
benzene + n-hexane	898	626	607
benzene + n-heptane	919	578	558
benzene + n-octane	969	528	513
benzene + n-hexadecane	1209	761	714
benzene + 224TMP	992	541	484
toluene + n-hexane	512	642	599
toluene + n-heptane	552	587	546
toluene + 224TMP	657	763	679
OMCTS + CCl_4	163	877	684
OMCTS + benzene	794	1421	1150
c-pentane + 23DMB	- 2	- 21	- 43
c-hexane + 23DMB	156	149	145
c-heptane + 23DMB	163	127	137
c-octane + 23DMB	176	143	187

(continued)

Table VII (continued)

Mixture	H^E/J mole		
	experiment	pseudo-2-fluid	simple-1-fluid
c-pentane + c-hexane	28	52	55
c-pentane + c-heptane	- 4	- 3	11
c-pentane + c-octane	- 41	- 38	- 5
c-hexane + c-heptane	6	1	4
c-hexane + c-octane	1	11	24
c-heptane + c-octane	- 4	4	8
benzene + c-pentane	630	414	406
benzene + c-hexane	799	658	640
benzene + c-heptane	758	677	661
benzene + c-octane	797	681	665
toluene + c-pentane	365	289	271
toluene + c-hexane	625	696	687
toluene + c-heptane	588	638	642
toluene + c-octane	618	714	733
benzene + toluene	68	- 13	- 2
benzene + o-xylene	216	103	115
benzene + m-xylene	223	101	115
benzene + p-xylene	164	2	18
toluene + o-xylene	47	47	55
toluene + m-xylene	43	43	43
toluene + p-xylene	19	1	1
o-xylene + m-xylene	11	10	9
o-xylene + p-xylene	6	8	8
m-xylene + p-xylene	- 8	- 10	- 10

tative mixtures at $x_1 = 0.5$ in Table VIII. Small changes in the relative values of m of the individual components are seen to have a marked effect on the magnitude of the excess enthalpy, while simultaneous changes in the values of m of both components, such that their relative magnitude is unchanged, have only minor effects. Vertical or horizontal movemement in any of the arrays (changes in the relative magnitude of m_1 and m_2) produces large changes in the excess property predictions, while diagonal movement does not. Excess enthalpy predictions for combinations of m_1 and m_2 whose values fall near the diagonal of these arrays agree best with experiment. With varying degrees of sensitivity, similar behavior was observed for all mixtures studied. Since the excess properties depend only on the relative contributions of the mixed and unmixed liquids, the observation that the relative magnitude of m_1 and m_2 is of primary importance is not unreasonable.

The ratios of pure component values of m which sucessfully predict the excess enthalpy of mixtures of the cycloalkanes and mixtures of the cycloalkanes with 2,3-dimethlybutane are closest to the ratios of the internal pressure-cohesive energy density "ratio method" values. This is not surprising, since application of the pseudo-2-fluid model using ratio method values of m was most sucessful for these mixtures.

Pairs of m_1 and m_2 values with nearly constant ratios slightly different from the pseudo-2-fluid ratios reproduced the excess enthalpy for most mixtures in the simple-1-fluid model; there were, however,

Table VIII

Dependence of the Excess Enthalpy on the Relative Magnitude of m_1 and m_2

benzene + toluene

m(toluene) \ m(benzene)	1.00	1.01	1.02	1.03	1.04
1.05	68	53	39	27	16
1.06	85	68	52	38	27
1.07	103	84	67	52	38
1.08	122	101	83	66	51
1.09	142	120	100	80	65

c-hexane + c-heptane

m(c-heptane) \ m(c-hexane)	1.12	1.13	1.14	1.15	1.16
1.13	6	10	16	23	31
1.14	2	5	10	15	23
1.15	0	2	5	10	15
1.16	- 1	0	2	5	9
1.17	- 2	- 1	0	2	5

c-pentane + 23DMB

m(23DMB) \ m(c-pentane)	1.07	1.08	1.09	1.10	1.11
1.13	- 4	-27	-47	-67	-84
1.14	17	- 7	-28	-48	-67
1.15	39	14	- 8	-30	-49
1.16	61	36	12	-10	-31
1.17	84	5[illegible]	33	11	-12

several important exceptions. Excess enthalpies computed from the simple-1-fluid model for hexane + hexadecane mixtures were always too high (≈ 200 joule/mole at $x_1 = 0.5$) for all combinations of m_1 and m_2 in the vicinity of their ratio method values; as the difference between m_1 and m_2 was increased, the decrease in H^E leveled off asymptotically without approaching the experimental values. The excess enthalpy predictions for cyclopentane + cyclooctane mixtures were similarly high and insensitive to changes in the individual values of m. The ratios, $m_{n\text{-alkane}}/m_{CCl_4}$, obtained from n-alkane + CCl_4 mixtures in the simple-1-fluid model for successive members of the n-alkane series, were higher and further separated from each other than ratios similarly obtained in the pseudo-2-fluid model and than ratios of the "ratio method" values of m. The simple-1-fluid model was frequently not as successful as the pseudo-2-fluid model in correctly predicting the concentration dependence of the excess enthalpy. These observations led us to choose the pseudo-2-fluid model as the basis for determining a single, consistent set of pure component values of m from which the excess properties of any binary mixture can be calcaulated.

The values of m we propose for the energy-volume exponents of the seventeen non-polar and weakly polar liquids studied are listed in the second column of Table III. These values have been normalized to the ratio method values of the cohesive energy-volume exponents of the cycloalkanes and 2,3-dimethlybutane. The cycloalkanes and 2,3-dimethylbutane were chosen as standards for the scaling process both because their physical properties had been recently determined in the same laboratory and because their mixture method m_i/m_j ratios closely follow the ratios of the appropriate "ratio method" values.

Since the magnitude of the excess enthalpy of the mixtures studied ranges from nearly zero to over a kilojoule and the accuracy and source of the experimental data varies widely, we felt it was unrealistic and overly rigid to represent overall agreement with experiment for a given set of pure component m values by a standard numerical function. We therefore chose not to use a complex 17-parameter curve fitting procedure with formalized weighting factors to identify the most representative set of pure component m values and instead identified them by inspection. Since three times as many mixtures were studied as there are pure components, the values of m are well overdetermined and may be considered theoretical constants of general validity rather than empirical parameters representative of a given mixture. Although all the values of m are scaled to the ratio method values of m of the cycloalkanes and of 2,3-dimethylbutane, the values were not chosen so as to best reproduce the excess enthalpy of only mixtures containing these molecules. All components appear in at least two mixtures, and most appear in four or more in combination with different types of molecules.

Within a given chemical class, the mixture method values of m presented in Table III increase with molecular weight and molar volume. Molecular size and weight do not absolutely determine m, however, for compounds that belong to different chemical classes. Cyclooctane and n-hexadecane have similar values of m but different molecular weights and molar volumes; n-hexane and 2,3-dimethylbutane have identical molecular weights and similar molar volumes but different values of m. Within the n-alkane series, the mixture method values of m increase with carbon number more smoothly than do the ratio method values. Branching and cyclization both lead to increased values of m for compounds with the same carbon number; the effect of branching is more pronounced for compounds with low carbon number. The values of m derived here for benzene and toluene are the reverse of those calculated by the ratio method; for aromatic molecules, the mixture method values of m increase with increasing methyl substitution while the ratio method values decrease equally with methyl substitution of any kind. The high value obtained by the ratio method for octamethylcyclotetrasiloxane is similar to fluoroalkane ratio method m values. Unlike the octamethylcyclotetrasiloxane mixtures studied here, however, mixtures containing fluoroalkanes usually have excess volumes of several cm^3/mole and excess enthalpies of several kilojoules/mole. The far lower value of m which we obtained for octamethylcyclotetrasiloxane seems to reflect the smaller magnitude of the excess properties for octamethyltetracyclosiloxane mixtures.

The excess enthalpy predictions of our model are compared with the predictions of Flory's model $(m=1)$ and with experimental data at $x_1 = 0.5$ in Table IX. The composition dependence of the predictions is compared with experimental data in Figures 1 - 46.

Table IX

Comparison of the Predicted Excess Enthalpies at $x_1 = 0.5$ with Values Obtained using the van der Waals $m = 1$ Approach

Mixture	H^E/J mol^{-1}		
	experiment	pseudo-2-fluid	m = 1
n-hexane + c-hexane	216	219	334
n-heptane + c-hexane	240	224	322
n-hexadecane + c-hexane	498	500	687
n-hexane + n-hexadecane	114	116	181
n-heptane + n-hexadecane	96	93	140
224TMP + n-hexadecane	233	223	275
CCl_4 + n-hexane	317	302	254
CCl_4 + n-heptane	339	326	257
CCl_4 + n-octane	364	364	262
CCl_4 + n-hexadecane	578	544	543
CCl_4 + c-hexane	166	177	191
CCl_4 + 224TMP	405	391	161
benzene + n-hexane	897	908	711
benzene + n-heptane	919	936	697
benzene + n-octane	969	988	692
benzene + n-hexadecane	1209	1139	911
benzene + 224TMP	992	991	460
toluene + n-hexane	512	521	438
toluene + n-heptane	552	532	426
toluene + 224TMP	657	672	374
OMCTS + CCl_4	163	162	-290
OMCTS + benzene	794	778	- 44
c-pentane + 23DMB	- 2	- 2	-190
c-hexane + 23DMB	156	154	134
c-heptane + 23DMB	163	162	99
c-octane + 23DMB	176	176	217

(continued)

Table IX (continued)

Mixture	H^E/J mol^{-1}		
	experiment	pseudo-2-fluid	m = 1
c-pentane + c-hexane	28	53	76
c-pentane + c-heptane	- 4	- 2	6
c-pentane + c-octane	- 41	- 37	- 30
c-hexane + c-heptane	6	5	3
c-hexane + c-octane	1	14	29
c-heptane + c-octane	- 4	5	8
benzene + c-pentane	630	523	519
benzene + c-hexane	799	801	813
benzene + c-heptane	758	790	842
benzene + c-octane	797	806	794
toluene + c-pentane	365	206	229
toluene + c-hexane	625	603	763
toluene + c-heptane	588	544	720
toluene + c-octane	618	610	804
benzene + toluene	68	67	37
benzene + o-xylene	216	215	208
benzene + m-xylene	223	218	208
benzene + p-xylene	164	166	106
toluene + o-xylene	47	55	71
toluene + m-xylene	43	43	59
toluene + p-xylene	19	15	8
o-xylene + m-xylene	11	6	10
o-xylene + p-xylene	6	8	6
m-xylene + p-xylene	- 8	- 6	- 13

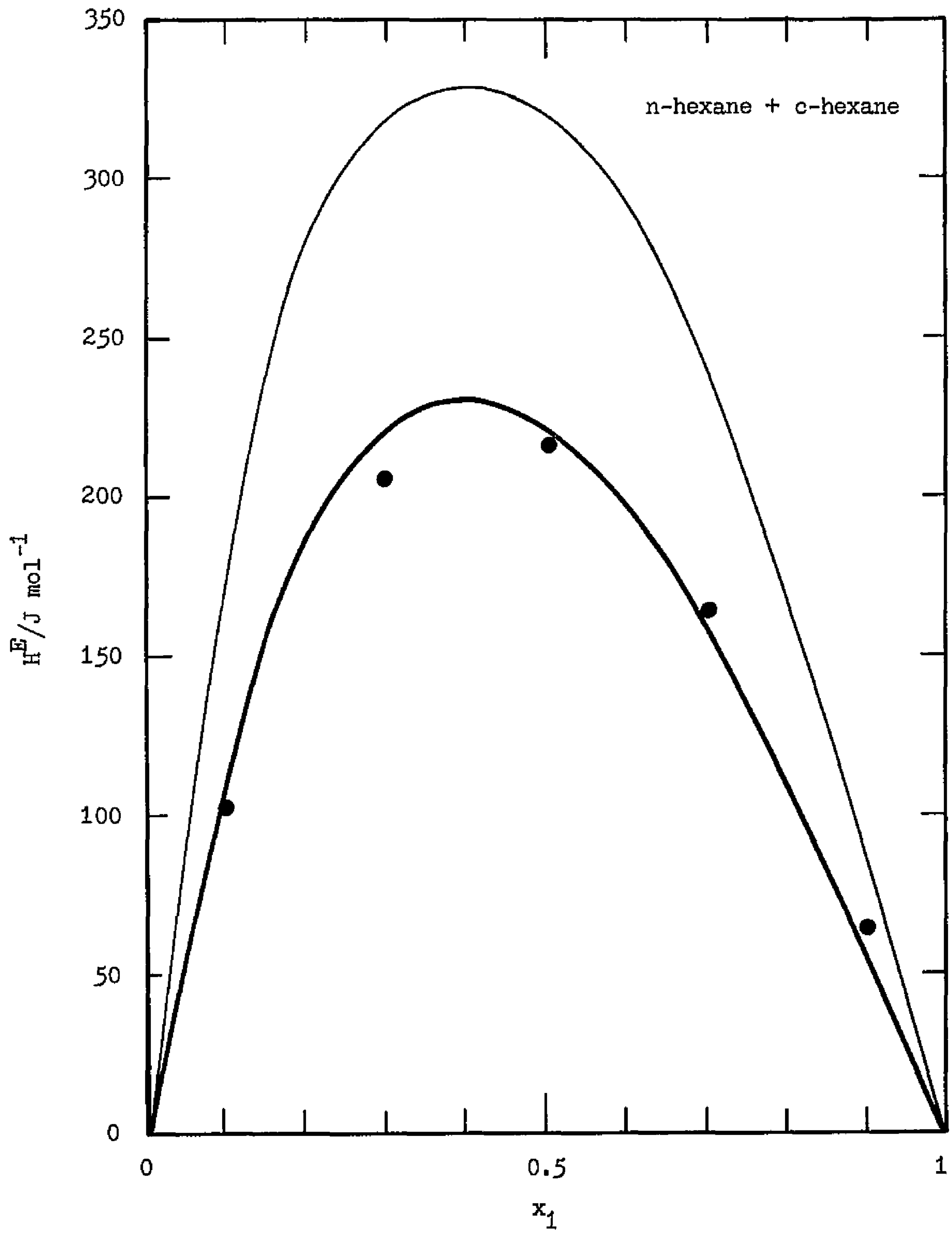

Figure 1. Dependence of the predicted excess enthalpy on composition for n-hexane + c-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

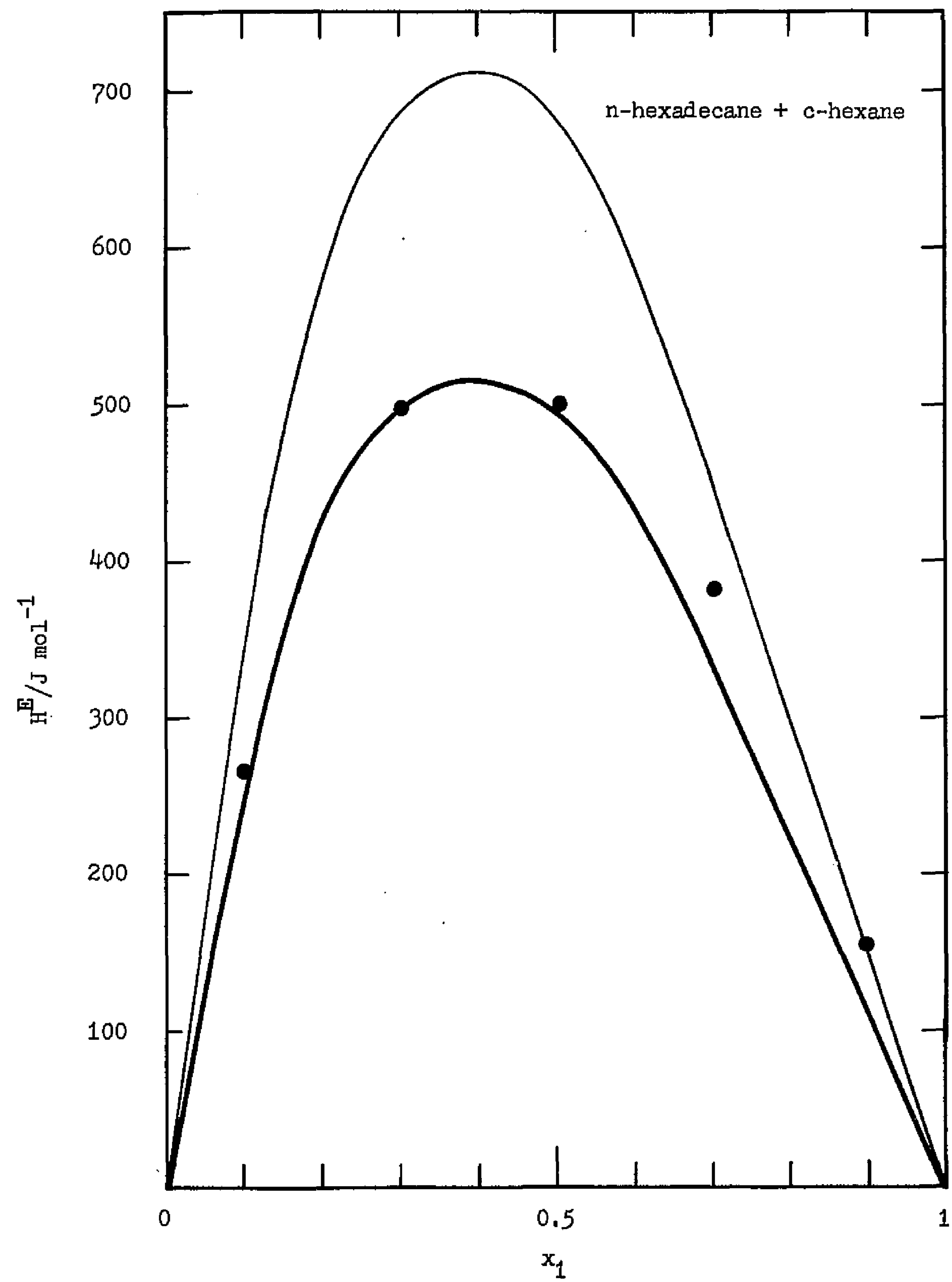

Figure 2. Dependence of the predicted excess enthalpy on composition for n-hexadecane + c-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

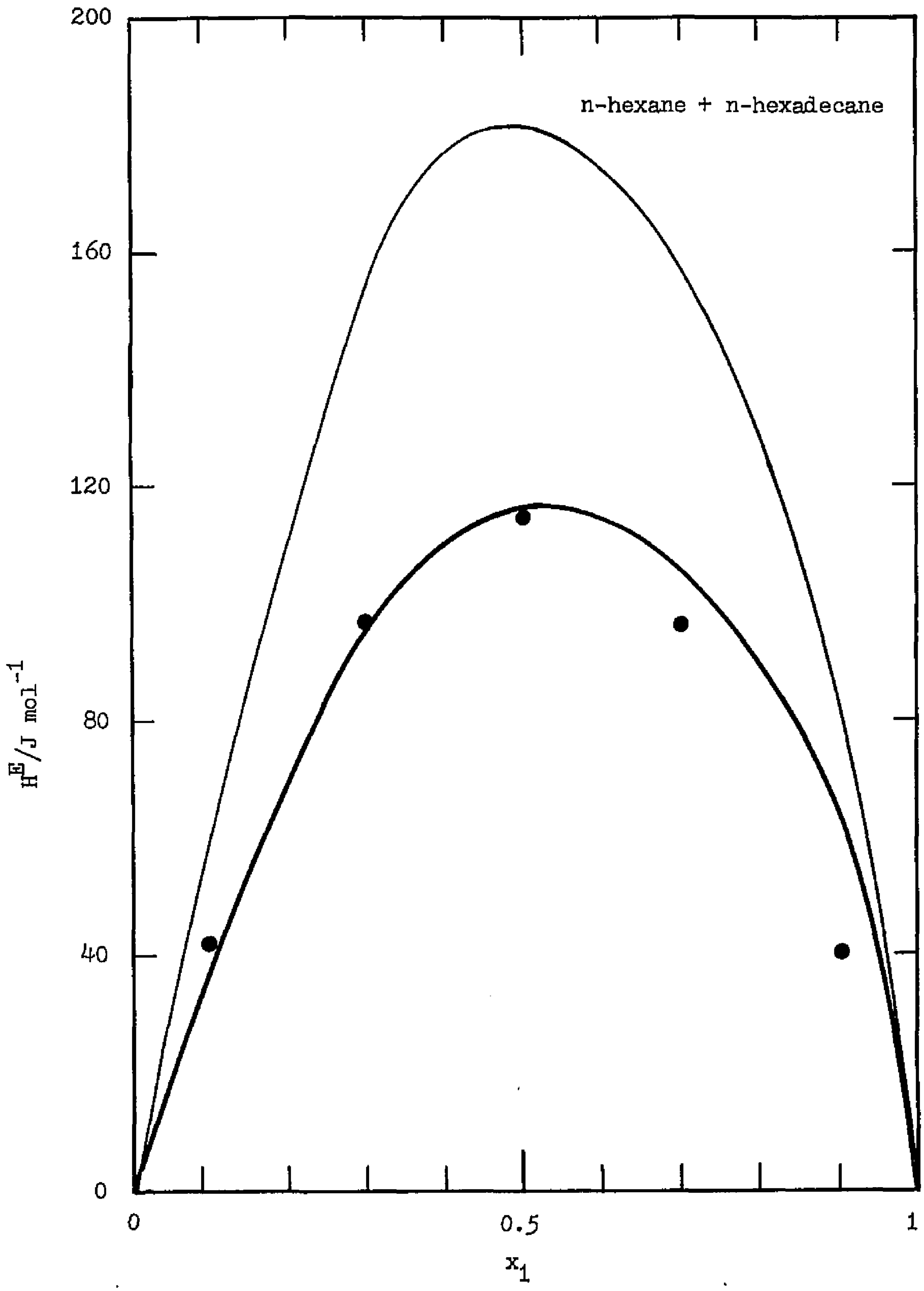

Figure 3. Dependence of the predicted excess enthalpy on composition for n-hexane + n-hexadecane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

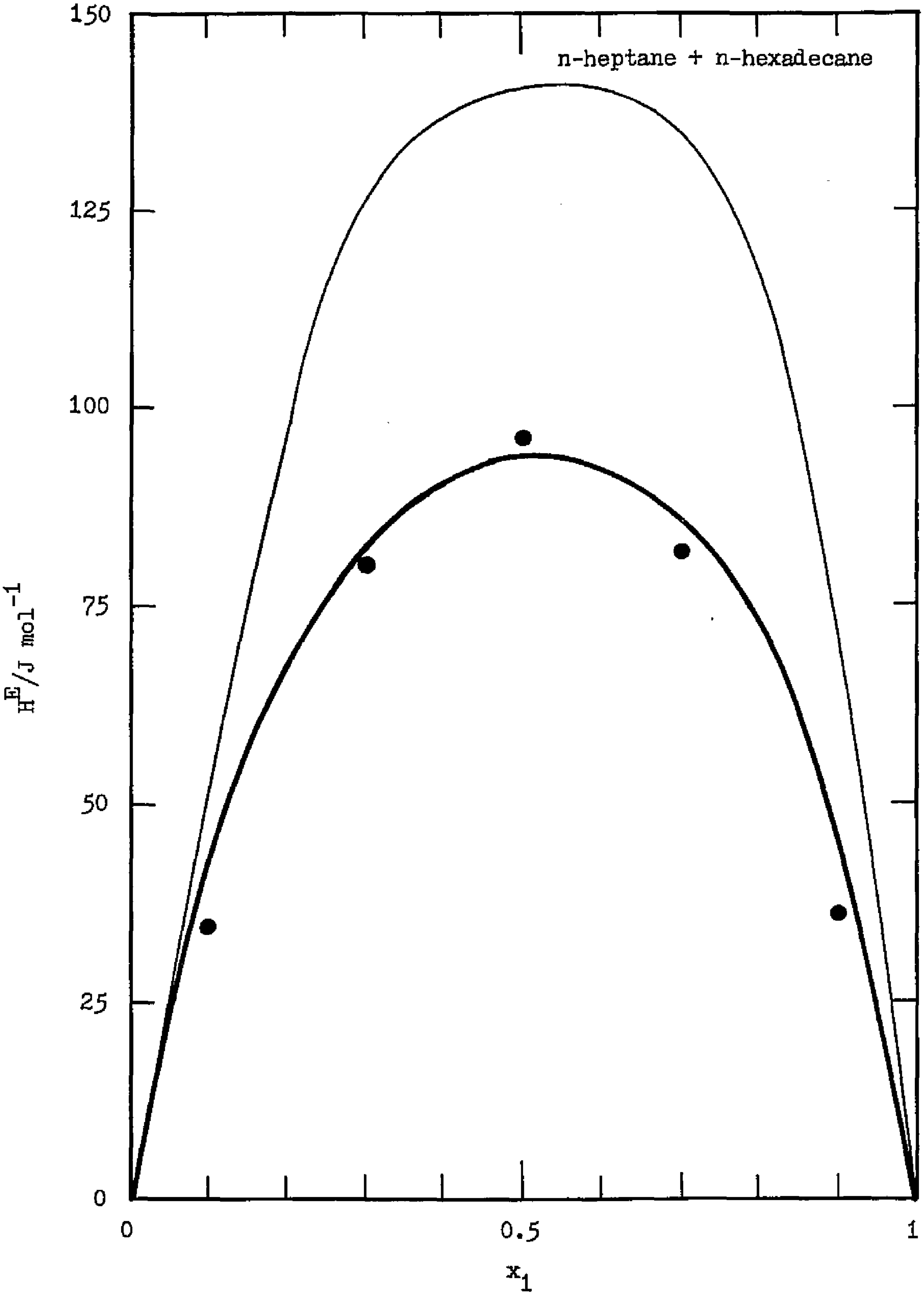

Figure 4. Dependence of the predicted excess enthalpy on composition for n-heptane + n-hexadecane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m=1$ predictions; circles: smoothed experimental data.

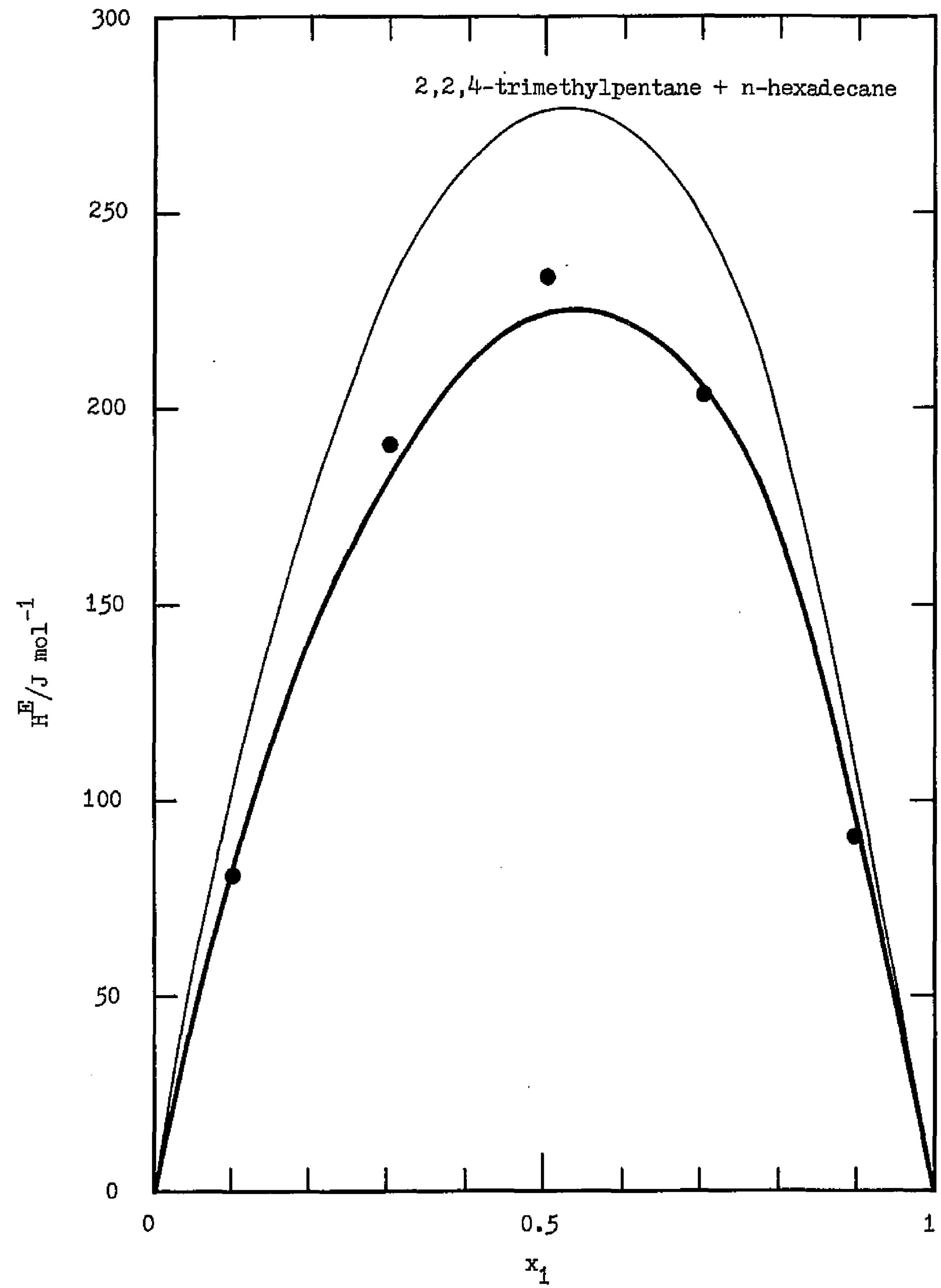

Figure 5. Dependence of the predicted excess enthalpy on composition for 2,2,4-trimethylpentane + n-hexadecane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

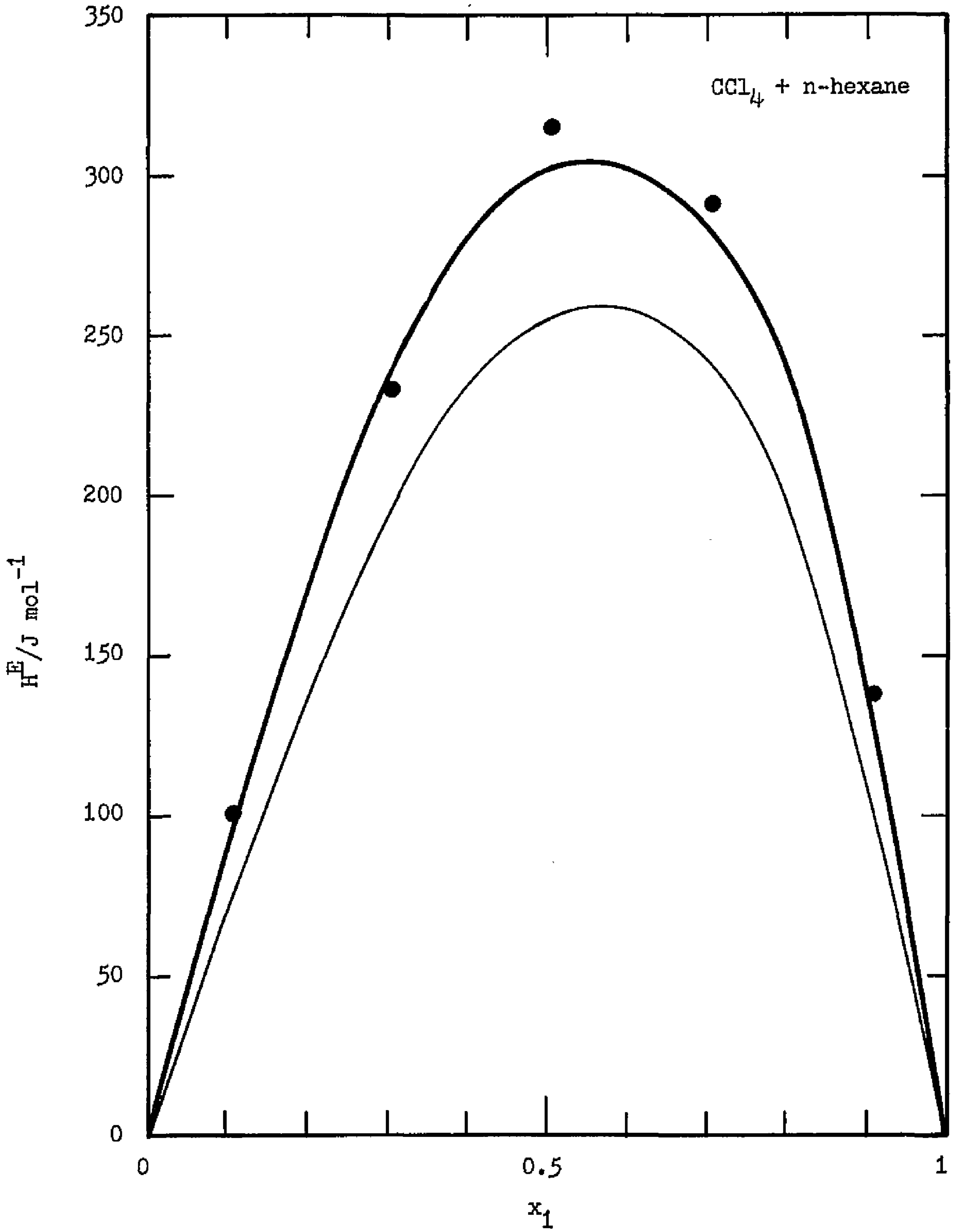

Figure 6. Dependence of the predicted excess enthalpy on composition for CCl_4 + n-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

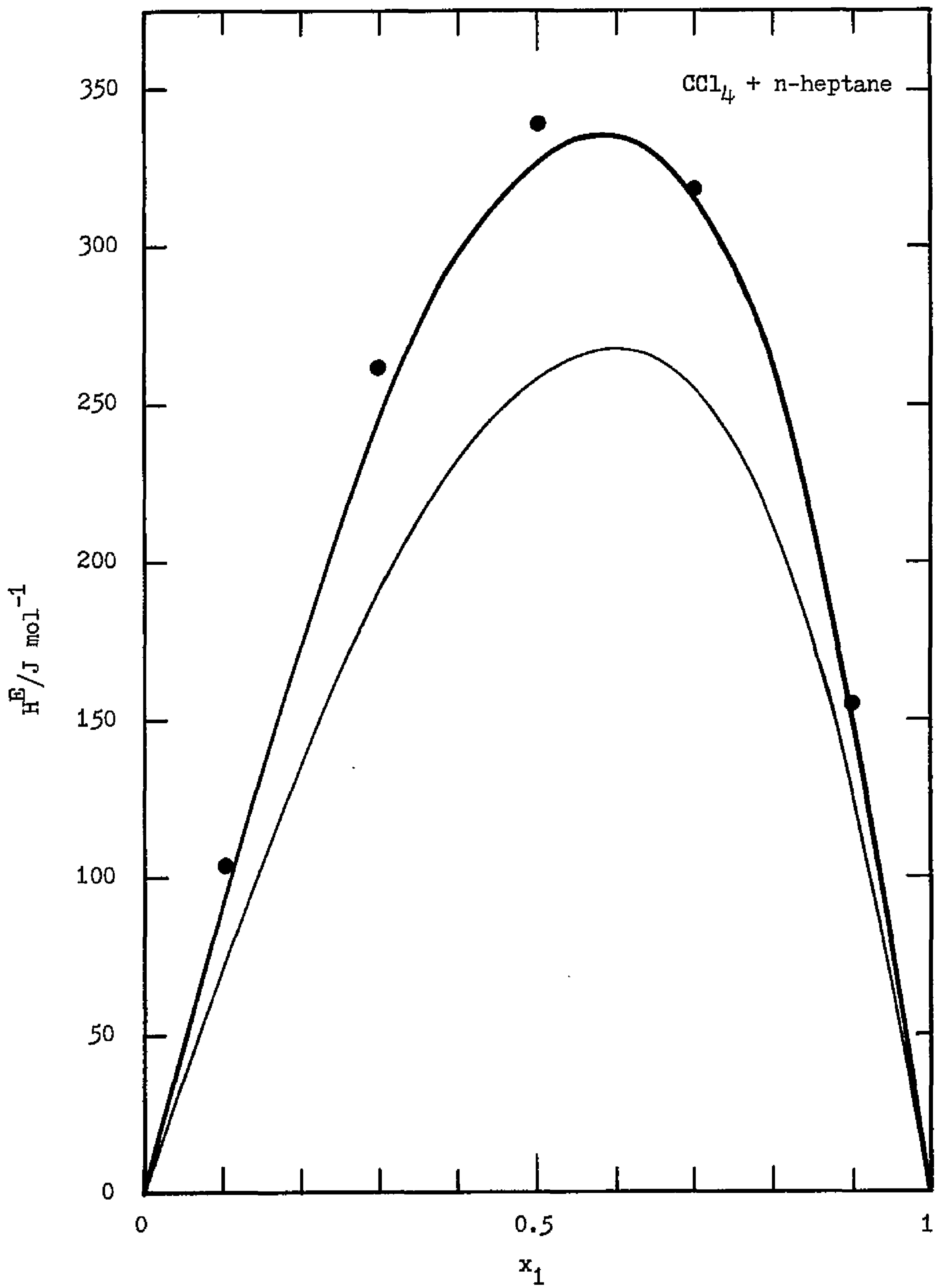

Figure 7. Dependence of the predicted excess enthalpy on composition for CCl_4 + n-heptane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

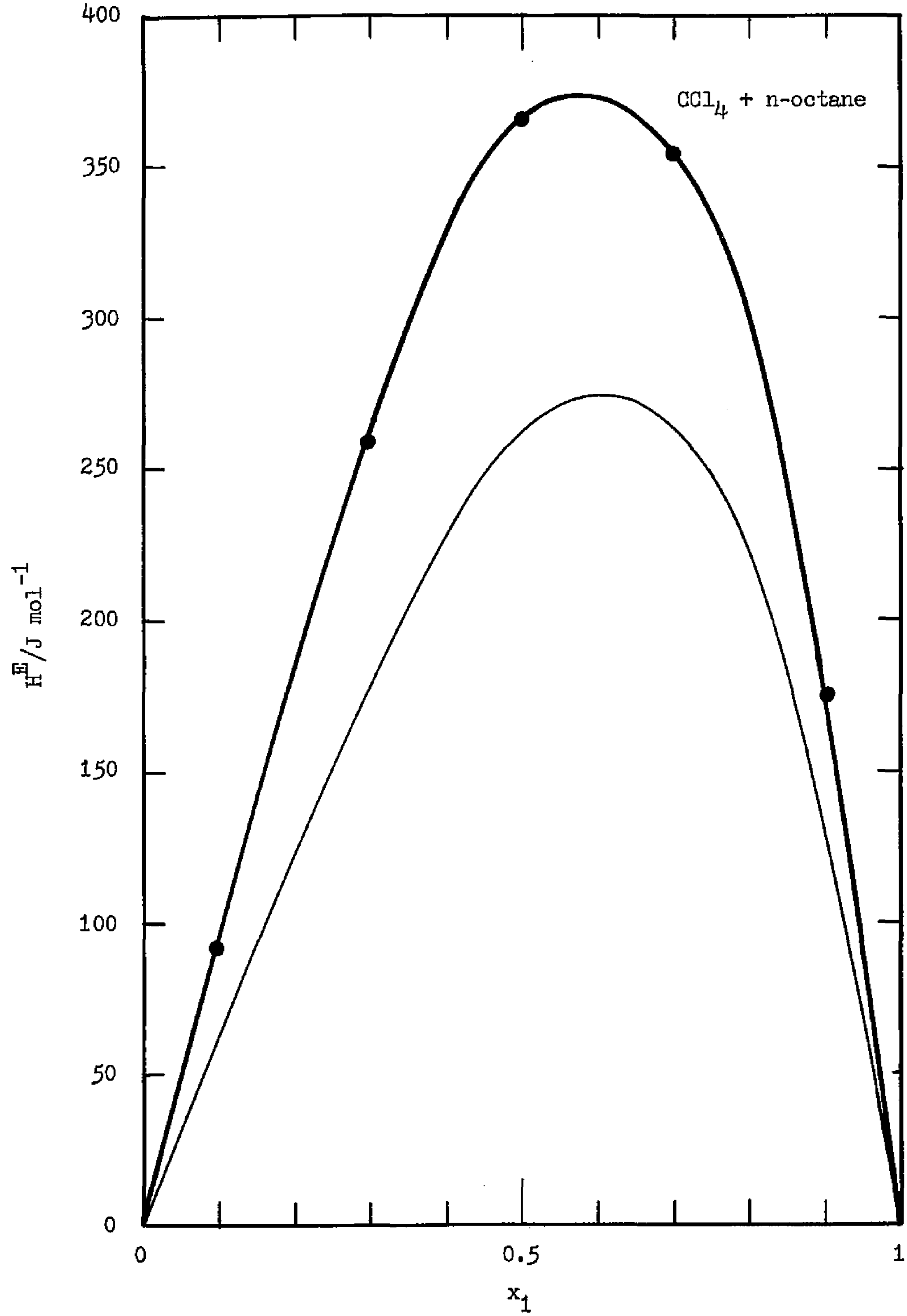

Figure 8. Dependence of the predicted excess enthalpy on composition for CCl_4 + n-octane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

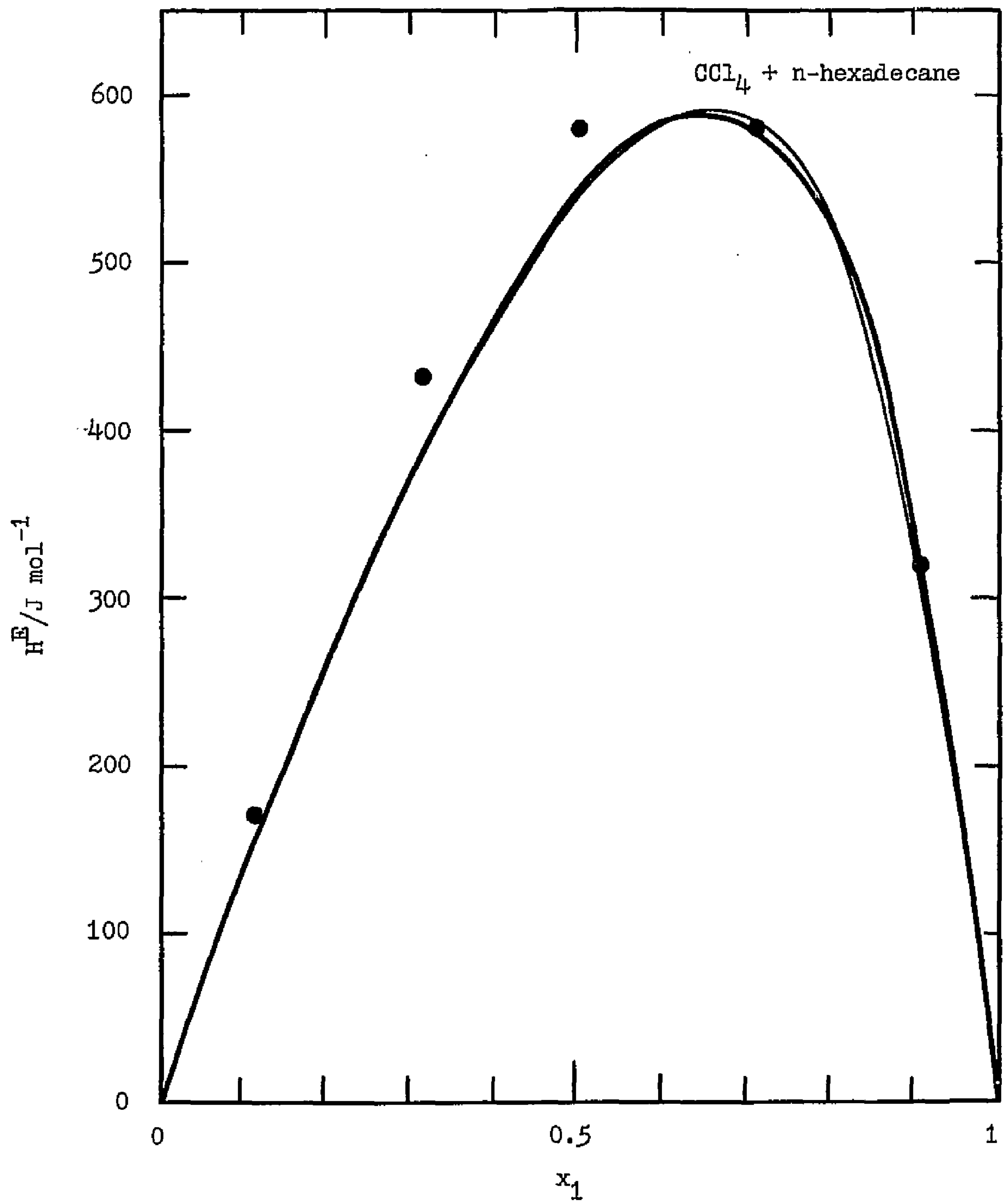

Figure 9. Dependence of the predicted excess enthalpy on composition for CCl_4 + n-hexadecane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

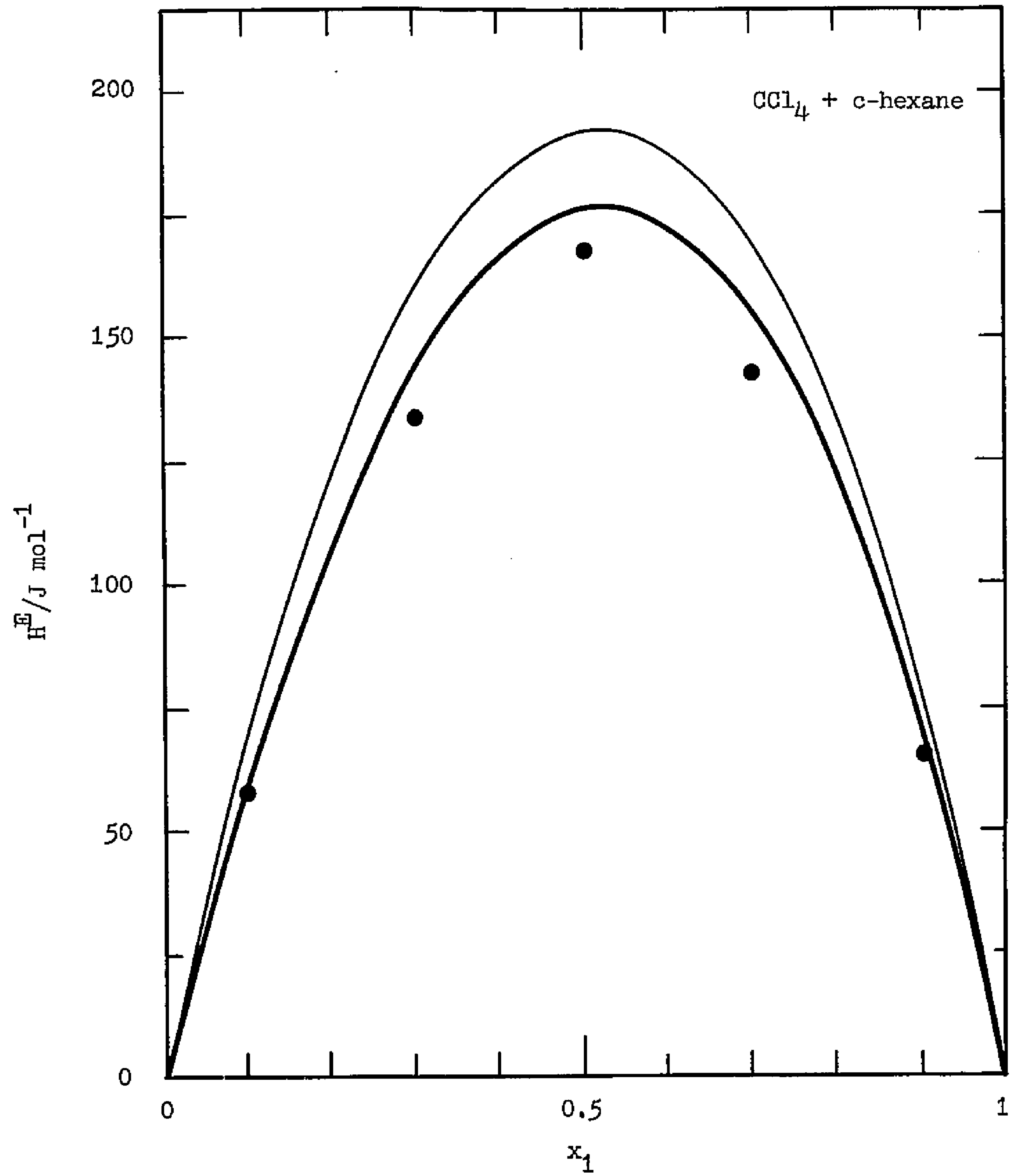

Figure 10. Dependence of the predicted excess enthalpy on composition for CCl_4 + c-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

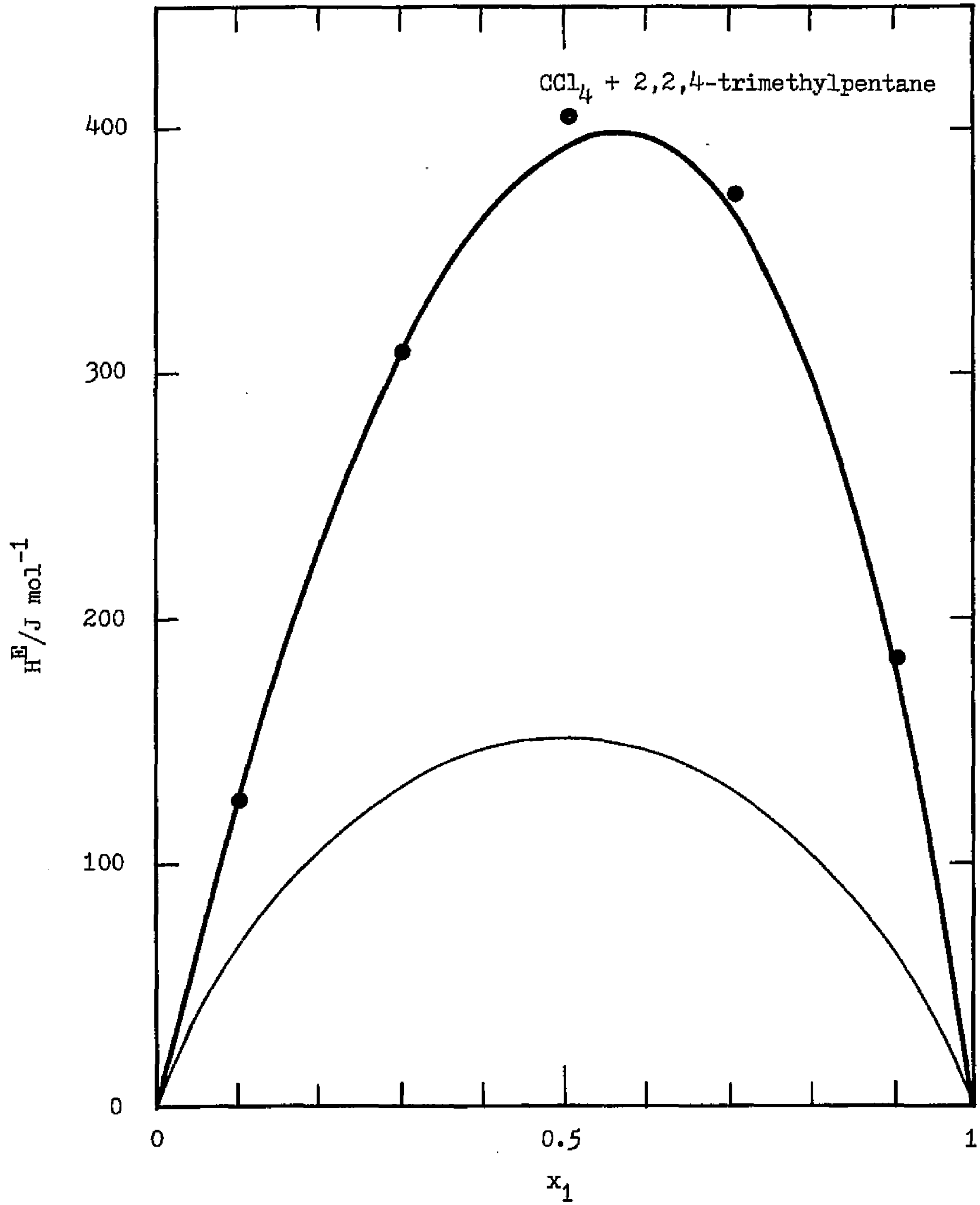

Figure 11. Dependence of the predicted excess enthalpy on composition for CCl_4 + 2,2,4-trimethylpentane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

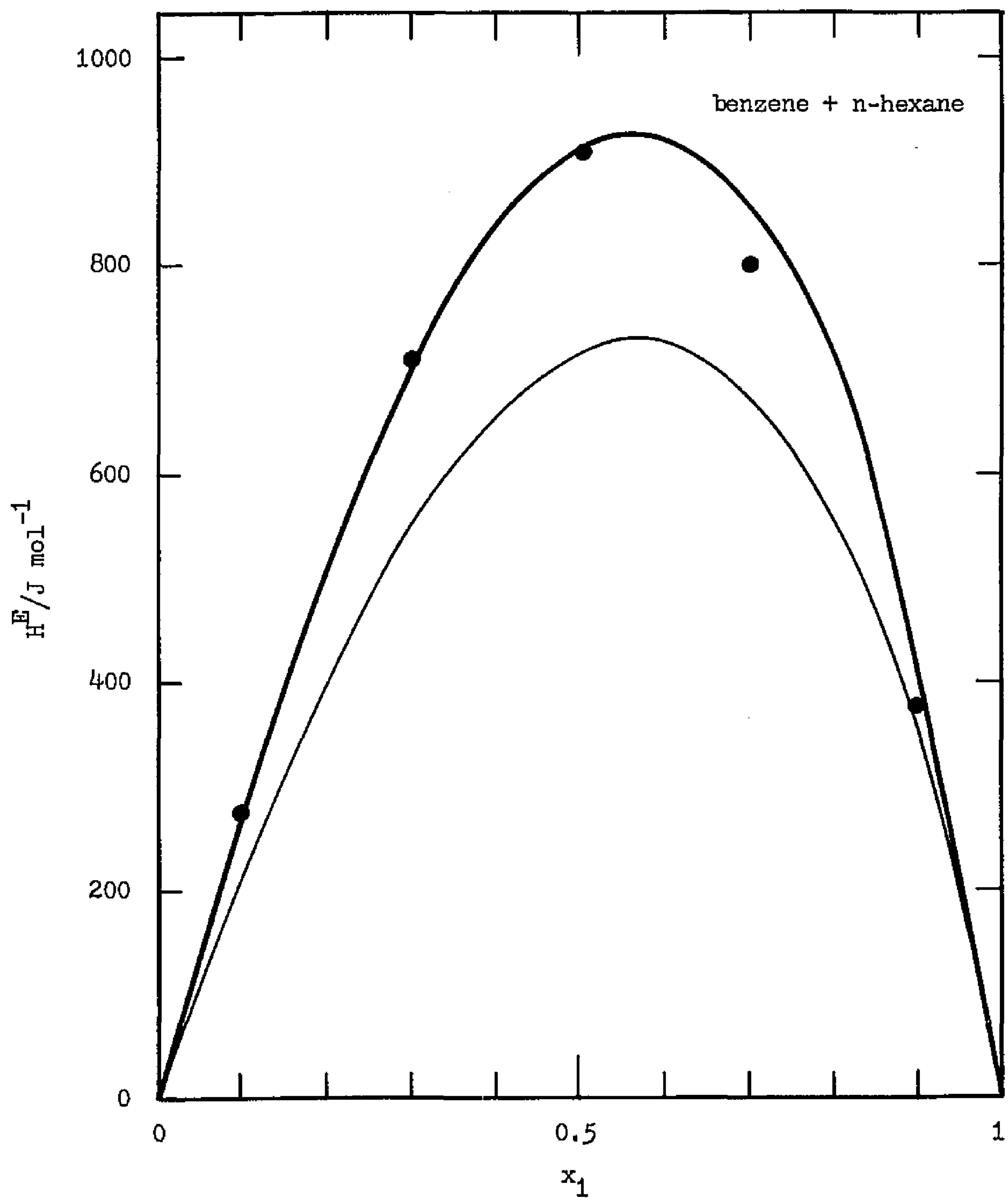

Figure 12. Dependence of the predicted excess enthalpy on composition for benzene + n-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

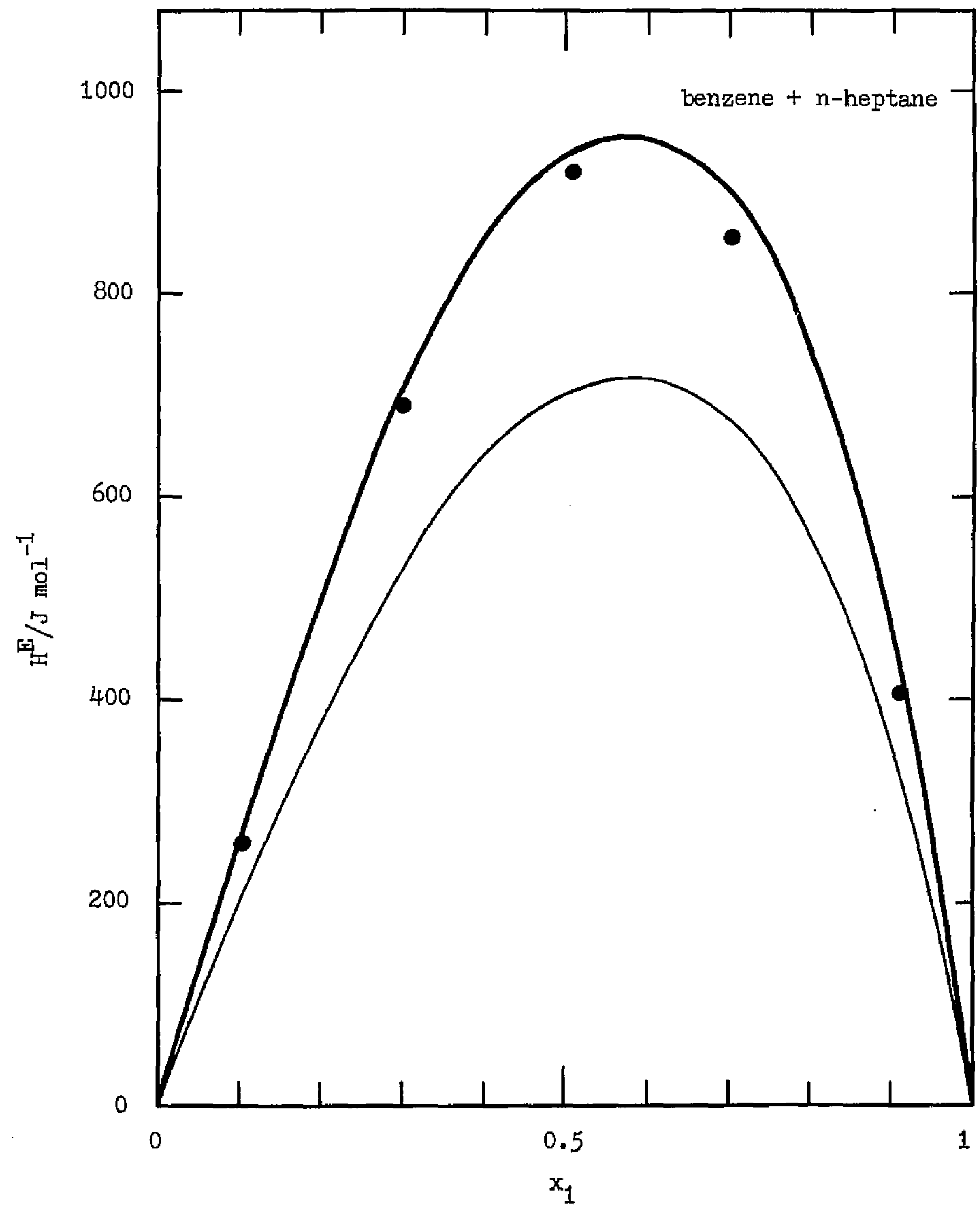

Figure 13. Dependence of the predicted excess enthalpy on composition for benzene + n-heptane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

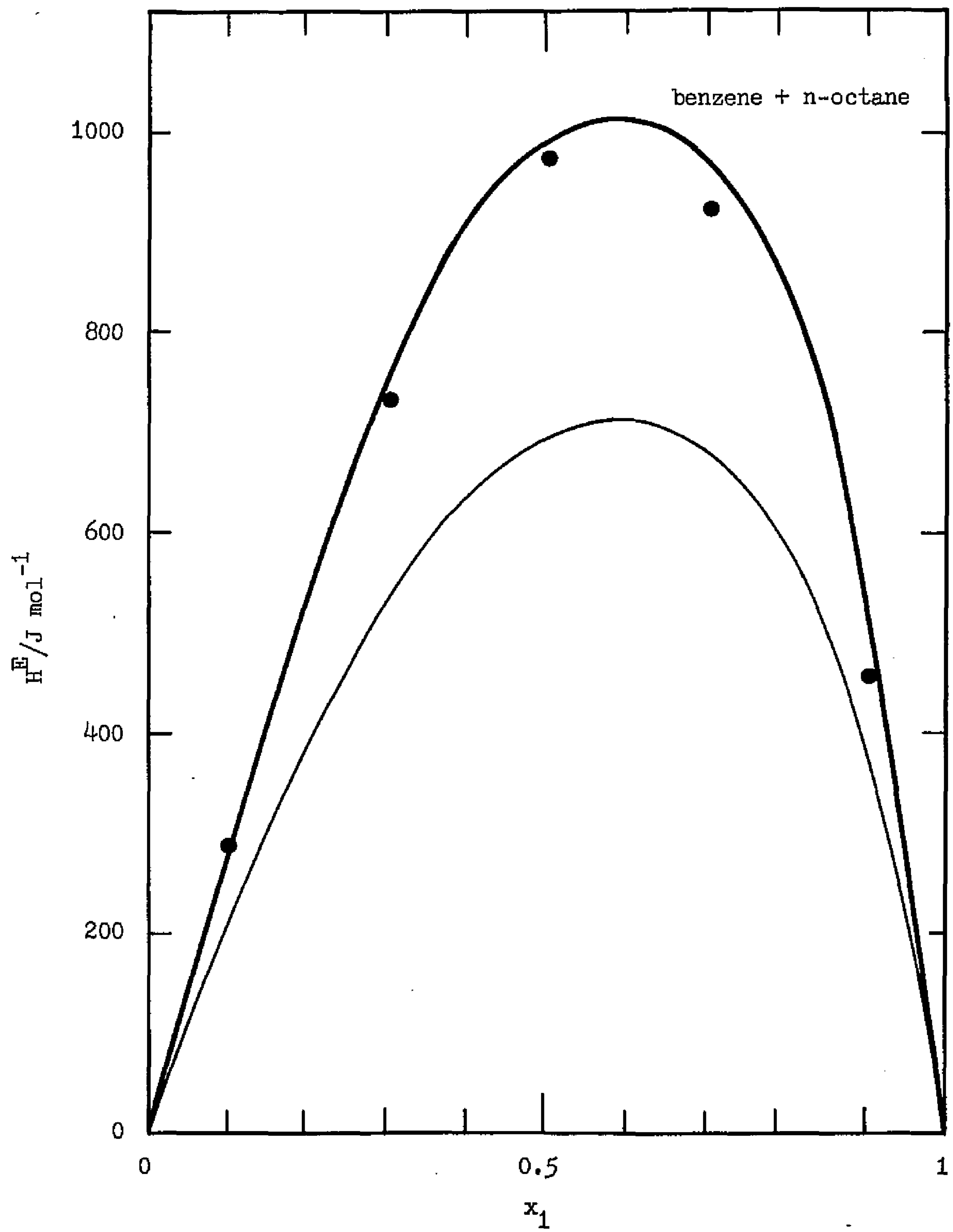

Figure 14. Dependence of the predicted excess enthalpy on composition for benzene + n-octane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

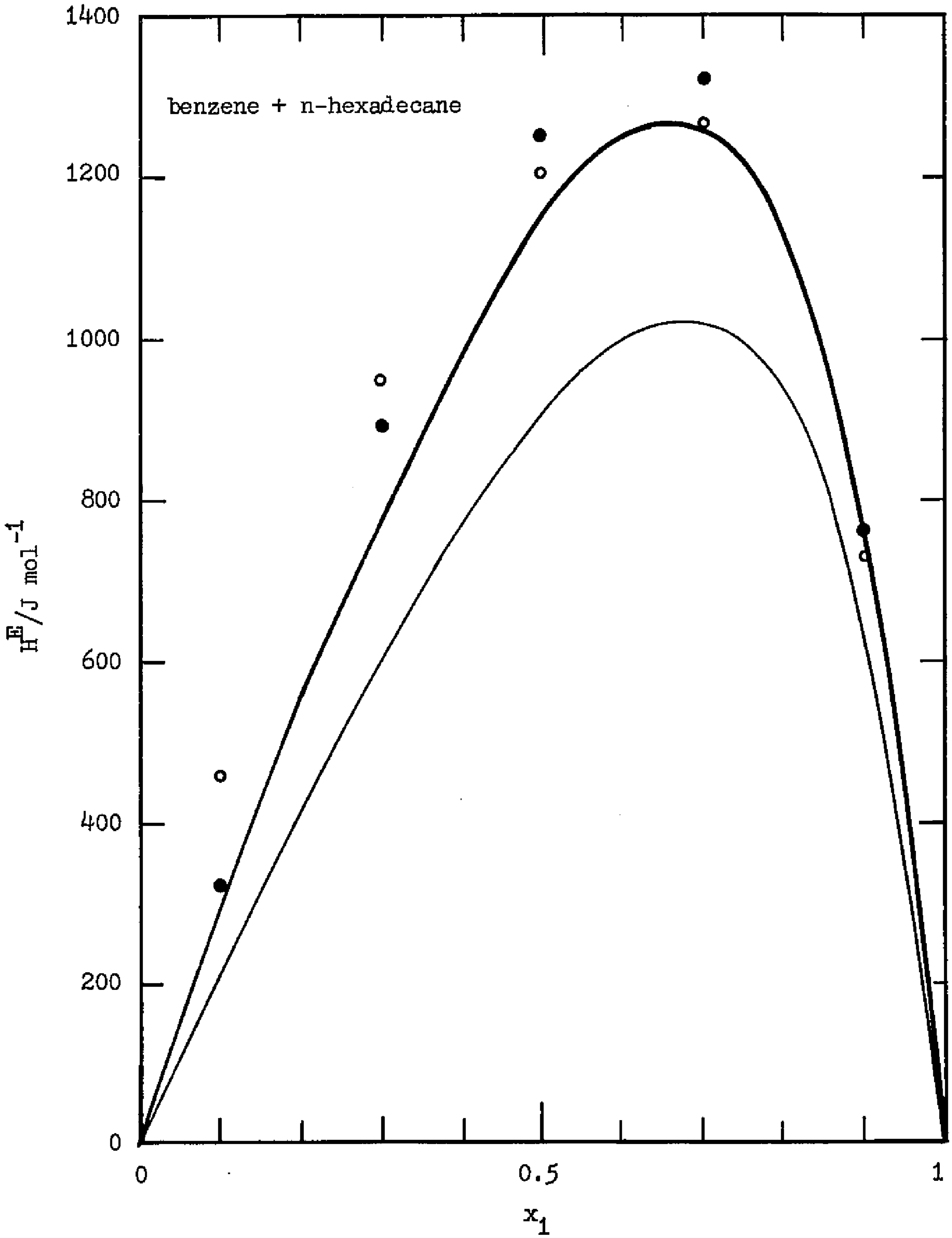

Figure 15. Dependence of the predicted excess enthalpy on composition for benzene + n-hexadecane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; o: smoothed experimental data, Diaz-Peña and Menduiña (223); ●: smoothed experimental data, Lundberg (204).

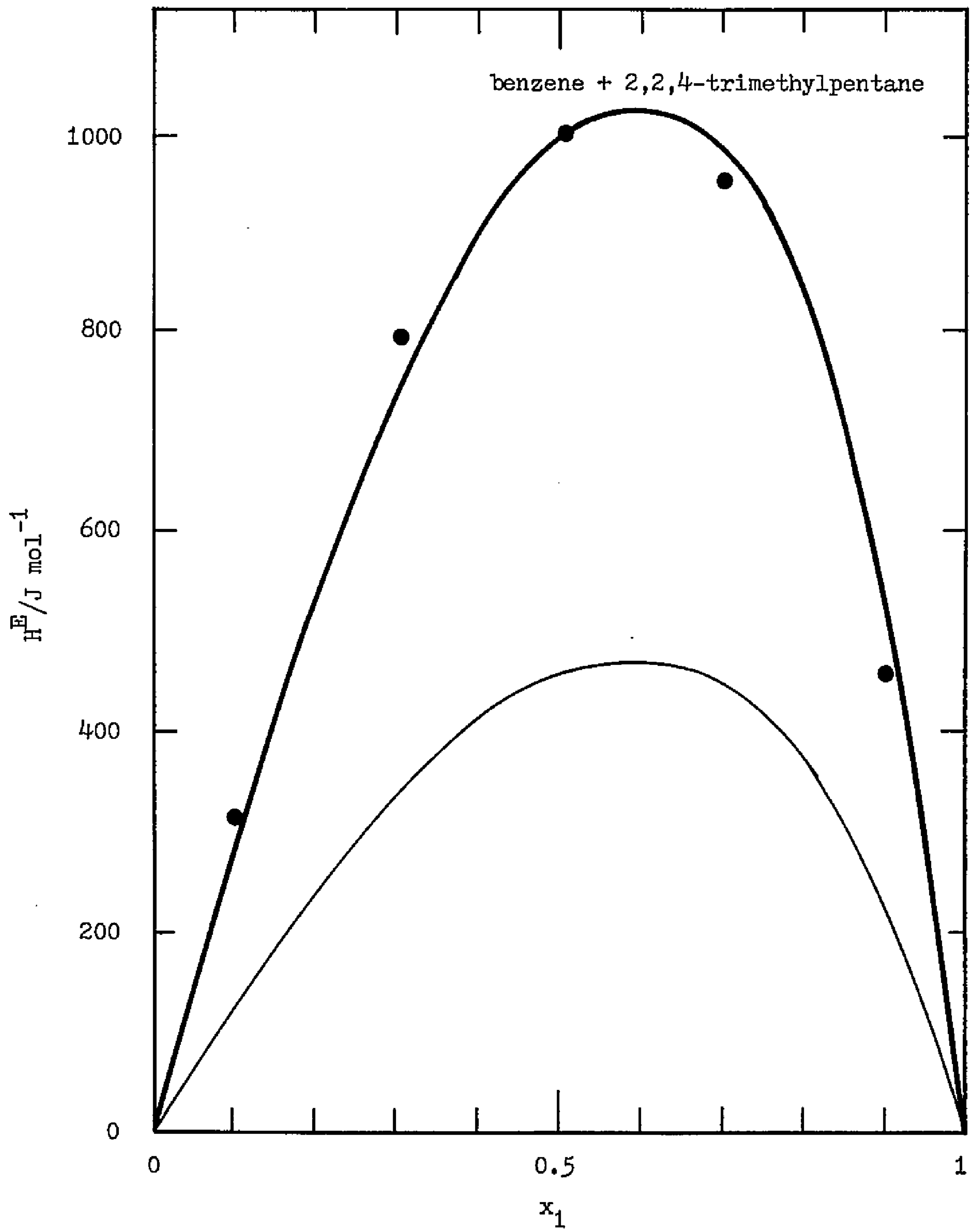

Figure 16. Dependence of the predicted excess enthalpy on composition for benzene + 2,2,4-trimethylpentane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

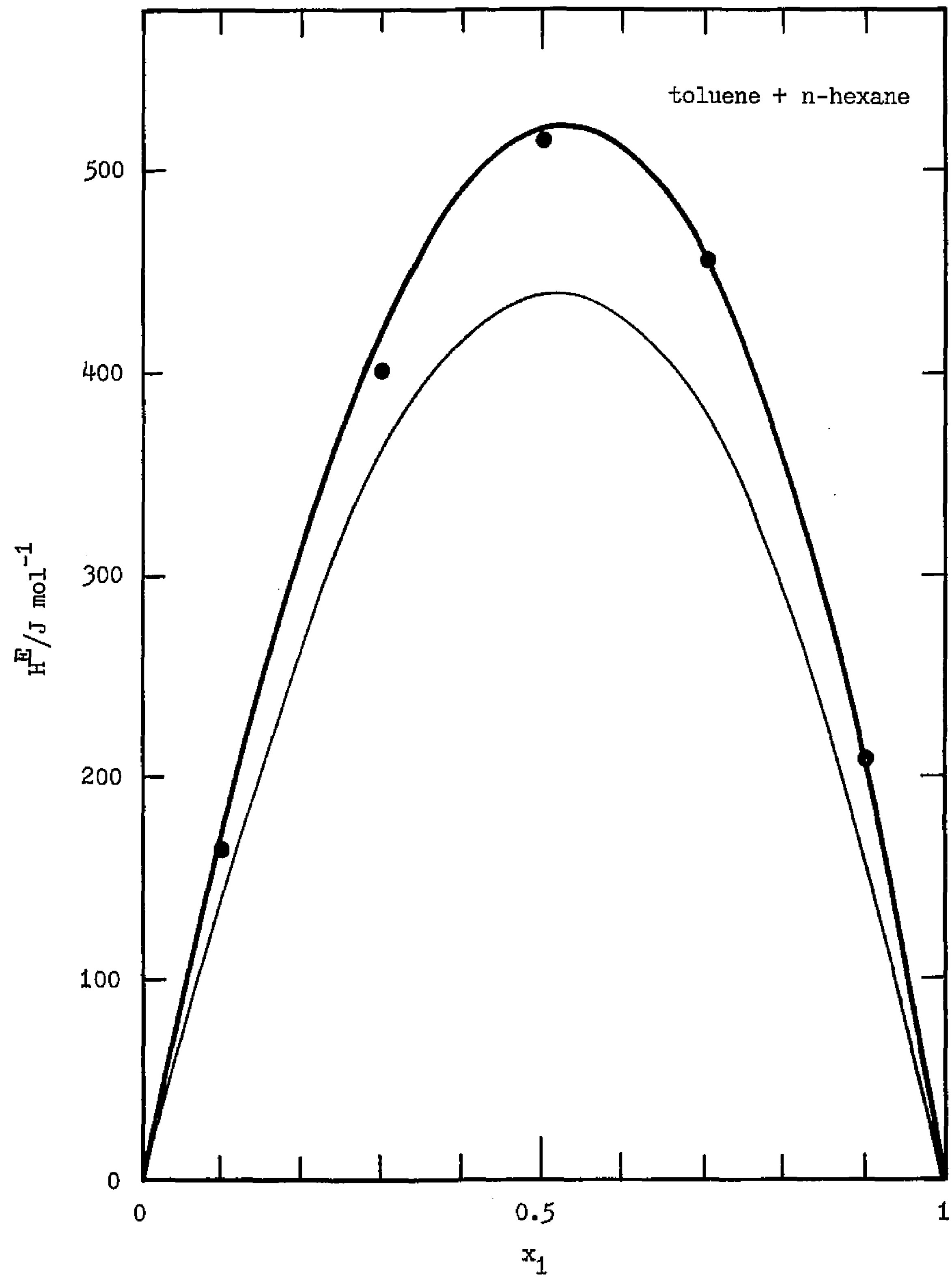

Figure 17. Dependence of the predicted excess enthalpy on composition for toluene + n-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

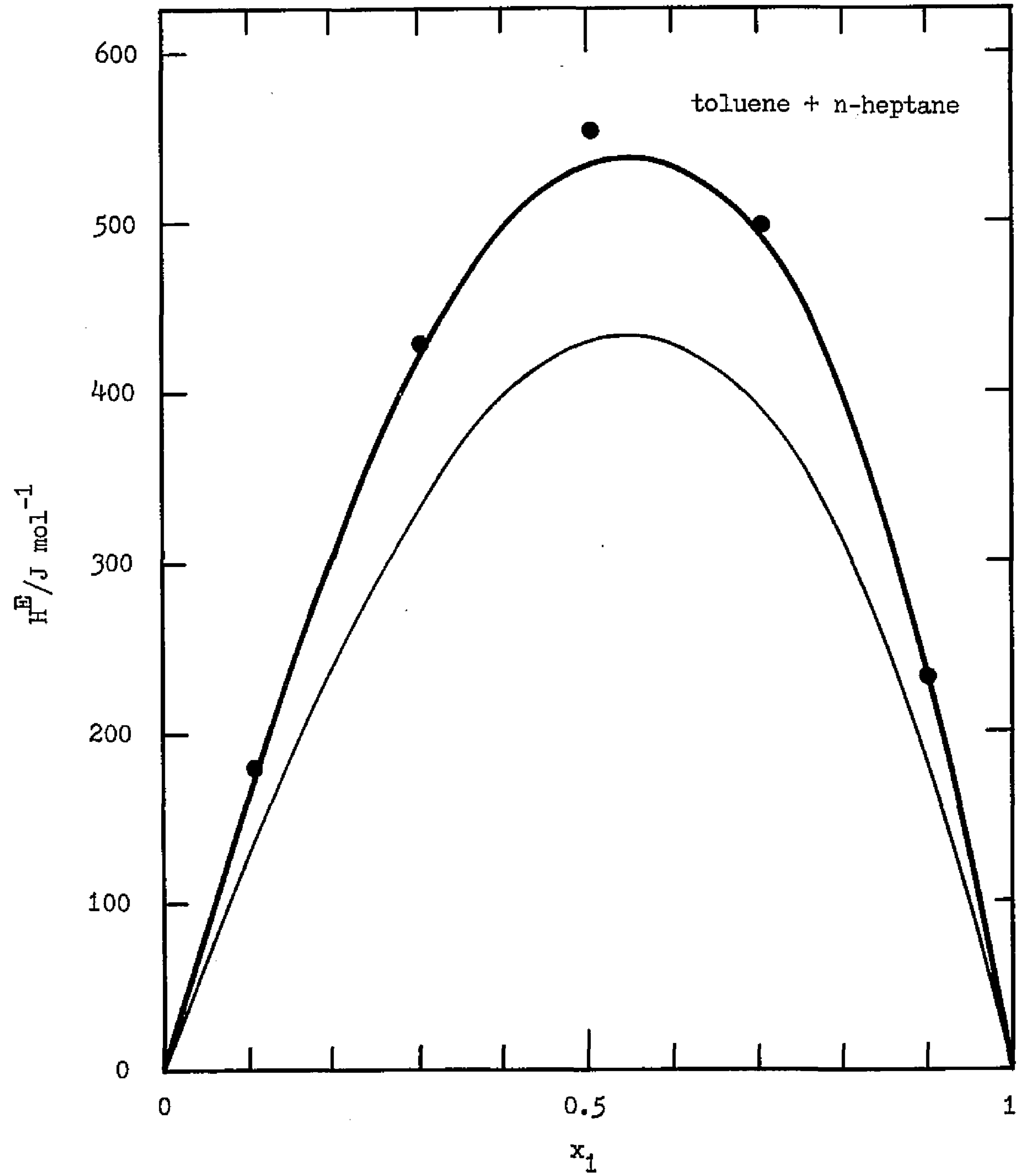

Figure 18. Dependence of the predicted excess enthalpy on composition for toluene + n-heptane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

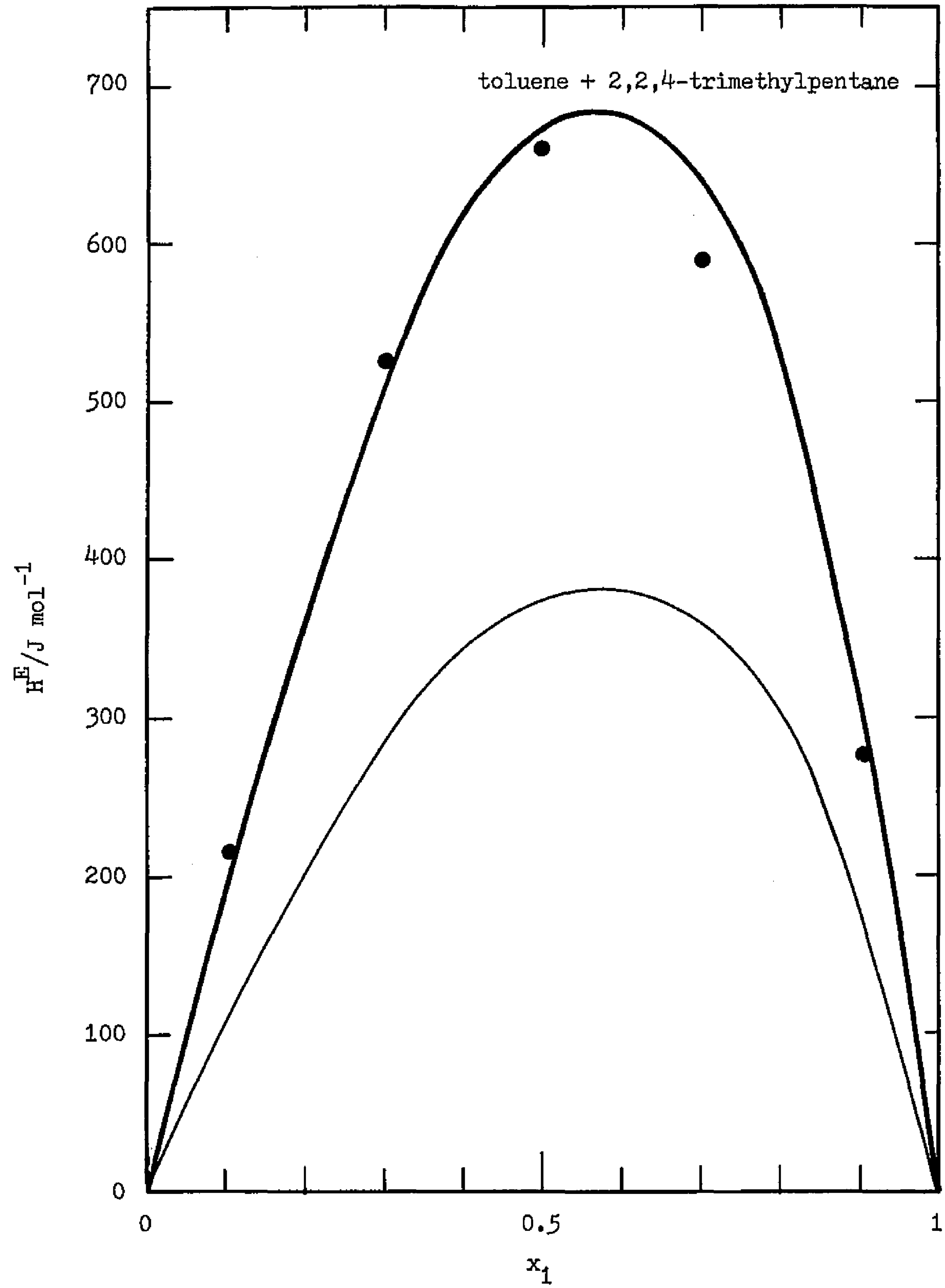

Figure 19. Dependence of the predicted excess enthalpy on composition for toluene + 2,2,4-trimethylpentane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

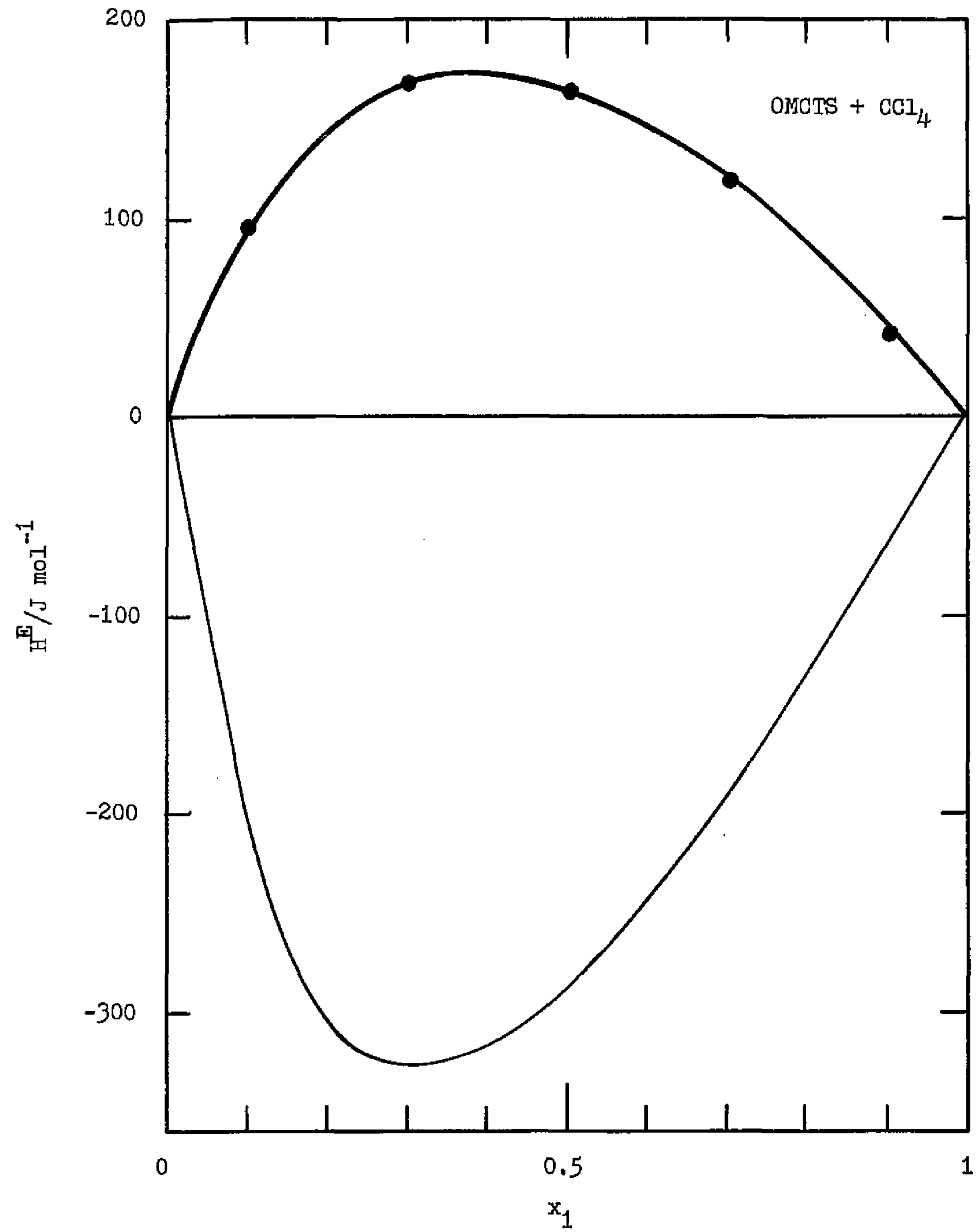

Figure 20. Dependence of the predicted excess enthalpy on composition for octamethylcyclotetrasiloxane + CCl_4 mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

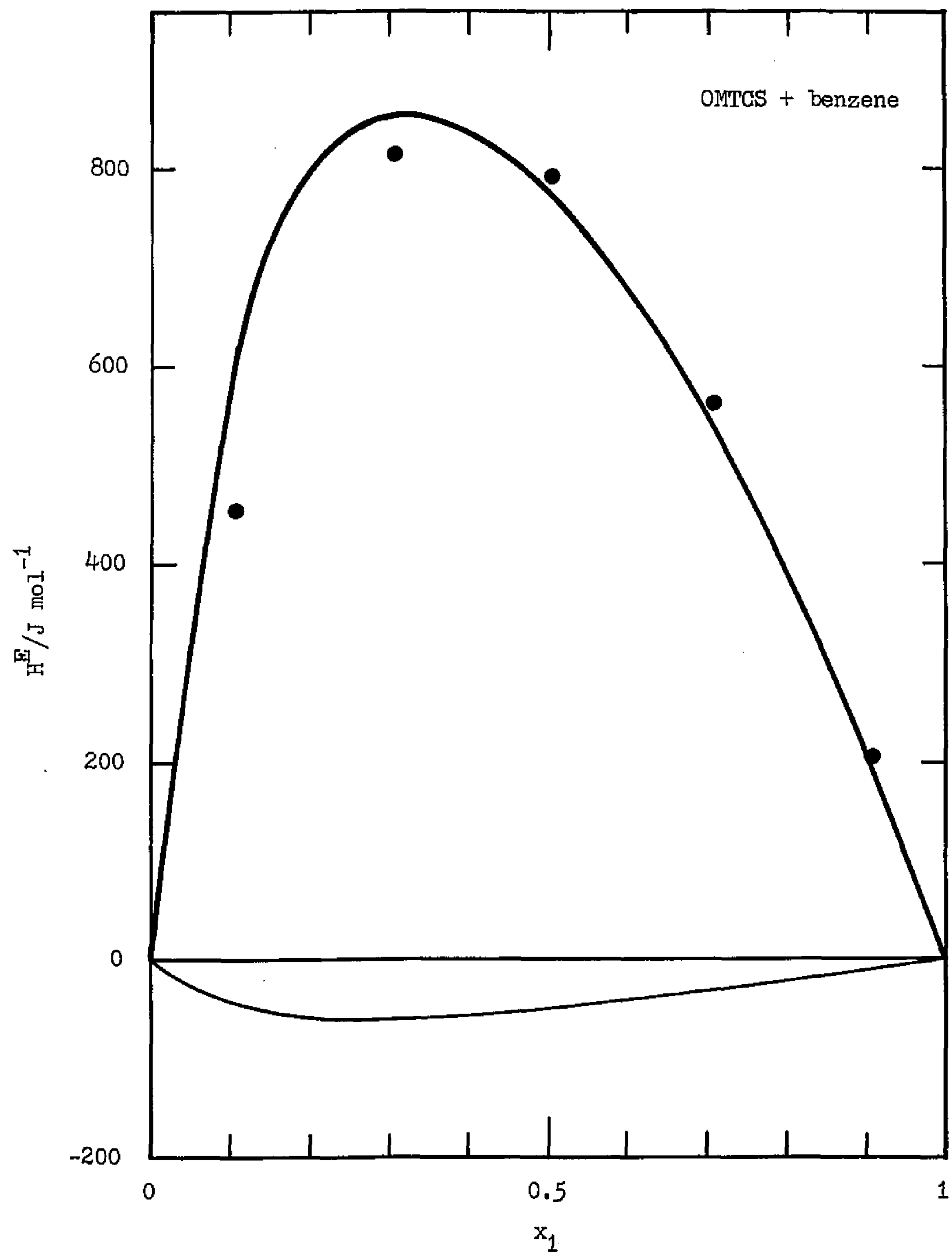

Figure 21. Dependence of the predicted excess enthalpy on composition for octamethylcyclotetrasiloxane + benzene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

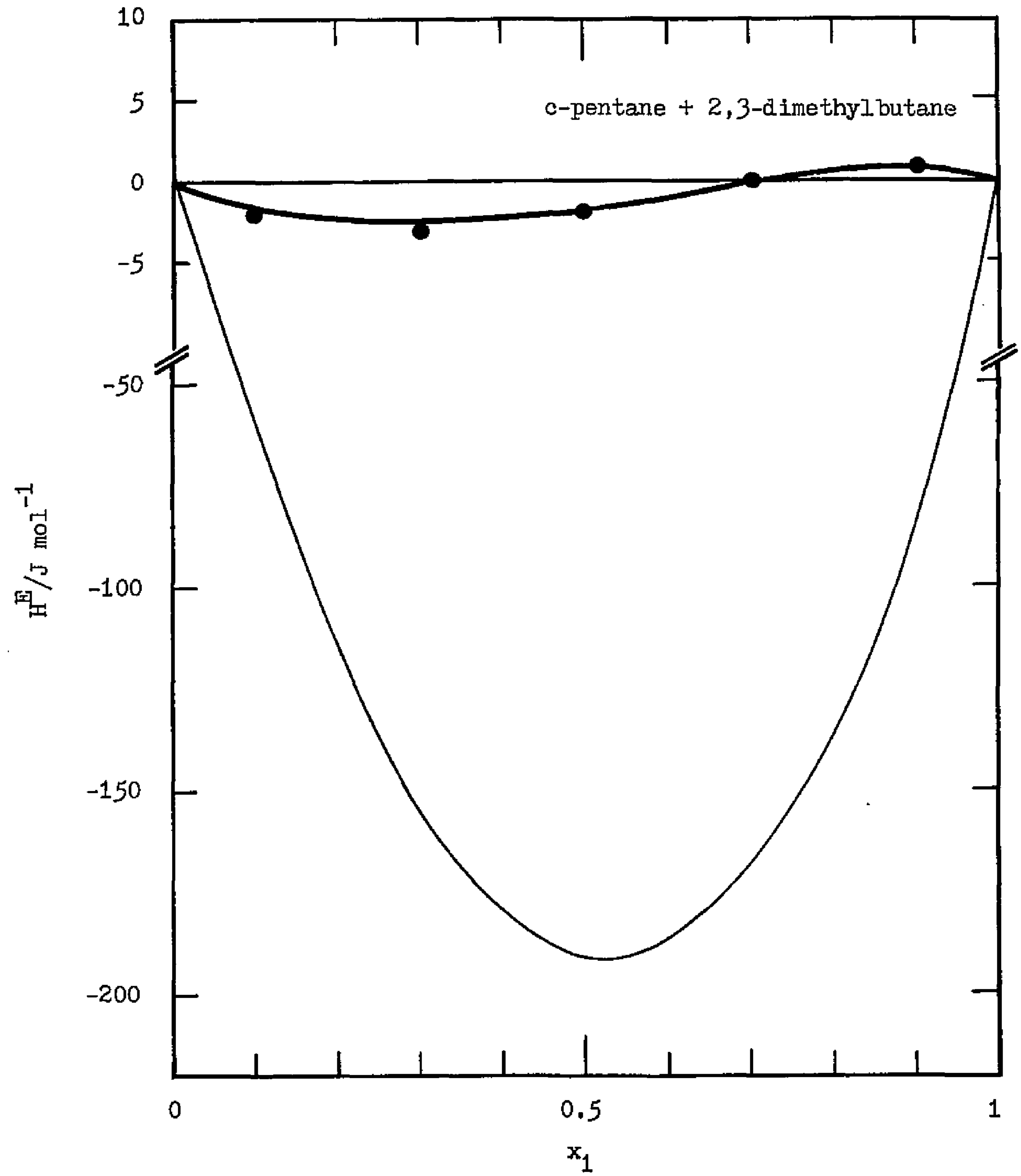

Figure 22. Dependence of the predicted excess enthalpy on composition for c-pentane + 2,3-dimethylbutane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

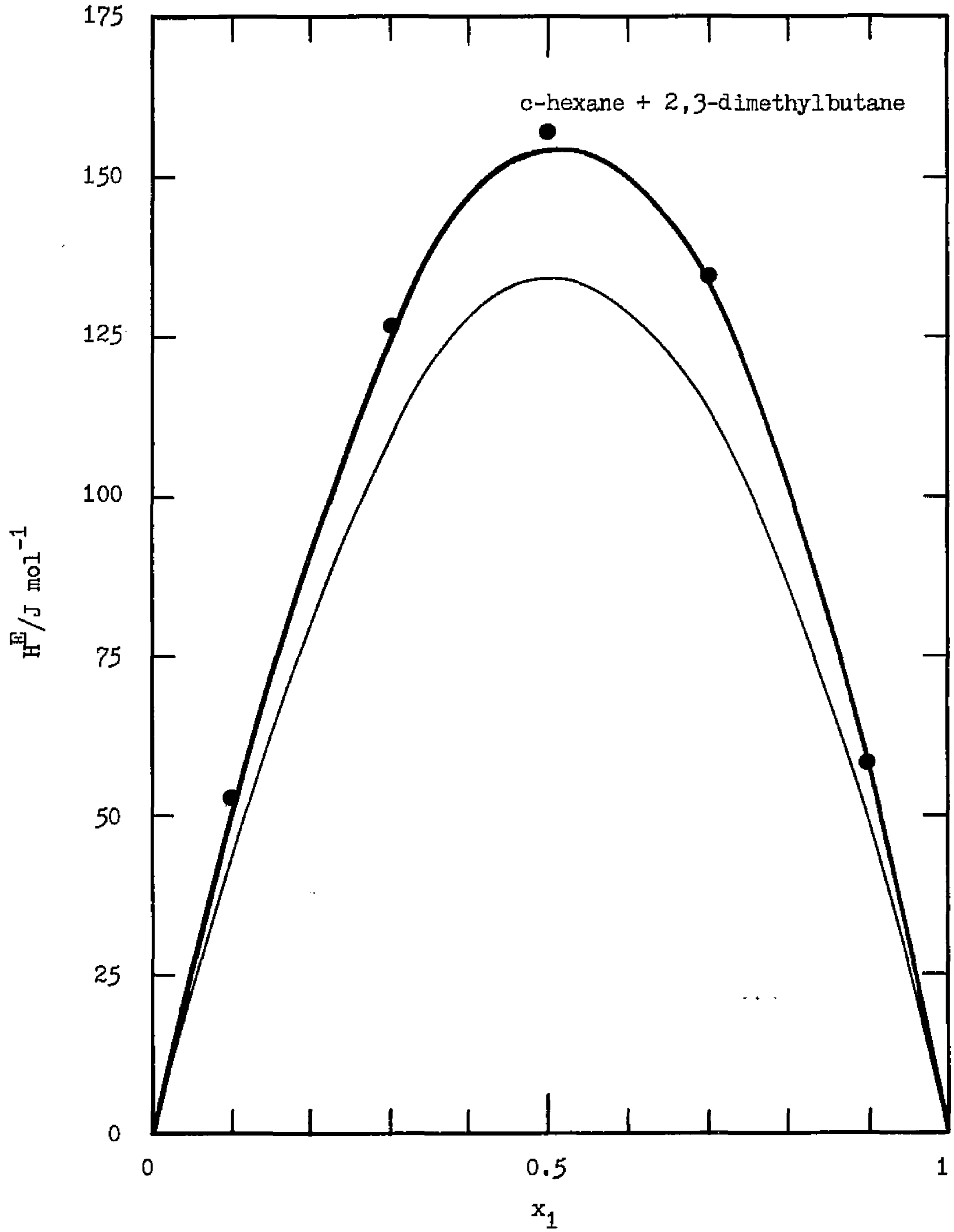

Figure 23. Dependence of the predicted excess enthalpy on composition for c-hexane + 2,3-dimethylbutane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m=1$ predictions; circles: smoothed experimental data.

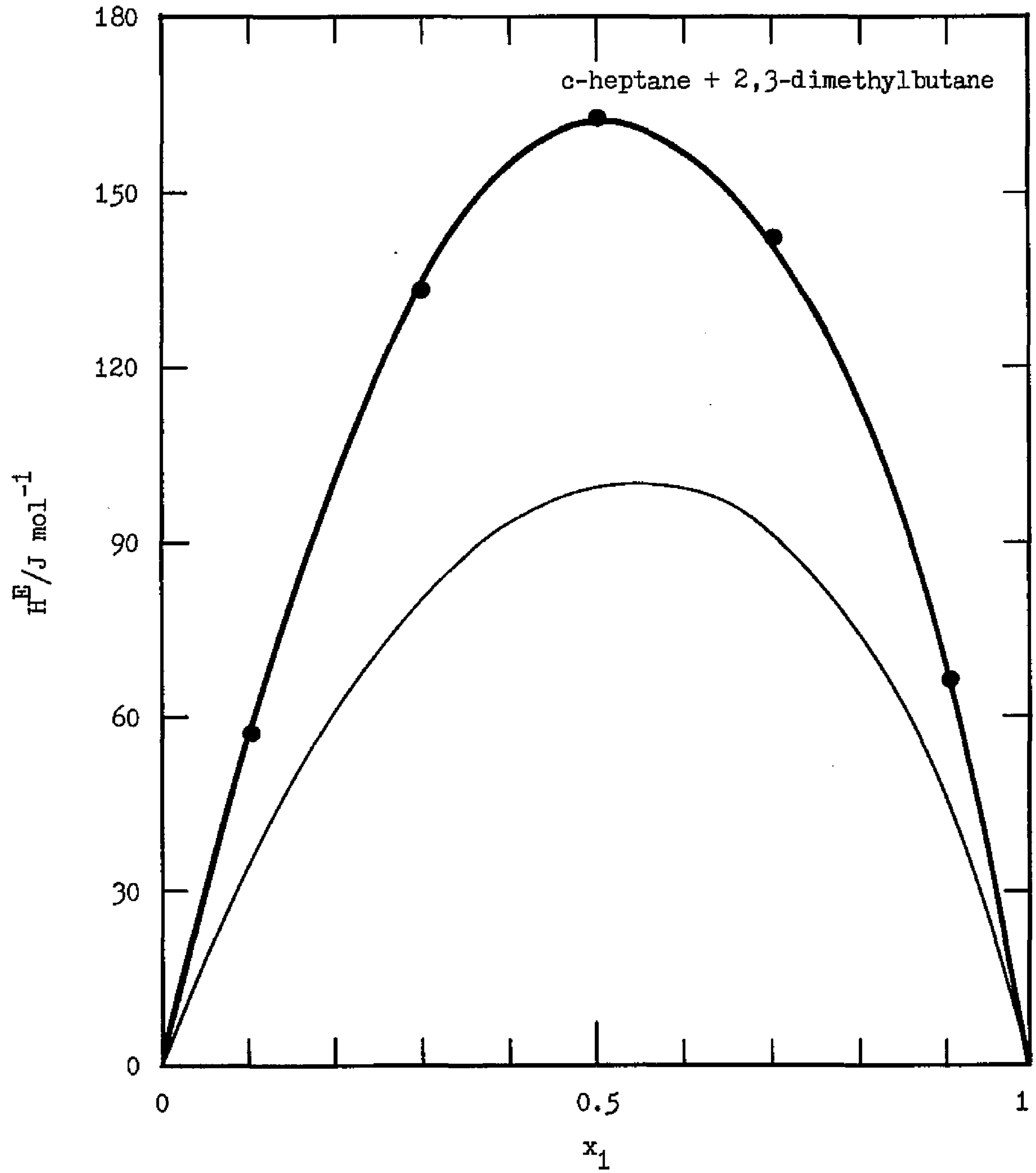

Figure 24. Dependence of the predicted excess enthalpy on composition for c-heptane + 2,3-dimethylbutane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

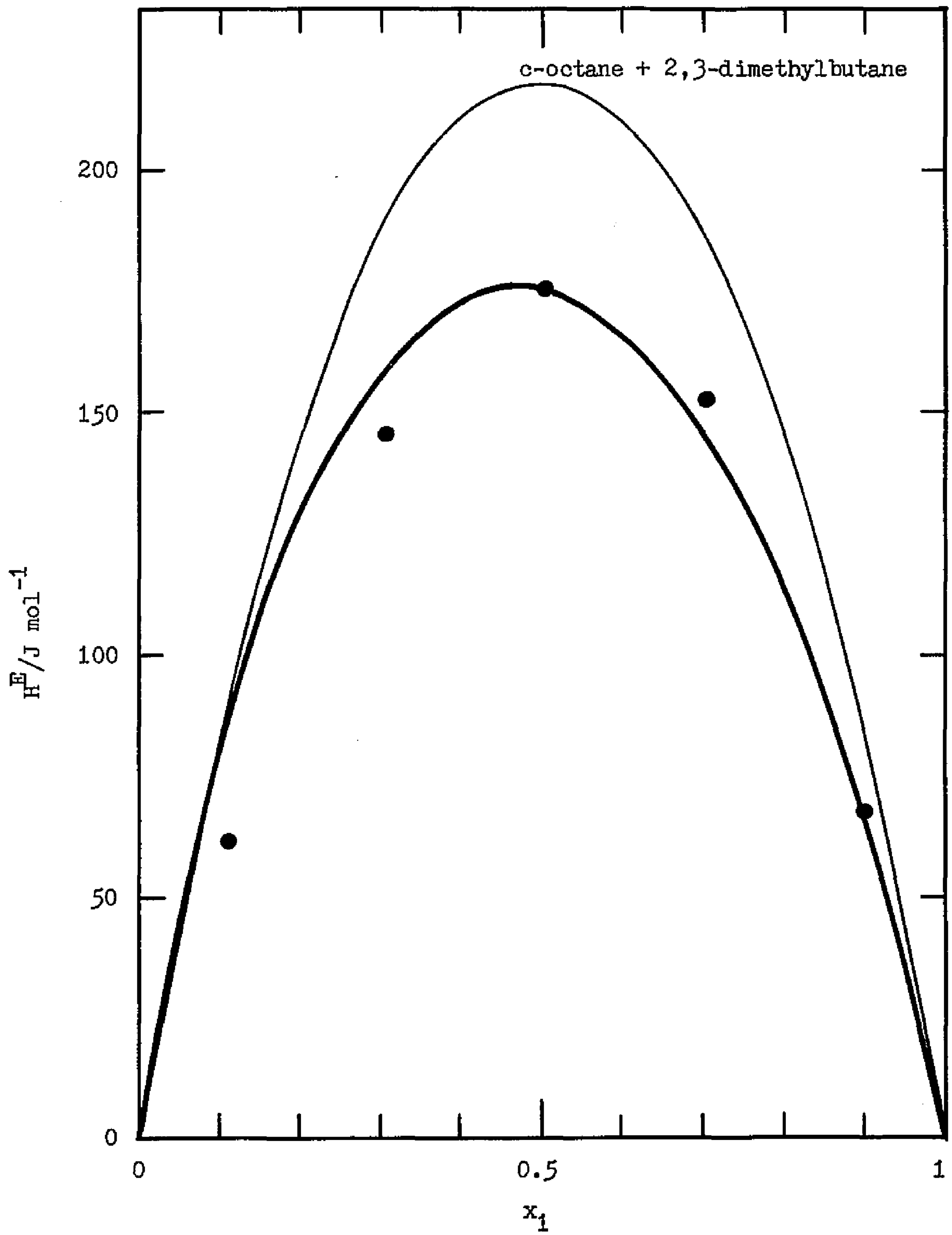

Figure 25. Dependence of the predicted excess enthalpy on composition for c-octane + 2,3-dimethylbutane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

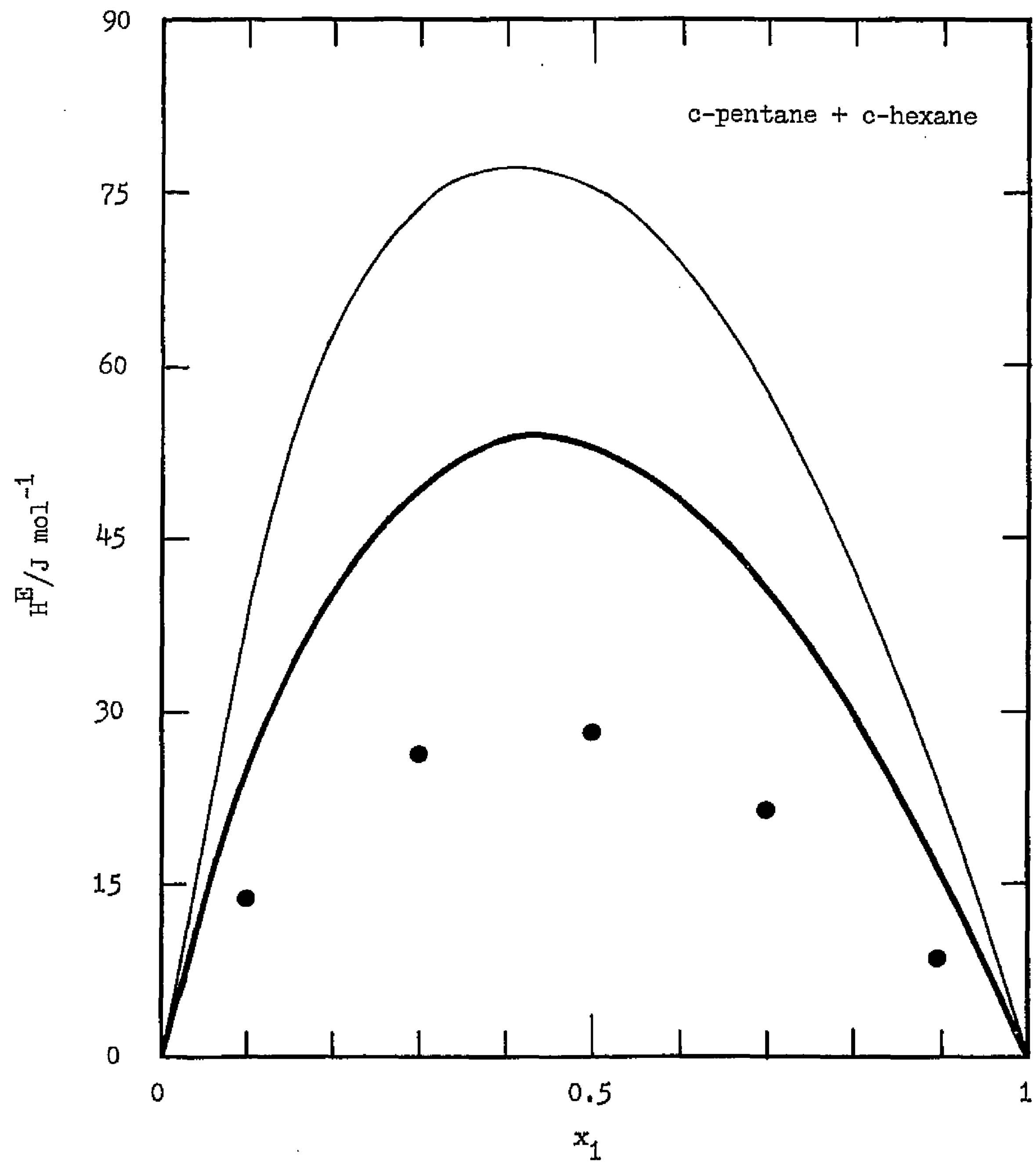

Figure 26. Dependence of the predicted excess enthalpy on composition for c-pentane + c-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

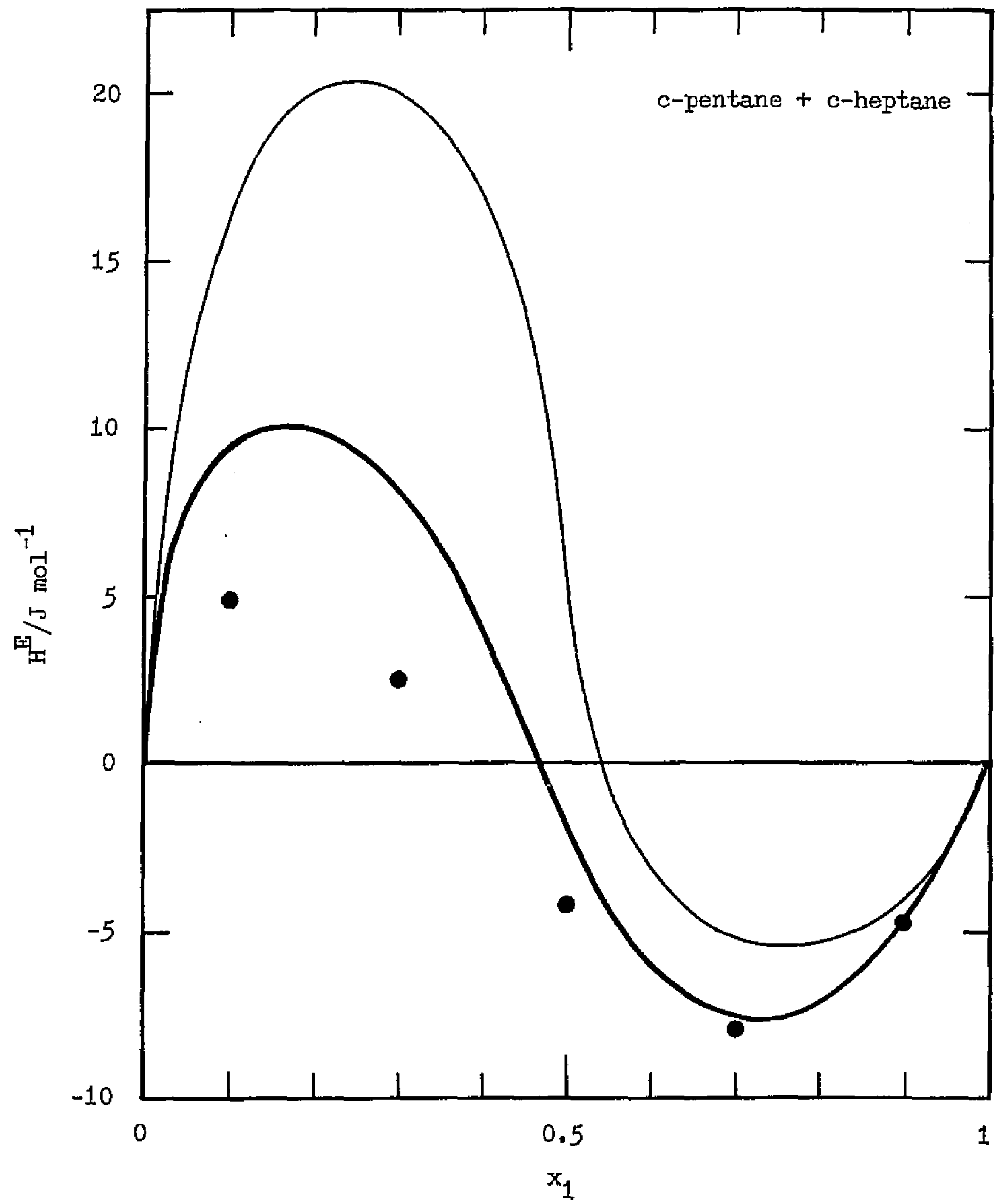

Figure 27. Dependence of the predicted excess enthalpy on composition for c-pentane + c-heptane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

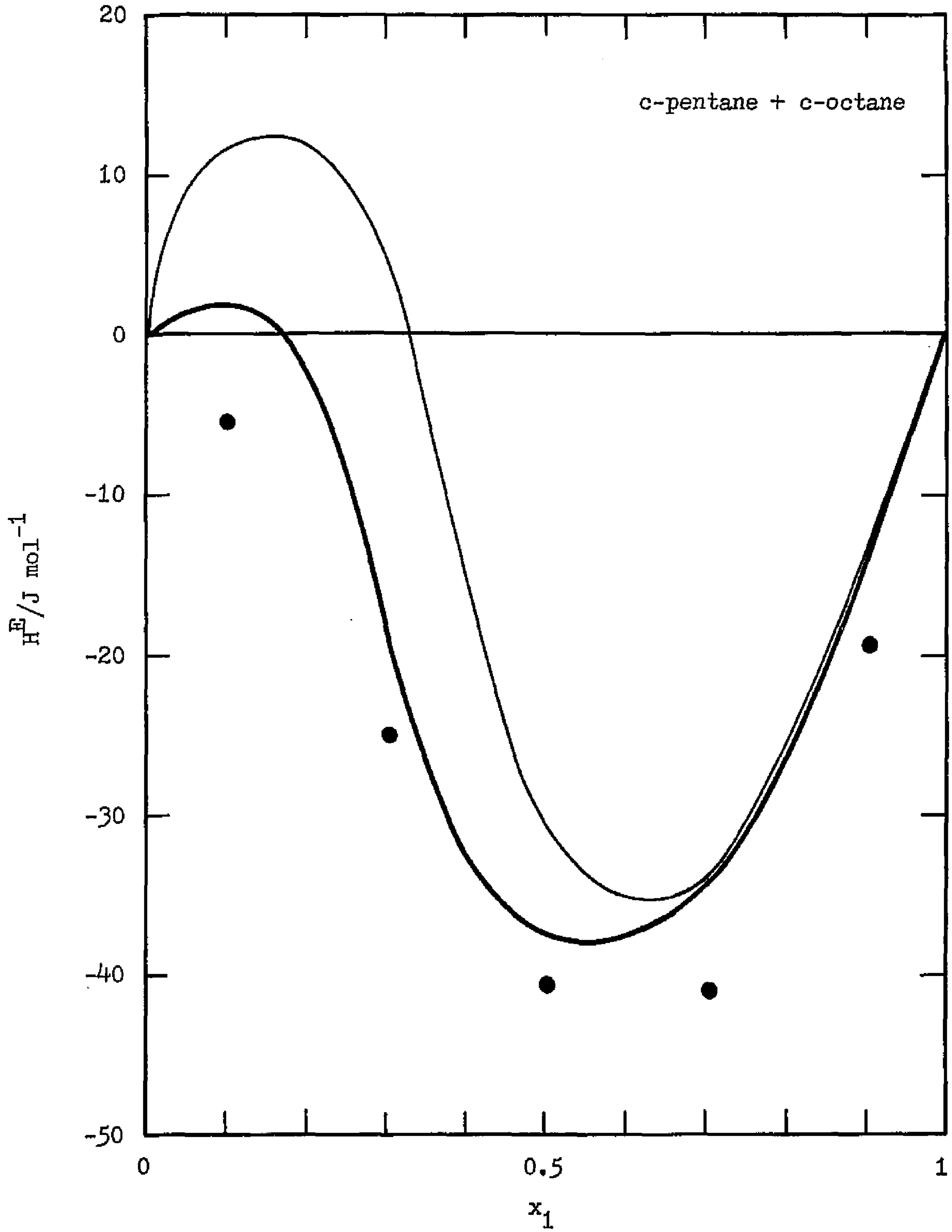

Figure 28. Dependence of the predicted excess enthalpy on composition for c-pentane + c-octane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

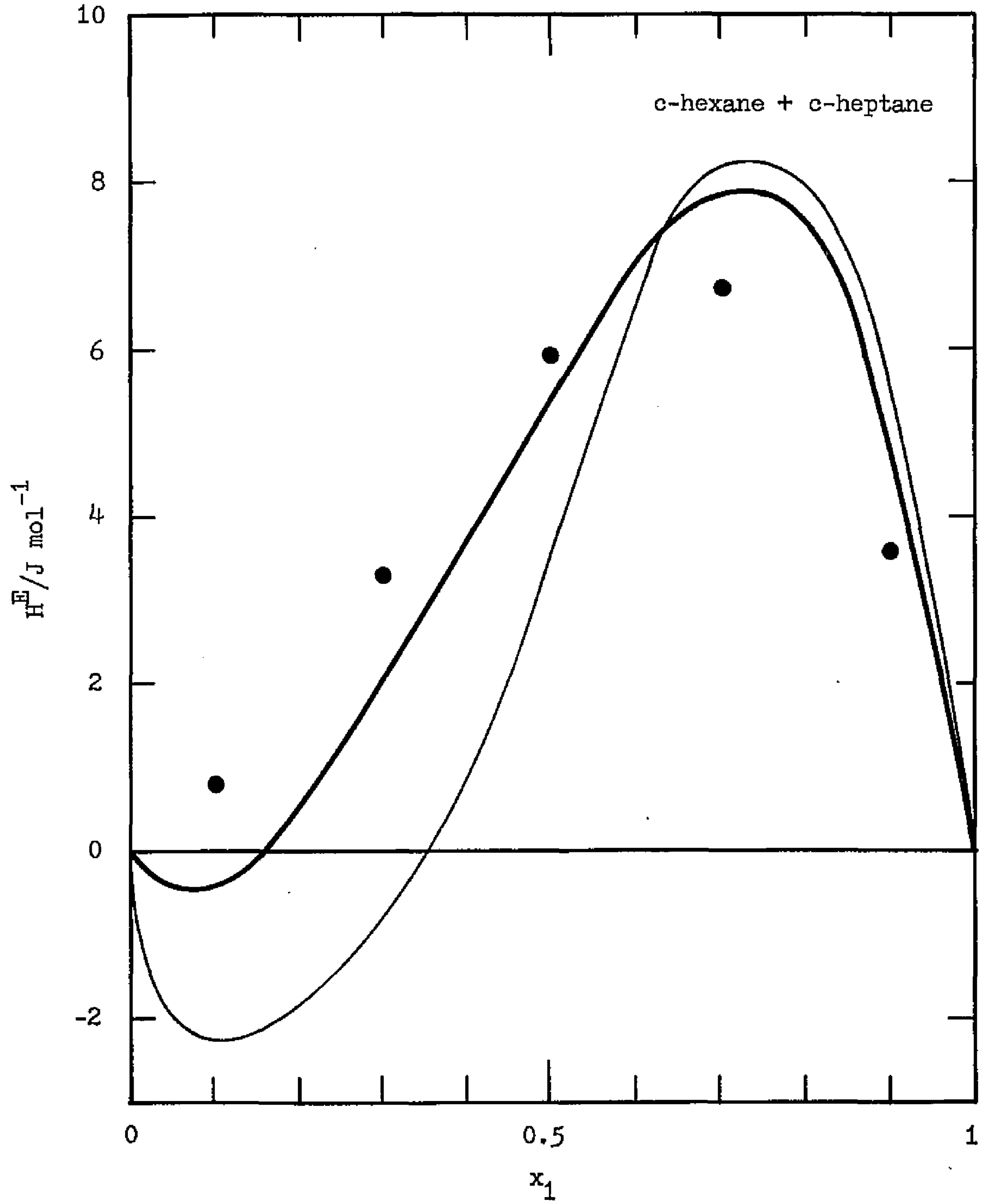

Figure 29. Dependence of the predicted excess enthalpy of composition for c-hexane + c-heptane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

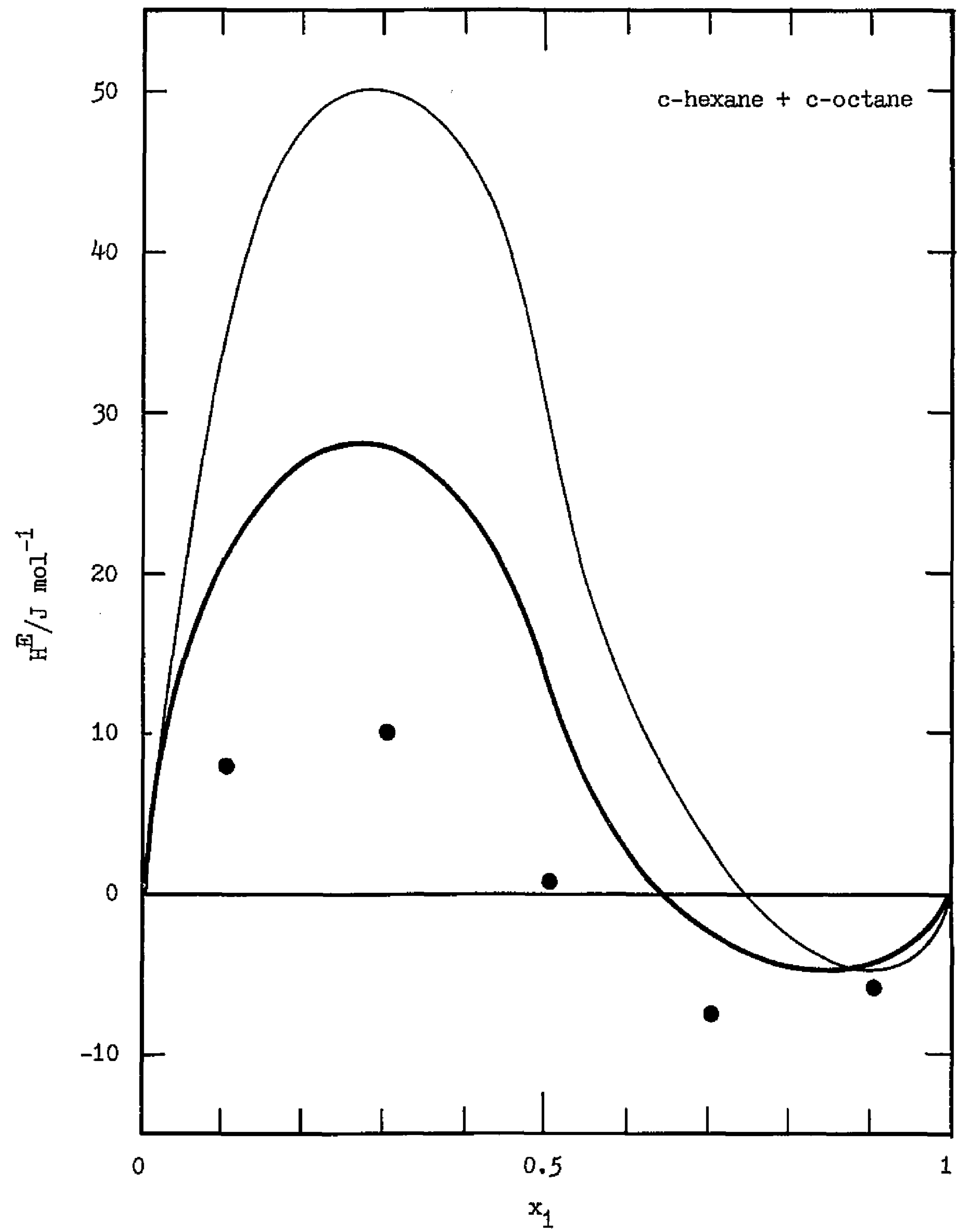

Figure 30. Dependence of the predicted excess enthalpy on composition for c-hexane + c-octane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

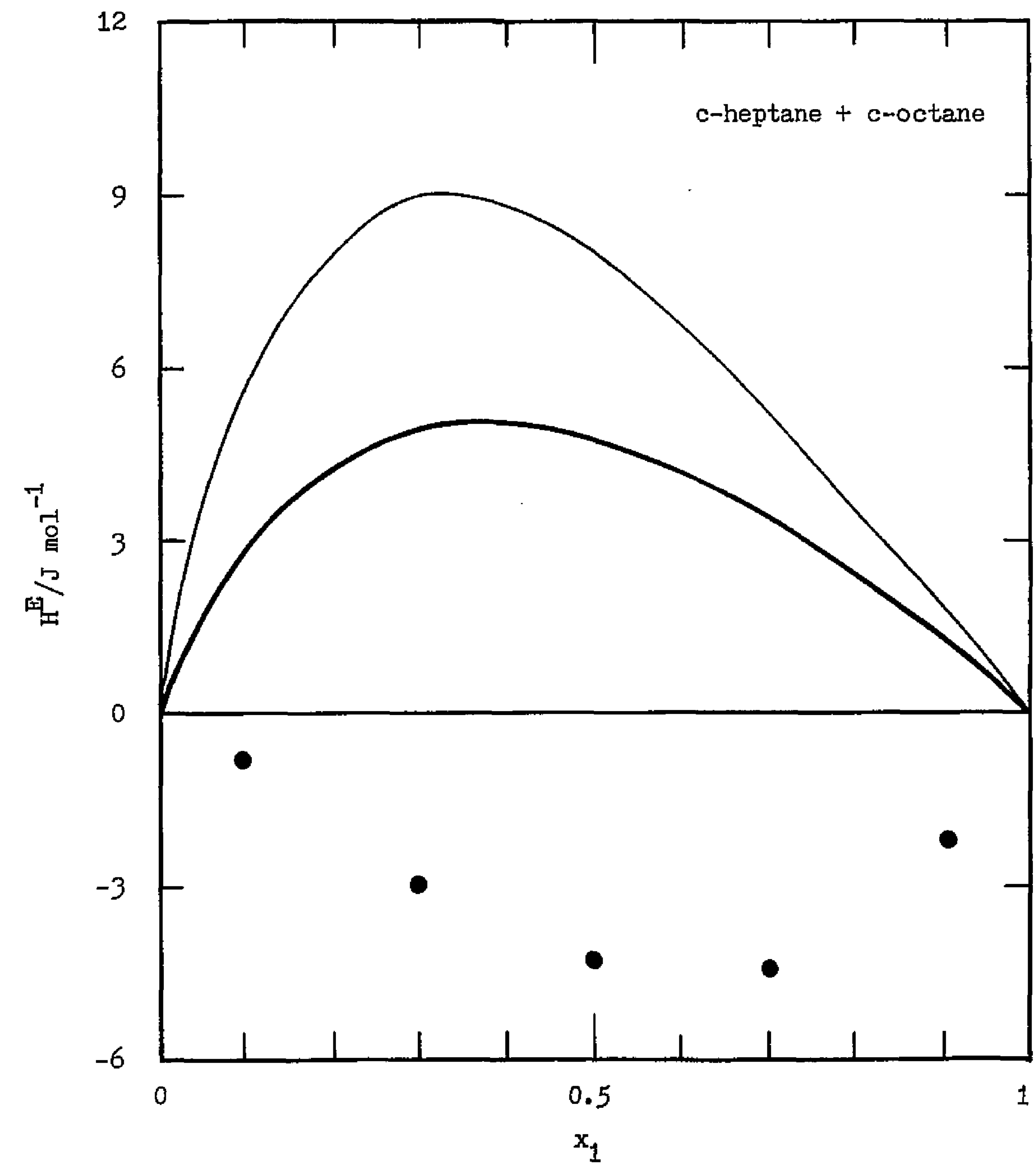

Figure 31. Dependence of the predicted excess enthalpy on composition for c-heptane + c-octane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

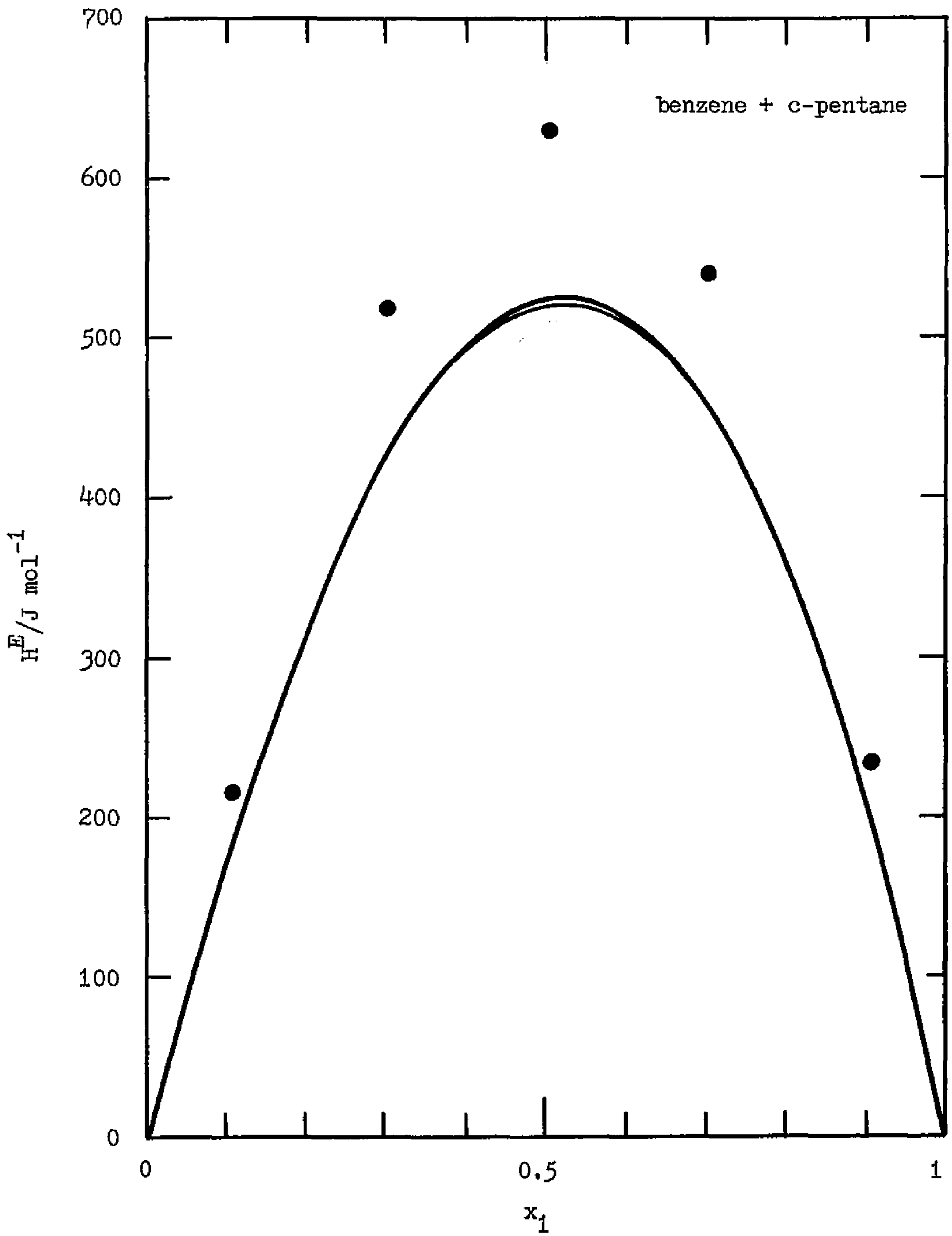

Figure 32. Dependence of the predicted excess enthalpy on composition for benzene + c-pentane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

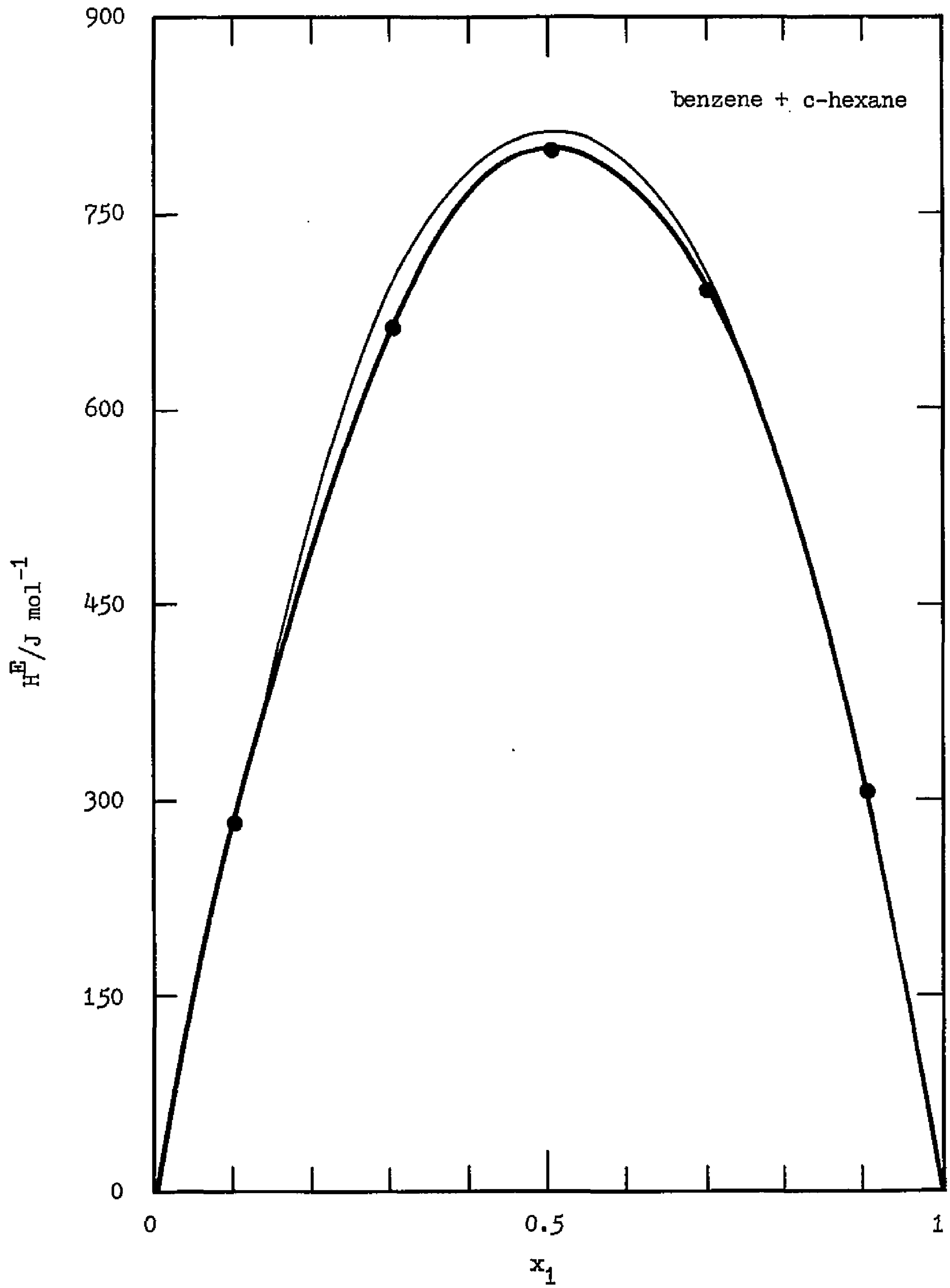

Figure 33. Dependence of the predicted excess enthalpy on composition for benzene + c-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

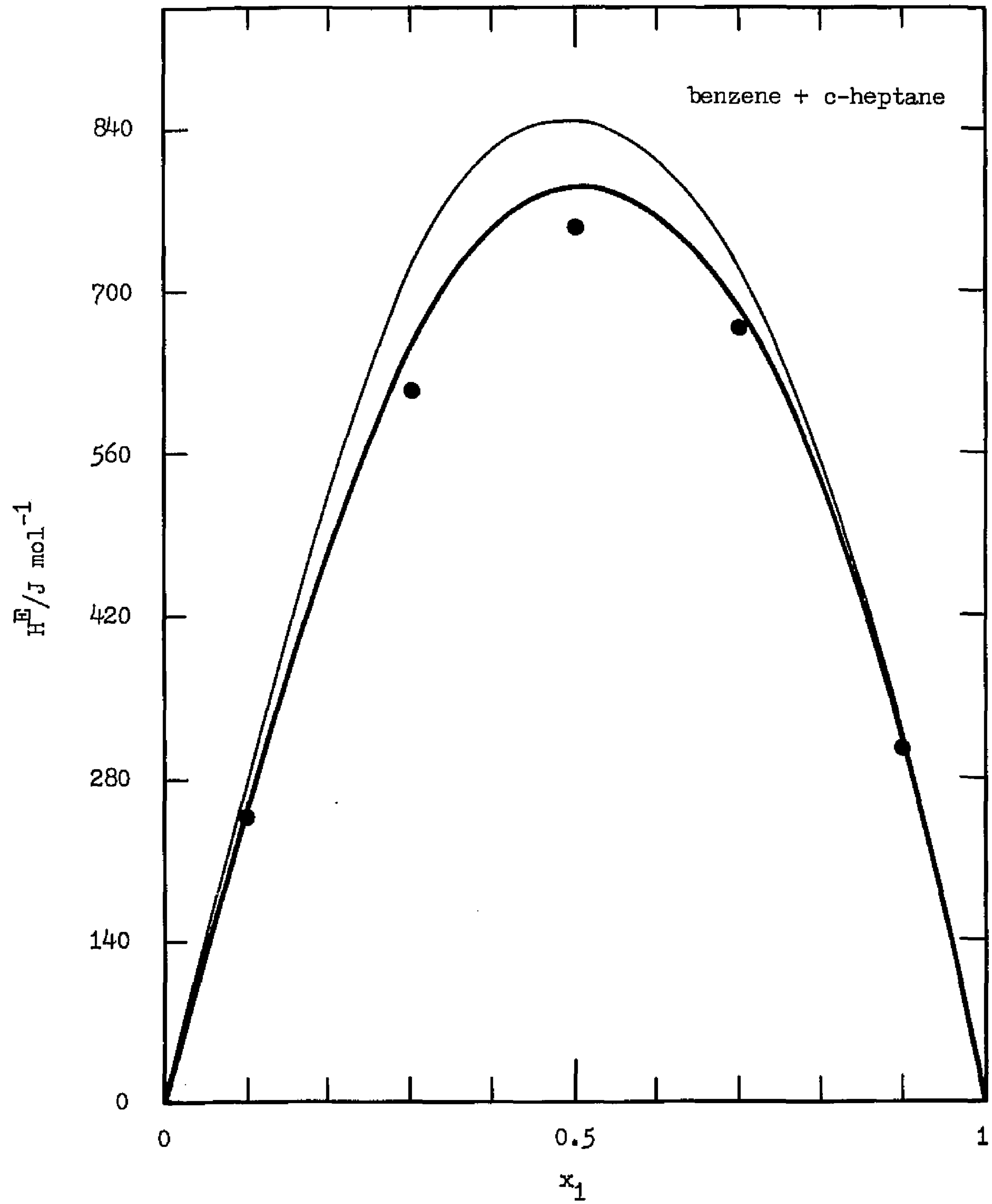

Figure 34. Dependence of the predicted excess enthalpy on composition for benzene + c-heptane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

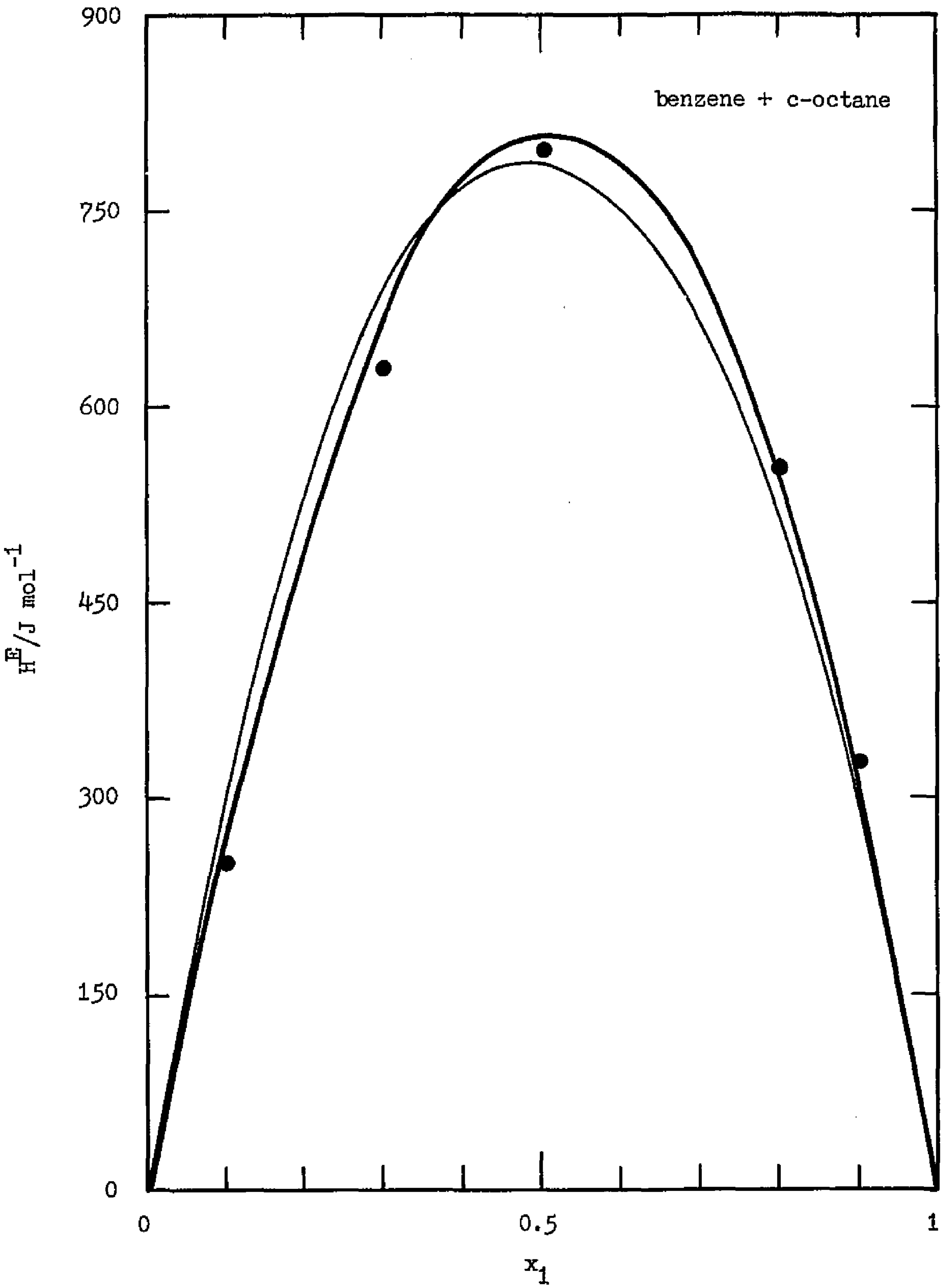

Figure 35. Dependence of the predicted excess enthalpy on composition for benzene + c-octane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

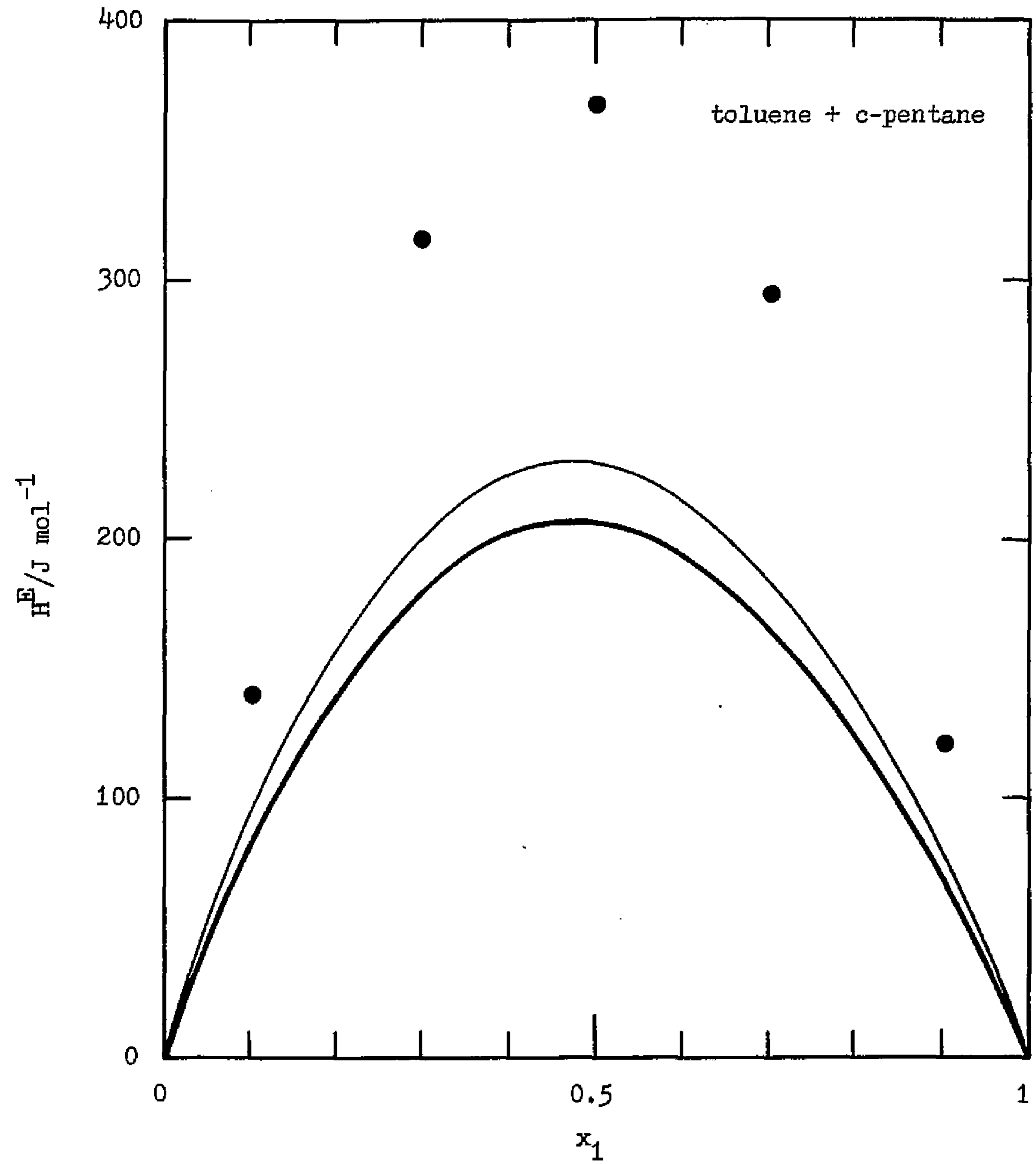

Figure 36. Dependence of the predicted excess enthalpy on composition for toluene + c-pentane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

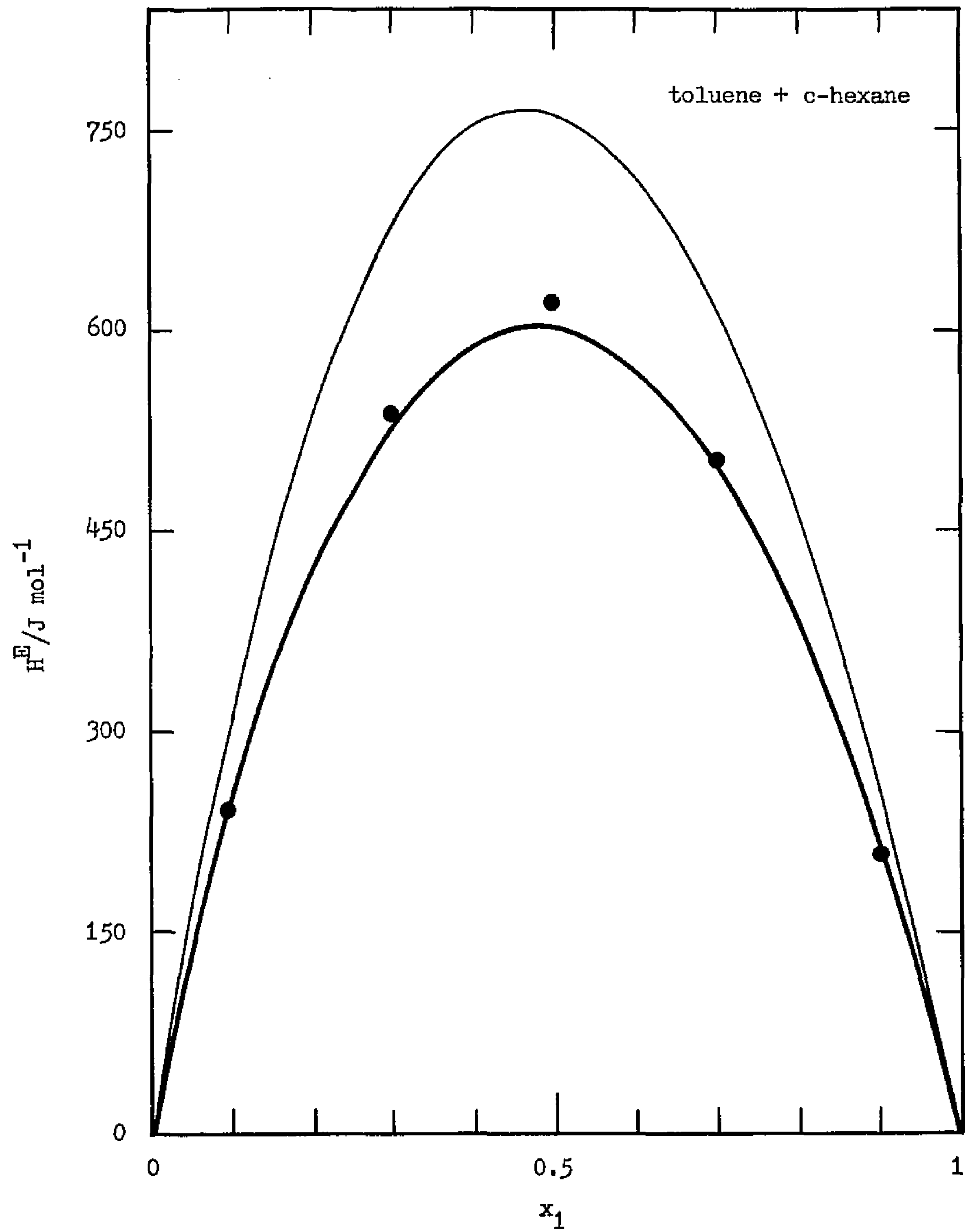

Figure 37. Dependence of the predicted excess enthalpy on composition for toluene + c-hexane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

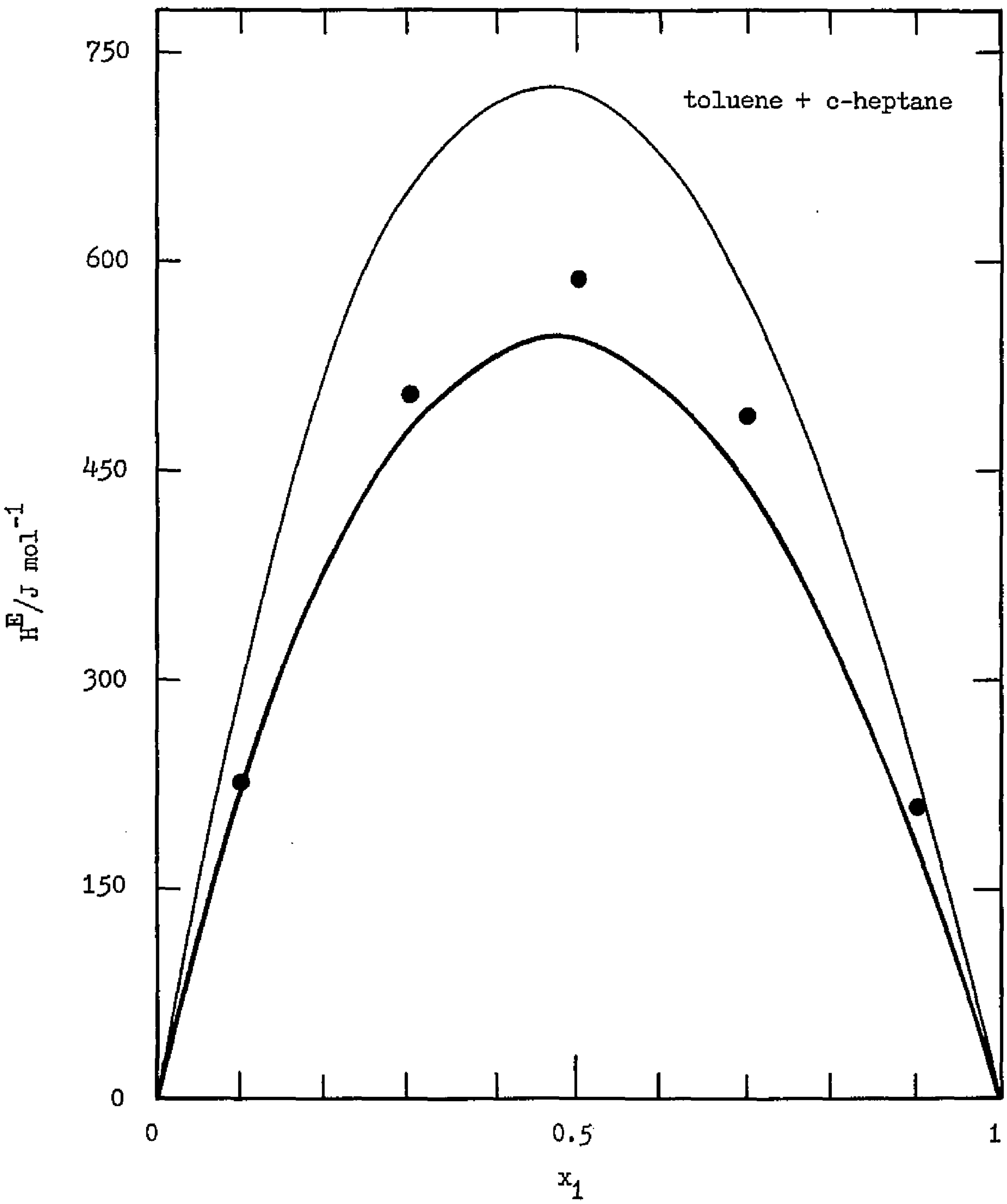

Figure 38. Dependence of the predicted excess enthalpy on composition for toluene + c-heptane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

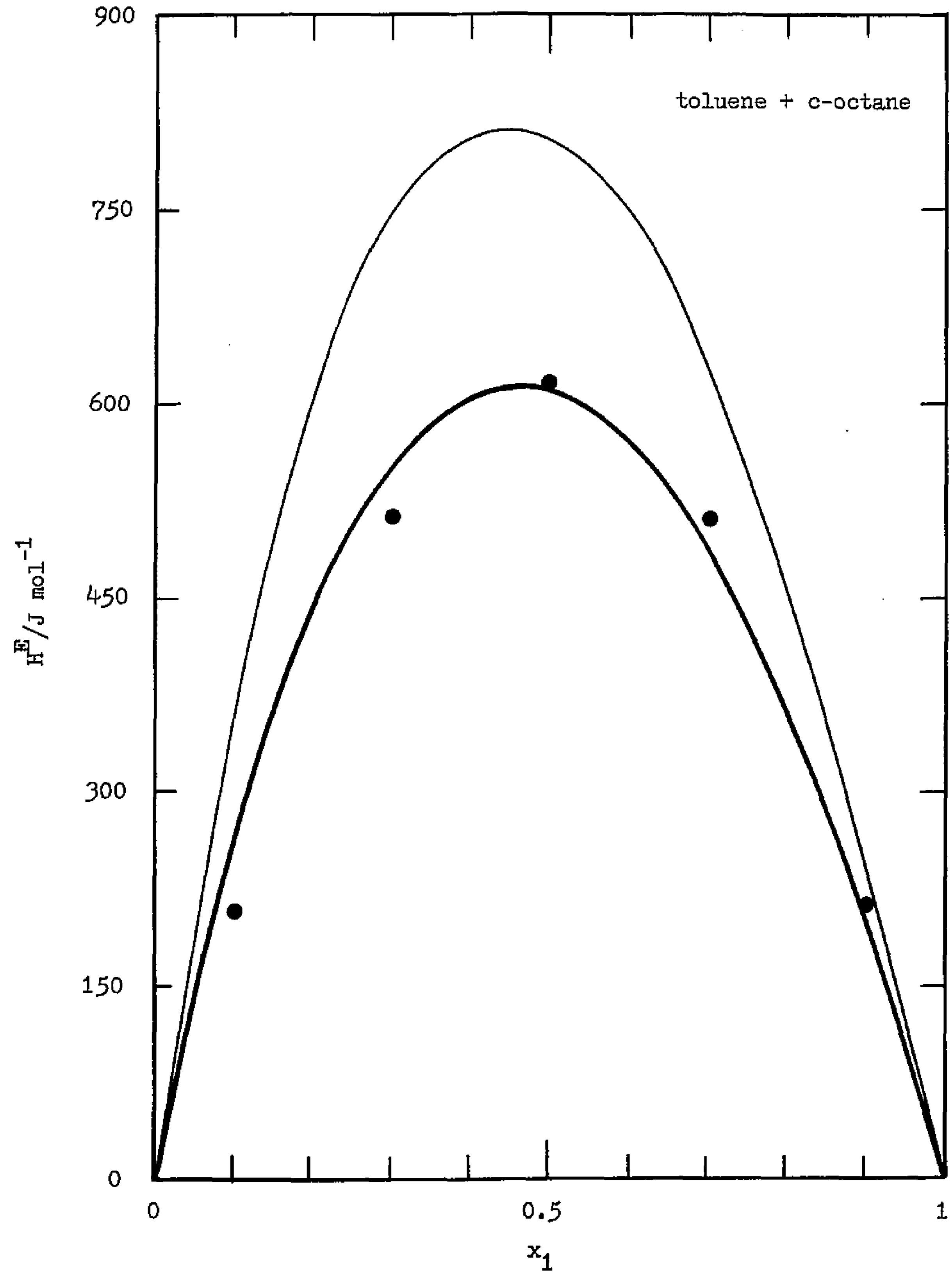

Figure 39. Dependence of the predicted excess enthalpy on composition for toluene + c-octane mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

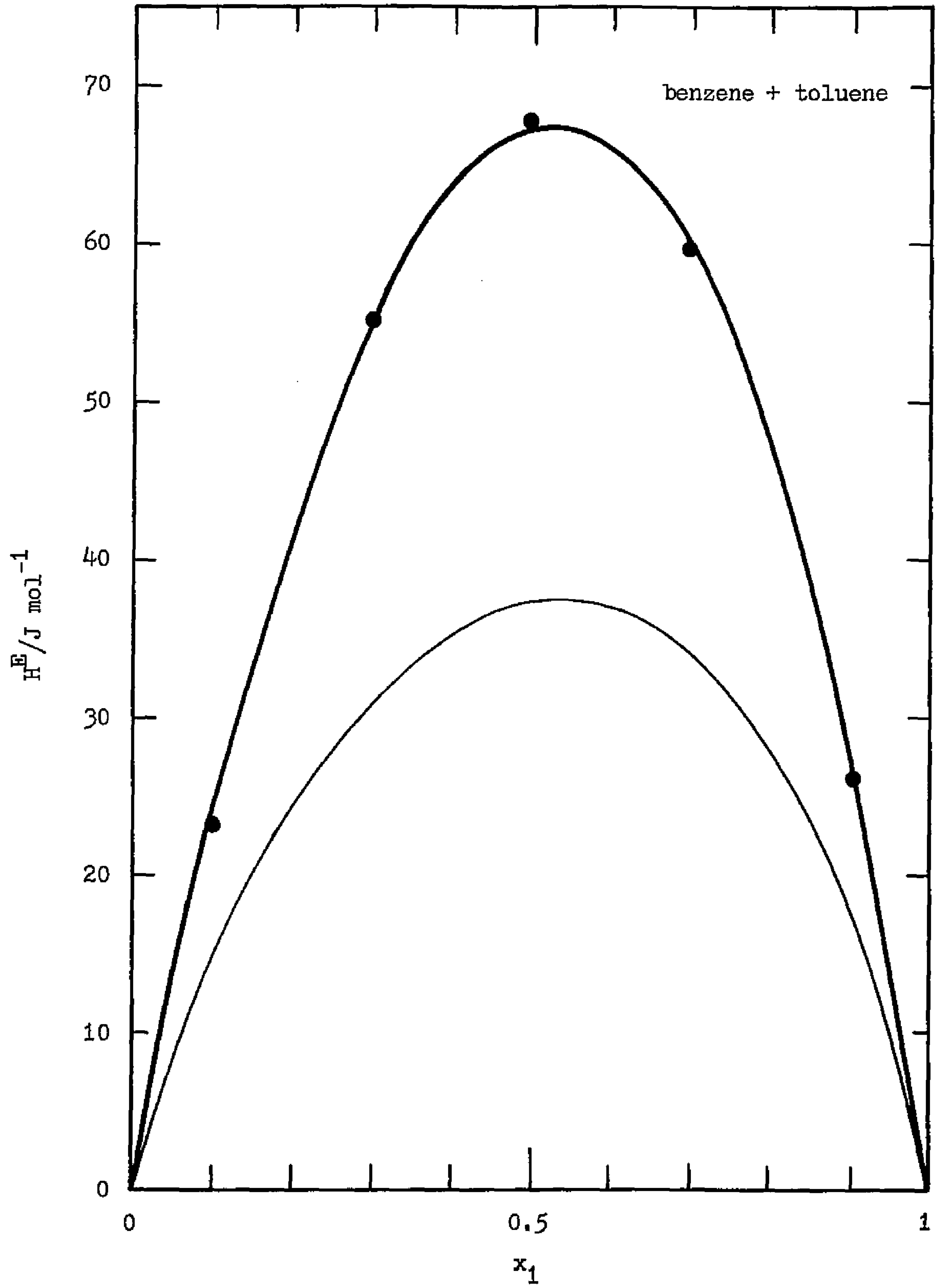

Figure 40. Dependence of the predicted excess enthalpy on composition for toluene + benzene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

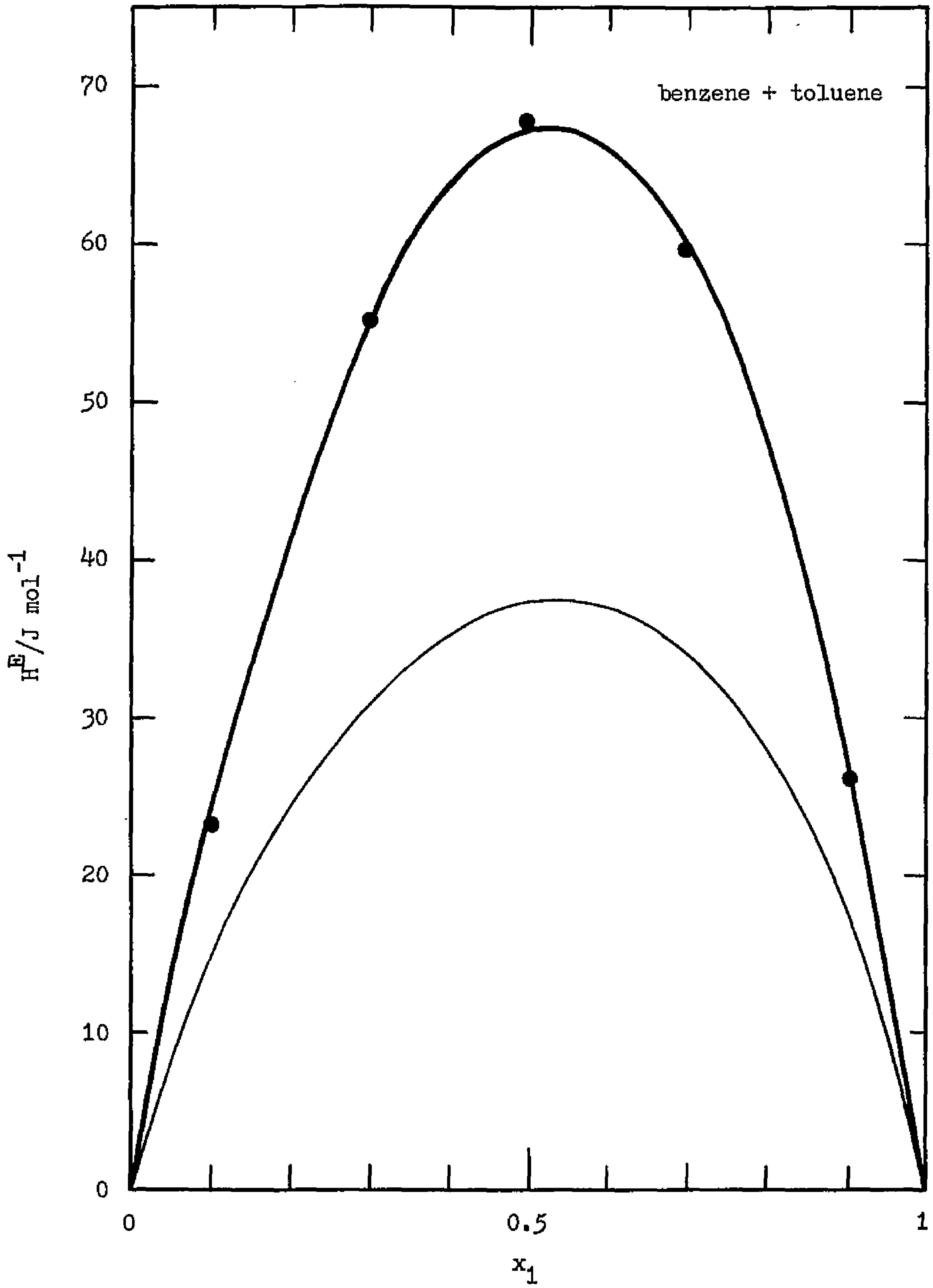

Figure 40. Dependence of the predicted excess enthalpy on composition for toluene + benzene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

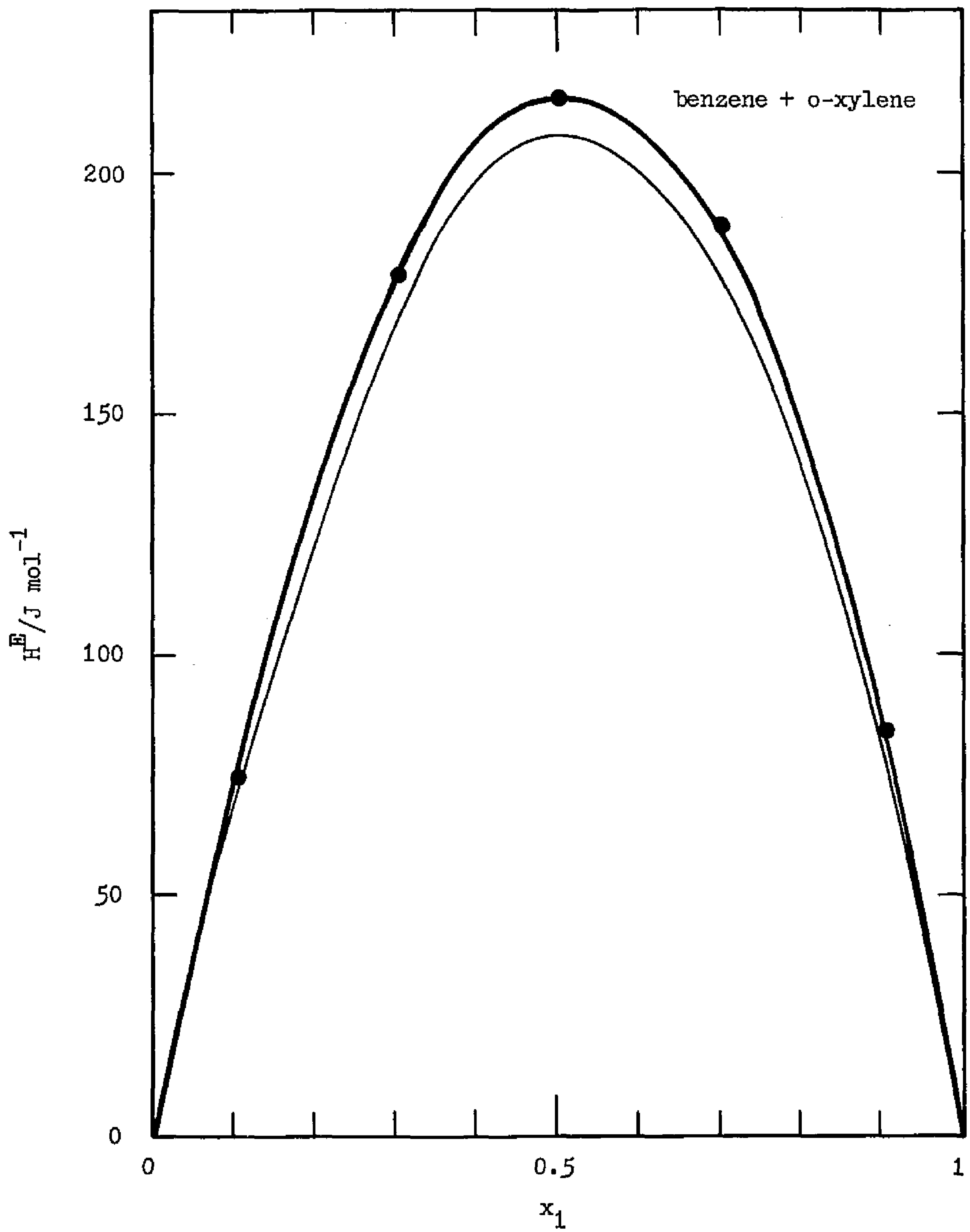

Figure 41. Dependence of the predicted excess enthalpy on composition for benzene + o-xylene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

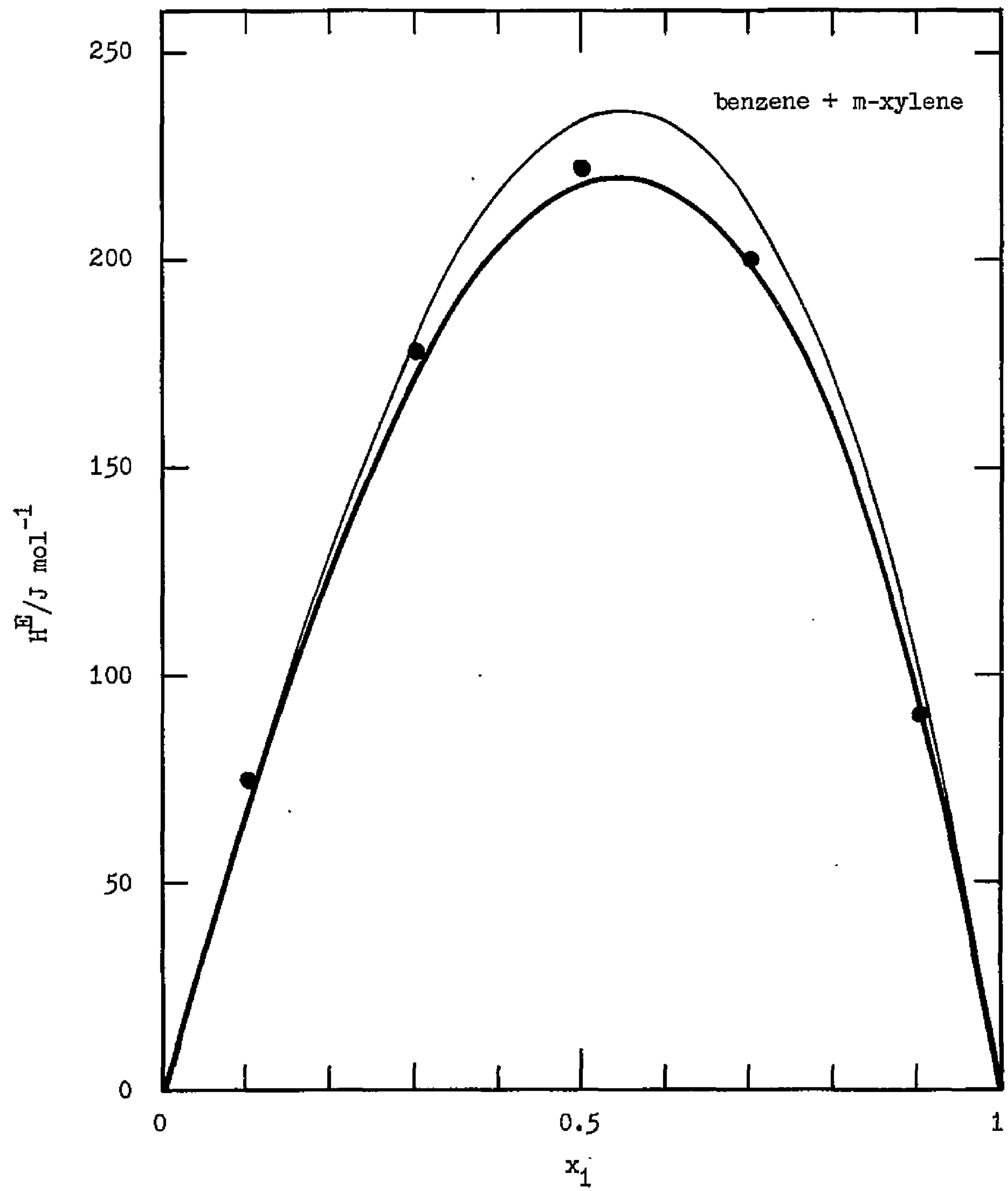

Figure 42. Dependence of the predicted excess enthalpy on composition for benzene + m-xylene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

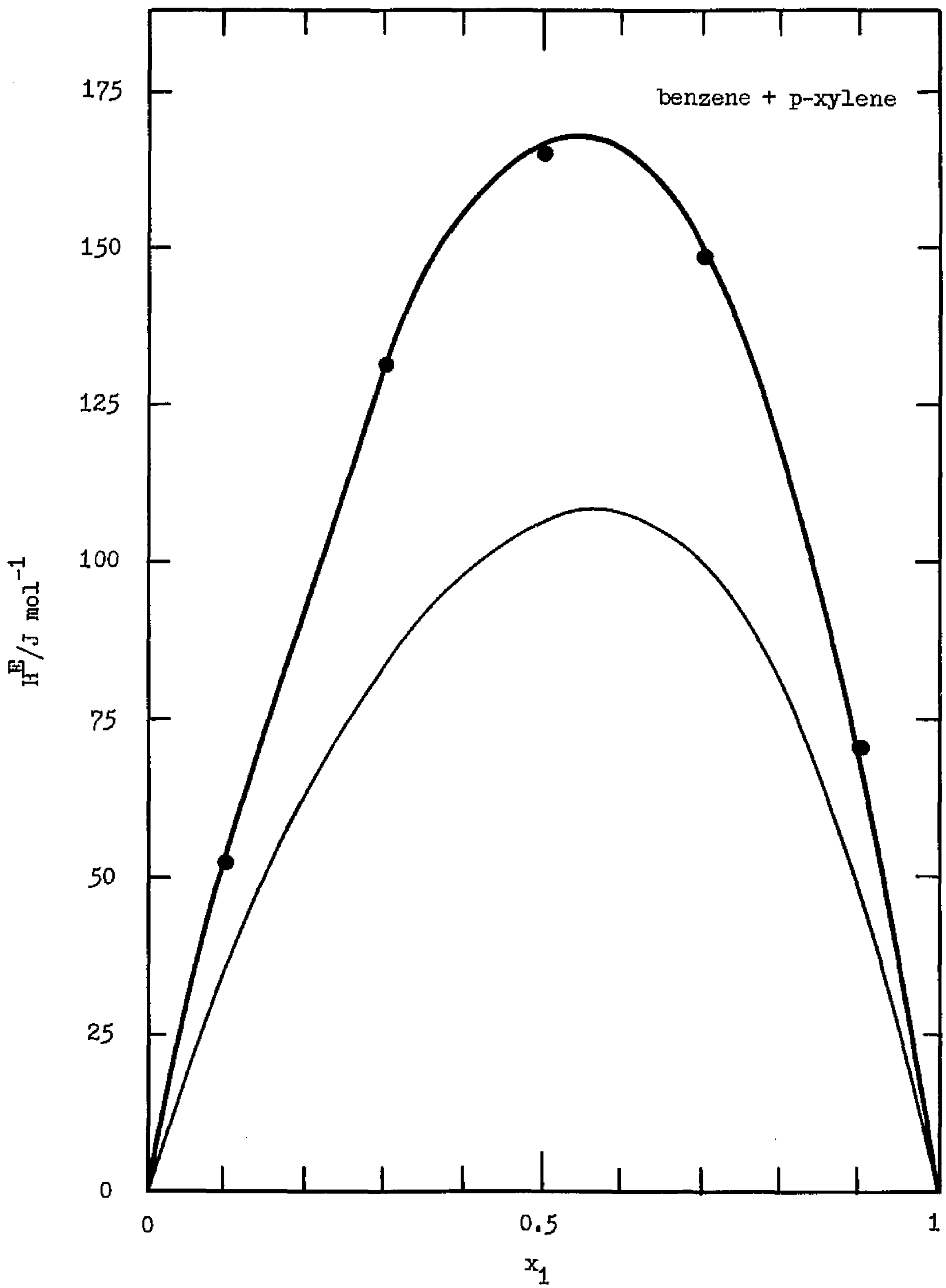

Figure 43. Dependence of the predicted excess enthalpy on composition for benzene + p-xylene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

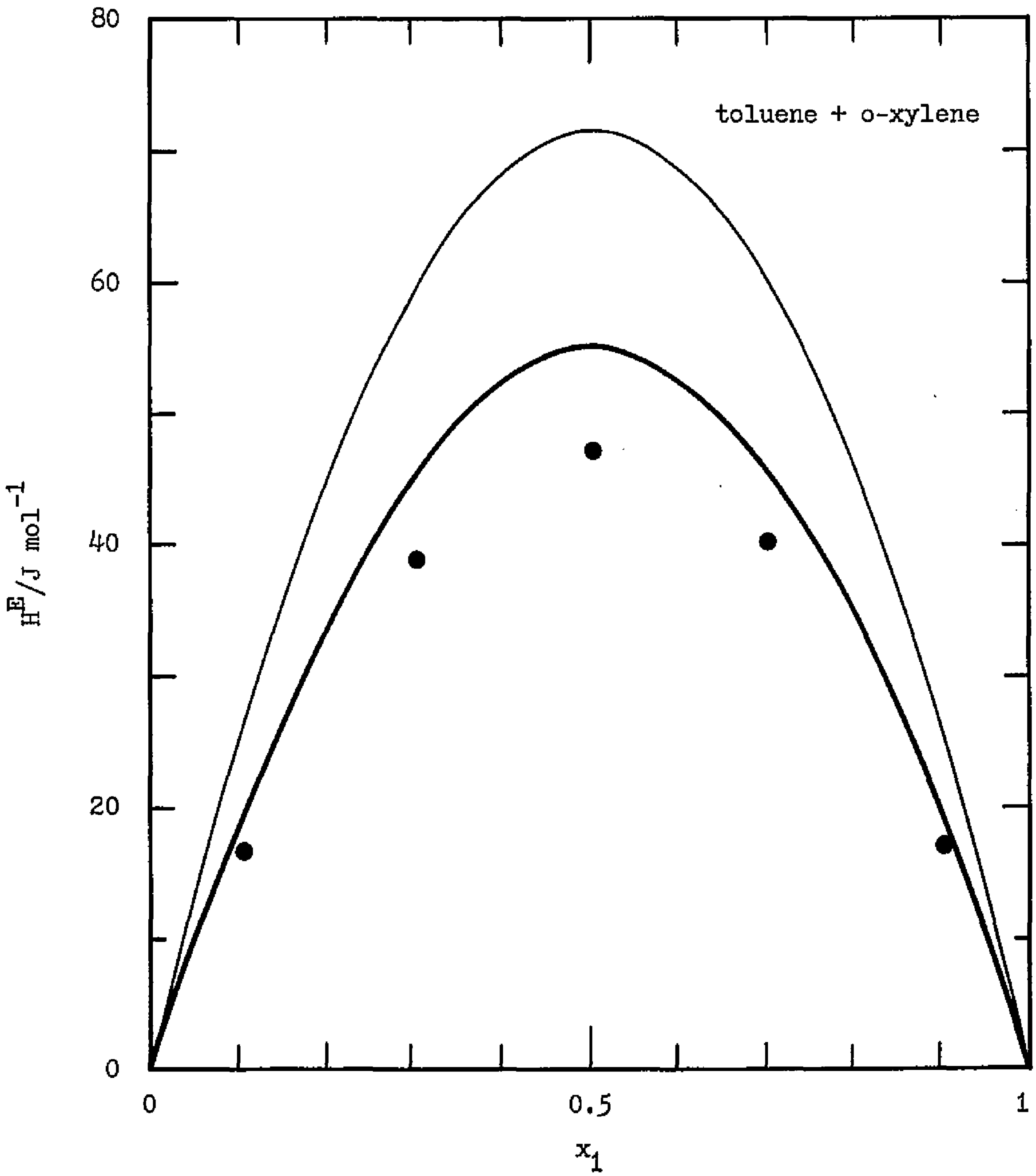

Figure 44. Dependence of the predicted excess enthalpy on composition for toluene + o-xylene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions. circles: smoothed experimental data.

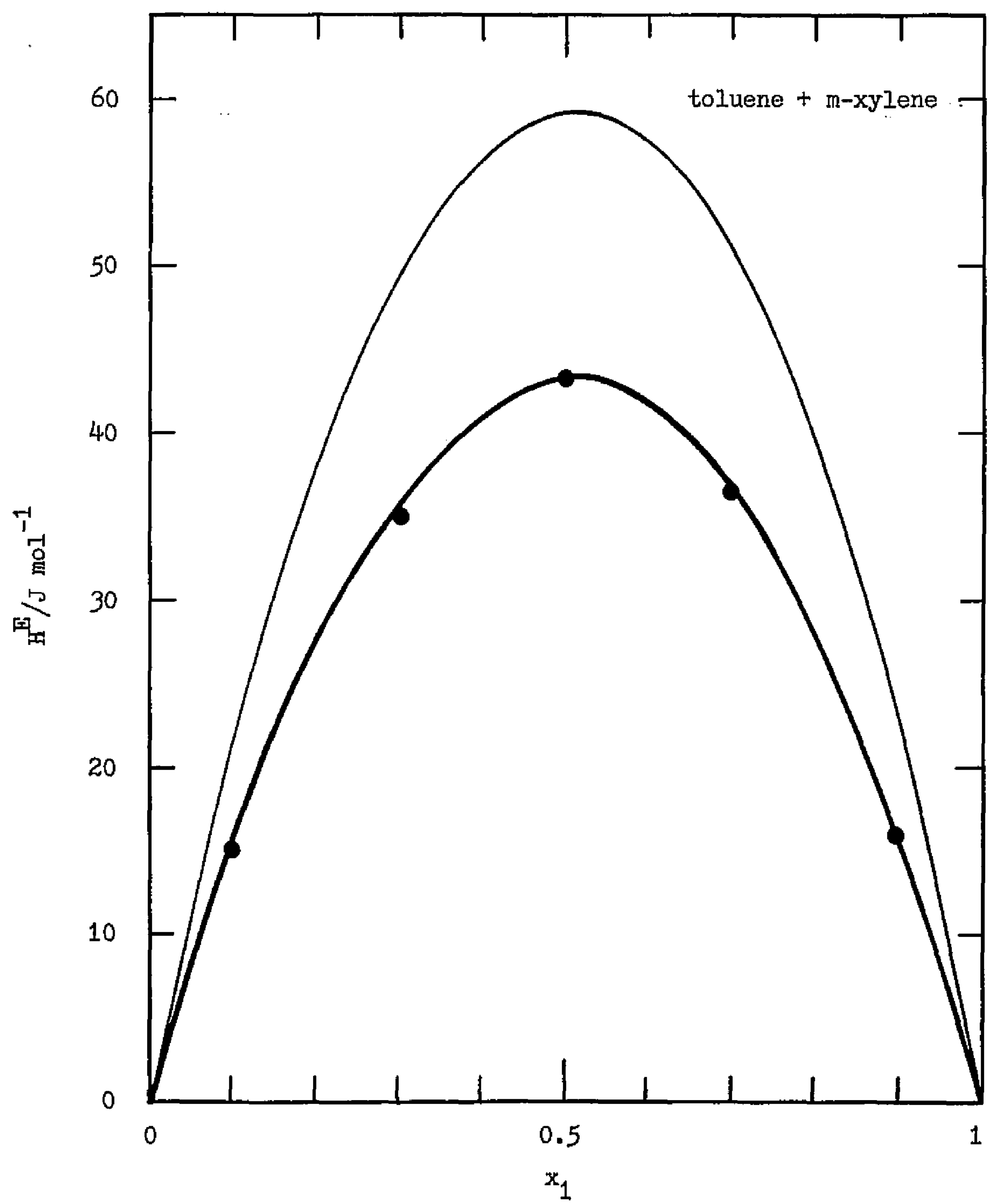

Figure 45. Dependence of the predicted excess enthalpy on composition for toluene + m-xylene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: $m = 1$ predictions; circles: smoothed experimental data.

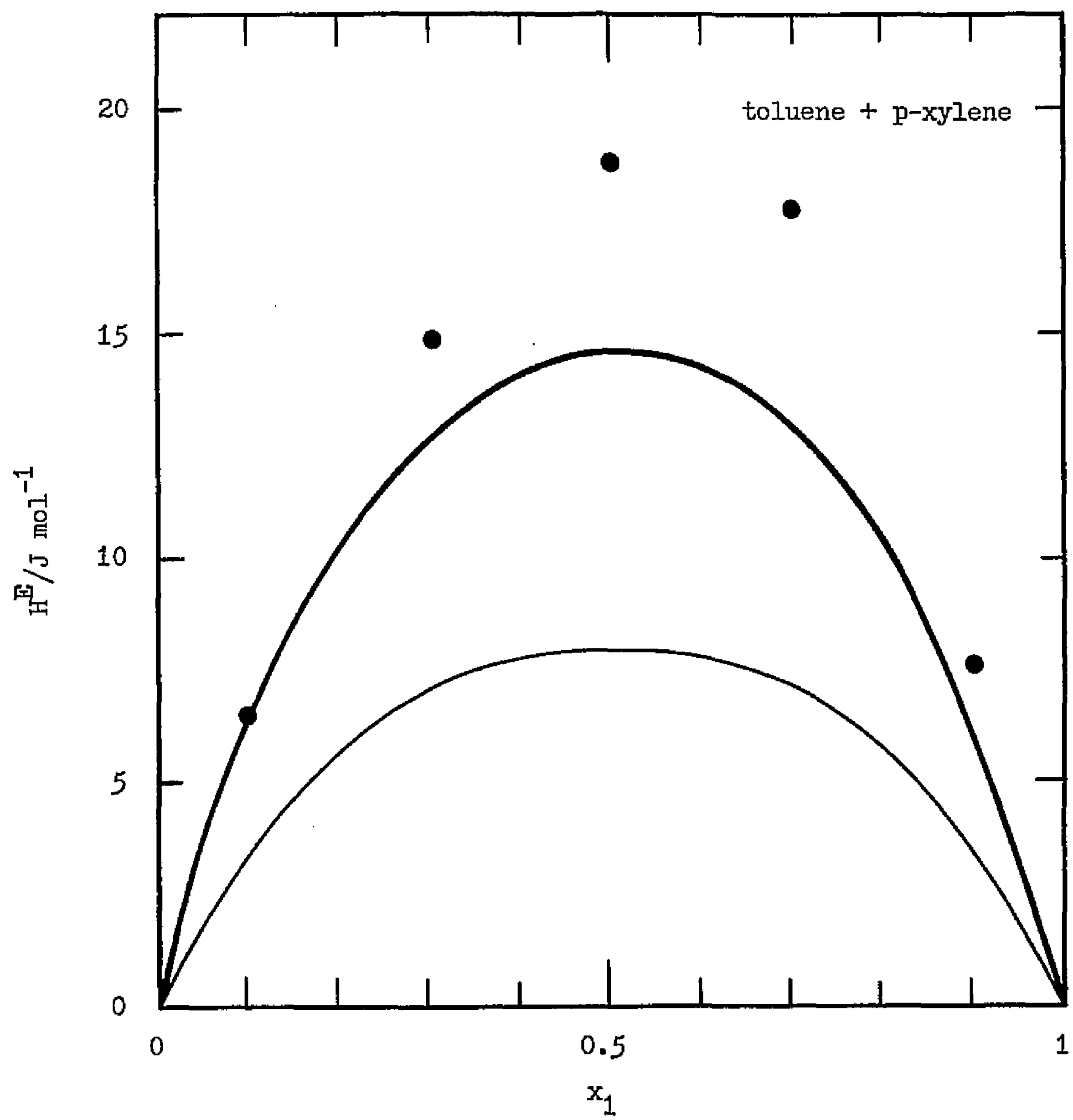

Figure 46. Dependence of the predicted excess enthalpy on composition for toluene + p-xylene mixtures. Broad curve: pseudo-2-fluid predictions; narrow curve: m = 1 predictions; circles: smoothed experimental data.

In each of the figures, x_1 refers to the mole fraction of the first named component; the broad curves represent the predictions of our model, the narrow curves represent the predictions of Flory's model (the van der Waals approximation) and the circles represent smoothed experimental excess enthalpy data at 298 K.

Figures 1 - 5 show mixtures of n-alkanes and mixtures of n-alkanes with branched and cyclic alkanes. The agreement of our predictions with experiment at $x_1 = 0.5$ ranges from within 0.4% to 6.5% while the predictions of the van der Waals approximation are consistently about 50% higher than experimental values at $x_1 = 0.5$. The shapes of the excess enthalpy curves were found to be highly sensitive to the shapes of the experimental excess volume curves; we will discuss the effect of the use of different sets of volumetric data on the excess enthalpy predictions for n-hexane + n-hexadecane mixtures in Section VI-3.

Figures 6 - 11 show the composition dependence of the excess enthalpy for mixtures of CCl_4 with alkanes. The deviation of our predictions at $x_1 = 0.5$ ranges from zero to 6.5%; deviations when $m = 1$ are as high as 63%. The predictions using the van der Waals approximation are usually low for mixtures containing CCl_4, although the two models yield virtually indistinguishable results for CCl_4 + n-hexadecane mixtures. The angular shape of the n-hexadecane rich region of the CCl_4 + n-hexadecane curve parallels similar angularity in the excess volume data used in the calculations.

Excess enthalpy predictions for mixtures of aromatic molecules with normal and branched alkanes are compared with experiment in Figures 12 - 19. The error in our predictions averages 2.7% at $x_1 = 0.5$; the predictions of Flory's model are again consistently low, with an average error of 29% at $x_1 = 0.5$. Disagreements of between 5 and 10% for independent sets of excess enthalpy measurements are not unusual. Figure 15 shows two such sets of experimental excess enthalpy measurements for benzene + n-hexadecane mixtures. At low benzene concentrations, our predictions more closely agree with the experimental data measured by Lundberg (204), while at middle and high benzene concentrations, they more closely agree with the data measured by Diaz-Peña and Menduiña (223).

As Figures 20 and 21 show, the pseudo-2-fluid model correctly predicts the magnitude and composition dependence of the excess enthalpy of octamethylcyclotetrasiloxane mixtures; the deviations are only 2% and 0.6% at $x_1 = 0.5$. Exothermic mixing is incorrectly predicted for $m = 1$.

The prediction of small values of H^E with reasonable accuracy is more difficult than the prediction of large values of H^E and represents a severe test for theories of liquid mixtures. As shown in Figure 22, the small magnitude and sigmoid shape of the excess enthalpy of c-pentane + 2,3-dimethylbutane mixtures is reproduced using our model, while use of the van der Waals approximation again incorrectly leads to highly exothermic predictions. The magnitude and concentration dependence of our excess enthalpy predictions for the other cycloalkane + branched alkane mixtures, shown in Figures 23 - 25, is also excellent.

Mixtures of cycloalkanes, shown in Figures 26 - 31, exhibit very unusual behavior. The closest homologs usually mix endothermically. As the size difference between the components increases, the excess enthalpy first becomes exothermic at high concentrations of the smaller component and endothermic at low concentrations of the smaller component and then becomes completely exothermic. While both models overestimate the endothermicity of c-pentane + c-hexane mixtures, our model reduces the deviation of the predictions by half. It more closely predicts the sigmoidal composition dependence of the excess enthalpy of c-pentane + c-heptane and c-hexane + c-octane mixtures, especially in the region richer in the larger molecule. The model also comes closer than Flory's model to predicting totally exothermic c-pentane + c-octane and totally endothermic c-hexane + c-heptane mixing processes. Both treatments predict positive excess enthalpies for c-heptane + c-octane mixtures analogous to the endothermic mixing of the smaller neighboring homologs. The influence of V^E on the very small H^E values of this system and of c-hexane + c-octane mixtures will be discussed in Section VI-3.

Use of the pseudo-2-fluid model leads to some improvement in the excess enthalpy predictions for mixtures of benzene with cycloalkanes, shown in Figures 32 - 35; the results closely trace the correct skew of the concentration dependence of H^E for benzene + c-octane mixtures. Marked improvement is obtained for mixtures of toluene with the larger cycloalkanes, shown in

Figures 36 - 39; the deviation at $x_1 = 0.5$ for these mixtures is reduced from 25% to 4%. Both theories underestimate the excess enthalpy of aromatic mixtures containing cyclopentane.

Figure 40 shows that use of our method results in excess enthalpy predictions for benzene + toluene mixtures within experimental error throughout the entire concentration range, while use of the van der Waals approximation results in an underestimate by 50% at $x_1 = 0.5$. Figures 41 - 46 show that substantial improvement also results for mixtures of benzene and toluene with each of the xylenes. Both theories predict the correct sign and magnitude of the very small mixing enthalpies of mixtures of the xylenes.

VI-3: Effect of Excess Volume on Excess Enthalpy Calculations

The excess enthalpy predictions are sensitive to the numerical values of the excess volume data on which they are based. The accuracy of the V^E data listed in Table VI to three decimal places is estimated as not usually better than 5×10^{-3} cm^3/mole; the accuracy of data given to two decimal places is probably about 2×10^{-2} cm^3/mole. The extensive compilation by Battino (262) of volumetric data for different types of mixtures shows that a wide range of V^E values have been obtained by different investigators for repeated studies of the same systems. Although dilatometric data is frequently cited as more accurate than pycnometric data, Smith (235) has shown that failure to correct for the effect of mechanical properties in dilatometric studies of benzene + cyclohexane mixtures causes values of V^E to be low by

1.0×10^{-2} cm^3/mole at $x_1 = 0.5$. Uncertainties are usually greater near the ends of the mole fraction scale since experimental data points are frequently concentrated in the mid-range region.

Figure 47 compares the smoothed excess volume data for n-hexane + n-hexadecane mixtures measured by Diaz- Peña (206) to that measured by Gomez-Ibañez (208). The two sets of data agree to within 0.002 cm^3/mole at $x_1 = 0.5$ but differ by 0.027 cm^3/mole and 0.026 cm^3/mole at $x_1 = 0.1$ and $x_1 = 0.9$; the curve obtained by Gomez-Ibañez indicates a greater volumetric contraction on mixing at all concentrations. The excess enthalpies predicted for n-hexane + n-hexadecane mixtures from these two sets of volumetric data are compared in Figure 48. While the equimolar predictions are essentially identical (the accuracy of the experimental excess enthalpy data is no better than several joules/mole and the enthalpy scale has been expanded for clarity) the concentration dependence of the predictions differs substantially. Our excess enthalpy predictions agree best with experiment if based on the low hexane concentration volumetric data measured by Diaz-Peña and the high hexane concentration data measured by Gomez-Ibañez. The excess volume curve predicted from the experimental excess enthalpy (the excess volume data which would predict excess enthalpies in perfect agreement with experiment) is virtually identical to that obtained by merging the two data sets of volumetric data, such that the resulting curve is more skewed towards high hexane concentrations.

Figures 49 and 50 show the volumetric properties of

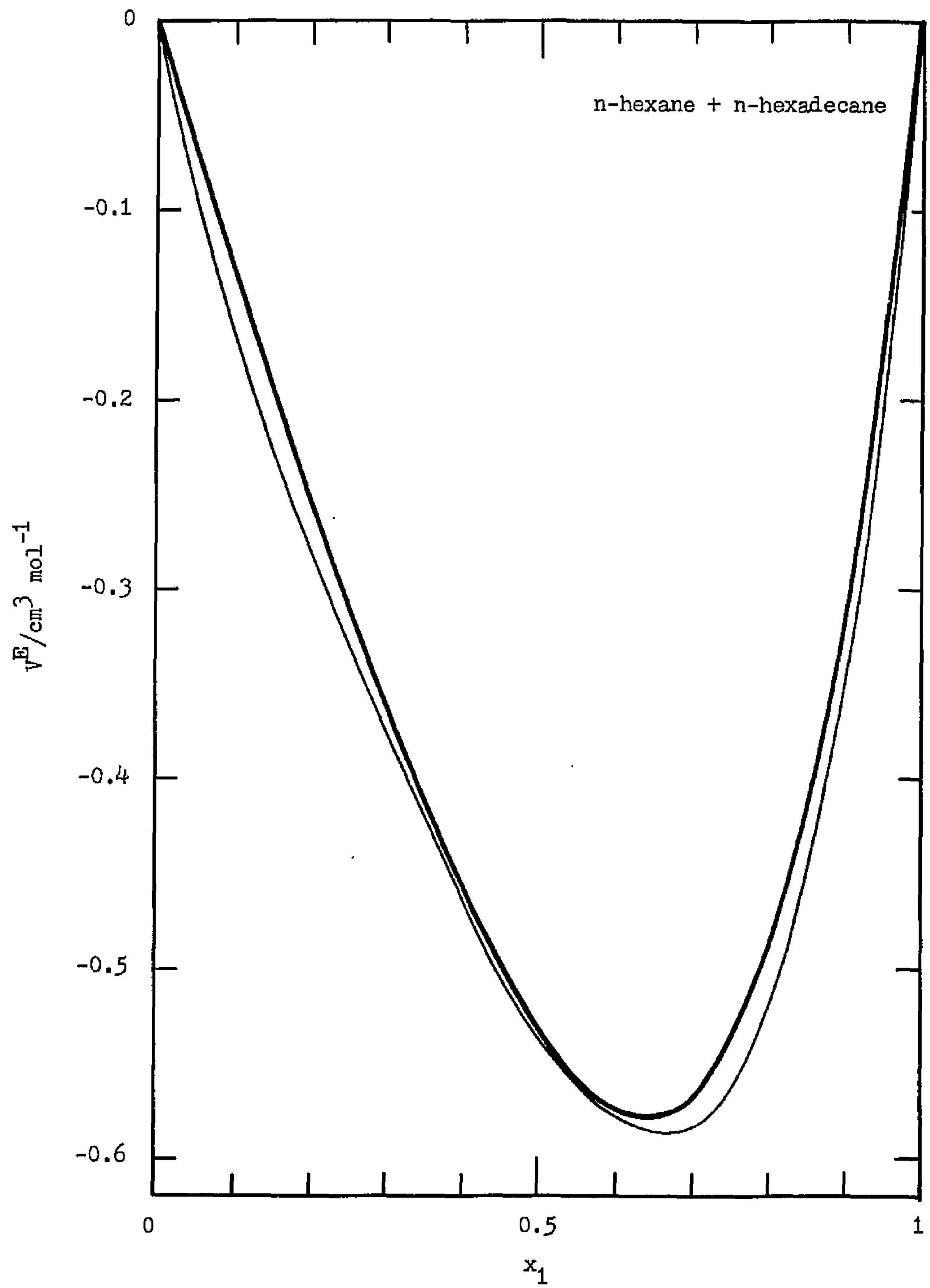

Figure 47. Excess volume of n-hexane + n-hexadecane mixtures. Broad curve: smoothed experimental data, Diaz-Peña (206); narrow curve: smoothed experimental data, Gomez-Ibañez (208).

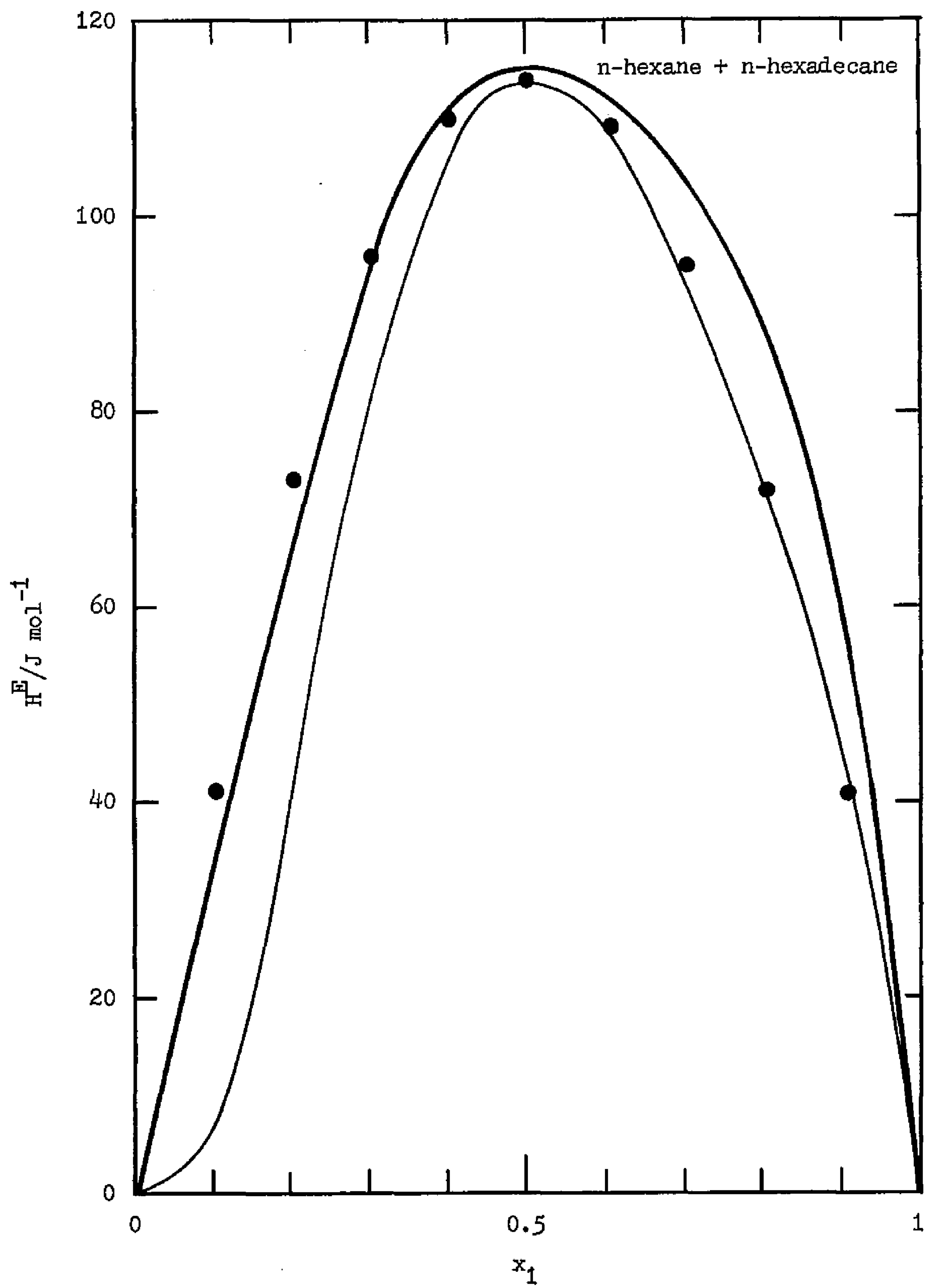

Figure 48. Effect of volumetric data on excess enthalpy predictions for n-hexane + n-hexadecane mixtures. Broad curve: predictions based on V^E data of Diaz-Peña (206); narrow curve: predictions based on V^E data of Gomez-Ibañez (208); circles: smoothed experimental data.

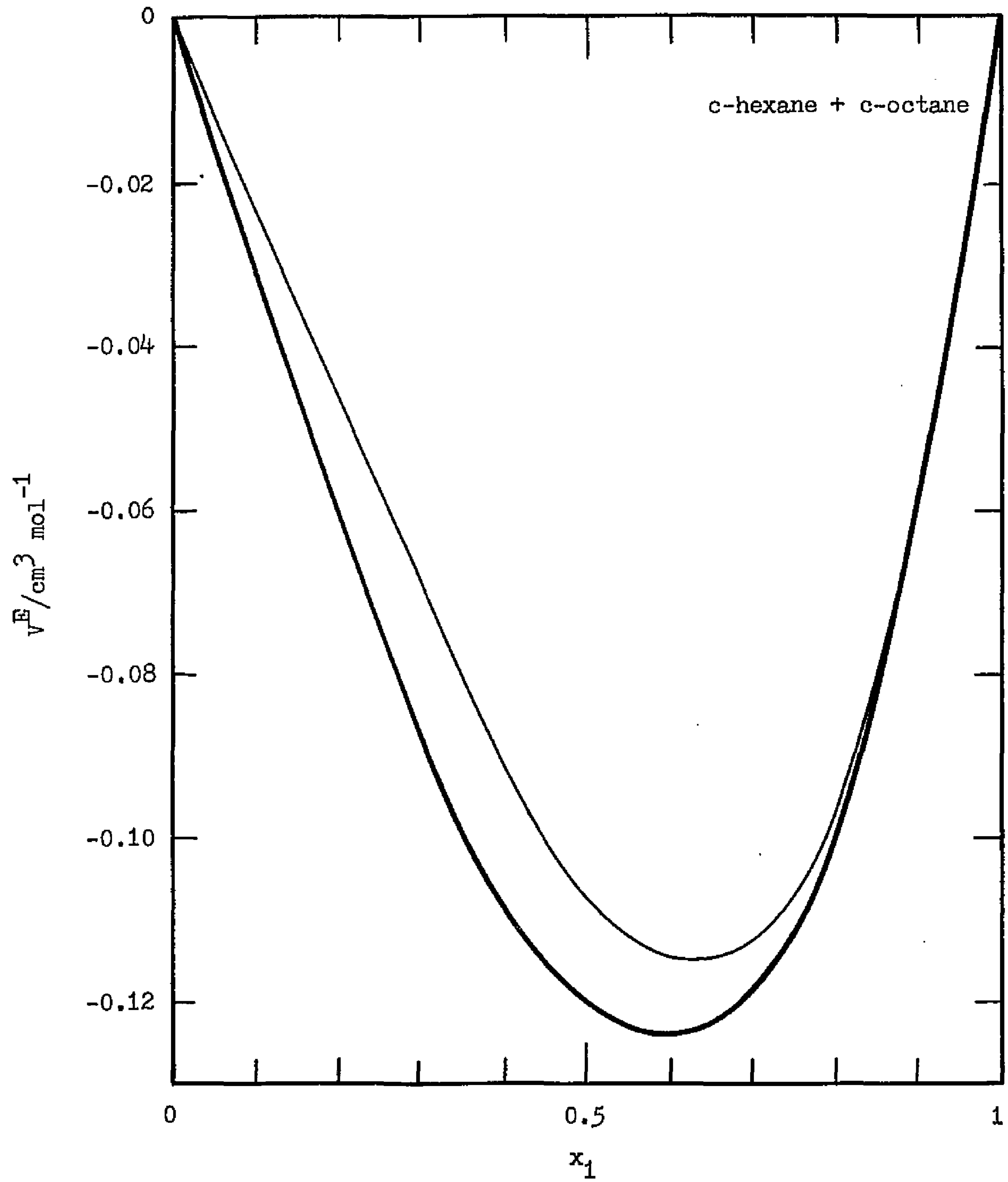

Figure 49. Excess volume of c-hexane + c-octane mixtures. Broad curve: predictions based on experimental excess enthalpy data; narrow curve: smoothed experimental V^E data.

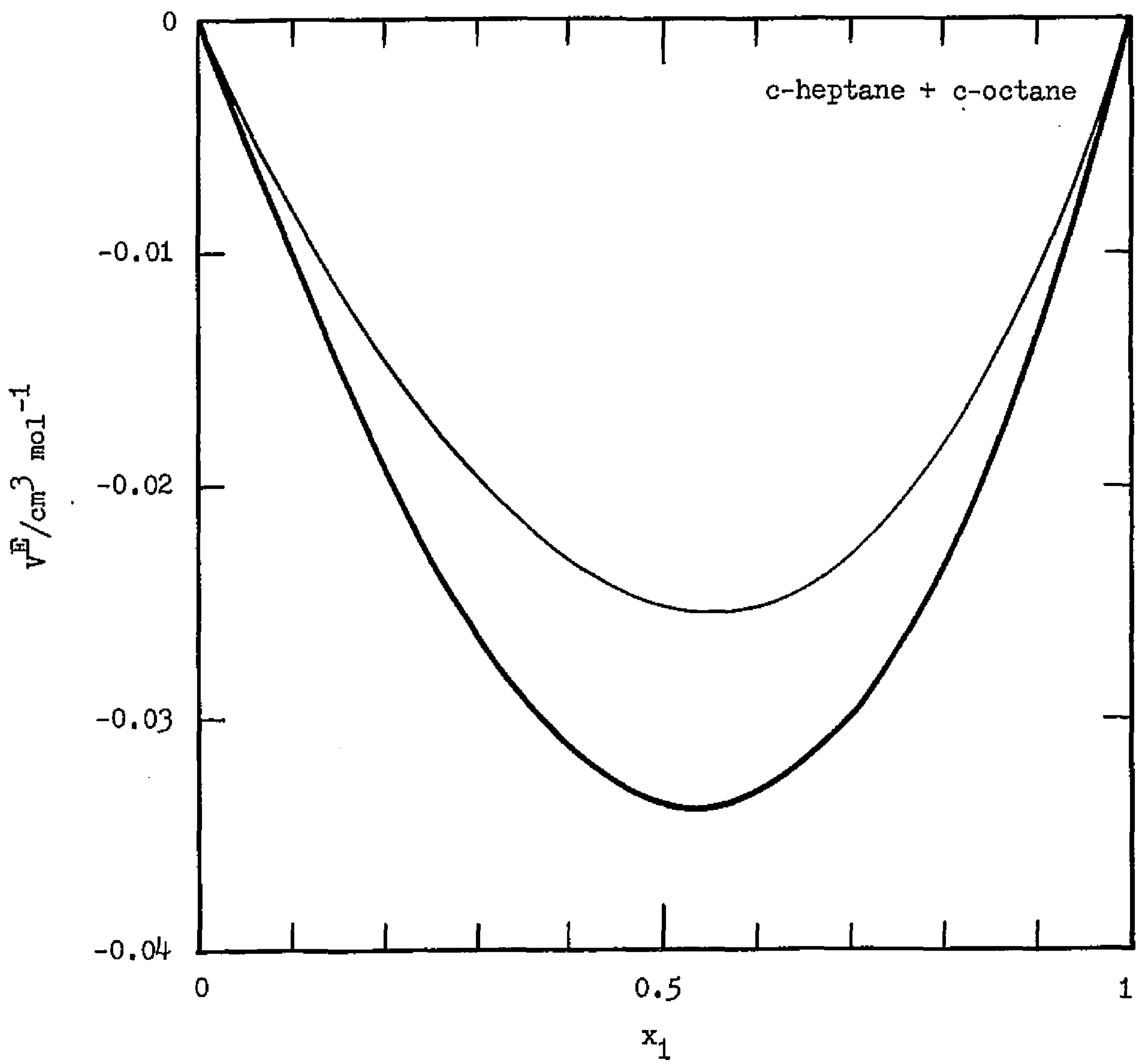

Figure 50. Excess volume of c-heptane + c-octane mixtures. Broad curve: predictions based on experimental excess enthalpy data; narrow curve: smoothed experimental V^E data.

the c-hexane + c-heptane and c-hexane + c-octane mixtures discussed in Section VI-2, for which the agreement between observed and predicted excess enthalpies is poor. The light curve in each figure shows the smoothed experimental values of V^E on which the H^E predictions were based. The heavy curves in each of the figures are the V^E values predicted from the experimental H^E data. The excess volume predictions from excess enthalpy data are in better accord with experiment for both systems than are the excess enthalpy predictions from volumetric data. This means that excess enthalpy predictions are more sensitive to numerical values of input data than are excess volume predictions and is the reason that use of the van der Waals approach results in better agreement for V^E calculated from H^E than for the reverse procedure. The V^E predictions of the van der Waals model may be reasonably accurate even though the H^E predictions are inaccurate.

The V^E curves predicted from excess enthalpy data are exactly those values of V^E needed to produce H^E curves in perfect agreement with experiment. It can be seen from Figures 49 and 50, that the differences between the experimental and predicted V^E values are almost at the limits of accuracy of the volumetric data. Slightly more negative, more symmetric values of V^E for c-hexane + c-octane mixtures will reproduce the symmetric excess enthalpy curve in Figure 30; slightly more negative excess volume values for mixtures of c-heptane + c-octane will both reverse the sign and correct the skew of the predicted excess enthalpy curve in Figure 31. Very accurate experimental volumetric data is therefore needed for accurate prediction of the very low H^E values of mixtures of similar components.

The effect of uncertainties of ± 0.005 cm^3/mole, ± 0.010 cm^3/mole and ± 0.020 cm^3/mole on excess enthalpy predictions at $x_1 = 0.5$ is shown in Table X. The absolute size of the effect produced by these uncertainties is virtually independent of the magnitude of both V^E and H^E. Uncertainties of 0.005 cm^3/mole in V^E produce changes in H^E of 3 - 6 joules, uncertainties of 0.010 cm^3/mole produce changes of 7 - 11 joules/mole and uncertainties of 0.020 cm^3/mole changes of 14 - 19 joules/mole. The relative effect of these uncertainties is more important for mixtures with small excess enthalpies, although even for mixtures with relatively high excess enthalpy values, effects of this magnitude are usually sufficient to bring prediction and experiment into perfect accord.

VI-4: Effect of α and γ on Excess Enthalpy Calculations

The influence of α and γ on excess property predictions is greater than generally realized. However, this sensitivity to pure component physical property data is not a serious obstacle to the application of our theory, since the accurate measurement of the mechanical properties of a few liquids provides the necessary input data for many mixtures.

Values of α calculated from either independent sets of density-temperature data or independent dilatometric measurements commonly differ by 1%. Recent piezometric measurements of γ are probably accurate to 2%; older, more indirectly obtained values

Table X

Effect of Uncertainties in V^E on H^E

Mixture	H^E/J mol^{-1} exp	H^E/J mol^{-1} calc	Uncertainty in V^E/cm^3 mol^{-1} (+) 0.005	(-)	(+) 0.010	(-)	(+) 0.020	(-)
n-hexane + c-hexane	216	219	223	216	226	213	232	206
n-heptane + c-hexane	240	224	227	221	231	218	240	210
n-hexadecane + c-hexane	498	500	505	495	509	491	519	482
n-hexane + n-hexadecane	114	116	120	112	124	107	132	99
n-heptane + n-hexadecane	96	93	98	89	102	85	111	76
224TMP + n-hexadecane	233	223	228	219	232	215	241	207
CCl_4 + n-hexane	315	302	306	299	309	296	315	289
CCl_4 + n-heptane	339	326	329	322	333	318	340	311
CCl_4 + n-octane	364	364	368.	360	371	356	379	349
CCl_4 + n-hexadecane	578	544	549	540	554	535	563	525
CCl_4 + c-hexane	166	177	181	173	185	169	193	160
CCl_4 + 224TMP	405	391	394	388	398	385	405	378
benzene + n-hexane	898	908	911	905	915	901	922	894
benzene + n-heptane	919	936	940	933	944	929	951	921
benzene + n-octane	969	988	992	984	995	980	1002	972
benzene + n-hexadecane	1209	1139	1144	1134	1149	1129	1154	1119
benzene + 224TMP	992	991	995	987	998	984	1004	977
toluene + n-hexane	512	521	525	518	528	514	535	506
toluene + n-heptane	552	532	535	528	539	524	547	517
toluene + 224 TMP	657	672	676	668	679	665	686	658

Table X (continued)

Mixture	H^E/J mol^{-1} exp	H^E/J mol^{-1} calc	Uncertainty in V^E/cm^3 mol^{-1} (+) 0.005	0.005 (-)	(+) 0.010	0.010 (-)	(+) 0.020	0.020 (-)
OMCTS + CCl_4	163	162	165	158	168	155	175	148
OMCTS + benzene	794	778	782	775	786	772	792	765
c-pentane + 23DMB	- 2	- 2	2	- 5	5	- 8	11	- 14
c-hexane + 23DMB	156	153	156	150	160	147	166	141
c-heptane + 23DMB	163	162	165	158	169	155	176	147
c-octane + 23DMB	176	176	180	172	184	168	192	160
c-pentane + c-hexane	28	53	57	49	61	45	68	38
c-pentane + c-heptane	- 4	- 2	2	- 6	7	- 10	15	- 19
c-pentane + c-octane	- 41	- 37	- 32	- 42	- 28	- 46	- 18	- 56
c-hexane + c-heptane	6	5	10	1	14	- 4	23	- 12
c-hexane + c-octane	1	14	18	9	23	4	33	- 6
c-heptane + c-octane	- 4	5	10	0	15	- 6	25	- 16
benzene + c-pentane	630	523	527	519	531	515	540	507
benzene + c-hexane	799	801	806	797	810	793	818	784
benzene + c-heptane	758	790	794	785	799	790	809	771
benzene + c-octane	797	806	811	801	816	795	826	785
toluene + c-pentane	365	206	210	202	214	198	223	189
toluene + c-hexane	625	603	607	599	612	595	620	586
toluene + c-heptane	588	544	549	539	553	535	563	525
toluene + octane	618	610	615	604	619	599	630	589

(continued)

Table X (continued)

Mixture	H^E/J mol^{-1}		Uncertainty in V^E/cm^3 mol^{-1}					
	exp	calc	(+) 0.005	(-)	(+) 0.010	(-)	(+) 0.020	(-)
benzene + toluene	68	67	72	61	77	57	87	46
benzene + o-xylene	216	215	221	210	226	205	237	194
benzene + m-xylene	223	218	223	213	228	208	239	197
benzene + p-xylene	164	166	171	161	175	155	186	145
toluene + o-xylene	47	55	60	49	65	44	76	33
toluene + m-xylene	43	43	48	38	53	33	64	22
toluene + p-xylene	19	15	19	9	24	4	35	- 6
o-xylene + m-xylene	11	6	11	0	16	- 6		
o-xylene + p-xylene	6	8	13	2	20	- 4		
m-xylene + p-xylene	- 8	- 6	0	- 11	6	- 16		

from isothermal and adiabatic compressibility measurements, are subject to larger errors.

Table XI shows the changes in the predicted H^E values at $x_1 = 0.5$ due to a 1% uncertainty in α; Table XII shows the changes due to a 2% uncertainty in γ. An increase in α_1 exerts approximately the same effect as a decrease in α_2, and an increase in γ_1 the same effect as a decrease in γ_2. Although small values of H^E are more noticeably affected, the general magnitude of the effect these changes produce is not absolutely or proportionally related to the size of H^E. The sensitivity to changes in α and γ varies from system to system, with mixtures of normal alkanes extremely sensitive to small variations. In general, mixtures whose components have dissimilar mechanical properties are not more sensitive to these changes than are mixtures whose components have similar properties. The magnitude of enthalpy changes on mixing is not directly related to the relative magnitudes of either α or γ of the pure components.

Because of the general sensitivity of the predicted excess enthalpy to the numerical values of α and γ used in the computations, the values of m proposed in Table III for pure components must be used in conjunction with the mechanical properties listed in Table II. As improved values for these physical properties become available, some small adjustments in the pure component m values may be desirable.

VI-5 Calculation of Second Law Properties

Values for TS^E at $x_1 = 0.5$, obtained by combining the

Table XI

Effect of Uncertainties in α on H^E

Mixture	H^E/J mol^{-1}		Uncertainty in α			
	exp	calc	α_1 +1%	α_1 -1%	α_2 +1%	α_2 -1%
n-hexane + c-hexane	216	219	231	208	207	232
n-heptane + c-hexane	240	224	235	214	212	236
n-hexadecane + c-hexane	498	500	502	499	493	507
n-hexane + n-hexadecane	114	116	131	100	109	129
n-heptane + n-hexadecane	96	93	106	80	81	105
224TMP + n-hexadecane	233	223	248	199	200	248
CCl_4 + n-hexane	315	302	287	318	317	288
CCl_4 + n-heptane	339	326	311	341	339	312
CCl_4 + n-octane	364	364	349	378	376	351
CCl_4 + n-hexadecane	578	544	534	555	550	538
CCl_4 + c-hexane	166	177	174	181	179	175
CCl_4 + 224TMP	405	391	370	413	411	371
benzene + n-hexane	898	908	886	930	926	890
benzene + n-heptane	919	936	915	958	953	919
benzene + n-octane	969	988	967	1009	1004	971
benzene + n-hexadecane	1209	1139	1119	1158	1149	1128
benzene + 224TMP	992	991	964	1018	1015	967
toluene + n-hexane	512	521	506	538	537	507
toluene + n-heptane	552	532	516	547	545	518
toluene + 224TMP	657	672	650	694	692	651
OMCTS + CCl_4	163	162	185	138	141	183
OMCTS + benzene	794	778	806	751	751	806
c-pentane + 23DMB	- 2	- 2	- 11	8	9	- 13
c-hexane + 23DMB	156	153	140	167	167	140
c-heptane + 23DMB	163	162	144	179	180	143
c-octane + 23DMB	176	176	155	197	199	152
c-pentane + c-hexane	28	53	55	51	51	55
c-pentane + c-heptane	- 4	- 2	4	- 8	- 7	3
c-pentane + c-octane	- 41	- 37	- 28	- 46	- 45	- 29
c-hexane + c-heptane	6	5	9	2	2	9
c-hexane + c-octane	1	14	20	7	7	20
c-heptane + c-octane	- 4	5	7	1	2	8

(continued)

Table XI (continued)

Mixtures	H^E/J mol^{-1}		Uncertainty in α			
	exp	calc	α_1 +1%	α_1 -1%	α_2 +1%	α_2 -1%
benzene + c-pentane	630	523	511	535	531	514
benzene + c-hexane	799	801	791	812	806	794
benzene + c-heptane	758	790	782	798	792	788
benzene + c-octane	797	806	800	811	806	805
toluene + c-pentane	365	206	200	211	210	202
toluene + c-hexane	625	603	598	608	603	603
toluene + c-heptane	588	544	543	546	541	547
toluene + c-octane	618	610	611	608	603	616
benzene + toluene	68	67	60	74	73	60
benzene + o-xylene	216	215	208	223	221	210
benzene + m-xylene	223	218	208	227	225	211
benzene + p-xylene	164	166	156	176	174	157
toluene + o-xylene	47	55	55	54	54	55
toluene + m-xylene	43	43	41	45	44	42
toluene + p-xylene	19	15	12	17	17	12
o-xylene + m-xylene	11	6	3	8	8	3
o-xylene + p-xylene	6	8	5	11	11	5
o-xylene + p-xylene	- 8	- 6	- 6	- 5	- 4	- 6

Table XII

Effect of Uncertainties in γ on H^E

Mixture	H^E/J mol^{-1}		Uncertainty in γ			
	exp	calc	γ_1 +2%	γ_1 -2%	γ_2 +2%	γ_2 2%
n-hexane + c-hexane	216	219	212	226	231	208
n-heptane + c-hexane	240	224	223	225	230	219
n-hexadecane + c-hexane	498	500	542	458	469	532
n-hexane + n-hexadecane	114	116	69	162	164	67
n-heptane + n-hexadecane	96	93	52	134	136	50
224TMP + n-hexadecane	233	223	185	262	181	266
CCl_4 + n-hexane	315	302	321	283	289	316
CCl_4 + n-heptane	339	326	339	312	319	333
CCl_4 + n-octane	364	364	373	354	361	266
CCl_4 + n-hexadecane	578	544	523	565	576	512
CCl_4 + c-hexane	166	177	186	168	172	182
CCl_4 + 224TMP	405	391	405	378	386	397
benzene + n-hexane	898	908	943	873	891	925
benzene + n-heptane	919	936	966	907	925	947
benzene + n-octane	969	987	1013	962	982	994
benzene + n-hexadecane	1209	1139	1134	1143	1166	1112
benzene + 224TMP	992	991	1020	961	981	1000
toluene + n-hexane	512	536	559	483	493	549
toluene + n-heptane	552	532	565	498	510	554
toluene + 224TMP	657	672	705	639	652	692
OMCTS + CCl_4	163	162	148	176	179	145
OMCTS + benzene	794	778	760	797	813	744
c-pentane + 23DMB	- 2	- 2	10	- 13	- 13	10
c-hexane + 23DMB	156	153	170	137	140	166
c-heptane + 23DMB	163	162	189	135	138	185
c-octane + 23DMB	176	176	211	141	144	208
c-pentane + c-hexane	28	53	51	55	56	50
c-pentane + c-heptane	- 4	- 2	- 14	10	10	- 14
c-pentane + c-octane	- 41	- 37	- 57	- 18	- 18	- 56
c-hexane + c-heptane	6	5	- 5	15	15	- 5
c-hexane + c-octane	1	14	- 4	31	31	- 4
c-heptane + c-octane	- 4	5	- 3	12	12	- 3

(continued)

Table XII (continued)

Mixture	H^E/J mol^{-1}		Uncertainty in γ			
	exp	calc	γ_1 +2%	γ_1 -2%	γ_2 +2%	γ_2 -2%
benzene + c-pentane	630	523	547	499	510	537
benzene + c-hexane	799	801	826	777	792	810
benzene + c-heptane	758	790	805	774	791	789
benzene + c-octane	797	806	814	798	814	798
toluene + c-pentane	365	206	233	179	183	229
toluene + c-hexane	625	603	633	573	585	620
toluene + c-heptane	588	544	565	524	535	554
toluene + c-octane	618	610	624	596	608	612
benzene + toluene	68	67	60	73	75	59
benzene + o-xylene	216	215	199	231	236	195
benzene + m-xylene	223	218	203	233	237	195
benzene + p-xylene	164	166	156	175	179	152
toluene + o-xylene	47	55	44	66	66	43
toluene + m-xylene	43	43	34	52	53	33
toluene + p-xylene	19	15	11	18	19	10
o-xylene + m-xylene	11	6	7	4	4	7
o-xylene + p-xylene	6	8	15	1	1	15
m-xylene + p-xylene	- 8	- 6	0	- 11	- 11	0

experimental G^E and H^E data in Table III, are shown in the last column of Table XIII. Values of TS^E, predicted from Flory's model with $m = 1$, $\nu_1^* = \nu_2^* = \nu^*$ and an ideal combinatory entropy of mixing, are listed in the first column. Values of TS^E predicted from the pseudo-2-fluid model using the approximations necessary to obtain a relation formally equivalent to Equation (213) are listed in the second column. Although the terms in Equation (213) have different numerical values in the two treatments, the effect of these differences on the excess entropy is not very great, and the magnitudes of the predictions are similar. The reason for the similarity is the lack of any term in Equation (213) explicitly involving the energy-volume exponent. Both models predict excess entropies consistently far below that found experimentally and frequently fail to predict the correct sign for this excess property. The reason for the disagreement with experiment can be traced to the necessity of approximating the combinatory entropy in Flory's model, and the collection of terms containing the combinatory entropy in our model, by the ideal entropy of mixing, since $TS^M \approx 2000$ joules/mole at $x_1 = 0.5$. It can be seen from the data in Table XIII that our values of m cannot be directly used to predict TS^E from the configurational partition function in Equation (132).

These values of m, however, may be used indirectly to predict TS^E from the semi-empirical equations discussed in Section V-2. The excess enthalpy vs. composition curves (Figures 1 - 46), predicted from volumetric data as described in

Table XIII

TS^E at $x_1 = 0.5$ for Mixtures of Non-polar and Weakly Polar Liquids

Mixture	TS^E/J mol^{-1}			
	Calculated directly from the partition function		Calculated from pseudo-2-fluid H predictions	experiment
	m = 1	pseudo-2-fluid		
n-hexane + c-hexane	84	75	121	145
n-heptane + c-hexane	87	79		
n-hexadecane + c-hexane	71	95	550	675
n-hexane + n-hexadecane	-101	- 78	253	182
n-heptane + n-hexadecane	- 61	- 47	189	151
224TMP + n-hexadecane	- 6	- 4	209	226
CCl_4 + n-hexane	64	66	178	166
CCl_4 + n-heptane	70	75	215	205
CCl_4 + n-octane	67	79	265	269
CCl_4 + n-hexadecane	49	82	632	694
CCl_4 + 224TMP	40	62	280	247
CCl_4 + c-hexane	51	46	92	96
benzene + n-hexane	193	198	487	513
benzene + n-heptane	189	206	528	489/562
benzene + n-octane	181	206	586	605/638
benzene + n-hexadecane	134	192	955	1118
benzene + 224TMP	120	164	595	592
toluene + n-hexane	80	82	271	-
toluene + n-heptane	95	98	295	351
toluene + 224TMP	88	115	390	303

(continued)

Table XIII (continued)

Mixture	TS^E/J mol^{-1}			
	Calculated directly from the partition function		Calculated from pseudo-2-fluid H^E predictions	experiment
	m = 1	pseudo-2-fluid		
OMCTS + CCl_4	- 77	- 39	150	296
OMCTS + benzene	- 12	52	725	677
c-pentane + 23DMB	- 56	- 42		- 15
c-hexane + 23DMB	26	27	89	69
c-heptane + 23DMB	- 11	- 7	82	28
c-octane + 23DMB	- 12	- 25	86	- 8
c-pentane + c-hexane	16	15	42	32
c-pentane + c-heptane	- 22	- 18		1
c-pentane + c-octane	- 68	- 54		- 39
c-hexane + c-heptane	- 6	- 5	6	- 3
c-hexane + c-octane	- 24	- 18		- 25
c-heptane + c-octane	- 7	- 5	4	- 9
benzene + c-pentane	140	136	259	359
benzene + c-hexane	220	215	403	468
benzene + c-heptane	210	210	412	-
benzene + c-octane	162	178	443	511
toluene + c-pentane	32	30	117	-
toluene + c-hexane	187	170	296	293
toluene + c-heptane	177	162	273	-
toluene + c-octane	184	172	315	322

(continued)

Table XIII (continued)

Mixture	TS^E/J mol^{-1}			
	Calculated directly from the partition function		Calculated from pseudo-2-fluid H predictions	experiment
	m = 1	pseudo-2-fluid		
benzene + toluene	- 1	5	43	-
benzene + o-xylene	13	23	135	-
benzene + m-xylene	28	34	141	-
benzene + p-xylene	3	15	116	-
toluene + o-xylene	8	9	33	-
toluene + m-xylene	9	9	28	-
toluene + p-xylene	- 1	1	14	-

Section VI-2, were used in an iterative, non-linear least squares curve fitting program to calculate D_{12} and D_{21} from Equation (222). D_{12} and D_{21} were both initialized at 0.5000 and usually converged to their final values after seven or eight iterations; convergence was considered achieved when $(|\delta D_{12}| + |\delta D_{21}|) \leq 2 \times 10^{-5}$.

The values of D_{12} and D_{21} obtained from our excess enthalpy predictions are listed in Table XIV. These values were used to predict G^E as a function of composition from Equation (215). Equimolar G^E predictions are listed in Table XIV; equimolar TS^E predictions, obtained by combining the G^E predictions with the H^E predictions from which they were derived, are listed for comparison in Table XIII. The approximation in Equation (219) limited the predictions to mixtures for which H^E is positive; compared to the partition function predictions, the agreement with experiment is exceptionally good. The concentration dependence of the excess free energy is also well predicted and a few representative curves are shown in Figure 51. As expected, the largest deviations occur for mixtures whose components have very different values of α. In view of the accuracy of the G^E predictions for those mixtures for which the excess free energy has been measured, the G^E predictions for those mixtures for which experimental data is unavailable should be reasonably reliable.

Table XIV

Prediction of G^E at $x_1 = 0.5$ from the Composition Dependence of Pseudo-2-fluid H^E Predictions

Mixture	D_{12}	D_{21}	G^E/J mol^{-1} predicted	G^E/J mol^{-1} experiment
n-hexane + c-hexane	0.6008	1.4051	98	71
n-hexadecane + c-hexane	0.5397	1.3085	- 52	-177
n-hexane + n-hexadecane	1.2602	0.7234	-137	- 68
n-heptane + n-hexadecane	1.0403	0.8904	- 96	- 55
224TMP + n-hexadecane	1.0544	0.8001	4	7
CCl_4 + n-hexane	1.1646	0.6863	124	149
CCl_4 + n-heptane	1.2279	0.6388	111	134
CCl_4 + n-octane	1.2615	0.6071	99	95
CCl_4 + n-hexadecane	1.4371	0.4682	- 88	-116
CCl_4 + c-hexane	1.0271	0.8512	85	70
CCl_4 + 224TMP	1.1012	0.6837	111	158
benzene + n-hexane	1.0229	0.5466	415	385
benzene + n-heptane	1.0418	0.5227	408	354/430
benzene + n-octane	1.0767	0.4897	402	331/364
benzene + n-hexadecane	1.3065	0.3585	184	91
benzene + 224TMP	1.0777	0.4895	396	400
toluene + n-hexane	0.9447	0.7391	250	332
toluene + n-heptane	1.0500	0.6582	237	201
toluene + 224TMP	1.0859	0.5841	282	354
OMCTS + CCl_4	0.5725	1.5309	-318	-133
OMCTS + benzene	0.3883	1.4750	53	116

(continued)

Table XIV (continued)

Mixture	D_{12}	D_{21}	G^E/J mol^{-1} predicted	G^E/J mol^{-1} experiment
c-hexane + 23DMB	1.0203	0.8725	65	87
c-heptane + 23DMB	1.0206	0.8653	80	135
c-octane + 23DMB	0.8463	1.0307	90	184
c-pentane + c-hexane	0.7325	1.3010	21	- 4
c-hexane + c-heptane	0.3193	3.1146	- 1	9
c-heptane + c-octane	0.5529	1.8015	1	5
benzene + c-pentane	0.8641	0.9914	264	291
benzene + c-hexane	0.8518	0.6969	400	331
benzene + c-heptane	0.8309	0.7176	378	-
benzene + c-octane	0.8437	0.7010	363	286
toluene + c-pentane	0.8641	0.9914	99	-
toluene + c-hexane	0.7658	0.8679	307	332
toluene + c-heptane	0.7403	0.9290	271	-
toluene + c-octane	0.6883	0.9583	295	296
benzene + toluene	1.0750	0.8815	24	-
benzene + o-xylene	1.0070	0.8449	80	-
benzene + m-xylene	1.1167	0.7602	77	-
benzene + p-xylene	1.1427	0.7704	50	-
toluene + o-xylene	1.0052	0.9529	22	-
toluene + m-xylene	1.0132	0.9536	15	-
toluene + p-xylene	1.0331	0.9563	1	-

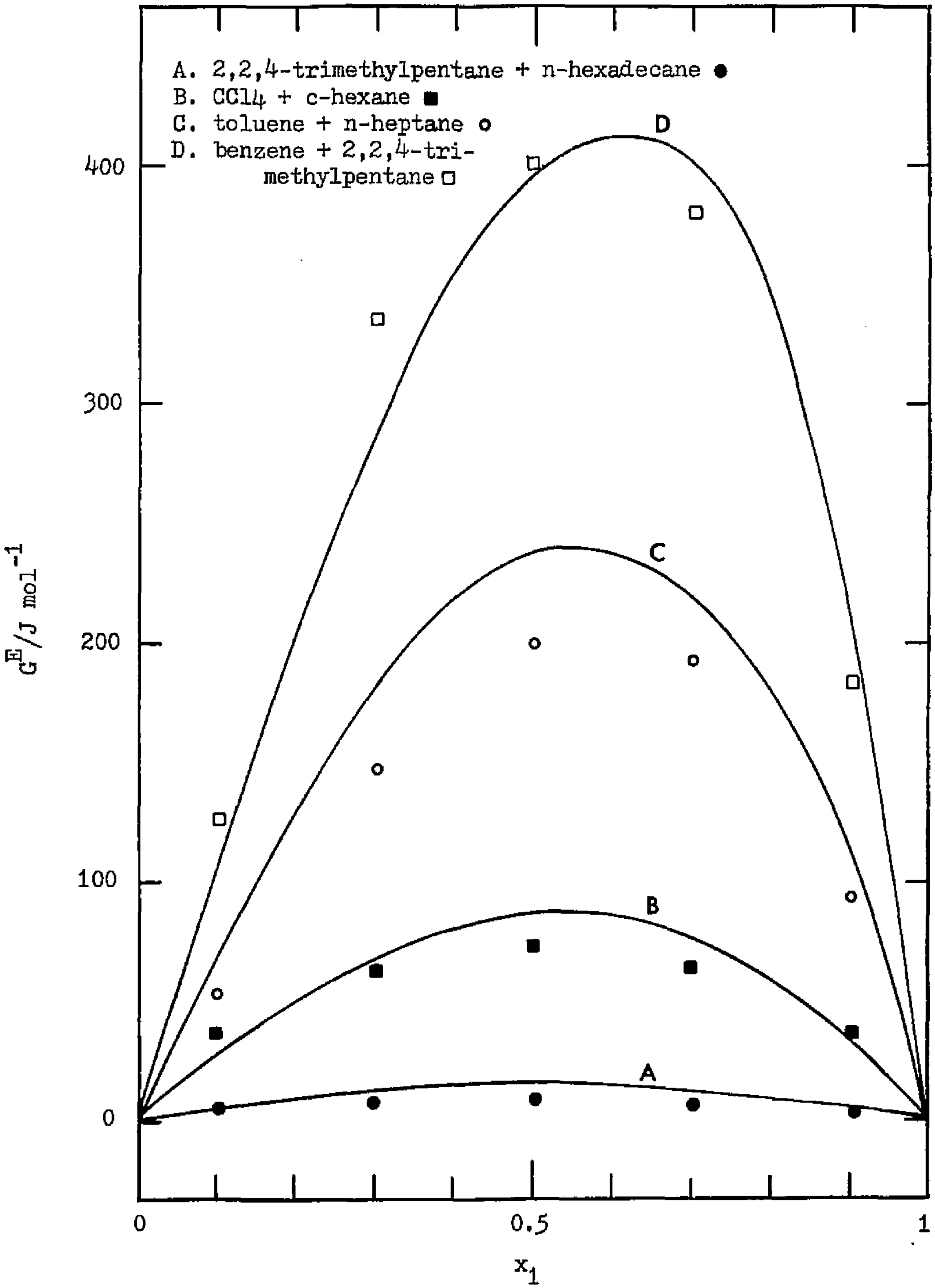

Figure 51. Dependence of the predicted excess free energy on composition. Symbols refer to smoothed experimental data.

VII. APPLICATION TO HYDROGEN BONDING LIQUIDS

The separation of the internal partition function from the translational partition function which was necessary to develop and apply the configurational partition function in Equation (132) is not rigorous for polar molecules since the rotations and vibrations of dipoles are strongly influenced by the positions of their neighbors. The assumption that the internal parition function is itself invarient on mixing is also not strictly valid for mixtures of polar molecules and is probably least accurate for mixtures of polar and non-polar molecules.

We expected, however, that the errors introduced by a non-rigorous application of the partition function in Equation (132) would be similar for members of a homologous series of polar liquids. While we did not expect to be able to determine absolute values of m for polar liquids (absolute in the sense that they could be combined with any of the m values of non-polar liquids in Table III), we expected to be able to determine an internally consistent relative scale of m values from which the excess enthalpy of mixtures of members of the series could be predicted.

We have examined mixtures of even carbon number normal alcohols with n-hexane and with each other and have found that the above expectation is fulfilled.

VII-1: Pure Components

The physical properties of the n-alcohols investigated are listed in Table XV. The values of α were computed from

Table XV

Physical Properties of n-Alcohols†

Liquid	$V/cm^3\ mol^{-1}$	$\alpha \times 10^3/K^{-1}$	$\gamma/J\ cm^{-3}\ K^{-1}$	$\Delta H^v/J\ mol^{-1}$
ethanol	56.68 (257)	1.083 (257)	0.942 (257)	42310 (256)
n-butanol	91.96 (257)	0.937 (257)	1.005 (257)	52380 (256)
n-hexanol	126.26 (257)	0.852 (257)	1.024 (257)	61920 (256)
n-octanol	158.42 (257)	0.818 (257)	1.050 (257)	65270 (256)

†at 298 K

density measurements at different temperatures; the values of γ were computed from the ratio of α to β, the isothermal compressibility. The isothermal compressibilities were derived from adiabatic compressibility values obtained from velocity of sound measurements, so that the uncertainty in these values is possibly somewhat higher than the uncertainty of most of the values used previously.

Values of m for the n-alcohols, calculated from the ratio of the internal pressure to the cohesive energy density, are listed in the first column of Table XVI. As before, the cohesive energy was approximated by the negative of the energy of vaporization assuming ideal gas phase behavior. Very low values of m were obtained by this method. This is because relatively small quantities of energy are associated with the minor changes in hydrogen bonding caused by the small intermolecular distance changes measured by the internal pressure, while much larger quantities of energy are associated with the total disruption of hydrogen bonding measured by vaporization to the ideal gas state. The rapid increase in the ratio method values of m with increasing carbon number results from the decreasing proportion of hydrogen bonding in the larger alcohols.

The characteristic properties of n-alcohols at three different values of m are tabulated in Table XVII. The values of m correspond to the ratio method values, to the van der Waals approximation and to values relative to n-hexane which will be discussed in Section VII-2. The characteristic properties at

Table XVI

Values of m for n-Alcohols

Liquid	m(ratio method)	m(relative to n-hexane)
ethanol	0.414	0.970
n-butanol	0.515	1.041
n-hexanol	0.643	1.085
n-octanol	0.790	1.126

Table XVII

Characteristic Parameters of n-Alcohols

Liquid	m	$V^*/cm^3\ mol^{-1}$	T^*/K	$P^*/J\ cm^{-3}$	C
ethanol	0.414	44.70	9296.0	996.6	0.597
	0.970	46.33	5103.0	461.2	0.504
	1.000	46.41	5010.7	449.1	0.500
n-butanol	0.515	72.72	8678.8	829.6	0.836
	1.000	74.47	5422.1	456.9	0.755
	1.041	74.62	5290.9	440.5	0.747
n-hexanol	0.643	101.45	7826.2	672.0	1.048
	1.000	102.96	5734.5	451.9	0.976
	1.085	103.29	5441.8	421.0	0.961
n-octanol	0.790	129.99	6914.6	564.7	1.277
	1.000	131.02	5876.7	457.7	1.227
	1.126	131.60	5442.1	412.4	1.200

ratio method m values are markedly different from those computed at the other values of m; T^* and P^* for the smaller alcohols are approximately twice as large at ratio method m values than at van der Waals and higher values of m. Values of C are always low for the smaller molecules, indicating very restricted motion in the liquid state; C increases as the carbon number of the alcohol increases and the proportion of hydrogen bonding decreases. Comparison of the magnitudes of C in hexanol and octanol with the magnitudes in the parent hydrocarbons (Table IV) not unexpectedly shows that molecular motion is more restricted in alcohols than in the corresponding alkanes.

Molar interaction energies of the different alcohols computed from their characteristic parameters at various values of m are listed in Table XVIII, along with the experimental energies of vaporization. The highest attractive interaction energies result from use of the ratio method values of m; such interaction energies include the total energy contributions arising from hydrogen bonding and most closely parallel the the energies of vaporization.

VII-2: Mixtures

The sources and equimolar values of the excess properties of the alkane + alcohol and alcohol + alcohol mixtures studied are tabulated in Table XIX. The concentration dependence of the excess properties of the n-hexane + n-alcohol systems has not been experimentally investigated.

Using $m_{n\text{-hexane}} = 1.115$ as determined in Section VI-2,

Table XVIII

Molar Interaction Energies of n-Alcohols

Liquid	ΔE^V/J mol^{-1}	Interaction energy/J mol^{-1}		
		m = 1	ratio method	relative to n-hexane
ethanol	39830	16483	39804	16989
n-butanol	49900	27555	53455	26441
n-hexanol	59440	38240	59533	35279
n-octanol	62790	49597	62778	44044

Table XIX

Excess Properties† at $x_1 = 0.5$ of Binary Mixtures Containing Hydrogen Bonding Liquids

Mixture	$V^E/cm^3\ mol^{-1}$		$H^E/J\ mol^{-1}$	
ethanol + n-hexane	0.41	(258)	555	(258)
n-butanol + n-hexane	0.08	(258)	510	(258)
n-hexanol + n-hexane	-0.16	(258)	465	(258)
n-octanol + n-hexane	-0.35	(258)	415	(258)
ethanol + n-butanol	0.012	(259)	48	(260)
ethanol + n-hexanol	0.036	(257)	126	(257)
ethanol + n-octanol	0.060	(259)	217	(260)
n-butanol + n-hexanol	0.012	(259)	27	(260)
n-butanol + n-octanol	0.041	(259)	104	(260)
n-hexanol + n-octanol	0.010	(259)	26	(260)

†at 298 K

values of m relative to n-hexane were computed for the n-alcohols by determining the values needed to reproduce perfectly the experimental excess enthalpy of the appropriate n-hexane + n-alcohol mixture. These values of m are listed in the second column of Table XVI. They are all higher than the ratio method values of m; this partially reflects the retention of some hydrogen bonding characteristics in the mixed state and partially reflects the artificiality of applying Equation (132) to polar molecules. Like the ratio method values, the mixture method values of m increase with increasing chain length.

The values of m obtained from hexane mixtures were directly used to compute the excess enthalpies of binary alcohol mixtures. Very satisfactory agreement with experiment was obtained, both at $x_1 = 0.5$ and throughout the concentration range. The equimolar predictions are tabulated in Table XX and the concentration dependences are shown in Figure 52. Use of the van der Waals approximation results in better predictions for alcoholic mixtures than it does for mixtures containing non-polar molecules.

The effects of small uncertainties in V^E, α and γ on H^E predictions are shown in Tables XXI, XXII and XXIII; the influence of these physical properties is analogous to that noted in Sections VI-3 and VI-4.

The values of m derived for the alcohols from alcohol + hexane mixtures should yield accurate excess enthalpy predictions for mixtures of alcohols and alkanes other than n-hexane. They should not be used to predict the excess enthalpy of mixtures

Table XX

Predicted Excess Enthalpies at $x_1 = 0.5$ of Mixtures Containing Hydrogen Bonding Liquids

Mixture	H^E/J mol^{-1}		
	experiment	pseudo-2-fluid	m = 1
ethanol + n-hexane	555	555	479
n-butanol + n-hexane	510	510	338
n-hexanol + n-hexane	465	464	420
n-octanol + n-hexane	415	416	421
ethanol + n-butanol	48	44	46
ethanol + n-hexanol	126	125	123
ethanol + n-octanol	217	215	213
n-butanol + n-hexanol	27	27	24
n-butanol + n-octanol	104	96	79
n-hexanol + n-octanol	26	22	22

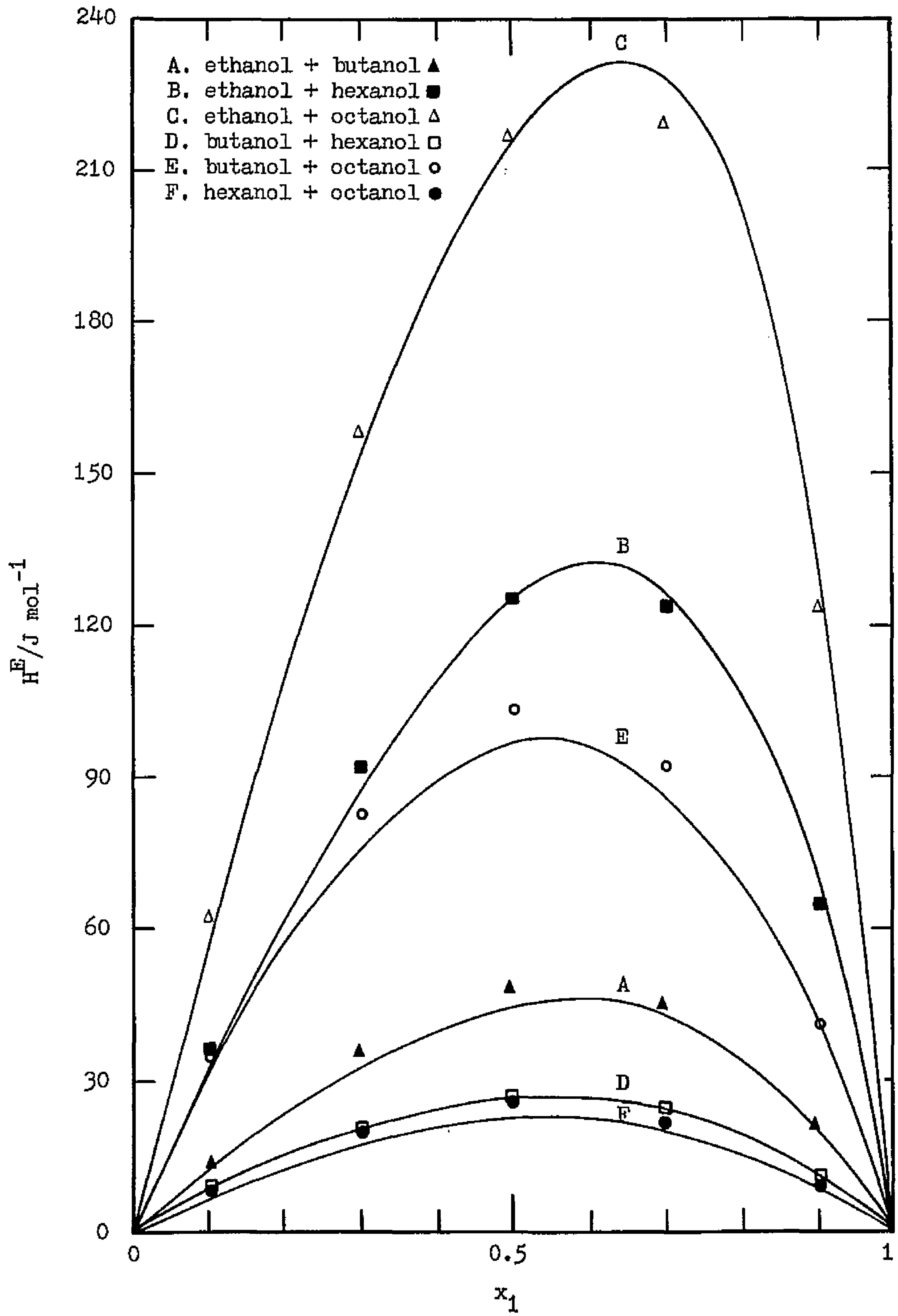

Figure 52. Dependence of the predicted excess enthalpy on composition for mixtures of n-alcohols. Symbols refer to smoothed experimental data.

Table XXI

Effect of Uncertainties in V^E on H^E of Mixtures Containing Hydrogen Bonding Liquids

Mixture	H^E/J mol^{-1}		Uncertainty in V^E/cm^3 mol^{-1}					
	exp	calc	(+) 0.005	(-)	(+) 0.010	(-)	(+) 0.020	(-)
ethanol + n-hexane	555	555	558	552	561	549	567	543
n-butanol + n-hexane	510	510	514	506	517	503	524	496
n-hexanol + n-hexane	465	464	468	460	472	456	480	448
n-octanol + n-hexane	415	416	420	411	424	407	432	399
ethanol + n-butanol	48	44	49	39	54	34		
ethanol + n-hexanol	126	126	131	120	136	115		
ethanol + n-octanol	217	215	221	210	226	205		
n-butanol + n-hexanol	27	27	32	21	38	16		
n-butanol + n-octanol	104	96	102	91	107	85		
n-hexanol + n-octanol	26	22	28	16	34	11		

Table XXII

Effect on Uncertainties in α on H^E of Mixtures Containing Hydrogen Bonding Liquids

Mixture	H^E/J mol^{-1}		Uncertainty in α			
	exp	calc	α_1 +1%	α_1 -1%	α_2 +1%	α_2 -1%
ethanol + n-hexane	555	555	550	559	556	553
n-butanol + n-hexane	510	510	503	518	517	504
n-hexanol + n-hexane	465	464	454	474	473	455
n-octanol + n-hexanol	415	416	403	427	428	403
ethanol + n-butanol	48	44	46	42	42	46
ethanol + n-hexanol	126	126	128	123	122	128
ethanol + n-octanol	217	215	219	212	211	220
n-butanol + n-hexanol	27	27	27	26	26	27
n-butanol + n-octanol	104	96	97	95	95	97
n-hexanol + n-octanol	26	22	23	21	20	24

Table XXIII

Effect of Uncertainties in γ on H^E of Mixtures Containing Hydrogen Bonding Liquids

Mixture	H^E/J mol^{-1}		Uncertainty in γ			
	exp	calc	γ_1 +2%	γ_1 -2%	γ_2 +2%	γ_2 -2%
ethanol + n-hexane	555	555	589	520	532	578
n-butanol + n-hexane	510	510	559	461	471	549
n-hexanol + n-hexane	465	464	526	403	412	516
n-octanol + n-hexane	415	416	482	349	357	474
ethanol + n-butanol	48	44	41	47	48	40
ethanol + n-hexanol	126	126	119	132	134	117
ethanol + n-octanol	217	215	210	221	225	206
n-butanol + n-hexanol	27	27	23	31	32	23
n-butanol + n-octanol	104	96	93	99	101	91
n-hexanol + n-octanol	26	22	24	21	21	23

containing molecules dissimilar to hexane. Mixtures of such molecules might interact differently with the hydroxyl group and produce deviations from the mixture partition function not accounted for in the hexane-derived values of m.

For completeness, the method described in Section V-2 has been used to predict excess free energies for the alcoholic mixtures studied. The predictions are listed in Table XXIV, along with the corresponding values of D_{12} and D_{21}. No experimental data is available for comparison.

Table XXIV

Prediction of G^E at $x_1 = 0.5$ for Mixtures of n-Alcohols
from the Composition Dependence of
Pseudo-2-fluid H^E Predictions

Mixture	D_{12}	D_{21}	G^E/J mol^{-1}
ethanol + n-butanol	1.3902	0.6940	40
ethanol + n-hexanol	1.5651	0.5768	111
ethanol + n-octanol	1.6334	0.5140	185
n-butanol + n-hexanol	1.1594	0.8437	16
n-butanol + n-octanol	1.1734	0.7898	42
n-hexanol + n-octanol	1.2061	0.8144	6

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