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Consideration of Some Dilute-Solution Phenomena Based on an Expression for the Gibbs Free Energy[1]

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Rigorous expressions based on the Lennard–Jones (6–12) potential, are presented for the Gibbs and Helmholtz free energy of a dilute mixture. These expressions give the free energy of the mixture in terms of the thermodynamic properties of the pure solvent, thereby providing a convenient means of correlating dilute mixture behavior with that of the pure solvent. Expressions for the following dilute binary solution properties are derived: Henry's constant, limiting activity coefficients with their derivatives, solid solubilities in supercritical gases, and mixed second virial coefficients. The Henry's constant expression suggests a linear temperature dependence; application to solubility data for various gases in methane and water shows a good agreement between theory and experiment. In the thermodynamic modeling of supercritical fluid extraction, we have demonstrated how to predict new solubility–pressure isotherms from a given isotherm, with encouraging results. The mixed second virial coefficient expression has also been applied to experimental data; the agreement with theory is good.

KEY WORDS: activity coefficient; dilute solution; Henry's constant; Lennard–Jones potential; mixture; solubilities; supercritical extraction; virial coefficients.

1. INTRODUCTION

Dilute solutions provide us with an ideal opportunity for relating mixture behavior to properties of the pure components. In dilute solutions, solute–

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solute contributions to the total potential energy are negligible, while the contribution from solute–solvent interactions is small enough to be considered a perturbation of the dominant solvent–solvent interactions. The appropriate combination of pure solvent properties to be used in such an approach is far from obvious, however. Emperical attempts at such correlations have been made; for example, Hildebrand's solubility parameters expression [1, 2] for limiting activity coefficients marks one of the earliest attempts at treatments with some theoretical basis. Rigorous approaches to the study of mixtures that yield a correlation with pure solvent properties are to be found in the corresponding states treatment of Longuet-Higgins and co-workers [3–5], Scott [6], Prigogine et al. [7], and Wojtowicz et al. [8].

In this paper, we exploit the special feature of dilute solutions already referred to above and perform a perturbation expansion about the state of the pure solvent. In a previous paper [9], such an expansion was made; however, some terms, which would have made this expansion correct to first order in solute mole fraction x_a, were neglected. These neglected terms are considered here.

2. EXPRESSION FOR THE GIBBS FREE ENERGY

We consider, to start with, a dilute binary mixture; the extension to a multicomponent system will be quite obvious.

The mixture consists of N molecules, N_a of species a, and N_b of species b, where $N_a \ll N_b$. For such a system, with total potential energy U, assuming that the internal degrees of freedom of the molecules are unaffected by the configurational state of the system, the molar Gibbs free energy may be written in the form,

$$\begin{aligned} g(T, p, x_a) &= \sum_i x_i[RT\ln x_i + \mu_i^\circ(T) + RT\ln(N/e)] - k_B T \ln \Delta_c \\ \mu_i^\circ(T) &= -RT\ln[\psi_i(T)/\Lambda_i^3] \qquad\qquad (1) \\ \Delta_c &\equiv \int_0^\infty \exp(-\beta p v)\, d(v/v^*) \int \exp(-\beta U)\, d(r^N)\, d(\omega^N) \end{aligned}$$

ψ_i and Λ_i^3 are, respectively, contributions to the partition function from the internal and translational degrees of freedom. Δ_c is the Gibbs phase integral for the system within the (N–p–T) ensemble; r^n, w^n abbreviate the center of mass and orientational coordinates $r_1, r_2, \ldots, r_n$ and $w_1, w_2, \ldots, w_n$, respectively, for the N molecules; $\beta \equiv 1/(k_B T)$, k_B denotes the Boltzmann constant. The volume v^* is an arbitrary, yet sufficiently small volume—typically of the order of the molecular volume—which does not affect the thermodynamic properties of the system [10].

In order to carry out a perturbation expansion about the pure solvent, we first need to identify the perturbation energy U_{pert} appropriately. As shown by Jonah et al. [9], the total potential energy U_{mix} of the dilute mixture can be written in the form,

$$U_{\mathrm{mix}} = U_{\mathrm{solv}} + U_{\mathrm{pert}} \tag{2}$$

where U_{solv} is the total potential energy for the pure solvent, component b, with the same number of molecules, N, as the mixture, while U_{pert} consists essentially of contributions arising from the solute–solvent and solute–solute interactions. (See Eq. (13) in Ref. 9.)

Expansion about the pure solvent state, using a procedure similar to those in Ref. 9 and based on the assumption of a Lennard–Jones 6–12 potential model, leads to the following expression for the molar Gibbs free energy g_{r}, which we give in residual form:

$$\begin{gathered}
g_{\mathrm{r}}(T, p, x_{\mathrm{a}}) = \mu_{\mathrm{br}}(T, p) + [\lambda_{\mathrm{ab}}^{(1)} - k^*(x_{\mathrm{a}})\lambda_{\mathrm{ab}}^{(2)}]x_{\mathrm{a}}x_{\mathrm{b}} + O(x_{\mathrm{a}}^2) \\
\lambda_{\mathrm{ab}}^{(1)} = \chi_{\mathrm{ab}} z_{\mathrm{r}} RT - 2(1 + \chi'_{\mathrm{ab}})U_{\mathrm{r}} \\
\lambda_{\mathrm{ab}}^{(2)} = C_{\mathrm{ab}}^{(2)}(TC_{\mathrm{pr}}) + [C_{\mathrm{ab}}^{(2)} + \chi_{\mathrm{ab}}](p^2 v\kappa_{\mathrm{T}} - pv\alpha) - \chi_{\mathrm{ab}} z_{\mathrm{r}} RT \\
\chi_{\mathrm{ab}} = st(t^2 - 1), \qquad \chi'_{\mathrm{ab}} = st(t^2 - 2) \\
C_{\mathrm{ab}}^{(2)} = 1 + \nu_{\mathrm{ab}} + 2\chi'_{\mathrm{ab}}, \qquad \nu_{\mathrm{ab}} = s^2 t^4 f(t^2) \qquad [f(1) = 1] \\
s = \varepsilon_{\mathrm{ab}}/\varepsilon_{\mathrm{bb}}, \qquad t = (\sigma_{\mathrm{ab}}/\sigma_{\mathrm{bb}})^3, \qquad k^*(x_{\mathrm{a}}) = k_1 + k_2 x_{\mathrm{a}}
\end{gathered} \tag{3}$$

[A residual (or excess) property P_{r} at temperature T, pressure p, and mole fraction x is being defined here as $P_{\mathrm{r}} \equiv P(T, p, x) - P(T, p^\circ, x)$, p° being sufficiently low for the system to be in an ideal-gas state.] μ_{br}, U_{r}, C_{pr}, and z_{r} denote, respectively, the molar residual chemical potential, internal energy, constant-pressure heat capacity, and compressibility factor of the pure solvent; α and κ_{T} are the pure solvent isobaric coefficient of volume expansion, and the isothermal coefficient of compressibility, respectively. $\varepsilon_{\mathrm{ab}}$, etc., denote the usual L–J molecular parameters, while k_1 and k_2 are empirical constants; f is an unknown function, which becomes unity for a system consisting of molecules of the same size, that is, $t = 1$.

The generalization of Eq. (3) to a multicomponent system with n components, in which 1 denotes the solvent component, and 2, 3,..., n, the solute components highly dilute in the solvent, is readily made; thus, we have

$$g_{\mathrm{r}}(T, p, x) = \mu_{1\mathrm{r}}(T, p) + \sum_{j=2}^{n} [\lambda_{j1}^{(1)} - k^*(x_j)\lambda_{j1}^{(2)}]x_1 x_j + O(x_2^2, x_3^2, \ldots) \tag{4}$$

Our interest is centered on the molar residual chemical potential μ_{ar} of the solute component a, and its limiting value $\mu_{\mathrm{ar}}^{\infty}$, at infinite dilution; we therefore write down expressions for these two quantities, using Eq. (3):

$$\begin{aligned}\mu_{\mathrm{ar}}(T, p, x_{\mathrm{a}}) &= \mu_{\mathrm{br}}(T, p) + \mu_{\mathrm{ar}}^{(\mathrm{ab})}(T, p, x_{\mathrm{a}}) \\ \mu_{\mathrm{ar}}^{(\mathrm{ab})}(T, p, x_{\mathrm{a}}) &= [\lambda_{\mathrm{ab}}^{(1)} - k^{*}(x_{\mathrm{a}})\,\lambda_{\mathrm{ab}}^{(2)}]\,x_{\mathrm{b}}^{2} - k_{2} x_{\mathrm{a}} x_{\mathrm{b}}^{2} \lambda_{\mathrm{ab}}^{(2)}\end{aligned} \tag{5}$$

with

$$\begin{aligned}\mu_{\mathrm{ar}}^{\infty} &= \mu_{\mathrm{br}} + \Lambda_{\mathrm{ab}} \\ \Lambda_{\mathrm{ab}} &\equiv \lambda_{\mathrm{ab}}^{(1)} - k_{1} \lambda_{\mathrm{ab}}^{(2)}\end{aligned} \tag{6}$$

The terms $\mu_{\mathrm{ar}}^{(\mathrm{ab})}$ and Λ_{ab} represent the solute–solvent interaction contributions to μ_{ar} and $\mu_{\mathrm{ar}}^{\infty}$, respectively.

We observe that in the limit $u_{\mathrm{aa}} = u_{\mathrm{bb}} = u_{\mathrm{ab}}$ (i.e., $s = 1$, $t = 1$) g_{r} in Eq. (3) and μ_{ar} in Eq. (5) reduce to the residual chemical potential μ_{br} of the pure solvent, as one would expect.

By reasoning completely analogous to that leading to Eq. (4), we can use the canonical ensemble partition function to derive the corresponding expression for the molar residual Helmholtz free energy A_{r}:

$$\begin{aligned}A_{\mathrm{r}}(T, v, x_{\mathrm{a}}) = {} & A_{\mathrm{br}}(T, v) + x_{\mathrm{a}} x_{\mathrm{b}} [\chi_{\mathrm{ab}} z_{\mathrm{r}} RT - 2(1 + \chi'_{\mathrm{ab}})\,U_{\mathrm{r}}] \\ & + x_{\mathrm{a}} x_{\mathrm{b}} \left\{ C_{\mathrm{ab}}^{(2)}(TC_{\mathrm{vr}}) - \chi_{\mathrm{ab}} \left[Tv \left(\frac{\partial p}{\partial T} \right)_{v} - RT \right] \right\} k^{*}(x_{\mathrm{a}}) + O(x_{\mathrm{a}}^{2})\end{aligned} \tag{7}$$

$A_{\mathrm{br}}(T, v)$ is the molar residual Helmholtz free energy for the pure-solvent b component with the same number N of molecules as the mixture, and C_{vr} the molar residual heat capacity at constant volume; other quantities have the same meanings as in Eqs. (3) and (5).

3. EXPRESSIONS FOR SOME THERMODYNAMIC PROPERTIES

In this section, we write down expressions for some dilute solution properties of interest, using Eq. (5) for the molar residual chemical potential of the solute component.

3.1. The Henry's Constant, Limiting Activity Coefficients, and Derivatives

From the definition of Henry's constant

$$H_{\mathrm{ab}} = \lim_{x_{\mathrm{a}} \to 0} (f_{\mathrm{a}}/x_{\mathrm{a}}) \tag{8}$$

we deduce at once from Eq. (5) that

$$H_{\mathrm{ab}} = f_{\mathrm{a}} \exp(\Lambda_{\mathrm{ab}}/RT) \tag{9}$$

This expression for Henry's constant may be compared with the standard form:

$$H_{\mathrm{ab}} = \exp(\Delta\mu^{\circ}/RT) \tag{10}$$

where $\Delta\mu^{\circ}$ is the standard change in partial molar free energies upon solution. It is seen at once that $\Delta\mu^{\circ} = \mu_{\mathrm{ar}}^{\infty}$ [see Eq. (6)], in which the contributions from the solvent–solvent and the solute–solvent interactions are explicitly displayed.

The limiting activity coefficients γ_i of a component i and derivatives can also be readily shown to be of the forms

$$\lim_{x_{\mathrm{a}} = 0} \gamma_{\mathrm{a}} \equiv \gamma_{\mathrm{a}}^{\infty} = (f_{\mathrm{a}}/f_{\mathrm{b}}) \exp(\Lambda_{\mathrm{ab}}/RT) \tag{11}$$

$$\lim_{x_{\mathrm{a}} \to 0} \left(\frac{\partial \ln \gamma_{\mathrm{a}}^{\infty}}{\partial x_{\mathrm{a}}} \right) \equiv \left(\frac{\partial \ln \gamma_{\mathrm{a}}}{\partial x_{\mathrm{a}}} \right)^{\infty} = -2[\lambda_{\mathrm{ab}}^{(1)} - (k_1 - k_2)\,\lambda_{\mathrm{ab}}^{(2)}]/RT \tag{12}$$

3.2. Solubility of Solids in Supercritical Gases

Assuming a dilute solution of the solid (component a) in the supercritical solvent gas (component b) such that terms of $O(y_{\mathrm{a}})$ in the solute mole fraction y_{a} may be neglected, it is readily shown that

$$y_{\mathrm{a}} = (f_{\mathrm{a}}^{\mathrm{solid}}/f_{\mathrm{a}}^{\mathrm{vap}}) \exp(-\Lambda_{\mathrm{ab}}/RT) \tag{13}$$

$$f_{\mathrm{a}}^{\mathrm{solid}} = p_{\mathrm{a}}^{\mathrm{sat}}\, \varphi_{\mathrm{a}}^{\mathrm{sat}} \exp[v_{\mathrm{a}}^{\mathrm{solid}}(p - p_{\mathrm{a}}^{\mathrm{sat}})/RT] \tag{14}$$

where φ is the fugacity coefficient, and the superscript sat refers to the saturated vapor.

3.3. Mixed Second Virial Coefficient

For a dilute binary gaseous mixture (solute component a and solvent component b), we find that the limiting fugacity coefficient φ_2^{∞} of the solute is given by

$$\ln \varphi_{\mathrm{a}}^{\infty} = \mu_{\mathrm{ar}}/RT + \ln(p^{\circ}/p) \tag{15}$$

p° being sufficiently low for the mixture to be considered ideal.

Using the standard thermodynamic expression for φ_2^{∞}, the mixed second virial coefficient B_{ab} is given by

$$B_{\mathrm{ab}} = (pv_{\mathrm{b}}/RT)B_{\mathrm{bb}} + (\Lambda_{\mathrm{ab}}/2RT)v_{\mathrm{b}} \tag{16}$$

B_{bb} being the second virial coefficient of the pure solvent.

4. COMPARISON WITH EXPERIMENT AND MACHINE CALCULATIONS

4.1. Simulation Data for Henry's Constant

In reduced variables, we have for the case $(\sigma_{ab}/\sigma_{bb})^3 = 1$, on using Eq. (7),

$$\ln(H_{ab}/\rho k_B T) = \mu_{br}/T^* - (2U_r^*/T^*)(1-s) - k_1(\partial U_r^*/\partial T^*)(1-s)^2$$
$$T^* \equiv k_B T/\varepsilon, \qquad \rho^* \equiv \rho\sigma^3, \qquad U_r^* \equiv U_r/N\varepsilon, \qquad \mu_{br}^* \equiv \mu_{br}/N\varepsilon \tag{17}$$

The L–J equation of state by Nicholas et al. [11] was used to obtain

$$U^*/T^* = -3.975, \qquad \partial U_r^*/\partial T^* = 0.71$$

the constant k_1 was assigned the value 0.5.

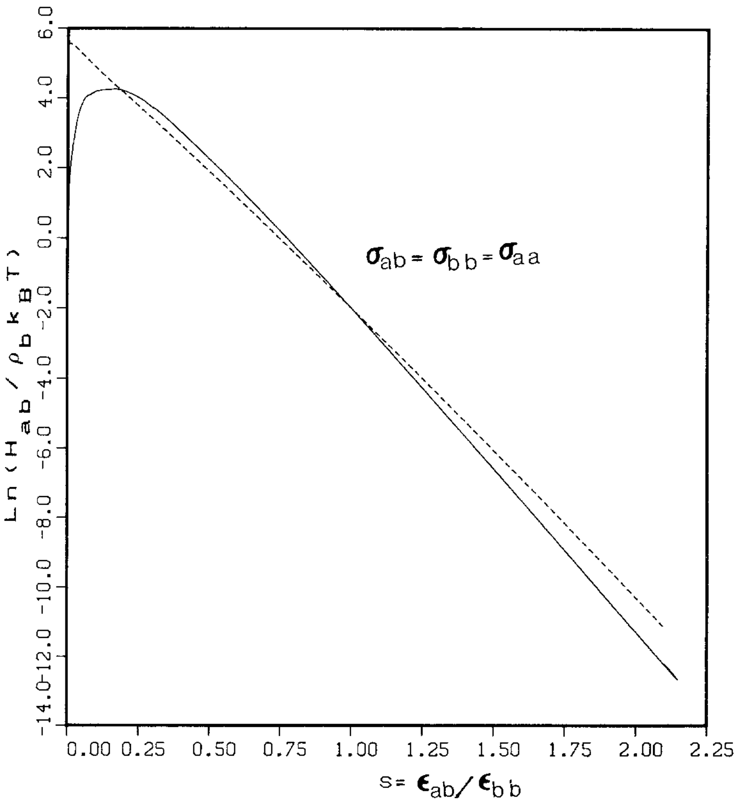

Fig. 1. Variation of Henry's constants with energy ratio, $s \equiv \varepsilon_{ab}/\varepsilon_{bb}$, for a binary mixture with molecules of the same size. (——) Machine calculation at reduced temperature $T \equiv k_B T/\varepsilon = 1.2$ and reduced density $\rho^* \equiv \sigma^3\rho = 0.7$ [12]; (----) theory according to Eq. (17) with $k_1 = 0.5$.

Figure 1 shows the comparison between our theory and the simulation data of Shing and Gubbins [12], for $\rho^* = 0.7$ and $T^* = 1$. In the range $0.25 < s < 2$, the agreement is seen to be quite good, becoming exact as $s = 1$.

4.2. Experimental Data for Henry's Constant

At liquid densities, the terms containing α and κ_T in Eq. (9), as well as the compressibility factor terms, are negligible. We may therefore write,

$$\ln(H_{ab}/f_b) = 2(1 + \chi'_{ab})(\Delta H^v/RT - 1) - k_1 C_{ab}^{(2)}(C_{pr}/R) \qquad (18)$$

where χ'_{ab} and $C_{ab}^{(2)}$ have been defined in Eq. (3); ΔH^v is the molar latent heat of vaporization.

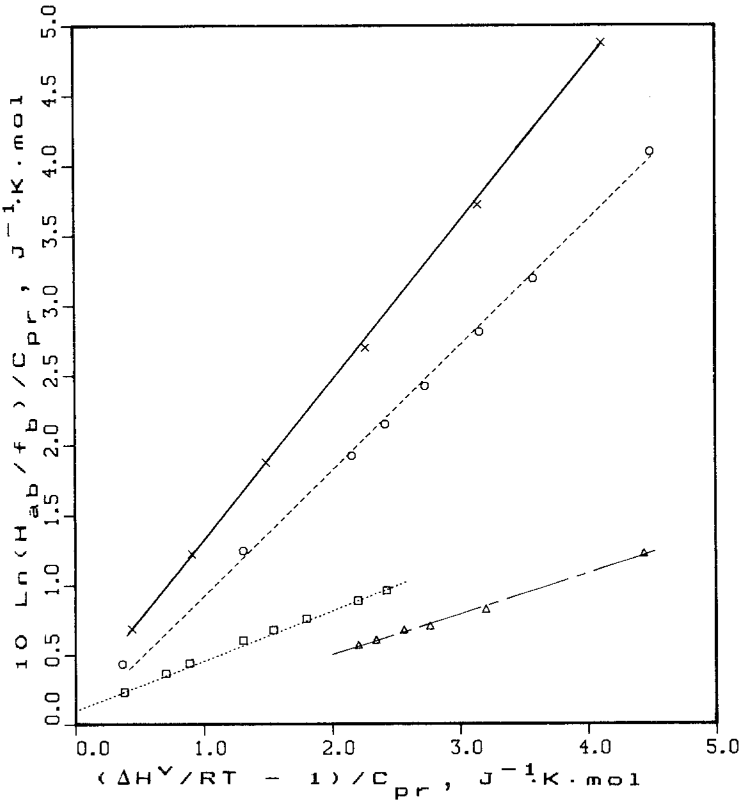

Fig. 2. Temperature variation of the solubility of gases He, H_2, and N_2 in liquid methane. ×, ○, □, and △, expt. points for He, H_2, N_2, and Ar, respectively. Data source, Ref. 18.

Equation (18) suggests that a plot of $F \equiv (R/C_{\mathrm{pr}}) \ln(H_{\mathrm{ab}}/f_{\mathrm{b}})$ versus $(R/C_{\mathrm{pr}})(\Delta H^{\mathrm{v}}/RT - 1)$ should be linear; Figs. 2 and 3 show such plots for various gases dissolved in liquid methane and water.

For the first set of mixtures with simple molecules, we have obtained the Lennard-Jones parameters from the critical constants of the pure components, according to the equations $s \equiv \varepsilon_{\mathrm{ab}}/\varepsilon_{\mathrm{bb}} = (1 - K_{\mathrm{ab}})(T_{\mathrm{ac}}/T_{\mathrm{bc}})^{1/2}$; $t \equiv (\sigma_{\mathrm{ab}}/\sigma_{\mathrm{bb}})^3 = (v_{\mathrm{ac}}^{1/3} + v_{\mathrm{bc}}^{1/3})^3/8v_{\mathrm{b}}^3$; T_{jc} and v_{jc} denote the critical temperature and critical volume, respectively, of a component j; K_{ab} gives the deviation from the geometric mean rule, which is evaluated from experimental data. The molecular parameter $f(t^2)$ defined in Eq. (3) is also to be obtained from experimental information.

Equation (18), with χ'_{ab} and $C_{\mathrm{ab}}^{(2)}$ obtained as above, has been used to calculate Henry's constant for the gases Ar, N_2, H_2, and He dissolved in

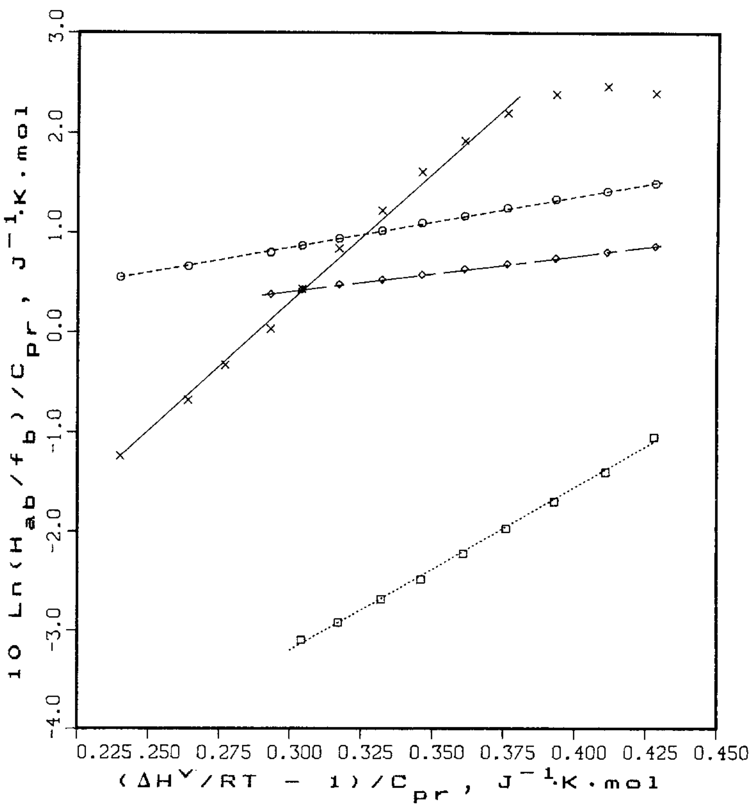

Fig. 3. Temperature variation of the solubility of various gases in water. ×, ○, □, and ◇, expt. points for HCN, H_2S, NH_3, and SO_2, respectively. Ordinates for H_2S and SO_2 have been multiplied by a factor of 10^2. Data source, Ref. 18.

Table I. Comparison Between Experimental[a] and Calculated[b] Henry's Constant According to Eq. (18)

		$\ln(H_{ab}/f_b)$	
	T (K)	Expt.	Calc.
He/CH_4			
	95	11.78	11.75
	110	9.58	9.69
	124.9	7.86	8.03
	139.9	6.48	6.49
	154.8	5.32	5.29
	170.0	4.20	4.18
H_2/CH_4			
	90.14	9.71	9.63
	102.97	7.95	8.06
	109.86	7.22	7.35
	116.51	6.56	6.71
	122.00	6.10	6.23
	127.00	5.71	5.83
	144.26	4.56	4.39
	171.92	2.98	2.40
Ar/CH_4			
	90.67	2.92	2.89
	109.0	2.12	2.19
	115.9	1.91	1.95
	119.6	1.88	1.84
	123.3	1.75	1.73
	126.0	1.68	1.65
N_2/CH_4			
	122.1	2.72	2.74
	126.2	2.62	2.62
	133.2	2.41	2.37
	138.7	2.31	2.22
	144.3	2.22	2.08
	155.4	1.94	1.76
	161.0	1.81	1.73
	171.5	1.57	1.58

[a] The experimental data were obtained from Refs. 17 and 18.

[b] The following parameter values were used for K_{ab} and $f(\sigma_{ab}^6/\sigma_{bb}^6)$: $(-2.15, -4.74)$ He/CH_4; $(-0.024, 1.878)$ Ar/CH_4; $(-0.489, 0.422)$ H_2/CH_4; $(-0.02, 1.75)$ N_2/CH_4.

liquid methane at various temperatures. Table I compares these calculated values with experimental values; the agreement is seen to be good.

Experimental data for the activity coefficients and their derivatives may be treated in analogous fashion to the above, making possible the interpolation of their values between two given temperatures; such interpolated values may then be used in empirical expressions (e.g., the Abbott-Van Ness [13] and conic equations [14]) for the excess Gibbs free energy-composition isotherms, to predict new isotherms. This has in fact been shown to be feasible and will be reported elsewhere.

Table II. Solubilities of 2,6-Dimethylnaphalene in Supercritical Ethylene as Predicted by Eq. (19)[a]

		$10^4 y_a$	
T	P (MPa)	Expt.	Calc.
308 K			
	9	9	7.73
	10	14	12.73
	14	34	34.7
	18	59	57.0
	22	81	79.5
	24	92.78[b]	90.3
	26	103	90.7
318 K			
	7.8	1.886	1.35
	12	21.99	21.3
	16	55.6	52.1
	20	90.82	82.1
	24	138.8	111.5
	28	171.3	139.6
328 K			
	7.8	2.364	1.44
	12	22.03	18.39
	16	67.43	56.14
	20	130.0	97.2
	24	200.2	132.9
	28	275.2	173.7

[a] The following values of $10^6 P_a^{sat}$ (MPa) and v_a^{solid} (liters) for 2,6-dimethylnaphthalene were used: (1.22, 0.137) 308 K; (3.45, 0.137) 318 K; (9.13, 0.137) 328 K.

[b] All experimental values for the 308 K isotherm, except this one, have been graphically interpolated.

4.3. Solid Solubilities in Supercritical Solvent

From Eq. (13), we may write for the solubility y_a of the solid

$$y_a = \frac{p_a^{\text{sat}}}{f_b^*}\exp\left[\frac{pv_a^{\text{solid}}}{RT} - (K_1 X + K_2 Y + K_3 Z + K_4 W)\right] \tag{19}$$

$$X = (p^2 v\kappa_T - pv\alpha T)/RT, \qquad Y = C_{pr}/R, \qquad Z \equiv 2U_r/RT, \qquad W \equiv z_r$$

where K_1, K_2, etc., are known functions of the L–J molecular parameters. In applying the above equation, however, to experimental data, $K_1, \ldots, K_4$ have been treated as empirical parameters. By using four experimental data points from the $T = 308$ K isotherm these parameters are evaluated for the system 2,6-dimethylnapthalene/ethylene [15]; with these same values of

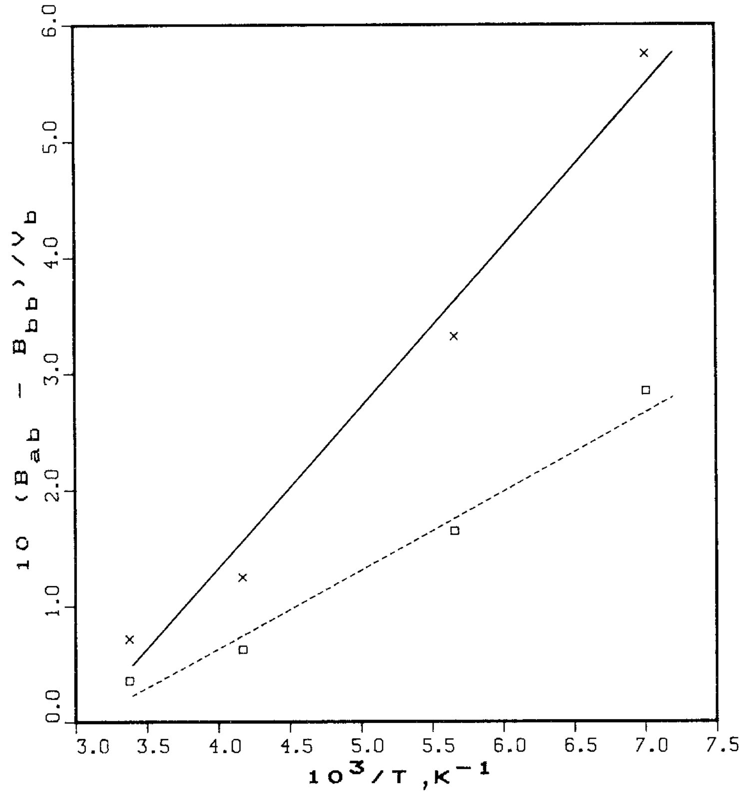

Fig. 4. Temperature variation of mixed second virial coefficient for gaseous mixture argon/methane. × and □, molar volume of methane at 0.1 and 0.05 MPa, respectively.

the parameters, isotherms at $T = 318$ and 328 K are predicted. The results shown in Table II indicate good agreement between experiment and theory.

4.4. Mixture Second Virial Coefficient

By approximating the compressibility factor of the pure solvent by unity and neglecting the residual properties in Eq. (16), the final form is suggestive of the following temperature variation of the second virial coefficients:

$$(B_{\mathrm{ab}} - B_{\mathrm{bb}})/V_{\mathrm{b}} = a + b/T + c/T^2 \tag{20}$$

where a, b, and c are temperature-independent constants.

The equation has been tested against two sets of experimental data: argon/methane and carbontetrafluoride/methane [16]. Figure 4 shows the lhs of Eq. (20) plotted against reciprocal temperature for Ar/CH_4, which is seen to be reasonably linear, indicating a negligible contribution from the c/T^2 term. A corresponding plot for the data set CF_4/CH_4 deviates from linearity; however, three data points at three temperatures, 273.15, 423.15, and 523.15 K, have been used to evaluate a, b, and c (with v_{b} corresponding to 0.1 MPa), to obtain $a = 1.096 \times 10^{-4}$, $b = 0.372$, and $c = -122$. Table III compares experimental with calculated values at other temperatures; the agreement is excellent.

Table III. Mixed Second Virial Coefficient for CF_4/CH_4[a]

	B_{ab} (cm^3)	
T(K)	Expt.	Calc.
298.15	−48.48	−48.69
303.15	−46.09	−46.26
323.15	−37.36	−37.69
348.15	−28.31	−28.49
373.15	−20.43	−20.7
398.15	−13.98	−14.09
448.15	−3.21	−3.39
498.15	4.94	4.83
548.15	11.39	11.28
573.15	14.10	13.96
596.15	16.55	16.37

[a] The calculated values are obtained from Eq. (20) for methane volumes at 0.1 MPa.

5. SUMMARY AND CONCLUSION

We have in this study identified a set of pure solvent thermodynamic properties, with which dilute solution behavior may be correlated. Although the interactions have been modeled by the L–J (6–12) potential, the success of our theory for simple as well as complex molecular mixtures encourages us to believe that the set of pure solvent properties identified on the basis of this model has a much wider range of validity.

In spite of the success of our theory, the divergence at the solvent's critical point of Eq. (3) for the Gibbs free energy presents a problem that needs to be resolved; on the other hand, the Helmholtz free energy, Eq. (7), is well behaved at this point.

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