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COMPARISON OF BENEDICT–WEBB–RUBIN AND STARLING EQUATIONS OF STATE FOR USE IN *P–V–T* CALCULATIONS OF BINARY MIXTURES

J. LIELMEZS

Chemical Engineering Department, The University of British Columbia, Vancouver, B.C. (Canada)

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ABSTRACT

Using the available experimental gas compressibility data, the predictive accuracy of the Benedict–Webb–Rubin and Starling equations of state was tested in $P-V-T$ calculations over a wide range of temperature, pressure and composition for the following binary mixtures: He–N_2, He–Ar, He–CO_2, H_2–CH_4, Ar–CO_2, N_2–CO_2, CH_4–CO_2, C_2H_6–CO_2 and C_3H_8–CO_2. New interaction parameters, $L_{ij} = L_{ij}(T,P,x)$, functionally dependent on temperature (T), pressure (P) and composition (x) were introduced. The root mean square (RMS) percent errors

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

where $\%\ \text{error} = [(Z_{\text{calculated}} - Z_{\text{experimental}})/Z_{\text{experimental}}]\times 100$, calculated over the $T-P-x$ range investigated for all binary mixtures, showed a degree of superiority for the Benedict–Webb–Rubin equation over the Starling equation of state.

INTRODUCTION

The eight-constant Benedict–Webb–Rubin (BWR) [1–6] equation and its modification, the eleven-constant Starling [7–10] equation of state have proved to be highly successful in providing a good description of the thermodynamic behaviour of real fluids for both vapour and liquid phases [11–19]. Lielmezs and coworkers [12] have shown that for pure gas compressibility factor calculations the generalized Starling equation gives good results for the following compounds: CH_4, C_2H_6, C_3H_8, CO_2, N_2, Ar, H_2 and He. They also noted that the BWR equation gives improved results if a reliable constant set is available for each compound [12].

This study examines the use of these two equations of state and the mixture combination rule* in predicting the compressibility factors for

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* A general introduction to various forms of these mixing rules is found in the texts of Reid et al. [20,21] and Prausnitz and Chueh [22].

TABLE 1

Experimental data used [a]

System	Reference	No. of data points	Pressure range, P (atm)	Temperature range, T (K)	Composition range, x, 1st component	Compressibility factor range Z	Average compressibility $Z_{AV} = (1/n)\Sigma_i Z_i$
$He-N_2$	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
$He-CO_2$	29	30	180–560	313–353	0.28–0.78	0.74–1.24	1.145
	31	19	1– 70	293	0.06–0.90	0.70–1.02	0.941
	32	39	16–440	340–700	0.12–0.95	0.62–1.06	0.991
	33	53	1–250	303–343	0.15–0.80	0.69–1.08	0.953
H_2-CH_4	23	71	13–340	200–283	0.20–0.78	0.73–1.22	0.993
$Ar-CO_2$	29	29	203–580	313–353	0.29–0.80	0.54–1.19	0.953
	30	20	1– 25	203–303	0.09–0.67	0.88–1.00	0.962
N_2-CO_2	29	50	88–580	313–353	0.32–0.77	0.65–1.36	0.978
CH_4-CO_2	26	38	13–340	310–444	0.20–0.67	0.80–1.01	0.865
$C_2H_6-CO_2$	27	66	6–620	277–511	0.21–0.80	0.31–1.64	0.773
$C_3H_8-CO_2$	28	76	13–680	311–478	0.18–0.83	0.32–1.43	0.800

[a] Property data for pure compounds taken from McFee et al. [12] and Reid et al. [20,21].

several non-hydrocarbon and hydrocarbon–non-hydrocarbon binary mixtures: $He-CO_2$, $He-N_2$, He–Ar, H_2-CH_4, $Ar-CO_2$, N_2-CO_2, CH_4-CO_2, $C_2H_6-CO_2$ and $C_3H_8-CO_2$. Experimental data were gathered from a number of sources [23–33] for the gas phase compressibilities and for near to the critical state condition. The BWR constants for individual pure components taken from McFee et al. [12] were supplemented by a set of new values for He (see Tables 1 and 2). The applicability of the BWR equation coefficients (eqns. (3)–(11)) for binary mixture calculations, was tested in three ways:

TABLE 2

Recommended binary mixture Benedict–Webb–Rubin constants [a] (eqn. (3)) for He

A	0.000231886
A_0	0.0524262
B	0.00056115
B_0	0.0150686
C	−0.000988
C_0	−1.0360223
α	0.00000472
γ	0.00092675

[a] Pure component critically evaluated BWR constant values for He given by McFee et al. [12].

using the original BWR mixing rules (eqns. (4)–(11)) which do not contain an empirical binary interaction parameter L_{ij}, i.e. L_{ij} is assumed to be 1.0; using mixing rules suggested by Bishnoi and Robinson (eqns. (12)–(15)) which contain a fixed binary interaction parameter L_{ij} ($L_{ij} = 1 - k_{ij}$) for coefficients A_0, C_0, A and C (Tables 3 and 5) and for coefficients B_0 and B (eqns. (16) and (17); Tables 3 and 5); and by introducing in the original BWR mixing rules (eqns. (4)–(11)), in place of the fixed interaction parameter L_{ij}, a new binary interaction parameter function $L_{ij}(T,P,x)$ such that $L_{ij} = e + fx + gP + hT$ (eqn. (41), Tables 4 and 5).

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

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

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 or "best" set of BWR coefficients and/or L_{ij} values was that set of coefficients and/or L_{ij} values which yields the lowest RMS% error over the same set of experimental data. Table 1 presents the summary of experimental data used. It also contains the parameter Z_{AV}*. A low Z_{AV} value indicates the presence of critical state data points in the given data set which are more difficult to curve-fit. Table 2 presents a new set of BWR constants for He to be used for gaseous mixtures ** containing He as a component. Table 3 sums up the fixed interaction parameter L_{ij} optimum values as calculated by several methods while Table 4 presents the calculated values of the dimensionless coefficients e, f, g and h of the interaction parameter function, $L_{ij}(T,P,x) = e + fx + gP + hT$, and shows the measure of the degree of fit for this equation. Table 5 compares the RMS% errors (eqns. (1) and (2)) in compressibility factor Z values calculated for binary mixtures by means of several methods. Table 6 points out the differences in fixed interaction parameter L_{ij} values as obtained by several authors. Figures 1–4 show the fixed interaction parameter L_{ij} dependence on the state parameters T,P and x for three binary systems, thus indicating the need for a state-dependent interaction parameter function $L_{ij}(T,P,x)$ such

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* Z_{AV} is defined as $Z_{AV} = (1/n)\sum_{i=1}^{n} Z_i$, where Z_i is the ith compressibility factor.

** Preliminary calculations, this work, indicated that the BWR coefficients for pure He [12] did not sufficiently describe the curve-fit of binary mixtures containing He as a component.

TABLE 3

Summary of fixed interaction parameter L_{ij} optimum values calculated by several methods

System	BWR equation (eqns. (3)–(17))							Starling generalized equation (eqns. (18)–(40)) A_0 and C_0 changed at the same time
	Original BWR equation mixing rules [a] BWR constants listed [a]						Bishnoi–Robinson [b] mixing rules (eqns. (12)–(15))	
	A_0 eqn. (5)	A eqn. (8)	B_0 eqn. (4)	B eqn. (7)	C_0 eqn. (6)	A_0 and C_0 both changed eqns. (5) and (6)		
	Optimum L_{ij} values calculated							
He–CO_2 [c]	2.15	3.00	2.22	1.67	4.44	1.94	1.60	2.50
He–N_2 [c]	0.80				−2.75	0.65	0.70	1.30
He–Ar [c]	1.65				1.60	1.60	1.50	2.99
H_2–CH_4 [c]	1.05				−1.00	0.97	0.90	1.30
CH_4–CO_2	0.60	−0.40	0.56	0.63	−0.60	0.77	0.80	0.75
C_2H_6–CO_2	0.90				0.94	0.96	0.96	0.96
C_3H_8–CO_2	0.85	0.87	0.69	0.87	0.91	0.94	0.95	0.95
N_2–CO_2	1.30	1.50	1.67	1.43	1.27	1.15	1.15	1.17
Ar–CO_2	1.07				1.04	1.02	1.02	1.08

[a] The listed BWR constant columns A_0, A, B_0, B, C_0 and A_0 and C_0 show obtained fixed interaction parameter L_{ij} optimum values when only the BWR constant is changed from the original simple BWR mixing rules (eqns. (4) and (11)) to a constant containing an interaction parameter.

[b] Constant A_0 and C_0 are changed simultaneously (footnote [a]); the constants D_0 and E_0 (eqns. (28), (29), (38) and (40) acquire that optimum L_{ij} value which has been obtained through this change.

[c] Calculations show that the system is very insensitive to small L_{ij} values changes.

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. (41) [a]

System	e	FR_e	f	FR_f	$g \times 10^3$	FR_g	$h \times 10^3$	FR_h	R
CH_4–CO_2									
I	0.3304	20	0.527978	107	0.506193	31	0.432724	5	0.8121
II	−0.3486	21	0.877605	287	0.636104	48	1.407550	46	0.9216
III	0.1137	4	0.570977	224	0.533789	62	0.932433	37	0.9089
N_2–CO_2									
I	1.2494	2858	−0.367444	139	0.258980	46	–	–	0.8073
II	1.5675	819	−0.892386	147	0.621234	47	–	–	0.8146
III	0.4536	24	–	–	0.270269	60	1.96966	46	0.7231
He–N_2									
I	−0.0473	0.1	0.624319	12	1.07685	21	1.72163	5	0.4973
II	−0.1997	1.1	0.743731	15	1.18828	24	2.99624	14	0.5827
III	−0.1184	0.2	–	–	3.03499	72	4.27556	13	0.6795
He–CO_2									
I	−3.4174	92	1.51846	213	0.91318	28	12.4164	133	0.9408
II	−5.5547	75	1.69012	81	1.95124	40	19.1073	97	0.9051
III	−5.4164	52	1.45396	43	1.91921	28	19.9601	76	0.8669
Ar–CO_2									
III	0.4113	3	–	–	–	–	2.06524	8	0.2330
H_2–CH_4									
III	0.9877	165	–	–	2.41307	47	–	–	0.4962
He–Ar									
III	0.7307	4	1.74845	13	7.00576	27	–	–	0.5909

[a] Symbols to Table 4: I BWR eqn. with Bishoi–Robinson mixing rules (eqns. (12)–(15)). II BWR eqn. with single $A_0 = A_0(L_{ij}(T,P,x)$ interaction term used. III Starling generalized equation, eqns. (18)–(40). FR_i, Measure of the degree of fit of the ith parameter ($i = e, f, g, h$) to experimental data [40,41]. R, Measure of the degree of fit of the entire eqn. (41) to experimental data [40,41].

TABLE 5

Comparison of RMS% error (eqns. (1) and (2)) in compressibility factor, Z, calculations for binary mixtures using several methods [a]

System	RMS% error values											
	Fixed interaction L_{ij} parameter BWR equation (eqns. (3)–(17))								Starling generalized equation (eqns. (18)–(40))	Interaction parameter function $L_{ij} = e + fx + gP + hT$ (eqn. (41))		
	BWR constants						Simple BWR eqn. mixing $L_{ij} = 1.0$ (eqns. (4)–(11))	Bishnoi–Robinson mixing rules (eqns. (12)–(15))		BWR equation		Starling generalized equation
	A_0 eqn. (5)	A eqn. (8)	B_0 eqn. (4)	B eqn. (7)	C_0 eqn. (6)	A_0 and C_0 eqns. (5) and (6)				$A_0(L_{ij}(T,P,x))$ parameter method (eqns. (5) and (41))	Bishnoi–Robinson mix. rules (eqns. (12)–(15))	
He–N_2	2.01					1.89	2.25	1.88	2.68	1.12	1.17	1.51
He–Ar	2.45					2.45	2.49	2.45	2.64			2.36
He–CO_2	3.14	4.17	2.90	3.76	3.56	3.14	6.37	3.40	3.09	0.96	1.35	0.91
H_2–CH_4	3.97					3.94	3.99	4.07	4.82			3.89
Ar–CO_2	2.48					2.49	2.72	2.47	2.67			2.29
N_2–CO_2	2.90	2.35	2.85	2.02	2.97	2.91	6.18	2.95	2.21	1.35	1.27	1.28
CH_4–CO_2	3.45	3.92	3.83	4.67	3.17	3.27	10.03	3.32	4.02	1.33	1.99	1.74
C_2H_6–CO_2	1.57					1.48	5.44	1.62	2.19			
C_3H_8–CO_2	1.28	2.02	1.36	2.12	1.51	1.37	3.96	1.44	1.83			
Average	2.58	3.12	2.74	3.14	2.80	2.55	4.83	2.62	2.91	1.19	1.45	1.36 (1.99) [b]

[a] For the numerical values of the fixed optimum L_{ij} parameters and the values of coefficients e, f, g and h found in the interaction parameter function $L_{ij}(T,P,x)$, eqn. (41), refer to Tables 3 and 4.

[b] Smaller average value (1.36) represents the same four binary systems as those for the BWR equation; larger average value (1.99) represents the average of all binary systems calculated by means of the Starling generalized equation.

TABLE 6

Comparison of interaction parameter L_{ij} values obtained by several authors

System	Method			
	Starling eqn. (eqns. (18)–(40))		BWR eqn. (eqns. (3)–(17))	
	This work (Tables 3 and 4)	Starling and Han [1–6]	This work (Tables 3 and 4)	Chueh and Prausnitz [22]
CH_4–CO_2	0.75	0.95	0.80	0.95
C_2H_6–CO_2	0.96	0.952	0.96	0.92
C_3H_8–CO_2	0.95	0.955	0.95	0.89
N_2–CO_2	1.17	1.00	1.15	–
H_2–CO_2 [a]	1.30	0.99	0.90	0.97

[a] Calculated including quantum effect correction [12].

as eqn. (41), Tables 3–5. In this, as in the previous work [12], the multiproperty linear regression method (BWR equation of state) proved to be overall more accurate than the generalized Starling equation even if the multiproperty regression approach is computer time consuming and not always in

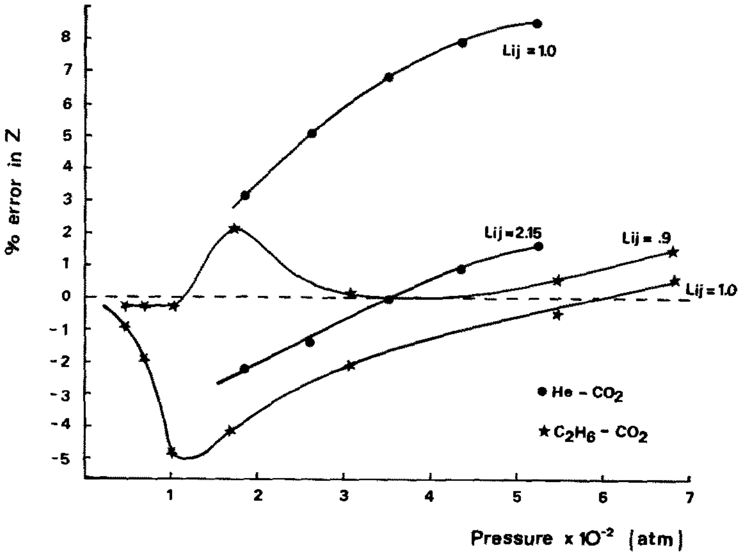

Fig. 1. Change of percentage-error in Z as a function of pressure, P, keeping interaction parameter L_{ij} fixed for: C_2H_6–CO_2 system at $x = 0.1777$; $T = 344.26$ K and $A_0 = f(L_{ij})$ only, and He–CO_2 system at $x = 0.5144$; $T = 313.05$ K and $A_0 = f(L_{ij})$

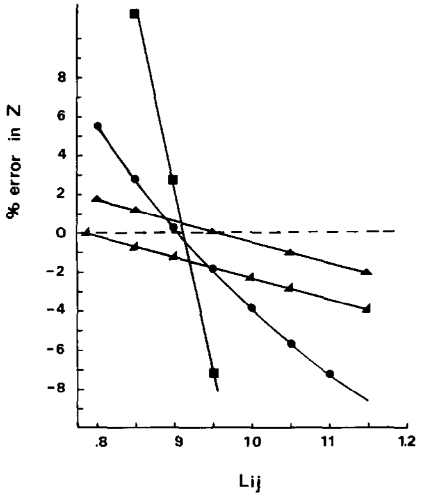

Fig. 2. Change of percentage error in Z as a function of the interaction parameter L_{ij} for C_2H_6–CO_2 system with $A_0 = f(L_{ij})$ at the following conditions: ■——■ $x = 0.1777$, $P = 85.03$ atm, $T = 310.93$ K, $Z = 0.3929$; ●——● $x = 0.1532$, $P = 170.07$ atm, $T = 310.93$ K, $Z = 0.467$; ◢——◢ $x = 0.1777$, $P = 40.82$ atm, $T = 310.93$ K, $Z = 0.7951$; ▲——▲ $x = 0.1777$, $P = 544.22$ atm, $T = 344.26$ K, $Z = 1.0177$.

itself successful (Tables 3–6). Varying the interaction parameter L_{ij} or introducing the interaction parameter function $L_{ij}(T,P,x)$ reduced errors for several binary mixtures (Tables 3–6).

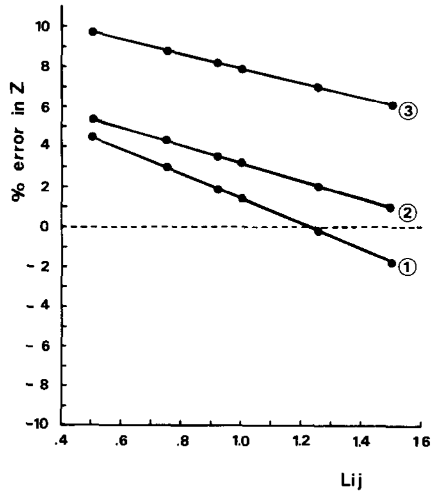

Fig. 3. Change in percentage error in Z as a function of interaction parameter L_{ij} for He–CO_2 system with $A_0 = f(L_{ij})$ only at fixed temperature $T = 313.05$ K for the following conditions: (1) $x = 0.2813$, $P = 184.56$ atm, $Z = 0.7450$; (2) $x = 0.5144$, $P = 184.43$ atm, $Z = 0.9395$; (3) $x = 0.7741$, $P = 522.25$ atm, $Z = 1.2315$.

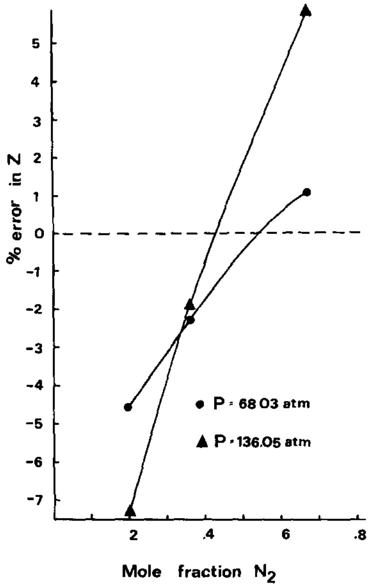

Fig. 4. Change of percentage error in Z as a function of mole fraction x for N_2–CO_2 system at fixed temperature $T = 310.93$ K and $L_{ij} = 0.60$, and with $A_0 = f(L_{ij})$ for two pressures $P = 68.03$ atm and $P = 136.05$ atm.

EQUATIONS OF STATE

Benedict–Webb–Rubin (BWR) equation

The BWR equation of state [1–6] is

$$P = RT\rho + \left(B_0RT - A_0 - \frac{C_0}{RT^2}\right)\rho^2 + (BRT - A)\rho^3 + A\alpha\rho^6 + \frac{C\rho^3}{T^2}(1 + \gamma\rho^2) + \exp(-\gamma\rho^2) \tag{3}$$

where B_0, A_0, C_0, B, A, C, α and γ are eight empirical constants [1,2].

The original mixture rules proposed by Benedict et al. [1–6] are

$$B_0 = \sum_i x_i B_{0i} \tag{4}$$

$$A_0 = \left[\sum_i x_i (A_{0i})^{1/2}\right]^2 \tag{5}$$

$$C_0 = \left[\sum_i x_i (C_{0i})^{1/2}\right]^2 \tag{6}$$

$$B = \left[\sum_i x_i (B_i)^{1/3}\right]^3 \tag{7}$$

$$A = \left[\sum_i x_i (A_i)^{1/3}\right]^3 \tag{8}$$

$$C=\left[\sum_i x_i (C_i)^{1/3}\right]^3 \tag{9}$$

$$\alpha=\left[\sum_i x_i (\alpha_i)^{1/3}\right]^3 \tag{10}$$

$$\gamma=\left[\sum_i x_i (\gamma_i)^{1/2}\right]^2 \tag{11}$$

These mixing rules (eqns. (4)–(11)) were shown to be adequate by the original investigators [1–6] for many of the hydrocarbon–hydrocarbon systems. To improve the mixing rule predictive accuracy for non-hydrocarbon–hydrocarbon systems at low temperatures and possibly at elevated pressures, researchers [16,17,34–37] have suggested that binary interaction parameters be introduced into the cross-interaction terms of the BWR original mixing rules. Thus Bishnoi and Robinson [16,17,34,35], utilizing the previous work of Stotler and Benedict [36] and Motard and Organick [37], proposed the following mixing rules involving the interaction parameter L_{ij}.

$$A_{0ij}=\left(A_{0i}A_{0j}\right)^{1/2}L_{ij} \tag{12}$$

$$C_{0ij}=\left(C_{0i}C_{0j}\right)^{1/2}L_{ij}^3 \tag{13}$$

$$A_{ij}=\left(A_iA_j\right)^{1/2}L_{ij} \tag{14}$$

$$C_{ij}=\left(C_iC_j\right)^{1/2}L_{ij}^3 \tag{15}$$

In this work the effect of the binary interaction parameter L_{ij} on the original B_0 term was considered to be (Tables 3 and 5)

$$B_{0ij}=\left(B_{0i}B_{0j}\right)^{1/2}/L_{ij} \tag{16}$$

$$B_{ij}=\left(B_iB_j\right)^{1/2}/L_{ij} \tag{17}$$

Starling equation

The Starling [7–10] equation * is an extension of the BWR equation of state with temperature corrections for C_0 (additional constants D_0 and E_0) and A (additional constant d)

$$P=RT\rho+\left(B_0RT-A_0-\frac{C_0}{T^2}+\frac{D_0}{T^3}-\frac{E_0}{T^4}\right)\rho^2+\left(bRT-a-\frac{d}{T}\right)\rho^3 \\ +\alpha\left(a+\frac{d}{T}\right)\rho^6+\frac{c\rho^3}{T^2}(1+\gamma\rho^2)\exp(-\gamma\rho^2) \tag{18}$$

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* All the data needed for the evaluation of the Starling equation for pure components are taken from McFee et al. [12].

Starling et al. [7–10] expressed the eleven pure component parameters (eqn. (18)) as the following functions of the component acentric factor ω_i, the critical temperature T_{ci} and critical density ρ_{ci}

$$\rho_{ci} B_{0i} = A_1 + B_1 \omega_i \tag{19}$$

$$\frac{\rho_{ci} A_{0i}}{RT_{ci}} = A_2 + B_2 \omega_i \tag{20}$$

$$\frac{\rho_{ci} C_{0i}}{RT_{ci}^3} = A_3 + B_3 \omega_i \tag{21}$$

$$\rho_{ci}^2 \gamma_i = A_4 + B_4 \omega_i \tag{22}$$

$$\rho_{ci}^2 b_i = A_5 + B_5 \omega_i \tag{23}$$

$$\frac{\rho_{ci}^2 a_i}{RT_{ci}} = A_6 + B_6 \omega_i \tag{24}$$

$$\rho_{ci}^3 \alpha_i = A_7 + B_7 \omega_i \tag{25}$$

$$\frac{\rho_{ci}^2 c_i}{RT_{ci}^3} = A_8 + B_8 \omega_i \tag{26}$$

$$\frac{\rho_{ci} D_{0i}}{RT_{ci}^4} = A_9 + B_9 \omega_i \tag{27}$$

$$\frac{\rho_{ci}^2 d_i}{RT_{ci}^2} = A_{10} + B_{10} \omega_i \tag{28}$$

$$\frac{\rho_{ci}^2 E_{0i}}{RT_{ci}^5} = A_{11} + B_{11} \omega_i \tag{29}$$

The mixing rules proposed by Starling et al. [7–10] are similar to the BWR rules *, and in effect are a combination of the suggestions of Stotler and Benedict [36], the A_0 term, and of Motard and Organick [37], the C_0 term but with the interaction parameter L_{ij} in the D_0 and E_0 terms also, as these terms modify the C_0 term.

The mixing rules used in this work are

$$B_0 = \sum_i x_i B_{0i} \tag{30}$$

$$A_0 = \sum_i \sum_j x_i x_j A_{0i}^{1/2} A_{0j}^{1/2} L_{ij} \tag{31}$$

$$C_0 = \sum_i \sum_j x_i x_j C_{0i}^{1/2} C_{0j}^{1/2} L_{ij}^3 \tag{32}$$

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* Nishiumi and Saito [38] define mixture behaviour for their fifteen-constant extended BWR equation by means of mixing rules set solely in terms of state parameters T_c, ρ_c and ω.

$$\gamma = \left[\sum_i x_i \gamma_i^{1/2}\right]^2 \tag{33}$$

$$b = \left[\sum_i x_i b_i^{1/3}\right]^3 \tag{34}$$

$$a = \left[\sum_i x_i a_i^{1/3}\right]^3 \tag{35}$$

$$\alpha = \left[\sum_i x_i \alpha_i^{1/3}\right]^3 \tag{36}$$

$$c = \left[\sum_i x_i c_i^{1/3}\right]^3 \tag{37}$$

$$D_0 = \sum_i \sum_j x_i x_j D_{0i}^{1/2} D_{0j}^{1/2} L_{ij}^4 \tag{38}$$

$$d = \left[\sum_i x_i d_i^{1/3}\right]^3 \tag{39}$$

$$E_0 = \sum_i \sum_j x_i x_j E_{0i}^{1/2} E_{0j}^{1/2} L_{ij}^5 \tag{40}$$

Interaction parameter function $L_{ij}(T,P,x)$

The binary interaction parameter L_{ij}, or as it is often referred to, $(1 - k_{ij})$, is generally assumed to be a constant *, characteristic of each binary system and independent of temperature, pressure and composition [20–22]. The original BWR mixing rules (eqns. (4)–(11)) involving mixtures of the same compound family (hydrocarbons–hydrocarbons) neglect the small same-compound family interactions and can be "normalized" * by the statement that for those particular mixing conditions, $L_{ij} = 1.0$. For mixtures characterized by interactions between dissimilar compounds, the original BWR mixing rules appear to be insufficient (Table 4) so that an interaction parameter, $L_{ij} \neq 1.0$, should be introduced.

Figure 1 illustrates this effect for the two systems C_2H_6–CO_2 and He–CO_2. Curves are presented with the mixing term for A_0 for these systems modified by including the binary interaction parameter $L_{ij} \neq 1.0$ and with the original BWR mixing rules ($L_{ij} = 1.0$).

Figures 2 and 3 show how changing the L_{ij} values affects the calculated compressibility factor Z for C_2H_6–CO_2 and He–CO_2 binary mixtures: the relationship between the percentage difference in the calculated and experimental compressibilities and the L_{ij} values is nearly linear; the slope of this

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* For similar molecules, identified as $i = j$, $k_{ii} = 0$, yielding $L_{ii} = 1.0$; for dissimilar molecules, $i \neq j$, so that $k_{ij} \neq 0$ and $L_{ij} \neq 1$.

relationship varies for different systems and for different conditions within a given system; L_{ij} becomes an important parameter near the critical point i.e. at low Z values, of a mixture where the original BWR mixing rules work least well and where small changes in L_i values (Fig. 2, C_2H_6–CO_2) may make large differences in the P–V–T relations; and the estimated errors in Z for some binary systems seem to cluster around an optimum L_{ij} value (for C_2H_6–CO_2 this occurs near $L_{ij} = 0.90$) while for other systems such as He–CO_2 there is no such distinct L_{ij} value.

Figure 1 indicates that the calculated compressibility factor for the He–CO_2 system varies with pressure while Fig. 4 shows a systematic change in Z values with composition for the N_2–CO_2 binary mixture. These observations prompt the suggestion that the binary interaction parameter L_{ij} is functionally dependent on the state parameters, temperature T, pressure P and composition x, i.e. instead of the fixed interaction parameter L_{ij}, an interaction parameter function $L_{ij}(T,P,x)$ curve-fitted by means of multiple linear regression methods to an equation of the form

$$L_{ij} = e + fx + gP + hT \qquad (41)$$

is introduced. The coefficients e, f, g and h are characteristic constants of the given binary system and are dimensionless because x, the mole fraction, is a dimensionless entity while the inputted state parameter P and T values have been referred to a reference state of unit pressure (atm) and unit absolute temperature (K). Tables 4 and 5 attest to the overall validity of the proposed relation (eqn. (41)). The proposed relation (eqn. (41)) is indirectly strengthened by the earlier work of Gugnoni et al. [39] who showed that the binary interaction parameter k_{ij} for the A_0 mixing term for the C_2H_6–CO_2 system, is a strong function of temperature.

EXPERIMENTAL DATA USED AND COMPUTER PROGRAMMING

The summary of experimental data used is given in Table 1. It is assumed that the data presented were of sufficient reliability so that further evaluation of their accuracy was not made.

Table 2 presents a set of new BWR constants of He to be used in mixture calculations containing He as a component *. This set of constants does not possess low temperature (quantum) corrections and hence is to be used for temperatures above 50 K. This set was obtained by means of the Starling generalized equations (eqns. (18)–(26), (30)–(37); constants d, D_0 and E_0 were not required) with the Prausnitz and Chueh [22] effective critical constants for He, $T_c = 10.47$ K; $V_c = 0.0375$ l mol^{-1}.

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* The presented constants (Table 2) supplement the set of BWR constants for pure He found in the work of McFee et al. [12].

The pure gas compressibility factor calculation programs of McFee et al. [12] were extended to include calculations of mixture compressibility factors. Experimental data for some difficult-to-fit mixtures involving CO_2 and the quantum gases He and H_2 were used to test the mixing rules (eqns. (30)–(40)) and the equations of state (eqns. (18)–(29)). The interaction parameter L_{ij} optimum value for a mixture (Tables 3–6) was found by varying the L_{ij} parameter until a minimum RMS% error value was found. The determination of the interaction parameter function $L_{ij}(T,P,x)$ value consisted of the evaluation of the coefficients e, f, g and h of eqn. (41) by iterating the L_{ij} valueuntil a preset tolerance limit in calculated compressibility factor value was reached. The calculations were performed by means of linear regression analysis program which curve-fitted the L_{ij} value against the corresponding T, P, x data till the final values of the coefficients e, f, g and h characterizing the state variables T, P and x (eqn. (41), Tables 4 and 5) were obtained. The measure of the closeness with which the regression plane fitted the experimental data points was established by means of the multiple correlation coefficient, R [40,41], such that $0 \leqslant R \leqslant 1.0$ (Table 4). The significance of each individual coefficient was tested by the F ratio (FR) or the F test [40,41]. Preset, low FR values served as criteria for omitting variables tested as insignificant from the correlation (eqn. (41), Table 4).

RESULTS AND DISCUSSION

Table 3 contains a summary of the fixed interaction parameter L_{ij} optimum values calculated by means of several methods. Table 4 presents the values of coefficients e, f, g and h for the calculation of the interaction parameter L_{ij} value using eqn. (41). Table 5 compares the RMS% error values obtained using both methods, the fixed interaction parameter L_{ij} optimum value approach (Table 3), and the interaction parameter function, $L_{ij}(T,P,x)$, using eqn. (41) to calculate "localized" L_{ij} values for the given T,P,x conditions (Table 4). The first five columns of Table 5 show results obtained when only the BWR equation constant listed is modified by the optimum value of the interaction parameter L_{ij}. The sixth column shows results when the constants A_0 and C_0 are simultaneously modified by the fixed binary interaction parameter L_{ij}. The next three columns compare results obtained by means of the original BWR mixing rules ($L_{ij} = 1.0$; eqns. (4)–(11), the Bishnoi–Robinson mixing rules ($L_{ij} \neq 1.0$, eqns. (12)–(15)) and the application of the fixed binary interaction parameter L_{ij} for the generalized Starling equation (eqns. (18)–(40)).

As seen from Table 5, when a fixed binary interaction parameter L_{ij} is used, the RMS% error for almost all systems is significantly lower than with the original BWR equation mixing rules. The decrease in RMS% error is due to an improved curve-fit in predicting the low Z values at the critical and near the critical state regions. These regions are not adequately described by the original BWR equation mixing rules. Table 5 indicates that for the fixed interaction parameter L_{ij}, almost the same accuracy may be obtained using a variety of mixing rules. Note however that the optimum value of the interaction parameter L_{ij} may somewhat depend on the mixing rule used. The results show (Table 5) that for binary mixture compressibility factor calculations, the BWR equation has a slight superiority over the generalized Starling equation. Whether the Starling equation might be more accurate than the BWR equation, due to the extra terms for binary mixture derivative property calculations, is a subject for further inquiry.

The second part of Table 5 shows that the use of the binary interaction parameter function $L_{ij}(T, P, x) = e + fx + gP + hT$ (eqn. (41)) improved the RMS% error curve-fit for He–N_2, He–CO_2, N_2–CO_2 and CH_4–CO_2 mixtures for both the BWR equation (two types of mixing rules) and the generalized Starling equation. Table 4 indicates that the certainty of this improved curve-fit, as measured by R (multiple correlation coefficient), is very good for these systems. The certainty of each individual coefficient e, f, g and h, as measured by their F ratios (FR) is also quite good. Less improvement is noted for the Ar–CO_2, He–Ar and H_2–CH_4 systems. Only for the C_2H_6–CO_2 and C_3H_8–CO_2 systems does the parameter L_{ij} seem to become constant for all the mixing rules listed.

Data sets for calculating L_{ij} values from eqn. (41) must include high pressure and critical region states if these regions are to be studied by means of a state equation. Kato et al. [42] imply that in addition to the state properties, interaction parameters may differ for different thermodynamic properties. Thus, Nishiumi and Saito [38] present a series of correlations of the binary interaction parameter with V_{c1} and V_{c2} to be used with their T_c, P_c mixing rules for vapour–liquid equilibrium calculations.

Table 6 shows that for the same binary mixture different investigators propose considerably varying fixed interaction parameter L_{ij} values. This may introduce large curve-fit RMS% error variations. For instance, for the C_2H_6–CO_2 system, for the BWR equation with the Bishnoi–Robinson mixing rules, use of $L_{ij} = 0.92$ as suggested by Prausnitz and Chueh [22] may lead to an RMS% error larger than 10% in the critical state region for the compressibility factor. If $L_{ij} = 0.96$ is used (this work *, Table 6), there is an overall RMS% error of 2.19.

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* To obtain the optimum L_{ij} value for the C_2H_6–CO_2 system (Table 6) the following calculated results were compared: for $L_{ij} = 0.97$, RMS% error = 3.13; for $L_{ij} = 0.96$, RMS% error = 2.19, for $L_{ij} = 0.95$, RMS% error = 2.26; for $L_{ij} = 0.94$, RMS% error = 3.20; for $L_{ij} = 0.90$, RMS% error = 8.37. From these results, $L_{ij} = 0.96$ was selected as the fixed optimum value.

This study indicated that both the BWR equation and the Starling generalized equation can predict with sufficient accuracy the gas phase binary mixture compressibility factor over a wide range of thermodynamic conditions if mixing rules used include reliable binary interaction parameters L_{ij} (Tables 3–6). If the ease of use of the state equation is considered, then the Starling generalized equation, or a version of the BWR equation where only the A_0 term for the mixture contains an interaction parameter L_{ij}, would appear to be suitable for calculating the compressibility factor of the binary gas mixture (Tables 3–5).

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LIST OF SYMBOLS

A_0, B_0, C_0, A, B, C, α, γ	B–W–R equation constants
A_0, B_0, C_0, D_0, E_0, a, b, c, d, α, γ	Starling equation constants
e, f, g, h	dimensionless coefficients of eqn. (41)
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 fraction
Z	compressibility factor
ρ	density
ω	acentric factor

Subscripts

c	critical state
i, j	components of binary mixture
r	reduced state (with respect to the vapor–liquid critical state)

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