A Modified Redlich-Kwong Equation for Supercritical Helium and Hydrogen

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A modified Redlich-Kwong equation of state is developed in which the two parameters are expressed as functions of temperature. The critical values for the two constants in the equation are completely determined by the values of the critical properties of the gas. The optimum values of the constants for each isotherm (Z vs. P) are found, followed by a curve-fitting routine that obtains the constants as functions of temperature. The resulting equation of state predicts experimental helium compressibility data to within an average of 0.90% absolute error for data in the range $0 < \text{pressure} \leqq 700$ atm., $5.26°\text{K.} \leqq \text{temperature} \leqq 1{,}500°\text{K}$. For hydrogen, the prediction is to within an average of 0.79% absolute error for temperatures from 34° to 600°K. and pressures up to 2,900 atm.

Since the pioneering work of Van der Waals (*31*) in 1873, there have been many equations of state proposed for predicting the P-V-T behavior of gases. Many of these equations contain several constants which must be determined empirically or semitheoretically. If a high order of precision is required in predicting experimental data for large temperature and pressure ranges, as many as forty-four constants may be necessary; however, two or three constants often suffice over smaller ranges. Martin (*19*) has given a detailed discussion on the nature of this problem.

The two constant equation developed by Redlich and Kwong (*26*) predicts the P-V-T behavior of gases with reasonable accuracy. Their equation has the following form:

$$P = \frac{RT}{(V - \underline{b})} - \frac{\underline{a}}{T^{1/2}\, V(V + \underline{b})} \tag{1}$$

The ability of this equation to predict experimental data has been substantiated by Estes and Tully (*8, 9*), Shah and Thodos (*28*), and Martin (*19*). The advantage of this equation is that the constants are directly related to the critical properties of the gas (when these constants are determined in this manner they will be referred to as the *critical constants*):

$$\underline{a}_c = \frac{\Omega_a R^2 T_c^{5/2}}{P_c} \tag{2}$$

$$\underline{b}_c = \frac{\Omega_b R T_c}{P_c} \tag{3}$$

There has been some question recently concerning the technique which should be used in finding the values for these constants. In the original formulation of the above equation of state, Redlich and Kwong state that $\underline{b}$ represents the limiting volume of a gas at high pressure. By using this information, Estes and Tully found that in the expression for $\underline{b}$ as a function of critical constants the coefficient Ω_b for helium should be 0.06372 rather than the original value of 0.0867 [obtained by solving $(\partial P/\partial V)_T = (\partial^2 P/\partial V^2)_T = 0$ at the critical point]. They also determined that the original Ω_a (0.4278) in the expression for $\underline{a}$ could not be improved. Their findings, therefore, indicate that Ω_a and Ω_b for a given substance are constant for all temperatures and pressures. Similar studies by Chueh and Prausnitz (*6, 7*) show that Ω_a and Ω_b depend on the substance but remain constant as temperature and pressure vary. Another modification of the equation has recently been presented by Barner, Pigford, and Schreiner (*1*).

Investigations by Wilson (*35, 36*), Robinson and Jacoby (*27*), and Mason (*20*) indicate that the constants $\underline{a}$ and $\underline{b}$ are actually functions of temperature. Mason's results indicate that for each noncritical isotherm there are optimum values for $\underline{a}$ and $\underline{b}$ which give better predictions of compressibility data than the critical constants. This temperature dependence is to be expected because $\underline{a}$ and $\underline{b}$ are related to the virial coefficients which are functions of temperature.

The purpose of this paper is to present a technique for finding the critical constants and expressions establishing the temperature dependence of $\underline{a}$ and $\underline{b}$. These results will then be used to propose a modified Redlich-Kwong equation. The paper will give the most general technique for finding $\underline{a}$ and $\underline{b}$ with specific results presented for helium and hydrogen.

METHOD FOR FINDING Ω_a AND Ω_b

The classical technique used for determining $\underline{a}_c$ and $\underline{b}_c$ is based on the behavior of the critical isotherm on a $P-V$ diagram. The critical point is a point of horizontal slope and inflection on this figure; therefore, the first two $P-V$ derivatives are

$$\left(\frac{\partial P}{\partial V}\right)_{T_c} = 0 \tag{4}$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T_c} = 0 \tag{5}$$

Differentiating Equation (1) twice and evaluating each partial derivative at the critical temperature we get expressions for $\underline{a}_c$ and $\underline{b}_c$ in terms of the critical properties. Eliminating $\underline{a}_c$ from the resulting equalities we get

$$\underline{b}_c = 0.26\, V_c \tag{6}$$

Substitution of Equation (6) into (1) at the critical point generates an equation for $\underline{a}_c$ in terms of the critical properties and the gas constant

$$\underline{a}_c = 0.4278\, \frac{R^2 T_c^{5/2}}{P_c} \tag{7}$$

from which

$$\underline{b}_c = 0.0867\,\frac{R\,T_c}{P_c} \tag{8}$$

This derivation has one major drawback; that is, it states that Ω_a and Ω_b are constant for all gases and at all temperatures. The following technique allows variation of these quantities with temperature and their calculation with knowledge of only the critical compressibility factor Z_c.

The first step involves consideration of Equations (2) and (3) where Ω_a and Ω_b are now variable. From the definition $Z_c = P_cV_c/RT_c$, the above equations become

$$\underline{a}_c = \alpha R T_c^{3/2}\,V_c \tag{9}$$

$$\underline{b}_c = \beta V_c \tag{10}$$

with $\alpha = \Omega_a/Z_c$ and $\beta = \Omega_b/Z_c$.
The new coefficients α and β have been introduced to simplify the final results. Equation (1) may be rewritten in terms of the compressibility factor as

$$Z \equiv \frac{PV}{RT} = \frac{V}{V-b} - \frac{a}{RT^{3/2}\,(V+b)} \tag{11}$$

Substitution of Equations (9) and (10) into (11) yields

$$Z = \frac{V}{V-\beta V_c} - \frac{\alpha T_c^{3/2}\,V_c}{T^{3/2}\,(V+\beta V_c)} \tag{12}$$

and at the critical point

$$Z_c = \frac{V_c}{V_c-\beta V_c} - \frac{\alpha T_c^{3/2}\,V_c}{T_c^{3/2}\,(V_c+\beta V_c)} \tag{13}$$

or

$$Z_c = \frac{1}{1-\beta} - \frac{\alpha}{1+\beta} \tag{14}$$

Rearranging Equation (14) we get

$$\alpha = \frac{(1+\beta) - Z_c(1-\beta^2)}{(1-\beta)} \tag{15}$$

Substituting Equations (15) and (10) into Equation (1) we get

$$P = \frac{RT}{V-\beta V_c} - \left[\frac{(1+\beta) - Z_c(1-\beta^2)}{(1-\beta)}\right]\frac{RT_c^{3/2}\,V_c}{T^{1/2}V\,(V+\beta V_c)} \tag{16}$$

Differentiating Equation (16) with respect to volume at constant temperature and then equating to zero (at the critical point) we obtain

$$\frac{1}{(1-\beta)} = [1 - Z_c\,(1-\beta)]\,\frac{(2+\beta)}{(1+\beta)} \tag{17}$$

Upon rearrangement, the result is

$$\beta^3 + \frac{1}{Z_c}\,\beta^2 + \frac{(2-3Z_c)}{Z_c}\,\beta + \frac{(2Z_c-1)}{Z_c} = 0 \tag{18}$$

Equation (18), therefore, allows β to be calculated with knowledge of only Z_c. The method for solving this cubic equation is given in Perry's (25), and there will be only one positive real root because Z_c is always positive. The value of α is then determined by Equation (15) because the values of β and Z_c are known.

The above method is more convenient than the previous methods for obtaining the critical constants because α and β (Ω_a and Ω_b) are determined for each substance by knowing only Z_c. This procedure establishes the values of the critical constants without requiring any trial-and-error techniques and forces the equation to predict the correct value of Z_c rather than 0.333 as when Equations (7) and (8) are used.

A MODIFIED REDLICH-KWONG EQUATION OF STATE

As stated earlier, $\underline{a}$ and $\underline{b}$ should be considered functions of temperature. To account for this temperature dependence, assume that Equations (2) and (3) have the following form:

$$\underline{a} = \Omega_a\,\frac{R^2\,T_c^{5/2}}{P_c}\,f(T_R) \tag{19}$$

$$\underline{b} = \Omega_b\,\frac{RT_c}{P_c}\,h(T_R) \tag{20}$$

The two arbitrary functions of reduced temperature have only one requirement; that is

$$f(T_R) = h(T_R) = 1 \quad \text{at} \quad T_R = 1 \tag{21}$$

This is a necessary condition, since at the critical point $\underline{a}_c$ and $\underline{b}_c$ must retain the critical values established by Equations (9) and (10). Multiplying the numerator and denominator of Equation (12) by $(1/V_c)$ we get

$$Z = \frac{V_R}{V_R - \dfrac{\underline{b}}{V_c}} - \frac{\underline{a}/V_c}{RT^{3/2}\left(V_R + \dfrac{\underline{b}}{V_c}\right)} \tag{22}$$

From Equations (19) and (20)

$$\frac{\underline{a}}{V_c} = \Omega_a\,\frac{RT_c^{3/2}}{Z_c}\,f(T_R) = \alpha R\,T_c^{3/2}\,f(T_R) \tag{23}$$

$$\frac{\underline{b}}{V_c} = \Omega_b\,\frac{h(T_R)}{Z_c} = \beta\,h(T_R) \tag{24}$$

Substitution of Equations (23) and (24) into Equation (22) gives the reduced equation of state

$$Z = \frac{V_R}{V_R - \beta\,h(T_R)} - \frac{\alpha\,f(T_R)}{T_R^{3/2}\,[V_R + \beta\,h(T_R)]} \tag{25}$$

The derivation of the above equation assumes that the law of corresponding states is applicable. It is a modification of the Redlich-Kwong equation of state for the following reason. The original R-K equation does not allow α and β to vary for different substances, nor $\underline{a}$ and $\underline{b}$ to vary with temperature. It should be emphasized that the addition of $f(T_R)$ and $h(T_R)$ does not necessarily make the above equation more complicated than other modifications because Ω_a and Ω_b are no longer adjustable.

OPTIMIZING AND CURVE FITTING $\underline{a}$ AND $\underline{b}$ AS FUNCTIONS OF TEMPERATURE

The optimum values for $\underline{a}$ and $\underline{b}$ by using the Redlich-Kwong equation are obtained at each isotherm for which experimental Z data are available. For each temperature, the optimal values are found by a nonlinear, least-squares analysis. The objective function is given by

$$S = \sum_{n=1}^{N}\,(Z_n^{o} - Z_n^{p})^2, \quad T = \text{constant} \tag{26}$$

TABLE 1. SOURCES OF EXPERIMENTAL P-V-T DATA FOR HELIUM AND PREDICTIVE ABILITY OF PROPOSED EQUATION

Source	Pressure range, atm.	Temperature range, °K.	Modified R-K equation MAE, %	AAE, %
Blancett (*4*)	2.9 to 695	220 to 320	0.41	0.07
Canfield (*5*)	2.2 to 530	130 to 270	0.45	0.05
Hall (*11*)	2.0 to 710	83 to 115	0.83	0.21
Hill (*13*)	1.3 to 100	7 to 20	12.67	3.78
Holborn and Otto (*14, 15*)	1.3 to 105	15 to 675	3.47	0.84
Keesom (*17*)	1.0 to 100	30 to 60	4.90	1.25
Michels (*21*)	9.1 to 290	270 to 420	0.24	0.05
Miller et al. (*24*)	6.3 to 275	250 to 330	0.41	0.06
Sullivan (*29*)	12.7 to 695	70 to 120	3.07	0.71
Wiebe et al. (*34*)	100.0 to 1,000	200 to 473	1.90	0.54
Yntema and Schneider (*38*)	6.0 to 75	770 to 1,470	0.02	0.01

and when S is a minimum the optimal values are obtained. For S to be a minimum

$$\left(\frac{\partial S}{\partial \underline{a}}\right)_{\underline{b}} = 0 \tag{27}$$

$$\left(\frac{\partial S}{\partial \underline{b}}\right)_{\underline{a}} = 0 \tag{28}$$

where these partials are obtained by differentiating Equation (26). If, however, the partials are not equal to zero when evaluated by using $\underline{a}_c$ and $\underline{b}_c$, then Equations (27) and (28) are set equal to

$$F_{\underline{a}}^{n} = \left(\frac{\partial S}{\partial \underline{a}}\right)_{n} \tag{29}$$

$$F_{\underline{b}}^{n} = \left(\frac{\partial S}{\partial \underline{b}}\right)_{n} \tag{30}$$

It then follows that

$$F_{\underline{a}}^{n} + \left(\frac{\partial F_{\underline{a}}}{\partial \underline{a}}\right)_{n} \Delta\underline{a} + \left(\frac{\partial F_{\underline{a}}}{\partial \underline{b}}\right)_{n} \Delta\underline{b} = F_{\underline{a}}^{n+1} \tag{31}$$

$$F_{\underline{b}}^{n} + \left(\frac{\partial F_{\underline{b}}}{\partial \underline{a}}\right)_{n} \Delta\underline{a} + \left(\frac{\partial F_{\underline{b}}}{\partial \underline{b}}\right)_{n} \Delta\underline{b} = F_{\underline{b}}^{n+1} \tag{32}$$

The equations will be equal to zero at the optimum because conditions (27) and (28) will be satisfied and Δa and Δb will be zero. Equations (31) and (32) are solved for Δa and Δb and iterated by letting

$$\underline{a}^{n+1} = \underline{a}^{n} + \Delta\underline{a} \tag{33}$$

$$\underline{b}^{n+1} = \underline{b}^{n} + \Delta\underline{b} \tag{34}$$

The new values for $\underline{a}$ and $\underline{b}$ are then used to recalculate all the partial derivatives, and this procedure is continued until $\Delta\underline{a}$ and $\Delta\underline{b}$ are arbitrarily near zero. When this occurs, the objective function has attained a minimum, and the conditions for an optimum are satisfied.

Once the optimum values for $\underline{a}$ and $\underline{b}$ are obtained for each isotherm, the variation with temperature can be determined. The least-squares procedure proposed by Hall and Canfield (*12*) was used extensively in this effort. One requirement for using this technique is that the form of the function of temperature must be stipulated.

RESULTS

Helium and hydrogen have been chosen as the gases for this initial study for two reasons. First, there are abundant experimental P-V-T data in the literature which can be converted into Z vs. *P* data (Tables 1 and 2 give the sources for the experimental helium and hydrogen data with corresponding temperature and pressure ranges). Second, because helium and hydrogen are quantum gases, their behavior should provide a stringent test of the ability of this method to predict compressibility data. Work is currently under way to extend the present modification to nonquantum gases.

Tables 1 and 2 contain data which the authors feel are representative and sufficient for this study. Calculation of the critical values for $\underline{a}$ and $\underline{b}$ requires only a knowledge

TABLE 2. SOURCES OF EXPERIMENTAL P-V-T DATA FOR HYDROGEN AND PREDICTIVE ABILITY OF PROPOSED EQUATION

Source	Pressure range, atm.	Temperature range, °K.	Modified R-K equation MAE, %	AAE, %
Bartlett et al. (*2*)	1.0 to 1,000	270 to 670	0.67	0.24
Bartlett et al. (*3*)	1.0 to 1,000	200 to 290	0.77	0.10
Goodwin et al. (*10*)	1.4 to 350	34 to 100	27.02	3.16
Holborn and Otto (*14* to *16*)	1.3 to 105	65 to 470	4.69	0.33
Johnston and White (*18*)	1.0 to 200	35 to 300	24.49	1.58
Michels et al. (*22*)	3.6 to 2,900	100 to 420	7.86	0.81
Michels et al. (*23*)	75.8 to 1,200	270 to 370	0.57	0.17
Townend and Bhatt (*30*)	1.0 to 600	270 to 300	0.34	0.10
Verschoyle (*32*)	46.1 to 205	270 to 290	0.45	0.19
Wiebe and Gaddy (*33*)	25.0 to 1,000	270 to 570	0.55	0.23
Woolley et al. (*37*)	0.2 to 1,700	38 to 600	10.71	0.74

of the critical properties. The critical values used for helium are $T_c = 5.25°K.$, $P_c = 2.26$ atm., and $Z_c = 0.300$; those used for hydrogen are $T_c = 33.25°K.$, $P_c = 12.80$ atm., and $Z_c = 0.304$. The value of Z_c allows the calculation of α and β from Equations (15) and (18). Table 3 compares the Ω_a and Ω_b values for both gases based on the original Redlich-Kwong equation, the Estes and Tully equations, and the modified R-K equation. The error associated with the original values is that Redlich and Kwong based their entire analysis on the behavior of the critical isotherm; therefore, the Z_c obtained does not correspond to the actual value. The values recommended by Estes and Tully differ from the proposed values because they ignore the quantum effects which become prevalent at very low temperatures.

By substituting the critical values, and the modified R-K equation Ω_a and Ω_b for each gas, Equations (19) and (20) become, respectively, for helium

$$\underline{a} = 79{,}480\, f(T_R) \tag{35}$$

$$\underline{b} = 16.241\, h(T_R) \tag{36}$$

and for hydrogen

$$\underline{a} = 14.2036 \times 10^5 f(T_R) \tag{37}$$

$$\underline{b} = 18.227\, h(T_R) \tag{38}$$

By using the critical values for $\underline{a}$ and $\underline{b}$ to start the iterative Newton-Raphson method, the optimum values are obtained for each isotherm. Figures 1 through 4 give the results for $\underline{a}$ and $\underline{b}$ as functions of temperature for both helium and hydrogen. All figures exclude those optimum values of $\underline{a}$ and $\underline{b}$ which, because of extreme scattering, do not follow the indicated trend. The choice of the critical values as a starting point for this optimization does not affect the final results, since the objective function represents a unimodal surface. This is verified by using several different starting points.

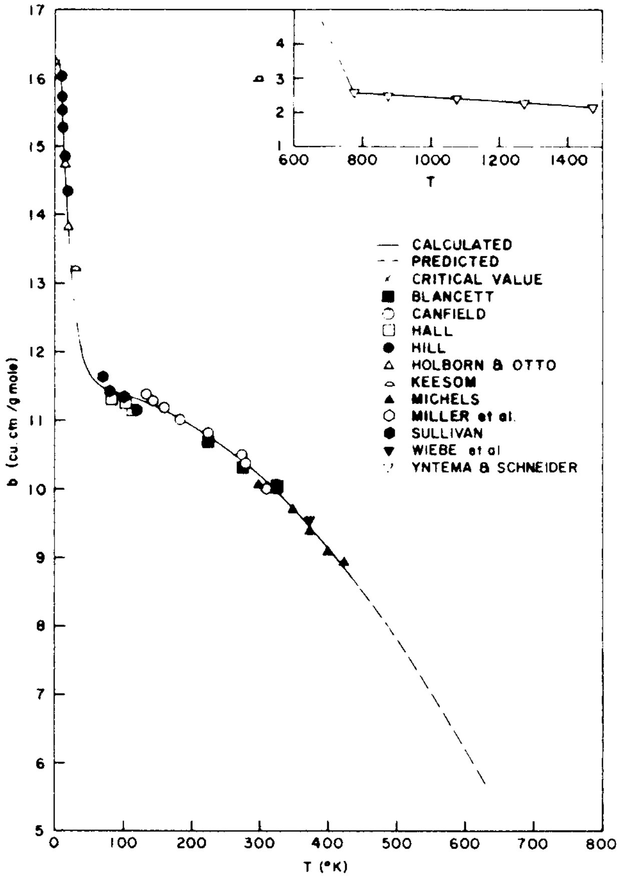

Fig. 2. Optimum values for $\underline{b}$ as a function of temperature for helium.

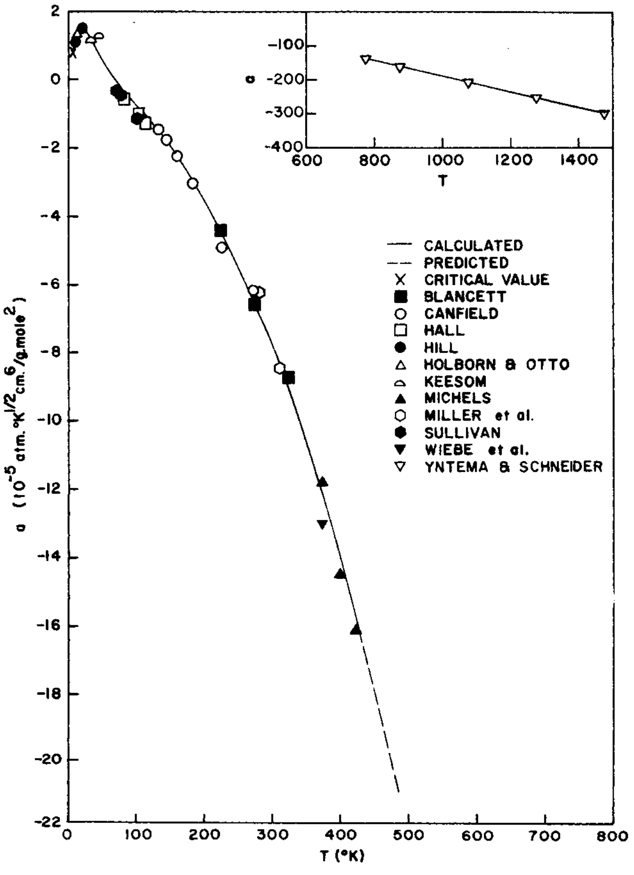

Fig. 1. Optimum values for $\underline{a}$ as a function of temperature for helium.

HELIUM

The variation of $\underline{b}$ with temperature (Figure 2) for helium exhibits three regions each signifying a different type of behavior. Below 70°K. the sharp rise up to the critical value can be associated with a quantum correction. The data between 70° and 750°K. have a trend which might be called *classical*. Above 750°K. there is a definite change in slope, and this region will be said to have "high temperature" behavior.

Table 3. Comparison of Different Values for Ω_a and Ω_b

	Helium	
	Ω_a	Ω_b
Modified R-K equation	0.4224	0.08520
Estes and Tully equation	0.4278	0.06372
Original R-K equation	0.4278	0.08670
	Hydrogen	
	Ω_a	Ω_b
Modified R-K equation	0.4235	0.08551
Tully and Estes equation	0.4278	0.08063
Original R-K equation	0.4278	0.08670

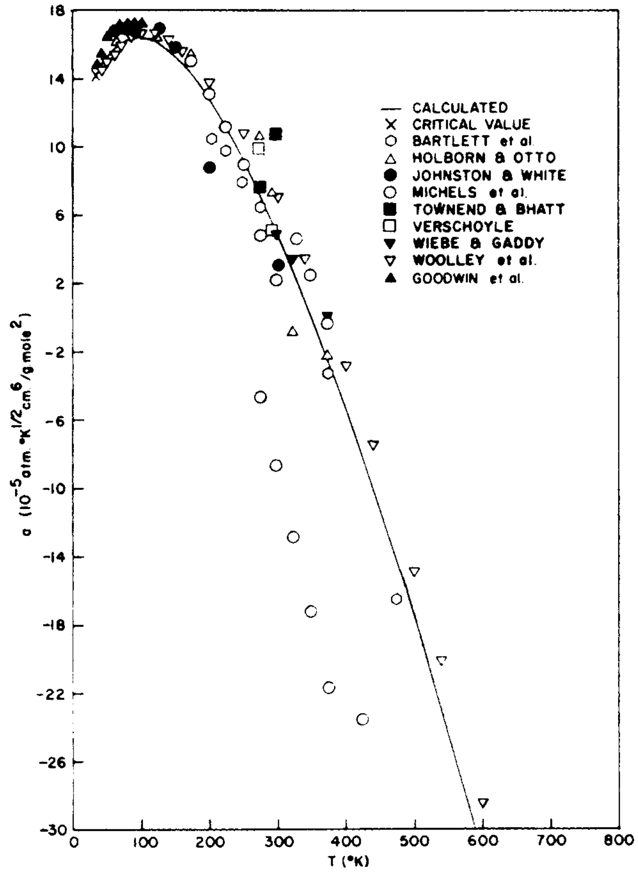

Fig. 3. Optimum values for $\underline{a}$ as a function of temperature for hydrogen.

It was decided that each region would be investigated separately. The classical region has a trend indicating that a parabola would fit the data, and this is found to be the case. An observation of Figure 2 also shows that an extension of this curve to $T_R = 1$ will give nearly the same value as that predicted by Estes and Tully which illustrates that their method neglects the quantum correction while the original Redlich-Kwong equation represents the classical region less accurately. Lacking good optimum values between 450° and 750°K., the behavior of this region is assumed classical.

The usual quantum correction term was applied to the data with disappointing results. Another expression was then constructed having an insignificant contribution above 70°K. to account for this effect. From Figure 2 it is clearly seen that the high temperature region data are easily expressed by the equation of a straight line.

A similar procedure can be applied to the variation of $\underline{a}$ with temperature (Figure 1), and when all these factors are considered simultaneously, the following equations are obtained:

$$\underline{a} = \underline{a}_c \left[f_1 - f_2 \{(1 - T_R)\, e^{1/T_R}\}^2 + QC_a\right] \qquad (39)$$

$$\underline{b} = \underline{b}_c \left[h_1 - h_2 \{(1 - T_R)\, e^{1/T_R}\}^2 + QC_b\right] \qquad (40)$$

where QC is the quantum correction term ($QC = 0$ for all gases except helium and hydrogen) and they have the following form:

$$QC_a = f_3\, T_R^{\gamma}\, e^{-T_R^{1.1/5}} \qquad (41)$$

$$QC_b = h_3\, T_R^{1/2}\, e^{-T_R/2} \qquad (42)$$

The values for the coefficients are given in Table 4. The above equations are applicable whenever $5.26°K. \leqq T \leqq 750°K.$ Otherwise use

$$\underline{a} = \underline{a}_c\, (47.4796 - 1.4984\, T_R) \qquad (43)$$

$$\underline{b} = \underline{b}_c\, (0.19149 - 0.0002216\, T_R) \qquad (44)$$

when $T \geqq 750°K.$

The above equations have been proposed since they could not be combined conveniently into two equations holding for all temperatures.

Table 4. The Helium and Hydrogen Coefficients for Equations (39) to (42)

Coefficient	Helium	Hydrogen
a_c	0.79480×10^5	14.204×10^5
b_c	16.421	18.227
f_1	0.04294	0.79170
f_2	0.03054×10^{-1}	0.09445×10^{-1}
f_3	1.17000	0.25490
h_1	0.70895	0.91010
h_2	0.25275×10^{-4}	0.32255×10^{-3}
h_3	0.47997	0.14810
γ	1.0	1.1

HYDROGEN

The $\underline{a}$ and $\underline{b}$ curves for hydrogen exhibit trends which are similar to those for helium. In this case, however, the

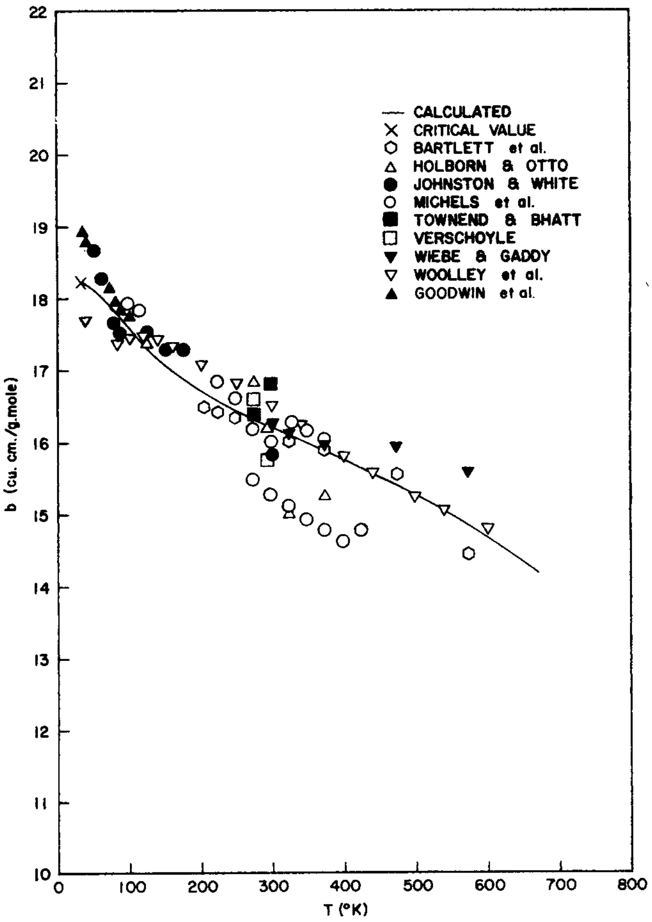

Fig. 4. Optimum values for $\underline{b}$ as a function of temperature for hydrogen.

distinction between the classical and quantum regions is less pronounced because the accuracy of the available data does not compare with the helium data. Furthermore, the high temperature region cannot be described because of lack of data. (See Figures 3 and 4.)

Both curves indicate that the quantum correction becomes significant at approximately 300°K. Use of the same procedure as for helium yields expressions for $\underline{a}$ and $\underline{b}$ as functions of temperature having the same form as Equations (39) and (40). The coefficients to be used for hydrogen are given in Table 4 and are appropriate for the temperature range $33°K. \leqq T \leqq 650°K.$

An independent check as to the accuracy of the above expressions for helium and hydrogen can be made by considering the behavior of the gases at their Boyle temperatures. Because the second virial coefficient is equal to zero at this point, it can be shown that

$$\underline{a} = \underline{b}\, R\, T_B{}^{3/2} \quad \text{at} \quad T = T_B \qquad (45)$$

This relationship is satisfied within expected limits at the reported Boyle points. It should also be noted that the $\underline{a}$ curves become negative. This result is surprising, but the accuracy obtained apparently verifies such behavior.

Use of the values for Ω_a, Ω_b, Z_c, and the equations for $\underline{a}$ and $\underline{b}$ as functions of temperature in conjunction with Equation (25) allows the prediction of compressibility data. The results are given in the form of tables. Table 1 gives the maximum absolute percent error and the average absolute percent error between the predicted and experimental helium compressibility data for each source. The corresponding results for hydrogen are given by Table 2.* Hill's helium data are represented by the proposed equation less satisfactorily than the other data. This is a result of the extreme slope of the $\underline{b}$ vs. T curve in the region of this data; here a small translation produces a vastly different $\underline{b}$. The overall average absolute percent error for all the helium data is 0.90%, but when Hill's data are excluded, the error becomes 0.28%. For hydrogen the overall error for all the data is 0.79%.

CONCLUSIONS

The modified Redlich-Kwong equation [Equation (25)] using Equations (39) and (40) predicts experimental helium and hydrogen compressibility data, respectively, more accurately than either the original Redlich-Kwong equation or the Estes and Tully form. From Tables* 5 and 6 the modified R-K equation has a significantly smaller or equivalent average absolute percent error for all but one source. The reason for this is that the $\underline{a}$ values associated with Keesom's data have a trend which can be more accurately predicted by using the critical value.

The conclusion to be drawn from these results is that the technique presented for finding a modified Redlich-Kwong equation substantially increases its ability to predict compressibility data.

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NOTATION

$\underline{a}, \underline{b}$ = constants in Redlich-Kwong equation of state
f, h = functions of reduced temperature
f_i, h_i = coefficients
P = pressure
QC = quantum correction
R = gas constant
T = objective function
V = temperature
S = volume
Z = compressibility factor
α, β = dimensionless coefficients related to Ω_a and Ω_b
Δ = change in variable
Ω_a, Ω_b = dimensionless coefficients in Redlich-Kwong parameters as defined by Equations (7) and (8)

Subscripts

B = Boyle temperature
c = critical
i = integer
R = reduced (actual divided by critical value)

Superscripts

n = integer
o = observed
p = predicted

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* Comparisons between the original Redlick-Kwong equation, the R-K equation using the values of Estes and Tully, the proposed modified R-K equation, and the R-K equation using the optimal values at each temperature have been deposited as document 01202 with the ASIS National Auxiliary Publications Service, c/o CCM Information Sciences Inc., 22 W. 34 St., New York 10001 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

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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