

species B

- $\bar{\alpha}, \tilde{\alpha}$ = lower and upper solutions of α
 $\bar{\beta}, \tilde{\beta}$ = lower and upper solutions of β
 θ = dimensionless variable of time
 ξ = dimensionless variable of the spatial coordinate x
 Δ = ratio of the coefficient of diffusion of species A to the coefficient of diffusion of species B
 Γ = ratio of the concentration of species B at $t = 0$ to the concentration of species A at $x = 0$
 G_p, R_p = domain and boundary of systems (1) and (2)
 R_n = subset of R_p
 R_p^+, R_n = boundary, defined in definition 1
 θ_k, ξ_k = sequences of θ and ξ , defined in definition 1
 ϕ, ψ = functions defined in G_p , see definition 1
 $||\xi_k||_e$ = Euclidean distance
 f, g = functions, defined by (7) and (8)
 $D(f), D(g)$ = domains of f and g
 ρ = function, defined in definition 2
 τ, δ = small number, defined in definition 2
 T = some large dimensionless variable of time
 $Z_0(f), Z_0(g, R_n)$ = function class, defined in definitions 3 and 4
 h = function, defined by (19)
 P_1, P_2 = differential operators, defined in (7) and (8)
 U = union, set notation

- ϵ = element of, set notation
 \subset = subset of, set notation
 E = function class, defined in definition 2

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Prediction of Partial Molar Volume from the Lee-Kesler Equation of State

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Based on Pitzer's three-parameter corresponding states principles (1955), Lee and Kesler (1975) developed an analytical method to represent the thermodynamic function of any fluid F in terms of a simple fluid contribution $F^{(o)}$ and of a reference fluid contribution $F^{(r)}$ as follows:

$$F = F^{(o)} + \frac{\omega}{\omega^{(r)}} [F^{(r)} - F^{(o)}] \quad (1)$$

The function for both the simple fluid $F^{(o)}$ and the reference fluid $F^{(r)}$ are derived from a reduced form of the modified BWR equation of state with a different set of constants:

$$Z = \left(\frac{P_r V_r}{T_r} \right) = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^3} + \frac{C_4}{T_r^3 V_r^3} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp \left(-\frac{\gamma}{V_r^2} \right) \quad (2)$$

where

$$B = b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \quad (3)$$

$$C = c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \quad (4)$$

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$$D = d_1 + \frac{d_2}{T_r} \quad (5)$$

and $b_1, b_2, b_3, b_4, c_1, c_2, c_3, c_4, d_1, d_2, \beta$, and γ are constants.

The set of constants for the simple fluid are determined from the data for argon, krypton, and methane and that of the reference fluid are from the data for *n*-octane. The Lee-Kesler correlation is accurate in estimating thermodynamic properties for nonpolar fluids (Reid et al., 1977; Danner et al., 1976). In this work, the Lee-Kesler equation of state is applied in the calculation of the partial molar volumes of nonpolar binary mixtures.

METHOD OF CALCULATION

If the thermodynamic function F in Equation (1) is the compressibility factor, then Equation (1) can be written as

$$Z = Z^{(o)} + \frac{\omega}{\omega^{(r)}} [Z^{(r)} - Z^{(o)}] \quad (6)$$

From the definition, $Z = P_r V_r / RT_r$, $Z^{(o)} = P_r V_r^{(o)} / T_r$, and $Z^{(r)} = P_r V_r^{(r)} / T_r$, we obtain

$$v = \frac{RT}{P} \left\{ \frac{P_r}{T_r} \left[V_r^{(o)} + \frac{\omega}{\omega^{(r)}} (V_r^{(r)} - V_r^{(o)}) \right] \right\} \quad (7)$$

TABLE 1. COMPARISON OF THE PARTIAL MOLAR VOLUME ESTIMATED BY THE LEE-KESLER EQUATION OF STATE AND THAT CALCULATED FROM DATA ON VOLUME CHANGE

System	Tempera- ture, °K	Pressure, atm	Composi- tion, x_1	Partial molar volume, cm ³ /g-mole				Data and source
				Component 1		Component 2		
				Estimate	Experiment	Estimate	Experiment	
Methane (1)								
<i>n</i> -butane (2)	344.3	40	0.1487	93.31	101.48	111.39	107.9	Reamer et al (1947)
Ethane (1)								
<i>n</i> -pentane (2)	344.3	272	0.6250	74.58	78.10	115.49	101.58	Sage (1965)
Benzene (1)								
2,2,4, trimethyl- pentane (2)	293.33	1	0.5	89.42	88.87	160.81	166.19	Graboski (1970)
Benzene (1)								
1-octene (2)	293.33	1	0.5	89.91	89.02	155.33	157.70	Graboski (1970)
Benzene (1)								
Ethylcyclohexane (2)	293.33	1	0.5	89.72	89.06	150.95	143.48	Graboski (1970)
Benzene (1)								
<i>n</i> -dodecane (2)	293.33	1	0.5	87.21	89.49	223.65	228.71	Graboski (1970)

The total volume V is equal to the total number of moles multiplied by the molar volume:

If derivatives of Equation (10) with respect to N_i are taken, and the final equation is rearranged

$$(\partial V_r / \partial N_i) = \frac{\left(\frac{\partial T_r}{\partial N_i} \right) \left[\frac{1}{V_r} \left(\frac{b_2}{T_r^2} + \frac{2b_3}{T_r^3} + \frac{3b_4}{T_r^4} \right) + \frac{1}{V_r^2} \left(\frac{c_2}{T_r^2} - \frac{3c_3}{T_r^3} \right) - \frac{d_2}{V_r^5 T_r^2} + \frac{P_r V_r}{T_r^2} - \frac{3c_4}{T_r^4 V_r^2} \right]}{\left\{ \frac{P_r}{T_r} + \frac{B}{V_r^2} + \frac{2C}{V_r^3} + \frac{5D}{V_r^6} + \exp \left(-\frac{\gamma}{V_r^2} \right) \left[\frac{2c_4}{T_r^3 V_r^3} \left(\beta + \frac{\gamma}{V_r^2} \right) + \frac{2\gamma c_4}{T_r^3 V_r^5} \right] \right\}}$$

$$V = \frac{N_T R T}{P} \left\{ \frac{P_r}{T_r} \left[V_r^{(o)} + \frac{\omega}{\omega^{(r)}} (V_r^{(r)} - V_r^{(o)}) \right] \right\} \quad (8)$$

Since

$$\left(\frac{\partial T_r}{\partial N_i} \right) = -\frac{T}{T_c^2} \left(\frac{\partial T_c}{\partial N_i} \right) \quad (12)$$

By the definition, the partial molar volume of component i in a mixture can be derived from Equation (8):

$$\frac{\partial P_r}{\partial N_i} = -\frac{P}{P_c^2} \left(\frac{\partial P_c}{\partial N_i} \right) \quad (13)$$

$$\bar{V}_i = \left(\frac{\partial V}{\partial N_i} \right)_{T, P, N_j (j \neq i)} = \frac{Z R T}{P} \left\{ 1 - \frac{N_T}{P_c} \left(\frac{\partial P_c}{\partial N_i} \right) \right\}$$

Substituting Equations (12) and (13) into Equation (11), we have

$$(\partial V_r / \partial N_i) = \frac{\frac{P_r V_r}{T_r} \frac{1}{P_c} \left(\frac{\partial P_c}{\partial N_i} \right) - T_r \frac{1}{T_c} \left(\frac{\partial T_c}{\partial N_i} \right) \left[\frac{1}{V_r} \left(\frac{b_2}{T_r^2} + \frac{2b_3}{T_r^3} + \frac{3b_4}{T_r^4} \right) + \frac{1}{V_r^2} \left(\frac{c_2}{T_r^2} - \frac{3c_3}{T_r^3} \right) + \frac{P_r V_r}{T_r} \right]}{\left\{ \frac{P_r}{T_r} + \frac{B}{V_r^2} + \frac{2C}{V_r^3} + \frac{5D}{V_r^6} + \exp \left(-\frac{\gamma}{V_r^2} \right) \left[\frac{2c_4}{T_r^3 V_r^3} \left(\beta + \frac{\gamma}{V_r^2} \right) + \frac{2\gamma c_4}{T_r^3 V_r^5} \right] \right\}}$$

$$\begin{aligned} & + \frac{N_T}{T_c} \left(\frac{\partial T_c}{\partial N_i} \right) \left\{ + \frac{N_T R T_c}{P_c} \left\{ \left(\frac{\partial V_r^{(o)}}{\partial N_i} \right) \right. \right. \\ & + \frac{\omega}{\omega^{(r)}} \left[\left(\frac{\partial V_r^{(l)}}{\partial N_i} \right) - \left(\frac{\partial V_r^{(o)}}{\partial N_i} \right) \right] \\ & \left. \left. + \frac{1}{\omega^{(r)}} (V_r^{(l)} - V_r^{(o)}) \left(\frac{\partial \omega}{\partial N_i} \right) \right\} \right\} \quad (9) \end{aligned}$$

In order to calculate the derivatives of reduced volume of both the simple and the reference fluid, $(\partial V_r^{(o)} / \partial N_i)$ and $(\partial V_r^{(l)} / \partial N_i)$, respectively, Equation (2) is rearranged as

$$\begin{aligned} P_r V_r = T_r \left\{ 1 + \left(b_1 - \frac{b_2}{T_r} - \frac{b_3}{T_r^2} - \frac{b_4}{T_r^3} \right) \frac{1}{V_r} \right. \\ + \left(c_1 - \frac{c_2}{T_r} + \frac{c_3}{T_r^3} \right) \frac{1}{V_r^2} + \left(d_1 + \frac{d_2}{T_r} \right) \frac{1}{V_r^5} \\ \left. + \frac{c_4}{T_r^3 V_r^2} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp \left(-\frac{\gamma}{V_r^2} \right) \right\} \quad (10) \end{aligned}$$

Equations for calculating $(\partial P_c / \partial N_i)$, $(\partial T_c / \partial N_i)$, $(\partial \omega / \partial N_i)$, and $(\partial V_c / \partial N_i)$ are given in the Appendix. If constants of simple fluids and reference fluids for Equation (2) are substituted into Equation (13), $(\partial V_r^{(o)} / \partial N_i)$ and $(\partial V_r^{(l)} / \partial N_i)$ are obtained. Equation (9) can then be utilized to estimate the partial molar volumes.

RESULTS

Table 1 compares the partial molar volumes estimated by the Lee-Kesler equation with experimental values. The estimates of Equation (9) are very close to those calculated from the data of volume change due to the variation of concentration in the mixture. Even at a pressure of 272 atm, the accuracy of the predicted values are still within 15% of the experimental values. Generally speaking, Equation (9) can predict accurate partial molar volumes of a component in a nonpolar binary mixture at moderate temperature and pressure. However, when the mixture approaches within about 5% of a pure component, the accuracy of the estimates of Equation (9) cannot be verified. Either the data for the volume change are not available, or they are subject to uncertainty.

APPENDIX

Equations to calculate the derivatives of the critical properties with respect to molar number.

For a binary system which contains N_1 moles of component 1 and N_2 moles of component 2, the critical volume of the mixture is

$$V_c = \frac{1}{N_T^2} \left\{ N_1^2 V_{c1} + N_2^2 V_{c2} + \frac{1}{4} N_1 N_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \right\} \quad (A1)$$

where $N_T = N_1 + N_2$.

Taking derivatives with respect to N_1 and N_2 , respectively, the following two equations result:

$$\left(\frac{\partial V_c}{\partial N_1} \right) = \frac{1}{N_T} \left\{ 2(x_1 V_{c1} - V_c) + \frac{1}{4} x_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \right\} \quad (A2)$$

$$\left(\frac{\partial V_c}{\partial N_2} \right) = \frac{1}{N_T} \left\{ 2(x_2 V_{c2} - V_c) + \frac{1}{4} x_1 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \right\} \quad (A3)$$

Here $x_1 = N_1/N_T$ and $x_2 = N_2/N_T$.

$$\left(\beta + \frac{\gamma}{V_r^2} \right) \exp \left(-\frac{\gamma}{V_r^2} \right) - \frac{V_r}{T_r} \left(\frac{\partial P_r}{\partial N_i} \right) \left(1 - \beta - \frac{\gamma}{V_r^2} \right) \right\} \quad (11)$$

According to the mixing rules recommended by Lee and Kesler, the critical temperature of the mixture is

$$T_c = \frac{1}{N_T^2 V_c} \left\{ N_1^2 V_{c1} T_{c1} + \frac{1}{4} N_1 N_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \sqrt{T_{c1} T_{c2}} + N_2^2 V_{c2} T_{c2} \right\} \quad (A4)$$

$$\left(1 - \beta - \frac{\gamma}{V_r^2} \right) \left\{ -\frac{3c_4}{T_r^4 V_r^2} \left(\beta + \frac{\gamma}{V_r^2} \right) \exp \left(-\frac{\gamma}{V_r^2} \right) \right\} \quad (14)$$

The following two equations are obtained by taking derivatives with respect to N_1 and N_2 , respectively:

$$\left(\frac{\partial T_c}{\partial N_1} \right) = \frac{1}{N_T V_c} \left\{ 2(x_1 V_{c1} T_{c1} - V_c T_c) + \frac{1}{4} x_2 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \sqrt{T_{c1} T_{c2}} - T_c N_T \left(\frac{\partial V_c}{\partial N_1} \right) \right\} \quad (A5)$$

$$\left(\frac{\partial T_c}{\partial N_2} \right) = \frac{1}{N_T V_c} \left\{ 2(x_2 V_{c2} T_{c2} - V_c T_c) + \frac{1}{4} x_1 (V_{c1}^{1/3} + V_{c2}^{1/3})^3 \sqrt{T_{c1} T_{c2}} - T_c N_T \left(\frac{\partial V_c}{\partial N_2} \right) \right\} \quad (A6)$$

Since the critical pressure of the mixture is

$$P_c = (0.2905 - 0.085 \omega) \frac{RT_c}{V_c} \quad (A7)$$

taking derivatives of Equation (A7) with respect to N_1 and N_2 yields

$$\left(\frac{\partial P_c}{\partial N_1} \right) = -0.085 \left(\frac{\partial \omega}{\partial N_1} \right) \frac{RT_c}{V_c} + (0.2905 - 0.085 \omega)^*$$

$$\left[\left(\frac{\partial T_c}{\partial N_1} \right) - \frac{T_c}{V_c} \left(\frac{\partial V_c}{\partial N_1} \right) \right] \frac{R}{V_c} \quad (A8)$$

$$\left(\frac{\partial P_c}{\partial N_2} \right) = -0.085 \left(\frac{\partial \omega}{\partial N_2} \right) \frac{RT_c}{V_c} + (0.2905 - 0.085 \omega)^*$$

$$\left[\left(\frac{\partial T_c}{\partial N_2} \right) - \frac{T_c}{V_c} \left(\frac{\partial V_c}{\partial N_2} \right) \right] \frac{R}{V_c} \quad (A9)$$

where R is the gas constant

$$\left(\frac{\partial \omega}{\partial N_1} \right) = \frac{1}{N_T} \{ \omega_1 - \omega \} \quad (A10)$$

$$\left(\frac{\partial \omega}{\partial N_2} \right) = \frac{1}{N_T} \{ \omega_2 - \omega \} \quad (A11)$$

According to the mixing rules proposed by Lee and Kesler, the acentric factor of the mixture is

$$\omega = \frac{1}{N_T} \{ N_1 \omega_1 + N_2 \omega_2 \} \quad (A12)$$

NOTATION

N_i	= molar number of component i in the mixture
N_T	= total molar number in the system
P	= pressure
P_c	= critical pressure of mixture
P_{ci}	= critical pressure of component i
P_r	= reduced pressure
T	= temperature
T_c	= critical temperature of mixture
T_{ci}	= critical temperature of component i
T_r	= reduced temperature
V	= total volume
V_c	= critical volume of the mixture
V_{ci}	= critical volume of component i
V_r	= reduced volume
Z	= compressibility
ν	= molar volume
ω	= acentric factor
ω^r	= acentric factor of reactor fluid

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