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A Molecular Theory of the Activity Coefficients and Their Reference Fugacities at the Supercritical State

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We take advantage of the recent advances in statistical mechanics on mixtures to examine a century-old problem in solution thermodynamics, specifically for the popular activity coefficient model, with regard to the absence of a standard state for the noncondensable gases in the mixture. This defect is traced back to the excess Gibbs free energy formalism where insistence on a pure liquid-state reference fluid is incorporated. By examining the molecularly derived counterparts, we propose a new division of the component chemical potential along the line of the molecular theory. A new definition of a reference fugacity and that of a molecular-inspired activity coefficients are formulated to cure this defect. We employ the Ornstein–Zernike equations to actually evaluate the molecular activity coefficients for a mixture of methane and *n*-pentane. The system temperature is 444 K. Thus, methane is the supercritical component and does not fit into the classical activity coefficient model. We demonstrate that the molecular activity coefficients of methane and *n*-pentane can be evaluated and do not suffer nonexistence. Furthermore, these values are used to determine the dew point and bubble point of the mixture. The results compare favorably with the experimental data of Sage and Lacey.

1. Introduction

Statistical mechanics has developed vigorously in the last half century and has impacted on all aspects of fluid properties: homogeneous and inhomogeneous, interfacial and bulk, small-molecule and polymer, chemical and biological, and polar and electrolyte solution properties. The conventional solution thermodynamics and study of phase equilibria of mixtures have been built on the pioneering work of Lewis and Randall¹ and other luminaries. In the last few decades, two classical approaches have emerged to gain widespread currency: (i) the equation of state approach (or abbreviated the ϕ - ϕ approach, ϕ being the fugacity coefficient) and (ii) the activity coefficient plus equation of state approach (the γ - ϕ approach). Both approaches have their merits and demerits. The ϕ - ϕ approach has the advantage of applicability at high pressures for compressible fluids but is plagued with uncertainties in the mixing rules. The γ - ϕ approach achieved great accuracy for liquid mixtures but suffers from the drawback of the nonexistence of the activity coefficients for light noncondensable gases (e.g., hydrogen, nitrogen, methane). This comes about, as is well-known, from the definition of the activity coefficient, which must depend on a *pure liquid state* reference fugacity. This pure liquid state does not exist at high system temperatures for the supercritical components in the mixture. We refer to this as the *referential nonexistence problem* (or simply the reference problem). Many noncondensable gases are important in industrial processes. In this work, we intend to examine what insights we might gain from recent statistical mechanical developments to treat this malaise. We propose, on the basis of the molecular theory of liquids, a parallel development by choosing a new reference fugacity and defining a new activity coefficient that is free from the referential nonexistence. It is a first step in an attempt to align this branch of solution thermodynamics with recent statistical mechanical advances.

Activity coefficient models, such as van Laar,² Wilson,³ NRTL,⁴ and UNIQUAC⁵ models, have the advantage of

possessing mixing rules for liquid mixtures that yield reasonably accurate answers where all of the components are genuine liquids. Values of these activity coefficients for many industrial mixtures have been extensively investigated, collected, and reported in handbooks and data compilations (e.g., DECHEMA⁶). Their theoretical basis is the excess Gibbs free energy, which essentially expresses the chemical potentials in mixtures as excesses over the pure-state chemical potentials. It is nice to base our knowledge on the *pure-state chemical potentials* at first because it would be very close to Rome when you had already reached Ostia. However, noncondensable gas, such as methane, can be supercritical at system temperature, say, $T = 444$ K (for methane, $T_c = 190.6$ K). Pure methane exists in the gas state. Gaseous methane can nonetheless dissolve in liquid *n*-pentane at this temperature and stay in the liquid phase. The activity coefficient γ_1 of methane cannot be defined because the liquid-state reference fugacity f_1^0 (i.e., the fugacity of pure *i* at T , P , and as a liquid) of methane does not exist; that in turn is because the liquid state of methane does not exist at 444 K.

$$\gamma_1(x_1, x_5; P, T, \text{liquid} - \text{state}) \equiv \frac{f_1(x_1, x_5; P, T, \text{liquid} - \text{state})}{xf_1^0(x_1 = 1, x_5 = 0; P, T, \text{pure} - \text{liquid} - \text{state})} \quad (1.1)$$

In literature, alternative choices of references were made: for example, using the asymmetric convention² (Henry's constants), and a number of other formulations (see, e.g., the five *F*'s, the *Five Famous Fugacity Formulas*⁷). On the other hand, in statistical mechanics, the chemical potentials of components in a mixture have been regularly computed, either by theory⁸ or by simulation.⁹ There is no problem regarding the referential nonexistence. When the state condition does not support the existence of a given mixture or a pure liquid there, either the integral equation diverges or the simulation fails to stabilize and phase-separate. If the state exists, there is an answer. No hypothetical value is required. We can take a clue here and examine if we can devise means based on the molecular formulation to obviate the reference problem: either (i) by finding new avenues of approach, revising the old, or (ii) by

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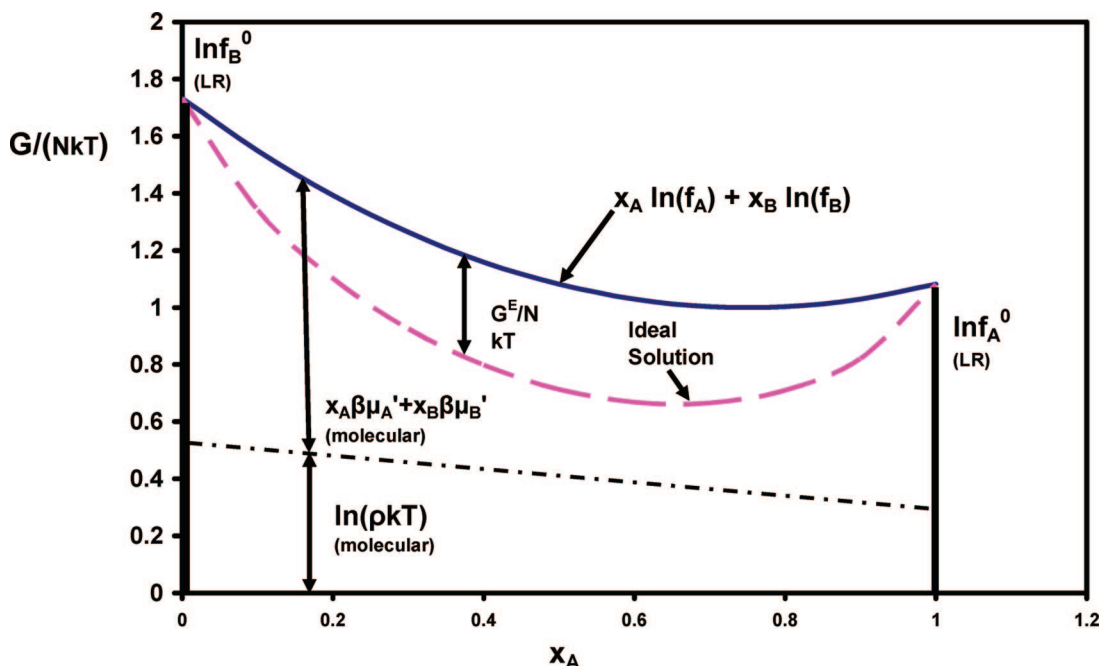


Figure 1. Total Gibbs free energy of the mixture. Comparison of the reference fugacities in the Lewis–Randall (LR) approach and in the molecular approach. At $x_A = 1$, we have pure A. The value of $\beta G/N$ is the pure-state fugacity $\ln f_A^0$ of A, whereas $x_B = 1$, $\beta G/N = \ln f_B^0$. The molecular approach reference fugacity is $\ln(p_kT)$. Note that all of the quantities exist here because even when A is supercritical it also has a fugacity f_A^0 (as a gas and not a liquid). Fugacities always exist (well defined), just like chemical potentials are well defined. The referential nonexistence happens when we begin to deal with activities a_A or activity coefficients γ_A as these are referred to a standard fugacity f_A^0 in a liquid state!

Table 1. Lennard–Jones Parameters for Methane (1) and Pentane-Type (Pentanoid 5) Species Used in This Work

	methane (1)	pentane (5) spherulized
ϵ/k (K)	152	350
σ (Å)	3.74	5.282

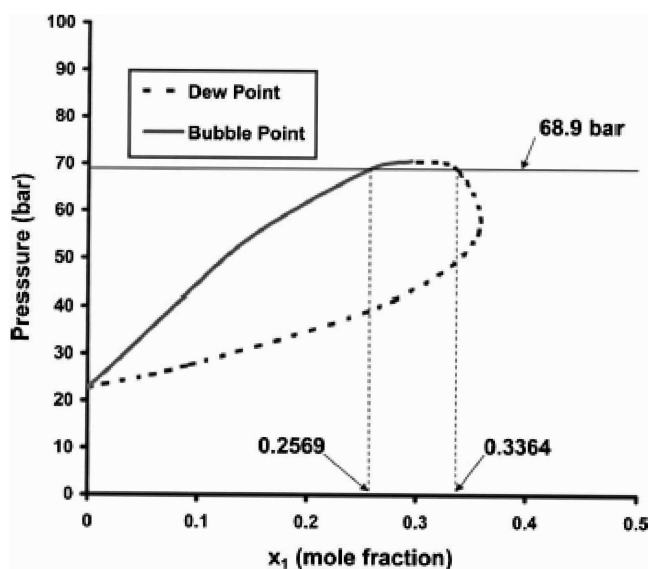


Figure 2. Experimental pressure- x - y diagram for the methane- n -pentane mixture at 444.26 K.

proposing a new formulation of the activity coefficient that is free of defects. In doing so, we found that the *excess Gibbs free energy* is the source of the problem. We propose a new choice for the reference fugacity and thus a new molecular-base activity coefficient that is in conformity with the formulas of the chemical potentials in the molecular theory.

The article is organized thusly. We review the excess Gibbs free energy in section 2. In section 3, we present the molecular-

Table 2. Parameters α_{jk} , ϕ_{jk} , and ζ_{jk} in the Bridge Function (δ_{15} Is the Binary Interaction Parameter for the Cross Energy Interaction in the Lennard–Jones Potential for the 1–5 Pair)^a

χ_1	ρ	δ_{15}	α_{11}	ϕ_{11}	ζ_{11}	α_{15}	ϕ_{15}	ζ_{15}	α_{55}	ϕ_{55}	ζ_{55}
0.1	0.199	-0.090	1.28	0.83	0.98	1.22	0.69	1.02	1.28	1.02	1.09
0.2	0.177	-0.012	1.36	0.81	0.98	1.41	0.75	0.95	1.54	1.03	0.92
0.25	0.151	-0.020	1.56	0.83	0.95	1.66	0.93	0.81	1.71	1.03	0.82
0.34	0.115	0.025	1.65	0.90	0.88	0.83	1.16	0.68	2.13	1.08	0.60
0.4	0.099	0.010	2.26	0.89	0.70	1.00	1.29	0.63	1.00	1.14	0.56
0.5	0.082	0.005	2.40	1.02	0.60	1.00	1.41	0.58	1.00	1.22	0.55
0.6	0.072	0.004	1.98	1.08	0.50	1.00	1.44	0.50	1.00	1.29	0.50
0.7	0.067	0.001	1.70	1.24	0.40	1.00	1.45	0.40	1.00	1.32	0.40
0.8	0.063	0.000	1.42	1.31	0.30	1.00	1.43	0.30	1.00	1.18	0.30
0.9	0.059	0.000	1.30	1.36	0.20	1.00	1.39	0.20	1.00	1.08	0.20

^a The pair correlations $g_{ij}(r) = h_{ij}(r) + 1$ obtained are shown in Figure 3. The data are compared with the molecular dynamics (MD) results. Good agreement is achieved between the integral equation (IE) results and MD results. The correlation functions are used to calculate the chemical potentials from the direct formula (eq 3.5). The results are given in Table 3. A plot is generated for these molecular configurational chemical potentials $\beta\mu_1'$ and $\beta\mu_5'$ (Figure 4).

Table 3. Configurational Chemical Potentials (Eq 3.5) Calculated from the Ornstein–Zernike Equations

x_1	$\beta\mu_1' (= \ln \gamma_1)$	$\beta\mu_5' (= \ln \gamma_5)$
0.1	-0.298	-2.17
0.2	-0.351	-2.02
0.4	-0.269	-1.18
0.5	-0.208	-0.919
0.6	-0.155	-0.733
0.7	-0.11	-0.583
0.8	-0.0777	-0.464
0.9	-0.0513	-0.368
1.0		-0.303

based activity coefficients. We capitalize on the direct chemical potential formula of molecular theory for this task. Next, we illustrate the connection between the new division and conventional activity coefficient by working on a van der Waals mixture (section 4). In section 5, we solve the Ornstein–Zernike

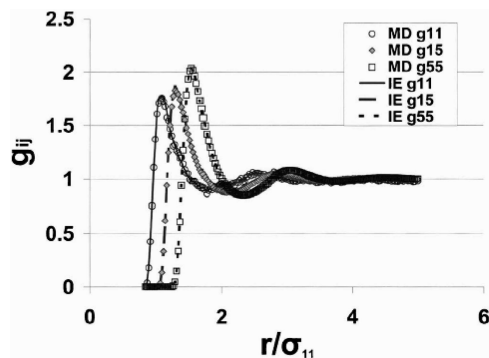


Figure 3. Pair correlation functions of the methane-*n*-pentane mixture. Lines are from the OZ integral equations (IE). Points are from the molecular dynamics (MD). Condition is at $x_1 = 0.1$, $T = 444.26$ K, and $P = 6.89$ MPa. We see that there is close agreement between the IE and the MD results.

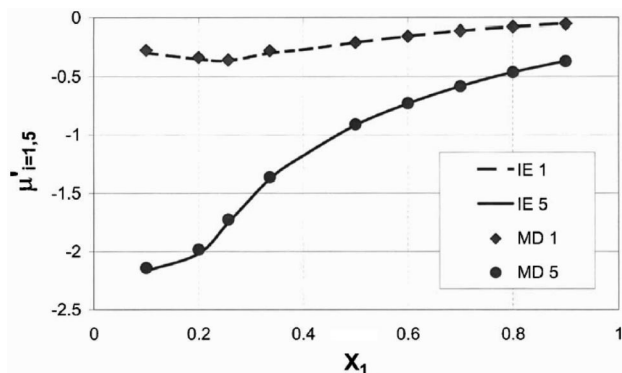


Figure 4. Configurational chemical potentials obtained from the direct formula eq 3.5. The molecular dynamics (MD) results confirm the accuracy of the OZ integral equation (IE) calculations.

equations to obtain the molecular distribution functions that figure in the new molecular activity coefficients. We test the formulation on a hydrocarbon mixture of methane and *n*-pentane, where methane is the supercritical component. In section 6, we draw the conclusions.

2. Review of the Excess Gibbs Free Energy

To bring into relief the essence of the new formulation, we recapitulate briefly the conventional excess Gibbs free energy approach. Without loss of generality, we consider a binary mixture of A and B (for example, A = methane, and B = *n*-pentane). We shall introduce, as usual, five types of Gibbs free energies: (i) the total Gibbs free energy G_m of n moles of mixture; (ii) the pure-state Gibbs free energies G_A^0 and G_B^0 of the components A and B (superscript 0 indicates pure state); (iii) the Gibbs free energy of mixing, $\Delta_{\text{mix}}G_m$; (iv) the ideal solution (*ids*) Gibbs free energy of mixing $\Delta_{\text{mix}}G_m^{\text{ids}}$; and (v) the excess Gibbs free energy G^E .

We prepare this mixture by mixing their pure constituents: n_A moles of A and n_B moles of B at constant temperature T , constant pressure P , and say, in the liquid state (namely, pure liquid A, pure liquid B, and the resulting liquid mixture). The total $n = n_A + n_B$ moles of the mixture will have a Gibbs free energy G_m (upon introducing the partial molar Gibbs free energies \bar{G}_A and \bar{G}_B)

$$G_m = n_A \bar{G}_A + n_B \bar{G}_B = n_A \mu_A + n_B \mu_B, (T, P, \text{liq.}) \quad (2.1)$$

Pure liquid A has a Gibbs free energy $n_A \bar{G}_A^0$ and pure liquid B has Gibbs free energy of $n_B \bar{G}_B^0$ (underscore means the

quantity is specific, i.e., in amount per mole), the Gibbs free energy of *mixing* is defined as the Gibbs free energy G_m of the mixture *after mixing* minus the sum of the pure-state Gibbs free energies *before mixing*:

$$\begin{aligned} \Delta_{\text{mix}}G_m &\equiv (n_A \bar{G}_A + n_B \bar{G}_B) - (n_A \bar{G}_A^0 + n_B \bar{G}_B^0) = n_A(\mu_A - \mu_A^0) + \\ &\quad n_B(\mu_B - \mu_B^0) = n_A RT(\ln f_A - \ln f_A^0) + n_B RT(\ln f_B - \\ &\quad \ln f_B^0) = RT[n_A \ln(x_A \gamma_A) + n_B \ln(x_B \gamma_B)] \quad (2.2) \end{aligned}$$

where we have introduced the activity coefficients as conventionally defined. We shall call this convention the Lewis–Randall (LR) form:

$$\gamma_i^{\text{LR}} \equiv \frac{f_i}{x_i f_i^0}(T, P, \text{liq.}) \quad (2.3)$$

Note that f_i^0 is the liquid-state reference fugacity of pure component i . This is the source of the reference-nonexistence problem.

For ideal solutions, the Gibbs free energy of mixing is purely entropic (this is the definition for ideal solution).

$$\Delta_{\text{mix}}G_m^{\text{ids}} \equiv n_A RT(\ln x_A) + n_B RT(\ln x_B) \quad (2.4)$$

The excess Gibbs free energy G^E is defined as the difference between the real mixture $\Delta_{\text{mix}}G_m$ and the ideal solution $\Delta_{\text{mix}}G_m^{\text{ids}}$.

$$G^E \equiv \Delta_{\text{mix}}G_m - \Delta_{\text{mix}}G_m^{\text{ids}} = n_A RT(\ln \gamma_A) + n_B RT(\ln \gamma_B), \quad (T, P, \text{liq.}) \quad (2.5)$$

where we have enclosed in angular brackets the quantity γ_A , indicating that it will cause the referential problem. All of the variables here are under what we call the LR convention. In classical solution thermodynamics, one would postulate an excess Gibbs free energy model (e.g., Wilson, NRTL, UNIQUAC, etc.). Then, one could derive the activity coefficients by differentiating (eq 2.5). However, it is well known that if the reference fugacity f_A^0 is not defined, γ_A is not defined. Then, we cannot proceed with the activity coefficient model.

3. The Molecular-Based Activity Coefficients

In statistical mechanics, a parallel development as in section 2 can be made. To contrast, we shall reinterpret all of the above quantities in terms of molecular formulas.

Let the Hamiltonian H_N of an N -body system be the sum of kinetic energies E_{kin} (translational, vibrational, and rotational kinetic energies) and the N -body potential energy V_N

$$H_N(p^N, r^N) \equiv E_{\text{kin}}(p^N) + V_N(r^N) \quad (3.1)$$

The partition function Z_N is then¹⁰

$$Z_N \equiv \frac{q_r^N q_v^N}{N! \Lambda^{3N}} \int dr^N e^{-\beta V_N(r^N)} \equiv \left(\frac{q_r^N q_v^N}{N! \Lambda^{3N}} \right) Q_N = \left(\frac{1}{N! q_{\text{trv}}^N} \right) Q_N \quad (3.2)$$

where Λ (the de Broglie thermal wavelength), q_r , and q_v are the factors derived from the translational, rotational, and vibrational kinetical energies, respectively. Note that the translational kinetic energy contributes a factor Λ^3 that has units of L^3 (length cubed). Q_N is the configurational integral that accounts for the contribution from the potential energy V_N of the N -body system. Q_N has units of L^{3N} (volume to the N th power). q_{trv} is a shorthand for the product of all three E_{kin} contributions. These formulas can also be written for a mixture

(see, e.g., Lee¹⁰). In 1992, a direct chemical potential formula was proposed.¹¹ The chemical potential of component i in a mixture can be directly related to the molecular correlation functions in the liquid-state theory as

$$\beta\mu_i = \ln\left(\frac{q_{trv,i}}{kT}(\rho kT)\right) + \ln x_i + \sum_{j=1}^n \left[\rho_j \int dr ((\ln y_{ji} - h_{ji} - (h_{ji}\gamma_{ji})/2 + \gamma_{ji}B_{ji} - S_{ji})) \right] \quad (3.3)$$

where $y_{ij}(r)$, $h_i(r)_j$, $\gamma_i(r)_j$, $B_i(r)_j$, and $S_{ij}(r)$ are molecular correlation functions (the cavity function, total correlation, indirect correlation, bridge function, and star function, respectively). This chemical potential is well defined at the given state, say, at T , P , and composition, in the liquid or gas states. (Note that to contrast with classical formulas, we split an ideal pressure factor ρkT out in the first logarithmic term.) If we retrace the developments of the excess Gibbs free energy, we obtain a parallel molecular counterpart (details omitted)

$$\beta G^E = n_A \left[\ln\left(\frac{\rho}{\rho_A^0}\right) + \beta\mu_A' - \beta\mu_A^{0'} \right] + n_B \left[\ln\left(\frac{\rho}{\rho_B^0}\right) + \beta\mu_B' - \beta\mu_B^{0'} \right] \quad (3.4)$$

where the superscripts 0 denote the pure-state properties and primes denote the configurational properties. The configurational part of the chemical potential $\beta\mu_i'$ (i.e., chemical potential after excluding the kinetic contributions) is known¹¹ to be

$$\beta\mu_i' = \sum_{j=1}^n \left[\rho_j \int dr ((\ln y_{ji} - h_{ji} - (h_{ji}\gamma_{ji})/2 + \gamma_{ji}B_{ji} - S_{ji})) \right] \quad (3.5)$$

Upon matching term by term between eqs 2.5 and 3.4, we obtain an expression for the LR activity coefficient γ_i in terms of molecular quantities.

$$\ln \gamma_i^{\text{LR}} = \ln\left(\frac{\rho}{\rho_i^0}\right) + \beta\mu_i' - \beta\mu_i^{0'}, (\text{at } T^0, P^0, \text{liq.}) \quad (3.6)$$

This equation inherits the pure liquid-state chemical potentials $\beta\mu_i^0$, because the excess Gibbs free energy itself refers to the pure-state chemical potentials. Equation 3.6 is not free from the reference problem because of G^E . To rid eq 3.6 of $\beta\mu_i^0$ and thus free it from the analogy with G^E , we recommence instead with the chemical potential itself. Chemical potential is a well-defined quantity. It is well defined in solution thermodynamics without reference to any pure state. It is equally well defined in statistical mechanics and does not depend on any reference state. We equate the classical expression with the molecular expression,

$$\beta\mu_i = \underbrace{\beta\mu_i^* + \ln f_i = \beta\mu_i^* + \ln(x_i \gamma_i^{\text{LR}} f_i^0)}_{\text{Classical Expression}} = \underbrace{\ln\left(\frac{q_{trv,i}}{kT} \rho kT\right) + \ln(x_i) + \beta\mu_i'}_{\text{Molecular Expression}} \quad (3.7)$$

(Note: The asterisk * denotes the temperature-dependent ideal gas part). Upon eliminating similar factors

$$\ln \gamma_i^{\text{LR}} + \ln f_i^0 = \ln(\rho kT) + \beta\mu_i' = \ln(\rho kT) + \sum_{j=1}^n \left[\rho_j \int dr ((\ln y_{ji} - h_{ji} - (h_{ji}\gamma_{ji})/2 + \gamma_{ji}B_{ji} - S_{ji})) \right] \quad (3.8)$$

where we have identified through statistical mechanics the temperature-dependent ideal gas term as (this expression was not known from the classical approach alone because it requires

molecular inputs such as the moment of inertia and vibrational frequencies),

$$\beta\mu_i^* = \ln\left(\frac{q_{trv,i}}{kT}\right) \quad (3.9)$$

If we express the pure-state fugacity in terms of the fugacity coefficient ν_i^0 and apply the compressibility factor Z_M for the mixture, that is,

$$\nu_i^0 \equiv \frac{f_i^0}{P}, Z_M \equiv \frac{P}{\rho kT}, (\text{at } T, P, \text{liq.}) \quad (3.10)$$

The LR activity coefficient $\ln \gamma_i^{\text{LR}}$ can be shown in an alternative form

$$\ln \gamma_i^{\text{LR}} + \ln \nu_i^0 = -\ln Z_M + \beta\mu_i' = -\ln Z_M + \sum_{j=1}^n \left[\rho_j \int dr ((\ln y_{ji} - h_{ji} - (h_{ji}\gamma_{ji})/2 + \gamma_{ji}B_{ji} - S_{ji})) \right] \quad (3.11)$$

To summarize, we have obtained three molecular expressions for the classical solution quantities, eq 3.4 for the excess Gibbs free energy, and eqs 3.8 and 3.11 for the activity coefficients of the LR form. In all of the expressions, we see the persistence of the pure fluid reference quantities: ν_i^0 , f_i^0 , and $\beta\mu_i^0$ in the LR activity but not in the molecular expressions. At supercritical states, the pure LR quantities have no liquid roots. On the other hand, for the molecular expressions, all of the quantities are well defined in the mixture state. For example, the quantities ρ and Z_M in eqs 3.8 and 3.11 refer to the mixture density at T and P , with compositions x_A and x_B . Whether the mixture is a liquid or a gas, all of the quantities are accessible from measurements or evaluation.

New Definitions of Activity Coefficients and Reference Fugacities. Here is our proposal. Because the reference fugacity f_A^0 or in general f_A^{ref} in the definition of the activity coefficient (the superscript ref denotes a general reference state to be specified) is allowed to be defined arbitrarily, for the sake of convenience, or for any future use, there is no reason why we cannot choose a new reference fugacity for A that exists at the mixture condition. So we propose a *new reference fugacity* $f_i^{0,\text{molecular}}$ as

$$\ln f_i^{0,\text{molecular}} \equiv \ln(\rho kT), (\text{at } T, P, x_i) \quad (3.12)$$

Consequently, we define the new molecular-base activity coefficient as equal to the molecular expression for the configurational chemical potential $\beta\mu_i'$

$$\ln \gamma_i^{\text{molecular}} \equiv \sum_{j=1}^n \left[\rho_j \int dr ((\ln y_{ji} - h_{ji} - (h_{ji}\gamma_{ji})/2 + \gamma_{ji}B_{ji} - S_{ji})) \right] = \beta\mu_i', (\text{at } T, P, \text{liq.}) \quad (3.13)$$

Clearly, these definitions do not involve any pure liquid-state quantities. Let us examine in depth the basic difference between the LR definition and the new molecular definition: neither approach violates the chemical potential values. First, we recognize that it is a matter of repartition or repportioning of a physical quantity $\beta\mu_i$ into parts. In fact, given a chemical potential $\beta\mu_i$, eqs 3.12 and 3.13 are repartitions of the total chemical potential into two parts $\ln(\rho kT)$ and $\beta\mu_i'$ (Figure 1). (Whereas the LR separation is a different repartition, see eq 3.7). To illustrate this concept, let us use a simple example: *the sum of numbers*, observe $10 = 3 + 7$ but also $10 = 6 + 4$. Then, why do we favor one partition over the other? Answer: the new partition is fashioned along the lines of the molecular expressions. It is advantageous to have statistical mechanics

serving as a guide in our choices. We remark that the molecular approach is mirrored in the equation of state approach, where the fugacity is also evaluated separately with one ideal gas part and one residual part! (see, e.g., eq 3.53 in ref 2).

4. Conversion between the Molecular Activity Coefficients and Lewis–Randall Activity Coefficients. The relation between the two scales are given by eqs 3.8, 3.12, and 3.13.

$$\ln \gamma_i^{\text{LR}} + \ln f_i^0 = \ln \gamma_i^{\text{molecular}} + \ln(f_i^{0,\text{molecular}}) \text{ or } = \beta \mu_i' + \ln(\rho kT), (\text{at } T, P, \text{liq.}) \quad (4.1)$$

So long as both pure A and pure B are subcritical at the given system T , all terms in (4.1) are defined. (Note that mathematically the logarithm should have dimensionless arguments. The fugacity f_i^0 has the units of pressure. Our usage here is a compromise to historical practice in thermodynamic texts). To illustrate these connections, we examine a van der Waals gas mixture.

Example of a van der Waals Gas. We illustrate the new activity coefficients via a well-known and simple equation of state, the van der Waals (*vdW*) equation with the usual van der Waals one-fluid mixing rules: $b = \sum x_i x_j b_{ij}$ and $a = \sum x_i x_j a_{ij}$. It is well-known² that the LR activity coefficient in a van der Waals mixture has the form

$$\ln \gamma_i^{\text{LR}} = \frac{b_i}{v-b} - \frac{2(x_1 a_{11} + x_2 a_{12})}{vRT} - \ln\left(\frac{f_i^0(v-b)}{RT}\right) \quad (4.2)$$

On the other hand, for the molecular approach we calculate the total chemical potential of the van der Waals gas. We choose the reference fugacity as $\ln(\rho RT)$. Subtracting the two, we obtain the molecular activity coefficient

$$\ln \gamma_i^{\text{molecular}} = \frac{b_i}{v-b} - \frac{2(x_1 a_{11} + x_2 a_{12})}{vRT} - \ln\left(\frac{v-b}{v}\right) \quad (4.3)$$

Further subtracting eq 4.2 from eq 4.3, we obtain,

$$\ln \gamma_i^{\text{molecular}} - \ln \gamma_i^{\text{LR}} = \ln \frac{f_i^0}{\rho RT} \quad (4.4)$$

This is precisely the relation in eq 4.1.

5. Solution of the Ornstein–Zernike Integral Equations. In this section, we shall carry out an actual evaluation of the molecular activity coefficients, as defined above, for a hydrocarbon mixture of methane and *n*-pentane. To obtain the molecular correlation functions, we shall solve the Ornstein–Zernike (OZ) equations for mixtures.¹⁰ The methane molecular interaction is modeled by the Lennard–Jones (spherical) potential. *n*-Pentane is a chain molecule and has been modeled in literature by a number of potentials. For simplicity, we use the concept of effective pair potentials as discussed by Rowlinson,¹² Stillinger,¹³ and others by assuming an effective Lennard–Jones potential for the pentane interaction. We call it the pentanoid effective potential. At high enough temperatures, the fast rotational motion of *n*-pentane will make it pseudo-spherical. The potential parameters used are listed in Table 1.

The OZ equations for mixtures of methane (component 1) and *n*-pentane (component 5) are written as a convolution integral (see, e.g., Lee¹⁰)

$$h_{jk}(r) - C_{jk}(r) = \sum_i \rho_i \int d\vec{s} h_{ji}(|\vec{r} - \vec{s}|) C_{ik}(s) \quad (5.1)$$

where $j, k = 1$ or 5 ; $h_{jk}(r)$ is the total correlation between a pair of molecules of species j and k ; $C_{jk}(r)$ is the direct correlation; and ρ_i is the number density of the molecules of species j (i, j ,

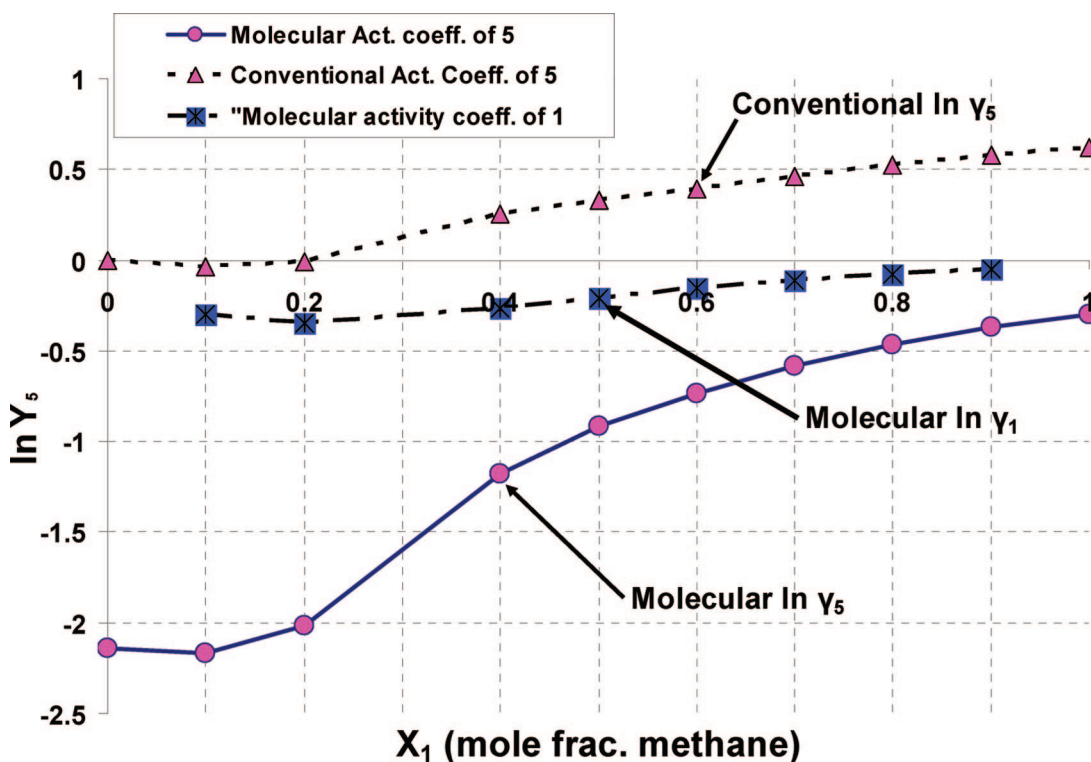


Figure 5. Comparison of the molecular activity coefficient for *n*-pentane (5) (circles) and the conventional Lewis–Randall (LR) activity coefficients (triangles) in the methane (1)–*n*-pentane (5) mixture at $T = 444.44$ K. The molecular activity coefficient for methane (squares) is also shown. The purpose of this graph is to exhibit the existence of the molecular activity coefficient of methane. γ_1^{mol} is well defined, whereas the LR convention activity γ_1' for methane does not exist.

k = labels of different species). The molecular pairs include the 11 pair, the 15 pair, and the 55 pair. For example, for the 15-pair, OZ appears as

$$\begin{aligned} (r) - C_{15}(r) = & \sum_i \rho_i \int d\vec{s} h_{1i}(|\vec{r} - \vec{s}|) C_{i5}(s) = \\ & \rho_1 \int d\vec{s} h_{11}(|\vec{r} - \vec{s}|) C_{15}(s) + \rho_5 \int d\vec{s} h_{15} \times \\ & (|\vec{r} - \vec{s}|) C_{55}(s) \quad (5.2) \end{aligned}$$

To solve for these equations, we need a closure relation, a second equation linking $h_{jk}(r)$ or its equivalents to $C_{jk}(r)$. We use the ZSEP closure¹⁴ that has been shown to work well for Lennard–Jones molecules.

$$B_{jk}(r) = -\frac{\zeta_{jk} \gamma_{jk}^*(r)^2}{2} \left[1 - \phi_{jk} + \frac{\phi_{jk}}{1 + \alpha_{jk} \gamma_{jk}^*(r)} \right] \quad (5.3)$$

where $B_{jk}(r)$ is the bridge function (bf), $\gamma_{jk}(r) = h_{jk}(r) - C_{jk}(r)$ is the indirect correlation function (icf), and $\gamma_{jk}^*(r)$ is the normalized¹⁵ icf. The parameters α_{jk} , ϕ_{jk} , and ζ_{jk} are to be determined by self-consistency conditions. For details of the solution, see Wilson 2005.⁸

The temperature of the system is 444.26 K and the pressure is 6.89 MPa. The mole fraction ranges from 0 to 1 ($x_A = 0.1, 0.2, 0.4, 0.5, 0.6, 0.7, 0.8$, and 0.9). According to the experimental data by Sage and Lacey (1959), there is detachment of the two-phase envelope from the methane-rich side of the P - x - y diagram (Figure 2) because methane is supercritical.

In the molecular formulation, the excess chemical potential $\beta\mu_i'$ can be calculated once the molecular correlation functions have been evaluated.

$$\beta\mu_i' \equiv \sum_{j=1}^n \left[p_j \int d\mathbf{r} (\ln \gamma_{ji} - h_{ji} - (h_{ji} \gamma_{ji})/2 + \gamma_{ji} B_{ji} - S_{ji}) \right] \quad (3.5)$$

This is the molecular activity coefficient

$$\ln \gamma_i^{\text{molecular}} \equiv \beta\mu_i', (\text{at } T, P, \text{liq.}) \quad (3.13)$$

Application to the Methane-*n*-Pentane Mixture System.

The OZ eqs (eq 5.1) were solved together with the closure (eq 5.3). The adjustable parameters α_{jk} , ϕ_{jk} , and ζ_{jk} in the bridge function were determined by using the thermodynamic consistency conditions (i) pressure consistency $P^v = P^c$, the virial pressure is equal to the compressibility pressure; (ii) the Gibbs–Duhem relation; and (iii) the zero-separation theorem.⁸ The values are listed in Table 2.

The pair correlations $g_{ij}(r) = h_{ij}(r) + 1$ obtained are shown in Figure 3. The data are compared with the molecular dynamics (MD) results. Good agreement is achieved between the integral equation (IE) results and MD results. The correlation functions are used to calculate the chemical potentials from the direct formula (eq 3.5). The results are given in Table 3. A plot is generated for these molecular configurational chemical potentials $\beta\mu_1'$ and $\beta\mu_5'$ (Figure 4).

Sage and Lacey¹⁶ have measured the vapor–liquid equilibrium data for the methane (1)-*n*-pentane (5) system at $T = 444.26$ K and $P = 68.9$ bar. The molecular activity coefficients are obtained from eqs 3.5 and 3.13. They are depicted in Figure 5. In it, we also show the conventional (LR) activity coefficient $\ln \gamma_5^{\text{LR}}$ of *n*-pentane, because *n*-pentane ($T_c = 469.7$ K) can be a pure liquid at system temperature. Methane does not have a

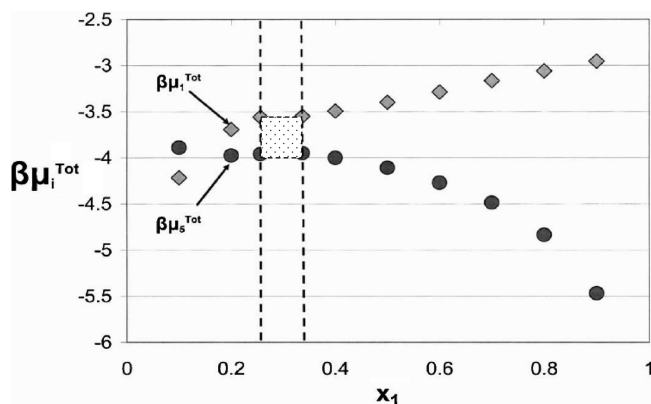


Figure 6. Total chemical potentials of methane and *n*-pentane as determined by the new formulation. The two vertical lines indicate the locations of the bubble and dew points for this mixture. $T = 444.26$ K and $P = 68.9$ bar. The dew-bubble points were determined by a floating-rectangle method, namely adjusting a variable-area rectangle with all four vertices anchored on the two branches (i.e., the $\beta\mu_1$ - x_1 curve and the $\beta\mu_5$ - x_1 curve) such that the rectangle fits without tilting (equal chemical potentials).

pure liquid state; we cannot calculate the conventional activity coefficient, but we can calculate the molecular $\ln \gamma_i^{\text{molecular}}$.

We used the data of chemical potentials from Table 3 to determine the vapor–liquid dew and bubble points for this state. The results are shown in Figure 6. Note that the total chemical potentials are the sum of the configurational chemical potentials and the ideal-gas chemical potentials

$$\beta\mu_i^{\text{Tot}} = \beta\mu_i' + \ln(x_i p k T) \quad (5.4)$$

Comparison with experimental data shows that we obtain very close agreement for the dew-bubble point. (Table 4)

6. Conclusions

In this work, we propose a new division of the chemical potential into a reference fugacity and a molecular activity coefficient, conforming to the molecular formula for the chemical potential. This new formulation does not depend on the pure-state reference fugacity, therefore it is free of the perennial referential nonexistence problem. Although we lose the convenience of the excess Gibbs free energy, we gain by harmonizing the new expressions with molecular theory. We demonstrated the operation of the new formulas by carrying out calculations via the OZ equations for the correlation functions of a methane-*n*-pentane mixture. Accurate results are obtained for the dew-bubble point calculations. We anticipate that future developments will allow us to incorporate a variety of new and existing results in statistical mechanics of mixtures into many areas of solution thermodynamics: from the hard sphere mixtures to polar fluids and from the polymer solutions to electrolyte solutions. Because supercritical gases, such as hydrogen, helium, hydrogen fluoride, methane, and nitrogen, are now treated on equal footing with subcritical components, the implication for industrially important mixtures will be far-reaching in vapor–liquid equilibrium calculations and in distillation, absorption, and extraction operations.

We offer some further reflections on the new activity coefficients. Because the reference state is arbitrary in the classical definition of activities, our formulation is by no means unique. However, our goal is to render classical solution thermodynamics consistent with statistical mechanical formulations. We believe that this is being achieved. Second, one might be concerned of the calculation of the molecular distribution

Table 4. Comparison of the Dew and Bubble Points from the Integral Equation Calculations and the Experimental Data of Sage and Lacey

	calculated value	experimental data
bubble point, $x_1 =$	0.25	0.2569
dew point, $x_1 =$	0.34	0.3364

functions. Their use necessitates the solution of the OZ equations, a time-consuming task, and at present not tolerable in industrial practice. However, for many systems in statistical mechanics, analytical expressions exist. This is the case for the hard sphere mixtures.¹⁰ Perturbation theories can be used to obtain results for more realistic potentials. For electrolyte systems, the mean spherical model gives adequate analytical expressions for the free energy. Note that these molecular theories were derived from statistical mechanics. Their mixing rules are well founded. Third, the utility of any new formulation must be tested for many industrial solutions and systems of interest. The earlier activity models have achieved this, witnessing the thousands of liquid mixtures that have been correlated by the UNIFAC, NRTL, and Pitzer models. The present method is in its infancy. Much work and effort lie in the future to achieve viability.

Acknowledgment

We are delighted to benefit from discussions with Dr. Frank Ting-Horng Chung.

Literature Cited

- (1) Lewis, G. N.; Randall, M. *Thermodynamics*; McGraw-Hill: New York, 1923.
- (2) Prausnitz, J. M.; Lichtenthaler, R. N.; de Azevedo, E. G. *Molecular Thermodynamics of Fluid Phase Equilibria*, 3rd ed.; Prentice Hall: Upper Saddle River, N. J., 1999.

- (3) Wilson, G. M. Vapor-Liquid Equilibrium. XI. A New Expression for the Excess Free Energy of Mixing. *J. Am. Chem. Soc.* **1964**, 86, 127.
- (4) Renon, H.; Prausnitz, J. M. Local Compositions in Thermodynamic Excess Functions for Liquid Mixtures. *AIChE J.* **1968**, 14, 135.
- (5) Abrams, D.; Prausnitz, J. M. Statistical Thermodynamics of Liquid Mixtures: A new Expression for the Excess Gibbs Energy of Partly or Completely Miscible Systems. *AIChE J.* **1975**, 21, 116.
- (6) Sorenson, J. M.; Arlt, W. *Liquid-liquid Equilibrium Data Collection*, Chemistry Data Series; DECHEMA, 1980.
- (7) O'Connell, J. P.; Haile, J. M. *Thermodynamics. Fundamentals for Applications*; Cambridge UP: Cambridge, 2005.
- (8) See, e.g., Wilson, D. S.; Lee, L. L. Chemical Potentials and Phase Equilibria of Lennard-Jones Mixtures: A self-Consistent Integral Equation Approach. *J. Chem. Phys.* **2005**, 123, 044512.
- (9) Panagiotopoulos, A. P.; Suter, U. W.; Reid, R. C. Phase Diagrams of Nonideal Fluid Mixtures from Monte Carlo Simulation. *Ind. Eng. Chem. Fundam.* **1986**, 25, 525.
- (10) Lee, L. L. *Molecular Thermodynamics of Nonideal Fluids*; Butterworths: Boston, 1988.
- (11) Lee, L. L. Chemical Potentials Based on the Molecular Distribution Functions. An Exact Diagrammatical Representation and the Star Function. *J. Chem. Phys.* **1992**, 97, 8606.
- (12) Rowlinson, J. S. Intermolecular Potentials that are Functions of Thermodynamic Variables. *Mol. Phys.* **1984**, 52, 567.
- (13) Stillinger, F. H.; Sakai, H.; Torquato, S. Statistical Mechanical Models with Effective Potentials: Definitions, Applications, and Thermodynamic Consequences. *J. Chem. Phys.* **2002**, 117, 288.
- (14) Lee, L. L.; Ghonasgi, D. The Fluid Structures for Soft-Sphere Potentials via the Zero-Separation Theorems on Molecular Distribution Functions. *J. Chem. Phys.* **1996**, 104, 8058.
- (15) Llano-Restrepo, M.; Chapman, W. G. Bridge Function and Cavity Correlation Function for the Lennard-Jones Fluid from Simulation. *J. Chem. Phys.* **1992**, 97, 2046.
- (16) Sage, H.; Lacey, W. N. *Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen*; Monograph on API Research Project, 37; American Petroleum Institute: New York, 1950.

Received for review September 10, 2007

Revised manuscript received November 20, 2007

Accepted November 27, 2007

IE071216D