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Statistical Thermodynamics of Chain Molecule Liquids. II. Liquid Mixtures of Normal Paraffin Hydrocarbons¹

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The partition function and equation of state of the preceding paper are reformulated for mixtures of homologous chain molecules. Thermodynamic properties of mixtures of *n*-alkanes are interpreted according to relationships thus derived. The excess volumes, always negative for these systems, are readily interpolated from the volumes of the pure components with the aid of the reduced equation of state. This scheme is formally equivalent to the Brønsted principle of congruence as it applies to the volume. The theoretical expression for the chemical potential affords an accurate and rational account of experimental results of McGlashan and Williamson for C₆-C₁₆ at 20° and at 50°, and those of van der Waals and Hermans for C₇-C₃₂ at 73° and C₇-C_∞ at 73°. A single choice in the value of one parameter suffices to establish agreement between theory and experiment for all of these systems. Previously neglected contributions from characteristics of the pure liquids, as expressed through parameters determined from their equations of state, are large. The contact term—the only one usually considered—is small for these systems. The theory correctly predicts a decrease in the excess enthalpy with temperature, its sign ultimately becoming negative as has been observed. Quantitative comparisons of observed with calculated enthalpies are less satisfactory, owing in part to the deficiency of equation of state data for the *n*-alkanes. The theory accounts in a straightforward way for the appearance of lower critical miscibility among mixtures of lower paraffins with higher homologs. LCST values are calculated for mixtures of several *n*-alkanes with polyethylene.

Mixtures of *n*-paraffin hydrocarbons have been subjects of some of the most painstaking experiments on solutions of nonpolar liquids. These studies have been concerned with the volume change on mixing,^{2,3} with the enthalpy of mixing,^{4,5} with the excess chemical potential,⁶⁻⁸ and, more recently, with the phenomenon of lower critical miscibility when one component is of low molecular weight and the other very high.^{9,10} The excess volume of mixing is negative^{2,3}; the excess enthalpy is small and positive at low temperatures,^{4,5} strongly dependent on temperature,⁵ and recently has been reported to be negative at higher temperatures.¹¹ The excess chemical potentials for mixtures of dissimilar *n*-paraffin hydrocarbons are negative, but considerably smaller in magnitude than lattice theories would predict.^{6,5} Studies of excess properties of these systems^{7,8,12} are monumental demonstrations of the inadequacy of lattice treatments of liquid mixtures.

The thermodynamic properties of mixtures of homologous chain molecules are derived in this paper by extension of the treatment of systems of one component set forth in the preceding paper,¹³ hereafter referred to as I. The application of the theory of mixtures of *n*-paraffin hydrocarbons is illustrated through comparisons with representative experimental data.

Adaptation of the Theory to Mixtures of Homologs

The theory sketched in I concerns a liquid comprising segments of two types: mid-chain segments and ter-

minal ones. The fact that the pure liquid consists of a single molecular species in which the two types of segments are combined in a uniquely specified manner did not enter explicitly into the argument. It was assumed, however, that mid-chain and terminal segments are distributed about one another at random. The validity of this assumption as applied to pure liquid hydrocarbons depends on the absence of order, or structure, in the disposition of segments about one another. The premise is a reasonable one. If it is valid for the pure components, it should hold *a fortiori* for their mixtures.

The absence of structure in this sense is not sufficient, however, to validate the assumption of random distribution of mid-chain and terminal segments in liquid mixtures of two hydrocarbons differing in chain length. The contiguity of segments in molecules of the two species introduces different correlations between terminal and mid-chain segments. The distribution of segments in space consequently must depart in some degree from that which would prevail if they were severed from one another by scission of the chains. Such correlations have been ignored in I in formulating the intermolecular energy and the segment partition function for a pure species, where the effect probably is of no consequence. It may, however, assume importance at the extremities of composition in mixtures of hydrocarbons differing considerably in chain length. The error involved in ignoring the correlations resulting from the integrity of chain molecules is well known from the analysis of thermodynamic properties of dilute polymer solutions.

The foregoing reservation notwithstanding, we shall for purposes of this paper adopt the assumption of randomness in the distribution of segments of the two kinds about one another in the liquid mixtures. The entire apparatus of the preceding paper¹³ is applicable in this approximation to mixtures of chain homologs. It is only necessary to effect nominal adaptations of terminology.

Starting with eq. 6 of I for the intermolecular energy, we find in analogy to the previous eq. I-5 and I-22

$$E_0 = -\bar{x}N_s\eta/2v = -\bar{x}N\rho^*v^*/\bar{v} \quad (1)$$

(1) Presented in part before the Division of Physical Chemistry of the American Chemical Society, Denver, Colo., Jan. 22, 1964.

(2) A. Desmyter and J. H. van der Waals, *Rec. trav. chim.*, **77**, 53 (1958).

(3) J. D. Gómez-Ibáñez and C.-T. Liu, *J. Phys. Chem.*, **67**, 1388 (1963).

(4) J. H. van der Waals and J. J. Hermans, *Rec. trav. chim.*, **69**, 949 (1950); J. H. van der Waals, *ibid.*, **70**, 101 (1951).

(5) M. L. McGlashan and K. W. Morcum, *Trans. Faraday Soc.*, **57**, 581, 907 (1961).

(6) J. H. van der Waals and J. J. Hermans, *Rec. trav. chim.*, **69**, 971 (1950).

(7) J. H. van der Waals, *Trans. Faraday Soc.*, **52**, 916 (1956).

(8) M. L. McGlashan and A. G. Williamson, *ibid.*, **57**, 588 (1961).

(9) P. I. Freeman and J. S. Rowlinson, *Polymer*, **1**, 20 (1960).

(10) A. J. Davenport and J. S. Rowlinson, *Trans. Faraday Soc.*, **59**, 78 (1963); J. S. Rowlinson and P. I. Freeman, *Pure Appl. Chem.*, **2**, 329 (1961).

(11) J. A. Friend, J. A. Larkin, A. Maroudas, and M. L. McGlashan, *Nature*, **198**, 683 (1963); T. Holleman, *Physica*, **29**, 274 (1963).

(12) M. L. McGlashan, K. W. Morcum, and A. G. Williamson, *Trans. Faraday Soc.*, **57**, 601 (1961).

(13) P. J. Flory, R. A. Orwoll and A. Vrij, *J. Am. Chem. Soc.*, **86**, 3507 (1964).

where \bar{x} is the number average defined by

$$\bar{x} = \sum x_i N_i / \sum N_i = \sum x_i N_i / N$$

all species i present in the mixture being included in the summations; s and η retain their previous definitions (see eq. I-1 and I-7). Thus

$$s = s_m + s_e/\bar{x} \quad (2)$$

$$\eta = (s_m^2/s^2)\eta_m + 2(s_m s_e/s^2\bar{x})\eta_{em} + (s_e^2/s^2\bar{x}^2)\eta_e \quad (3)$$

The various parameters are conveniently expressed in terms of their analogs for the pure components as

$$1/\bar{x} = \sum \varphi_i/x_i \quad (4)$$

$$s = \sum \varphi_i s_i \quad (5)$$

where φ_i is the segment fraction for species i

$$\varphi_i = x_i N_i / \sum x_i N_i$$

The parameter c applicable to the mixture is given by

$$c = \sum \varphi_i c_i \quad (6)$$

With these revisions the relationship derived in I may be adopted at once for mixtures of chain homologs. It is required merely to replace x by \bar{x} , and to use the definitions of s and η given above, whereby these quantities become functions of the composition. The reduced partition function, eq. I-12, is immediately applicable. The reduced equation of state given in I, and the various relationships which follow from it, are thus validated for mixtures.

Throughout the remainder of the paper attention is restricted to systems of two components.

The Excess Volume

Let \bar{v}^0 represent the reduced volume per segment if no volume change occurred on mixing. For a binary mixture

$$\bar{v}^0 = \varphi_1 \bar{v}_1 + \varphi_2 \bar{v}_2 \quad (7)$$

where \bar{v}_1 and \bar{v}_2 are the reduced volumes of the pure components at the same temperature and pressure. The reduced excess volume per segment is

$$\bar{v}^E = \bar{v} - \bar{v}^0 = \bar{v} - \varphi_1 \bar{v}_1 - \varphi_2 \bar{v}_2 \quad (8)$$

\bar{v} being the reduced volume of the mixture.

According to results shown in Fig. 2 of the preceding paper¹³ and summarized by eq. I-32, $1/T^*$ increases linearly with $1/x$ within experimental error over the range of interest (*i.e.*, for $x > 6$). Equation I-30 written in this approximation is

$$\bar{T} \cong \bar{T}_\infty [1 + (c_e/c_m - a)/\bar{x}] \quad (9)$$

Since $1/\bar{x}$ is linear in the φ_i (see eq. 4), it follows that \bar{T} for a binary mixture should vary linearly with the segment fraction composition at constant temperature; *i.e.*

$$\bar{T} = \varphi_1 \bar{T}_1 + \varphi_2 \bar{T}_2 \quad (10)$$

in the aforementioned approximation. The reduced volume \bar{v} for the reduced temperature \bar{T} may then be calculated from the equation of state for $p = 0$.

$$\bar{T} = (\bar{v}^{1/3} - 1)/\bar{v}^{4/3} \quad (11)$$

The difference compared to \bar{v}^0 determined by linear

interpolation from the reduced volumes \bar{v}_1 and \bar{v}_2 of the components gives the excess reduced volume \bar{v}^E .

Calculation of \bar{v}^E in this manner is rendered difficult by the fact that eq. 11 is not explicitly solvable for \bar{v} . Moreover, \bar{v} must be calculated accurately from \bar{T} in view of the small difference involved. A procedure that circumvents these difficulties is as follows. Given \bar{v}_1 and \bar{v}_2 and the \bar{T}_1 and \bar{T}_2 corresponding to them according to eq. 11, obtain \bar{T} by linear interpolation. Also calculate the reduced temperature \bar{T}^0 corresponding to \bar{v}^0 given by eq. 7. Then with negligible error

$$\bar{v}^E = (\partial \bar{v} / \partial \bar{T})(\bar{T} - \bar{T}^0) = 3(\bar{v}^0)^{2/3} [4 - 3(\bar{v}^0)^{1/3}]^{-1} \times (\bar{T} - \bar{T}^0) \quad (12)$$

The equation of state prescribes an isobar (\bar{v} vs. \bar{T}) with positive curvature. The "ideal" reduced volume \bar{v}^0 for the mixture being linear with φ , the excess volume \bar{v}^E must be negative. This is evident also from eq. 12 by noting, on the same grounds as above, that $\bar{T} < \bar{T}^0$.

Numerical calculations carried out as prescribed above are compared in Fig. 1 with experimental results of van der Waals and Desmyter^{2,14} for the system C₆-C₁₆. The calculations for a given composition depend entirely on the values assigned to the reduced volumes of the pure components, and the result is quite sensitive to them. These, in turn, depend on the thermal expansion coefficients α . In order to minimize the effect of errors in α for individual homologs, reduced volumes have been calculated on the basis of the empirical relationship between $1/T^*$ and $1/x$ afforded by eq. I-32. Thus, $\bar{T} = T/T^*$ was calculated for the respective homologs using the relationship, eq. I-32, representing data at 20°, and from it the reduced volumes \bar{v} for the pure components were calculated according to the equation of state, eq. 11. In interests of consistency, the same relationship (for 20°) was used to calculate \bar{T} values, and from them the \bar{v} values, applicable at 50°. In light of the small drift of the parameters with temperature, previously noted in I, a more satisfactory calculation of \bar{v}^E might have been realized by using an empirical equation adjusted to data taken at 50°. As pointed out in I (see especially Fig. 2) however, the slope of the relationship at this temperature is anomalous. Excess volumes calculated on the basis of eq. I-32 for 50° were appreciably smaller in magnitude than those shown in Fig. 1, and the disparity is directly traceable to the lower value of \bar{v}_1 (1.3601 vs. 1.3718) for *n*-hexane given by the 50° relationship.

The calculated curve for 20° in Fig. 1 agrees very well with experiment. A small difference is apparent at 50°, but this is within the limits of internal consistency of the calculation, which, as previously noted, is very sensitive to the precise values of the reduced volumes.

It was established in I that the combination of eq. I-32 or I-30 and the equation of state provides the basis for successfully correlating data, at a given temperature, for all members of the normal paraffin series with $n \geq 6$. The further demonstration of the applicability of these relationships to mixtures amounts to reaffirmation of Brønsted's principle of congruence¹⁵

(14) The results for 50° are taken from interpolated values quoted by McClashan, Morcum, and Williamson¹² and attributed to Holleman and van der Waals, who measured excess volumes for this system at 50.6°; see T. Holleman, *Physica*, **29**, 585 (1963).

(15) J. N. Brønsted and J. Koefoed, *Kgl. Danske Videnskab. Selskab. Mat.-fys. Medd.*, **22**, No. 17, 1 (1946); see van der Waals and Hermans, *ref. 1*

as applied to the excess volume. According to this principle the volume of a mixture of n -paraffins equals the volume of a homolog having the same ratio of CH_3 to CH_2 groups as the mixture. That this should be the case is implicit in the present formulation.

The Free Energy and Chemical Potential

The configurational free energy according to eq. I-12 is

$$F_{\text{conf}} = F^\dagger - \bar{x}NkTc[\ln(\gamma v^*) + 3 \ln(\bar{v}^{1/3} - 1) + 1/\bar{v}\bar{T}] \quad (13)$$

The free energy of mixing follows as

$$\begin{aligned} \Delta F_M = & \bar{x}NkT[(\varphi_1/x_1) \ln \varphi_1 + (\varphi_2/x_2) \ln \varphi_2] + \\ & 3\bar{x}NkT\{\varphi_1c_1 \ln [(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1)] + \\ & \varphi_2c_2 \ln [(\bar{v}_2^{1/3} - 1)/(\bar{v}^{1/3} - 1)]\} + \\ & \bar{x}Nv^*(\varphi_1p_1^*/\bar{v}_1 + \varphi_2p_2^*/\bar{v}_2 - p^*/\bar{v}) \quad (14) \end{aligned}$$

where the substitutions $kT\bar{c}\bar{T}^{-1} = p^*v^*$ and corresponding expressions for the pure components have been incorporated; ΔF^\dagger has been replaced by the lattice theory result (first term in brackets in eq. 14). The higher approximation of Huggins,¹⁶ Miller,¹⁷ and Orr¹⁷ could be used if advantage were to be gained thereby. It is to be noted that segment fractions φ_2 have been substituted for the usual volume fractions in the lattice. This substitution is proper in light of the way in which a segment has been defined and its role in the theory propounded in I.

The reference pressure p^* equals $s\eta/2v^{*2}$ according to eq. I-22, where $s\eta$ is given by eq. 3. The substitutions $1/\bar{x} = \varphi_1/x_1 + \varphi_2/x_2$ and $s = \varphi_1s_1 + \varphi_2s_2$ permit the result to be rearranged, without approximation, to

$$p^* = \varphi_1p_1^* + \varphi_2p_2^* - \varphi_1\varphi_2p_{12}^* \quad (15)$$

where

$$p_{12}^* = p_\infty^*(1/x_1 - 1/x_2)^2b/(1 + s_e/s_m\bar{x})(1 + s_e/s_mx_1)(1 + s_e/s_mx_2) \quad (16)$$

The parameters p_∞^* and b have been defined by eq. I-34 and I-29, respectively. The first of the factors appearing in the denominator of eq. 16 depends on the composition through $1/\bar{x}$. Since s_e/s_m may be assumed to occur in the range from 1 to 2, the change in this factor is not large. Moreover, for n -alkanes b turns out to be small and the importance of the terms containing p_{12}^* is minor compared with other terms. It may therefore suffice to write

$$p_{12}^* = p_\infty^*(1/x_1 - 1/x_2)^2b' \quad (17)$$

where

$$b' = b/(1 + s_e/s_m\bar{x})(1 + s_e/s_mx_1)(1 + s_e/s_mx_2)$$

and to treat b' as constant for all n -alkanes.

The chemical potential of component 1 relative to the pure component is

$$\begin{aligned} \mu_1 - \mu_1^0 = & -RT[\partial \ln(Z/Z_1^0)/\partial N_1]_{T,V,N_2} \\ = & (\partial \Delta F_M/\partial N_1)_{\bar{T},\bar{v},N_2} + (\partial \Delta F_M/\partial \bar{v})_{\bar{T},N_1,N_2} \times \\ & (\partial \bar{v}/\partial N_1)_{\bar{T},V,N_2} \quad (18) \end{aligned}$$

(16) M. L. Huggins, *Ann. N. Y. Acad. Sci.*, **43**, 1 (1942).

(17) E. A. Guggenheim, "Mixtures," Oxford University Press, London, 1952. Chapters 10-12.

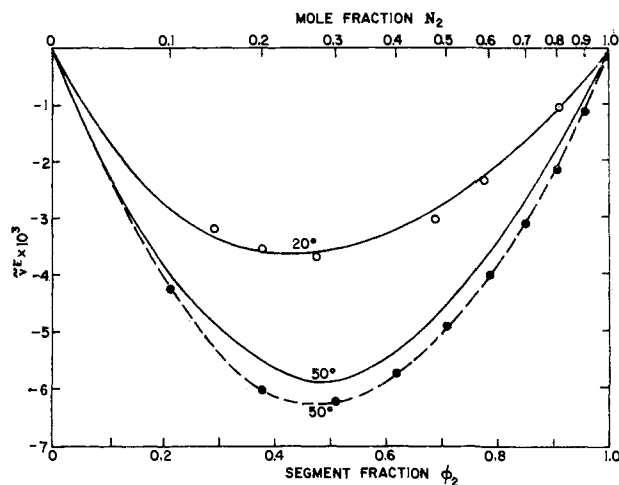


Fig. 1.—Reduced excess volumes for C_6 - C_{16} mixtures plotted against the segment fraction φ_2 of the latter component. The mole fraction N_2 is shown along the upper margin. Solid curves have been calculated from the reduced equation of state as described in the text. Open circles represent experimental results of Desmyter and van der Waals² at 20°; filled circles have been interpolated¹² from experimental results at 50.6° attributed to Holleman and van der Waals.¹⁴ The dashed line has been drawn through these experimental points.

where Z_1^0 is the partition function for the pure component. The second term in eq. 18 makes a contribution of magnitude $p v^*(\bar{v} - \bar{v}_1)$. It may therefore be neglected at all ordinary pressures. On this basis we obtain from eq. 14, 15, and 18

$$\begin{aligned} (\mu_1 - \mu_1^0)/RT = & [\ln(1 - \varphi_2) + (1 - x_1/x_2)\varphi_2] + \\ & 3x_1c_1 \ln [(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1)] - \\ & (x_1p_1^*v^*/RT)(1/\bar{v} - 1/\bar{v}_1) + \\ & (x_1p_{12}^*v^*/RT\bar{v})\varphi_2^2 \quad (19) \end{aligned}$$

where v^* is to be expressed in units of volume per mole of segments. The substitution

$$p_1^*v^*/RT = c_1/\bar{T}_1 = c_1\bar{v}_1^{1/3}/(\bar{v}_1^{1/3} - 1) \quad (20)$$

provides the alternative expression

$$\begin{aligned} (\mu_1 - \mu_1^0)/RT = & [\ln(1 - \varphi_2) + (1 - x_1/x_2)\varphi_2] + \\ & x_1c_1\{3 \ln [(\bar{v}_1^{1/3} - 1)/(\bar{v}^{1/3} - 1)] - \\ & (\bar{v}_1 - \bar{v})\bar{v}_1^{1/3}/\bar{v}(\bar{v}_1^{1/3} - 1)\} + \\ & (x_1\beta_{12}/T\bar{v})\varphi_2^2 \quad (21) \end{aligned}$$

where

$$\beta_{12} = p_{12}^*v^*/R = (p_\infty^*v^*b'/R)(1/x_1 - 1/x_2)^2 \quad (22)$$

Equations 19 and 21 relate the chemical potential to the composition of the mixture using only one parameter (either p_{12}^* or β_{12}) beyond those (x_1 , x_2 , c_1 , v^* , \bar{v}_1 , and p_∞^*) characterizing the pure components; the reduced volume \bar{v} for the mixture is calculable from characteristics of the pure components, as related above. This parameter occurs as the coefficient of the term in φ_2^2 . It depends on b , which according to I reflects the difference in the interactions of terminal segments as compared to internal ones. Equation 21 offers the advantage over eq. 19 of expressing the volume sensitive term as a function of \bar{v}_1 and \bar{v} only.

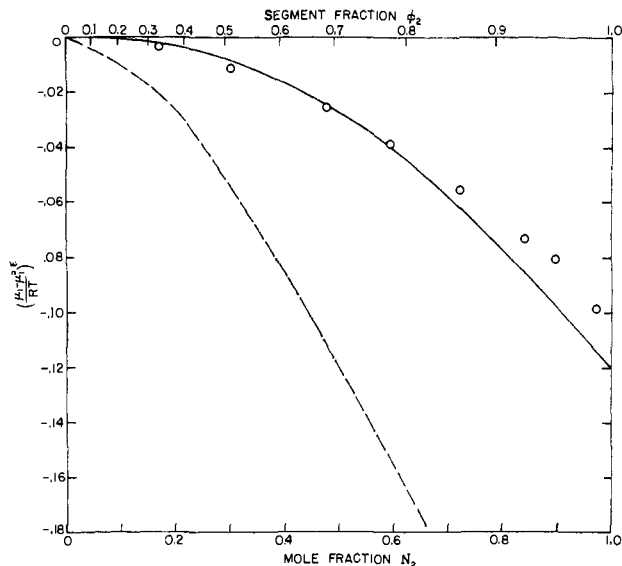


Fig. 2.—Excess chemical potential for the system C_6-C_{16} at 20° plotted against the mole fraction N_2 . The segment fraction ϕ_2 is shown along the upper margin. Experimental points are those of McGlashan and Williamson.⁸ The solid line has been calculated from eq. 21 using parameters for the pure components found in the preceding paper and taking $b' = 0.40$. The dashed line represents the lattice theory contribution alone (first bracket in eq. 21).

Excess chemical potentials

$$(\mu_1 - \mu_1^0)^E/RT = (\mu_1 - \mu_1^0)/RT - \ln(1 - N_2)$$

are plotted against the mole fraction N_2 of *n*-hexadecane in the system *n*-hexane-*n*-hexadecane (C_6-C_{16}) at 20° in Fig. 2. The experimental points are from the precise measurements of McGlashan and Williamson.⁸ The solid curve has been calculated according to eq. 21 with $\beta_{12} = 2.4^\circ K.$, corresponding to $b' = 0.40$. The agreement is remarkably good. Departures of experimental data from the theoretical curve amount to no more than about 1% in the activity over most of the range in composition.

The contribution from the lattice entropy, expressed by the first bracketed term in eq. 21, is shown by the dashed curve in Fig. 2. Other terms in eq. 21, which are the ones contributed by the present theory, are comparable to the lattice excess free energy in magnitude but are opposite in sign. The calculated excess chemical potentials for this system (C_6-C_{16}) consequently are fairly small. The measure of disagreement with experiment should be judged by the absolute amount of the departure and not by the ratio of observed and calculated values.

Experimental results of McGlashan and Williamson⁸ for the same system at 50° are similarly compared with theoretical calculations in Fig. 3. Also included are data of van der Waals and Hermans⁶ on C_7-C_{32} mixtures at 73° . The curves shown have been calculated using the same values of b' quoted above. The agreement with experiment is comparable to that shown in Fig. 2. Thus, the arbitrary choice of a value for only one parameter, b' , suffices to fit data for two diverse systems and for the same system at different temperatures. Moreover, the resulting value of β_{12} being small, the contribution of the contact term governed by it is minor. The volume sensitive term, involving only such param-

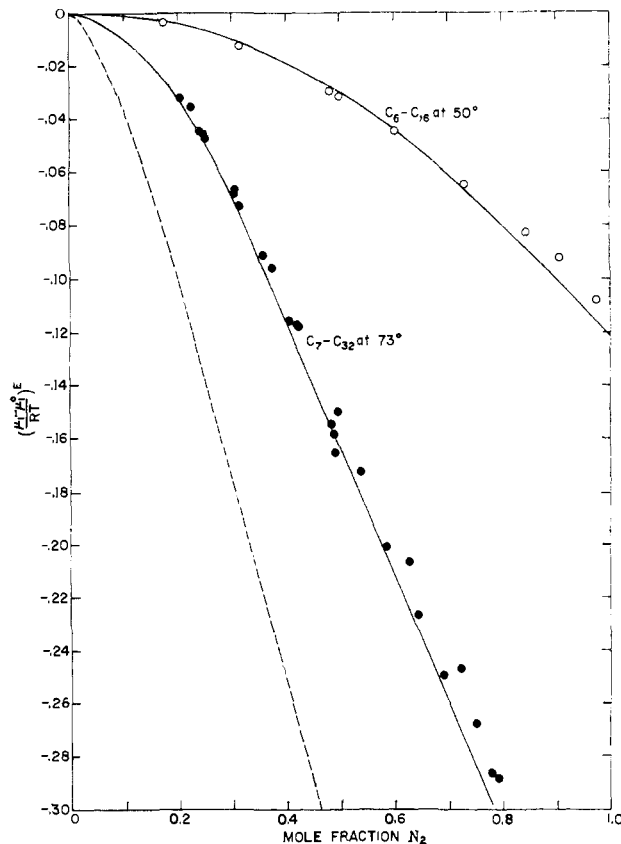


Fig. 3.—Excess chemical potentials for the system C_6-C_{16} at 50° (McGlashan and Williamson⁸) and for C_7-C_{32} at 73° (van der Waals and Hermans⁶) plotted against the mole fraction N_2 of the component of higher molecular weight. Solid lines were calculated from eq. 21 with $b' = 0.40$. The dashed line represents the lattice contribution for the latter system.

eters as are determined by properties of the pure components, is dominant for the systems considered.

Conventional interpretations proceeding from the lattice model would prescribe an excess chemical potential consisting of the lattice entropy term in eq. 21 supplemented by a contact energy term. Since the latter is small, it alone would raise the dashed curve in Fig. 2 by only a small fraction of the difference between this curve and experiment.

If one should choose to supplement the lattice entropy with the observed enthalpy of mixing (see below), the resultant curve for C_6-C_{16} mixtures at 20° would, to be sure, fall not far below the experimental points. Such agreement as would be achieved is peculiar to this temperature, however. The observed excess enthalpy for this system decreases rapidly with temperature, becoming negative above about 65° .¹¹ Inasmuch as the excess chemical potential changes little with temperature,⁸ interpretation of the excess chemical potentials in this manner becomes increasingly unsatisfactory for temperatures above 20° . These remarks are by way of illustrating the serious failure of lattice theories alone to account for excess thermodynamic properties of these systems. Their deficiencies are abundantly documented.

Calculations carried out using the lattice theory in the higher approximation of Huggins,¹⁵ Orr, Miller, and Guggenheim¹⁷ have little effect on the agreement attainable, despite the availability of a further parameter, namely, the lattice coordination number z .

The value of β_{12} required to achieve optimum agreement is lowered however. For $z = 12$, the experimental data require $b' \cong 0.15$.

van der Waals and Hermans⁶ also measured activities of *n*-heptane mixtures with polyethylene at 108.9°. Their polyethylene sample consisted of a highly branched fraction having a CH₃:CH₂ ratio of about 0.05 and a molecular weight of 26,000. Calculations carried out again on the basis of $b' = 0.40$ reproduce the experimental data fairly well. The significance of this comparison, based on parameters deduced from properties of the *n*-alkanes, is obscured by the nonlinearity of the polymer component. We have not therefore included the analysis of this set of results.

The calculated curves shown in Fig. 2 and 3 would not be altered significantly by taking account of the small dependence of b' on the composition of the mixture. To have performed the calculation in this manner would have required assignment of a numerical value to the ratio s_e/s_m , which can only be estimated crudely from the molecular geometry.

The Excess Enthalpy

Ignoring the small difference between enthalpy and energy for a condensed system, we have for the excess enthalpy per mole of mixture

$$H^E = [E_0(\text{mixture}) - E_0(1) - E_0(2)]/N$$

which, in light of eq. 1, can be written

$$H^E = \bar{x}v^*(\varphi_1 p_1^*/\bar{v}_1 + \varphi_2 p_2^*/\bar{v}_2 - p^*/\bar{v}) \quad (23)$$

Substitution of eq. 15 for p^* converts this result to

$$H^E = \bar{x}v^*[\varphi_1 p_1^*(1/\bar{v}_1 - 1/\bar{v}) + \varphi_2 p_2^*(1/\bar{v}_2 - 1/\bar{v}) + \varphi_1 \varphi_2 p_{12}^*/\bar{v}] \quad (24)$$

Since \bar{v}^E is very small, the reciprocal of \bar{v} may be approximated with negligible error by

$$1/\bar{v} = 1/\bar{v}^0 - \bar{v}^E/(\bar{v}^0)^2$$

substitution of which in eq. 24 permits the excess molar enthalpy to be expressed as a sum of three terms as

$$H^E/\bar{x}v^* = (p_{12}^*/\bar{v})\varphi_1\varphi_2 + [(\bar{v}_1 - \bar{v}_2)/\bar{v}^0](p_2^*/\bar{v}_2 - p_1^*/\bar{v}_1)\varphi_1\varphi_2 + [\bar{v}^E/(\bar{v}^0)^2](\varphi_1 p_1^* + \varphi_2 p_2^*) \quad (25)$$

$$\cong (p_{12}^*/\bar{v})\varphi_1\varphi_2 + [(\bar{v}_1 - \bar{v}_2)/\bar{v}](p_2^*/\bar{v}_2 - p_1^*/\bar{v}_1)\varphi_1\varphi_2 + (\bar{v}^E/\bar{v}^2)(\varphi_1 p_1^* + \varphi_2 p_2^*) \quad (25')$$

The first term in eq. 25, or in 25', represents the contribution to the excess enthalpy from change in contact pairs upon mixing. This term should be positive, and such is observed to be the case. The second term takes account of the effect on the enthalpy arising from the difference in the volumes available to segments in the two pure components. It vanishes for $\bar{v}_1 = \bar{v}_2$, but does not depend on the change in volume on mixing. Depending on values of the parameters, it could conceivably be either positive or negative. For the *n*-paraffin hydrocarbons it is decidedly positive. The third term accounts for the effect of the volume change on mixing. It varies directly as \bar{v}^E , and since $\bar{v}^E < 0$ for the paraffin hydrocarbon mixtures, its contribution is negative. Three such contributions to the excess thermodynamic properties were recognized by McGlashan, Morcum, and Williamson.¹²

Excess enthalpies per mole of mixture calculated according to eq. 25 are compared in Table I with values observed for various systems. All data refer to compositions $\varphi_1 = \varphi_2 = 1/2$. Experimental results are from the investigations of van der Waals and Hermans⁴ and McGlashan and Morcum.⁵ Values of p_1^* and p_2^* required for calculation according to eq. 25 were computed from I-35 wherein the constant a has been assigned the value -1.5 for the express purpose of achieving approximate agreement with the enthalpies of mixing, as previously acknowledged.¹³ The required p_{12}^* were computed according to eq. 17 with b' being assigned the same value, 0.40, used for calculating the chemical potentials. Reduced volumes \bar{v}_1 and \bar{v}_2 were taken from Table I of the previous paper¹³; those for 73° were obtained by interpolation from the tabulations for 50 and 100°. Experimental reduced excess volumes \bar{v}^E were used, except for the system C₁₀-C₃₂ for which experimental excess volumes are unavailable. The required \bar{v}^E in this instance was calculated in the manner described earlier.

TABLE I
MOLAR EXCESS ENTHALPIES FOR VARIOUS HYDROCARBON MIXTURES

System	Temp., °C.	H^E FOR $\varphi_2 = 1/2$, cal. mole ⁻¹	
		Calcd.	Obsd.
C ₆ -C ₁₆	20	28	25, ^a 27 ^b
C ₇ -C ₁₆	20	19	22, ^a 23 ^b
C ₈ -C ₁₆	20	14	18, ^a 19 ^b
C ₆ -C ₁₆	50	16	7 ^b
C ₈ -C ₁₆	50	10	8 ^a
C ₁₀ -C ₃₂	73	20	22 (±4) ^a

^a See ref. 4. ^b See ref. 5.

The relative magnitudes of the three terms in eq. 25 calculated in this way for the C₆-C₁₆ system at 20° are illustrative. They are 9.4, 50.5, and -31.9 cal. mole⁻¹, respectively. The first is comparatively small, and the latter two are of opposite sign. The second term is sensitive to the differences between the reduced volumes \bar{v}_1 and \bar{v}_2 and also to the difference between p_1^* and p_2^* . Although the former are obtained with reasonable accuracy from the thermal expansion coefficients (see I), their difference is disturbingly sensitive to small errors in the α 's. The p^* are subject to large errors stemming from inaccuracies in existing compression data,¹³ which we have attempted to circumvent by exercising an arbitrary choice of the parameter a . Moreover, we assume implicitly that the constants p_{∞}^* and a in eq. I-35 are independent of temperature. The third term amounts to at least half of the sum of the first two. Hence, the final result is precariously dependent also on the values of p_1^* and p_2^* and \bar{v}^E .

The theory correctly predicts a decrease in the excess enthalpy with temperature and it provides an approximate correlation of the enthalpies of mixing for different pairs of *n*-alkanes. The calculated change with temperature for the C₆-C₁₆ system is less than that observed. An error in either \bar{v} or p^* for *n*-hexane at the higher temperature would account for this most serious discrepancy between calculated and observed results. In any case, the theory correctly depicts the direction of changes in the excess enthalpy. It may be quantitatively inaccurate in its account of their magnitudes.

It will be observed from figures quoted above that the contact term amounts to less than 20% of the second

term for the C₆-C₁₆ mixtures. This term is the only one normally considered in the treatment of the excess enthalpies of solutions. It alone could account for the change of sign of μ^E only by *ad hoc* identification of b' as a free energy parameter¹⁷ whose entropic contribution is very large, thereby rendering b' strongly dependent upon temperature. According to the present treatment, the excess enthalpy for *n*-paraffin mixtures arises in a natural way from characteristics of the pure liquids. It depends only to a minor degree on the contact energy between unlike species or segments.

Lower Critical Solution Temperatures (LCST)

The series expansion of the chemical potential as given by eq. 21 can be written

$$(\mu_1 - \mu_1^0)/RT = - (x_1/x_2)\varphi_2 - (1/2)[1 - 3x_1c_1(1 - T_1^*/T_2^*)^2 / (1 - 4\bar{v}_1T/T_1^*) - 2x_1\beta_{12}/T\bar{v}_1]\varphi_2^2 - \dots \quad (26)$$

where the coefficients of φ_2^2 have been expressed in terms of the T^* instead of the corresponding p^* values.

We confine present considerations to liquid-liquid miscibility for a solute of infinite chain length, *i.e.*, $x_2 = \infty$. In this case, the conditions for critical miscibility, namely

$$(\partial\mu_1/\partial\varphi_2)_{T,p} = 0$$

$$(\partial^2\mu_1/\partial\varphi_2^2)_{T,p} = 0$$

are fulfilled at $\varphi_2 = 0$ provided that

$$3x_1c_1(1 - T_1^*/T_\infty^*)^2 / (1 - 4\bar{v}_1T/T_1^*) + 2x_1\beta_{12}/T\bar{v}_1 = 1 \quad (27)$$

This equation immediately predicts the occurrence of LCST in mixtures of *n*-paraffin hydrocarbons with polyethylene. The numerical calculations listed in Table II have been carried out using the parameters given in the preceding paper together with $b' = 0.40$ as above. The T^* have been obtained at each temperature by graphical interpolation of T^* evaluated from eq. I-32.

TABLE II
LCST VALUES FOR *n*-ALKANES AND POLYETHYLENE AS
CALCULATED FROM EQ. 27

<i>n</i>	LCST, calcd., °C.
5	Incompletely miscible at all <i>T</i>
6	85
7	130
8	155
9	175

Freeman and Rowlinson⁹ report the absence of a range of total miscibility for *n*-pentane and polyethylene above the temperature (*ca.* 110°) at which the latter

melts in presence of the former.¹⁸ In the case of *n*-hexane total miscibility was observed⁹ within a small temperature interval, its upper limit being an LCST reported at 400°K. The calculated LCST given in Table II for hexane is somewhat lower. The calculated result for *n*-heptane agrees approximately with that reported for *n*-hexane. The assumption of random dispersion of segments commented upon early in this paper should perhaps be called into question in this connection. The infinitely dilute solution of the polyethylene solute in a lower hydrocarbon presents a situation in which the error attending this assumption should be of maximum effect. It is also to be noted that the LCST occur well above the boiling points of the solvents; hence a considerable extrapolation beyond the range of the data for the pure liquids is involved.

The progressive increase in the calculated LCST with chain length of the solvent is of interest. Experiments to provide comparisons with these predictions are being undertaken.

Conclusions

The successful correlation of the chemical potentials for several binary systems affords a critical demonstration of the accuracy with which the free energy of mixing can be represented by the present theory. The parallel treatment of the enthalpies of mixing, although less impressive in terms of quantitative numerical comparisons, appears nonetheless to give a consistent account of the main features. Departures from numerical agreement between calculated and observed enthalpies may reflect more on inaccuracies of equation of state data for the pure components than on the theory as applied to mixtures. As is generally recognized, the free energy gains a degree of insensitivity to the liquid structure from the condition $(\partial F/\partial V)_{T,p} \cong 0$ at low pressures, which is not shared by the companion enthalpy and entropy functions.

The present investigation is preliminary. It is not comprehensive; a number of related systems remain to be treated similarly. We have not presented an explicit analysis of the excess entropy. The character of the comparison of calculated with observed entropies is of course foreshadowed by the analysis given of the chemical potentials and the enthalpies of mixing.

Of foremost importance, the present study establishes the significance of characteristics of the liquid state in determining the thermodynamic properties of liquid mixtures. The excess thermodynamic functions of mixtures cannot be adequately comprehended without taking proper account of these characteristics.

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(18) P. Ehrlich and J. J. Kurpen, *J. Polymer Sci.*, **A1**, 3217 (1963), report an LCST of about 90° for *n*-pentane and branched polyethylene. As they have pointed out (private communication), the extent of branching in their sample (*ca.* 1.7% of total CH₂) probably has little effect on the LCST in this instance.