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NOTATION

A = molar Helmholtz free energy
a = attraction parameter
b = van der Waals covolume
C_p = heat capacity at constant pressure
G = molar Gibbs free energy
M = critical state determinant
n = number of components
P = pressure
R = gas constant
T = temperature
U = critical state determinant
V = molar volume
x = mole fraction
α = scaling factor
δ = interaction coefficient
κ = characterization constants
ω = Pitzer's acentric factor

Superscript

(r) = r^{th} iteration
$*$ = ideal gas state

Subscripts

c = critical property
i, j, k = component identifications
o = reference state

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A Group Contribution Molecular Model of Liquids and Solutions

A group contribution molecular model is developed for the thermodynamic properties of polar and nonpolar liquids and their solutions, including energy of vaporization, pVT relations, excess properties, and activity coefficients. The model is based on the cell theory in which the repulsive forces of molecules are expressed with a modified cell partition function derived from the Carnahan-Starling equation of state for hard spheres. The attractive forces are made up of group pair interaction contributions. Group and interaction properties have been determined for methyl, methylene, hydroxyl, and carbonyl. Extensive comparisons are made of predictions of the model with data for pure liquids and their solutions.

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SCOPE

The objective of this work is twofold:

1. To develop a comprehensive theory of group contribution for the estimation of various thermodynamic properties of polar and nonpolar liquids and their solu-

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tions that are needed in engineering design and analysis.

2. To demonstrate the theory by applying it to several groups of common occurrences, thus making possible wide ranging predictions for a large number of molecular systems.

Group contribution methods are capable of making predictions of properties for systems for which only the molecular structure may be known. Since many molecules are made up of a few common structural units (or groups), the potential of group contribution methods for making predictions for large numbers of molecular systems is great.

Past efforts with group contribution have been numerous, but the correlations developed were limited in scope, one correlation being devoted exclusively to one property such as heat of vaporization, activity coefficients at one temperature, etc. In contrast, the present theory describes various thermodynamic properties of pure liquids and their solutions, including activity coefficients, over a wide temperature range.

CONCLUSIONS AND SIGNIFICANCE

A group interaction molecular model has been developed for the quantitative description of the thermodynamic properties of liquids of polar and nonpolar substances and their solutions. Properties of the methyl, methylene, hydroxyl, and carbonyl groups and all their mutual interactions have been evaluated from analysis of pure fluid data over a wide temperature range and adjusted by referring to excess property data of a few binary systems at one or two temperatures. The molecular model with the properties of the four groups is capable of predicting thermodynamic properties for a large number of molecular systems over a wide temperature range. Extensive comparisons of the predicted values with literature data have been made at conditions for which the cell model is known to be applicable: where the liquids are not expanded, the reduced density is greater than 2, and the temperature is not much above the normal boiling point. The results show that the model gives reliable results for:

Energies of vaporization and densities for all fluids at all temperatures studied except for the heaviest fluids at the higher temperatures.

Activity coefficients in all the liquid solutions studied.

Excess enthalpies, where the deviations may be acceptable in terms of calories per mole but can be large in percent figures where the values are very small, as for *n*-alkane solutions.

These results show that the model can be applied for making useful estimates for systems for which experimental data are incomplete or lacking when the properties of all of the groups making up the system are determined and are available.

The model will be extended to include additional groups and to describe larger classes of molecular systems. Experience to date shows that the hard core volumes of the groups can be closely estimated from Bondi's van der Waals volumes. The procedure for the determination of the other properties of the groups is well developed.

There has been a sustained interest in the recent literature about group contributions to activity coefficients in highly nonideal solutions. This interest stems from the simple fact that large numbers of molecules are made up of a few common structural units or groups. Group contribution models, therefore, offer the potential of making wide ranging predictions in numerous mixture systems using the properties of a few groups. Notable in this development are the pioneering work by Pierotti, Deal, and Derr (1959), Wilson and Deal (1962), and subsequent contributions by Scheller (1965), Ratcliff and Chao (1969), Derr and Deal (1969), and Fredenslund, Jones, and Prausnitz (1975).

Lee, Greenkorn, and Chao (1972) extended the group contribution concept by expressing it in terms of a partition function description of a molecular model. These results are no longer restricted to activity coefficients but applicable to various thermodynamic properties at the same time, including those of pure liquids. Indeed, from the group viewpoint there is no clear distinction between pure liquids and solutions, and a practical consequence is that many of the properties of the groups of interest can be determined from analysis of data on pure liquids. The partition function formulation also releases the model from being fixed at a given temperature, and extrapolation can be made with respect to temperature. The degree of practical success of these extrapolations with a partition function from pure liquids to mixtures and from one temperature to another depends on the physical model described by the partition function. In this work, we improve the physical model of Lee et al. and achieve extrapolation of considerable range. Data on pure liquids are used for the determination of all the properties of the groups. Subsequently, fine adjustments are made of the group exchange energy by referring to excess properties of one binary system at one or two temperatures. The completed model is then compared with data on several thermodynamic properties for various molecular systems.

A MOLECULAR MODEL EXPRESSED AS GROUP CONTRIBUTIONS

Following Lee et al. (1972), we adopt the cell theory as our molecular model. Thus, the partition function Q for a liquid is given by

$$Q = g\left(\prod_A \psi_A^{N_A} \right) \exp(-E/kT) \qquad (1)$$

The molecular cell partition function is expressed in terms of contributions by its constituent groups

$$\psi_A = \prod_i \psi_i^{n_{iA} c_i} \qquad (2)$$

According to Prigogine (1957*a*), the external degrees of freedom c expresses the equivalent translational motions of the group that are dependent on the external environment but independent of the valency forces. By the assumption of homogeneity of cells, all the ψ_i's are equal in a given liquid. Hence, c_i is the only variable characteristic of group i in Equation (2).

Our experience (Lee et al., 1972) with the usual cell partition function showed it is not entirely satisfactory in the description of the change of properties over wide temperature ranges. In this work we use a new cell partition function derived from the Carnahan-Starling (1969) hard sphere equation of state given by

$$\psi_t = \tilde{v} \exp\left[-\frac{(4\tilde{v}-3)}{(\tilde{v}-1)^2} \right] \tag{3}$$

where $\tilde{v} = V/V^*$, reduced volume. The derivation of Equation (3) is given in Appendix A. The Carnahan-Starling equation is the result of a long series of investigations on radial distribution and the fine structure of fluids due to short-range repulsive forces. It is applicable to dense fluids in which multiple collisions predominate, a condition that is found in the liquids of interest in this work. In reexpressing the Carnahan-Starling equation, we convert the radial distribution functions into the practically more convenient partition functions.

The hard core volume has been found to decrease with increasing temperature (Bienkowski and Chao, 1975). The hard core volume of groups as a function of T is represented in this work by the empirical expression

$$V_i^* = V_{io}^* \exp\left[a_i \left(\frac{1}{T} - \frac{1}{T_o} \right) \right] \tag{4}$$

where V_{io}^* denotes the hard core volume at the base temperature T_o, and a_i expresses the dependence of V^* on T. We chose the base temperature T_o to be 298.15°K.

Attractive forces are of comparable importance to the repulsive forces expressed by the hard sphere derived partition function of Equations (2) and (3). The attractive forces are more long ranged and do not play a direct role in determining the fine structure. We express the attractive forces by the lattice energy and decompose it into group contributions as follows:

$$E = \sum_{i \geq j} \sum N_{ij} \phi_{ij} \tag{5}$$

The pairwise interaction energy is made up of two terms:

$$\phi_{ij} = -\frac{\epsilon_{ij}}{\tilde{v}} \exp\left(\frac{\kappa}{\tilde{v}} \right) - \sigma_{ij} \tag{6}$$

The first term on the right-hand side of Equation (6) expresses the dispersive energy and the second term the chemical association energy. For nonassociating pairs, $\sigma = 0$, and all the energy is dispersive. However, for associating pairs, $\epsilon \neq 0$, and dispersive energy still makes a contribution.

Hildebrand and Scott (1950) and Flory, Orwoll, and Vrij (1964) expressed the dispersive energy in the form $1/\tilde{v}$, which is justified if the radial distribution function is independent of density. Lee et al. raised the volume to a power of 1.15 from consideration of internal pressure data by Allen et al. (1960 *a, b*) and by Bagley et al. (1970). The exponential function used in Equation (6) improves agreement with internal pressure data and was adopted after extensive comparison of calculated results with those of other functions.

The chemical association energy is temperature dependent and is given by

$$\frac{\sigma}{T} = \frac{\sigma_o}{T_o} + \sigma' \left(\frac{1}{T} - \frac{1}{T_o} \right) \tag{7}$$

where σ_o and σ' are constants for given ij pairs.

Internal pressure data indicate σ is independent of volume. Wiehe and Bagley (1967) observed that hydrogen bonds appear to remain intact in a small isothermal expansion; the volume change occurs primarily due to increases in the spacing of the inert backbone portions of the molecules. Winnick (1972) arrived at the same conclusion from consideration of canonical preaveraging of dipole energy.

The energy expressed by Equation (6) represents the average energy of interaction of an ij pair in contact averaged over the configurations of a contact and must not be confused with instantaneous interaction energy of a pair. The average pairwise energy is a function of macroscopic variables such as $\tilde{v}$ and possibly T, but the instantaneous energy of a pair must depend on microscopic variables such as distances and angles.

The number of ij pairs in a liquid N_{ij} is governed by the abundance of contacts offered by i and j and by the energy ϕ_{ij} relative to the energies of other modes of interaction of i and of j. Two sets of equations simultaneously determine N_{ij}:

$$\frac{N_{ij}^2}{N_{ii}N_{jj}} = 4 \exp\left(-\frac{2w_{ij}}{kT} \right) \tag{8}$$

and

$$2N_{ii} + \sum_{j(\neq i)} N_{ij} = Q_i n_i N \tag{9}$$

where $w_{ij} = \phi_{ij} - (\phi_{ii} + \phi_{jj})/2$, exchange energy. Equation (8) expresses Guggenheim's quasichemical relation and Equation (9) the stoichiometry of contacts.

The contacts Q of a group are determined by the surface area of the group for which we use the van der Waals surface area values compiled by Bondi (1968). The calculation of Q is described in Appendix B. The lattice coordination number is set equal to 10 in the calculations.

The combinatorial factor g in Equation (1) is made up of two parts:

$$g = g_o g_1 \tag{10}$$

$$\ln g_1 = \sum_i \ln \frac{N_{ii}^*!}{N_{ii}!} + \sum_{i>j} \sum \ln \frac{N_{ij}^*! 2^{N_{ij}}}{N_{ij}! 2^{N^*_{ij}}} \tag{11}$$

where N^*_{ij} denotes the number of ij pairs in the liquid if specific preferential interactions were absent.

The complete expression for our molecular model is obtained upon combining the preceding equations:

$$\ln Q = \ln g_o + \ln g_1 + Nc\left[\ln \tilde{v} - \frac{(4\tilde{v}-3)}{(\tilde{v}-1)^2} \right] - \sum_{i \geq j} \sum \frac{N_{ij}\phi_{ij}}{kT} \tag{12}$$

where $c = \sum_i c_i n_i = \sum_A c_A x_A$ average external degrees of freedom per molecule, and $c_A = \sum_i c_i n_i^A$, external degrees of freedom of molecule A.

THE WORKING EQUATIONS

Working equations are obtained from the partition function Equation (12) by following standard procedures of statistical thermodynamics. The results are given below with brief comments.

Equation of state

Upon differentiating Equation (12) with respect to V at constant T and N_A, we obtain the equation of state

$$\frac{pV}{NkT} = c + \frac{c\tilde{v}(4\tilde{v} - 2)}{(\tilde{v} - 1)^3} - \frac{n\overline{Q\epsilon}}{2kT\tilde{v}}\left(1 + \frac{\kappa}{\tilde{v}}\right)\exp\left(\frac{\kappa}{\tilde{v}}\right) \quad (13)$$

Equation (13) is applicable to liquids but not to gases, inasmuch as it does not approach the ideal gas limit of $pV = NkT$ at infinite volume. Equation (13) may be expressed completely in reduced variables:

$$\frac{\tilde{p}\tilde{v}}{\tilde{T}} = 1 + \frac{\tilde{v}(4\tilde{v} - 2)}{(\tilde{v} - 1)^3} - \frac{(1 + \kappa/\tilde{v})}{\tilde{T}\tilde{v}}\exp\left(\frac{\kappa}{\tilde{v}}\right) \quad (14)$$

The reduced variables are defined by

$$\tilde{p} = p/p^* \quad (15)$$

$$\tilde{v} = V/V^* = v/v^* \quad (16)$$

$$\tilde{T} = T/T^* \quad (17)$$

and the reducing variables by

$$p^* = cNkT^*/V^* \quad (18)$$

$$V^* = N(v^*/\tilde{N}) \quad (19)$$

$$T^* = n\overline{Q\epsilon}/2ck \quad (20)$$

In Equation (16), V and V^* represent liquid and core volumes of a given liquid, while v and v^* are the corresponding molal quantities.

In Equation (20), n denotes the average number of groups per molecule

$$n = \sum_i n_i \quad (21)$$

and $\overline{Q\epsilon}$ denotes the average interaction coefficient defined by

$$\overline{Q\epsilon} = \frac{2}{nN}\sum_{i \geqq j}\sum N_{ij}\epsilon_{ij} \quad (22)$$

For random mixtures in which preferential orientation effects are absent, Equation (22) simplifies to

$$\overline{Q\epsilon} = \sum_i \frac{n_i Q_i}{n}\sum_j \frac{n_j Q_j \epsilon_{ij}}{\sum_k n_k Q_k} \quad (23)$$

The derivation of Equation (13) from Equation (12) simplifies, since a number of volume derivatives in combination vanish:

$$\left(\frac{\partial \ln g_1}{\partial \tilde{v}}\right)_T - \sum_{i \geqq j}\sum \left(\frac{\partial N_{ij}}{\partial \tilde{v}}\right)\frac{\phi_{ij}}{kT}$$

$$= -\frac{1}{2}\sum_i \left(\ln N_{ii} + \frac{\phi_{ii}}{kT}\right)\frac{\partial\left(2N_{ii} + \sum_{j\ (\neq i)} N_{ij}\right)}{\partial \tilde{v}}$$

$$= -\frac{1}{2}\sum_i \left(\ln N_{ii} + \frac{\phi_{ii}}{kT}\right)\frac{\partial(Q_i N_i n)}{\partial \tilde{v}} = 0 \quad (24)$$

Configurational energy and internal energy of vaporization

The configurational energy is given by

$$U_{\text{conf}} = kT^2\left(\frac{\partial \ln Q}{\partial T}\right)_{V,N} \quad (25)$$

Substituting Equation (12) in Equation (25), we obtain

$$\frac{U_{\text{conf}}}{NkT} = \sum_{i \geqq j}\sum \left[\frac{N_{ij}\phi_{ij}}{NkT} + \frac{N_{ij}}{Nk}\left(\frac{\partial \sigma_{ij}}{\partial T}\right)_V\right] - \left(\frac{d \ln V^*}{d \ln T}\right)\left(\frac{pV}{NkT}\right) \quad (26)$$

or

$$\frac{U_{\text{conf}}}{NkT} = -\sum_{i \geqq j}\sum \frac{N_{ij}}{NkT}\left[\frac{\epsilon_{ij}}{\tilde{v}}\exp\left(\frac{\kappa}{\tilde{v}}\right) + \sigma'_{ij}\right] - \left(\frac{\partial \ln V^*}{\partial \ln T}\right)\left(\frac{pV}{NkT}\right) \quad (27)$$

For low pressure liquids $p \doteq 0$ with nonspecific interactions, $w_{ij} = 0$ for all i, j. Equation (27) simplifies to

$$\frac{U_{\text{conf}}}{NkT} = -\frac{n\overline{Q\epsilon}}{2KT\tilde{v}}\exp\left(\frac{\kappa}{\tilde{v}}\right) \quad (28)$$

or

$$\frac{U_{\text{conf}}}{NkT} = -\frac{c}{\tilde{T}\tilde{v}}\exp\left(\frac{\kappa}{\tilde{v}}\right) \quad (29)$$

The derivation of Equation (26) from Equation (25) simplifies, since a number of temperature derivatives in combination vanish:

$$\left(\frac{\partial \ln g_1}{\partial T}\right)_V - \sum_{i \geqq j}\sum \left(\frac{\partial N_{ij}}{\partial T}\right)_V \frac{\phi_{ij}}{kT}$$

$$= -\frac{1}{2}\sum_i \left(\ln N_{ii} + \frac{\phi_{ii}}{kT}\right)\frac{\partial(Q_i n_i N)}{\partial T} = 0 \quad (30)$$

The configurational energy given above will be identified in the following calculations with the internal energy of vaporization into vacuum $U_{\text{conf}} = \Delta U_v$. The equality is rigorous for simple molecules for which there is no difference in rotational and vibrational modes in the gas and liquid states. The equality is assumed to hold also for complex molecules such as those studied in this work. Possible errors are likely small, as the energy of vaporization is mainly due to molecular interaction energy which is accounted for in the configurational energy. Prigogine (1957*b*) and Hijmans and Holleman (1969) assumed the same equality in their work on chain molecules.

Chemical potential and activity coefficient

The chemical potential of A is obtained from Equation (12) by differentiation at constant T, V, and $N_{B \neq A}$:

$$\frac{\mu_A}{kT} = -\left(\frac{\partial \ln g_o}{\partial N_A}\right) - c_A\left[\ln \tilde{v} - \frac{(4\tilde{v} - 3)}{(\tilde{v} - 1)^2}\right] + \frac{1}{2}\sum_i Q_i n_i^A\left[\ln\left(\frac{N_{ii}}{N_{ii}^*}\right) + \frac{\phi_{ii}}{kT}\right] \quad (31)$$

Activity coefficient is derived from Equation (31), based on $\ln \gamma_A = (\mu_A - \mu_{AO})kT - \ln x_A$:

$$\ln \gamma_A = \ln\left(\frac{V_A^*}{V^*}\right) + 1 - \frac{V_A^*}{V^*} + c_A\left[\ln\left(\frac{\tilde{v}_{A0}}{\tilde{v}}\right)\right.$$

$$+\frac{4\tilde{v}-3}{(\tilde{v}-1)^2}-\frac{(4\tilde{v}_{A0}-3)}{(\tilde{v}_{A0}-1)^2}\Bigg]$$

$$+\frac{1}{2}\sum_i Q_i n_i^A(\phi_{ii}-\phi_{ii}^{A0})/kT$$

$$+\sum_i Q_i n_i^A \ln\left(\frac{Y_i}{Y_i^*}\cdot\frac{Y_i^{*A0}}{Y_i^{A0}}\right) \qquad (32)$$

where the index $A0$ expresses that the quantity is for pure liquid A, and Y is defined by

$$Y_i=\frac{1}{Q_i n_i}\sqrt{\frac{N_{ii}}{N}} \qquad (33)$$

The first three terms on the right-hand side of Equation (32) represent Flory-Huggins' entropy contribution. The next two terms reflect the effect of changes in reduced volume associated with the mixing of liquids. The last term shows the effect of changes of specific interaction due to mixing and is zero for fluids of nonspecific interactions.

With N_{ii} expressed in terms of Y_i, the quasichemical relation Equation (8) and the stoichiometry of contacts Equation (9) are combined to give

$$Y_i\sum_j Q_j n_j \eta_{ij} Y_j=\frac{1}{2} \qquad (34)$$

where, by definition

$$\eta_{ij}=\exp(-w_{ij}/kT) \qquad (35)$$

There is one equation like Equation (34) for each group. The set of equations for all the groups simultaneously determines Y_i for use in Equation (32). In general, a numerical procedure has to be followed to find Y_i. However, for liquids of nonspecific interactions, an explicit solution is obtained:

$$Y_i^*=1/\sqrt{2\sum_j Q_j n_j} \qquad (36)$$

The main advantage gained in replacing N_{ii} with Y_i is the fact that Y_i has a nonzero value even at infinite dilution of group i. The algorithm for finite concentrations can be extended to infinite dilution without alteration.

Heat of mixing

The molal heat of mixing is strictly given by

$$H^E=H-\sum_A x_A H_{A0} \qquad (37)$$

For low pressure liquids, we use the approximate equation

$$H^E=U_{\text{conf}}-\sum_A x_A U_{A0\text{conf}} \qquad (38)$$

Substitution of Equation (27) in Equation (38) gives, for low pressure liquids

$$\frac{H^E}{RT}=-\sum_i Q_i n_i\sum_j Q_j n_j\Bigg\{Y_iY_j\eta_{ij}\left[\frac{\epsilon_{ij}}{RT\tilde{v}}\exp\left(\frac{\kappa}{\tilde{v}}\right)\right.$$

$$\left.+\sigma'_{ij}\right]-\sum_A x_A Y_i^{A0}Y_j^{A0}\eta_{ij}^{A0}\left[\frac{\epsilon_{ij}}{RT\tilde{v}_{A0}}\exp\left(\frac{\kappa}{\tilde{v}_{A0}}\right)\right.$$

$$\left.+\sigma'_{ij}\right]\Bigg\} \qquad (39)$$

Coefficient of thermal pressure

The coefficient of thermal pressure is defined by

$$\gamma_V=(\partial p/\partial T)_V \qquad (40)$$

and is of much interest because of its close relationship to the internal pressure of a liquid $-(\partial U/\partial V)_T$ through the equation

$$-\left(\frac{\partial U}{\partial V}\right)_T=p-T\left(\frac{\partial p}{\partial T}\right)_V \qquad (41)$$

For low pressure liquids, $p \doteq 0$:

$$-\left(\frac{\partial U}{\partial V}\right)_T=-T\gamma_V \qquad (42)$$

From Equation (13) we differentiate to obtain a dimensionless expression for γ_V:

$$\frac{\gamma_V V}{Nk}=c\left[1+\frac{\tilde{v}(4\tilde{v}-2)}{(\tilde{v}-1)^3}\right]+\left(\frac{d\ln V^*}{d\ln T}\right)$$

$$\left(\frac{V}{\beta_T NkT}-\frac{pV}{NkT}\right)-\sum_{i\geqq j}\sum\frac{N_{ij}}{NkT}\left(\frac{\partial\phi_{ij}}{\partial\ln\tilde{v}}\right)_T$$

$$\left[\left(\frac{\partial\ln N_{ij}}{\partial\ln T}\right)_V+\left(\frac{\partial\ln N_{ij}}{\partial\ln\tilde{v}}\right)_T\left(\frac{d\ln V^*}{d\ln T}\right)\right] \qquad (43)$$

For liquids of nonspecific interactions, Equation (43) simplifies to

$$\frac{\gamma_V V}{Nk}=c\left[1+\frac{\tilde{v}(4\tilde{v}-2)}{(\tilde{v}-1)^3}\right]+\left(\frac{d\ln V^*}{d\ln T}\right)$$

$$\left(\frac{V}{\beta_T NkT}-\frac{pV}{NkT}\right) \qquad (44)$$

The coefficient of isothermal compressibility β_T required in Equations (43) and (44) is given below. The derivatives of N_{ij} with T and with $\tilde{v}$ also required in these equations are discussed in Appendix C.

Coefficient of isothermal compressibility

The coefficient of isothermal compressibility is defined by

$$\beta_T=-\frac{1}{V}\left(\frac{\partial V}{\partial p}\right)_T \qquad (45)$$

We obtain a dimensionless expression for β_T upon differentiating Equation (13):

$$\frac{V}{\beta_T NkT}=\frac{pV}{NkT}+\frac{c\tilde{v}(4\tilde{v}^2+4\tilde{v}-2)}{(\tilde{v}-1)^4}$$

$$+\sum_{i\geqq j}\sum\frac{N_{ij}}{NkT}\left[\frac{\partial}{\partial\ln\tilde{v}}\left(\frac{\partial\phi_{ij}}{\partial\ln\tilde{v}}\right)_T\right.$$

$$\left.+\left(\frac{\partial\ln N_{ij}}{\partial\ln\tilde{v}}\right)\left(\frac{\partial\phi_{ij}}{\partial\ln\tilde{v}}\right)_T\right] \qquad (46)$$

For liquids of nonspecific interactions, Equation (46) simplifies to

$$\frac{V}{\beta_T NkT}=\frac{c\tilde{p}\tilde{v}}{\tilde{T}}+\frac{c\tilde{v}(4\tilde{v}^2+4\tilde{v}-2)}{(\tilde{v}-1)^2}$$

Table 1. Properties of Groups and Their Interactions

Group	V_o^* (cm³/mole)	a (°K)	c	ϵ_{ii} (cal/mole)	Q	V_w (cm³/mole)
CH_3 methyl	13.46	23.7	0.338	601	6.71	13.67
CH_2 methylene	10.25	23.7	0.093	601	4.27	10.23
OH hydroxyl	8.01	39.6	0.245	1 646	3.62(O) 1.00(H)	8.04
C=O carbonyl	11.60	11.2	0.147	1 558	5.06	11.70

$\Delta\epsilon = -\epsilon_{ij} + (\epsilon_{ii} + \epsilon_{jj})/2$

	CH_3	CH_2	OH	C=O
CH_3	0	0	230	228
CH_2		0	230	228
OH			0	0.0
C=O				0

σ^0 and σ'

	O	H	C=O
O	0	$\sigma^0 = 3\,000$ $\sigma' = 4\,100$	0
H		0	$\sigma^0 = 3\,050$ $\sigma' = 3\,870$
C=O			$\sigma^0 = 700$ $\sigma' = 700$

$$-\frac{c}{\tilde{\tilde{T}}\tilde{\tilde{v}}}\left(1+\frac{3\kappa}{\tilde{v}}+\frac{\kappa^2}{\tilde{v}^2}\right)\exp\left(\frac{\kappa}{\tilde{v}}\right) \qquad (47)$$

NORMAL ALKANES AND THEIR SOLUTIONS

n-alkanes and their solutions are made up of only two groups: methyl and methylene. The properties of these two groups and their interactions are determined by referring to data on several pure alkane liquids. Subsequently, the external degrees of freedom of methyl and methylene are finely adjusted by referring to activity coefficient data on one binary system.

Data on five pure n-alkane liquids are used in the group property determination, and they are C_6, C_7, C_8, C_{12}, and C_{16}. The data used are molal volume v, thermal pressure coefficient γ_v, and configurational energy U_{conf} at temperatures from −20° to 210°C but not to exceed reduced temperature (based on critical) of 0.75. The molal volumes are based on the density data of Orwoll and Flory (1967). The thermal pressure coefficient data are from the same source. Internal energy of vaporization values are obtained from heat of vaporization values at 25°C and the normal boiling point from American Petroleum Institute Research Project 44 tables of 1965. The two values of ΔH_v are fitted with an equation of the Watson type for interpolation and extrapolation:

$$\frac{\Delta H_v}{\Delta H_{vb}} = \left(\frac{1 - T_r}{1 - T_{rb}}\right)^x \qquad (48)$$

The heats are converted to energies with the use of vapor pressure values computed from the Antoine equation with constants given by API 44 tables of 1974.

Activity coefficient data on nC_6 in solution with nC_{16} at 20° and 60°C by McGlashan and Williamson (1961) are used for the fine adjustment of c for methyl and methylene.

Marquardt's (1963) nonlinear optimum seeking procedure is used to find the values of the properties of methyl and methylene that best represent the various types of data.

Table 1 shows the result. The contact points Q are separately obtained from the procedure described in Appendix B and are input to the Marquardt calculations. The van der Waals volumes V_w from Bondi (1968) used in the determination of Q are shown in the table for convenient reference. They agree closely (within 1.5%) with the hard core volumes V_o^* obtained in this work.

The interaction energy coefficients ϵ_{ii} have the same value for methyl and methylene. Their exchange coefficient $\Delta\epsilon$ is zero. To the best of our knowledge, methyl and methylene interact with the same energy. But they differ significantly in size and greatly in degrees of freedom.

Figure 1 shows the calculated molar volumes of n-alkanes for comparison with data. Deviations are generally within 1% except for the heaviest alkanes at the higher temperatures. Figure 2 shows the calculated energies of vaporization for comparison with data. Deviations are generally within 1% except for the heaviest alkanes at the higher temperatures.

Figure 3 shows the activity coefficients of nC_6 in nC_{16}. Data on this system have been used for the fine adjust-

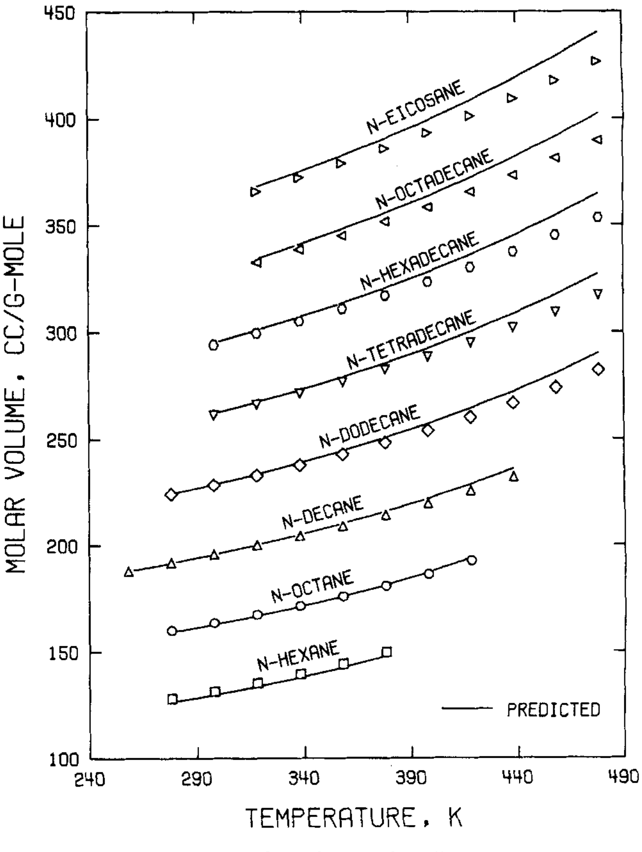

Fig. 1. Molar volumes of n-alkanes.

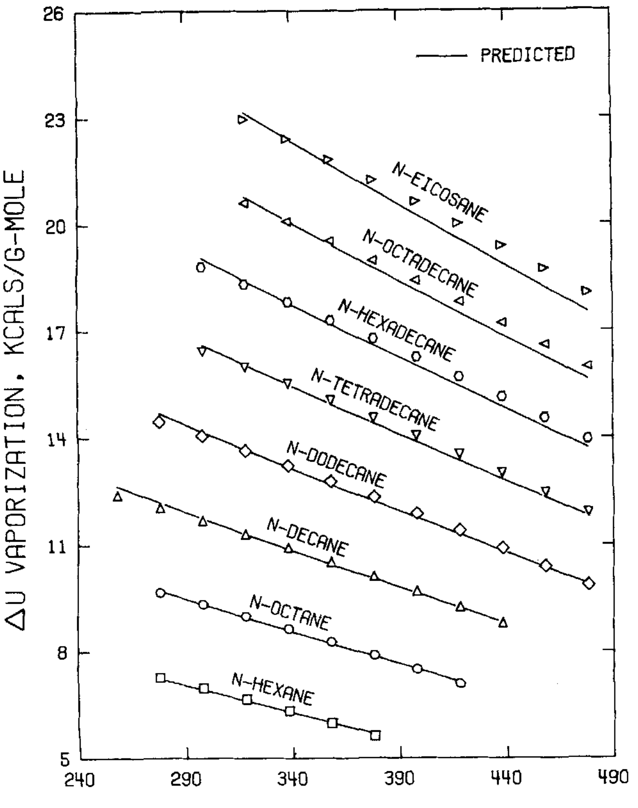

Fig. 2. Energies of vaporization of *n*-alkanes.

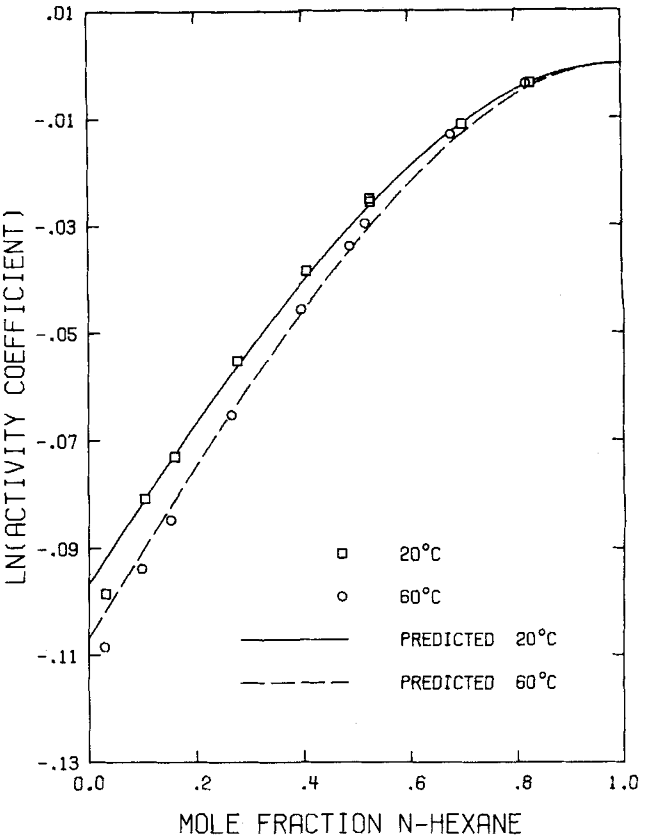

Fig. 3. Activity coefficients of *n*-C_6 in *n*-C_{16}.

ment of *c*. Figure 4 shows the activity coefficients of nC_7 in nC_{32}. Data on this system have not been used in any way in obtaining the group properties. The predicted results are in good agreement with data with deviations below 2%. Better results have been obtained in predictions for activity coefficients in systems studied by Broensted and Koefoed (1946), that is, C_6 in C_{16} and C_{12}, and C_7 in C_{16}. Cruickshank et al. (1968) reported activity coefficients of C_6, C_7, and C_8 at infinite dilution in C_{18}. About the same agreement is obtained between these data and our model.

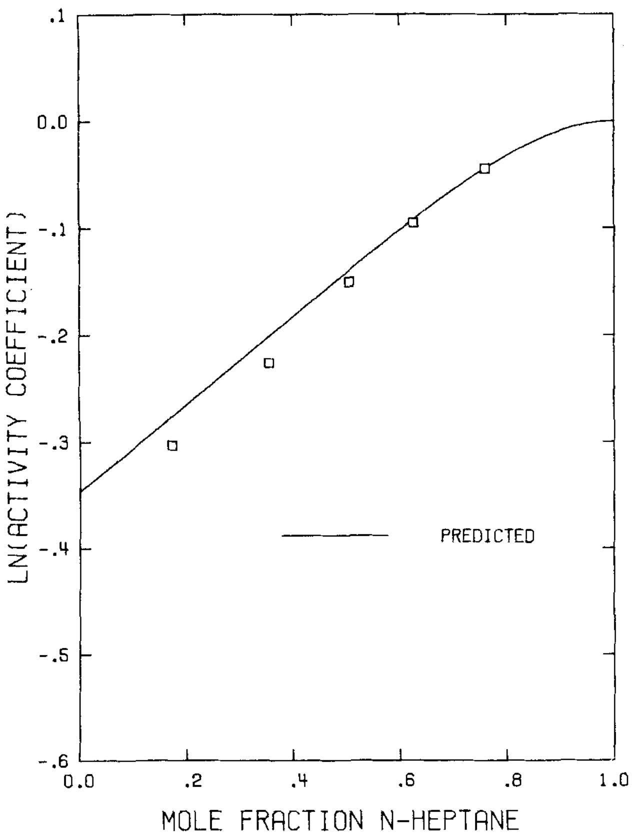

Fig. 4. Activity coefficients of *n*-C_7 in *n*-C_{32} at 73°C.

Figure 5 shows the excess enthalpy data of mixtures of C_8/C_{24} and comparison with predictions from our model. Our model predicts the correct order of magnitude and the correct trend of decreasing excess enthalpy with increasing temperature. But the predicted rate of change with temperature is too small. Deviations of the predictions are small in terms of calories per mole but large in percent figures owing to the small magnitude of the excess enthalpies. Similar results have been obtained for excess enthalpy of nC_6/nC_{16} at 20° and 50°C (McGlashan and Morcom 1961) and at 76°C (Holleman, 1965) and of C_8/C_{32} at 76°C (Holleman, 1965).

n-ALKANOLS AND THEIR SOLUTIONS WITH *n*-ALKANES

The alkanols contain the hydroxyl group in addition to methyl and methylene groups. With the properties of methyl and methylene already known, we determine the properties of hydroxyl by analyzing data on pure *n*-alkanol-1 liquids. Subsequently, fine adjustment is made of the exchange energy coefficient $\Delta\epsilon$ between hydroxyl and methyl-methylene and of the chemical association energy σ of the hydroxyls by referring to excess properties of one binary alkanol-1/alkane mixture system.

Data on four pure *n*-alkanol-1 liquids are used to determine properties of the hydroxyl, and they are ethanol, propanol, pentanol, and hexanol. The data used

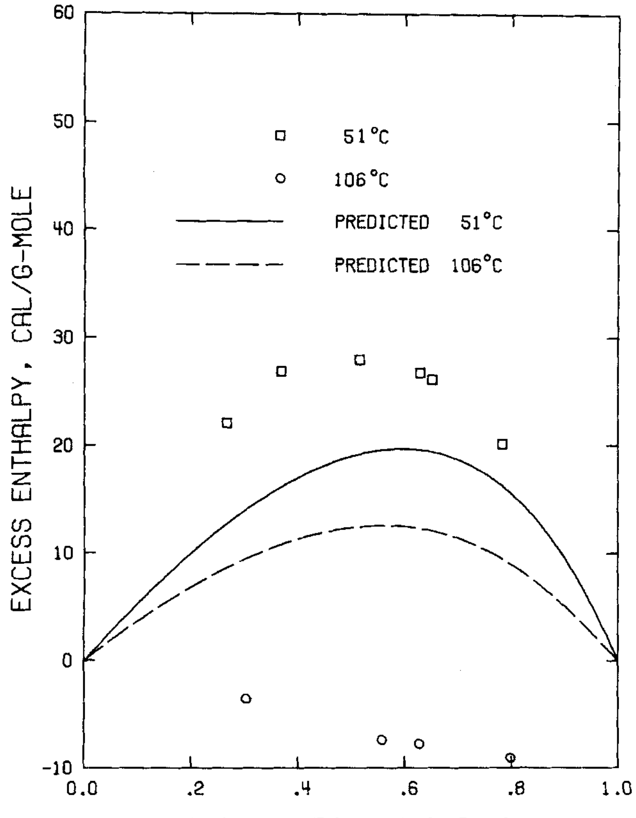

Fig. 5. Excess enthalpy of n-C$_8$/n-C$_{24}$.

are molal volume v and internal energy of vaporization at temperatures from −20° to 170°C but not to exceed reduced temperature (based on critical) of 0.75. The molal volumes are based on density data from TRC (1968) data tables. Heat of vaporization data at 25°C and the normal boiling point are also from the same source. The two values of ΔH_v are fitted with Equation (48) for interpolation and extrapolation. The heats are converted to energies with the use of vapor pressure values computed from the Antoine equation with constants given by TRC (1968) data tables.

Marquardt's (1963) nonlinear optimum seeking procedure is used to find the values of the properties of hydroxyl that best represent the pure alkanol data. Fine adjustment is subsequently made on σ_o of the hydrogen bond and on $\Delta\epsilon$ of hydroxyl and methyl-methylene exchange energy coefficient by referring to data on activity coefficients in n-propanol/n-heptane at 30° and 60°C reported by Van Ness et al. (1967b). Finally, adjustment is made on σ' of the hydrogen bond by referring to data on excess enthalpy of n-propanol/n-heptane at 30° and 45°C by Savini et al. (1965). The fine adjustments are also made with Marquardt's procedure. The activity coefficients have been found to be sensitively dependent on $\Delta\epsilon$ and σ_o and excess enthalpies on σ'.

The group and interaction properties of the hydroxyl are included in Table 1. The entire OH group (Q = 4.62) has the same dispersive interaction energy. However, in the formation of a hydrogen bond the total value of Q is composed of two parts (Q = 1 for H and 3.62 for O). Values are presented for the chemical association of O and H. This is the only association mode in alkanol and alkanol/alkane liquids.

Figure 6 shows the calculated molar volumes on n-alkanol-1 for comparison with data. Deviations are generally well within 1% except for the heaviest alkanols

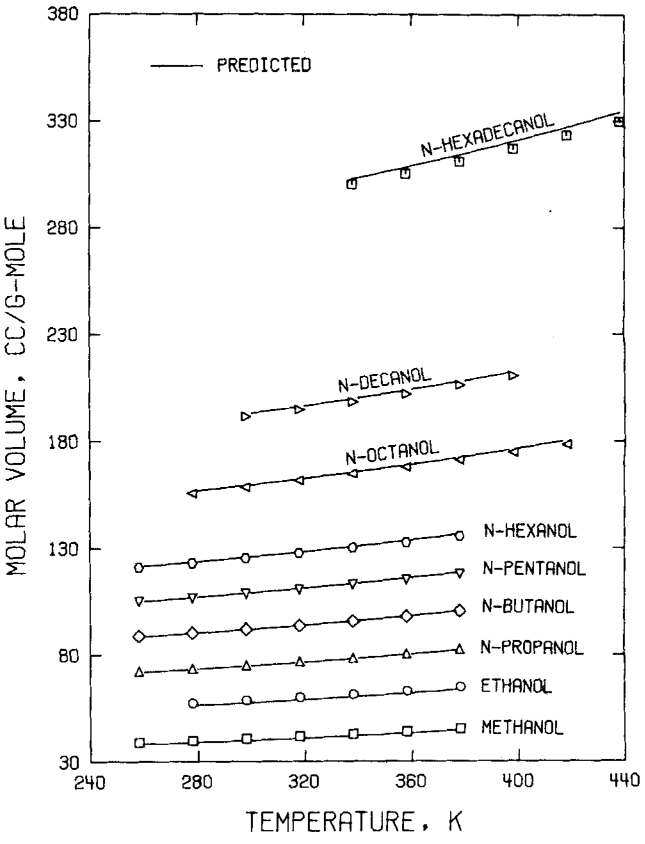

Fig. 6. Molar volumes of n-alkanols.

at the highest temperatures. Figure 7 shows the calculated energies of vaporization for comparison with data. Deviations are generally within a few percent but larger than for the n-alkanes.

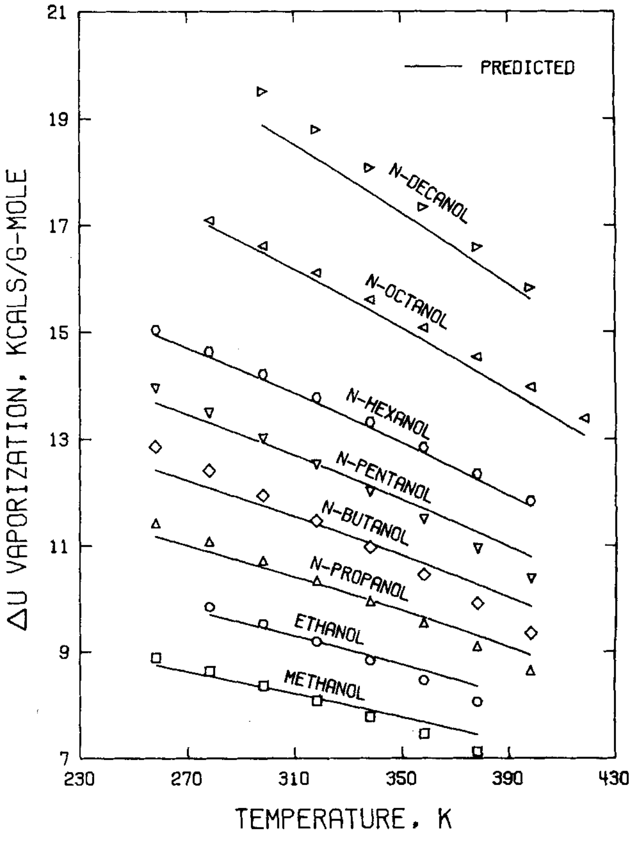

Fig. 7. Energies of vaporization of n-alkanols.

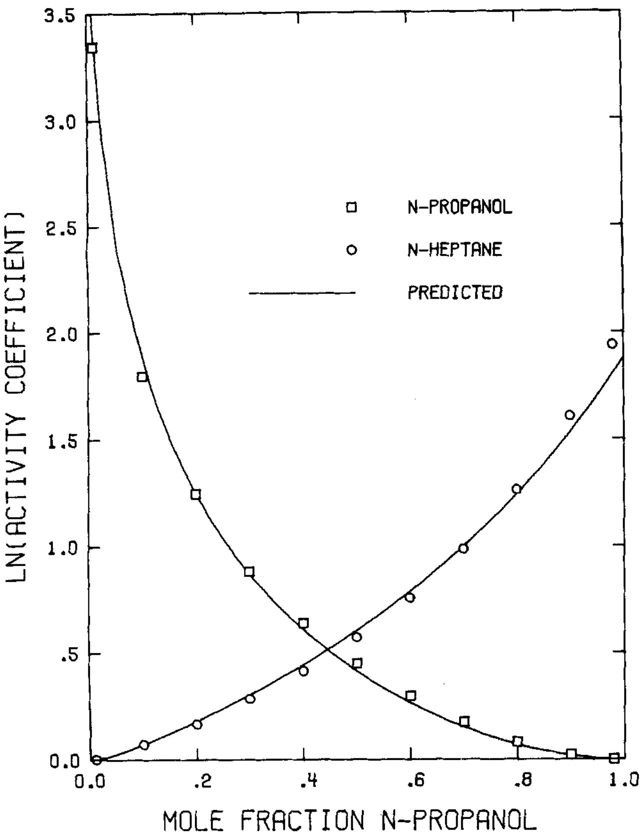

Fig. 8. Activity coefficients in *n*-propanol/*n*-heptane at 30°C.

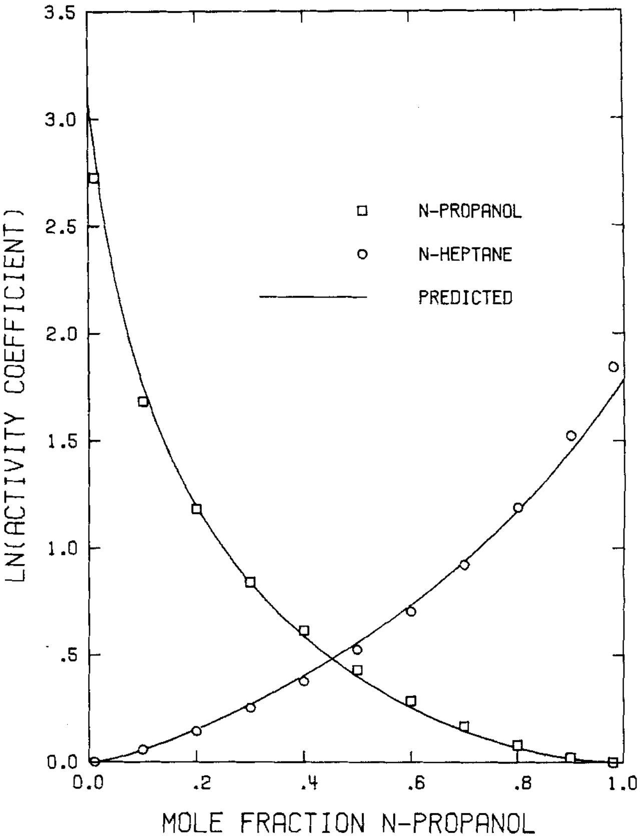

Fig. 9. Activity coefficients in *n*-propanol/*n*-heptane at 60°C.

Figure 8 shows the activity coefficients in *n*-propanol/*n*-heptane at 30°C, and Figure 9 shows the same system at 60°C. Figure 10 shows the excess enthalpy of the same system at 30° and 45°C. The data shown in the figures have been used for the determination of the properties of the hydroxyl group. Generally good agreement is obtained between the calculated values and the data.

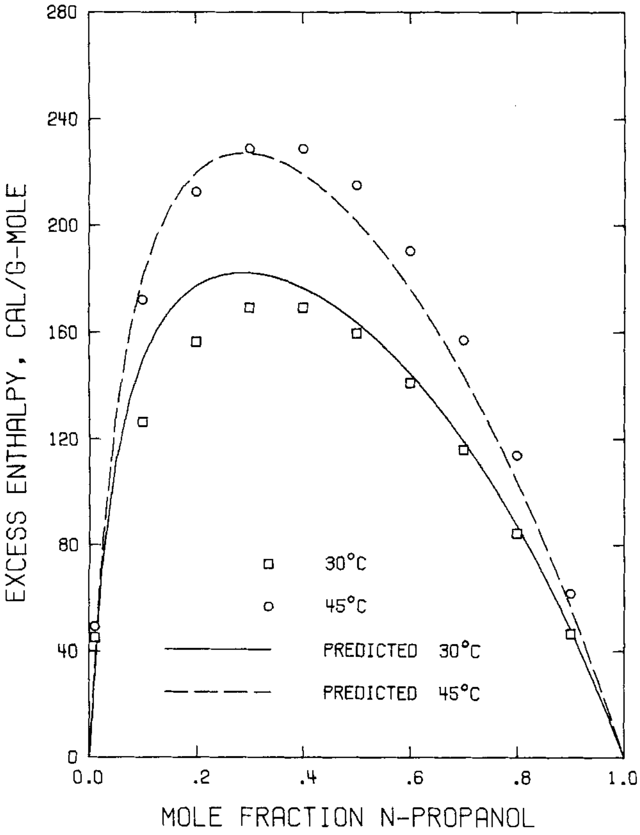

Fig. 10. Excess enthalpy of *n*-propanol/*n*-heptane.

Predicted activity coefficients are shown in Figure 11 for ethanol/*n*-octane for comparison with data by Boublikova and Lu (1969) and in Figure 12 for *n*-butanol/*n*-decane for comparison with data by Lee and Scheller. Generally good agreement is obtained except for decane in dilute solution in butanol. The reported large activity coefficient values cannot be reproduced by our model. Data on alkanes in the dilute range in other alkanol mixtures, for example, Figure 9, do not show a similar abrupt change.

Additional comparisons of our model have been made with data on excess Gibbs energy data on *n*-propanol/*n*-hexane by Brown, Fock, and Smith (1969) and activity coefficient data on *n*-heptane/*n*-butanol by Vijayaraghavan, Despande, and Kuloor (1966), *n*-decane/*n*-heptanol by Cova and Rains (1974), and *n*-heptane/*n*-butanol by Aristovich et al. (1965). The results are generally comparable to those shown in Figures 8, 9, 11, and 12.

Our predictions of excess enthalpy for the system ethanol/*n*-heptane measured by Van Ness et al. (1967) at 10°, 45°, and 75°C are shown in Figure 13. The model reproduces the magnitude and the composition dependence well but does not change with temperature quite as much as the data.

n-ALKANONES AND THEIR SOLUTIONS WITH *n*-ALKANES

The alkanones contain the carbonyl group in addition to methyl and methylene groups. We determine the properties of the carbonyl group by analyzing data on pure alkanone liquids, making use of the known properties of

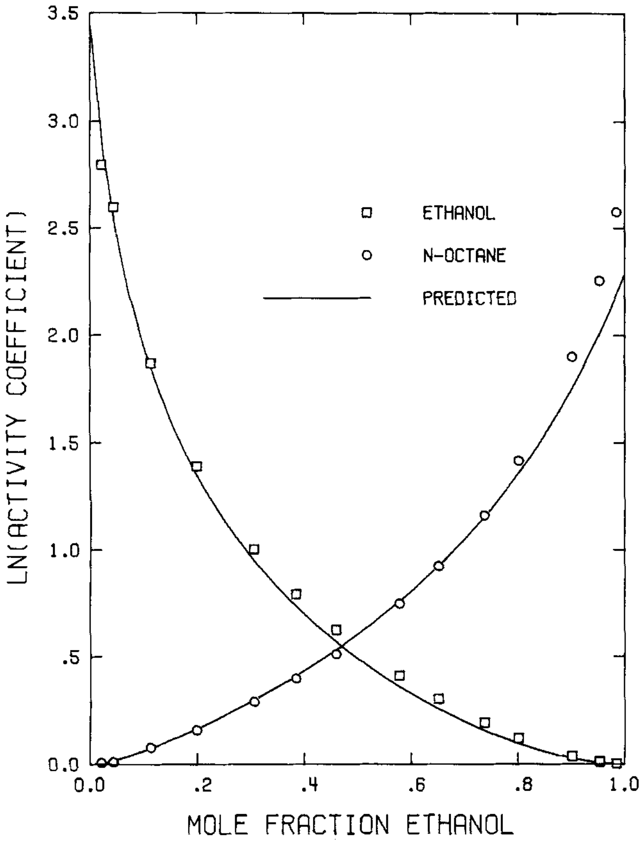

Fig. 11. Activity coefficients in ethanol/*n*-octane at 45°C.

methyl and methylene. Subsequently, fine adjustment is made of the exchange energy coefficient $\Delta\epsilon$ between carbonyl and methyl-methylene and of the chemical association energy σ of carbonyl by referring to excess property data of one binary alkanone/alkane system. The procedure is similar to that followed in the preceding section for alkanols and their alkane solutions.

Data on densities of 2-propanone and 2-butanone are taken from Timmermans (1950, 1965) and on 2-pentanone and 2-heptanone from Meyer and Wagner (1966). Heats of vaporization of 2-propanone are taken from Pennington and Kobe (1957) and of 2-butanone and 2-pentanone from Nickerson, Kobe, and McKetta (1961). The heats are converted into energies by using vapor pressure values from TRC (1968) data tables for 2-propanone and 2-butanone and from Meyer and Wagner (1966) for 2-pentanone.

Marquardt's (1963) optimization procedure is used to find the values of the properties of carbonyl that best represent the pure alkanone data. Fine adjustment is subsequently made on $\Delta\epsilon$ and σ by referring to activity coefficient data on 2-propanone/*n*-hexane by Schäfer and Rall (1958) at 45°C and by Rall and Schäfer (1959) at 20°C and excess enthalpy data on the same system and on 2-butanone/*n*-hexane both by Murakami, Amaya, and Fujishiro (1964) at 25°C.

The group and interaction properties of carbonyl are included in Table 1. The calculated molar volumes are compared with data in Figure 14. Agreement is generally within 1% except for the highest alkanones at the higher temperatures. The calculated energies of vaporization shown in Figure 15 are in good agreement with data for the two lower alkanones but appear to be high for 2-pentanone. Unfortunately, data are lacking on higher alkanones, so it cannot be established if systematic deviations might exist for the higher alkanones.

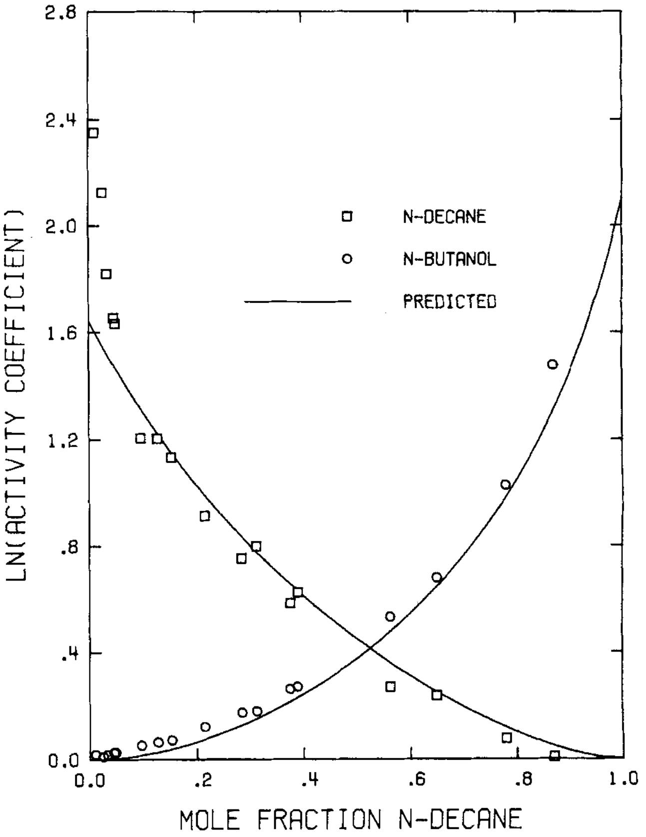

Fig. 12. Activity coefficients in *n*-butanol/*n*-decane at 100°C.

Figure 16 shows the activity coefficients in 2-propanone/*n*-hexane at 45°C. Figure 17 shows the excess enthalpy of the same systems and Figure 18 that of 2-butanone/

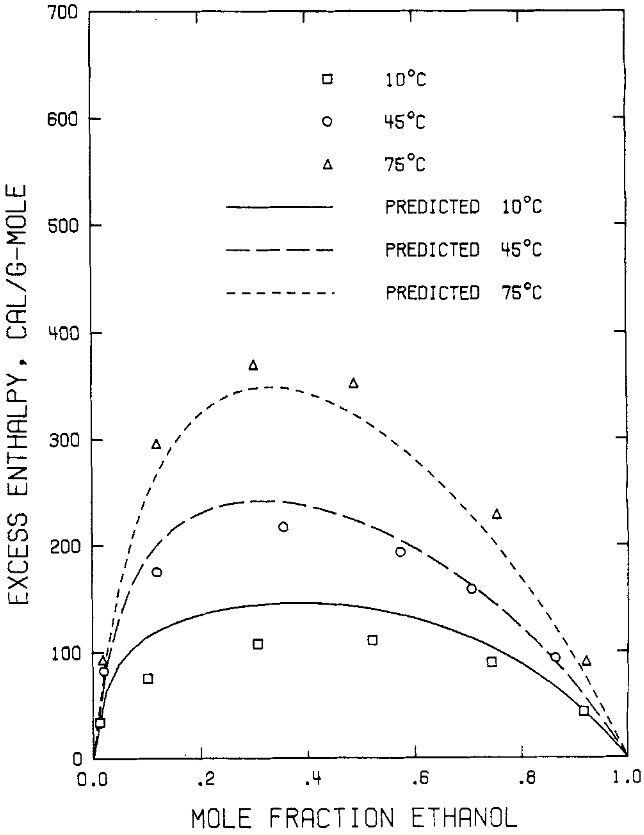

Fig. 13. Excess enthalpy of ethanol/*n*-heptane.

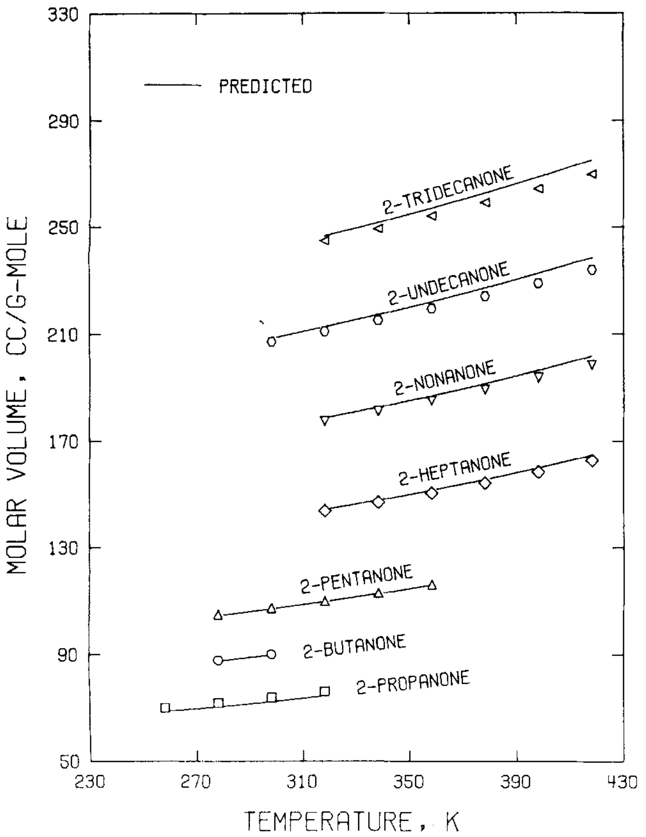

Fig. 14. Molar volumes of *n*-alkanones.

n-hexane. Data shown in all three figures have been used in determining the properties of carbonyl. Agreement between the data and the calculations appears excellent.

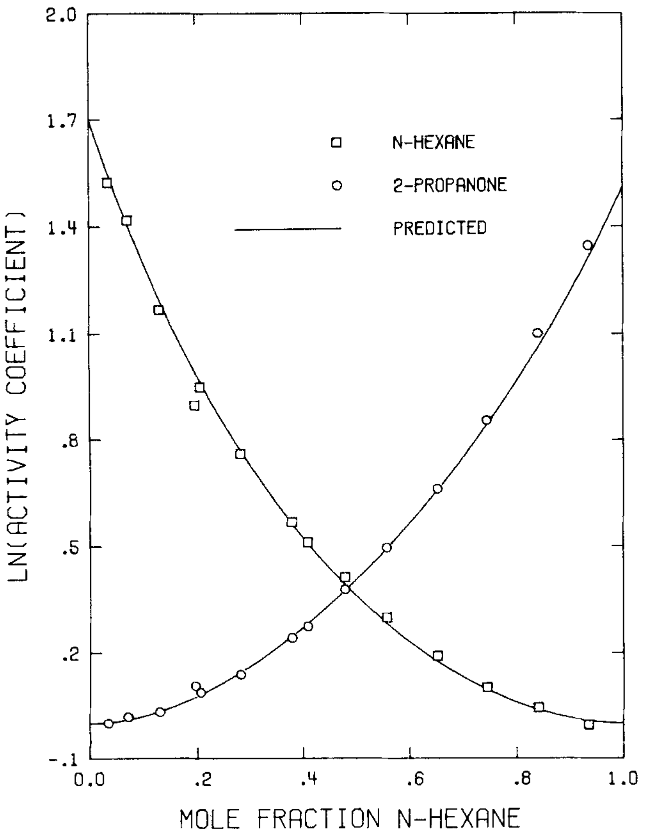

Fig. 16. Activity coefficients in 2-propanone/*n*-hexane at 45°C.

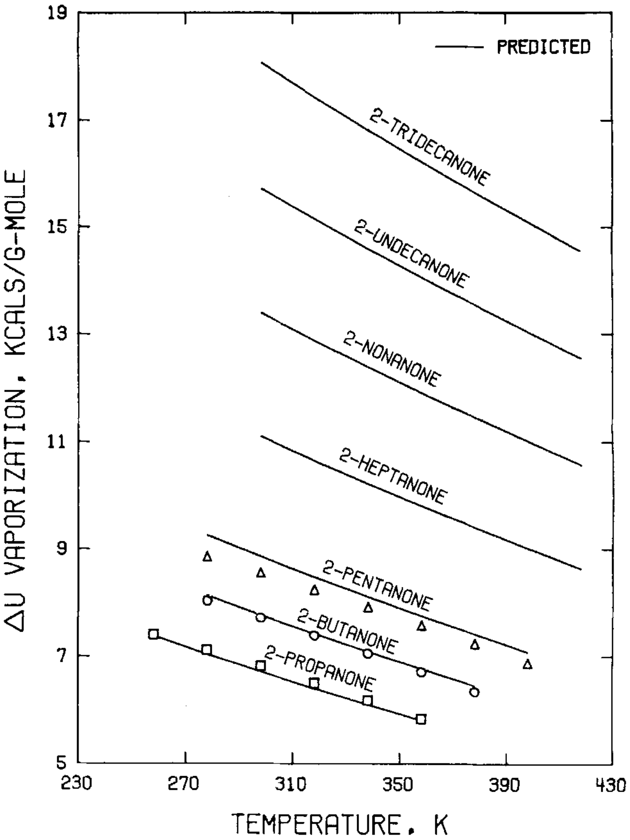

Fig. 15. Energies of vaporization of *n*-alkanones.

Predictions of the model are compared with data in Figure 19 for 2-propanone/*n*-hexane at −20°C reported by Schäfer and Rall (1958). Data on the same system at higher temperatures (see Figure 16) have been used

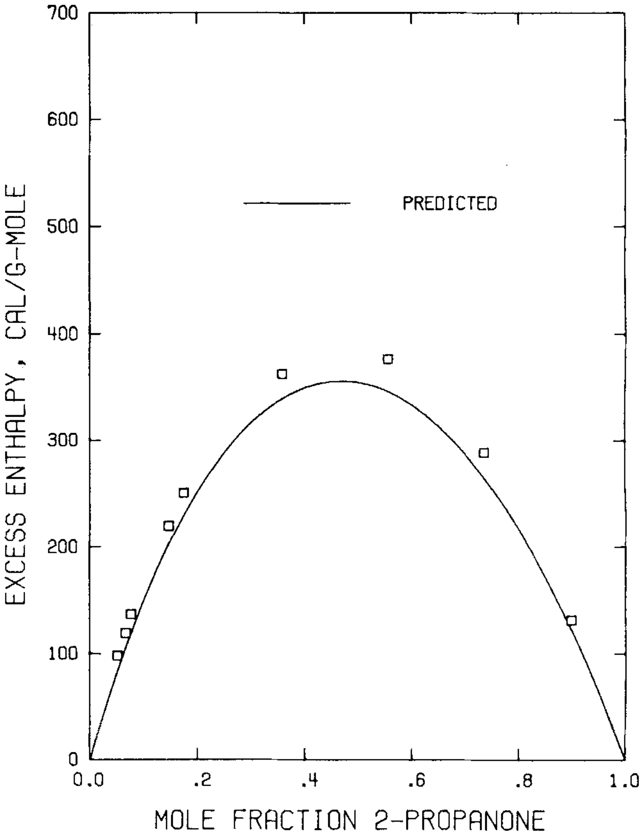

Fig. 17. Excess enthalpy of 2-propanone/*n*-hexane at 25°C.

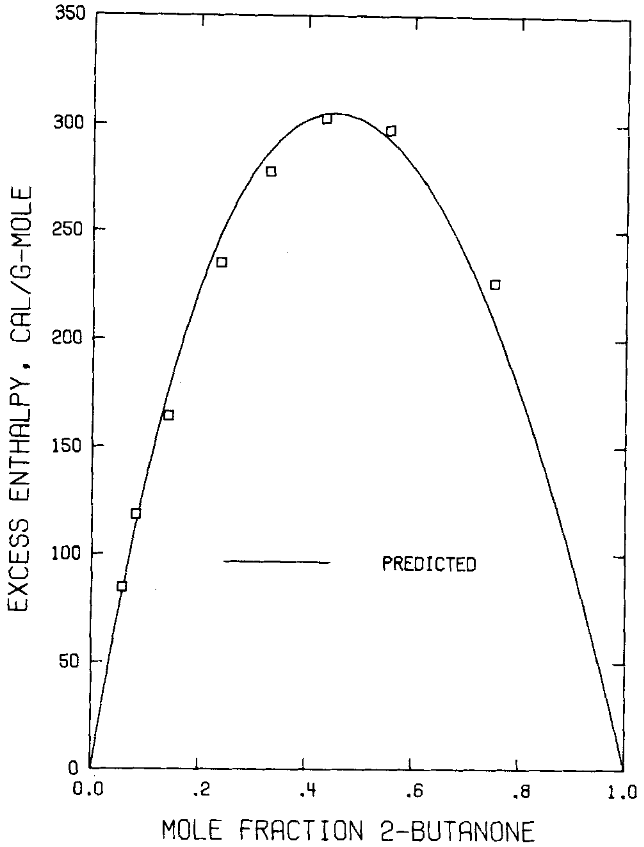

Fig. 18. Excess enthalpy of 2-butanone/*n*-hexane at 25°C.

to determine the properties of carbonyl. Figure 19, therefore, illustrates extrapolation to a lower temperature by means of our model. The extrapolated results are in excellent agreement with data.

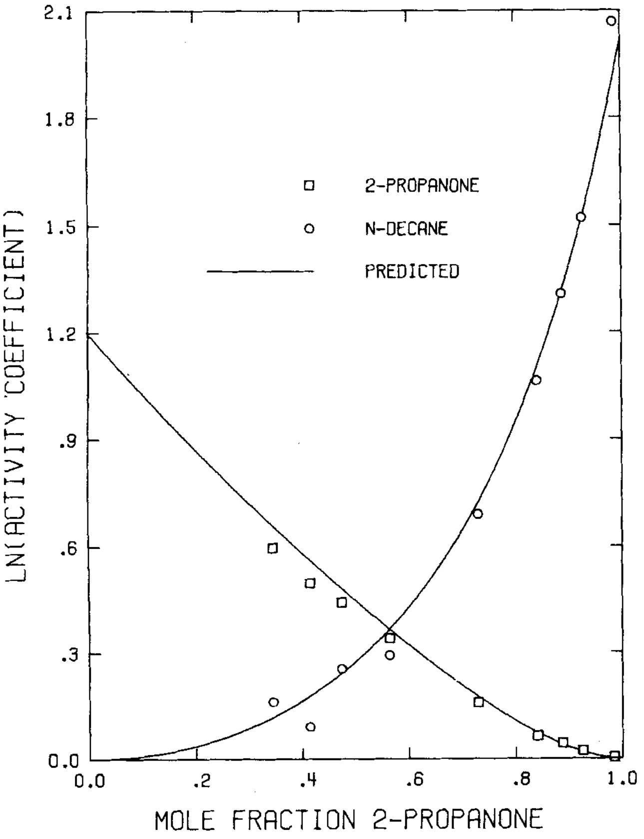

Fig. 20. Activity coefficients in 2-propanone/*n*-decane at 65°C.

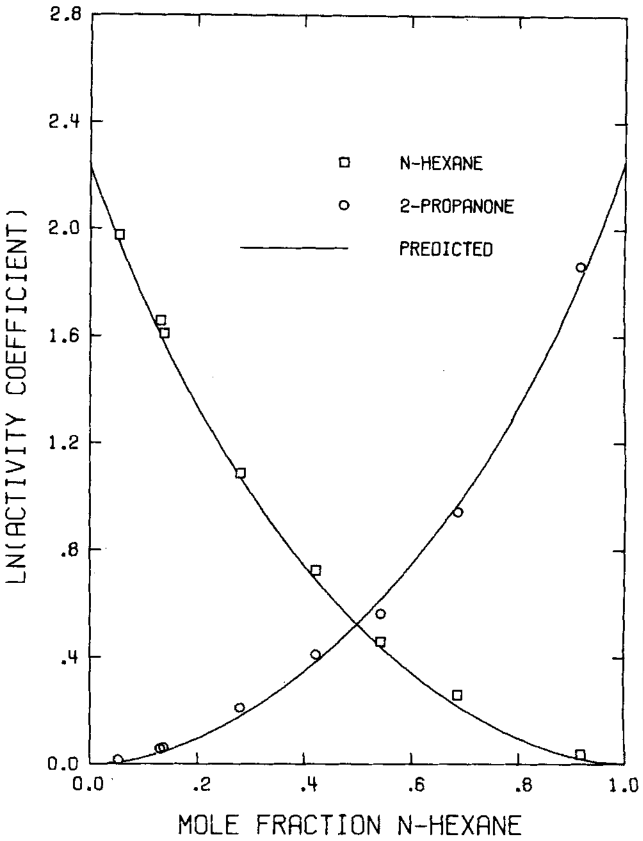

Fig. 19. Activity coefficients in 2-propanone/*n*-hexane at —20°C.

Extrapolation to activity coefficients of other molecular systems are shown in Figure 20 for 2-propanone/*n*-decane, for comparison with data by Maripuri and Ratcliff (1972*b*), and in Figure 21 for 2-butanone/*n*-octane for

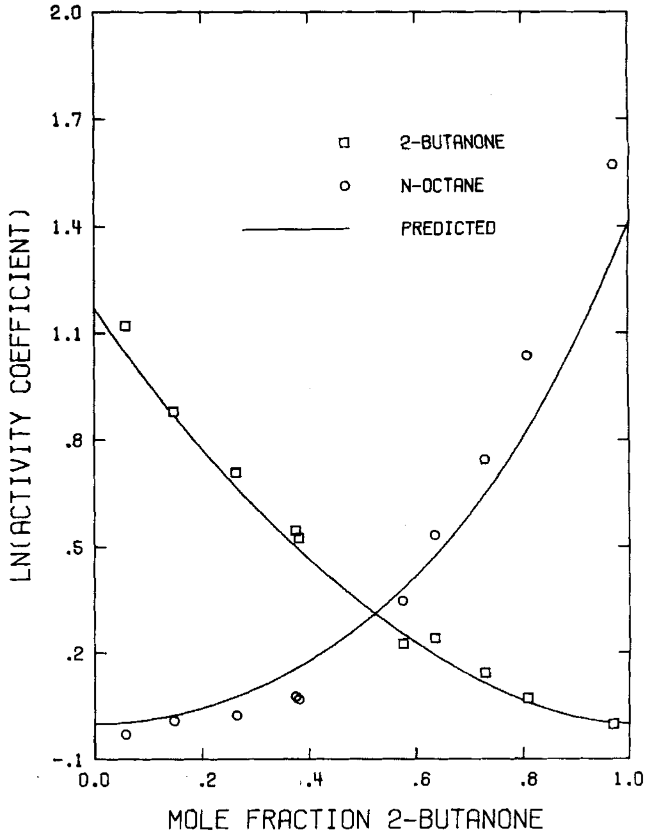

Fig. 21. Activity coefficients in 2-butanone/*n*-octane at 65°C.

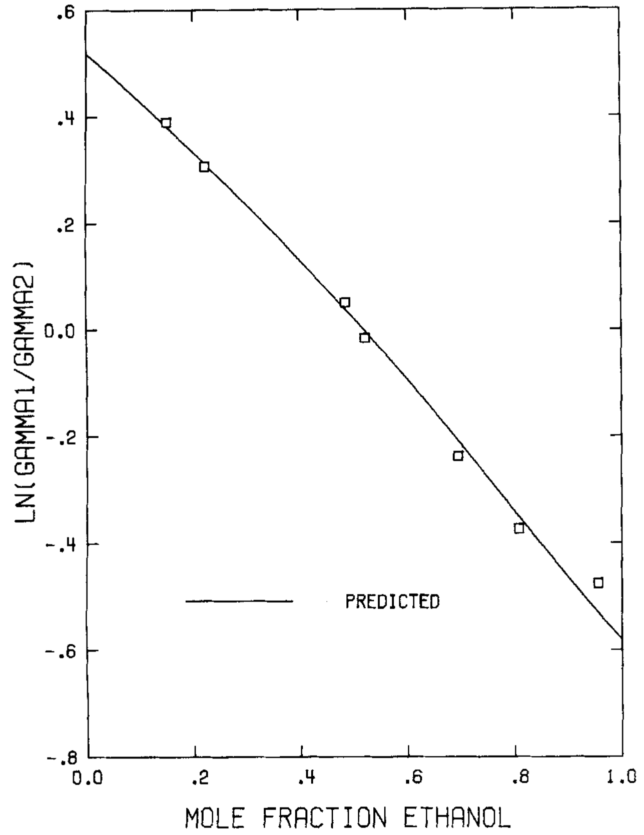

Fig. 22. Activity coefficients in ethanol/2-butanone at 1 atm.

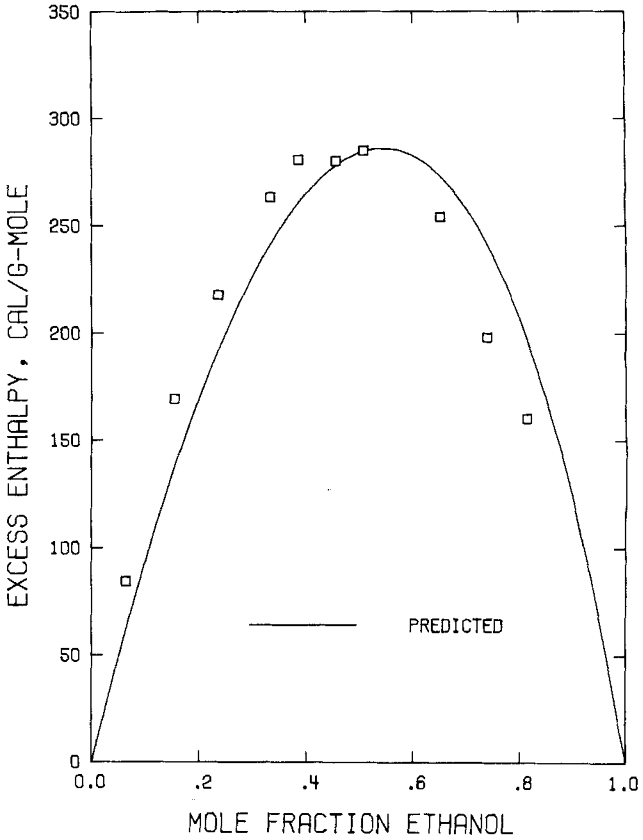

Fig. 23. Excess enthalpy of ethanol/2-butanone at 25°C.

comparison with data reported by the same authors.

Additional calculations have been made with comparable results for the activity coefficients of the following systems:

2-propanone/*n*-heptane at 65°C by Maripuri and Ratcliff (1972*a*)

2-propanone/*n*-heptane at 50°C by Schäfer, Rall, and Lindemann (1958)

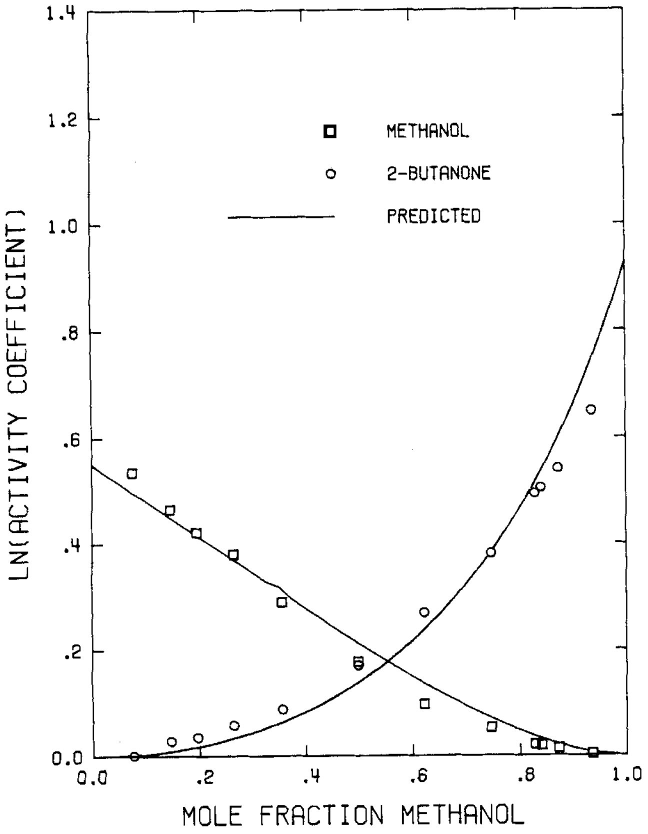

Fig. 24. Activity coefficients in methanol/2-butanone at 1 atm.

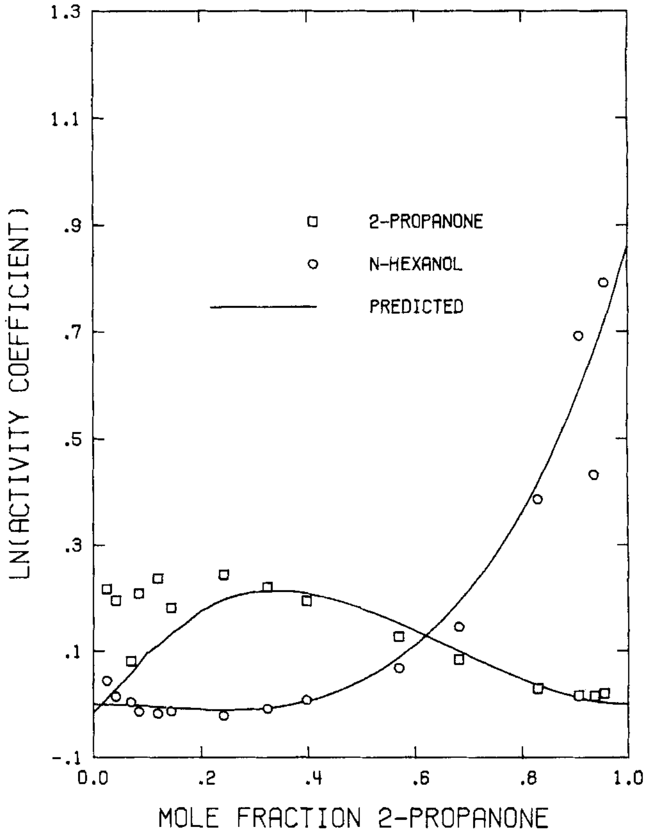

Fig. 25. Activity coefficients in 2-propanone/*n*-hexanol at 1 atm.

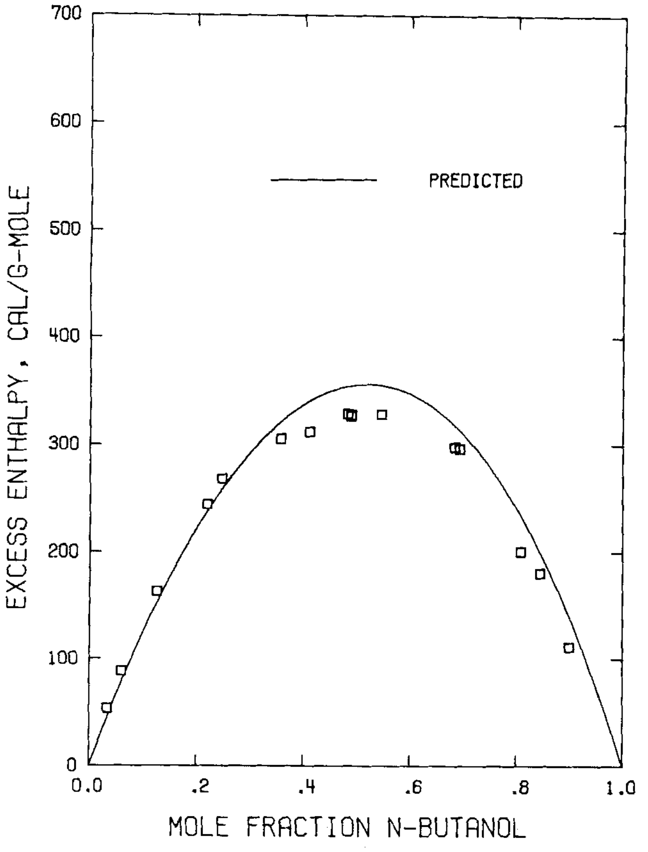

Fig. 26. Excess enthalpies of n-butanol/2-propanone at 25°C.

2-butanone/*n*-hexane at 65°C by Maripuri and Ratcliff (1972*b*)

2-pentanone/*n*-heptane at 90°C by Scheller and Rao (1973)

SOLUTIONS OF *n*-ALKANOLS AND *n*-ALKANONES

Extension of the group properties to the description of solutions of alkanols and alkanones requires the determination of the interaction properties of OH and carbonyl groups. The determination is made by referring to the activity coefficient data on ethanol/2-butanone at 1 atm reported by Hellwig and Van Winkle (1953) and excess enthalpy data on the same system at 25°C reported by Takami, Murakami, and Fujishiro (1965).

The resulting values of σ_o and σ' are included in Table 1. The exchange energy coefficient $\Delta\epsilon$ is presumed to be zero, since the values of ϵ_{ii} for OH and carbonyl groups are almost the same.

Figure 22 shows the fitted activity coefficients in ethanol/2-butanone and Figure 23 the fitted excess enthalpies of the same system. Fitting of the activity coefficients appears excellent, but excess enthalpies appear not to correctly respond to composition changes.

Predictions from our model are compared in Figure 24 with data on methanol/2-butanone at 1 atm reported by Privott et al. (1966). Agreement seems excellent. Figure 25 shows the predicted activity coefficients in comparison with data on 2-propanone/*n*-hexanol at 1 atm reported by Rao, Chiranjivi, and Dasarao (1967). The activity coefficient of hexanol goes through a minimum value at a mole fraction of 2-propanone of about 0.2. This minimum is correctly predicted by our model. The occurrence of a maximum activity coefficient for 2-propanone is also predicted. However, at dilute concentrations of 2-propanone, the propanone data are excessively scattered, and the hexanol data do not approach the correct limit. Our model diverges from the data in that range.

Figure 26 shows the predicted excess enthalpies of *n*-butanol/2-propanone at 25°C. Excellent agreement is obtained with data by Murakami and Fujishiro (1966).

ACKNOWLEDGMENT

This work was supported by National Science Foundation through grant GK-16573.

NOTATION

a = coefficient in Equation (4) to express change of hard core volume with changing temperature
A_w = Van der Waals surface area
c = external degrees of freedom
E = lattice energy
F_i = quantity defined by Equation (C1)
g = combinatorial factor of molecular occupancy of cell lattice
g_o = Flory-Huggins combinatorial factor for random distribution
g_1 = Guggenheim factor for effect of quasichemical interaction on combinatorial factor
H = enthalpy
H^E = excess enthalpy
ΔH_v = heat of vaporization
ΔH_{vb} = heat of vaporization at normal boiling point
k = $R/\tilde{N}$, Boltzmann constant
N = total number of molecules
N_A = number of molecules A
N_{ij} = number of group pairs ij
N_{ij}^* = N_{ij} in the case of $w = 0$ for all group pairs
$\tilde{N}$ = Avogadro number
n_i^A = number of group i per molecule A
n_i = $\sum_A n_i^A x_A$ average number of i groups per molecule
p = pressure
p^* = reducing pressure defined by Equation (18)
$\tilde{p}$ = reduced pressure defined by Equation (15)
Q = configurational partition function
Q_i = number of contacts of group i
R = universal gas constant
r_i = number of lattice sites occupied by group i
T = absolute temperature
$\tilde{T}$ = reduced temperature defined by Equation (17)
T_c = critical temperature
T_r = T/T_c reduced temperature
T^* = reducing temperature defined by Equation (20)
U = internal energy
U_{conf} = configurational energy
ΔU_v = internal energy of vaporization
V = volume of the fluid
v = volume of the fluid per mole
$\tilde{v}$ = reduced volume defined by Equation (16)
V_w = Van der Waals volume
V^* = hard core volume
v^* = hard core volume per mole
w = exchange energy
x = exponent in Equation (48)
x_A = mole fraction of A
Y_i = quantity defined by Equation (33)
Y_i^* = Y_i in the case of $w = 0$ for all group pairs
z = lattice coordination number (= 10 in this work)

Letters

β_T = coefficient of isothermal compressibility

γ_A = activity coefficient of A

γ_V = coefficient of thermal pressure

ϵ = interaction energy constant

ϵ_{ij} = constant for given i and j

η = quantity defined by Equation (35)

η = dimensionless density in Equation (A1)

κ = a constant in Equation (6), equal to 0.7

σ = chemical association energy of groups i and j

σ_0 = value of chemical association energy at T_0

σ' = coefficient in Equation (7) to express change of σ with T

ϕ_{ij} = potential energy of ij pairwise interaction

ψ = cell partition function

Subscripts and Superscripts

A = molecule A

$A0$ = pure liquid A

i = group i

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APPENDIX A: CELL PARTITION FUNCTION FROM CARNAHAN-STARLING EQUATION OF STATE

The Carnahan-Starling equation of state (1969) for hard sphere is expressed by

$$\frac{pV}{NkT} = \frac{1+\eta+\eta^2-\eta^3}{(1-\eta)^3} \tag{A1}$$

where η is a dimensionless density defined by $\eta \equiv [(\Pi/6) N\sigma^3/V]$, and σ is the diameter of the hard sphere. Thus, $\eta = 1/\tilde{v}$. Reexpressing Equation (A1) in $\tilde{v}$, we have

$$p = \left(\frac{NkT}{V}\right)\frac{(\tilde{v}^3+\tilde{v}^2+\tilde{v}-1)}{(\tilde{v}-1)^3} \tag{A2}$$

The equation of state is related to configurational partition function by

$$p = kT\left(\frac{\partial \ln Q}{\partial V}\right)_{T,N} \tag{A3}$$

Combining the two equations, we get

$$\frac{\partial \ln Q}{\partial \ln \tilde{v}} = N\frac{(\tilde{v}^3+\tilde{v}^2+\tilde{v}-1)}{(\tilde{v}-1)^3} \tag{A4}$$

Integrating, we get

$$Q^{1/N} = \tilde{v}\exp\left[-\frac{(4\tilde{v}-3)}{(\tilde{v}-1)^2}\right] \tag{A5}$$

which shows the right-hand side to be like the cell partition function for an unbonded hard sphere ψ.

APPENDIX B: CONTACTS OF GROUPS

The number of contacts Q_i of group i is proportional to its surface area A:

$$Q_i = zA_{wi}/A_{ws} \tag{B1}$$

The van der Waals surface areas compiled by Bondi (1968) are used in this work to express the surface area A_{wi}. The lattice coordination number z is equal to 10 as recommended by Bondi. Equation (B1) proposed by Abrams and Prausnitz (1975) states that the proportionality constant between Q_i and A_{wi} is determined by referring to a standard group having as many contacts as z. It remains to determine the standard group.

The standard group in this work is determined by referring to properties of CH_3 and CH_2 groups for which the following three equations also apply:

$$r_i = V_{wi}/V_{ws} \tag{B2}$$

$$Q_{CH_3} = (z-2)r_{CH_3} + 1 \tag{B3}$$

$$Q_{CH_2} = (z-2)r_{CH_2} \tag{B4}$$

Simultaneous solution of these equations with Equation (B1) for CH_3 and CH_2 gives $Q_{CH_3} = 6.71$ and $Q_{CH_2} = 4.27$. The standard group turns out to have $A_{ws} = 3.161 \times 10^9$ cm^2/mole, and $V_{ws} = 19.15$ cm^3/mole. In this determination, the standard group is no longer spherical as assumed in Abrams and Prausnitz (1975).

APPENDIX C: CALCULATION OF N_{ij}, $\partial N_{ij}/\partial \tilde{v}$, AND $\partial N_{ij}/\partial T$

We first calculate N_{ij} by solving Equation (34) for Y_i using the Newton-Raphson iterative procedure. For this purpose, we define F_i by

$$F_i = \sum_j a_{ij}Y_iY_j - 0.5 \tag{C1}$$

where $a_{ij} = Q_jn_j\eta_{ij}$. Initial values of Y_i are chosen to be Y_i^*, and $X_i \equiv \Delta Y_i/Y_i$ are found by solving the simultaneous linear equations

$$\sum_j A_{ij}X_j = -F_i \tag{C2}$$

where

$$A_{ij} = a_{ij}Y_iY_j \quad \text{for} \quad i \neq j \tag{C3}$$

$$A_{ii} = \sum_j a_{ij}Y_iY_j + a_{ii}Y_i^2 \tag{C4}$$

From the converged solution, we compute N_{ij}:

$$N_{ij} = 2NQ_iQ_jn_in_jY_iY_j\eta_{ij} \tag{C5}$$

$$N_{ii} = N(Q_in_iY_i)^2 \tag{C6}$$

To obtain the derivatives of N_{ij}, we differentiate Equation (C5):

$$\left(\frac{\partial \ln N_{ij}}{\partial \ln \tilde{v}}\right)_T = \left(\frac{\partial \ln \eta_{ij}}{\partial \ln \tilde{v}}\right)_T + \left(\frac{\partial \ln Y_i}{\partial \ln \tilde{v}}\right)_T + \left(\frac{\partial \ln Y_j}{\partial \ln \tilde{v}}\right)_T$$

and

$$\left(\frac{\partial \ln N_{ij}}{\partial \ln T}\right)_V = \left(\frac{\partial \ln \eta_{ij}}{\partial \ln T}\right)_V + \left(\frac{\partial \ln Y_i}{\partial \ln T}\right)_V + \left(\frac{\partial \ln Y_j}{\partial \ln T}\right)_V \tag{C7}$$

where

$$\left(\frac{\partial \ln \eta_{ij}}{\partial \ln \tilde{v}}\right)_T = -\frac{\Delta\epsilon_{ij}}{kT}\cdot\frac{(1+\kappa/\tilde{v})}{\tilde{v}}\exp(\kappa/\tilde{v})$$

and

$$\left(\frac{\partial \ln \eta_{ij}}{\partial \ln T}\right)_V = -\frac{\Delta \underset{\sim}{e_{ij}}}{kT\,v}\exp\left(\frac{\underset{\sim}{\kappa}}{v}\right)\left[1 - \left(1+\frac{\underset{\sim}{\kappa}}{v}\right)_v\left(\frac{d\ln V^*}{d\ln T}\right)\right] - \frac{\Delta\sigma_{ij}'}{\substack{kT\\ kT}} \qquad \text{(C8)}$$

where

$$\Delta e_{ij} = e_{ij} - \frac{e_{ii}+e_{jj}}{2} \qquad \text{(C9)}$$

$$\Delta \sigma_{ij}' = \sigma_{ij}' - \frac{\sigma_{ii}'+\sigma_{jj}'}{2} \qquad \text{(C10)}$$

The derivatives $(\partial \ln Y_i/\partial \ln \tilde{v})_T$ and $(\partial \ln Y_i/\partial \ln T)_V$ in Equation (C7) are found by solving simultaneous linear equations obtained by differentiating Equation (34) with respect to $\tilde{v}$ and T, respectively. Since the equations are similar, we will write them only in the case of $\tilde{v}$, and they are

$$\sum_j A_{ij}X_j' = -F_i' \qquad \text{(C11)}$$

where

$$X_j' = \frac{\partial \ln Y_j}{\partial \ln \tilde{v}} \qquad \text{(C12)}$$

and

$$F_i' = Y_i \sum_j a_{ij}Y_j\left(\frac{\partial \ln \eta_{ij}}{\partial \ln \tilde{v}}\right) \qquad \text{(C13)}$$

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Influence of Schmidt Number on the Fluctuations of Turbulent Mass Transfer to a Wall

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Measurements are presented on the influence of Schmidt number on the frequency of the mass transfer fluctuations at a solid boundary. The shape of the spectral function is similar at all Schmidt numbers. A relation between the mass transfer fluctuations and the fluctuating velocity field can be obtained only at high frequencies. A comparison of the scale and the frequency of the mass transfer fluctuations and the velocity fluctuations suggests that the rate of mass transfer is controlled by convective motions in the flow oriented eddies described by a number of previous investigators. However, the concentration fluctuations caused by these convective motions are greatly dampened close to the wall by molecular diffusion. Thus the mass transfer fluctuations reflect only the scale and not the frequency of the convective motions in the flow oriented eddies.

SCOPE

When mass is exchanged between a turbulent fluid and a solid boundary, the local rate of mass transfer varies erratically with time. In two previous studies from this laboratory (Van Shaw and Hanratty, 1964; Sirkar and Hanratty, 1970), the fluctuations in the rate of mass transfer to a pipe wall were measured in order to better understand the role that the turbulent convective motions play in the transfer process. It was found that mass transfer fluctuations are of much lower frequency than velocity fluctuations close to the wall and that the spatial extent of the mass transfer fluctuations is much smaller in the transverse direction than in the direction of flow.

In order to examine in greater detail how the concentration boundary layer dampens concentration fluctuations close to a wall, Shaw (1976) recently performed experiments in which he measured the spectral function and the spatial correlation functions characterizing the mass transfer fluctuations. The results of his studies and their implications with respect to modeling turbulent mass transfer to a solid boundary are presented in this paper.

Two general postulates proposed by Sirkar and Hanratty (1970) are used to relate the mass transfer fluctuations to the velocity fluctuations. One of these is the assumption that linear theory describes the high frequency mass transfer fluctuations. The other is a pseudo steady state assumption whereby the limiting behavior at low frequencies is described by a steady state form of the mass balance equation.

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