Prediction of Vapor-Liquid Equilibria with the Benedict-Webb-Rubin Equation of State

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The prediction of vapor-liquid equilibria with the Benedict-Webb-Rubin (BWR) equation of tate has been restudied. It was found that the suitability of the equation of state to represent ully the behavior of the constituents is the main factor which affects the accuracy of the pre-liction. To improve the representation of the pure component data by means of equation of state t is necessary to modify the present form of the BWR equation of state. A tentative form of nodification of the BWR equation of state has been chosen. Although the modified equation is still subject to further evaluation and refinement, satisfactory results have been obtained for the prediction of four binary systems containing nitrogen and carbon dioxide (nitrogen-methane. methane-carbon dioxide, propane-carbon dioxide, and n-butane-carbon dioxide).

The method of nonlinear estimation has been used to fit the coefficients in the equation of state to either vapor-pressure data or P-V-T data.

The need for consistent thermodynamic properties for engineering practice has been recognized (*18*). It is also known theoretically that an equation of state is one of the key functions from which thermodynamic properties can be derived. To predict thermodynamic properties which involve more than one phase, such as *K*-factor for vapor-liquid equilibria, the equation should at least represent the behavior of both the vapor and liquid phases. In addition, as can be seen from the theoretical derivations, the prediction of *K*-factors is a more severe test of accuracy since it requires not only the use of the equation of state but also its partial derivatives and integrals. These requirements are unattainable at present with any equation of state based purely on theoretical deduction.

To date, the most accurate equation of state which may be used to predict *K*-factors is the Benedict-Webb-Rubin (BWR) equation of state. It has been used to predict the *K*-factors of light hydrocarbon mixtures of up to twelve components (*4, 5, 6, 7*) and the *K*-factors of nitrogen-carbon monoxide mixtures (*34*) with satisfactory results. However, the predictions of the *K*-factors of nitrogen-methane (*36*), propane-carbon dioxide (*15*), and light hydrocarbons containing hydrogen (*26*) were found to be far from satisfactory. Poor results were also reported when some of the simpler thermodynamic properties were predicted such as the densities of mixture of *n*-butane and carbon dioxide (*29*) and the compressibilities of binary mixtures of carbon dioxide and light hydrocarbons (*17*). Even for the systems consisting purely of light hydrocarbons, the predicted *K*-factors were not satisfactory when the temperature is low and the pressure is high (*30*).

Several modifications have been suggested to improve the *K*-factor prediction. Stotler and Benedict (*36*) suggested two modifications. One was the modification of the equations of the pure components achieved when the numerical value of one of the coefficients, C_o, is changed at different temperature levels so that the low temperature vapor pressure of the component concerned can be adequately represented. The second was to fit one of the interaction constants (corresponding to the constant A_o in Equation (3) to the experimental values of *K*-factor. Even with this modified method, however, Cullen and Kobe (*15*) still obtained unsatisfactory results in the prediction of the *K*-factors of propane-carbon dioxide system. Recently, Motard and Organic (*26*) found that in the case of the mixtures of light hydrocarbons with hydrogen it is necessary to follow the first suggestion proposed by low the second one. Instead, they found that adjustment Stotler and Benedict (*36*), but it is not necessary to fol- of the coefficient, γ, for hydrogen according to the temperature level can yield better prediction except for the *K*-factors of propane at very low temperatures (*26*).

The first suggestion of Stotler and Benedict implied that the BWR equation was not accurate enough in the low-temperature region; the second meant that the mixing rule which was set up to compute the interaction constants may not be applicable to all cases. One objective of the present work is to determine which of these two factors is more important and how, if possible, to improve *K*-factor prediction without major revision of the BWR equation.

THE QUESTION OF FITTING THE INTERACTION CONSTANTS TO THE EXPERIMENTAL DATA

The reported improvements (*36*) in *K*-factor correlation, after one of the binary interaction constants (*4*) corresponding to A_o had been fitted to the experimental data, encouraged the further study of fitting the interaction constants to the experimental data. The previous work of Stotler and Benedict (*36*) was based on the results with six out of the original ninety-six data points (*14*). This is possibly owing to the manpower limitation in the attempt to do such a large-scale computation manually.

The major problem in the attempt to fit the interaction constants is owing to the fact that the form of the equation is nonlinear in terms of the coefficients. For this reason the conventional method of least squares cannot be used. Recently, the method of nonlinear estimation, which can be applied to the present case, has been developed by Box (*9* to *11*). In essence, it is a variation of method of least squares. The equation is linearized by the applica-

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tion of first-order Taylor's expansion to all the coefficients. The method of least squares is then applied to the linearized equation. From this, a set of corrections to the initial values of the coefficients is obtained. The coefficients are then corrected and the method of least squares applied again. The iteration proceeds until a minimum in the sum of squares of the errors has been reached or until there is no further significant improvement. A more detailed illustrative description of the method is available elsewhere (*8, 24*).

It is apparent that the execution of such a task by manual computation is impractical if not impossible. The use of an electronic digital computer is inevitable. An IBM-704 program for the method of nonlinear estimation has been made available by Booth and Peterson (*8*). However, for the purposes of the present application, the program was modified. The modification was made to increase the flexibility of the operation and to make possible the combination of the program with a sub-program written in Fortran. The details of the modification, a brief write-up, and the listing of the modified program are available elsewhere (*24*).

With the aid of an electronic digital computer and method of nonlinear estimation program, the significance of fitting the interaction constants has been studied more closely. The same nitrogen-methane data (*14*) as employed by Stotler and Benedict (*36*) have been used in fitting the interaction constants. The fitting was conducted without complying with the first suggestion given by Stotler and Benedict (*36*) as quoted earlier in this paper. The results of fitting all twelve of the interaction constants in the binary system (*4, 24*) reduced the overall average absolute deviation by 0.9%, from 11.4% to 10.5% in *K*-factor.[*] The gain was in the area where the errors in prediction were not serious in the first place. For those points where the initial deviations were excessive, the deviations were increased instead of being reduced.

It was also found that the suggestion to adjust the numerical value of C_o at each temperature level is more effective than the fitting of the interaction constants. For example, at 99.85°K., when the suggested values (*36*) of C_o for both nitrogen and methane were used, the average absolute deviation was found to be 17.1% as compared to 32.7% found when the C_o values were not adjusted.

This demonstrates that the perfection of the equation of state for the pure components can be far more important than the fitting of the interaction constants.

REEXAMINATION OF THE BWR EQUATION OF STATE

It was suggested (*36*) that C_o should be adjusted so that the equation of state for the pure component can be used to predict the vapor pressure of the same pure component. No explanation was given as to why the coefficient C_o, and not the others, should be adjusted. In fact it was found that in the *K*-factor prediction of the nitrogen-methane system at 99.85°K., when only the suggested C_o value for methane was used, the average absolute deviation was 16.4% while the deviation was 17.1% when both adjusted C_o's were used.

The suggestion to alter the numerical value of C_o so that it will represent the vapor pressure at the temperature of interest is apparently a compromise. The equation of state should correctly predict vapor pressure. One method of assuring this is to fit the BWR equation of state to the vapor-pressure data. Theoretically this can be done (*3, 24*), but because of the complexity and the nonlinearity of the problem no previous attempts have been made along these lines although the problem involved is less complicated than fitting the interaction constants to *K*-factor data.

With the aid of the nonlinear estimation program, a machine program for obtaining the coefficients in the BWR equation of state from vapor-pressure data has been developed (*24*). However, the coefficients obtained from fitting the vapor-pressure data cannot be used to predict the P-V-T relation far from the two-phase region without serious error.

A study has also been made to find the best dependent variable is to use in fitting the equation of state to P-V-T data. Again the main problem has been how to fit the experimental data with a nonlinear equation (the form of BWR equation). For this purpose, a program for fitting the BWR equation to P-V-T data which is based on a method of nonlinear estimation has also been developed (*24*). The program will accept pressure or compressibility factors as the dependent variable.

The original method proposed by BWR (*3*) for fitting P-V-T data is essentially a graphical method. Pressure was used as the dependent variable. Sage, et al. (*13, 28, 35*) and others (*17*) have developed methods based on the method of least squares. They all use the compressibility factor, Z, as the dependent variable for simplicity in the mathematical treatment.

The results obtained when compressibility factors and pressure as the dependent variable in P-V-T data fitting were used have been compared. A smaller average percentage deviation, defined as $(1/n)\Sigma|(P_{obs} - P_{cal}) \times 100/P|$, was obtained when the compressibility factor was used as the dependent variable. On the other hand, a smaller average deviation defined as $(1/n)\Sigma|P_{obs} - P_{cal}|$, was obtained when pressure was used as the dependent variable. Further comparison was carried out to determine the effect of choosing the dependent variable in P-V-T data fitting on *K*-factor prediction. The results shown in Table 1. favor the use of pressure as the dependent variable.

The numerical values of the pressure in a whole range of P-V-T data may vary from a fraction of an atmosphere to several hundred atmospheres. The same percentage deviation at the low pressure end may be merely a minute deviation, while on the other extreme, it can be a difference of several atmospheres or even more. It is less likely that error of such a magnitude will be encountered in

TABLE 1. THE EFFECT OF CHOOSING THE DEPENDENT VARIABLE IN P-V-T DATA FITTING ON *K*-FACTOR PREDICTION

System *A*	System *B*	Dependent variable for *A*	Dependent variable for *B*	Dev. in *K*-factor prediction, % Max. dev.	Min. dev.	Avg. abs. dev.
Propane	Carbon Dioxide	Z(*M*)	P(*M*)	73.4	0	15.0
		P(*M*)	P(*M*)	22.0	0	6.7
		P(BWR)	Z(*M*)	79.5	0	7.4
		P(BWR)	P(*M*)	17.4	0	5.2
n-butane	Carbon Dioxide	P(BWR)	Z(*M*)	60.3	0	5.7
		P(BWR)	P(*M*)	36.4	0	4.8

Note: (*M*) means based on the proposed modified BWR equation, and (BWR) means based on original BWR equation.

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[*] Most of the data cited in this paper is available in tabular form and has been deposited as document 7641 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $6.25 for photoprints or $2.50 for 35-mm. microfilm.

TABLE 2. COMPARISON OF THE DEVIATIONS IN THE COMPUTED LIQUID AND VAPOR PHASE FUGACITIES IN THE TWO-PHASE REGION USING THE ORIGINAL AND THE PROPOSED MODIFIED FORM OF THE BWR EQUATION

System	Dependent variable*	Original form Max. dev.	Original form Min. dev.	Original form Avg. abs. dev.	Modified form Max. dev.	Modified form Min. dev.	Modified form Avg. abs. dev.
Propane	P	99.35	0.77	36.15	95.35	0.76	27.98
Propane	Z	99.54	1.06	41.06	65.18	10.40	17.34
CO_2	P	29.88	1.30	10.67	13.51	0.62	4.64
CO_2	Z	14.47	0.476	4.59	12.98	0.48	4.68
Hydrogen	P	100.0	99.5	99.9	100.0	87.5	97.8
Hydrogen	Z	100.0	93.6	98.9	98.5	30.0	75.2

* Dependent variable used to fit the equation to P-V-T data:
Dev. $= 100(1 - f_L/f_V)$

actual experimental measurements. Hence, average deviation is preferred as a criterion to average percentage deviation.

The definition of compressibility factor, $Z = P/RTd$, demonstrates that the use of the compressibility factor as the dependent variable in P-V-T data fitting tends to give more weight to the low temperature and low density data. This may be undesirable.

The need for adjusting the coefficient C_o at different temperature levels so that the BWR equation represents vapor-pressure data suggests that C_o be expressed as a function of temperature. The justification for expressing the coefficient C_o as a function of temperature has been shown qualitatively (*24*) after a study of the possibilities of adjusting other coefficients (such as c or γ) with several test systems such as nitrogen, *n*-butane, propane, methane, hydrogen (*21*), and carbon dioxide (*25*). Based on the results on these same systems, it was found that in the two-phase region better agreement in the computed liquid and vapor phase fugacities (Table 2.) can be improved if the second virial coefficient in the BWR equation is expressed as

$$B_oRT - A_o - C_o/T^\beta \tag{1}$$

instead of the original

$$B_oRT - A_o - C_o/T^2 \tag{2}$$

The modified equation is

$$P = RTd + (B_oRT - A_o - C_o/T^\beta)d^2 + (bRT - a)d^3 + a\alpha d^6 + (cd^3/T^2)(1 + \gamma d^2) \exp(-\gamma d^2) \tag{3}$$

However, the results as a whole are still not satisfactory. Even with the modified form, it is still not possible to use one set of BWR coefficients to represent fully the behavior in the single and two-phase regions.

The adequacy of an equation of state merely to reproduce the P-V-T behavior within experimental error is not sufficient to insure its use to predict derived properties adequately. The derivatives and the integrals of the equation must also be sufficiently accurate. To assure this quality, at least one of the derived properties should be included as a test during the course of data fitting. Fugaciy is a fairly important derived property; like most of the derived properties, however, it cannot be measured directly. It is well known that at the two-phase region when equilibrium is established the fugacities of the two phases are equal. This can be used as the required test, and it has been used when the BWR coefficients were fitted to vapor-pressure data. However, since in most cases vapor-pressure data do not include the equilibrium vapor and liquid densities, there is no means to test whether the equation will predict the equilibrium densities correctly as a result of fitting the coefficients to vapor-pressure data. If such data are available, they can be used as a constraint in the coefficient data fitting process to improve the results. They can also be used as an indicator to show whether the equation needs further improvement. Several improved forms may have to be tried before the one that satisfies this additional condition can be obtained.

THE PRESENT STATUS OF THE PREDICTION OF K-FACTORS

In the absence of a full-range equation of state, two sets of coefficients were used (one from P-V-T data fitting, the other from vapor-pressure data fitting) to represent the behavior of the pure component in the different regions. The *K*-factor predictions of four binary systems were computed, and the results were compared with the experimental data. The systems are nitrogen-methane (*14*), methane-carbon dioxide (*16*), propane-carbon dioxide (*32*), and *n*-butane-carbon dioxide (*27*). Two hydrocarbon binary systems, methane-*n*-butane and ethane-*n*-butane (*4*), were included primarily for comparative purposes.

Since the modified BWR equation has been found to cover a wider range than the original equation, the prediction was based on the modified BWR equation. The results of fitting the coefficients in the modified BWR equation to the vapor-pressure data (*21, 25*) for all of the pure components involved in the aforementioned four binary systems are shown in Table 3. The work of fitting the coefficients in the modified BWR equation to the P-V-T data, however, has been limited to propane (*2, 31*), carbon dioxide (*22*), and hydrogen (*38*) and is shown in Table 4. For nitrogen, methane, ethane, and *n*-butane, the coefficients in the modified BWR equation fitted to the P-V-T data were not carried out in this investigation. For these components, the published constants based on the original equation were used with β, the added coefficient in the modified form considered to have a numerical value of 2.

RESULTS OF THE PREDICTIONS

The computations show that in most cases the coefficients obtained as a result of P-V-T data fitting give better

TABLE 3. COEFFICIENTS IN THE MODIFIED BWR EQUATION OF STATE AS DETERMINED FROM VAPOR-PRESSURE DATA

System	N_2	CO_2	H_2	CH_4	C_3H_8	n-C_4H_{10}
A_o	0.5719747	−1.684630	0.2063201	1.589113	6.245638	20.52172
$B_o \times 10$	0.4618903	*5.169879	0.184970	0.4335033	0.8182161	3.735933
$C_o \times 10^{-5}$	0.001064597	0.01543682	0.0001133076	0.02143107	0.2803237	0.2194065
$\gamma \times 10^2$	0.7605651	0.3327236	0.6058854	0.6426799	2.048722	3.544808
$a \times 10$	0.1536841	2.251909	−0.01974672	0.6661414	6.855057	34.38312
$b \times 10^3$	2.012855	6.720486	0.3595485	4.363266	23.53479	87.4850
$c \times 10^{-4}$	0.05513302	1.435322	0.001004429	0.2551919	6.583077	28.38896
$\alpha \times 10^{-4}$	2.890314	0.3846211	−0.5624030	1.228510	5.249580	16.39037
β	0.9725759	1.023405	1.380643	1.484483	1.533527	2.214998

* This figure should be multiplied by 10^{-26}.

TABLE 4. COEFFICIENTS IN THE MODIFIED BWR EQUATION OF STATE AS DETERMINED FROM P-V-T DATA (PRESSURE AS THE DEPENDENT VARIABLE)

System	CO_2	C_3H_8	H_2*
A_o	1.506609	4.291380	0.1392109
$B_o \times 10^2$	2.034075	3.625513	1.955537
$C_o \times 10^{-5}$	2.057525	2.331544	0.001962048
$\gamma \times 10^2$	0.3302648	1.786940	0.6308159
$a \times 10$	2.117938	10.26809	—0.02048868
$b \times 10^3$	6.150275	27.64357	0.3588767
$c \times 10^{-4}$	1.435392	9.071040	0.0009925807
$\alpha \times 10^4$	0.3782074	4.155765	—0.5774094
β	2.037402	1.872571	1.803368

* Only part of the extensive data ($P = 0.31 \rightarrow 1{,}060$ atm., $T = 85 \rightarrow 372$°K. and $d = 0.045 \rightarrow 22.3$ g.mole/liter) have been used.

results than the coefficients obtained from fitting the vapor pressure. However, when the system temperature is below about 0.7 times the critical temperature of one of the constituents, the right set of constants for that component should be chosen with care. In the case of nitrogen-methane some of the system temperatures are below 0.7 of the critical temperature of methane. In this low temperature range both sets of coefficients must be considered. The choice depends upon the system pressure in relation to the vapor pressure of methane. When it is not more than about 15 atm. above the vapor pressure of methane, the coefficient from vapor pressure data should be used; otherwise those coefficients from P-V-T data should be chosen. When this is done, the average absolute deviation in the low-temperature range was reduced from 1.2 mole % to 0.7 mole %; the overall average absolute deviation is reduced from 1.8 mole % to 1.0 mole %. For the other systems, including the two hydrocarbon systems, the predictions are rather straightforward because the temperature and the pressure ranges are not within the aforementioned limits. These results are summarized in Table 5.

In Table 5, the results of recomputing the *K*-factor predictions of the systems methane-*n*-butane and ethane-*n*-butane, based on the work of BWR (*4*), were included. The result of predicting the *K*-factor of methane-*n*-butane system is the most accurate in the table. The prediction of ethane-*n*-butane system, however, is nearly as good as those of the other systems.

Comparison with the Experimental Data

In most cases, the published tabulated data are the experimental data which has been smoothed. It is generally believed that the smoothed data is more accurate than the original data. The deviation in *K*-factor prediction in this work had been based on the smoothed data. To compare the results of the prediction to the results of experimental measurements, the deviation of the experimental measurements from the smoothed values should be used. Such deviations, however, are not readily available from the published data; the only reported deviation is actually the experimental reproducibility based on the repeated sample analysis. From some of the published data-smoothing graphs one can conclude that the deviation of the experimental measurements from the smoothed values are generally greater than the reported reproducibility. The present predicted values are nearly as good as the experimentally measured values.

Application to the System Containing Hydrogen

Some attempts have also been made to apply the method to the systems of hydrocarbons containing hydrogen such as hydrogen-methane (*20, 33*), -ethane (*20, 37*), -propane (*12*, *37*), and -butane (*1*). The results are not comparable to the other systems studied in this investigation. The main difficulty encountered was owing to the negative coefficients in the equation of state. The fitting of the coefficients in the BWR or the modified BWR equation to the P-V-T data does not present any problem except that two of the resulting coefficients are found to be negative as was reported by Eubanks (*19*) and Motard and Organick (*26*). It is these negative coefficients which present the problem for *K*-factor prediction. The method proposed by Eubanks (*19*) has been applied, extended (*24*), and found unsatisfactory. Perhaps the solution to such systems at the present time is to follow the procedure shown by Motard and Organick (*26*). It should be noted here that the coverage of the hydrogen P-V-T data employed in this work (Table 4.) was much wider than those used by Motard and Organick (*26*).

SUMMARY

An equation of state can, in principle, be used to predict vapor-liquid equilibria for the whole temperature and pressure range. The constants in the pure component equation of state are made functions of composition, and interaction constants are introduced. In the case of the Benedict-Webb-Rubin equation, a method of computing interaction constants from pure component data led to a scheme which permitted prediction of vapor-liquid equilibria for a wide range of temperature and pressure without the use of any experimental data for the mixture in question. The fact that this scheme succeeds with a homologous series of hydrocarbons and fails with other systems led to speculation that a method of fitting interaction constants to mixture data would extend the usefulness of the equation of state.

It has been found that unless the equation of state adequately fits the pure components, including the two-phase region, improvement of the interaction constants was not effective as a means of improving prediction of *K*-factor.

Pressure, not the compressibility factor, should be used as the dependent variable to fit the constants in both the modified and the original form of BWR equation of state for pure components.

It has been found that the original form of BWR equation of state will not fully represent the P-V-T behavior of a substance in all regions with comparable precision. Although it is not yet adequate, a simple modification has been found to extend the range of the coverage of the equation. For this reason, it has been necessary to use two sets of constants per component to represent fully the P-V-T behavior in all regions. One of these should be ob-

TABLE 5. SUMMARY OF *K*-FACTOR PREDICTION OF VARIOUS SYSTEMS

System	Deviation in *K*, % Avg. abs. dev.	Deviation in *K*, % Max. dev.	Deviation in mole fraction, % Avg. abs. dev.	Deviation in mole fraction, % Max. dev.
CH_4-CO_2	8.4	28.2	1.2	2.8
C_3H_8-CO_2	5.2	17.5	0.9	2.2
n-C_4H_{10}-CO_2	4.6	36.4	0.6	2.3
N_2-CH_4	8.1	38.4	1.0	5.8
CH_4-*n*-C_4H_{10}	1.1	4.8	0.25	0.76
C_2H_6-*n*-C_4H_{10}	3.5	21.0	0.75	3.9

Note: The prediction was made in *K*-factor. The deviation in mole fraction was calculated according to

$$dK = (\partial K/\partial x)dx + (\partial K/\partial y)dy = -(y/x^2)dx + (1/x)dy$$

Assume

$$|\Delta x| = |\Delta y|$$

from which

$$|\Delta y| = |\Delta x| = \frac{x^2}{x + y} \Delta K$$

tained when the constant is fitted to the P-V-T data with pressure as the dependent variable; the other should be obtained through fitting the vapor-pressure data.

Although it requires two sets of constants to describe fully the behavior of a pure component, the constants from vapor-pressure data will be needed for the purpose of predicting the *K*-factor only when the temperature is sufficiently low (lower than $T_r = 0.7$) and the pressure is close to the saturated vapor pressure. Otherwise, the constants from P-V-T data in the modified equation of state can be used to predict the *K*-factors with reasonable results.

In conclusion, the authors wish to stress that, although progress has been made in this investigation, further improvement can be expected. Such improvement should be directed toward making possible the representation of both P-V-T and vapor-pressure data by one set of constants. These requirements are owing to the fact that in order to predict the *K*-factor of a mixture, the equation must be used to predict all of the P-V-T behavior for the pure components. This includes the states of superheated liquid and supercooled vapor which are known to be unstable. It is also necessary that the integrals and the derivatives of the equation be correct. These requirements can only be met by an equation of state which fully represents the behavior of a pure component.

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NOTATION

A_o, a, B_o, b, C_o, c = coefficients in BWR equation
d = density, g. mole/liter
f_L, f_V = liquid and vapor phase fugacity, respectively
K = y/x, *K*-factor
n = number of data point
P = pressure, atm.
P_{obs} = pressure, experimentally observed
P_{cal} = pressure, calculated with equation
R = gas constant, atm. liter/g. mole °K.
T = absolute temperature, °K.
T_r = reduced temperature
x = mole fraction in liquid phase
y = mole fraction in vapor phase
Z = P/RTd, compressibility factor
α = a coefficient in BWR equation
β = a coefficient in the modified BWR equation
γ = a coefficient in BWR equation

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