Table II. Dilation Constants of Some Binary Systems

System	T, ° R	$\eta_{2(1)}$
Methane(2)–propane(1)	407.7	0.31
	499.7	1.46
	559.7	4.12
	619.7	28.35
Methane(2)–*n*-pentane(1)	559.7	1.19
	619.7	1.62
	679.7	2.25
	739.7	8.39
Propane(2)–*n*-pentane(1)	679.7	0.27
	739.7	1.23
	799.7	26.24
Methane(2)–ethane(1)	359.7	0.90
	409.7	1.29
	459.7	3.06
	509.7	27.10
Ethane(2)–propane(1)	559.7	1.30
	599.7	4.41
	619.7	12.28
	639.7	43.54

Table III. Henry's Constants of Some Solutes in Solvents

System	T, ° R	$H_{2(1)}^{(PO)}$ psia
Methane(2)–ethane(1)	359.7	690
	409.7	1029
	459.7	1330
	509.7	1500
Methane(2)–propane(1)	359.7	870
	409.7	1360
	459.7	1800
	491.7	2044
	509.7	2130
	559.7	2141
	619.7	1844
Methane(2)–*n*-pentane(1)	559.7	2821
	619.7	3185
	679.9	3256
	739.7	2943
Ethane(2)–propane(1)	559.7	449
	579.7	503
	599.7	573
	619.7	616
	639.7	631
Propane(2)–*n*-pentane(1)	619.7	289
	679.7	447
	739.7	610
	799.7	750

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function of the mole fraction, especially in the vicinity of the critical composition. The liquid solution dilates as x_2 rises, and van Laar's model must be modified to take this effect into account.

For practical reasons (since experimental data are usually not plentiful), it is desirable to derive equations for the constant-pressure activity coefficients which contain no more than two parameters. Because of this limitation, we assume that whereas q_1 and q_2 depend on composition, their ratio does not. Since the van Laar treatment is a two-body (quadratic) theory, we assume that q_1 and q_2 are given by a quadratic function of the effective volume fraction:

$$q_1 = v_{c_1}[1 + \eta_{2(1)}\Phi_2^2] \tag{30}$$

$$q_2 = v_{c_2}[1 + \eta_{2(1)}\Phi_2^2] \tag{31}$$

(From Equations 30 and 31, it follows that the volume fraction Φ_i is given by $\Phi_i = x_i v_{c_i}/\Sigma_i\, x_i v_{c_i}$.)

In Equations ~~B-13~~ 30 and ~~B-14~~ 31 we have arbitrarily used the pure-component critical volumes as our measure of the molecular cross sections at infinite dilution, when $\Phi_2 = 0$. Some other constant (for example, van der Waals b or Leonard-Jones σ^3) could just as easily be used. The dilation constant $\eta_{2(1)}$ is a measure of how effectively the light component dilates (swells) the liquid solution.

When Equations 30 and 31 are substituted into Equation 26, the pressure-independent activity coefficients are

$$\ln \gamma_1^{(P^r)} = A\Phi_2^2 + B\Phi_2^4 \tag{32}$$

$$\ln \gamma_2^{*(P^r)} = A\left(\frac{v_{c_2}}{v_{c_1}}\right)(\Phi_2^2 - 2\,\Phi_2) + B\left(\frac{v_{c_2}}{v_{c_1}}\right)\left(\Phi_2^4 - \frac{4}{3}\,\Phi_2^3\right) \tag{33}$$

where

$$A \equiv \alpha_{22(1)} v_{c_1} \tag{34}$$

$$B \equiv 3\,\eta_{2(1)}\alpha_{22(1)} v_{c_1} \tag{35}$$

Equations 32 and 33 are the desired two-parameter equations. These equations provide accurate representation of the constant-pressure activity coefficients of nonpolar binary mixtures from the dilute region up to the critical composition. To illustrate, Figures 3 and 4 present typical results of data reduction for two binary systems, propane-methane (*30*) and carbon dioxide–nitrogen (*21*).

Self-interaction constants, dilation constants, and Henry's constants for some binary systems are given in Tables I, II, and III. The magnitude of the dilation constant shows a consistent and meaningful variation with respect to the temperature and the properties of the constituent components; the dilation constants are

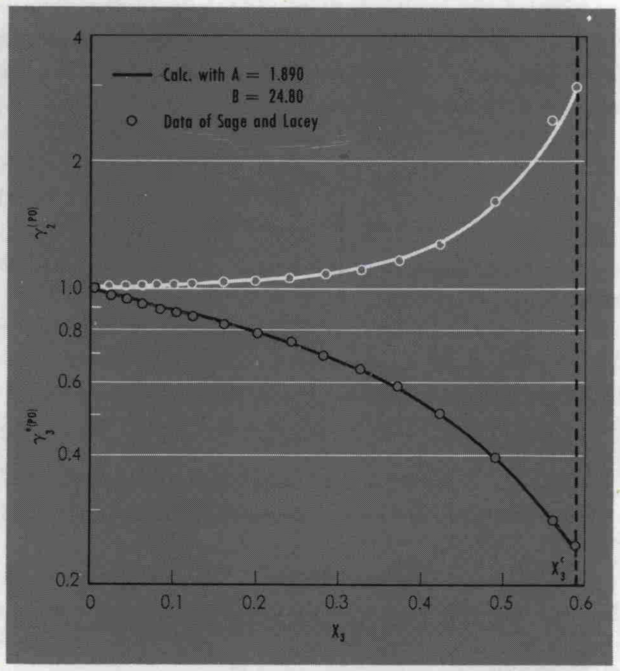

Figure 3. Activity coefficients for the propane(2)–methane(3) system at 100° F.

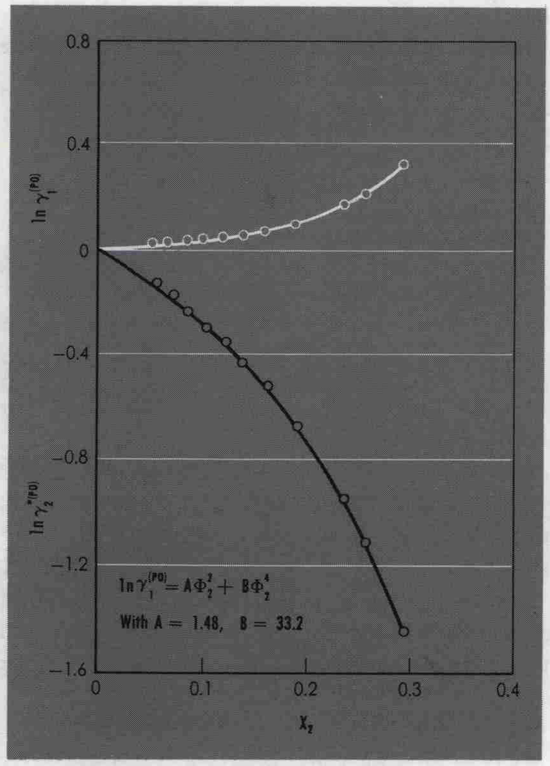

Figure 4. Activity coefficients for the carbon dioxide(1)–nitrogen(2) system at 32° F.

larger for those systems at temperatures approaching the critical temperature of the heavy component (component 1); also, they are larger for those systems in which the light component is highly supercritical. This behavior of dilation constants is in agreement with their physical significance in the dilated van Laar model—i.e., the liquid phase is swelled or dilated most when the subcritical heavy component itself is near its critical temperature, or when the light component is far above its critical temperature. Under these conditions the liquid molar volume increases sharply with dissolved gas.

Plots of ln $\eta^{1/2}$ *vs.* $1/T$ show a similar shape for all systems. It has been possible to unify all the curves into a single reduced plot, as shown in Figure 5. The curve can be represented by

$$\ln (\eta/\eta^{\ddagger})^{1/2} = -30.2925 + 39.1396\ (T^{\ddagger}/T) - 17.2182\ (T^{\ddagger}/T)^2 + 2.81464\ (T^{\ddagger}/T)^3 - 2.78571/(T^{\ddagger}/T) - 5.26736 \ln (T^{\ddagger}/T - 0.9) \quad (36)$$

where $\eta^{\ddagger}$ is a constant characteristic of the light component and $T^{\ddagger}$ is a constant characteristic of the binary system. Some values of $\eta^{\ddagger}$ and $T^{\ddagger}$ are given in Figure 5.

Mixtures of condensable components. At temperatures sufficiently lower than the critical temperature of the light component (component 2), the dilation constant η obtained from data reduction becomes so small that it can be effectively equated to zero. Under these conditions, the constant-pressure activity coefficients of both components can be correlated with only one parameter, α. We found empirically that this occurs for T_{R_2} less than 0.93. Therefore, components with a reduced temperature smaller than 0.93 are treated as heavy components (solvent), and those with T_R larger than 0.93 are treated as light components (solute). Systems for which both T_{R_1} and T_{R_2} are smaller than 0.93 are correlated with $\eta = 0$ and only one parameter, α. Systems for which the critical temperatures of the two components are very close (such as acetylene–ethane) are also analyzed with only one parameter, α, even though T_{R_2} is larger than 0.93; the terms "heavy" and "light" component lose their conventional meaning for such systems. In fact, it sometimes happens that the component with the higher critical temperature ("heavy") may actually have a higher vapor pressure and critical pressure than the component with the lower critical temperature ("light").

For those systems where both components can exist in the pure liquid state, it is not necessary to use the unsymmetric convention for normalization of activity coefficients. Instead, such a system can be analyzed with a one-parameter, symmetric-convention expression for the excess Gibbs energy: