Statistical Thermodynamics of Liquid Mixtures

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Liquid mixtures of nonpolar molecules are treated on the basis of a simple partition function affording an approximate, but satisfactory, representation of liquid state properties. Parameters characterizing the pure components (specifically, the density, thermal expansion coefficient, and thermal pressure coefficient) are thus brought to bear on the analysis of properties of mixtures. Theoretical expressions for the "equation of state" contributions to the free energy, enthalpy, entropy, chemical potential, and excess volume are derived. The theoretical entropy of mixing in excess of the combinatorial, or "ideal," entropy depends on the reduced volumes of the two components and of the mixture; it does not vanish, in general, when the excess volume is reduced to zero, contrary to a tenet of regular solution theory. The treatment is applicable to mixtures of molecules differing in size.

Introduction

Traditional theories of solutions dwell exclusively on two aspects of liquid mixtures. One of these is the entropy associated with dispersion of the two molecular species, or of their constituent elements in the case of complex molecules, among one another. A lattice model often serves as the device for estimating this "combinatorial" entropy. The other aspect relates to the interactions between neighboring molecules and, in particular, to the difference in the interactions between unlike and like neighbor pairs. Treatment of the properties of liquid mixtures has progressed little beyond the level of interpretation possible within the framework supported by these two considerations alone.[1,2]

The equilibrium properties of a liquid are strongly dependent on what may be loosely called its local structure, often expressed in terms such as packing density, free volume, or, more exactly, in terms of the radial distribution function. Inasmuch as this local structure depends on the forces between molecules and on the form and volume of the molecules, in general, it will change with the composition. This change in turn will be reflected in the thermodynamic properties of the mixture. Contributions of this nature have either been ignored altogether, or correction to a state of null volume change on mixing has been adopted as a means of compensating for the effects referred to.[2] By this device, the various properties of the mixture are altered by the changes they would sustain if the volume were adjusted to the value linearly interpolated between the volumes of the pure components. It will be apparent, however, that adjustment of one thermodynamic quantity (*e.g.*, the volume) in this manner will not, in general, effect a simultaneous correction of

others (*e.g.*, the free energy or that part of it relating to the local structure) to their linearly interpolated values. The choice of volume as the property to be "conserved" is arbitrary, and there is no assurance that nullity of volume change obviates consideration of other characteristic properties of the liquid.

More sophisticated treatments[3,4] of liquid mixtures derive their conceptual basis from (a) the cell model for liquids and (or) from (b) the postulation of a universal form for the intermolecular potential expressed by $\epsilon_{ij} = \epsilon^*_{ij}\varphi(r_{ij}/r^*_{ij})$, where r_{ij} is the distance between centers of molecules i and j, ϵ^*_{ij} and r^*_{ij} are characteristic parameters for the pair, and $\varphi(r/r^*)$ is a universal function of its argument. The corresponding states approach, including conformal theory, proceeds from the latter of these premises.[4] Insofar as giving account of experimental results is concerned, these approaches have failed to establish decisive advantage over treatments recalled in the preceding paragraphs. Reasons therefore undoubtedly relate to limitations of the cell model and to severe departures from proposition b above for component molecules which differ appreciably in size, shape, or composition.

The definition of the cell, consisting of neighbor molecules in fixed array about the central "wanderer," erroneously ascribes crystal-like characteristics to the liquid. Each molecule is required to perform dual, mutually inconsistent roles: it must function both as a fixed neighbor and as the wanderer within its own cell. Thus, not only does the cell model incorporate the acknowledged deficiencies of the Einstein model for a solid, but it also fails to take account of those features which set a liquid apart from a solid. These shortcomings of the cell model have been stressed by Hildebrand and his co-workers.[1,2]

By computing the mean intermolecular energy for a set of molecules in perfect array, each being assigned to the center of its cell, the cell model prescribes a dependence on the volume which is too great. This error can be seen to be an inevitable consequence of the order implied by this model and would follow for any acceptable representation of the intermolecular energy for a pair of molecules. That the energy–volume relationship according to the cell model is at variance with experiment has been abundantly shown[2,5] by analysis of $(\partial E/\partial V)_T$ coefficients.

The intermolecular energy is usually discussed on the basis of the familiar Lennard-Jones potential operating between molecular centers. Even in comparatively simple polyatomic molecules, *e.g.*, CH_4 or CCl_4, the acentric distribution of polarizable electrons neces-

(1) J. H. Hildebrand and R. L. Scott, "Solubility of Non-Electrolytes," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1950.
(2) J. H. Hildebrand and R. L. Scott,"Regular Solutions," Prentice-Hall, Englewood Cliffs, N. J., 1962.

(3) I. Prigogine, "The Molecular Theory of Solutions," North-Holland Publishing Co., Amsterdam, 1957.
(4) J. S. Rowlinson, "Liquids and Liquid Mixtures," Butterworth and Co., Ltd., London, 1959.
(5) R. L. Scott, *Discussions Faraday Soc.*, 15, 44, 113 (1953); *J. Chem. Phys.*, 25, 193 (1956); H. Benninga and R. L. Scott, *ibid.*, 23, 1911 (1955).

sitates fairly drastic modification of this potential.[2] Kihara,[6] Hamann and Lambert,[7] and Pitzer[8] have offered modified intermolecular potentials for polyatomic (globular) molecules, especially those approximating spherical symmetry in form. Pitzer replaces each molecule with a smooth distribution of interacting elements (electrons), these being distributed uniformly either on the surface of a spherical core or throughout the volume of the core. In either case, a Lennard-Jones interaction is ascribed to each pair of elements, one from the distribution for each of two neighboring molecules, and the total interaction is obtained by integrating over the respective cores. The form of the potential is modified considerably by acentricity, irrespective of which of the two models is used. Both the attractive and the repulsive terms are rendered more steeply dependent on the distance between molecular centers,[7-9] but to a degree which is highly dependent on the particular molecule.

An extension of these considerations which suggests itself as a basis for treating the intermolecular energy in liquids consists in integrating the interactions of elements of the core of one molecule with the elements of all surrounding molecules, these latter being treated as a continuum occupying the space outside the cavity reserved for the molecule in question. The result obtained[10] departs markedly from the form of the intermolecular energy according to the theory of Lennard-Jones and Devonshire. For a ratio of core to cavity diameters greater than $^1/_5$, the energy is approximately proportional to the density; it depends also on a simple function of the cavity diameter. Inasmuch as the form of the potential depends on parameters peculiar to the molecular species, it does not lend itself to reduction to a parametric expression such as is required to sustain a law of corresponding states.[10] Limitations[11] of the corresponding states scheme advanced by Prigogine and co-workers[3] are probably related to considerations of this nature.

In the limit of very large particles such that the range of intermolecular interactions, attractive as well as repulsive, is small compared to the molecular diameter and to the distance between boundaries of the domains of neighboring molecules, the intermolecular energy can be treated as arising effectively from interactions between the surfaces of adjoining molecules. The calculations[10] described briefly above support an account of the intermolecular energy on this basis, and they indicate further that this manifestly naive approximation should be satisfactory even for small polyatomic molecules such as CCl_4. Certainly this approximation, which has a long history of usage in solution theory, is preferable to central force potentials of the Lennard-Jones type for virtually all molecules of interest. It offers the additional advantage of being adaptable to treatment of nonspherical molecules and of mixtures of molecules differing in size.

Recently,[12] we have explored the application of a comparatively simple partition function suitable for liquids comprising chain molecules to homologs of the normal paraffin hydrocarbon series, $H-(CH_2)_n-H$ with $n > 5$. A coherent correlation of the properties of the pure hydrocarbons has been achieved, which, as it involves relationships expressed in algebraic form, is much to be preferred over the various corresponding states schemes which have been propounded.[3,11] The same partition function has been adapted to *mixtures* of the straight-chain hydrocarbons.[13] Thermodynamic properties of these mixtures are thus related to parameters obtained from equation of state characteristics of the pure component hydrocarbons. The peculiar patterns of the excess chemical potentials and the excess enthalpies for these systems are well explained by the theory. Especially striking is the excellent agreement between calculated and observed chemical potentials for a variety of systems C_n/C_m at different temperatures with arbitrary choice of a single parameter for all.

The previous formulation[12,13] was addressed specifically to chain molecules and to mixtures of chain homologs. Here we present a rendition for mixtures of molecules of unrelated types. One of the merits of the theory is its adaptability to mixtures of molecules differing in size and shape. Calculations performed to date encourage the expectation that it may be broadly applicable to mixtures of homopolar molecules.[14]

The Partition Function and Equation of State

Consider a one-dimensional system comprising N particles each of length $l*$ distributed within a space of length L. Overlaps of particles are assumed to be excluded. Then as Tonks[15] pointed out a number of years ago, the totality of configuration space available to the system is

$$\Omega = (L - Nl*)^N/N! \qquad (1)$$

$$\cong [(l - l*)e]^N \qquad (1')$$

where $l = L/N$ is the space available per particle.

The configuration integral for such a system can be written

$$Z = \int \ldots \int \exp[-E(x)/kT]dx \qquad (2)$$

where x denotes the set of configuration coordinates $x_1, x_2, \ldots, x_N$ in the one-dimensional space, and $dx = dx_1 dx_2 \ldots dx_N$. In accordance with conventional procedure, let

$$Z = \Omega \exp(-E_0/kT) \qquad (3)$$

where E_0 is the "mean" intermolecular energy defined formally by eq. 2 and 3. By obvious extension of the argument to three dimensions, one obtains for a system of spheres analogous to the one-dimensional particles considered[15,16]

$$Z = [\gamma e^3 (v^{1/3} - v*^{1/3})^3]^N \exp(-E_0/kT) \qquad (4)$$

where γ is a geometric factor which establishes the connections $(\gamma v*)^{1/3} = l*$ and $(\gamma v)^{1/3} = l$. The form of the result is equivalent to that given by the cell model.

(6) T. Kihara, *Rev. Mod. Phys.*, **25**, 831 (1953).
(7) S. D. Hamann and J. A. Lambert, *Australian J. Chem.*, **7**, 1 (1954).
(8) K. S. Pitzer, *J. Am. Chem. Soc.*, **77**, 3427 (1955); K. S. Pitzer and G. O. Hultgren, *ibid.*, **80**, 4793 (1958).
(9) See ref. 3, p. 259 ff.
(10) Unpublished.
(11) R. Simha and A. J. Havlik, *J. Am. Chem. Soc.*, **86**, 197 (1964).
(12) P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3507 (1964).
(13) P. J. Flory, R. A. Orwoll, and A. Vrij, *ibid.*, **86**, 3515 (1964).
(14) P. J. Flory and A. Abe, *ibid.*, **86**, 3563 (1964); see especially the following paper, A. Abe and P. J. Flory, *ibid.*, **87**, 1838 (1965).
(15) L. Tonks, *Phys. Rev.*, **50**, 955 (1936).
(16) O. K. Rice, *J. Chem. Phys.*, **12**, 1 (1944); *ibid.*, **14**, 348 (1946).

The communal entropy[15,16] factor e^{3N} is not, of course, included in the cell model treatment.[17]

With the objective of arriving at a formulation not limited to spherical molecules, and one which may be adapted to the treatment of mixtures of molecules differing in size, we define an *element* (or *segment*) as an arbitrarily chosen isometric portion of the molecule. Its definition is otherwise left open for later specification in such manner as may prove most convenient in a given instance. Let there be r such elements, or segments, in a molecule. Following Prigogine's treatment[3,18] of "r-mer" chain molecules, we let $3c$ represent the number of external degrees of freedom per segment. Also following Prigogine, we assume the partition function to take the form

$$Z = Z_{\text{comb}}[\gamma(v^{1/3} - v^{*1/3})^3]^{rNc} \exp(-E_0/kT) \quad (5)$$

where Z_{comb} is a combinatorial factor which takes account of the number of ways of interspersing the rN elements among one another, without regard to the precise location of each relative to its chosen neighbor (this latter being within the province of the Tonks[15] estimation of Ω). If it should be important to identify the communal entropy factor e^{3N}, we may consider it to have been absorbed into Z_{comb}. In general, however, this factor along with γ^N will be lost in the process of differentiation involved in deducing the equation of state or in the taking of differences with respect to the pure components in treating mixtures.

The device of modifying the exponent of the bracketed expression in eq. 5 by the factor c, where we anticipate defining an element in such a way as to render $c \leqq 1$, is intuitive rather than rigorous. Its basis is equally obscure in terms of the cell model used by Prigogine.[3,18] The form of the result is plausible enough, but the literal significance of c should be regarded with caution.

Prigogine and co-workers[3,18] adhered to the cell model as a guide to formulation of the mean intermolecular energy E_0. Quite apart from its intrinsic physical inconsistencies, the cell model is known empirically to lead to an energy which depends much too steeply on the volume.[5] We therefore reject this approach in favor of one suggested by considerations of the radial distribution function. The arguments for this preference have been eloquently presented by Hildebrand and Scott.[1,2] They have shown that the energy is usually well represented by an expression of the form suggested by Frank[19]

$$E_0 = \text{constant}/V^m$$

where m may be treated as a constant, usually in the range of 1.0 to 1.5 for nonpolar liquids.[20] In interests

(17) The communal entropy is usually considered to be Nk, apparently by analogy to a gas. Support for the larger communal entropy ($3Nk$) in the case of liquids has been clearly set forth by Rice.[16]

(18) I. Prigogine, N. Trappeniers, and V. Mathot, *J. Chem. Phys.*, **21**, 559, 560 (1953); *Discussions Faraday Soc.*, **15**, 93 (1953); I. Prigogine, A. Bellemans, and C. Naar-Colin, *ibid.*, **26**, 751 (1957); see also Chapters XVI and XVII of ref. 3.

(19) H. S. Frank, *J. Chem. Phys.*, **13**, 495 (1945).

(20) Hildebrand and Scott's[1,2] values of m rest on comparison of $(\partial E/\partial V)_T \cong T(\partial p/\partial T)_V$ with the energy of vaporization, the latter of which represents the energy change for infinite expansion of the liquid. Their values of m reflect therefore the energy-volume relationship over a much greater range than that with which we shall be concerned. Departures of m from unity according to the method of Hildebrand and Scott do not necessarily imply a corresponding deviation within the normal range of density of the liquid.

of restricting the number of parameters permitted, we take $m = 1$, and write

$$E_0 = -Nrs\eta/2v \quad (6)$$

where s is the number of intermolecular contact sites per segment, η is a constant characterizing the energy of interaction for a pair of neighboring sites, and v is the volume per segment in accord with terminology used above. The choice of a reciprocal power of unity for v finds further justification in the fact that the treatment will generally be applied over only a limited range of volume. Application over wider ranges has been forfeited implicitly in the designation of c as a constant parameter. At the larger volumes characterizing the liquid near its critical point, for example, the number c of intermolecular degrees of freedom must necessarily decrease.

Also to be noted is the implication of eq. 6 that the intermolecular energy can be reckoned according to the number of contact sites or the area of contact. Short of an inordinately detailed accounting of correlation interactions (London forces) between all intermolecular pairs of atoms in the interacting molecules, this should afford a good approximation for molecules of a complexity not less that that of methane, as was pointed out in the Introduction.

The partition function expressed by eq. 5 resembles that proposed a number of years ago by Hirschfelder and Eyring.[21] It differs from their partition function through introduction of the parameter c, whereby application to liquids comprising nonspherical molecules is made possible. The reduced partition function which follows from eq. 5 and 6

$$Z = Z_{\text{comb}}(\gamma v^*)^{rNc}(\tilde{v}^{1/3} - 1)^{3rNc} \exp(rNc/\tilde{v}\tilde{T}) \quad (7)$$

and the reduced equation of state

$$\tilde{p}\tilde{v}/\tilde{T} = \tilde{v}^{1/3}/(\tilde{v}^{1/3} - 1) - 1/\tilde{v}\tilde{T} \quad (8)$$

obtained from it are identical with those of the Hirschfelder and Eyring theory. Departures occur however in the definitions of the various reduced quantities. Changing from molecular to molar units per segment for v, v^*, and η, we have

$$\tilde{v} = v/v^* \quad (9)$$

$$\tilde{T} = T/T^* = 2v^*cRT/s\eta \quad (10)$$

$$\tilde{p} = p/p^* = 2pv^{*2}/s\eta \quad (11)$$

Thus

$$p^* = cRT^*/v^* \quad (12)$$

where $3c$ is the number of external degrees of freedom *per element*, or

$$p^* = CRT^*/\text{v}^* \quad (12')$$

where $C = rc$ and $\text{v}^* = rv^*$ are the corresponding quantities per mole. The reduced equation of state at $p = 0$ is

$$(\tilde{v}^{1/3} - 1)/\tilde{v}^{4/3} = \tilde{T} \quad (13)$$

The characteristic quantities v^* and T^* can be evaluated readily from the specific volume and the thermal ex-

(21) H. Eyring and J. O. Hirschfelder, *J. Phys. Chem.*, **41**, 249 (1937); J. O. Hirschfelder, D. P. Stevenson, and H. Eyring, *J. Chem. Phys.*, **5**, 896 (1937).

pansion coefficient α as shown previously.[12,14] These quantities depend, of course, on the arbitrary specification of an element or segment. The compressibility, κ, or the thermal pressure coefficient, $\gamma \equiv (\partial p/\partial T)_v = \alpha/\kappa$, serve to define p^*. From v^*, T^*, and p^*, the set of primary parameters v^* (or $\mathrm{v}^* = rv^*$), $s\eta$, and c (or C) can be determined.

That the theory presented is approximate cannot be denied. Its purpose, namely the treatment of liquid mixtures, precludes an elaborate scheme, and it is doubtful that a better representation of liquid state properties can be achieved without disproportionate sacrifice of facility of application. The formulation given should, at the very least, afford a substantial improvement in treating liquid mixtures over ignoring altogether the characteristics of the pure components denoted by their equation of state parameters.

Binary Mixtures

The following analysis is confined to binary mixtures, the components being indexed by subscripts 1 and 2. The molecular element or segment is to be defined in correspondence for the two species such that r_1 and r_2 shall be in the ratio of the respective molar core volumes $\mathrm{v}^*{}_1$ and $\mathrm{v}^*{}_2$. Similarly, s_1 and s_2 shall be in the ratio of the molecular surface areas of contact *per segment*.

Let A_{11}, A_{12}, and A_{22} represent the numbers of contact pairs between the respective species, and let η_{11}/v, etc., be the energies associated with each. Then

$$-E_0 = (A_{11}\eta_{11} + A_{22}\eta_{22} + A_{12}\eta_{12})/v$$

Since

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

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

it follows that

$$-E_0 = (s_1 r_1 N_1 \eta_{11} + s_2 r_2 N_2 \eta_{22} - A_{12}\Delta\eta)/2v \quad (14)$$

where

$$\Delta\eta = \eta_{11} + \eta_{22} - 2\eta_{12} \quad (15)$$

Random mixing of the two species will be assumed. As a further approximation, we take the expectation that a species of kind i neighbors any given site to be equal to its site fraction θ_i, defined for a binary mixture by

$$\theta_2 = 1 - \theta_1 = s_2 r_2 N_2 / s\tilde{r}N \quad (16)$$

On this basis

$$A_{12} = s_1 r_1 N_1 \theta_2 = s_2 r_2 N_2 \theta_1 \quad (17)$$

where

$$\tilde{r} = (r_1 N_1 + r_2 N_2)/N \quad (18)$$

$$s = (s_1 r_1 N_1 + s_2 r_2 N_2)/\tilde{r}N \quad (19)$$

$$N = N_1 + N_2$$

By substitution of eq. 16 and 17 in 14

$$-E_0/\tilde{r}N = (s/2v)(\theta_1\eta_{11} + \theta_2\eta_{22} - \theta_1\theta_2\Delta\eta) \quad (20)$$

or

$$-E_0/\tilde{r}N = (s/2v)(\theta_1{}^2\eta_{11} + \theta_2{}^2\eta_{22} + 2\theta_1\theta_2\eta_{12}) \quad (20')$$

Defining the segment fractions φ_1 and φ_2 by

$$\varphi_2 = 1 - \varphi_1 = r_2 N_2/\tilde{r}N \quad (21)$$

we have

$$1/\tilde{r} = \varphi_1/r_1 + \varphi_2/r_2 \quad (18')$$

$$s = \varphi_1 s_1 + \varphi_2 s_2 \quad (19')$$

$$\theta_2 = (s_2/s)\varphi_2 \quad (22)$$

The characteristic pressures for the pure components (see eq. 11) are

$$p_1^* = s_1 \eta_{11}/2v^{*2}; \quad p_2^* = s_2\eta_{22}/2v^{*2}$$

By analogy, we define[22]

$$X_{12} = s_1\Delta\eta/2v^{*2} \quad (23)$$

Then

$$-E_0/\tilde{r}N = p^*v^*/\bar{v} = ckT^*/\bar{v} \quad (24)$$

where

$$p^* = \varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1\theta_2 X_{12} \quad (25)$$

$$c = (c_1 r_1 N_1 + c_2 r_2 N_2)/\tilde{r}N \quad (26)$$

$$= \varphi_1 c_1 + \varphi_2 c_2 \quad (26')$$

On the basis of eq. 24, 25, and 26, the characteristic temperature T^* for the mixture is given by

$$1/T^* = (\varphi_1 p_1^*/T_1^* + \varphi_2 p_2^*/T_2^*)(\varphi_1 p_1^* + \varphi_2 p_2^* - \varphi_1\theta_2 X_{12})^{-1} \quad (27)$$

where the characteristic temperatures T_1^* and T_2^* are defined in accordance with eq. 10.

Adoption of the familiar Berthelot relationship[1,4]

$$\eta_{12} = (\eta_{11}\eta_{22})^{1/2} \quad (28)$$

for homopolar species whose interactions are dominated by the intermolecular dispersion energy leads to

$$\Delta\eta = (\eta_{11}{}^{1/2} - \eta_{22}{}^{1/2})^2 \quad (29)$$

$$X_{12} = p_1^*[1 - (s_1/s_2)^{1/2}(p_2^*/p_1^*)^{1/2}]^2 \quad (30)$$

$$p^* = [(\varphi_1\theta_1 p_1^*)^{1/2} + (\varphi_2\theta_2 p_2^*)^{1/2}]^2 \quad (31)$$

The intermolecular energy is given in terms of p^* by eq. 24. It may be expressed alternatively (see eq. 20') by

$$-E_0/\tilde{r}N = (s/2v)(\theta_1\eta_{11}{}^{1/2} + \theta_2\eta_{22}{}^{1/2})^2 \quad (32)$$

Equations 28 and 32 will not be incorporated in the subsequent development. Hence, the relationships which follow are not restricted to systems for which eq. 28 is applicable.

Enthalpy of Mixing. Ignoring the difference between the energy and enthalpy of a condensed system at low pressure, we have for the enthalpy of mixing (*i.e.*, the "excess" enthalpy)

$$\Delta H_M = E_0(\text{mixture}) - E_0(1) - E_0(2)$$
$$= \tilde{r}Nv^*[\varphi_1 p_1^*/\bar{v}_1 + \varphi_2 p_2^*/\bar{v}_2 - p^*/\bar{v}] \quad (33)$$

which is equivalent in form to the corresponding expression derived for mixtures of *n*-alkanes.[13] Equations given above allow this result to be expressed in the

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(22) It will be observed that $X_{21} \neq X_{12}$ according to this definition.

alternative forms

$$\Delta H_{\text{M}} = \tilde{r}Nv^*[\varphi_1 p_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + \varphi_2 p_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + (\varphi_1\theta_2/\tilde{v})X_{12}] \quad (34)$$

$$= N_1 p_1^* v_1^*(1/\tilde{v}_1 - 1/\tilde{v}) + N_2 p_2^* v_2^*(1/\tilde{v}_2 - 1/\tilde{v}) + (N_1 v_1^*\theta_2/\tilde{v})X_{12} \quad (34')$$

The latter rendition is preferred for mixtures of molecules comparable in size.

The last term in each of these equations for the mixing enthalpy represents the contributions from contact interactions attributable to a difference between 1,2 pairs and the mean of 1,1 and 2,2 contact pairs. It is the only term normally considered. We designate this term the *contact interaction term*. The terms preceding it in the mixing enthalpy expressions will be referred to as the *equation of state terms*. Their contribution depends on the reduced volume of the solution compared to those of the pure components. It may be quite large, sometimes dominating the contact interaction term.

The equation of state terms may, if desired, be rearranged into two terms, one of which is proportional to the volume change on mixing, i.e., to $\Delta\tilde{v}_{\text{M}} \equiv \tilde{v}^{\text{E}}$, the "excess" reduced volume.[13] The other term depends only on the difference between $\tilde{v}_1$ and $\tilde{v}_2$, being zero for $\tilde{v}_1 = \tilde{v}_2$; this term is independent of $\tilde{v}^{\text{E}}$. It is important to observe that the equation of state terms do not vanish for $\tilde{v}^{\text{E}} = 0$, provided of course that $\tilde{v}_1 \neq \tilde{v}_2$.

The Residual Free Energy and Entropy. The configuration partition function, eq. 5 (or in reduced form, eq. 7), is directly applicable to mixtures, subject merely to replacement of r by $\tilde{r}$, and to use of the mean values of s and c as prescribed by eq. 19 and 26. The reduced equation of state (8) is applicable without revision.

According to eq. 5 for the partition function and eq. 34 for ΔH_{M}, the free energy of mixing comprises a combinatory term $\Delta G_{\text{comb}} = -T\Delta S_{\text{comb}} = -kT \ln Z_{\text{comb}}$, a contact interaction term, and equation of state terms. Contributions of the equation of state and contact interaction terms are the ones of present concern. If the molecules of the two components are of comparable size and shape, then ΔG_{comb} should be given appropriately by the ideal mixing law, and the remaining terms may be identified with the excess free energy G^{E}. Inasmuch as the present treatment is not intended to be so restricted, we require a quantity analogous to G^{E}, but so defined as to represent the sum of the contact and equation of state terms without limitation on the nature of the combinatorial expression which may be appropriate for ΔS_{comb} and, hence, for ΔG_{comb}.

We therefore define the *residual free energy* G^{R} as[23]

$$G^{\text{R}} = \Delta G_{\text{M}} - \Delta G_{\text{comb}} \quad (35)$$

Obviously, G^{R} is identical with G^{E} if ΔG_{comb} can be represented by the ideal mixing law. If, however, the component molecules differ in size, at least one of

(23) Rowlinson[4] has applied "residual" in another sense. We are constrained to commit this expropriation of a term previously used for another purpose in consequence of the seeming exhaustion of the bountiful resources of the English language by the terminology of solution theory.

them being a chain molecule, then ΔS_{comb} may be expressed by polymer solution theory, i.e.

$$\Delta G_{\text{comb}} = -T\Delta S_{\text{comb}} = RT(N_1 \ln \varphi_1 + N_2 \ln \varphi_2) \quad (36)$$

The definition of G^{R} requires no revision in these circumstances. Other *residual* thermodynamic functions can be similarly defined. The residual free energy for binary mixtures is given according to eq. 7 by

$$G^{\text{R}} = 3\tilde{r}Nv^*\{\varphi_1 p_1^*\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + \varphi_2 p_2^*\tilde{T}_2 \ln [(\tilde{v}_2^{1/3} - 1)/(\tilde{v}^{1/3} - 1)]\} + \Delta H_{\text{M}} \quad (37)$$

Here, and in the equations which follow, the reduced temperatures $\tilde{T}_1$ and $\tilde{T}_2$ could be expressed in terms of the respective reduced volumes $\tilde{v}_1$ and $\tilde{v}_2$ according to eq. 13. The number of variables appearing in the equations would be diminished by these substitutions but at the expense of more lengthy expressions.

The residual entropy S^{R} is implicit in the term in braces in eq. 37. It may be written alternatively as

$$S^{\text{R}} = -3(N_1 p_1^* v_1^*\tilde{T}_1/T) \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] - 3(N_2 p_2^* v_2^*\tilde{T}_2/T) \ln [(\tilde{v}_2^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] \quad (38)$$

According to these equations, the residual entropy will not vanish, in general, when the volume change on mixing is reduced to zero, i.e., for $\tilde{v} = \varphi_1\tilde{v}_1 + \varphi_2\tilde{v}_2$. This assertion is at variance with the concept of a regular solution[1,2] as one whose entropy of mixing is ideal when its volume corresponds to the additive volumes of the components. The contribution of equation of state terms to the entropy depends on the reduced volume $\tilde{v}$ of the solution, but it does not vanish in general for $\Delta\tilde{v}_{\text{M}} = \tilde{v} - (\varphi_1\tilde{v}_1 + \varphi_2\tilde{v}_2) = 0$. As may be shown by numerical calculations, the magnitude of S^{R} may be fairly large.

The Chemical Potential and Related Partial Molar Quantities. The chemical potential of component 1 is given by $(\mu_1 - \mu_1^0)/RT = (\partial\Delta G_{\text{M}}/\partial N_1)_{T,N_2,\tilde{v}}$ apart from a trivial, pressure-dependent term from the companion partial derivative of ΔG_{M} with respect to $\tilde{v}$. By differentiation of eq. 37 followed by substitution from the equation of state (13) as applied both to the mixture and to the pure components

$$(\mu_1 - \mu_1^0)^{\text{R}} = p_1^* v_1^*\{3\tilde{T}_1 \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] + (\tilde{v}_1^{-1} - \tilde{v}^{-1})\} + (v_1^* X_{12}/\tilde{v})\theta_2^2 \quad (39)$$

Equation 39 is equivalent in form to the expression for the chemical potential in n-alkane mixtures,[13] apart from the replacement of the segment fraction φ_2 by the site fraction θ_2 in the last term.

The partial molar enthalpy of dilution is

$$\bar{H}_1^{\text{R}} = \bar{H}_1 - H^0 = p_1^* v_1^*[(\tilde{v}_1^{-1} - \tilde{v}^{-1}) + (\alpha T/\tilde{v})(\tilde{T}_1 - \tilde{T})/\tilde{T}] + (v_1^* X_{12}/\tilde{v})(1 + \alpha T)\theta_2^2 \quad (40)$$

where $\tilde{T} = T/T^*$, the characteristic temperature T^* for the mixture being defined by eq. 27. The thermal expansion coefficient α appearing in this equation and those which follow is given according to the equation of state (13) by

$$\alpha T = 3(\tilde{v}^{1/3} - 1)/[1 - 3(\tilde{v}^{1/3} - 1)] \quad (41)$$

The partial molar residual entropy is

$$\bar{s}_1^{\text{R}} = -p_1^* v_1^*\{(3\tilde{T}_1/T) \ln [(\tilde{v}_1^{1/3} - 1)/(\tilde{v}^{1/3} - 1)] - (\alpha/\tilde{v})(\tilde{T}_1 - \tilde{T})/\tilde{T}\} + \alpha(v_1^* X_{12}/\tilde{v})\theta_2^2 \quad (42)$$

Series expansion of the residual chemical potential leads to

$$(\mu_1 - \mu_1{}^0)^R = (A^2\alpha_1 T/2 + Y_{12})(p_1^*v_1^*/\bar{v}_1)\varphi_2{}^2 +$$

$$\{2Y_{12}(1 - s_2/s_1) + [2Y_{12} + (1 - p_2^*T_1^*/p_1^*T_2^*)A] \times$$

$$(A\alpha_1 T) - (6\alpha_1 T + 4\alpha_1{}^2 T^2 + 4\alpha_1{}^3 T^3)(A^3/9)\} \times$$

$$(p_1^*v_1^*/\bar{v}_1)\varphi_2{}^3 + \ldots \quad (43)$$

where

$$A = (1 - T_1^*/T_2^*)(p_2^*/p_1^*) - (s_2/s_1)(X_{12}/p_1^*) \quad (44)$$

$$Y_{12} = (s_2/s_1)^2(X_{12}/p_1^*) \quad (45)$$

α_1 is the thermal expansion coefficient of pure component 1 (see eq. 41). If $s_1 = s_2$, the coefficients simplify in eq. 43–45.

Series expansions for the partial molar enthalpy and entropy may be obtained from eq. 43 by differentiation.

Concluding Remarks

Adaptation of the reduced partition function expressed by eq. 7 to mixtures and adoption of eq. 20 for the intermolecular energy on the assumption of random mixing underlies the theory developed above.

The expressions derived for the various residual (or excess) properties of a binary mixture involve a single parameter, X_{12}, beyond those furnished by the properties of the two pure components. The thermodynamic properties (e.g., H, V, and S) are thus related explicitly to one another in terms of this parameter characterizing the given mixture. Treatment of mixtures of small, nonpolar molecules on this basis is demonstrated in the following paper.[14] Application to polymer solutions will be presented in a future communication.

The Thermodynamic Properties of Mixtures of Small, Nonpolar Molecules

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The excess enthalpies, volumes, and entropies of 23 equimolar binary liquid mixtures for which necessary data are available in the literature are interpreted according to the relationships presented in the preceding paper. Most of the mixtures comprise pairs of small globular molecules from the group c-C_6H_{12}, C_6H_6, $C(CH_3)_4$, CCl_4, $SiCl_4$, $TiCl_4$, and $SnCl_4$ or from the condensed gases CH_4, Ar, O_2, and N_2. Also included are mixtures of C_6H_6 and of c-C_6H_{12} with n-hexane and n-heptane, the benzene–diphenyl system, and two hydrocarbon–fluorocarbon mixtures. Previously unaccounted equation of state terms, which depend on properties of the pure components, make important contributions to each of the excess quantities. Through use of pair interaction parameters chosen to achieve agreement with the observed excess enthalpies, excess volumes are calculated which agree in nearly all cases with those observed within limits set by experimental errors. Although excess entropies calculated on the same basis tend to be somewhat lower than those observed, the agreement is favorable for most systems. Exceptions involve benzene as one component or cyclohexane in admixture with n-alkanes. Because account was taken of equation of state contributions, the present interaction parameters differ from those deduced from experimental results by previous procedures. Departures from the Berthelot geometric mean rule are discussed.

Introduction

In this paper we present an analysis of the experimental excess thermodynamic functions V^E, H^E, and S^E for binary liquid mixtures of nonpolar molecules.

The systems considered comprise pairs of molecules which (i) are small rather than polymeric, (ii) do not differ greatly in size, and (iii) in general are approximately spherical. The analysis is carried out on the basis of the relationships formulated in the preceding paper[1] and, hence, serves to put to test the theory there set forth.

A preliminary examination of experimental data for several representative systems in the category specified above was presented in a recent communication.[2] The results seemed to warrant an exhaustive investigation of mixtures of globular, nonpolar molecules. A wealth of experimental material is at hand for such systems,[3] and we have accordingly undertaken to include in the present report an account of all of those for which the necessary data are available. Deviations from ideality or from regularity are generally small for such systems, and this fact places greater demands on experimental accuracy and at the same time provides, in some respects, a more stringent test of theory.

Treatment of excess properties according to the theoretical scheme set forth in the preceding paper[1] and elsewhere[4,5] depends first of all on reliable equation of state parameters for the pure liquids. These comprise the molar volume v, the thermal expansion coefficient α, and the isothermal compressibility κ, or,

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