Generalized Temperature Dependence of the Redlich-Kwong Constants

WALTER F. VOGL and KENNETH R. HALL

University of Virginia, Charlottesville, Virginia

Recently, the literature has indicated a resurgence in the popularity of two-parameter equations of state. The primary driving force behind this shifting stance is the relative ease of adapting theoretical insight to these equations through their parameters. On a more practical basis, the simple equations of state can be more easily adapted to the techniques of computer aided design. In these applications, a small loss of accuracy is offset by ease of implementation and speed of calculation.

When one speaks of two-parameter equations in chemical engineering, the Redlich-Kwong equation assumes primacy. Indeed, several investigators have been actively working with this relationship in recent years. Their efforts have demonstrated its accuracy: Estes and Tully (*6*), Shah and Thodos (*12*), Martin (*9*); as well as proposing modifications to improve this accuracy: Barner, Pigford, and Schreiner (*1*), Chueh and Prausnitz (*2* to *5*), Zudkevitch and Joffee (*16*). Others have noted that the accuracy of two-parameter equations (primarily the Redlich-Kwong) can be improved considerably by allowing the constants to vary with temperature: Wilson (*14*, *15*), Robinson and Jacoby (*11*), Mason (*19*), Haar and Sengers (*8*), Vogl and Hall (*13*). The results of this study are generalized correlations for the Redlich-Kwong constants as functions of reduced temperature.

DISCUSSION

Mason (*10*) demonstrated that the Redlich-Kwong equation possessed remarkable predictive ability if applied to an isotherm via least mean squares. For many gases, it surpassed the Benedict-Webb-Rubin equation in overall performance. The results presented here represent an extention and amplification of his work.

The values of $\underline{a}$ and $\underline{b}$ for the Redlich-Kwong equation

$$Z = \frac{v}{v - \underline{b}} - \frac{\underline{a}}{RT^{1.5}(v + \underline{b})} \tag{1}$$

were evaluated for multiple isotherms of fifteen common gases: helium, neon, argon, xenon, hydrogen, methane, ethane, ethylene, propane, acetylene, oxygen, nitrogen, carbon monoxide, carbon dioxide, and ammonia. Nonlinear least mean squares was applied by using the Newton-Raphson convergence technique.

Because the idea of corresponding states is such an attractive concept, these values were reduced by using $\underline{a}_c$ and $\underline{b}_c$, where

$$\underline{a}_c = \frac{\Omega_a R^2 T_c^{2.5}}{P_c} \tag{2}$$

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

the usual values obtained by noting that $(\partial P/\partial v)_{T_c} = (\partial^2 P/\partial v^2)_{T_c} = 0$ at the critical point. Ω_a is 0.4278 and Ω_b is 0.0867 in these equations. For helium and hydrogen, the critical properties vary with temperature as demonstrated by Gunn, Chueh, and Prausnitz (*7*). These authors recommend that if hydrogen and helium are to correspond with other substances in generalized correlations, then

$$T_c = \frac{T_c^\circ}{1 + \dfrac{21.8}{MT}} \tag{4}$$

$$P_c = \frac{P_c^\circ}{1 + \dfrac{44.2}{MT}} \tag{5}$$

where M is the molecular weight and T_c° and P_c° are the high temperature limits of T_c and P_c. Table 1 lists the values of T_c° and P_c°.

This contention was substantiated in the present work. By using the observed T_c and P_c, the helium and hydrogen data did not correspond, while the temperature adjusted

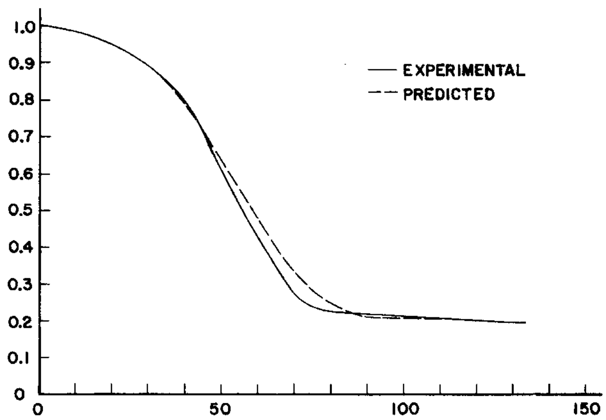

Fig. 1. b_R vs. T_R.

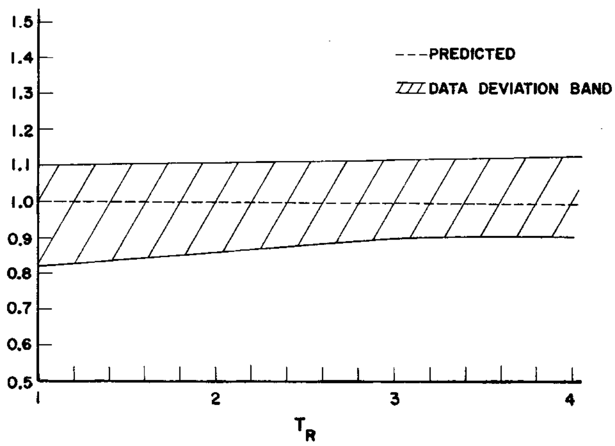

Fig. 2. b_R vs. T_R (expanded scale).

Kenneth R. Hall is with the ChemShare Corporation, Norman, Oklahoma.

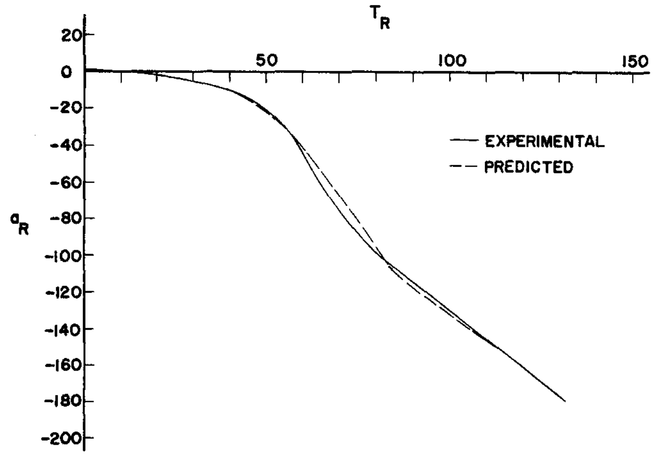

Fig. 3. a_R vs. T_R.

T_c and P_c allowed these data to merge smoothly with those for the other gases.

A final note of explanation concerning the data: most of the gases are represented in the range $1 < T_R < 5$. Data were employed for argon and nitrogen up to $T_R < 20$. Hydrogen data were found extending to $T_R < 30$. Therefore, the results presented in this paper are based upon helium alone in the range $30 < T_R < 150$.

RESULTS

Figures 1 through 4 present the results as plots of $\underline{b}_R = \underline{b} / \underline{b}_c$ and $\underline{a}_R = \underline{a} / \underline{a}_c$ as a function of reduced temperature. Figure 1 represents b_R (T_R) over a very large temperature range. It should be noted that the curve is poorly defined (lack of data) in the region $40 < T_R < 80$ and that the solid line is merely a smooth extension of the curve in the well-defined regions. Figure 2 is an expanded scale providing more detail in the commonly encountered temperature region. The data deviation band represents the scatter of over 200 points. Analogous comments apply to Figures 3 and 4 for $\underline{a}_R$ (T_R). The only strange indication is that $\underline{a}_R$ becomes negative. This is also predicted by Wilson (*15*).

Because the curves are smooth functions, they have been correlated. The geometric feature which is apparent is that both Figures 1 and 3 bear some resemblance to a probability function. This observation has been exploited to produce equations which are useful for computer applications:

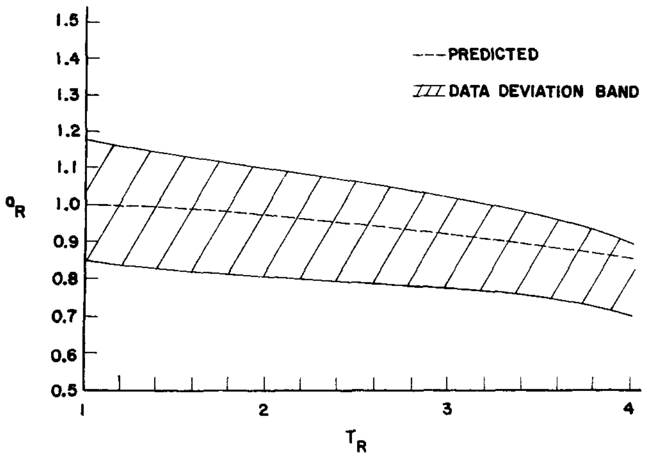

Fig. 4. a_R vs. T_R (expanded scale).

TABLE 1. HIGH TEMPERATURE LIMIT CRITICAL PROPERTIES FOR HELIUM AND HYDROGEN

Gas	$T_c°$, K.	$P_c°$, atm.
Helium	10.47	6.67
Hydrogen	43.6	20.2

$$\underline{a}_R = 1 - 0.00863 T_R^2 - 48.1 \exp\left\{\frac{-(T_R - 90)^2}{600}\right\} - 31.0 \exp\left\{\frac{-(T_R - 125)^2}{400}\right\} \quad (6)$$

$$\underline{b}_R = \exp\left\{\frac{-(T_R - 1)^2}{7500}\right\} - 0.2 \exp\left\{\frac{-(T_R - 75)^2}{800}\right\} + 0.125 \exp\left\{\frac{-(T_R - 150)^2}{1400}\right\} \quad (7)$$

These equations have been plotted in Figures 1 through 4 and represent the data quite satisfactorily. The worst deviation occurs in the poorly defined region of Figure 1. Clearly, Equations (6) and (7) are satisfactory in the normal regions represented by Figures 2 and 4.

CONCLUSIONS

Generalized correlations have been established for the temperature dependence of the constants $\underline{a}$ and $\underline{b}$ in the Redlich-Kwong equation. The equations are relatively simple, and they adequately represent the data. It is also interesting to note that below $T_R = 4$, the usual equations for calculating $\underline{a}$ and $\underline{b}$ are optimal within the scatter of the data.

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