Generalized Equation of State for Vapors and Liquids

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The Redlich-Kwong equation of state (*23*) is generally recognized as one of the best generalized two-parameter equations. Many attempts (*1, 8, 23, 24*) have been made in the literature to improve its accuracy. In general, the acentric factor of Pitzer ω has been used as a third parameter, in addition to the critical temperature and pressure of the original equation. In an earlier article (*27*), a generalized pressure-explicit equation of state has been proposed for nonpolar gases in the $T_r \geqq 1.0$ region. In the development, the Redlich-Kwong equation of state was modified by means of a deviation function approach and Pitzer's tables (*20*) were used as a guide. The purpose of this investigation is to develop a suitable equation for the vapor and liquid regions using the same approach. It is expected that the resulting equation is applicable in the $0.56 < T_r \leqq 1.0$ region of Pitzer's tables, and is suitable for predicting the vapor and the liquid compressibility factors, enthalpy departures in the vapor phase, and vapor-phase fugacities of nonpolar pure substances and mixtures. In addition, it satisfies Z_c and the usual first two pressure-volume derivatives at the critical point.

DEVELOPMENT OF PROPOSED EQUATION

Following the approach developed in the previous article (*27*), the critical isotherm of the original Redlich-Kwong equation of state was first linearly transformed to pass through the true critical point by the introduction of a constant c in the original equation. Hence

$$P = \frac{RT}{v - b + c} - \frac{aT^{-0.5}}{(v+c)(v+b+c)} \tag{1}$$

in which

$$a = a^* \left(\frac{R^2 T_c^{2.5}}{P_c}\right), \qquad a^* = 0.42748 \tag{2}$$

$$b = b^* \left(\frac{R T_c}{P_c}\right), \qquad b^* = 0.08664 \tag{3}$$

$$c = c^* \left(\frac{R T_c}{P_c}\right), \qquad c^* = \frac{1 - 3Z_c}{3} \tag{4}$$

The constants a^* and b^* are those obtained from the original Redlich-Kwong equation by setting the first two pressure-volume derivatives to zero at the critical point. Since this linear transformation carried the critical isotherm too far to the left in the $P - v$ diagram at the left of the critical point, further modification was necessary. A pressure-explicit deviation function approach was followed and the three-parameter tabular correlation of Pitzer et al. (*20*) was used as the basis of the curve fitting in the determination of the coefficients of the deviation function.

Pitzer et al. (*20*) suggested that a linear equation in ω is usually adequate for representing Z. At the critical point, the following relationship was used in this investigation:

$$Z_c = 0.291 - 0.080\ \omega \tag{5}$$

The expression for the deviation function ΔP was chosen as follows:

$$\Delta P = \sum_{j=1}^{m} \frac{f_j(T)}{(v - K)^{j+1}} \tag{6}$$

Furthermore, three conditions were set at the critical point as follows:

$$(\ \Delta P\ )\ \text{critical} = 0 \tag{7}$$

$$\left(\frac{\partial \Delta P}{\partial v}\right) \text{critical} = 0 \tag{8}$$

$$\left(\frac{\partial^2 \Delta P}{\partial v^2}\right) \text{critical} = 0 \tag{9}$$

Following the suggestions of Redlich and Kwong (*22*), Beattie and Bridgeman (*3*), and Martin and Hou (*13*), the following expressions were considered in this investigation for choosing the temperature function $f_j(T)$:

$$f_j(T) = d_j T + e_j T^{-0.5} \tag{10}$$

$$f_j(T) = d_j + e_j T + g_j T^{-2} \tag{11}$$

$$f_j(T) = d_j + e_j T + g_j e^{-5.475\ T_r} \tag{12}$$

where d_j, e_j, and g_j are constants for pure substances. For

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the constant K of Equation (6), three cases were considered: $K = 0$, $K = b$, and $K = b - c$. Values of Pitzer's tables in the $0.56 < T_r \leqq 1.0$ region were fitted by means of Equation (6) with an assumed value of m together with one of the three $f_j(T)$ expressions and one of the three K values. The best results were obtained when $K = 0$. Furthermore, all three expressions of $f_j(T)$ were found to be satisfactory. Equation (10) was adopted not only because its expression is shorter but extension of its coefficients to mixture is simpler as no additional mixing rules will be required. The value of m was chosen to be 10. Hence, the final expression of the deviation function was obtained as follows:

$$\Delta P = \sum_{j=1}^{10} \frac{d_j T + e_j T^{-0.5}}{v^{j+1}} = \sum_{j=1}^{10} \frac{d_j^* T_r + e_j^* T_r^{-0.5}}{(Z T_r/P_r)^{j+1}} \tag{13}$$

where d_j^* and e_j^* are functions of the acentric factor ω. In order to satisfy the conditions set at the critical point [Equations (7) to (9)], the expressions for e_1^*, e_2^*, and e_3^* were fixed as follows:

$$e_1^* = -\sum_{j=1}^{10} \frac{(j-2)(j-3)}{2} \frac{d_j^*}{Z_c^{j-1}} - \sum_{j=4}^{10} \frac{(j-2)(j-3)}{2} \frac{e_j^*}{Z_c^{j-1}} \tag{14}$$

$$e_2^* = \sum_{j=1}^{10} (j-1)(j-3) \frac{d_j^*}{Z_c^{j-2}} + \sum_{j=4}^{10} (j-1)(j-3) \frac{e_j^*}{Z_c^{j-2}} \tag{15}$$

$$e_3^* = -\sum_{j=1}^{10} \frac{(j-1)(j-2)}{2} \frac{d_j^*}{Z_c^{j-3}} - \sum_{j=4}^{10} \frac{(j-1)(j-2)}{2} \frac{e_j^*}{Z_c^{j-3}} \tag{16}$$

By using the standard curve fitting technique, d_j^* ($1 \leqq j \leqq 10$) and e_j^* ($4 \leqq j \leqq 10$) were finally determined, and were found to be linear functions of ω. The results are listed in Table 1.

Furthermore, when these results, together with Equation (5), were substituted into Equations (14) to (16), the quantities e_1^*, e_2^*, and e_3^* were also found to be practically linear in ω as shown in Figure 1. Hence

$$e_1^* = -5.1775 \times 10^{-2} - 6.8365 \times 10^{-1} \omega \tag{17}$$

$$e_2^* = 3.5828 \times 10^{-2} + 2.8289 \times 10^{-1} \omega \tag{18}$$

$$e_3^* = -1.5493 \times 10^{-2} - 8.9116 \times 10^{-2} \omega \tag{19}$$

Finally, the proposed generalized equation of state, which is explicit in pressure, is given as follows:

$$P = \frac{RT}{v - b + c} - \frac{aT^{-0.5}}{(v + c)(v + b + c)} + \sum_{j=1}^{10} \frac{d_j T + e_j T^{-0.5}}{v^{j+1}} \tag{20}$$

where

$$d_j = d_j^* \left(\frac{R^{j+1} T_c^j}{P_c^j} \right) \tag{21}$$

$$e_j = e_j^* \left(\frac{R^{j+1} T_c^{j+1.5}}{P_c^j} \right) \tag{22}$$

MIXING RULES

In order to extend the proposed equation to mixtures, mixing rules are required for the coefficients. The expressions for d_j and e_j [Equations (21) and (22)] may be rearranged to give

$$d_j = d_j^* R^{j+1} \left(\frac{T_c}{P_c} \right)^j \tag{23}$$

$$e_j = e_j^* R^{j+1} \left(\frac{T_c^{2.5}}{P_c} \right) \left(\frac{T_c}{P_c} \right)^{j-1} \tag{24}$$

By considering Equations (2) to (4) and (23) and (24), the following mixing rules are proposed:

$$a_M = a_M^* R^2 \left(\frac{T_c^{2.5}}{P_c} \right)_M \tag{25}$$

$$b_M = b_M^* R \left(\frac{T_c}{P_c} \right)_M \tag{26}$$

Table 1. Numerical Values of Coefficients of Equation (20)

$$a^* = 0.42748$$

$$b^* = 0.08664$$

$$c^* = (1 - 3Zc)/3$$

$$d_1^* = 9.7806 \times 10^{-2} + 7.0750 \times 10^{-1} \omega$$

$$d_2^* = -6.5927 \times 10^{-2} - 3.0890 \times 10^{-1} \omega$$

$$d_3^* = 1.4085 \times 10^{-2} + 1.0353 \times 10^{-1} \omega$$

$$d_4^* = 2.8115 \times 10^{-3} - 9.8715 \times 10^{-3} \omega$$

$$d_5^* = -1.1178 \times 10^{-3} + 6.6578 \times 10^{-4} \omega$$

$$d_6^* = 2.3658 \times 10^{-5} + 4.6647 \times 10^{-5} \omega$$

$$d_7^* = 1.6314 \times 10^{-5} - 2.6384 \times 10^{-5} \omega$$

$$d_8^* = -2.6225 \times 10^{-7} + 4.4515 \times 10^{-7} \omega$$

$$d_9^* = -1.1441 \times 10^{-7} + 1.8492 \times 10^{-8} \omega$$

$$d_{10}^* = 2.6681 \times 10^{-9} + 1.3076 \times 10^{-8} \omega$$

$$e_1^* = -\sum_{j=1}^{10} \frac{(j-2)(j-3)}{2} \frac{d_j^*}{Zc^{j-1}} - \sum_{j=1}^{10} \frac{(j-2)(j-3)}{2} \frac{e_j^*}{Zc^{j-1}}$$

$$e_2^* = \sum_{j=1}^{10} (j-1)(j-3) \frac{d_j^*}{Zc^{j-2}} + \sum_{j=4}^{10} (j-1)(j-3) \frac{e_j^*}{Zc^{j-2}}$$

$$e_3^* = -\sum_{j=1}^{10} \frac{(j-1)(j-2)}{2} \frac{d_j^*}{Zc^{j-3}} - \sum_{j=4}^{10} \frac{(j-1)(j-2)}{2} \frac{e_j^*}{Zc^{j-3}}$$

$$e_4^* = 2.1163 \times 10^{-3} + 5.8262 \times 10^{-3} \omega$$

$$e_5^* = 4.3405 \times 10^{-5} - 4.6678 \times 10^{-4} \omega$$

$$e_6^* = -1.9517 \times 10^{-5} + 8.8237 \times 10^{-5} \omega$$

$$e_7^* = -9.1644 \times 10^{-7} + 4.7942 \times 10^{-6} \omega$$

$$e_8^* = 2.1117 \times 10^{-8} - 4.7493 \times 10^{-8} \omega$$

$$e_9^* = -1.4070 \times 10^{-8} - 1.3246 \times 10^{-8} \omega$$

$$e_{10}^* = 3.1756 \times 10^{-9} - 8.3832 \times 10^{-9} \omega$$

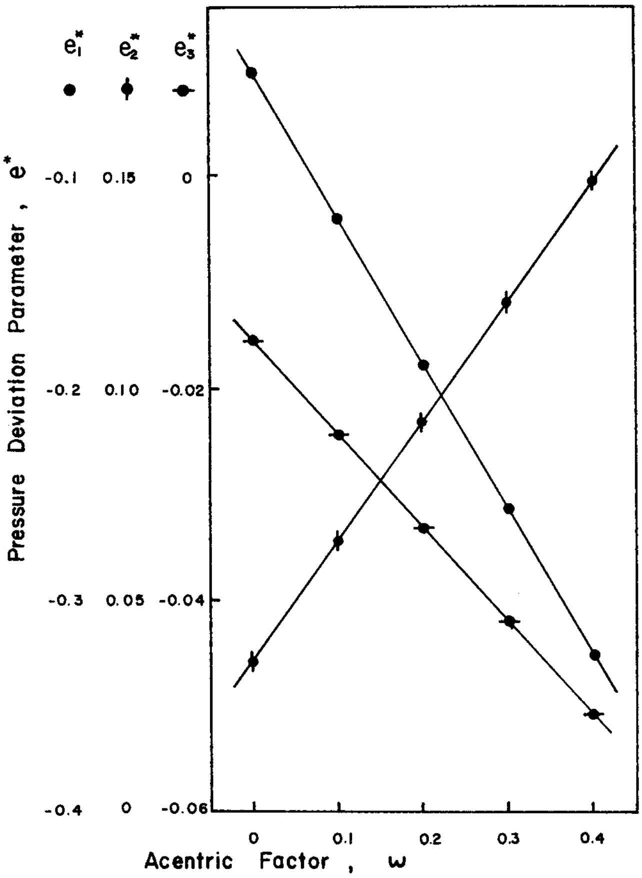

Fig. 1. Illustration of the linear relationship between e_1^*, e_2^*, e_3^*, and ω. All the points represent calculated values.

$$c_M = c_M^* \, R \left(\frac{T_c}{P_c}\right)_M \tag{27}$$

$$d_{jM} = d_{jM}^* \, R^{j+1} \left(\frac{T_c}{P_c}\right)_M^j \tag{28}$$

$$e_{jM} = e_{jM}^* \, R^{j+1} \left(\frac{T_c^{2.5}}{P_c}\right)_M \left(\frac{T_c}{P_c}\right)_M^{j-1} \tag{29}$$

In these expressions, the quantities, a_M^*, b_M^*, c_M^*, d_{jM}^*, and e_{jM}^* are identical to the quantities, a^*, b^*, c^*, d_j^*, and e_j^*, respectively. However, ω and Z_c are replaced, respectively, by ω_M and Z_{cM}, which are defined by

$$\omega_M = \sum_i y_i \, \omega_i \tag{30}$$

$$Z_{cM} = 0.291 - 0.080 \, \omega_M \tag{31}$$

In addition, the quantities $(T_c/P_c)_M$ and $(T_c^{2.5}/P_c)_M$ are further defined as follows:

$$\left(\frac{T_c}{P_c}\right)_M = \sum_i y_i \left(\frac{T_{ci}}{P_{ci}}\right) \tag{32}$$

$$\left(\frac{T_c^{2.5}}{P_c}\right)_M = \sum_i \sum_j y_i \, y_j \, (1 - k_{ij}) \sqrt{\left(\frac{T_{ci}^{2.5}}{P_{ci}}\right)\left(\frac{T_{cj}^{2.5}}{P_{cj}}\right)} \tag{33}$$

In Equation (33), the quantity k_{ij} is a characteristic constant for the $i - j$ interaction. Zudkevitch and Joffe (*31*) adopted a similar constant c_{ij} in the following manner:

$$a_M = \sum_i \sum_j y_i \, y_j \, (1 - c_{ij}) \, (a_i \, a_j)^{0.5}$$

The difference between the two methods lies in the treatment of the constant a^*, which is considered as a universal constant in this investigation for all substances.

APPLICATIONS OF THE PROPOSED EQUATION

The proposed equation may be applied to the prediction of the compressibility factors, enthalpy departures in the vapor phase, and vapor-phase fugacities of pure substances and mixtures.

Compressibility Factors

The compressibility factors for argon ($\omega = -0.002$) and *n*-butane ($\omega = 0.200$) in the vapor and in the liquid states, and for hydrogen sulfide ($\omega = 0.100$) and carbon dioxide ($\omega = 0.225$) at saturated conditions, were arbitrarily chosen for testing the applicability of the proposed equation.

The predicted values, together with those calculated using the equations of Redlich and Kwong (*22*) and Redlich et al. (*24*), are compared with the experimental values (*15, 18, 26*) in Tables 2 to 4.* The average absolute deviations obtained in Z values for argon and *n*-butane are summarized as follows:

		Average absolute deviation		
	T_r	Redlich Kwong (*22*)	Redlich et al. (*24*)	This work
Argon	0.833 to 0.999	0.0074	0.0044	0.0023
n-Butane	0.731 to 0.967	0.0203	0.0036	0.0016

TABLE 4. COMPARISON OF EXPERIMENTAL AND CALCULATED Z VALUES

(v = vapor; l = liquid; c = critical)

					% Deviation	
	T_r	P_r		Z exp (26)	Redlich et al. (24)	This work
Hydrogen sulfide	0.760	0.153	v	0.845	3.20	1.89
			l	0.0246	2.03	−0.70
	0.886	0.459	v	0.689	3.48	2.10
			l	0.0749	2.67	−0.74
	0.959	0.766	v	0.529	6.05	4.17
			l	0.139	10.07	−3.27
	0.988	0.919	v	0.420	9.05	7.47
			l	0.190	21.58	−4.15
	1.000	1.000	c	0.283	2.83	0.00
Carbon dioxide	0.931	0.608	v	0.6233	4.12	0.83
			l	0.09692	4.21	−1.98
	0.957	0.748	v	0.5481	4.36	−0.33
			l	0.1262	9.35	−3.64
	0.981	0.888	v	0.4575	4.04	−4.96
			l	0.1641	17.61	−5.20
	1.000	1.000	c	0.2746	4.88	−0.58
Average absolute % deviation					6.85	2.63

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The results indicate that the proposed equation gives the least deviations.

The compressibility factors of the binary mixtures methane ($\omega = 0.013$) — *n*-pentane ($\omega = 0.252$), and *n*-butane–carbon dioxide were investigated by Redlich et al. (*24*). The proposed equation was used to evaluate the compressibility factors for the same mixtures. The calculated results together with those obtained by Redlich et al. (*24*) are compared with the experimental values (*19, 25*) in Tables 5 and 6. The proposed equation gives better agreement with the experimental values.

TABLE 5. COMPARISON OF EXPERIMENTAL AND CALCULATED Z VALUES AND FUGACITIES FOR METHANE–*n*-PENTANE
(v = vapor; l = liquid; c = critical)

Experimental data (*25*)						ΔZ		Δf_1		Δf_2	
P, lb./sq.in.abs.		Mole fraction of methane	Z	f_1	f_2	Redlich et al.*	This work ($k_{12} = -0.05$)	Redlich et al.*	This work ($k_{12} = -0.05$)	Redlich et al.*	This work ($k_{12} = -0.05$)
Temperature = 100°F.											
15.69	v	0.0	0.9574	0	15.10	0.0070	−0.0030	0.0	0.0	0.0	−0.1
	l	0.0	0.0050			0.0002	0.0001				
1,000	v	0.947	0.8602	861	17.9	−0.0140	−0.0048	0	13.4	1.8	−0.5
	l	0.308	0.2693			−0.0060	0.0104				
2,000	v	0.920	0.7409	1,548	18.1	−0.0170	−0.0316	27	27.3	−1.5	−3.1
	l	0.579	0.4809			−0.0290	0.0161				
2,455	c	0.824	0.6345	1,773	20.2	−0.0360	−0.0274	117	47.1	−6.3	−3.9
Temperature = 220°F.											
94.91	v	0.0	0.8398	0	82.02	0.0180	−0.0040	0.0	0.0	1.0	−0.7
	l	0.0	0.0284			−0.0005	0.0002				
1,000	v	0.798	0.8432	808	85.0	−0.0070	−0.0043	−4	5.6	−7.5	4.2
	l	0.251	0.2704			−0.0070	0.0102				
2,081	c	0.671	0.6446	1,620	96.4	−0.0460	−0.0150	128	7.2	−17.3	−1.1
Temperature = 340°F.											
329.16	v	0.0	0.5920	0	238.68	−0.0510	0.0032	0.0	0.0	−6.1	−2.0
	l	0.0	0.1077			−0.0070	−0.0021				
1,025	c	0.295	0.4396	522	236.9	−0.0910	0.0230	138	68.2	−28.9	14.8
Average absolute deviation						0.0225	0.0104 (0.0106)†	46.0	18.7 (10.4)†	7.8	3.4 (2.5)†

* Values were taken from Table III of reference *24*.
† Average absolute deviation of all points reported in Table II of reference *25*.

TABLE 6. COMPARISON OF EXPERIMENTAL AND CALCULATED Z VALUES AND FUGACITIES FOR *n*-BUTANE (1) CARBON DIOXIDE (2)
(v = vapor; l = liquid; c = critical)

Experimental data (*19*)						ΔZ		Δf_1		Δf_2	
P, lb./sq.in.abs.		Mole fraction of *n*-butane	Z	f_1	f_2	Redlich et al.*	This work ($k_{12} = 0.10$)	Redlich et al.*	This work ($k_{12} = 0.10$)	Redlich et al.*	This work ($k_{12} = 0.10$)
Temperature = 100°F.											
51.5	v	1.0	0.899	47.0	0	0.0160	0.0023	0.5	−0.2	0	0.0
	l	1.0	0.0143			0.0007	0.0001				
300	v	0.202	0.851	40.8	222	−0.0110	−0.0011	−0.6	0.4	2	−0.8
	l	0.804	0.0766			0.0014	0.0003				
700	v	0.100	0.675	29.1	505	−0.0320	−0.0032	−4.2	0.0	0	2.2
	l	0.416	0.151			−0.0070	−0.0016				
1,095	c	0.060	0.279	12.5	722	−0.0810	0.0381	−7.9	−1.0	3	−9.6
Temperature = 280°F.											
436	v	1.0	0.527	303	0	0.0240	0.0029	3	0.8	0	0.0
	l	1.0	0.1374			0.0206	−0.0036				
600	v	0.839	0.501	294	139	−0.0550	−0.0065	0	2.5	−10	−0.9
	l	0.927	0.1952			0.0058	−0.0057				
758	c	0.812	0.328	293	258	−0.0540	0.0076	−10	−1.6	−21	0.5
Average absolute deviation						0.0257	0.0061 (0.0039)†	3.7	0.9 (1.5)†	5.3	2.0 (3.1)†

* Values were taken from Table IV of reference *24*.
† Average absolute deviation of all points reported in Table III of reference *19*.

Vapor-Phase Fugacities

The fugacity f_i of a component i in the vapor phase is related to its mole fraction y_i in the vapor phase and to the system pressure P by the fugacity coefficient φ_i.

$$\varphi_i = \frac{f_i}{y_i P} \tag{34}$$

which can be evaluated by means of the relationship (*2*, *21*)

$$RT \ln \varphi_i = \int_v^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - RT \ln Z \tag{35}$$

In Equation (35) V represents the total volume of the mixture.

Substituting the proposed equation [Equation (20)] and the proposed mixing rules [Equations (25) to (33)] into Equation (35), one obtains the following expression for the fugacity coefficient of component k in the mixture:

$$\begin{aligned}\ln \varphi_k = \ln \varphi &+ \frac{(b-c)\beta_k - 0.08\, R\, \gamma_k\, \epsilon}{v - b + c} \\ &+ \frac{a(\beta_k - \alpha_k)}{RT^{1.5}\, b} \ln \frac{v+b+c}{v+c} \\ &+ \frac{a}{RT^{1.5}\,(v+b+c)} \left(\frac{c\,\beta_k + 0.08\, R\, \gamma_k\, \epsilon}{v+c} - \beta_k \right) \\ &+ \frac{1}{RT} \sum_{j=1}^{10} \frac{1}{j v^j} \left[\left\{ j\,\beta_k + \gamma_k \frac{d_{\omega j}^*}{d_j^*} \right\} d_j\, T \right. \\ &\left. + \left\{ \alpha_k + (j-1)\beta_k + \gamma_k \frac{e_{\omega j}^*}{e_j^*} \right\} e_j\, T^{-0.5} \right]\end{aligned} \tag{36}$$

in which $\ln \varphi$ is for the pure component

$$\begin{aligned}\ln \varphi = Z - 1 - \ln Z &+ \ln \frac{v}{v-b+c} + \frac{a}{RT^{1.5}\, b} \ln \frac{v+c}{v+b+c} \\ &+ \frac{1}{RT} \sum_{j=1}^{10} \frac{d_j\, T + e_j\, T^{-0.5}}{j v^j}\end{aligned} \tag{37}$$

and

$$\alpha_k = 2 \left[\frac{\sum_i y_i\, \delta_{ik} - \delta}{\delta} \right] \tag{38}$$

$$\beta_k = \frac{\epsilon_k - \epsilon}{\epsilon} \tag{39}$$

$$\gamma_k = \omega_k - \omega \tag{40}$$

$$\delta = \sum_{ij} y_i\, y_j\, \delta_{ij} \tag{41}$$

$$\delta_{ij} = \sqrt{\left(\frac{T_{ci}^{2.5}}{P_{ci}} \right) \left(\frac{T_{cj}^{2.5}}{P_{cj}} \right)}\; (1 - k_{ij}) \tag{42}$$

$$\epsilon = \sum_i y_i\, \epsilon_i \tag{43}$$

TABLE 7. COMPARISON OF EXPERIMENTAL AND CALCULATED $(H^0 - H^P)_T$ VALUES FOR SATURATED PURE VAPORS

P, lb./sq.in.abs.	T, °F.	Experimental, B.t.u./lb.	Redlich-Kwong (*22*)	Barner et al. (*1*)	This work
Methane (9)					
190	−178.4	20.7	−1.0	−0.8	0.7
240	−168.5	25.5	−1.0	−0.8	0.8
298	−159.6	31.1	−0.6	−0.4	1.4
367	−148.1	38.9	−1.9	−1.6	0.2
443	−138.5	48.0	−2.6	−2.3	−0.5
530	−129.0	60.5	−4.1	−3.7	−1.8
579	−124.2	68.8	−4.9	−4.5	−2.3
631	−119.3	81.2	−7.9	−7.4	−4.5
669	−116.6	109.8	−9.3	−8.7	0.7
Propane (30)					
14.7	−43.7	1.9	−0.4	0.4	0.1
50	14.1	6.7	−2.3	−0.5	−1.0
100	55.0	10.7	−2.6	0.2	−0.3
150	82.7	14.6	−2.9	0.7	0.3
200	104.5	18.6	−3.3	1.0	0.6
250	122.5	23.0	−4.1	0.9	0.6
300	137.6	26.9	−4.1	1.6	1.2
350	151.4	31.7	−4.9	1.4	1.0
400	163.5	37.0	−5.9	1.2	0.8
450	174.7	43.5	−7.6	0.2	−0.2
500	184.8	50.8	−9.3	−0.5	−0.9
550	194.4	59.0	−10.7	−0.9	−0.6
588	201.0	66.1	−10.0	1.8	5.1
600	203.5	69.7	−11.3	−0.4	3.4
617	206.3	86.7	−15.4	−4.2	3.3
Average absolute deviation			5.3	2.0	1.4

TABLE 8. COMPARISON OF EXPERIMENTAL AND CALCULATED $(H^0 - H^P)_T$ VALUES FOR VAPOR MIXTURE CONTAINING 5 MOLE % PROPANE IN METHANE AT −27°F.
$(H^0 - H^P)_T$ (B.t.u./lb.)

P, lb./sq.in.abs.	Experimental*	BWR (4, 5)*	Lydersen et al. (*11*)*	Yen (*29*)*	Curl-Pitzer (*7*)*	Redlich-Kwong (*22*)	Barner et al. (*1*)	This work $k_{12} = 0$	This work $k_{12} = 0.2$
500	25.9	26.2	21.4	25.7	24.1	25.2	25.0	26.5	26.4
1,000	60.3	61.1	55.2	58.4	56.9	58.2	57.2	61.6	61.1
1,500	96.9	98.0	83.7	89.3	90.7	92.5	90.6	97.0	96.0
2,000	116.0	117.5	100.9	108.6	111.2	110.4	108.9	117.0	116.1
Average absolute deviation		0.9	9.5	4.3	4.1	3.2	4.4	0.8	0.4

* Values reported by Mather, Powers, and Katz (*14*).

TABLE 9. COMPARISON OF EXPERIMENTAL AND CALCULATED $(H^0 - H^P)_T$ VALUES FOR VAPOUR MIXTURES

System	Number of points	Redlich-Kwong (*22*)*	Average Absolute Deviation, B.t.u./lb. Barner et al. (*1*)*	BWR (*4, 5*)*	This work $k_{ij} = 0$	$k_{ij} \neq 0$
Methane-propane (*12*)	5	1.8	2.1	—	0.8	0.8 ($k_{12} = 0.02$)
Propane-benzene (*17*)	10	7.5	4.8	4.6	4.3	4.0 ($k_{12} = 0.03$)
Propane-n butane-n pentane (*28*)	14	5.6	2.2	2.2	2.4	

* Values reported by Barner, Pigford and Schreiner (*1*).

$$\epsilon_i = \left(\frac{T_{ci}}{P_{ci}}\right) \tag{44}$$

and the quantities $d_{\omega j}{}^*$ and $e_{\omega j}{}^*$ are the slopes of the linear functions of $d_j{}^*$ and $e_j{}^*$ in ω, respectively. The values for $d_{\omega j}{}^*$ $(1 \leqq j \leqq 10)$ and $e_{\omega j}{}^*$ $(4 \leqq j \leqq 10)$ are given in Table 1, while the values for $e_{\omega j}{}^*$ $(1 \leqq j \leqq 10)$ are given in Equations (17) to (19).

TABLE 10. COMPARISON OF EXPERIMENTAL AND CALCULATED PRESSURES AT CRITICAL AND SLIGHTLY OVER CRITICAL ISOTHERMS WHEN $Pr \leqq 1$

			% Deviation		
	V_r	P_r exp	Redlich-Kwong (22)	Sugie-Lu (27)	This work
Carbon dioxide (*16*) $T_r = 1$	12.626	0.26084	0.14	−0.09	−0.09
	10.091	0.31809	0.17	−0.10	−0.11
	8.4020	0.37221	0.22	−0.08	−0.11
	7.2217	0.42217	0.26	−0.07	−0.12
	6.2922	0.47156	0.32	−0.03	−0.12
	5.5805	0.51755	0.38	0.01	−0.12
	5.1732	0.54786	0.42	0.05	−0.13
	5.0239	0.55983	0.43	0.06	−0.13
	4.5599	0.60021	0.49	0.12	−0.14
	3.4234	0.72387	0.71	0.44	−0.16
	2.5984	0.83872	0.94	1.00	−0.23
	2.1103	0.91211	1.05	1.63	−0.30
	1.7737	0.95806	1.00	2.24	−0.35
	1.5393	0.98235	0.80	2.69	−0.31
	1.3890	0.99281	0.51	2.81	−0.24
	1.0000	1.00000	1.09	0.20	−0.00
Sulfur dioxide (*10*) $T_r = 1$	287.15	0.01285	0.03	0.02	0.02
	142.90	0.02570	0.06	0.03	0.04
	56.343	0.06426	0.13	0.07	0.07
	27.488	0.12852	0.21	0.09	0.10
	17.860	0.19278	0.27	0.09	0.10
	13.035	0.25704	0.32	0.09	0.09
	9.9876	0.32130	1.62	1.32	1.31
	8.1808	0.38556	0.44	0.11	0.08
	6.7772	0.44983	0.52	0.15	0.08
	5.7094	0.51409	0.66	0.27	0.13
	4.8647	0.57835	0.83	0.43	0.21
	4.1780	0.64261	0.95	0.58	0.22
	3.5973	0.70687	1.13	0.82	0.26
	3.0941	0.77113	1.29	1.09	0.26
	2.6453	0.83539	1.33	1.36	0.13
	2.2087	0.89965	1.45	1.92	0.08
	1.7206	0.96391	1.34	2.79	0.02
Argon (*15*) $T_r = 1.015$	300.4	0.01157	−0.05	−0.05	−0.05
	150.2	0.02305	−0.06	−0.05	−0.05
	60.08	0.05699	−0.09	−0.07	−0.06
	30.04	0.11188	−0.12	−0.09	−0.07
	15.02	0.21547	−0.18	−0.12	−0.08
	7.510	0.39902	−0.24	−0.10	−0.07
	3.755	0.68067	−0.16	0.19	−0.10
	2.5033	0.86616	0.09	0.79	−0.24
	1.8775	0.97780	0.36	1.51	−0.42
Average absolute % deviation			0.54	0.61	0.17

Fugacities of components in the two binary mixtures studied above were evaluated. The calculated values, together with those obtained by Redlich et al. (*24*), are compared with the experimental values (*19, 25*) in Tables 5 and 6 for the mixtures methane–*n*-pentane and *n*-butane–carbon dioxide, respectively. Significant improvements are obtained at the critical point of the mixtures.

Isothermal Enthalpy Departures

The isothermal enthalpy departures from the ideal gas state may be derived from Equation (20):

$$(H^P - H^0)_T = PV - RT - \int_\infty^v \left[P - T\left(\frac{\partial P}{\partial T}\right)_v \right]_T dv$$

$$= \frac{(b-c)\,RT}{(v-b+c)} - \frac{aT^{-0.5}\,v}{(v+c)(v+b+c)}$$

$$- \frac{1.5\,aT^{-0.5}}{b} \ln\left(\frac{v+b+c}{v+c}\right)$$

$$+ \sum_{j=1}^{10} \frac{j\,d_j\,T + (j+1.5)\,e_j\,T^{-0.5}}{jv^j} \tag{45}$$

The isothermal enthalpy departures at the dew point for pure substances were evaluated for methane and propane ($\omega = 0.105$). The predicted results are compared with the experimental values (*9, 30*) in Table 7. Calculated values obtained by the equations of Redlich and Kwong (*22*) and of Barner, Pigford, and Schreiner (*1*) are also included for the comparison. The proposed method gives the lowest average absolute deviation.

Mather, Powers, and Katz (*14*) experimentally determined the isothermal enthalpy departures for a vapor mixture containing 5% propane in methane. The predicted values obtained by the proposed method for this mixture are compared with the experimental values in Table 8. The calculated values from other methods reported by Mather, Powers, and Katz (*14*) are also included for the comparison. The proposed method again gives the lowest average absolute deviation.

Barner, Pigford, and Schreiner (*1*) calculated the isothermal enthalpy departures for three systems: methane-propane, propane-benzene ($\omega = 0.211$), and propane–*n*-butane–*n*-pentane. The predicted values obtained by the proposed method are compared with the experimental values (*12, 17, 28*) and with the calculated values reported by Barner et al. (*1*) in Table 9.[*] The proposed method gives better results for the two binary systems. For the ternary system, the calculated values of Barner et al. (*1*) gives an average absolute deviation of 2.2% and the proposed method, 2.4%.

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[*] See footnote on p. 1070.

DISCUSSION AND CONCLUSIONS

In conclusion, a generalized pressure-explicit equation of state has been developed which is suitable for nonpolar vapors and liquids in the $1 \geqq T_r > 0.56$ region. The limiting pressure for the proposed equation is that of Pitzer's table ($P_r < 9.0$).

The generalized equation of state previously proposed for nonpolar gases in the $T_r \geqq 1$ region (*27*) does not satisfy the conditions that $(\partial P/\partial v)_{T_c} = 0$ and $(\partial^2 P/\partial v^2)_{T_c} = 0$, although it does pass through the critical point. For this reason, it was not recommended to apply the equation to the narrow region where $1.02 > T_r > 1.0$ and $1 > P_r > 0.8$. The equation developed in this investigation satisfies Z_c and the first two pressure-volume derivatives at the critical point.

The applicability of the proposed equation to this narrow region is demonstrated in Table 10, in which the predicted pressures are compared with the experimental values for carbon dioxide at $T_r = 1.0$ (*16*), sulfur dioxide at $T_r = 1.0$ (*10*), and argon at $T_r = 1.015$ (*15*). The calculated values obtained from the previously proposed equation (*27*) and the Redlich-Kwong equation (*22*) are also included in this table. The comparison indicates that the results obtained from the equation developed in this investigation are superior, and agree extremely well with the experimental values.

The proposed equation has predicted successfully the compressibility factors, vapor-phase fugacities, and enthalpy departures in the vapor phase of pure substances and mixtures. Comparison with the methods available in the literature indicates that the proposed equation represents a good improvement in the specified region.

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NOTATION

a, b, c, d_j, e_j = coefficients in Equation (20)
$a^*, b^*, c^*, d_j^*, e_j^*$ = functions as defined by Equations (2) to (4) and (21) and (22)
c_{ij}, k_{ij} = interaction constants for pair of components i and j
$d_{\omega j}^*, e_{\omega j}^*$ = slopes of the linear functions of d_j^* and e_j^* in ω
f = fugacity
$f_j(T)$ = temperature function as defined by Equation (6)
H_T^P = enthalpy of a real gas at T and P
H_T^0 = enthalpy of an ideal gas at T
K = constant as defined by Equation (6)
P = pressure
ΔP = deviation function as defined by Equation (6)
R = gas constant
T = absolute temperature
V = total volume
v = molar volume
y = molar fraction
Z = compressibility factor

Greek Letters

$\alpha, \beta, \gamma, \delta, \epsilon$ = functions as defined by Equations (38) to (44)
φ = fugacity coefficient
ω = acentric factor

Subscripts

c = critical property
i, j, k = component i, j, k
r = reduced property
M = mixture property

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