Equilibrium Constants From a Modified Redlich–Kwong Equation of State

1 author:

Giorgio Soave
retired

79 PUBLICATIONS   **6,954** CITATIONS

Equilibrium constants from a modified Redlich–Kwong equation of state

GIORGIO SOAVE

Snam Progetti, Div. Sviluppo, Milano, Italy

Abstract — A modified Redlich–Kwong equation of state is proposed. Vapor pressures of pure compounds can be closely reproduced by assuming the parameter a in the original equation to be temperature-dependent. With the introduction of the acentric factor as a third parameter, a generalized correlation for the modified parameter can be derived. It applies to all nonpolar compounds.

With the application of the original generalized mixing rules, the proposed equation can be extended successfully to multicomponent-VLE calculations, for mixtures of nonpolar substances, with the exclusion of carbon dioxide. Less accurate results are obtained for hydrogen-containing mixtures.

INTRODUCTION

THE REDLICH–KWONG equation[1] is commonly considered the best of two-parameter equations of state proposed until now. While it can be used to calculate, with a good degree of accuracy, volumetric and thermal properties of pure compounds and of mixtures, its application to multicomponent -VLE calculations often gives poor results.

This fact cannot be attributed solely to the imperfection of the mixing rules (although several authors have tried to improve the equation by introducing empirical binary interaction constants[2]), but it must be ascribed partly to the equation's lack of accuracy in expressing the influence of temperature.

As a matter of fact, the accuracy is not better when calculating the vapor pressures of pure substances, which are not influenced by any mixing rule.

This conclusion was attained by several authors[3] who tried to improve the original equation by assuming temperature-dependent parameters.

This work arises from the assumption that an improvement in reproducing saturation conditions of pure substances also leads to an improvement for mixtures. Good agreement between calculated and experimental vapor pressures of pure compounds is of course not a sufficient condition for a good fitting for mixtures also, but is a necessary one.

The original Redlich–Kwong equation of state is:

$$p = \frac{RT}{v-b} - \frac{a/T^{0.5}}{v(v+b)}. \qquad (1)$$

In this work, it has been modified by replacing the term $a/T^{0.5}$ with a more general temperature-dependent term $a(T)$:

$$p = \frac{RT}{v-b} - \frac{a(T)}{v(v+b)}. \qquad (1')$$

Letting:

$$v = z\frac{RT}{p}$$

$$\frac{ap}{R^2T^2} = A \qquad (2)$$

$$\frac{bp}{RT} = B \qquad (3)$$

Eq. (1') can also be written:

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0. \qquad (4)$$

PURE SUBSTANCES

Supposing that, at the critical point, the first and second derivatives of pressure with respect

to volume be zero, we obtain:

$$a_i(T_{ci}) = a_{ci} = 0 \cdot 42747 \frac{R^2 T_{ci}^2}{p_{ci}} \qquad (5)$$

$$b_i = 0 \cdot 08664 \frac{RT_{ci}}{p_{ci}}. \qquad (6)$$

At temperatures other than the critical, let:

$$a_i(T) = a_{ci} \alpha_i(T) \qquad (7)$$

where $\alpha_i(T)$ is an adimensional factor which becomes unity at $T = T_{ci}$.

Applying Eqs. (5)–(7), Eqs. (2) and (3) become, for pure substances:

$$A = 0 \cdot 42747 \, \alpha_i(T) \frac{p/p_{ci}}{(T/T_{ci})^2} \qquad (8)$$

$$B = 0 \cdot 08664 \frac{p/p_{ci}}{T/T_{ci}}. \qquad (9)$$

The fugacity coefficient of a pure component can be calculated from the equation:

$$\ln \frac{f}{P} = Z - 1 - \ln (Z - B) - \frac{A}{B} \ln \left(\frac{Z+B}{Z} \right) \qquad (10)$$

which can be easily derived by applying to Eq. (1) the general thermodynamic relationship:

$$\ln \frac{f}{P} = \int_0^P \left(\frac{v}{RT} - \frac{1}{P} \right) dP. \qquad (11)$$

The compressibility factor Z to be used in Eq. (10) is previously obtained by solving Eq. (4) (one or three real roots can be obtained; in the latter case, the smallest root will be taken for a liquid phase and the highest one for a vapor phase).

For a pure substance at a given temperature and for a given value of $a(T)$, a single value of P exists which satisfies the saturation condition:

$$f_i^L = f_i^V. \qquad (12)$$

This pressure can be found by trial and error,

for each value of the pressure solving twice Eq. (4), once for the liquid phase and once for the vapor phase, and introducing the two roots into Eq. (10); the right pressure is such that the two values of f/P calculated are equal.

Vice versa, imposing an experimental value of the saturation pressure, Eq. (12) is satisfied by a single value of $a(T)$, that is of $\alpha(T)$.

It is possible thus to obtain from experimental vapor pressures a set of values of $\alpha(T)$ for each substance.

This has been done for a number of hydrocarbons, assuming as experimental vapor pressures the accurate Antoine expressions reported by API Project 44 [4].

When plotting the values of $\alpha_i(T)$ obtained against $T_{Ri} = T/T_{ci}$, separate curves are obtained, showing similar trends. By plotting $\alpha_i^{0.5}$ against $T_{Ri}^{0.5}$, almost straight lines are obtained (Fig. 1). As all lines must pass through the same point $(T_R = \alpha = 1)$, we can write:

$$\alpha_i^{0.5} = 1 + m_i(1 - T_{Ri}^{0.5}). \qquad (13)$$

The slopes m_i can be connected directly with the acentric factors ω_i of the related compounds. As a matter of fact, each value of ω defines a value of the reduced vapor pressure at a reduced temperature of 0.7:

$$p_{Ri}^{sat}(T_R = 0 \cdot 7) = 10^{-1-\omega_i}.$$

From the pair $(T_R = 0 \cdot 7, p_R = 10^{-1-\omega})$ a value of $\alpha_i(0 \cdot 7)$ is obtained, which depends only on the assumed ω (See Table 1). Forcing all the straight lines, as defined by Eq. (13), to pass through the points $(T_R = 0 \cdot 7, \alpha = \alpha(0 \cdot 7))$ we obtain:

$$m_i = \frac{\alpha_i^{0.5}(0 \cdot 7) - 1}{1 - (0 \cdot 7)^{0.5}}. \qquad (14)$$

The m_i values obtained by substitution into Eq. (14) of the $\alpha_i(0 \cdot 7)$ values of Table 1 have been correlated against ω_i:

$$m_i = 0 \cdot 480 + 1 \cdot 574 \omega_i - 0 \cdot 176 \omega_i^2. \qquad (15)$$

Equations (7), (13) and (15) yield the desired
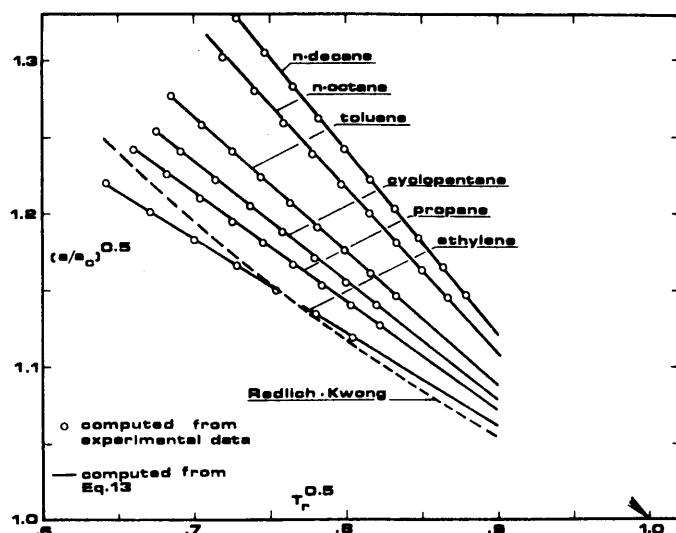
Fig. 1.

Table 1. Values of $\alpha_i(0\cdot7)$ and m_i (Eq. 14).

ω_i	$\alpha_i(0\cdot7)$	m_i
0·00	1·162881	0·47979
0·05	1·190635	0·55811
0·10	1·218377	0·63549
0·15	1·246101	0·71194
0·20	1·273802	0·78749
0·25	1·301478	0·86215
0·30	1·329124	0·93594
0·35	1·356737	1·00888
0·40	1·384314	1·08099
0·45	1·411854	1·15229
0·50	1·439354	1·22279

value of $a_i(T)$ of a given substance at any temperature, the only quantities needed being the critical constants and the acentric factor.

To prove the effectiveness of the proposed modifications, the vapor pressures of a number of hydrocarbons were calculated and compared with experimental data[4]. Accurate values of the acentric factors were derived from experimental data. The same was done for the original Redlich–Kwong equation.

While the original equation yielded vapor pressures diverging sharply from experimental

values, particularly for substances having high values of the acentric factor, the proposed equation fairly fitted to the experimental data (Table 2). All the vapor pressures computed from the latter equation showed slightly S-shaped deviations, with a tendency to diverge at the end of the range of temperatures examined, that is at reduced temperatures lower than about 0·4.

Table 2. Comparison of calculated vapor pressures

Compound		Root mean square deviation %	
		Original Eq.	modified Eq.
Ethylene	0·087	20·1	2·0
Propylene	0·144	23·5	0·7
Propane	0·152	28·8	2·0
Isobutane	0·185	52·4	2·4
Cyclopentane	0·195	66·0	0·8
Toluene	0·260	129·0	0·8
n-hexane	0·301	159·0	1·9
n-octane	0·402	268·0	2·1
n-decane	0·488	402·0	1·0

This demonstrates the possibility of further improvement with a more refined expression for $\alpha(T)$; this problem will be raised when dealing with mixtures containing very light components,

particularly hydrogen, which require an extrapolation of $\alpha(T_R)$ to high reduced temperatures.

MIXTURES

For the sake of simplicity. the original generalized mixing rules:

$$a = (\Sigma\, x_i a_i^{0.5})^2 \qquad (16)$$

$$b = \Sigma x_i b_i. \qquad (17)$$

were first tried.

It was found that these rules could be applied with acceptable results to mixtures of nonpolar fluids, such as hydrocarbons, nitrogen. carbon monoxide, with the exclusion of carbon dioxide and hydrogen sulfide.

No particular deviation was found to occur in mixtures of components of widely different volatilities. so it was concluded that the above mixing rules are adequate.

By applying mixing rules (16) and (17) to Eqs. (2). (3). (5) and (6), we obtain:

$$A = 0.42747\,\frac{p}{T^2}\left(\sum x_i\frac{T_{ci}\alpha_i^{0.5}}{p_{ci}^{0.5}}\right)^2 \qquad (18)$$

$$B = 0.08664\,\frac{p}{T}\sum x_i\frac{T_{ci}}{p_{ci}}. \qquad (19)$$

The fugacity coefficient of a component in a mixture is given by:

$$\ln\frac{\bar{f_i}}{px_i} = \int_{\infty}^{v}\left[\frac{1}{v}-\frac{1}{RT}\left(\frac{dp}{dn_i}\right)_{T,v,n_j}\right]dv - \ln Z. \qquad (20)$$

From Eq. (20) we obtain:

$$\ln\frac{\bar{f_i}}{px_i} = \frac{b_i}{b}\,(Z-1) - \ln\,(Z-B)$$

$$-\frac{A}{B}\left(2\frac{a_i^{0.5}}{a^{0.5}}-\frac{b_i}{b}\right)\ln\left(1+\frac{B}{Z}\right) \qquad (21)$$

in which the ratios b_i/b and a_i/a are given by:

$$\frac{a_i^{0.5}}{a^{0.5}} = \frac{\alpha_i^{0.5}T_{ci}/p_{ci}^{0.5}}{\Sigma\, x_i\alpha_i^{0.5}T_{ci}/p_{ci}^{0.5}} \qquad (22)$$

$$\frac{b_i}{b} = \frac{T_{ci}/p_{ci}}{\Sigma\, x_iT_{ci}/p_{ci}} \qquad (23)$$

and the compressibility factor Z is obtained by solving previously Eq. (4) (the smallest root must be taken for a liquid phase and the greatest one for a vapor phase.)

The above equations were applied to several binary systems and the results compared with the experimental data. The same was done for the original equation.

Figure 2 shows the results obtained for the binary methane/n-butane at 100°F and the experimental data from Sage and Lacey[5]. The proposed modified equation fits the experimental curve well, particularly for the vapor phase. However, for the liquid phase also, the error in computed bubble-pressures is small.

It is noteworthy that the calculated vapor and liquid curves converge almost exactly at the experimental critical pressure and composition. This fact was verified in almost all cases examined, so it can be concluded that the proposed equation is able to predict the phase behaviour of mixtures in the critical zone also.

To prove the accuracy of the adopted mixing rules. some binaries of components having largely different volatilities were investigated. The results for the binary methane/n-decane are shown in Fig. 3. No loss of accuracy can be noticed in comparison to the first binary. The same was found in other similar cases, so it was concluded that the mixing rules adopted (the same as in the original equation) are adequate.

Greater deviations. however, were found for hydrogen-containing mixtures (see Fig. 4). The classical hydrogen's critical constants were used, together with a value -0.22 of the acentric factor. as derived from hydrogen's experimental vapor pressures. No improvement was obtained using effective, critical constants. A marked improvement was instead realized, in limited pressure ranges (up to 1000–2000 psia), using a suitable value of the acentric factor.

Some empirical correction becomes necessary for systems containing carbon dioxide, hydrogen sulfide and polar compounds, for which large
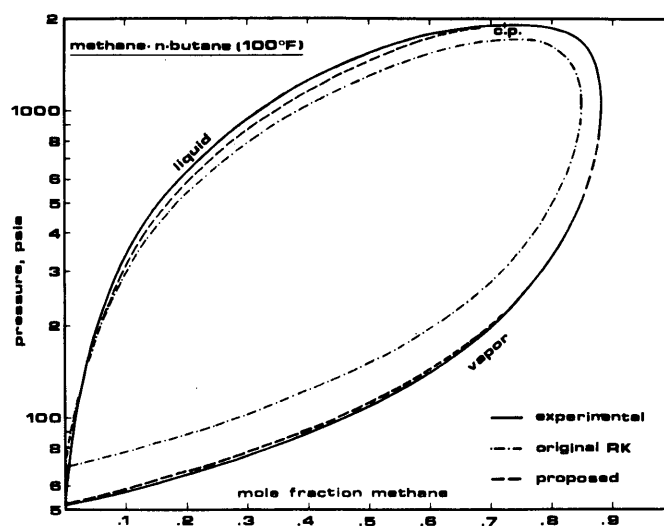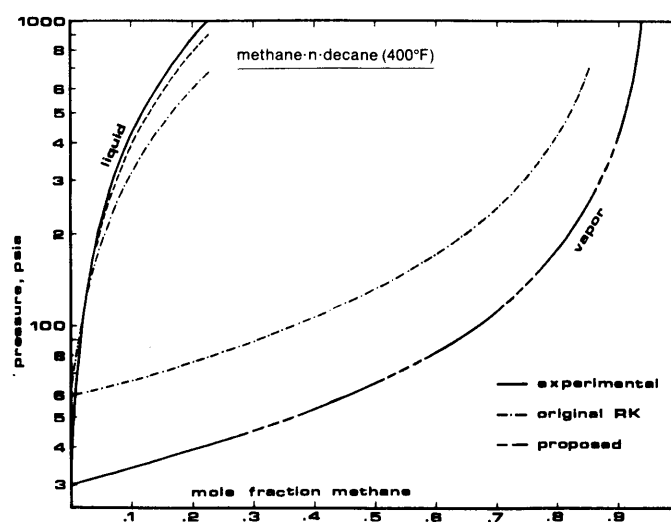
Fig. 2.

Fig. 3.

deviations were obtained, although the vapor pressures of the single pure components were reproduced well (see Fig. 5).

In such cases one cannot any longer use the generalized mixing rules given above since these assume that

$$a_{ij} = (a_i a_j)^{1/2}.$$

More generally, one could write:

$$a_{ij} = (1 - K_{ij})\,(a_i a_j)^{1/2}$$

where K_{ij} is an empirical correction factor, to be determined from the experimental data, for each binary present in the mixture (if n is the number
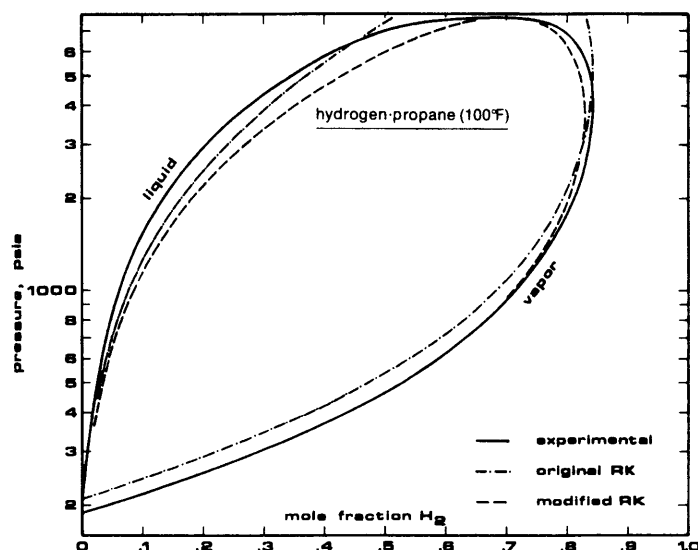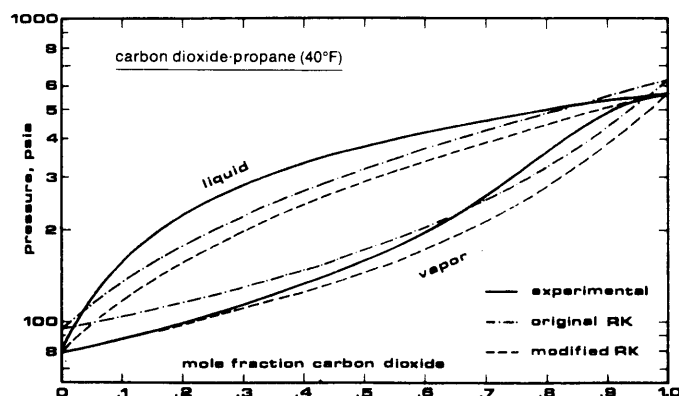
Fig. 4.

Fig. 5.

of the components in a mixture, the binaries will be $n(n-1)/2$.

As pointed out by several authors, each K_{ij} factor can be considered independent of system temperature, pressure and composition. The derivation of such parameters from experimental data will be attempted in future work. It is possible that the introduction of such correction factors may also improve the results for mixtures of more 'normal' components, such as the hydrocarbons and hydrogen.

NOTATION

T	absolute temperature
P	pressure
v	specific volume
T_c	critical temperature
P_c	critical pressure
$T_R = T/T_c$	reduced temperature
$P_R = P/P_c$	reduced pressure
ω	acentric factor
a, b	parameters in Redlich–Kwong equation

$a(T)$	parameter in the modified Eq. (1')	m	slope of $\alpha^{0.5}$ against $T_R^{0.5}$, Eq. (13)
a_c	value of $a(T)$ at $T = T_c$	$B = bP/RT$	Eqs. (3), (9) and (19)
$\alpha = a/a_c$	correction factor in the modified equation	$A = aP^2/R^2T^2$	Eqs. (2), (8) and (18)
		$Z = Pv/RT$	compressibility factor

REFERENCES

[1] REDLICH-KWONG, *Chem. Rev.* 1949 **44**, 233.
[2] CHUEH and PRAUSNITZ, *Ind. Engng Chem.* 1967 **6** 4, 492; HISSONG and McKAY, *A.I.Ch.E.Jl* 1970 **16** 4, 580.
[3] WILSON, *Adv. Cryogenic Engng* 1966 **9**, 392; JOFFE, SCHROEDER and ZUDKEVITCH, *A.I.Ch.E.Jl* 1970 **16** 496; 1970 **16** 112.
[4] Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds, API Research Project 44 1953.
[5] SAGE and LACEY, *Thermodynamic Properties of the Lighter Paraffin Hydrocarbons and Nitrogen* 1950.
[6] SAGE and LACEY, *Some Properties of the Lighter Hydrocarbons, Hydrogen Sulfide and Carbon Dioxide* 1955.

Résumé—Les auteurs proposent une équation modifiée de Redlich–Kwong de l'état. Il est possible de reproduire, avec précision, les pressions de vapeur de composés purs en considérant que le paramètre 'a' dans l'équation originale est dépendant de la température. En introduisant le facteur assymétrique comme troisième paramètre, on peut dériver une corrélation généralisée pour le paramètre modifié. Il s'applique à tous les composés non-polaires. En appliquant les régles originales généralisées de mélange, l'équation proposée peut être étendue à des calculs VLE à composantes multiples, pour les mélanges de substances non-polaires, à l'exception du bioxyde de carbone. Des résultats moins précis sont obtenus pour des mélanges contenant de l'hydrogène.

Zusammenfassung – Es wird eine abgeänderte Redlich–Kwongsche Zustandsgleichung vorgeschlagen.
Dampfdrucke reiner Stoffe können mit guter Annäherung reproduziert werden, wenn der Parameter a in der ursprünglichen Gleichung als temperaturabhängig angesehen wird. Mit der Einführung des nicht-zentrischen Faktors als dritten Parameter kann eine verallgemeinerte Korrelation für den abgeänderten Parameter abgeleitet werden. Sie gilt für alle unpolaren Verbindungen.
Bei Anwendung der ursprünglichen verallgemeinerten Mischregeln kann die vorgeschagene Gleichung erfolgreich auf Mehrkomponenten VLE Berechnungen, für Mischungen unpolarer Stoffe, mit Ausnahme von Kohlendioxyd ausgedehnt werden. Für wasserstoffhältige Mischungen werden weiger genaue Resultate erhalten.