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APPLICABILITY OF THE LEE–KESLER EQUATION OF STATE IN P–V–T CALCULATIONS FOR BINARY MIXTURES

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ABSTRACT

The predictive applicability of the Lee–Kesler equation of state was studied over a wide range of P–V–T–x values for 17 binary mixtures by means of the available gas and liquid state experimental compressibility data.

New optimum fixed value interaction parameters $L_{ij} = L_{ij}(T, P, x)$, functionally dependent on temperature (T), pressure (P) and composition (x), were introduced for several binary systems.

The root mean square percent errors calculated over the P–T–x range investigated showed a degree of superiority of the Lee–Kesler equation over the Benedict–Webb–Rubin (BWR) and Starling equations of state.

LIST OF SYMBOLS

B, C, D, b_1, b_2, b_3, b_4, c_1, c_2, c_3, c_4, d_1, d_2, β, γ	Lee–Kesler equation constants
e, f, g, h	dimensionless coefficients of eqn. (21)
k_{ij}	binary interaction parameter
L_{ij}	binary interaction parameter defined as $L_{ij} = 1 - k_{ij}$
P	pressure
R	universal gas constant
T	temperature
V	volume
x	composition, mole fractions
Z	compressibility factor
ω	acentric factor

Subscripts

c	critical state
i, j, k	components

m	mixture
r	reduced state, with respect to the vapour–liquid critical point

INTRODUCTION

Despite the large number of new equations of state recently suggested [1,2], the Benedict–Webb–Rubin (BWR) equation [3–8] and its modifications, the Starling [9–13] and the Lee–Kesler [14] equations continue to be popular and widely used. The Lee and Kesler generalization of the BWR equation is particularly attractive as it is relatively easy to use. Also, within the context of Pitzer's macroscopic three-parameter theorem of corresponding states [15–18], it possesses a more analytical form than the semi-empirical BWR and Starling equations. This study has examined the predictive accuracy of the Lee–Kesler equation of state by means of the available experimental binary mixture compressibility data for use in $P–V–T$ calculations. The following 17 binary systems were selected: $CH_4–C_2H_6$, $CH_4–C_4H_{10}$, $CH_4–C_5H_{12}$, $CH_4–C_{10}H_{22}$, $C_2H_6–C_5H_{12}$, $C_3H_8–C_{10}H_{22}$, $H_2–CH_4$, $H_2–C_6H_{14}$, $He–CO_2$, $He–Ar$, $He–N_2$, $He–C_3H_8$, $CH_4–CO_2$,$C_2H_6–CO_2$, $C_3H_8–CO_2$, $N_2–CO_2$ and $Ar–CO_2$.

Experimental data were gathered from a number of sources [19–38] for the gas and liquid compressibilities and the compositions near the critical state condition. The constants and physical properties needed for individual pure components taken from McFee et al. [39] were supplemented by a set of additional values listed in Table 1. The applicability of the Lee–Kesler

TABLE 1

Experimental pure compound data [a]

Compound [b]	Ref.	No. of data points	Reduced pressure range, P_r (atm.)	Reduced temperature range, T_r (K)	Average compressibility factor, Z_{AV} [c]	Compressibility factor range, Z
C_4H_{10}						
gas	19	38	0.26–10.53	0.89–1.20	0.754	0.08–1.39
liquid	20	33	0.04– 5.44	0.69–0.93	0.552	0.07–0.98
C_5H_{12}	19, 22	46	0.30–20.43	0.62–1.09	0.528	0.05–1.50
C_6H_{14}	21	25	0.25– 9.24	0.61–0.94	0.531	0.04–1.47
$C_{10}H_{22}$	23	36	0.82– 9.81	0.48–0.72	0.715	0.09–1.61

[a] Data for pure compounds not presented here are listed by McFee et al. [39].

[b] Physical properties for compounds listed in this Table have been taken from Reid et al. [1,2].

[c] Average compressibility factor $Z_{AV} = (1/n) \sum_i^n Z_i$.

TABLE 2

Summary of experimental data used for binary systems [a]

Binary mixture	Ref.	No. of data points	Pressure range, P (atm.)	Temperature range, T (K)	Composition range, x (1^{st} component)	Compressibility factor range, Z	Average compressibility factor, Z_{AV} [b]
He–N_2	24	45	13–530	183–273	0.16–0.75	0.60–1.71	1.116
He–Ar	25	32	80–320	303–773	0.12–1.00	0.99–1.11	1.040
He–CO_2	26	30	180–560	313–353	0.28–0.78	0.74–1.24	1.145
H_2–CH_4	27	71	13–340	200–283	0.20–0.78	0.73–1.22	0.993
Ar–CO_2	26	29	203–580	313–353	0.29–0.80	0.54–1.19	0.953
N_2–CO_2	26	50	88–580	313–353	0.32–0.77	0.65–1.36	0.978
CH_4–CO_2	28	38	13–340	310–444	0.20–0.67	0.80–1.01	0.865
C_2H_6–CO_2	29	66	6–620	277–511	0.21–0.80	0.31–1.64	0.773
C_3H_8–CO_2	30	76	13–680	311–478	0.18–0.83	0.32–1.43	0.800
CH_4–C_2H_6	31	49	7–204	294–361	0.32–0.92	0.36–0.99	0.853
CH_4–C_4H_{10}	32						
gas		50	7–153	294–394	0.29–0.97	0.54–0.99	0.837
liquid		39	27–153	294–394	0.08–0.78	0.11–0.66	0.423
CH_4–C_5H_{12}	33						
gas		28	1–167	310–444	0.21–0.95	0.44–0.97	0.776
liquid		24	1–160	310–444	0.01–0.77	0.11–0.66	0.286
CH_4–$C_{10}H_{22}$	34	23	6–238	310–444	0.03–0.99	0.04–0.96	0.699
C_2H_6–C_5H_{12}	35	48	13–170	277–410	0.10–0.90	0.05–0.71	0.419
C_3H_8–$C_{10}H_{22}$	36	50	13–170	277–477	0.10–0.90	0.05–1.24	0.504
He–C_3H_8	37	18	5– 62	393–423	0.19–0.61	0.79–1.00	0.938
H_2–C_6H_{14}	38	30	34–204	277–477	0.04–0.99	0.16–1.13	0.744

[a] For pure compound property data listings, see Table 1.

[b] Defined in Table 1, footnote c.

equation (eqns. (3–8)) for binary mixture calculations (Table 2) was tested in three ways: (i) by means of the original Lee–Kesler mixing rules (eqns. (9–14)); (ii) by mixing rules which contain a fixed optimum binary interaction parameter L_{ij}, where $L_{ij} = 1 - k_{ij}$ (eqns. (5–20)); and (iii) following Lielmezs' [40] work on the BWR and Starling equations, by introducing, instead of the fixed optimum interaction parameter L_{ij}, a new binary interaction function $L_{ij}(T, P, x)$ such that $L_{ij} = e + fx + gP + hT$ (eqn. (21)). The Lee–Kesler equation test results obtained were compared with the performance of the BWR and Starling equations tested earlier [40].

The results of the testing were evaluated by comparing the compressibility factors calculated via the equations of state with the experimental binary mixture compressibility factor data over the entire data set by means of the root mean square (RMS) percent error

$$\text{RMS\% error} = \left[\sum_{i=1}^{n} \frac{(\%\ \text{error})^2}{n} \right]^{1/2} \tag{1}$$

TABLE 3

Fixed interaction parameter L_{ij} optimum values calculated by the BWR, Starling and Lee–Kesler equations

Binary mixture	Equation		
	BWR $A_0 = f\ (L_{ij})$ [a]	Starling	Lee–Kesler modified [b]
He–CO_2 [c]	2.15	2.50	0.3
He–N_2 [c]	0.80	1.30	−0.8
He–Ar [c]	1.65	2.99	−0.7
H_2–CH_4 [c]	1.05	1.30	0.8
CH_4–CO_2	0.60	0.75	0.59
C_2H_6–CO_2	0.90	0.96	0.89
CH_3H_8–CO_2	0.85	0.95	0.88
N_2–CO_2	1.30	1.17	1.15
Ar–CO_2	1.07	1.08	1.02
CH_4–C_2H_6		1.04	1.04
CH_4–C_4H_{10}			
gas		1.04	1.05
liquid		1.02	1.05
CH_4–C_5H_{12}			
gas		1.02	1.00
liquid		0.99	1.05
CH_4–$C_{10}H_{22}$ [c]		1.10	1.85
C_2H_6–C_5H_{12}		1.02	1.08
C_3H_8–$C_{10}H_{22}$		0.98	1.60
He–C_3H_8		0.81	−1.50
H_2–C_6H_{14} [c]		1.50	0.99

[a] Term $A_0 = A_0\ (L_{ij})$ only; see discussion by Lielmezs [40].

[b] This work, eqns. (15–20).

[c] Systems insensitive to L_{ij} values; see also discussion by Lielmezs [40].

TABLE 4

Values of the interaction parameter function $L_{ij} = e + fx + gP + hT$, coefficients and the measure of the degree of fit of eqn. (21)

Binary mixture	e	FR_e	f	FR_f	$g \times 10^3$	FR_g	$h \times 10^3$	FR_h	R
CH_4–CO_2									
I	−0.34860	21	0.87761	287	0.63610	48	1.40755	46	0.9216
II	0.11370	4	0.57098	224	0.53379	62	0.93243	37	0.9089
III	−0.19857	12	0.69095	307	−0.22301	10	1.76190	124	0.9306
N_2–CO_2									
I	1.56750	819	−0.89239	147	0.62123	47	–	–	0.8146
II	0.45360	24	–	–	0.27027	60	1.96966	46	0.7233
III	1.04114	68	−0.43842	132	–	–	1.06706	8	0.7518
H_2–CH_4									
II	0.98770	165	–	–	2.41307	47	–	–	0.4962
III	1.45843	86	−1.68254	40	0.93155	5.5	–	–	0.5407
Ar–CO_2									
II	0.41133	3	–	–	–	–	2.06524	8	0.2330
III	1.14614	300	−0.24639	5	–	–	–	–	0.1477

I = BWR equation, single $A_0 = A_0(L_{ij}(T, P, x))$ interaction term [40]. II = Starling equation [40]. III = Modified Lee–Kesler equation (eqns. (15–20)). FR_i = Measure of the degree of fit of the i^{th} parameter ($i = e, f, g, h$) to experimental data [54,55]. R = Measure of degree of fit of the entire eqn. (21) to experimental data [54,55].

TABLE 5

Comparison of RMS% error in compressibility factor Z calculations for binary mixtures using several methods [a]

Binary mixture	RMS% error values						
	Fixed interaction parameter L_{ij}				Interaction parameter function $L_{ij} = e + fx + gP + hT$ (eqn. (21))		
	Original Lee-Kesler equation (eqns. (3)-(13))	Starling equation (ref. 40)	BWR equation $A_0 = A_0(L_{ij})$ (ref. 40)	Modified Lee-Kesler equation (eqns. (15)-(20))	BWR equation $A_0 = f(L_{ij})$	Starling [b] equation	Modified Lee-Kesler equation [b] (eqns. (15)-(20))
He-CO_2	5.00	3.09	3.14	1.95			
He-N_2	2.67	2.68	2.01	1.02			
He-Ar	2.12	2.64	2.45	2.08			
He-C_3H_8	1.10	0.17	0.23	0.43			
CH_4-CO_2	11.07	4.02	3.45	3.69	1.33	1.74	0.80
C_2H_6-CO_2	10.67	2.19	1.57	0.93			
C_3H_8-CO_2	8.96	1.83	1.28	0.97			
N_2-CO_2	5.89	2.21	2.90	1.79	1.35	1.28	0.94
Ar-CO_2	2.87	2.67	2.48	2.37	–	2.29	2.14
CH_4-C_2H_6	2.14	2.03		1.65			
CH_4-C_4H_{10}							
gas	2.37	1.92		2.06			
liquid	1.69	1.63		3.23			
CH_4-C_5H_{12}							
gas	3.76	1.58		1.88			
liquid	4.74	3.83		2.93			
CH_4-$C_{10}H_{22}$	2.83	3.47		5.86			
C_2H_6-C_5H_{12}	2.39	3.50		2.13			
C_3H_8-$C_{10}H_{22}$	1.15	0.47		1.87			
H_2-CH_4	4.08	4.82	3.97	4.02	–	3.89	3.43
H_2-C_6H_{14}	2.49	1.34		4.96			
Average value					1.34	2.30 (1.51)	1.83 (0.87)

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[a] Tables 3 and 4 list the numerical values of the fixed optimum L_{ij} parameters and the values of coefficients e, f, g and h in the interaction function $L_{ij}(T, P, x)$, eqn. (21).

[b] Values in parentheses represent the same two binary systems as those for the BWR equation.

where for each data point 'i'

$$\% \text{ error} = \left[\frac{Z_{\text{calculated}} - Z_{\text{experimental}}}{Z_{\text{experimental}}}\right] \times 100 \tag{2}$$

The optimum set of L_{ij} parameter values was that set of parameters which yielded the lowest RMS% error over the same set of experimental data used. It also contains the average compressibility factor Z_{AV} defined as $Z_{\text{AV}} = (1/n) \Sigma_i^n Z_i$, where Z_i is the i^{th} binary mixture compressibility factor. A low Z_{AV} value indicates the presence of the critical state data points in the given data set. Table 3 gives the fixed interaction parameter L_{ij} optimum values as obtained by different equations of state. Table 4 presents the calculated values of the binary interaction parameter function $L_{ij}(T, P, x) = e + fx + gP + hT$, the dimensionless coefficients e, f, g and h, and shows the measure of the degree of fit for this equation *. Table 5 compares the RMS% errors (eqns. (1,2)) in binary mixture compressibility factor Z values calculated by means of the Lee–Kesler, BWR and Starling equations of state. In this, as in the previous work regarding the pure compounds [39,41,42], the generalized Lee–Kesler method appears to have a slight superiority over the BWR and Starling equations of state in P–V–T calculations.

EQUATIONS OF STATE

Lee–Kesler equation

The Lee–Kesler equation is a classical corresponding-states correlation [14–18,39,41–48]. To predict the compressibility factor Z, Lee and Kesler [14] took the macroscopic states correlation of Pitzer et al. [15–18]

$$Z = Z^{(0)} + \omega Z^{(1)} \tag{3}$$

and used a modified BWR equation given in reduced coordinates as

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^5} + \frac{c_4}{T_r^3 V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right) \tag{4}$$

to calculate the values of $Z^{(0)}$ and $Z^{(1)}$ (eqn. (3)). Constants B, C and D in eqn. (4) are defined as **

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* Compare with the discussion of ref. 40.

** Constants used in eqns. (5–7) are given by McFee et al. [39] and Manji and Lielmezs [41]. Note that ω in the Pitzer relation (eqn. (3)) is replaced by $\omega/0.3978$ for the Lee–Kesler equation. A value of 0.3978 represents the ω value for the reference fluid used (n-octane).

$$B = b_1 - \left(\frac{b_2}{T_r}\right) - \left(\frac{b_3}{T_r^2}\right) - \frac{b_4}{T_r^3}\Bigg) \qquad (5)$$

$$C = c_1 - \left(\frac{c_2}{T_r}\right) + \left(\frac{c_3}{T_r^3}\right) \qquad (6)$$

$$D = d_1 + \left(\frac{d_2}{T_r}\right) \qquad (7)$$

The pseudo-reduced volume, V_r, is given as

$$V_r = \frac{P_c V}{RT_c} \qquad (8)$$

The theoretical basis of the Lee–Kesler equation is found in Pitzer's use of the macroscopic theorem of corresponding states [15–18] and the range of applicability of the modified BWR relation [49] (eqn. (4)). The Pitzer macroscopic theorem of corresponding states, being a first-order perturbation about simple fluid (reference fluid, acentric factor $\omega = 0$) corresponding states, can effectively be applied to moderately large non-spherical molecules to correct non-idealities caused by the molecular size and shape. As such, the work of Lee and Kesler is based on experimental data for hydrocarbons ranging from methane to *n*-octane as the heaviest reference fluid. It is questionable whether the linear form of the Z–ω relation (eqn. (3)) may be extended through the inclusion of higher order Taylor expansion terms [15–18,43]. Attempts have been made [39,42–46] to extend the applicability of the linear Z–ω relation (eqn. (3)) at intervals of $0.2 \leqslant T_r \leqslant 5.0$ and $0.0 \leqslant P_r \leqslant 30$. These extensions are only valid for simple compounds, mostly hydrocarbons, and for certain groups of compounds. Highly polar compounds and quantum fluids may not be included in this type of 3-parameter correlation [39,43]. Recently, however, Chao and Zhong [48] extended the applicability of the Lee–Kesler equation to polar fluids over the range of $T_r = 0.3$–4.0 and $P_r = 0.01$–10 by the addition of a fourth parameter to eqn. (3). The original mixing rules proposed by Lee and Kesler [14] are

$$V_{c_i} = Z_{c_i} \frac{RT_{c_i}}{P_{c_i}} \qquad (9)$$

$$Z_{c_i} = 0.2905 - 0.085\omega_i \qquad (10)$$

$$V_c = \tfrac{1}{8} \sum_j \sum_k x_j x_k \left(V_{c_j}^{1/3} + V_{c_k}^{1/3}\right)^3 \qquad (11)$$

$$T_c = 1/8V_c \sum_j \sum_k x_j x_k \left(V_{c_j}^{1/3} + V_{c_k}^{1/3}\right)^3 \sqrt{T_{c_j} T_{c_k}} \qquad (12)$$

$$\omega = \sum_j x_j \omega_j \qquad (13)$$

$$P_c = Z_c RT_c/V_c = (0.2905 - 0.085\omega)RT_c/V_c \qquad (14)$$

Lee and Kesler [14] suggested these mixing rules, eqns. 9–14, on the basis of a relatively small number of hydrocarbon–hydrocarbon mixtures in the gas and dense gas–liquid phases. Since then, additional sets of mixing rules including the use of an interaction parameter $(1 - k_{ij})$, have been proposed for the Lee–Kesler equation of state [1,2]. The mixing rules adopted for use in this work, however, are those used successfully by Sugie and Lu [50,51] for their equation of state

$$\omega_{\mathrm{m}} = \sum_i x_i \omega_i \tag{15}$$

$$Z_{\mathrm{c_m}} = 0.291 - 0.08\omega_{\mathrm{m}} \tag{16}$$

$$P_{\mathrm{c_m}} = \frac{T_{\mathrm{c_m}}}{\sum_i \left(x_i T_{\mathrm{c}_i}/P_{\mathrm{c}_i}\right)} \tag{17}$$

$$T_{\mathrm{c_m}} = \left\{ \frac{\left[\sum_i \sum_j x_i x_j (1 - k_{ij})\left(T_{\mathrm{c}_i}^{2.5}/P_{\mathrm{c}_i}\right)\left(T_{\mathrm{c}_j}^{2.5}/P_{\mathrm{c}_j}\right)\right]^{1/2}}{\sum_i \left(x_i T_{\mathrm{c}_i}/P_{\mathrm{c}_i}\right)} \right\}^{2/3} \tag{18}$$

Equation (18) was modified by rewriting by binary interaction term $(1 - k_{ij})$ by means of an empirical, optimum binary interaction parameter L_{ij} [1,2,40] as

$$L_{ij} = 1 - k_{ij} \tag{19}$$

Following earlier work of Lielmezs [40], the value of the interaction parameter L_{ij} (eqn. (19)) was estimated two ways: (a) as a fixed optimum binary interaction parameter L_{ij}, independent of thermodynamic state parameters T, P, x; and (b) as a binary parameter function, $L_{ij} = L_{ij}(T, P, x)$ dependent on state variables T, P, x. This empirical mode of estimating the binary interaction parameter L_{ij} value yielded surprisingly large improvements in RMS% errors over a wide state variable T, P, x range for the given equation of state (Tables 1 and 5).

The initial L_{ij} values were obtained by means of eqn. (19) by calculating the corresponding k_{ij} value from the Tarakad and Danner [52] relation

$$k_{ij} = 1 - \frac{8\left(V_{\mathrm{c}_i} V_{\mathrm{c}_j}\right)^{1/2}}{\left(V_{\mathrm{c}}^{1/3} + V_{\mathrm{c}}^{1/3}\right)^3} \tag{20}$$

modified when required for the quantum effects (He, H_2, Ne) [53].

Benedict–Webb–Rubin and Starling equations

For both the BWR and Starling equations of state, the representative mixing rules and the constant sets used in this work were taken from the study by Lielmezs [40] regarding the applicability of these equations in $P-V-T$ calculations of binary mixtures. Tables 1 and 2 supplement the data sets listed by McFee et al. and Lielmezs [39,40].

Interaction parameter function L_{ij}

Following Lielmezs [40], instead of a fixed interaction parameter L_{ij} (eqns. (18,19)), we have introduced an interaction parameter function $L_{ij} = L_{ij}(T, P, x)$, curve-fitted by means of multiple linear regression methods to an equation of the form

$$L_{ij} = e + fx + gP + hT \tag{21}$$

The coefficients e, f, g and h of eqn. (21) are characteristic constants of the given binary system and are dimensionless as x, the mole fraction, is dimensionless, while the state parameter T and P values have been referred to a unit pressure (atm) and unit absolute temperature (K). Results shown in Tables 4 and 5 verify the overall validity of the proposed relation (eqn. (21)).

Experimental data used and computer programming

The summary of experimental data used is given in Tables 1 and 2. As it was assumed that the data presented were of sufficient reliability, further evaluation of their accuracy was not made. The compressibility factor calculation programs of McFee et al. [39] and of Lielmezs [40] were extended to include calculations of binary mixture compressibility factors using the Lee–Kesler equation of state. The determination of the interaction parameter L_{ij} fixed optimum value (Table 3) and the interaction parameter function $L_{ij} = L_{ij}(P, T, x)$ value (eqn. (21), Table 4) for binary mixtures was done following the estimation method of Lielmezs [40].

The measure of the closeness with which the regression surface (eqn. (21)) fitted the experimental data points was established by means of the multiple correlation coefficient R [54,55] such that $0.0 \leqslant R \leqslant 1.0$ (Table 4). The significance of each individual coefficient was tested by the F ratio (FR) or the F test [54,55]. Preset, low FR values served as criteria for omitting variables tested as insignificant from the correlation (eqn. (21), Table 4).

RESULTS AND DISCUSSION

The results are presented in Table 5. For hydrocarbon–hydrocarbon systems the RMS% error indicates that the Lee–Kesler and Starling equations yield similar results. Errors are somewhat larger for the Lee–Kesler equation with CH_4–C_5H_{12} mixtures. However, the original Lee–Kesler equation (eqns. (3–14)) requiring no binary interaction parameter L_{ij} appears to offer an ease of use over the Starling equation. The modified Lee–Kesler equation (eqns. (15–20)) with a fixed binary interaction parameter L_{ij} in the mixing rules (eqns. (19) and (20)) is adequate for hydrocarbon mixtures and shows an edge in accuracy overall when compared to the BWR and Starling equations. Lielmezs [40] has shown that for the BWR and Starling equations of state, the introduction of a single binary interaction parameter L_{ij} as a continuously varying function of T, P and x, presents results of considerable accuracy. Table 5 confirms this by displaying results obtained by means of the modified Lee–Kesler equation (eqns. (15–20)) and the BWR and Starling equations [40] for the CH_4–CO_2, N_2–CO_2, H_2–CH_4 and Ar–CO_2 binary systems. Table 4 amplifies these observations by showing that the introduced interaction parameter function $L_{ij} = L_{ij}(T, P, x)$, eqn. (21), for all state equations considered (Lee–Kesler, BWR and Starling) displays a large dependence on x, although there is also a weaker correlation with T and P (Table 4). The high value of the FR and the multiple correlation coefficient R indicate the relative strength of the proposed $L_{ij} = e + fx + gP + hT$ relation (eqn. (21), Table 4).

Concluding we observe that the Lee–Kesler equation is relatively easy to use and quite accurate for gas and liquid binary mixture compressibility factor calculations. For hydrocarbon–hydrocarbon mixtures, the Lee–Kesler equation may be used with the original mixing rules (eqns. 9–14)), Table 5). The modified Lee–Kesler equation (eqns. (15–20)) with mixing rules containing the fixed optimum value, empirical binary interaction parameter L_{ij} (Table 3), will quite accurately predict the compressibility factors for non-hydrocarbon mixtures (Table 5). Considerable additional improvement in compressibility factor calculations has been achieved by the use of the binary interaction parameter function $L_{ij} = L_{ij}(T, P, x)$, eqn. (21), as shown in Table 5 for some of the more difficult binary mixtures.

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