

PHASE EQUILIBRIUM DATA AND METHODS: IMPLICATION OF PRESENT  
STATE ON HEAVY PETROLEUM FRACTIONS AND COAL PROCESSING  
PART II: THE EQUATION OF STATE APPROACH TO PREDICTING  
VAPOR - LIQUID EQUILIBRIUM

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ABSTRACT

The need to produce liquid fuel and chemical fuel stocks from heavy and highly aromatic petroleum fractions, residues, and coal poses the questions whether the existing thermodynamic data correlations are applicable and what new data should be measured.

Evaluations of existing correlations as to their applicability to the conditions of processing coal fluids and heavy oil are presented in a series of four articles. Such evaluations are considered important in planning the measurement of new data and further research.

In this second article of the series, the equation of state approach to predicting vapor-liquid equilibrium is discussed.

RESUMEN

La necesidad de producir combustibles líquidos y productos químicos a partir de fracciones y residuos pesados y altamente aromáticos del petróleo y de carbón, plantea la pregunta de si los datos y correlaciones termodinámicos existentes son aplicables y qué nuevos datos deben ser medidos.

La evaluación de las correlaciones existentes en cuanto a su aplicabilidad a las condiciones de procesamiento de fluidos del carbón y aceite pesado se presenta en una serie de cuatro artículos. Tales evaluaciones son consideradas importantes en la planificación de la medición de nuevos datos e investigación.

En este segundo artículo de la serie, los métodos basados en el uso de la ecuación de estado para predecir equilibrio entre vapor - líquido son discutidos.

## GENERAL DISCUSSION

The classical , "Standard State" method for calculating VLE at high pressure , has difficulties in attempting to meet the primary requirement that all the fugacity ratios and K values must converge to unity at the true critical point of the mixture . Thus , an equation of state applicable for all fluid phases has several advantages . It is based on a rigorous analytic thermodynamic approach with empiricism reduced to a minimum . Hypothetical standard states are eliminated and there is no need to develop relationships between activity coefficients . However, the method places great demands on the equation of state because it must be capable of representing both the vapor and liquid states, their pressures , and their fugacities.

The main objective in usage of equations of state in VLE calculations is to obtain the parameters and relationships for integrating the basic equation for the fugacity of a component in a mixture. In any phase and for every component  $i$

$$\hat{f}_{i_v} = \hat{f}_{i_\ell} \quad (18)$$

and

$$\ln \hat{f}_i = \frac{1}{RT} \int_v^\infty \left[ \left( \frac{\partial P}{\partial n_i} \right)_{T,V,n_j} - \frac{RT}{V} \right] dV - \ln \frac{V}{n_i RT} \quad (19)$$

where  $n_i$  = moles of  $i$ ;  $V$  = mixture molar volume.

For an equation to be acceptable for phase equilibrium calculations, it must meet the following criteria.

- (1) The equation must have a reasonable number of parameters.
- (2) The model should overcome the limitations of the "standard state" method at high pressures, especially in the vicinity of the critical point, and in liquid density calculations.
- (3) The constants in the equation should be expressible in terms of known thermodynamic properties, vapor pressure  $P_c$ ,  $T_c$ , and either  $Z_c$  or  $\omega$ . Hence, it requires reliable correlations for predicting the equations' parameters from other measurable properties such as petroleum inspection data.
- (4) The predicted fugacities for a compound should result in  $K_i = 1$  at any of the boundary conditions: pure compound under its own vapor pressure, an azeotrope, and the true critical point of a mixture.
- (5) The mixing rules for evaluating mixture constants should not contain more than one fitted binary interaction parameter, and, if possible, this parameter should be independent of temperature, pressure, and composition.
- (6) The equation should be sufficiently general in its applicability so that a single equation can be used to handle all fluid property calculations.

Most of the many equations of state in the literature (about 75 of them) represent modifications of van der Waals theories of the behavior of fluids. Consequently, any equation of general usefulness represents either a modified form of the van der Waals equation, or either the virial equation of state or the theorem of the corresponding states. The latter two are concepts that were also advanced by van der Waals. Any graphical presentation of variations of thermodynamic variables as functions of reduced properties is, in the author's opinion, also an equation of state without explicitly determined form or coefficients.

Two equations of state are widely used in the natural gas and petroleum processing industry. These are the BWR [I-9, I-10, II-3] and some of its modifications [II-11, II-13, II-15, I-72, II-20] and that of Redlich and Kwong [I-62]. The proponents of the latter

did not propose their equation (R-K equation) for liquids. However, in 1964 Wilson [II-25] showed that the K-K equation with and without modifications can be used for predicting fugacities in both phases, hence K values. Since that time the R-K equation in various modified forms [I-25, I-71, II-1, II-2, II-4, II-5, II-6, II-8, II-10, II-12, II-17, II-26, II-28] has become a main tool of the fuel and chemical process designers.

Recently an equation proposed by Peng and Robinson [II-16] has gained some consideration [I-25, II-19].

#### THE BWR EQUATION

The BWR equation was originally developed for use in VLE calculations and was applied to systems containing light paraffin and olefin hydrocarbons. The equation-of-state constants for mixtures are established, as recommended by Benedict, Webb, and Rubin, according to combining rules analogous to those first proposed by van der Waals.

The original BWR equation uses eight parameters for each component in a mixture plus a tabular temperature dependence for one of the parameters to improve the fit of vapor-pressure data. Originally the BWR equation was applied to twelve light paraffinic and olefinic hydrocarbons and their mixtures. This equation is reasonably accurate for light paraffin mixtures at reduced temperature of 0.6 and above [I-11]. It is less satisfactory with low temperatures, non-hydrocarbons, non-paraffins and heavy paraffins.

Improved fits to mixture data have been obtained by correlating the parameter variations with temperature [I-11, I-72], by including temperature dependence of additional parameters, and by use of an empirical correction factor in parameter-combination rules [II-15, II-20].

Parameters have been developed for a wide variety of compounds extending to  $C_{22}H_{46}$  and including several non-hydrocarbons, such as sulphur dioxide, nitrogen, hydrogen, argon, and carbon monoxide and

dioxide [II-3]. Ranges of applicability for some compounds are given in Table 4. (The latter compounds play an important role in coal conversion). Also, generalized forms of the parameters have been developed.

The BWR equation expresses the pressure  $P$  as a function of the molal density,  $d$  of each phase.

$$P = RTd + \left( B_0 RT - A_0 - C_0/T^2 \right) d^2 + (bRT - a) d^3 + a\alpha d^6 + (cd^3/T^2) (1 + \gamma d^2) \exp(-\gamma d^2) \quad (20)$$

where:  $A_0, B_0, C_0, a, b, c, \alpha,$  and  $\gamma$  are empirical coefficients,

$R$  is the gas constant,

$T$  is the absolute temperature, and

$d$  is density in moles/unit volume

In the past, correlations have been proposed to relate the coefficients to those for the virial expansion

$$P = B_1(T)d + B_2(T)d^2 + B_3(T)d^3 + \dots \quad (21)$$

However, one should bear in mind that Equation 20 is empirical and that its complicated last term cannot be regarded as a substitute for the missing powers in the virial expansion. Hence, it should only be used at conditions for which it was designed.

The proponents of the method also recommended the rules for calculating the coefficients for a mixture from those of the individual components. Since the compositions of the vapor phase and the liquid phase are different, two sets of coefficients, one for each phase, are needed for every computation of equilibrium condition.

The fugacity of a component in a phase, related to a standard

state of zero pressure, is calculated from Equation 22, below. It should be noted that since fugacity is not additive (the free energy  $G$  is), partial molal metal fugacities  $\bar{f}_{i\ell}$  and  $\bar{f}_{iV}$  can not be calculated; their equivalents, by the Lewis and Randall definition, are the

ratios  $\left(\frac{\hat{f}_{i\ell}}{x_i}\right)$  and  $\left(\frac{\hat{f}_{iV}}{y_i}\right)$  calculated instead.

$$\begin{aligned}
 RT \ln \frac{\hat{f}_{i\ell}}{x_i} = & RT \ln d + \left[ (B_0 + B_{0i})RT - 2(A_0 A_{0i})^{\frac{1}{2}} - 2(C_0 C_{0i})^{\frac{1}{2}} / T^2 \right] d \\
 & + \frac{3}{2} \left[ RT(b^2 b_i)^{\frac{1}{3}} - (a^2 a_i)^{\frac{1}{3}} \right] d^5 + \frac{3}{5} \left[ a(\alpha^2 \alpha_i)^{\frac{1}{3}} + \alpha(a^2 a_i)^{\frac{1}{3}} \right] d^5 \\
 & + \frac{3d^2 (c^2 c_i)^{\frac{1}{3}}}{T^2} - \left[ \frac{1}{\gamma d^2} - \left( \frac{1}{2} + \frac{1}{\gamma d^2} \right) \exp(-\gamma d^2) \right] \\
 & - \frac{2d^2}{T^2} c \left( \frac{\gamma_i}{\gamma} \right)^{\frac{1}{2}} \left[ \frac{1 - \exp(-\gamma d^2)}{\gamma d^2} - \exp(-\gamma d^2) \right. \\
 & \left. - \frac{\gamma d^2}{2} \exp(-\gamma d^2) \right] \tag{22}
 \end{aligned}$$

In predicting the VLE  $K_i$  for each component  $i$ , Equation 22 must be used twice, for calculating  $\hat{f}_{i\ell} / x_i$  in the liquid phase and for calculating  $\hat{f}_{iV} / y_i$  in the vapor phase, respectively. Then

$$K_i = \left( \hat{f}_{i\ell} / x_i \right) / \left( \hat{f}_{iV} / y_i \right) \tag{23}$$

where the ratios  $\left(\frac{\hat{f}_{i\ell}}{x_i}\right)$  and  $\left(\frac{\hat{f}_{iV}}{y_i}\right)$  are calculated from Equation 22 each as an inseparable single value.

Trial values of all  $x_i$  and  $y_i$  must be assumed in order to calculate the eight parameters  $B_0, A_0$ , etc. of the BWR equation, sixteen for both phases, for use with Equations 20 and 22.

Of course, the mixtures' coefficients must be established first and the phase density,  $d$  in Equation 20, must be arrived at by trial and error before Equation 22 is used.

Equation 23 is more clearly understood if the basic concept it implies is derived from

$$f_{i\ell} = \hat{\phi}_{i\ell} x_i P \quad (24)$$

which is the equivalent of Equation 2 for the components in the liquid phase.

Substitution of Equation 2 and 24 into Equation 23, with the fugacity coefficients  $\hat{\phi}_{i\ell}$  and  $\hat{\phi}_{iV}$  calculated at system's pressure, yields,

$$K_i = \frac{\hat{\phi}_{i\ell}}{\hat{\phi}_{iV}} \quad (25)$$

As can be seen in Table 4 [II-3], the number of compounds for which coefficients are available is limited. Applicability of the equation is therefore correspondingly limited. Moreover, programming the BWR procedure for flash and VLE calculations requires skill and experience with the method and its intricacies to account for unconverged cases. Modified versions of the BWR method are widely used in process calculations for natural gas systems [II-22].

Experience has shown that the arbitrarily proposed mixing rules,

following van der Waals, do not always work and at least one adjustable binary constant is needed. This adjustable parameter is obtained by fitting experimental data. As was shown by Orye [II-15], the adjustable parameter, using Orye's nomenclature,  $\mu_{ij}$ , has a strong effect, especially on the liquid fugacity. Small variations in  $\mu_{ij}$  cause large deviations in bubble point pressure calculations.

Starling [I-72] has proposed an eleven coefficient BWR equation for better fitting the volumetric and thermal properties, as well as the vapor pressure of the pure components. In all cases where the Starling form of the BWR equation is used, an adjustment parameter  $k_{ij}$  is required in addition to the original mixing values.

Although the BWR equation provides a tool for computing VLE and other thermodynamic data, it is clear that more than a few pieces of information are required for establishing coefficients. There is little expectation that the BWR equation could be utilized for mixtures of petroleum or coal liquid fractions. However, for synthetic gases that contain compounds for which BWR constants and mixing parameters are available, this method can be used successfully, provided that the flash program contains all the necessary tests and flexibility required for converging on the correct answer, especially near the critical point and within the retrograde region.

Although not intended for exclusive utilization as an accurate prediction of liquid volumetric properties the Starling Han version of the BWR equation [II-22] does quite well. This is illustrated in Table 5.

#### THE REDLICH AND KWONG (R - K) EQUATION

The simplest successful variation of the van der Waals equation was proposed by Redlich and Kwong [I-62]. Before 1964, the Redlich-Kwong equation had been used conveniently for calculating the fugacities of compounds in the vapor phase [I-15]. However, since 1964, when Wilson proposed that a modified version be used for both phases in predicting K ratios [II-25], almost a hundred modifi-

cations [I-59] have been proposed.

Important advantages of the two-parameter Redlich-Kwong equation of state are the ease of predicting its coefficients from the critical properties of pure compounds and the simple way in which binary interaction constants enter into the expressions for the mixtures, as first demonstrated by van der Waals for the van der Waals equation. The two-constant R-K equation is admittedly less accurate than the BWR equation. The R-K equation is:

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}} V(V+b)} \quad (26)$$

The standard values of the constants are given by the equations (D-14):

$$a = 0.4278 R^2 T_c^{2.5} / P_c \quad (27)$$

and

$$b = 0.0867 RT_c / P_c \quad (28)$$

For a one component system, the fugacity coefficient of the mixture,  $\Phi$ , in either phase is calculated from:

$$\ln \Phi = \ln [RT/P (V-b)] + (PV/RT) - 1 - \left( a/RT^{\frac{3}{2}} b \right) \ln [(V+b)/V] \quad (29)$$

Wilson [II-25] proposed that constant  $a$  be made temperature dependent and its value adjusted for each pure component so as to make

the liquid-phase fugacity coefficient equal to the vapor-phase fugacity coefficient at the component vapor pressure. Subsequently, he proposed establishing the temperature dependence of constant  $a$  from the slope of the vapor-pressure curve at the critical point. The latest form of the temperature function proposed by Wilson is:

$$\left( a/RT^{\frac{3}{2}} b \right) = 4.934 \left[ 1 + (1.45 + 1.62) \left( \frac{1}{T_r} - 1 \right) \right] \left( 1/T_r \right)^{0.12} \quad (30)$$

In Wilson's treatment of the R-K equation a single set of parameters is used for the gas and liquid phases, the parameter  $b$  is taken as a constant calculated from Equation 28 and the parameter  $a$  is a generalized function of temperature and acentric factor,  $\omega$ .

Without detracting from the originality and usefulness of Wilson's method, which is widely used as the MARK V program [II-26] distributed by the GPA, the use of Equation 27 leads to erroneous liquid and vapor densities [II-1]. Chueh and Prausnitz [II-1, I-16] proposed two sets of constants for the R-K equation, one for the vapor phase, the other for the liquid phase. They replace Equations 27 and 28 with:

$$a = \Omega_a R^2 T_c^{2.5} / P_c \quad (31)$$

and

$$b = \Omega_b RT_c / P_c \quad (32)$$

The dimensionless constants for the gaseous phase,  $\Omega_a$  and  $\Omega_b$ , are determined for each pure component by fitting Equation 30 to P-V-T data. The saturated vapor data yields vapor-phase values of

the constants. Similarly the liquid-phase values of  $\ell^{\Omega_a}$  and  $\ell^{\Omega_b}$  are obtained by fitting Equation 26 to P-V-T data for the saturated liquid.

Zudkevitch and Joffe [II-28] indicated that if the proposals of Chueh and Prausnitz are followed four temperature-dependent parameters are required for every compound in the mixture. They also discovered that when these four constant sets are used, the densities are calculated with some degree of reliability, but the fugacity equality requirement is not met. (See Figure 8). At none of the three points where K must equal unity is this requirement satisfied. Zudkevitch and Joffe [II-28] and Hamam [II-8] also indicated that the temperature dependent parameters a and b must, at any point along the vapor pressure curve of the compound, satisfy only two of the four requirements below.

- (1) Fit the liquid density (Point A in Figure 8)
- (2) Fit the vapor density (Point B in Figure 8)
- (3) Satisfy the fugacity equality requirement

$$\int_{\text{sat.v}}^{\text{sat.l}} V dP = 0$$

where  $S_\ell$  and  $S_v$  are saturated liquid and vapor respectively

- (4) Predict the exact fugacity.

Originally, Zudkevitch and Joffe [II-28] selected the first and fourth requirements. Later [II-10], recognizing that the fugacity equalization cannot be sacrificed, they chose to satisfy requirements 1 and 3. In the last ten years there have been quite a few suggestions were made on which of the four requirements can be sacrificed. Some of such suggestions were reviewed by Medani and Hasan [II-12].

Due to the need to calculate the values of  $\Omega_a$  and  $\Omega_b$  for each compound at each temperature while meeting requirements 1 and 3,

this method, though the most accurate among the modifications of the Redlich-Kwong procedure, did not achieve wide utilization. However, recently, Hamam and Lu [II-8] proposed generalized analytical formulas for  $\Omega_a$  and  $\Omega_b$  which simplify use of the method.

Peters and Wenzel [II-17, II-18] proposed that the agreement between experimental and calculated VLE K data could be improved by modifying the pure component data which are used in establishing the R-K parameter of the supercritical component. Per Deiters and Schneider [II-4] only a small (<1%) adjustment of the V of methane is needed.

In all of the above approaches for calculating fugacities in multicomponent mixtures, Equation 33 below is used. As mentioned earlier [II-31], in some versions of the classical approach such as that of Chao and Seader [I-15] the fugacity coefficients  $\phi_{iV}$  are calculated only for the components in the vapor mixture only. When an equation of state method is used for calculating the fugacity coefficients in both phases Equation 26 and Equation 33, below, are used twice, as in the case when the BWR method is used.

The Redlich-Kwong equation in the form

$$P = \frac{RT}{V-b} - \frac{a}{T^{\frac{1}{2}} V(V+b)} \quad (\text{Equation 26})$$

is integrated to provide the fugacity coefficient  $\phi_k$  of component k in the mixture.

$$\begin{aligned} \ln \hat{\phi}_k &= \ln \left( \frac{V}{V-b} \right) + \frac{b_k}{V-b} + \ln \left( \frac{RT}{PV} \right) - \frac{2 \sum_{i=1}^m y_i a_{ik}}{RT^{\frac{3}{2}} b} \\ &\times \ln \left( \frac{V+b}{V} \right) + \frac{ab_k}{RT^{\frac{3}{2}} b^2} \left[ \ln \left( \frac{V+b}{V} \right) - \frac{b}{V+b} \right] \end{aligned} \quad (33)$$

where  $V$ ,  $a$  and  $b$  in the equation are those calculated for the specific mixture, either that of the liquid or that of the vapor.

For a binary system equation (A2-1) reduces to:

$$\ln \hat{\phi}_1 = \ln \left( \frac{V}{V-b} \right) + \frac{b_1}{V-b} + \ln \left( \frac{RT}{PV} \right) - \frac{2(y_1 a_{11} + y_2 a_{12})}{RT^{\frac{3}{2}} b} \\ \times \ln \left( \frac{V+b}{V} \right) + \frac{ab_1}{RT^{\frac{3}{2}} b^2} \left[ \ln \left( \frac{V+b}{V} \right) - \frac{b}{V+b} \right] \quad (34)$$

The reader may recall that in the original presentation by Redlich and Kwong [I-63] Equations 32, 33 and 34 were presented in terms of the compressibility factor  $Z$  and the coefficients  $A$  and  $B$ . Regardless of the form of the equation used, the calculated properties should be the same if the same data and combination rules are used in establishing the parameters.

Another formula derived from the Redlich-Kwong provides for the partial molal volumes of the component of a mixture

$$\bar{V}_k = \frac{\frac{RT}{V-b} \left( 1 + \frac{b_k}{V-b} \right) - \frac{2 \sum_i x_i a_{ik} - \frac{ab_k}{V+b}}{V(V+b) T^{\frac{1}{2}}}}{\frac{RT}{(V-b)^2} - \frac{a}{T^{\frac{1}{2}}} \left( \frac{2V+b}{V^2(V+b)^2} \right)} \quad (35)$$

When the R-K equation is applied to mixtures the constants are given by:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (a_{ii} = a_i) \quad (36)$$

and

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (b_{ii} = b_i) \quad (37)$$

Wilson [II-25] and Chueh and Prausnitz [I-16] have proposed that Equation 37 be replaced with the simpler relationship:

$$b = \sum_i x_i b_i \quad (38)$$

Equation 35 is equivalent to assuming the combining rule:

$$b_{ij} = \frac{1}{2} (b_i + b_j) \quad (39)$$

This combining rule appears to represent a reasonably good approximation in most systems.

Wilson proposed that the interaction constants,  $a_{ij}$ , of Equation 32 be obtained from experimentally determined binary vapor-liquid equilibrium data. Chueh and Prausnitz [II-1], on the other hand, have used binary mixture volumetric data (second virial coefficients of gases and saturated liquid volumes) to calculate the  $a_{ij}$  for either phase. Zudkevitch and Joffe [II-28, II-29] proposed the use of experimental VLE data to obtain the interaction parameter  $C_{ij}$  for every binary mixture. This is done by either working backwards from the experimental data through Equations 35 and 36 to obtain  $a_{ij}$  and  $C_{ij}$  from:

$$a_{ij} = (1 - C_{ij}) \sqrt{a_i a_j} \quad (40)$$

For practical reasons the value of  $C_{ij}$  is established by trial and error procedure for minimizing the discrepancies between calculated and experimental VLE K values [II-28]. An equivalent of Equation 40 was derived and used by Lu and his students [II-2, II-8].

From the early utilization of the R-K equation for correlating VLE [II-28] it was assumed that a single binary interaction constant is sufficient to describe the interaction of two components and that only binary interaction constants suffice to describe all interactions in multicomponent mixtures. It was further assumed that each binary interaction parameter is independent of temperature and pressure, though, it was also recognized that better results could be

obtained if interaction parameter were applied to the calculation of the parameter  $b$  of the equation [II-28, II-30]. The validity of the above simplifying assumption has been proven for many systems in many publications. An example of the accuracy level achieved is shown in Table 6.

Deiters and Schneider [II-4] suggested a general equation for the (second) interaction parameter for the parameter  $b$ .

$$b_{ij} = (1 - \xi_{ij})^{1/2} (b_{ii} + b_{jj}) \quad (41)$$

Deiters also showed that for better prediction  $b$  cannot be a linear function of the concentration. Gray [II-7] suggested that since the equation is simple and limited, the users and correlators must be careful in selecting the objectives, e.g., predicting the critical point of mixture, and the variables that must be adjusted to meet these objectives. In Gary's opinion, this is especially important in correlating the behavior of hydrogen containing systems, which constitute a major part of the subject of this writing. He also suggested that in predicting K values in the vicinity of the mixture critical, the sensitivity of the predictions' validity to  $C_{ij}$  variations in the interaction parameter increases with the increase in the difference between the molar volumes of compounds  $i$  and  $j$ .

Soave [I-71] expanded the utilization of the concept of "fugacity equality" when using the R-K equation for establishing the coefficient  $a$  and predicting  $K$  values. He expressed the R-K  $a$  by an empirical function of the reduced temperature and the acentric factor  $\omega$ . The empirical factor  $\alpha_i$  introduced by Soave, illustrated in Figure 9, enters all calculations of properties of mixtures.

Soave used the rigorous R-K expression for the fugacity coefficient calculations

$$\begin{aligned} \ln \hat{\phi}_{iL} &= \ln \frac{\hat{f}_{iL}}{P x_i} \\ &= \frac{b_i}{b} (Z-1) - \ln (Z-B) - \frac{A}{B} \left[ \frac{a_i^{0.5}}{a^{0.5}} - \frac{b_i}{b} \right] \ln \left( 1 + \frac{B}{Z} \right) \end{aligned} \quad (42)$$

The following expressions are used to obtain the ratios.

$$\frac{a_i^{0.5}}{a^{0.5}} = \frac{\alpha_i^{0.5} T_{C_i} / P_{C_i}^{0.5}}{\sum_{j=1}^n x_j \alpha_j^{0.5} T_{C_j} / P_{C_j}^{0.5}} \quad (43)$$

$$\frac{b_i}{b} = \frac{T_{C_i} / P_{C_i}}{\sum_{j=1}^n x_j T_{C_j} / P_{C_j}} \quad (44)$$

Soave's formulas for  $A$  and  $B$

$$A = \frac{0.42747 P}{T^2} \left[ \sum_{i=1}^n x_i \frac{T_{C_i} \alpha_i^{0.5}}{P_{C_i}^{0.5}} \right]^2 \quad (45)$$

$$B = \frac{0.08664 P}{T} \left[ \sum_{i=1}^n x_i \frac{T_{C_i}}{P_{C_i}} \right] \quad (46)$$

are different from those of the standard R-K, though similar to those used in recent modified forms.

Soave showed a direct relationship between the proportionality

$$\alpha_i = \frac{a_i(T_{C_i})}{a_i(T)} \quad \text{and} \quad T_R^{0.5}$$

with the compound parameter  $m_i$  directly related to its acentric factor  $\omega_i$ , see Figure 9.

$\alpha_i^{0.5}$  is calculated from

$$\alpha_i^{0.5} = 1 + m_i (1 - T_{R_i}^{0.5}) \quad (47)$$

$$m_i = 0.480 + 1.574 \omega_i - 0.176 \omega_i^2 \quad (48)$$

This method leads to a very general procedure which requires only the critical temperature and pressure and the acentric factor for each component to calculate the K values.

Equation 42 to 46 are also used for calculating  $\hat{\phi}_{iV}$  and  $\hat{f}_{iV}$ , substituting the properties of the vapor mixture (a, b, A, B, and Z) for those of the liquid above. The VLE K ratios are calculated by substituting  $\hat{\phi}_{iL}$  and  $\hat{\phi}_{iV}$  from Equation 42 in Equation 25.

An early review by West and Erbar [1-77] illustrated its simplicity and applicability to natural gas systems. However, Soave's

original method, though very widely used, did not rely on interaction parameters, and thus did not give good predictions for mixtures containing  $H_2$ ,  $CO_2$  and  $H_2S$ . It does not provide good predictions of liquid densities.

In adapting the Soave procedure for the API Data Book, Graboski and Daubert [I-25, I-26] developed and incorporated binary interaction coefficients into the Soave equation. Their final formula, based on the London dispersion coefficients, is

$$(\alpha\alpha)_{\text{mix}} = x_i^2 (\alpha\alpha)_i + 2x_i x_j (\alpha\alpha)_i (\alpha\alpha)_j^{\frac{1}{2}} (1-k_{ij}) + x_j^2 (\alpha\alpha)_j \quad (49)$$

The term  $(1-k_{ij})$  can not be generalized; it must be determined from binary mixture data. In their report they also discussed the invalidity of the Soave equation when applied to  $H_2$  at temperatures above  $0^\circ C$ .

These investigators suggested a new relationship for Soave's. They also proposed varying the criticals of  $H_2$  with the temperature of the system. They offered a special equation for  $H_2$ .

$$\alpha_{H_2} = 1.202 \exp [-0.30228] T_R \quad (50)$$

The reader is referred to the API Data Book Report VII [I-26] and the revision of Chapter 8 for further information on the modification and for tables of interaction coefficients.

#### EQUILIBRIUM IN THE CRITICAL REGIONS & THE REDLICH - KWONG EQUATIONS

The equation of state approach in general, and due to its sim-

plicity the Redlich-Kwong equation, has been proposed for correlating high pressure equilibria in following the assumption that critical convergence could be achieved if the interaction parameters are known from low pressure data [II-1, II-10, II-29, II-30]. This is illustrated in Figure 6 and Figure 7 in Part I. However, enough evidence exists to verify that this is not always true.

Deiters and Schneider [II-9] showed, see Figure 10, that even by using interaction parameters  $C_{ij}$  and  $\xi_{ij}$  for Equation 40 and 41 respectively, established from moderate pressure data did not provide for predicted convergence that is in agreement in with the experimentally observed critical point. As shown in Figure 10 agreement was achieved when the coefficients a and b of the supercritical compound, methane, were "adjusted". Gray [II-7] on the other hand, suggested that interaction parameters must change with temperature and pressure.

#### THE PENG-ROBINSON EQUATION (PR)

Peng and Robinson [II-16, II-19] introduced an equation somewhat different from that of Redlich and Kwong.

The equation has the form:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b) + b(V-b)} \quad (51)$$

In this equation:

$$a = a(T_c) \alpha(T_R, \omega) \quad (52)$$

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad (53)$$

$$b = 0.07780 \frac{RT_c}{P_c} \quad (54)$$

The above implies that  $Z_c = 0.307$  for all compounds.  
The function  $\alpha(T_R, \omega)$  is calculated from

$$\alpha^{\frac{1}{2}}(T_R, \omega) = 1 + k \left( 1 - T_R^{\frac{1}{2}} \right) \quad (55)$$

where the factor  $k$ , not the same as that in Equation 49, is defined as:

$$k = 0.37464 + 1.54226\omega - 0.26992\omega^2 \quad (56)$$

With the constant  $Z_c = 0.307$  applied universally, one should expect significant deviations in predictions of  $K$  ratios and other properties within the critical region.

In a comparison for light hydrocarbon systems, Peng and Robinson showed that the use of the PR equation has improved the RMS relative error by about 40 percent over the Soave-R-K (SRK) predictions of vapor pressures of pure compounds (II-19 Table 1). They further contended that the SRK predictions are biased high in every case but one, and that the PR predictions are evenly split between positive and negative departures, with a resulting overall positive bias that is only 16 percent of the value obtained using the SRK equation.

In addition, the proponents pointed out that the PR equation gives a universal critical compressibility factor of 0.307 compared to 0.333 for the SRK equation.

In a manner similar to those of BWR, Wilson, Joffe and Zudkevitch, and Soave, the vapor/liquid equilibrium ratio,  $K_1$ , is

calculated from the fugacity coefficients via Equation 25. The Peng-Robinson equivalent of Equation 42 is:

$$\ln \hat{\phi}_{i\ell} = \ln \frac{\hat{f}_{i\ell}}{x_i P} = \frac{b_i}{b} (Z-1) - \ln (Z-B) - \frac{A}{2\sqrt{2B}} \left( \frac{2 \sum_j x_j a_{ji}}{a} - \frac{b_i}{b} \right) \times \ln \left( \frac{Z + 2.414 B}{Z - 0.414 B} \right) \quad (57)$$

The mixture parameters are:

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (58)$$

and

$$b = \sum x_i b_i \quad (59)$$

The cross coefficient  $a_{ij}$  is derived from experimental data and the equation is equivalent to Equation 40 with  $\delta_{ij}$  replacing  $C_{ij}$

$$a_{ij} = (1 - \delta_{ij}) \sqrt{a_i a_j} \quad (60)$$

As in other procedures that use equations of state, Equation 57

is used twice, once for the vapor to establish  $\hat{\phi}_{iV}$  and once to establish  $\hat{\phi}_{iL}$ . The VLE K is calculated from the latter values and Equation 25.

Figure 11 illustrates the performance of the two equations for predicting the molal volume of saturated liquids and vapors for pure n-pentane. At reduced temperatures above about 0.8, the average error in liquid density has been reduced by a factor of about 4 by using the PR equation. At lower reduced temperatures, the predictions by the new equation are better by a factor of about 2. Both equations give acceptable predictions of the vapor density.

The ability of the PR equation to predict the V/L ratios (percent liquid by volume) in flash calculations of multicomponent systems is illustrated in Figure 12 which shows comparisons for a 9-component system containing  $N_2$ ,  $CO_2$  and  $H_2S$  in addition to the 6 hydrocarbons [II-27].

It should be noted, however, that neither method is as applicable to liquid density predictions as are the methods of Joffe and Zudkevitch [II-10] and of Chang and Lu (per Hamam, reference II-8), which utilize the properties of each component hence the proper  $Z_c$  in establishing the parameters.

#### EQUATIONS OF STATE FOR WATER-CONTAINING GASES

On many occasions, especially when water is a major component, the use of the classical method with activity coefficients, etc. for defining fugacities of the components in the liquid phase is most promising. However, at high pressures, equations of state are recommended for the vapor phase. Unlike the "equation-of-state" approach, in this case, the equation is used only for the vapor phase. Such conditions usually prevail when steam is used in liquefaction and gasification of coal and heavy residues.

A modification to the Redlich and Kwong equation was developed by de Santis and Breedveld [II-5]. The Redlich-Kwong coefficients for water are given as

$$b_{\text{H}_2\text{O}} = 14.6 \text{ cm}^3 / \text{mole}$$

and the coefficient  $a$  is composed of a non-polar component  $a^{(0)}$  and a polar component  $a^{(1)}$ . The value  $a(T)$  at  $T$  is:

$$a(T) = a^{(0)} + a^{(1)}(T) \quad (61)$$

where  $a^{(1)}$  is a function of temperature ( $T$ ).

For water  $a^{(0)}$  and  $a^{(1)}$  were developed by de Santis and Breedveld from data in the Steam Tables.

For binary mixtures containing a non-polar gas with water, the following equations were proposed.

$$b = y_1 b_1 + y_2 b_2 \quad (62)$$

$$a = y_1^2 a_{11} + y_2^2 a_{22} + 2y_1 y_2 a_{12} \quad (63)$$

$$a_{12} = \left( a_1^{(0)} a_2^{(0)} \right)^{\frac{1}{2}} \quad (64)$$

To find  $a_1^{(0)}$ , data for mixtures of water with a non-polar compound ( $\text{N}_2$ ,  $\text{Ar}$ ,  $\text{CH}_4$ , etc.) have been used [II-9].

The "cross coefficient"  $a_{12}$  in Equation 56 is found from the "geometric mean" assumption of Equation 57 applied only to the non-polar part of coefficient  $a$ .

The equation of de Santis and Breedveld has been used by Heidemann et al [II-9] to calculate water fugacity coefficients in wet air oxidation. The vapor/liquid  $K$  values, calculated from the classical Equation 6, was used to predict water content in  $\text{N}_2$  and in

combustion gas, i.e.,  $N_2$ ,  $H_2O$  and  $CO_2$ . The computation results, shown in Figure 13 for two compositions of the dry gas, 20/80 mole %  $CO_2/N_2$  and 13/87, indicated that the  $CO_2$  substantially raises the saturated water content. It should be mentioned here, that these are computation results only, not experimental.

Fuller [II-6] added parameters to the Soave equation (SRK). The R-K equation then becomes:

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+cb)} \quad (65)$$

Using the constraints of the derivatives at the critical point, Fuller derived new forms for  $\Omega_a, \Omega_b, a(T)$  and  $m$  of the Soave form of the R-K equation. These parameters were made functions of a new parameter  $\beta$ , which in turn is a function of temperature and the compounds parachor. Fuller's predictions of volumetric properties of water shown in Figure 14 are quite encouraging, though the claimed average error of 3.63% leaves space for improvement.

Chung and Lu [II-2] proposed to relate  $\Omega_a$  and  $\Omega_b$  of the R-K equation as polynomial functions of  $(1-T_R)$ . The coefficients for their polynomials were obtained from fitting experimental data on pure compounds in the liquid phase. Results from comparisons given in Chung and Lu's paper suggest a high level of accuracy. For liquid water the average error reported in 0.23% vs. 3.19% obtained by Fuller's method and 24.63% by the Peng Robinson equation.

Neither Fuller nor Chang and Lu applied their correlations to mixtures containing water and steam. Wenzel and Rupp [II-24] applied their idea of establishing the desired  $\Omega_a$  and  $\Omega_b$  values not from the experimental liquid volumes but from "adjusted" values for water. Using the adjusted values of  $a$  and  $b$  and strong interaction parameters, Wenzel and Rupp showed quite impressive agreements between predicted and experimental VLE data on systems containing water and  $CO_2, N_2, H_2S$ , methane and butane.

Nakamura et al [II-14] utilized the concept of polar / nonpolar interaction with a perturbed hard sphere equation and obtained good results in predicting VLE and thermal properties on many binar mixtures of compounds encountered in processing coal.

The applicability of the various equations of state to prediction of phase behavior in different parts of the schemes for processing heavy petroleum fractions and coal to produce fluid fuels is discussed in a later part of this series.

REFERENCES FOR PART II

- [II-1] CHUEH, P.L. and PRAUSNITZ, M.M., *AIChE Jour.* 13, 1099 (1967).
- [II-2] CHUNG, W.K. and LU, B. Y-C J., "On the Representation of Liquid Properties of Pure Polar Compounds by Means of a Modified Redlich-Kwong Equation of State", *The Canad. Jour. of Chem. Eng.* 55, 707, (1977).
- [II-3] COOPER, H.W. and GOLDFRANK, J.C., "BWR Constants and New Correlation", *Hydrocarbon Processing* 46, N°12, 141 (December 1967).
- [II-4] DEITERS, U. and SCHNEIDER, G.M., "Fluid Mixtures at High Pressures, Computer Calculations of the Phase Equilibria and the Critical Phenomena in Fluid Binary Mixtures from the Redlich-Kwong Equation of State", *Ber. Bunsenges. Phys. Chem.* 86, 1316, (1976).
- [II-5] DeSANTIS, R., BREEDVELD, G.J.F. and PRAUSNITZ, J.M., *Ind. Eng. Chem. Process Des. Dev.*, 13, 374 (1974).
- [II-6] FULLER, G.G., "A Modified Redlich-Kwong-Soave Equation of State Capable of Representing the Liquid", *Ind. Eng. Chem. Fundamentals* 15, N°4, 254, (1976).
- [II-7] GRAY, R.D. Jr., Comments made at the Annual Meeting of the AIChE, New York (Nov. 1977).
- [II-8] HAMAM, S.E.M., "A Study on Phase Behavior of Selected Carbon Dioxide-Alkane Systems and Equations of State", Ph.D. Dissertation, Univ. of Ottawa (May 1976).
- [II-9] HEIDEMANN, R.A. and PRAUSNITZ, J.M., "Equilibrium Data for Wet-Air Oxidation, Water Content and Properties of Saturated Combustion Gases", *Ind. Eng. Chem. Process Des. Dev.* 16, 375 (1977).
- [II-10] JOFFE, J., SCHROEDER, G.M. and ZUDKEVITCH, D., Communication to the Editor *AIChE Jour.* 16, (May 1970).

- [II-11] LEE, B.I., KESLER, M.G., "A Generalized Thermodynamic Correlation Based on Three-Parameter Corresponding States", *AIChE Jour.* 21 (1975).
- [II-12] MEDANI, M.S. and HASAN, M.A., "Phase Equilibria Calculations with a Modified Redlich-Kwong Equation of State", *The Canad. Jour. of Chem. Eng.* 56, 251, (1978).
- [II-13] MOTARD, R.L., and ORGANICK, E.I., "Thermodynamic Behavior of Hydrogen-Hydrocarbon Mixtures", *AIChE Jour.*, 6, 36 - 43 (March 1960).
- [II-14] NAKAMURA, R., BREEDVELD, G.J.F. and PRAUSNITZ, J.M., *Ind. Eng. Chem., Process Des. Dev.* 15, 557, (1976).
- [II-15] ORYE, R.V., *Ind. Eng. Chem. Process Des. Dev.* 8, 579, 59 (1969).
- [II-16] PENG, D.Y. and ROBINSON, D.B., *Ind. Eng. Chem. Fundamentals* 15, 1, 59 (1976).
- [II-17] PETERS, S. and WENZEL, H., "Berechnung von Binaren Verdampfungsgleichgewichten mit Hilfe der Zustandsgleichung nach Redlich und Kwong", *Chem. Ing. Techn.* 43, 623, (1971).
- [II-18] PETERS, S. and WENZEL, H., "Berechnung von Binaren Verdampfungsgleichgewichten mit Einer überkritischen Komponente", *Chem. Eng. Tech.* 43, 856, (1971).
- [II-19] ROBINSON, D.B., PENG, D.Y. and NG, H.J., "Application of the Peng-Robinson Equation of State", A paper presented at the Engineering Foundation Conference, Asilomar, Pacific Grove, California (Jan. 16, 1977).
- [II-20] STARLING, K.E., *Hydrocarbon Proc.*, 50, (3), 101 (1971).
- [II-21] STARLING, K.E. and HAN, M.S., *Hydrocarbon Proc.*, 51, 107 (1972).
- [II-22] STARLING, K.E. and HAN, M.S., *Hydrocarbon Proc.*, 51, 129 (1972).

- [II-23] TEJA, A.S., and ROWLINSON, J.S., "The Prediction of Thermodynamic Properties of Fluids and Fluid Mixtures - IV, Critical and Azeotropic States", *Chemical Engineering Science* 28, 529, (1973).
- [II-24] WENZEL, H. and RUPP, W., "Calculation of Phase Equilibria in System, Containing Water and Supercritical Components", *Chemical Engineering Science*, 33, 683, (1978).
- [II-25] WILSON, G.M., *Advances in Cryogenic Engineering*, 9, 168 (1964).
- [II-26] WILSON, G.M. and DeVANEY, W.E., "Mark V Computer Program", available either from P-V-T or the Gas Processors Association.
- [II-27] YARBOROUGH, L., "Vapor-Liquid Equilibrium Data for Multi-component Mixtures Containing Hydrocarbons and Nonhydrocarbon Components", *Jour. Chem. Eng. Data* 17, 129 (1972).
- [II-28] ZUDKEVITCH, D. and JOFFE, J., "Correlation and Prediction of Vapor Liquid Equilibria with the Redlich-Kwong Equation of State", *AIChE Jour.*, 16, 112 (1970).
- [II-29] ZUDKEVITCH, D., JOFFE, J. and SCHROEDER, G.M., "Prediction of Vapor-Liquid Equilibria within the Critical Region: The Use of Equations of State", *Inst. Chem. Eng. (London) Symp. Ser.*, N°32, 21 (1969).
- [II-30] ZUDKEVITCH, D., Statement in *Inst. Chem. E. Symposium Series N°32*, Page 3:156, (1969).
- [II-31] ZUDKEVITCH, D., Part I of this Series.

TABLE 4

COMPOUNDS FOR WHICH COEFFICIENTS FOR THE BWR EQUATION ARE AVAILABLE  
[II - 3]

Substance	VAPOR PHASE				LIQUID PHASE			
	Density		Temperature		Pressure		Temperature	
	From	To	From	To	From	To	From	To
Methane.....	2.0	18.0	- 70	200	4.5	41.8	-140	-35
Methane.....	.75	12.5	0	350	Not Studied		Not Studied	
Ethane.....	.5	10.0	25	275	5.5	41.4	- 50	25
Propane.....	1.0	9.0	96.8	275	2.0	26.0	- 25	75
n-Butane.....	.5	7.0	150	300	1.2	23.5	- 4.0	121
i-Butane.....	.5	7.0	104.4	237.8	1.0	27.2	- 12	119
n-Pentane.....	.46	4.8	140	250	2.1	25.5	60	150
i-Pentane.....	.5	5.0	130	250	.34	21.5	0	160
i-Pentane.....	1.5	5.5	200	300	Not recommended for liquid region -			
2, 2 Dimethyl Propane.....	1.0	6.0	160	275	Not Studied		Not Studied	
n-Hexane.....	2.5	5.0	225	275	1.0	23.8	70	220
n-Hexane.....		Not recommended for gas phase			0	670	35	238
i-Hexane.....	1.5	5.5	250	275	Not recommended for liquid region			
3-methane pentane.....	3.2	6.0	250	275	Not recommended for liquid region			
2, 2 dimethyl butane.....	1.8	5.0	225	275	Not recommended for liquid region			
2, 3 dimethyl butane.....	1.5	5.0	250	275	Not recommended for liquid region			
n-Heptane.....	1.0	4.0	275	350	1.0	13.6	100	221
n-Heptane.....		Not recommended for gas phase			0	27	-177	257
3 methyl hexane.....	1.5	5.0	250	275	Not recommended for liquid region			
2, 2 dimethyl pentane.....	1.8	5.0	225	275	Not recommended for liquid region			
n-Nonane.....		Not recommended for gas phase			0	6.5	204	235
n-Decane.....		Not recommended for gas phase			0	5.3	35	238
methyl chloride.....	.05-17	4.0	35	225	8.013	102.71	35	140
Perfluorocyclobutane.....	.75	7.0	30	350	1.0	27.412	- 6	115
Tetrafluoromethane.....	.75	12.5	0	350	Not Studied		Not Studied	
Pentafluoro-mono-chloroethane.....	.64	10.5	- 68	174	.03	27.	- 76	67
Ethylene.....	1.0	12.8	0	198.5	2.1	31.9	- 90	-10
Ethylene.....	.15	18.9	50	125	Not recommended for liquid region			
Propylene.....	.5	8.0	25	300	2.1	24.9	- 30	60
Propylene.....	.5	9.5	100	250	Not Studied		Not Studied	
i-Butylene.....	1.0	7.0	150	275	1.0	27.2	- 7	123
i-Butylene.....	1.0	8.0	150	250	Not given		Not given	
Propyne.....	.3	11.4	50	200	Not given		Not given	
Benzene.....	.6	8.1	240	350	Not given		Not given	
Ammonia.....	0	2.6	27	307	Not recommended for liquid region			
Ammonia.....		Not recommended for gas phase			20	800	37	127
Argon.....	.02	29.8	-111	327	Not recommended for liquid region			
Carbon Dioxide.....	0	14.5	Up to	138	0	66	- 23	31
Carbon Dioxide.....	0	14.5	138	238	Not recommended for liquid region			
Carbon Dioxide.....	.15	15.9	50	125	Not recommended for liquid region			
Carbon Monoxide.....	.15	9.0	-140.2	- 25	3.13	34.53	-150	- 25
Carbon Monoxide.....	.09	1.8	- 25	200	Not recommended for liquid region			
Diborane.....	.04	15.7	- 93	27	1	39.5	- 93	9
Diborane.....	.04	8.35	- 93	27	Not recommended for liquid region			
Helium.....	2.0	50.0	-270	-253	0	100	-270	-267
Nitrogen.....	.02	24.34	-170	93	Not recommended for liquid region			
Nitrogen.....	0	22.2	-173	100	Not given		Not given	
Nitric Oxide.....	.04	1.6	5	105	Not given		Not given	
Nitric Oxide.....	0	10.0	27	105	Not given		Not given	
Nitrous Oxide.....	0	25.0	- 30	150	Not recommended for liquid region			
Oxygen.....	0	2.4	27	727	Not given		Not given	
Sulfur Dioxide.....	0	22.8	10	250	Not recommended for liquid region			

Table 5

PREDICTIONS OF VLE K RATIOS BY THE ZUDKEVITCH-JOFFE  
VERSION OF THE REDLICH-KWONG EQUATION

Summary of Results from Sample Cases in the Critical Region [I-81]

System **	Reference	Component	Number of K-values	Error in K (%)			
				***		Other Method	
				Average ±	Maximum	Average	Maximum
C <sub>1</sub> -C <sub>7</sub>	42	—	36	3.02			
		Methane	18	2.98	7.75		
		Heptane	18	3.06	8.93		
C <sub>2</sub> -C <sub>3</sub>	39	—	20	2.63			
		Ethane	10	1.44	3.30		
		Propane	10	3.82	11.77		
C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	38	—	39	6.83		B-W-R <sup>19,56</sup>	
		Methane	13	4.62	11.54	5.5	23.0
		Ethane	13	5.91	23.48	10.2	28.8
		Propane	13	9.95	38.36	20.2	42.2
H <sub>2</sub> -C <sub>7</sub>	51	—	16	2.81	—		
		Hydrogen	8	2.88	6.04		
		Heptane	8	2.74	4.05		
C <sub>3</sub> -CO <sub>2</sub>	52	—	86	2.48	—		
		Propane	43	3.39	29.9		
		CO <sub>2</sub>	43	1.57	6.95		
C <sub>1</sub> -H <sub>2</sub> S	48	—	48	4.30	—		
		Methane	24	6.04	19.75		
		H <sub>2</sub> S	24	2.56	5.58		
N <sub>2</sub> -C <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -C <sub>5</sub> -C <sub>7</sub> -C <sub>10</sub>	55	—	63	5.78	—	Chao-Seader <sup>4</sup>	
		Nitrogen	9	4.84	9.43	*17.13	
		Methane	9	1.18	2.89	21.39	47.17
		Ethane	9	6.05	7.89	7.04	11.62
		Propane	9	2.59	5.52	20.28	33.45
		Pentane	9	9.09	12.49	6.49	15.85
		Heptane	9	1.59	2.97	7.26	21.81
		Decane	9	15.11	34.39	11.99	56.52
						37.45	72.22

\* Seven values used for each component; 49 values total for the system.

\*\* Note For Reference see [I - 81]

\*\*\* Zudkevitch, Joffe

TABLE 6

SUMMARY OF LIQUID DENSITY EVALUATION  
FOR LOW MW SYSTEMS  
PER ERBAR [I - 71]

Source of 780 Data Points: Provence, Weiner and Walton, NGPA TP-2, 1972)

Range of Absolute Average Error %	Approximate Reduced Temp. Range	Number of Points		
		OSU/GPA	SHBWR	SRK
0.0 to 0.5	$\langle T_r < 0.85$	578	66	0
0.5 to 1.0	$\langle T_r < 0.85$	139	234	0
1.0 to 2.0	$0.85 < T_r < 0.90$	45	381	1
2.0 to 5.0	$0.85 < T_r < 0.90$	7	25	2
5.0 to	$0.95 < T_r$	22	3	706
Overall Abs.		0.88%	1.14%	9.78%

Range of Data: 32° to 140°F and 200 psia to 2000 psia

Symbols: OSU/GPA = is a computerized version of the Rackett method [I-4]  
SHBWR = Starling, Han BWR [I-22]  
SRK = Soave, Redlich-Kwong [I-71]