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A Modified Redlich-Kwong Equation of State

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A new modification of the Redlich-Kwong equation of state is presented. The modification follows the procedure suggested by Redlich, Ackerman, et al., in which a deviation function (a function of temperature, pressure, and acentric factor) is added to the compressibility factor from the original equation to improve the agreement with data. The purpose of the present modification was to improve predictions of the Redlich-Kwong equation in the saturated vapor region up to the critical point while retaining a relatively simple form to make analytical relations for derived properties possible. The equation for pressure correction to vapor enthalpy, derived from the compressibility factor by standard thermodynamic procedures, is also presented. Comparisons of predicted vapor compressibility factors and vapor enthalpy pressure corrections with literature data are given, demonstrating the advantages of the proposed modification when the saturated vapor region is of principal interest.

The Redlich-Kwong equation of state, first introduced in 1949 (*22*), has found wide use in recent years in computer procedures for predicting real gas behavior. It is generally conceded to be one of the best generalized two-parameter equations of state available. In addition, it is remarkably compact, which makes it attractive for inclusion in large scale process design computer programs which require efficient data calculation procedures to be effective. Several workers (*4, 24, 29*) have reported the incorporation of the Chao-Seader vapor liquid equilibrium procedure (which uses vapor fugacity coefficients predicted by the Redlich-Kwong equation) into distillation and/or flash computation; one of these also uses the equation in computing vapor enthalpies.

There has been continuing interest in modifications to the Redlich-Kwong equation to improve its accuracy while maintaining its basic simplicity. In most cases, a third parameter (generally the acentric factor of Pitzer) has been added to the two parameters (critical temperature and pressure) of the original equation. There have been a considerable number of such modifications proposed; those relevant to the present work are summarized below.

The multiplicity of these modifications may be explained by the general difficulty of developing a reasonably compact equation of state applicable over a wide range of conditions. The comprehensive review of Martin (*14*), summarizing the extensive research to develop analytical equations of state over the past 20 yr., gives a cogent explanation of this difficulty. For pure components, the three parameter tabular correlation introduced by Pitzer et al. in 1955 (*18*) still remains the bench mark for analytical equations. No compact analytical equation can equal it in accuracy for predicting vapor densities over a wide range of conditions.

One may conclude that any modification to the Redlich-Kwong equation will include two kinds of compromise: accuracy vs. complexity and accuracy in one region vs. accuracy in another. The present modification is no exception. It was developed to fill a need for a relatively compact equation to predict vapor compressibility factors and the isothermal pressure correction to vapor enthalpy for light hydrocarbon mixtures and other related mixtures of nonpolar compounds. The saturated vapor region was of principal interest, but it was desirable to maintain reasonable accuracy up to a reduced temperature of 1.1 to a reduced pressure of approximately 2.0 and to have correct low pressure limiting behavior to a reduced temperature of 2.

The modification follows closely the work of Barner et al. (3) in an effort to retain relative simplicity. However, it uses the deviation function approach, developed by Redlich and co-workers (*1, 20, 21*), in order to obtain better accuracy at higher pressures. The deviation function was based on a curve fit of vapor density data for pure light hydrocarbons in the region of interest. The compressibility factor predictions have been tested against mixture data for eight hydrocarbons and the enthalpy predictions spot checked against both data derived from P-V-T measurements and some available calorimetric data.

We expect that our modification of the Redlich-Kwong equation will be useful for those who require a computer procedure valid for the range of components and conditions covered. In addition, our experience in developing a deviation function valid for a particular region may be of interest to those who might wish to develop a similar function with better accuracy in other regions.

THE ORIGINAL REDLICH-KWONG EQUATION OF STATE

It will be useful in the discussion that follows to have available the original equation given by Redlich and Kwong (*22*):

$$Z = \frac{1}{1-h} - \frac{A^2}{B}\left(\frac{h}{1+h}\right) \qquad (1)$$

where

$$A^2 = a/R^2T^{5/2}$$

$$a = \frac{1}{(\sqrt[3]{2}-1)9} \cdot \frac{R^2T_c^{5/2}}{P_c} = 0.42748022\,\frac{R^2T_c^{5/2}}{P_c}$$

$$B = b/RT$$

$$b = \frac{(\sqrt[3]{2}-1)}{3}\,\frac{RT_c}{P_c} = 0.08664034\,\frac{RT_c}{P_c}$$

$$h = BP/Z$$

$$Z = \frac{PV}{RT}$$

The expression for the constants a and b were determined by Redlich and Kwong using the standard theoretical conditions for the critical point: that the first and second partial derivatives of pressure with respect to volume are zero. The mixing rules proposed for application to Equation (1) by Redlich and Kwong for determining mixture constants given pure component constants are

$$a_{\mathrm{mix}}^{1/2} = \sum_i y_i a_i^{1/2} \qquad (2)$$

$$b_{\mathrm{mix}} = \sum_i y_i b_i \qquad (3)$$

Equation (1) is not explicit in Z as written, since h depends on Z. For pressures above the critical pressure, Equation (1) has only one real root, so a computer trial-and-error solution for Z given T and P is not difficult. We use the Newton-Raphson procedure given by Shelton and Wood (*24*), with some modification to assure that the correct (vapor) root is identified below the critical temperature and pressure where Equation (1) may have one or three real roots.

Equation (1) is fairly accurate over a wide range of vapor conditions (with the exception of the critical region) for compounds which consist of spherical molecules, that is, compounds obeying Pitzer's definition of a simple fluid, those with an acentric factor ω of zero, where $\omega = -1.0 - \log_{10} P_r^0$ (@ $Tr = 0.7$) and $P_r^0 = P^0/P_c$ reduced vapor pressure.

While Equation (1) is empirical, it rests on a semi-theoretical framework in its behavior at the high and low pressure limits. The behavior at these limits also provides justification for the mixing rules given in Equations (2) and (3). Of particular importance is the low pressure limiting behavior, which allows a direct comparison with the virial equation of state (truncated to two terms), which has a solid theoretical and experimental base in the low pressure region. This is discussed further in the Appendix.

The inadequacies of the Redlich-Kwong equation of state are related to the fact that it contains only two parameters, the critical temperature and the critical pressure. The R-K equation shows increasing errors as the acentric factor of the compound in question increases. In addition, it predicts a value of one-third for the critical compressibility factor Z_c for all compounds, whereas Z_c varies from a value of about 0.290 for compounds with spherical molecules down to value of 0.260 for *n*-heptane. Finally, the mixing rules, particularly the mixing rule for the constant a, are inadequate for mixtures including components of widely different molecular size. This inadequacy is most marked in the prediction of fugacity coefficient for components in a mixture.

PREVIOUS WORK IN IMPROVING THE R-K EQUATION

Previous modifications suggested in the literature to improve the Redlich-Kwong equation were investigated before the present work was begun. These modifications may be conveniently divided into four categories:

1. Improvement of the Redlich-Kwong mixing rules.
2. Improvement of the Redlich-Kwong equation by changing the temperature dependence of the term A.
3. Improvement of the Redlich-Kwong equation by changing the expression for determining the constants.
4. Improvement of the Redlich-Kwong equation by adding a correction term to the original equation.

Wilson (*30, 31*) had some success for specific binary systems in modifying the mixing rules for both a and b empirically. A study of experimental and theoretical bases for determination of interaction terms for Equations (2) and (3) was developed in the paper by Joffe and Zudkevitch (*11*), who were concerned principally with systems having unusual critical loci, for example, carbon dioxide—light hydrocarbon binaries. Chueh and Prausnitz (*6*) have determined an interaction term for a large number of binary mixtures, with particular emphasis on the improvement of the fugacity coefficient prediction. Their improvement incorporates both acentric factor and critical volume as well as an interaction constant specific to each binary mixture.

Wilson (*30*) and Barner et al. (*3*) investigated the possibility of changing the temperature dependence of the term A. Also, they all introduced the acentric factor into the equation as a third parameter. The Barner et al. modification is based on empirical evidence for a wider range of conditions. Their modification involves a graphical averaging procedure to force agreement with the two-term virial equation of state in the low pressure limit for compounds with nonzero acentric factor. It uses Pitzer and Curl's empirical correlation for the effect of acentric factor on the second virial coefficient (*15*).

The modification of Barner et al. has the advantage of being relatively simple. The principal disadvantage is that no information above the critical temperature is included in its development. It is of interest that the Barner et al. modification predicts $Z_c = 1/3$, unchanged from the original equation; in fact, it can be shown that no change in the temperature dependence of the A term can change Z_c, which remains one-third.

Chueh and Prausnitz (5) have shown that the prediction of saturated vapor density of pure components by the Redlich-Kwong equation is improved by changing the expression for determining the constants a and b. Instead of the constant premultipliers, 0.0866... and 0.427..., they use values determined from saturated vapor density for each component. In addition, they have shown that adjusting the premultipliers is effective in improving the liquid partial molal volume prediction of the equation. The best value of the premultiplier for the saturated liquid is different from that for saturated vapor. Generally the best premultiplier increases with increasing acentric factor for the saturated vapor and decreases for the saturated liquid. With the change in premultiplier advocated by Chueh and Prausnitz, the condition at which $(\partial P/\partial V)_T = 0$ and $(\partial^2 P/\partial V^2)_T = 0$ no longer corresponds to the component critical temperature and pressure. This introduces a slight inconsistency in the extent of the two-phase region.

Redlich and his co-workers (*1, 20, 21*) have maintained a continuing interest in improving the R-K equation by adding a correction term

$$Z = Z_{RK} + Z_2\,(T_r, P_r, \omega) \tag{4}$$

where Z_{RK} is the vapor root of Equation (1). Here the correction Z_2 need be evaluated only once at each set of conditions (T_r, P_r, ω) and does not enter into the iterative solution of Equation (1). Therefore, little extra logic or computation time is needed to accommodate a Z_2 correction of moderate complexity.

The additivity of the correction term is carried over into the evaluation of the isothermal pressure correction to vapor enthalpy. The pressure correction is given by (*28*)

$$\Delta H^P = -RT_r^2\,T_c \frac{\partial}{\partial T_r}\left\{\int_0^{P_r} (Z)\,\frac{dP_r}{P_r}\right\} \tag{5}$$

TABLE 1. SOURCES FOR COMPRESSIBILITY FACTOR DATA

A. Pure compounds	Data sources	Bibliography reference
Methane	Din, Vol. 3	*9*
Ethane	Din, Vol. 3	*9*
Propane	Din, Vol. 2	*9*
Butane	Sage and Lacey (1950)	*23*
Pentane	Timmermans, Sage, and Lacey (1950)	*23, 27*
Hexane	Timmermans	*27*
Heptane	Timmermans, Smith, et al.	*25, 27*
Ethylene	Din, Vol. 2	*9*
Propylene	Timmermans, Marchman, et al.	*15, 27*
Benzene	Organick and Studhalter	*17*
Hydrogen	Dean (NBS)	*8*
Nitrogen	Strobridge (NBS)	*26*
Water	Combustion Engineering Steam Tables	*7*
B. Mixtures		
Methane-propane	Sage and Lacey (1950)	*23*
Methane-butane	Sage and Lacey (1950)	*23*
Propane-pentane	Sage and Lacey (1950)	*23*
Ethane-propylene	Sage and Lacey (1955)	*23*
Butane-heptane	Kay (1940)	*13*
Ethane-butane	Kay (1940)	*12*
Propane-octane	Genco	*10*

For use with derived properties, it can be seen from Equations (4) and (5) that it is important that Z_2 may be integrated analytically with respect to $\ln P_r$.

The tentative conclusion of the analysis of previous work was that none of the modified R-K equations were really well suited to our needs. It was also concluded that a combination of the features of several of the modifications was possible. We therefore gathered experimental data from the literature to aid in the development of a modified form and provide the basis for a critical comparison of this form with those previously proposed.

CHOOSING DATA FOR COMPARISON

The most important data used were pure component light hydrocarbon data (C_1-C_7 *n*-paraffins, ethylene, and propylene). These data formed the basis for the primary comparison between methods and the development of the new correlation. These data were therefore carefully selected, mainly on the basis of the critical reviews of Din (*9*) and Timmermans (*27*). The data consisted of ninety-nine vapor density points along the vapor pressure curve up to the critical point, and 297 points along isotherms of reduced temperature ranging from 0.8 to 1.1 in the reduced pressure range 0 to 1.5.

In order to check the behavior of the methods when applied to components of less than primary interest, vapor Z data were gathered for benzene, nitrogen, water, and hydrogen. In addition, vapor Z's for light hydrocarbon mixtures were compiled, mostly for the saturation region. Data sources are summarized for all pure components and mixtures in Table 1.

DEVELOPMENT OF NEW CORRELATION

It was decided that a correlation of the general form of that proposed by Redlich and his students [that is, Equation (4)] was most suitable for our purposes. This form has the advantage of being expandable because Z_2 can be changed with no basic logic changes in the program. It is inherently capable of better accuracy than the Barner form. However, the constraint on second virial coefficient employed by Barner was adapted for use as a limiting condition of the new correlation. In addition, a separate term was added for better agreement near the critical point.

Two steps were involved in developing the function. Pure component compressibility factors from the original Redlich-Kwong equation were first calculated at the experimental conditions. Then the values of $Z - Z_{RK}$ were plotted as a guide to choice of a functional form for Z_2 and tabulated for input to a linear regression program. The linear regression program made use of a sequential application of the F test to throw out terms which did not contribute significantly to the reduction of variance. This is a useful curve fit artifice which has no statistical significance, since no independent estimate of the variance was used in forming the F ratios.

The form finally chosen is

$$\begin{aligned} Z_2 = {} & D_1 T_r^2 P_r^2 e^{-7{,}000(1-T_r)^2 - 770(1.02-P_r)^2} \\ & + \omega\,[-0.464419 + 0.424568\,T_r^2]\,\frac{P_r}{T_r^4 + P_r^4} \\ & + \omega\,[D_3 + D_4\,T_r]\,\frac{P_r^2}{(1+T_r)^4 + P_r^4} \\ & + [D_2 + \omega\,(D_5 + D_6\,T_r)]\,\frac{P_r^3}{(1+T_r)^4 + P_r^4} \end{aligned} \tag{6}$$

Table 2. Comparison of Vapor Z's Predicted by Redlich-Kwong Variants with Data from Normal Paraffins (C_1-C_7) and Olefins (C_2-C_3)

Region	No. pts.	Original RK	Dunlop form	Ackerman form	Barner form	Present modification
		Root-mean-square error in Z				
Saturation	99 (90)*	0.0342 (0.0307)*	0.0236 (0.0187)*	0.0219 (0.0157)*	0.0225 (0.0145)*	0.0098 (0.0100)*
Superheat	297	0.0186	0.0147	0.0101	0.0295	0.0085
Total	396	0.0263	0.0174	0.0149	0.0276	0.0094

* Numbers in parentheses: saturation region excluding critical point.

Table 3. Critical Compressibility Factors by the Various Methods

Component	Acentric factor	Experi- mental	Barner and original R-K	Dunlop	Ackerman	Present modifi- cation
		Zc				
Methane	0.001	0.2900	0.3333	0.334	0.290	0.2922
Propane	0.157	0.2776	0.3333	0.327	0.287	0.2771
Pentane	0.256	0.2685	0.3333	0.322	0.285	0.2676
Heptane	0.352	0.2597	0.3333	0.317	0.283	0.2586
Ethylene	0.089	0.2691	0.3333	0.329	0.289	0.2838
Propylene	0.147	0.2739	0.3333	0.326	0.287	0.2782

Only the constants D_1 through D_6 were determined by regression. The values are $D_1 = -0.04666626$, $D_2 = -0.11386032$, $D_3 = -41.76451266$, $D_4 = 40.47298767$, $D_5 = 12.55135462$, and $D_6 = -12.55831122$. By comparison, the Redlich-Dunlop form (*20*) contains nine adjustable constants; the Ackerman form (*1*) contains twenty-three. The first term was designed to make the equation fit at or near the critical point, and the exponents were estimated by using the curvature predicted by the Pitzer correlation for Z near the critical. The second term was designed to force agreement with Pitzer and Curl's correlation for the dependence of the second virial coefficient on ω and T_r (*19*). See the Appendix for more detail.

Equation (6) contains a number of compromises, the most significant of which is the choice of the form for the first term. A rather good fit is obtained for saturated vapor densities right up to the critical point. This is done only at the expense of a slight kink in the critical isotherm above the critical pressure. This will not normally be important. In addition, the accuracy will suffer outside the range of the data built into the correlation, although the limiting forms of the correlation insure against any wild behavior.

COMPARISON OF CORRELATION WITH PURE COMPONENT Z DATA

Table 2 gives an overall comparison with the pure component paraffin and olefin data of Z values predicted with the original Redlich-Kwong and the various modifications. The advantage of Equation (6) for data in this region is clearly decisive. The advantage over the Ackerman form almost entirely depends on the better representation of the saturation region. The Ackerman form is probably superior to Equation (6) at reduced temperatures greater than 1.1 and reduced pressures above 2.0.

The Barner modification gives accuracy as good as the forms of Ackerman and Dunlop in the saturation region, although not as good as Equation (6). It yields errors larger than those obtained from the original form for the superheated region because of its inability to reproduce the region where both *Pr* and *Tr* are greater than 1. In

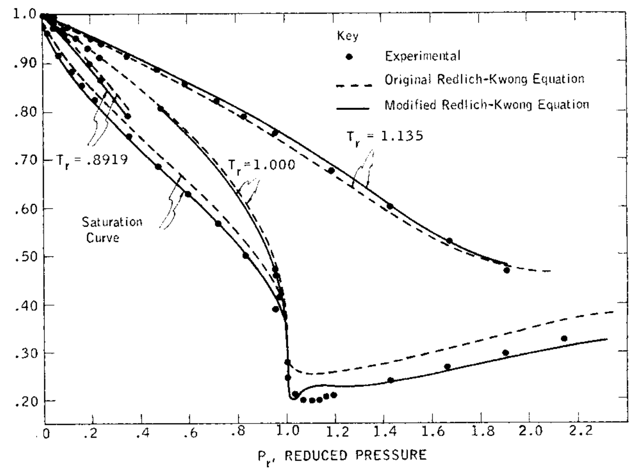

Fig. 1. Comparison of experimental and predicted compressibility factors for propane.

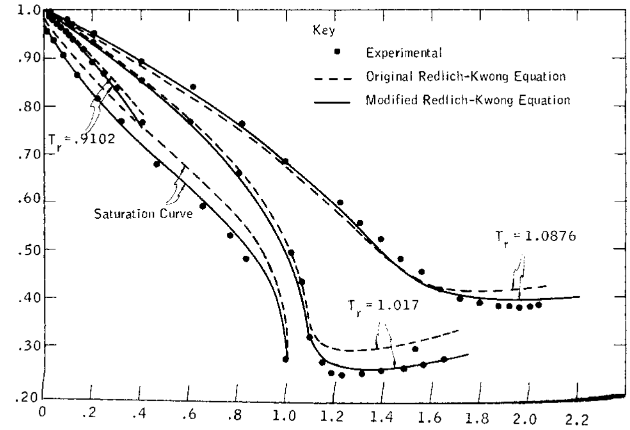

Fig. 2. Comparison of experimental and predicted compressibility factors for pentane.

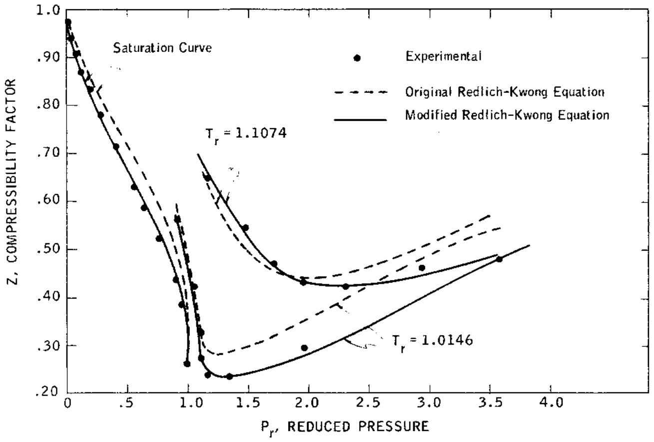

Fig. 3. Comparison of experimental and predicted compressibility factors for heptane.

view of its simplicity, it is useful when only the saturation region is of interest.

Note that comparisons for the saturated region in Table 2 include the critical point. Since the original Redlich-Kwong, the Dunlop modification, and the Barner modification were not intended to fit the critical point accurately, the errors quoted for the saturated region are somewhat misleading. Therefore, comparisons for the saturated region excluding the critical point are also given (in parentheses) in Table 2. The relative ranking of the methods is unchanged, but the attractiveness of the simple Barner modification in the saturated region is shown more strongly.

A comparison of the critical compressibility factors is given in Table 3. It can be seen that Equation (6) is the only one of the four modifications which reproduces the variation of Z_c with acentric factor (ω). The relatively large error in the Z_c predicted for ethylene is a reflection of the fact that ethylene does not follow the Z_c vs. ω relation of the paraffins.

Figures 1 through 3 show predicted vs. experimental Z's for propane, pentane, and heptane for both the original R-K equation and the R-K equation modified by Equation (6). These figures show how the improvement of the original equation varies with Tr, Pr, and ω. For methane (not shown) the improvement is negligible (except at the critical point), but as the acentric factor increases, the advantage of Equation (6) becomes marked. The saturation region and the critical region show the most improvement.

The kink in the critical isotherm is shown for propane, the only component for which extensive critical isotherm data were readily available. This was judged not too great a price to pay for the fit up to the critical point.

In Table 4, the original R-K equation and the new modification are compared with data for nitrogen, water, benzene, and hydrogen. The advantage of the modification is maintained, although not necessarily at as large a margin. The most important result of this comparison is that an acentric factor of zero should be used for hydrogen rather than the experimental value of −0.21. This follows the usual practice with the Pitzer tables. Also, it should be noted that true critical temperature and pressure were used for hydrogen, rather than adjusted values for quantum gases (5).

COMPARISONS WITH MIXTURE DATA

There were two purposes in examining the performance of the modified Redlich-Kwong with reference to mixture compressibility factors. The first was to establish the effectiveness of the correlation for mixtures. The second was to examine the effect of different mixture rules on Equation (6).

Mixtures rules enter Equation (6) through the definition of pseudocritical temperature and pressure. Several definitions can be used, the most obvious being a simple linear molal average (Kay's rule). However, as has been

TABLE 4. COMPARISON OF ORIGINAL AND MODIFIED REDLICH-KWONG EQUATION
DATA: VAPOR Z'S FOR NONPARAFFINS

Component	No. data points	Root-mean-square error in Z Original R-K	Modified R-K
Benzene	58	0.0223	0.01265
N_2	45	0.01612	0.00742
H_2O	10	0.04658	0.01739
H_2	25	0.02074	0.0532* 0.01304†

* $\omega = -0.21$.
† $\omega = 0.00$.

TABLE 5. COMPARISON OF ORIGINAL REDLICH-KWONG AND MODIFIED REDLICH-KWONG. DATA: VAPOR Z'S FOR MIXTURES

System	Mole frac. heavy comp.	(°F)	Pressure, lb./sq.in.abs.	No. points	Root-mean-square error Original	Modified
C_1-C_3	1.0	160	150 to 350	3	0.0181	0.0035
	0.8	160	150 to 550	5	0.0197	0.0138
	0.7	160	150 to 750	7	0.0143	0.01413
	0.6	160	150 to 1,150	10	0.0155	0.0196
	0.2	160	150 to 1,150	10	0.0023	0.0084
C_1-C_4	0.1 to 1.0*	100	100 to 1,912	23	0.0222	0.0241
	0.45 to 1.0*	220	100 to 1,520	14	0.0443	0.0469
C_3-C_5	0.248 to 0.853	160	40 to 190	16	0.0108	0.0028
	0.145 to 0.853	220	40 to 250	32	0.0150	0.0080
	0.145 to 0.752	280	40 to 250	14	0.0264	0.0089
	0.145 to 0.752	340	40 to 440	20	0.0275	0.0149
C_2-$C_3^=$	0.2 to 0.8	220	200 to 10,000	66	0.0207	0.0144
	0.1 to 0.9*	10 to 100	64 to 687	30	0.0299	0.0134
C_4-C_7	0.059 to 0.841*	159 to 446	40 to 440	37	0.0279	0.0121
C_2-C_4	0.053 to 0.825*	35 to 282	100 to 700	35	0.0175	0.0100
C_3-C_8	0.041 to 0.786*	252 to 504	250 to 840	38	0.0572	0.0551

* Saturated vapor data.

Table 6. Isothermal Pressure Corrections to Enthalpy Compared with Sage and Lacey's Derived Values for Pentane

Range of reduced temperature	Range of reduced pressure	Number of points	Root-mean-square error, B.t.u./lb. mole (B.t.u./lb.)	
			Original R-K	Modified R-K
0.94 to 1.08	0 to 2.0	20	789 (11.0)	248 (3.4)
1.00 to 1.08	2.0 to 4.0	12	1,321 (18.5)	462 (6.4)
Saturated vapor		10	344 (4.8)	73.5 (1.0)

Table 7. Isothermal Pressure Correction to Enthalpy at the Critical Temperature and Pressure

Compound	$\Delta H_C{}^P$ B.t.u./lb. mole Original R-K	Modified R-K	Pitzer
Methane	1,680	1,623	1,608
Ethane	2,589	2,804	3,029
Propane	3,251	3,642	3,664
Butane	3,607	4,214	4,407
Pentane	4,000	4,834	5,095
Hexane	4,314	5,376	5,730
Heptane	4,580	5,898	6,351
Ethylene	2,401	2,577	2,618
Propylene	3,107	3,479	3,577

pointed out by Joffe and Zudkevitch (*11*), the mixing rules for an equation of state also imply pseudocritical properties. That is, if the pseudocritical concept is valid, the definitions of *a* and *b* in terms of pure component criticals also express the relations of the mixture pseudocriticals to the mixture constants given by Equations (2) and (3). This yields two equations which may be solved to give mixture pseudocritical temperature and pressure in terms of pure component values.

It was found that the pseudocriticals which agree with the R-K mixing rules [Equations (2) and (3)] had a slight advantage over the simple Kay's rule in predicting mixture vapor Z's. Use of the R-K pseudocriticals introduces little complication into the derived properties. However, no advantage was found for using the very complicated empirical modification to the Redlich-Kwong pseudocriticals proposed by Redlich et al. (*21*). The Redlich-Kwong pseudocriticals were therefore chosen, since they are also the most consistent with the assumptions of the original equation.

Results of comparisons made for mixtures are shown in Table 5. The improvement over the original R-K equation is substantial, except for methane systems and propane-octane, where the root-mean-square error is about the same. The errors in methane-propane are relatively small, and the lack of improvement largely reflects the good fit of the original Redlich-Kwong equation. The larger errors in predicting the behavior of the methane-butane and propane-octane mixtures indicate difficulty in characterizing vapor densities at saturation when the difference in molecular size is substantial. Addition of an interaction term of the kind proposed by Chueh and Prausnitz and Joffe and Zudkevitch to the mixing rules of the original R-K equation might improve the equation for such mixtures.

ENTHALPY PREDICTION BY THE MODIFIED REDLICH-KWONG EQUATION

The pressure correction to vapor enthalpy by the modified Redlich-Kwong equation is given by applying Equation (5) to Equation (4):

$$\Delta H^P = \Delta H_{R-K} + \Delta H_2 \tag{7}$$

where

$$\Delta H_{R-K} = RT\,(Z_{R-K} - 1) - \frac{3A^2RT}{2B}\ln\left(1 + \frac{BP}{Z_{R-K}}\right) \tag{8}$$

and

$$\Delta H_2 = -\,RT_r{}^2\,T_c\,\frac{\partial}{\partial T_r}\left\{\int_0^{P_r} (Z)_2\,\frac{dP_r}{P_r}\right\} \tag{9}$$

Here ΔH_{R-K} is the value given by the original Redlich-Kwong equation (note that Z_{R-K} is the value from the original equation), and ΔH_2 is the correction for the modified equation. The integration in Equation (9) must be carried out analytically for computational efficiency. The derivative of the resulting integral can be carried out either analytically or (with some care) numerically. Both analytical and numerical derivatives were taken in this work as a check. Equation (9) is worked out in more detail in the Appendix.

Equation (7) was checked for consistency by comparing the predicted pressure correction for pure components with literature values derived from P-V-T data. This was necessary because few calorimetric data are available. One such comparison is shown in Table 6 for normal pentane. It can be seen that substantial improvement over the original Redlich-Kwong equation is obtained in both saturated and superheated regions, although both equations show a decrease in accuracy for superheated conditions.

Another kind of consistency check is shown in Table 7 where the pressure correction to enthalpy at the critical temperature and pressure for several light hydrocarbons is compared with value given by the Pitzer correlation. This shows that the modified Redlich-Kwong equation gives the proper trend with acentric factor and the right order of magnitude at critical conditions.

Comparisons with experimental data for two systems considered by Barner et al. (*3*) for their modification of the Redlich-Kwong equation are shown in Table 8. These

Table 8. Isothermal Pressure Correction to Vapor Enthalpy Compared with Experimental Values

System	No. points	Root-mean-square error, B.t.u./lb. mole (B.t.u./lb.) Original R-K	Present modification	Barner et al. modification	Barner et al. B-W-R
Propane-benzene* (saturated vapor)	10	569 (10.4)	365 (6.4)	386 (7.0)	401 (7.3)
Propane-butane-pentane† (near saturation)	14	393 (6.2)	142 (2.2)	161 (2.5)	165 (2.6)

* Data from Yarborough and Edmister (*32*) as reported by Barner et al. (*3*).
† Data from Nelson and Holcomb (*16*) as reported by Barner et al. (*3*).

comparisons correspond to Tables 3 and 5 of their paper. The present equation agrees closely with the Barner modification for these systems, since they are near saturation. Both modifications agree closely with the B-W-R equation (as reported by Barner).

For the propane-butane-pentane system, the modified equation shows considerable improvement over the original equation, and agreement with data is satisfactory. For the propane-benzene system, some improvement is shown, but the modified form still shows substantial error. As noted by Barner et al., this may be the result of inadequate mixing rules for the coefficients a and b, or it may be the result of experimental error, since too few data points are available to estimate the precision of the data.

CONCLUSIONS

The present modification should be useful when a relatively compact analytical equation suitable for computer use is needed for predicting vapor compressibilities and vapor enthalpy pressure correction in the saturated and immediately superheated region.

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NOTATION

a, b = constants of Redlich-Kwong equation
A, B = temperature dependent term related to constants of Redlich-Kwong equation [see Equation (1)]
B = second virial coefficient (Appendix only)
B_{R-K} = second virial coefficient predicted by Redlich-Kwong equation
D_i = constants (i = 1-6) in deviation function determined by regression
H^0 = enthalpy of pure component or mixture at zero pressure
H^P = enthalpy of pure component or mixture at a pressure P
ΔH^P = $H^0 - H^P$, isothermal pressure correction to enthalpy
$\Delta H^P{}_{R-K}$ = isothermal pressure correction predicted by Redlich-Kwong equation [Equation (8)]
$\Delta H_2{}^P$ = deviation function for isothermal pressure correction (Appendix)
P = system pressure, lb./sq.in.abs.
P_c = component critical pressure or mixture pseudocritical pressure, lb./sq.in.abs.
P_r = P/P_c reduced pressure
R = gas constant
T = system temperature, °R.
T_c = component critical temperature or mixture pseudocritical temperature, °R.
T_r = reduced temperature
V = molar volume cu.ft./lb. mole
y_i = mole fraction component i in vapor
Z = PV/RT compressibility factor
Z_{R-K} = compressibility factor from Redlich-Kwong equation
Z_2 = deviation function correction to Redlich-Kwong Z
θ = Z_2RT/P
ω = Pitzer's acentric factor

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APPENDIX

Determination of Constants for the Modified Redlich-Kwong Equation

Redlich and his students seem to have assumed that adding a deviation function to the original Redlich-Kwong equation will not change the expressions for a and b. While this is true, an additional requirement on the deviation function must be met. Equation (4) may be written in the form

$$P = \frac{RT}{V - \theta - b} - \frac{a}{T^{1/2}} \frac{1}{(V - \theta + b)(V - \theta)} \qquad (A1)$$

where

$$\theta = \frac{Z_2RT}{P} \qquad (A2)$$

and Z_2 is the deviation function of Equation (4).

The partial derivatives of P with respect to V may then be taken and set equal to zero at the critical point by using the chain rule to avoid the difficulty that θ is a function of T and P rather than T and V. Provided only that $(\partial\theta/\partial P)_T$ and $(\partial^2\theta/\partial P^2)_T$ are finite at the critical point, the equations relating a and b to T_c and P_c are unchanged. However, two other expressions related to determination of the constants, that $Z_c = 1/3$ and that $b = (\sqrt[3]{2} - 1)\ V_c$ are no longer true for the modified equation.

Low Pressure Limits and the Virial Equation

The second virial coefficient B can be defined as (*24*)

$$B = \lim_{\substack{P \to 0 \\ V \to \infty}} (Z - 1)V$$

It is fairly easy to show, by expansion in series, that (assuming Z_2T_r/P_r has a low pressure limit) we can write the second virial coefficient in dimensionless form as

$$\frac{BP_c}{RT_c} = \frac{B_{R\text{-}K}P_c}{RT_c} + \lim_{P \to 0}\left(\frac{Z_2T_r}{P_r}\right) \qquad (A3)$$

where

$$\frac{B_{R\text{-}K}P_c}{RT_c} = 0.08666 - T_r^{3/2}$$

Here $B_{R\text{-}K}$ is the second virial coefficient as a function of temperature predicted by the original Redlich-Kwong equation. As Barner (*3*) points out, this fits the data rather well for spherical molecules. Thus the second term in Equation (3) should include the effect of acentric factor on the virial coefficient but should have no terms to affect B when the acentric factor is zero. This was arranged in choosing the form for Z_2 in Equation (6) by the following:

- No terms in the numerator of lower order than first in P_r were used so the second term in (A-3) would be defined.
- No terms in numerator of lower order than second were included in terms not multiplied by acentric factor ω.
- The terms of first order in P_r multiplied by ω [second term in Equation (6)] were determined from Pitzer and Curl's correlation for the dependence of B on ω (*15*).

Pitzer and Curl's function $f_0\ (T_r)$ is very close to $B_{R-K}\ P_c/RT_c$. The function $f_1\ (T_r)$ was represented by a much simplified form which reproduces Pitzer and Curl's function for $T_r < 0.6$.

Use of the second virial coefficient correlation to guide the low pressure limit in this way makes Equation (6) valid over a larger range of reduced temperatures in the low pressure limit than would otherwise be true. It should be pointed out that the pressure dependence of the denominator in the second term of Equation (6) was not fixed by this procedure, and a certain amount of trial and error was necessary to obtain a satisfactory fit to the data.

Pressure Correction to Enthalpy For The Modified Equation

The deviation of the isothermal pressure correction to enthalpy from that given by the original equation is given by Equation (9). Equation (9) requires the evaluation of the integral

$$I = \int_0^{P_r} Z_2 \frac{dP_r}{P_r}$$

where Z_2 is given by Equation (6).

The integral is given by

$$\begin{aligned} I = {} & D_1T_r^2\ [\exp\ (-7{,}000\ (1 - T_r)^2)]I_1 \\ & + \omega\ [-0.464419 + 0.424568\ T_r^2]I_2 \\ & + \omega\ [D_3 + D_4T_r]I_3 \\ & + [D_2 + \omega\ (D_5 + D_6T_r)]I_4 \end{aligned}$$

Where

$$I_1 = \int_0^{P_r} x[\exp\ (-770\ (1.02 - x)^2)]dx$$

$$I_2 = \int_0^{P_r} \frac{1}{T_r^4 + x^4}\, dx$$

$$I_3 = \int_0^{P_r} \frac{x}{(1 + T_r^4) + x^4}\, dx$$

$$I_4 = \int_0^{P_r} \frac{x^2}{(1 + T_r)^4 + x^4}\, dx$$

By standard procedures

$$\begin{aligned} I_1 = {} & \frac{-1.02}{\sqrt{770}}\frac{\sqrt{\pi}}{2}\{\mathrm{erf}[\sqrt{770}(1.02 - P_r)] - \mathrm{erf}[1.02\sqrt{770}]\} \\ & - \frac{1}{2(770)}[\exp(-770(1.02 - P_r)^2 - \exp(-770(1.02)^2)] \end{aligned}$$

$$\begin{aligned} I_2 = {} & \frac{1}{4\sqrt{2}\,T_r^3}\ln\left[\frac{P_r^2 + \sqrt{2}\,P_rT_r + T_r^2}{P_r^2 - \sqrt{2}\,P_rT_r + T_r^2}\right] + \frac{1}{2\,T_r^3\sqrt{2}} \\ & \left\{\tan^{-1}\left(\frac{2\,P_r + \sqrt{2}\,T_r}{\sqrt{2}\,T_r}\right) + \tan^{-1}\left(\frac{2\,P_r - \sqrt{2}\,T_r}{\sqrt{2}\,T_r}\right)\right\} \end{aligned}$$

$$I_3 = \frac{1}{2(1 + T_r)^2}\tan^{-1}\left(\frac{P_r^2}{(1 + T_r)^2}\right)$$

$$\begin{aligned} I_4 = {} & -\frac{1}{2\sqrt{2}(1 + T_r)}\ln \\ & \left[\frac{P_r^2 + \sqrt{2}(1 + T_r)P_r + (1 + T_r)^2}{P_r^2 - \sqrt{2}(1 + T_r)P_r + (1 + T_r)^2}\right] + (1 + T_r)^2\, I_2^* \end{aligned}$$

where I_2^* is I_2 with T_r replaced by $1 + T_r$.

It is interesting to note that the inverse tangent term in I_2 is not the one obtained from standard integral tables, which give a contracted form based on an identity for the tangent of the sum of two angles. This contracted form introduces a spurious discontinuity if the principal value of the argument of the inverse tangent is used.

Equation (9) also requires differentiation of I by T_r. This is rather lengthy, but it has been performed. The analytical derivative has been checked by numerical differentiation; the analytical derivative is slightly more efficient in computer time and storage. The isothermal pressure correction deviation given by analytical differentiation is

$$\Delta H_2 = -RT_r^2\,T_c\{A_1I_1 + A_2I_2 + A_3I_3 + A_4I_4 + A_5 + A_6\}$$

where

$$A_1 = 2D_1T_r[7{,}000\ T_r(1 - T_r) + 1]\exp[-7{,}000(1 - T_r)^2]$$

$$A_2 = \omega\left[2(0.424568)T_r + \frac{3}{T_r}(0.464419 - 0.424568\ T_r^2)\right]$$

$$A_3 = \omega\left[D_4 - \frac{2}{(1 + T_r)}(D_3 + D_4T_r)\right]$$

$$A_4 = \omega D_6 - \frac{D_2 + \omega(D_5 + D_6\,T_r)}{(1 + T_r)}$$

$$A_5 = \omega\ (0.464419 - 0.424568\ T_r^2)\frac{P_r}{T_r(P_r^4 + T_r^4)}$$

$$\begin{aligned} A_6 = {} & -\frac{P_r^2}{(1 + T_r)[P_r^4 + (1 + T_r)^4]}\left\{\omega(D_3 + D_4\,T_r)\right. \\ & \left. + \frac{P_r}{2}[D_2 + \omega(D_5 + D_6T_r)]\right\} \end{aligned}$$