# Benedict Equation of State: Application to Vapor—Liquid Equilibria

**Edward J. Cullen and Kenneth A. Kobe**
University of Texas, Austin, Texas

The Benedict-Webb-Rubin equation of state (*3, 4, 5, 6*) has been used extensively and successfully by its authors to represent the *P-V-T* data of the hydrocarbons and to predict the vapor-liquid equilibria existing in binary and ternary mixtures of hydrocarbons (*6*). Sage and coworkers (*8, 12*) have subsequently shown the utility of this equation of state for hydrocarbons over much wider ranges of pressure. The equation has also been applied to the nitrogen–carbon monoxide system by Schiller and Canjar (*13*), who showed that it could satisfactorily predict vapor-liquid equilibria in that system. The latter investigation is the only one in systems outside the hydrocarbons and, as it was successful, the present authors decided to investigate the possibility of a general application of this equation of state to binary systems. The nitrogen–carbon monoxide system is a rather special case in that the two gases have isosteric molecules and consequently very similar physical properties. This is well illustrated by the similarity in the values of their constants in the equation of state. The more general system chosen for this work was that of carbon dioxide and propane, which have molecules differing both in molecular size and chemical type.

## CONSTANTS FOR CARBON DIOXIDE

The method originally used by its authors for evaluating the constants is tedious, and a more refined technique using a statistical method has been developed by Sage and coworkers (*7*), who later facilitated the calculations by the use of a digital computing machine (*14*). Unfortunately the means to make use of these better methods were not available for this work, and so recourse had to be made to the original method of the authors. The details of the methods employed in this work are available in the literature (*3, 4*).

Kendall and Sage (*8*) have conveniently tabulated the isothermals for carbon dioxide in the temperature range from 40° to 460°F. and for pressures up to 10,000 lb./sq.in. abs., and these data were used to evaluate the constants. For the vapor pressure of liquid carbon dioxide the extensive data of Meyer and Van Dusen (*9*) in the temperature range from —60°F. to the critical temperature were used.

The constants for propane are available in the literature from two sources. The first source is in the summary of the original work by Benedict, Webb, and Rubin (*5*), in which they present values of the constants for twelve hydrocarbons. The second source is in the paper by Selleck *et al.* (*14*) in which a different set of constants is given, determined by the more refined technique and applicable over a wider range of pressures; the latter are consistent with those of Benedict, Webb, and Rubin up to pressures of about 4,000 lb./sq.in. abs., but deviate increasingly at higher pressures.

Since the method of Benedict, Webb, and Rubin was used to determine the values of the constants for carbon dioxide in this study, it was considered wiser to select their values. Then the two sets of constants used for the determination of the vapor-liquid equilibria in the carbon dioxide–propane system would be consistent in their method of determination. In any case, in the binary system investigated the pressure does not exceed 1,000 lb./sq.in. abs., and so the two sets of constants are consistent.

The equation of state may be written in the following form:

$$P = RTd + (B_oRT - A_o - C_o/T^2)d^2 + (bRT - a)d^3 + a\alpha d^6 + \frac{cd^3}{T^2}(1 + \gamma d^2)\, e^{-\gamma d^2} \qquad (1)$$

Subsequently for purposes of comparing the observed and predicted values, the pressure will be considered as the dependent variable.

Figures 1, 2, and 3 show the graphs from which the preliminary values of the constants were determined. An attempt was made to fit the equation to the vapor-pressure data, but it was impossible to adjust the constants $A_o$, $B_o$, and $C_o$ so that the equation would represent the data over the whole range from —10° to 460°F. Therefore, it was decided to present two sets of constants to obtain adequate representation over the whole range of temperatures. Set *A*, to which vapor-pressure corrections have been applied, is to be used for the calculation of vapor pressures, the critical point, and pressures in the gaseous region up to 280°F. Set *B*, the preliminary values determined from Figures 1, 2, and 3, is to be used for the calculation of all pressures in the temperature range of 280° to 460°F. These constants are presented in Table 1.

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Edward J. Cullen is at present at Cambridge University, Cambridge, England.

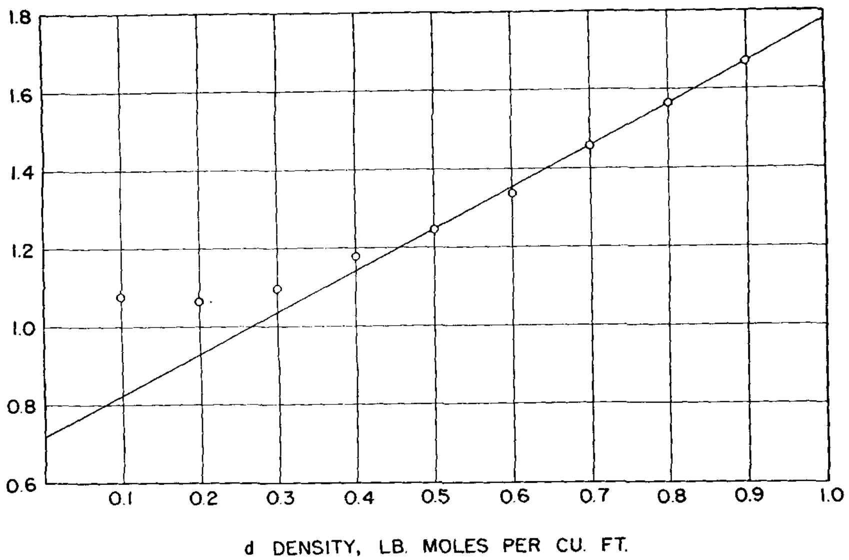

Fig. 1. Determination of function $B$ for Benedict-Webb-Rubin equation of state for carbon dioxide.

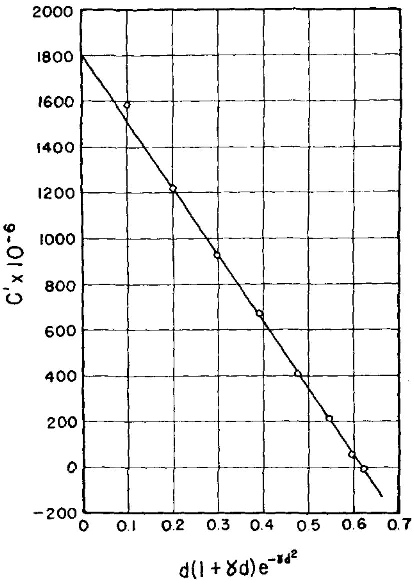

Fig. 2. Determination of function $C'$ for Benedict-Webb-Rubin equation of state for carbon dioxide.

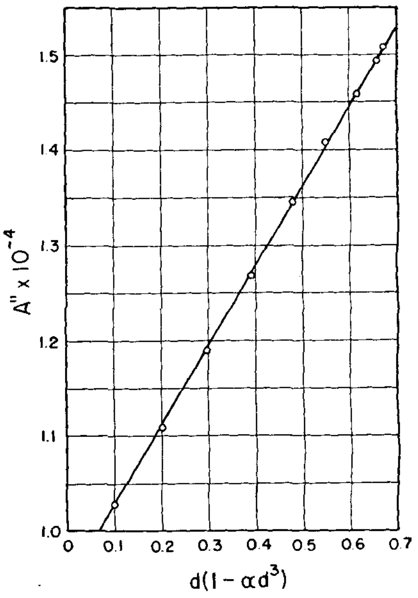

Fig. 3. Determination of function $A''$ for Benedict-Webb-Rubin equation of state for carbon dioxide.

The equation of state fits the $P$-$V$-$T$ data on carbon dioxide with an over-all deviation in the dependent pressure variable of 0.32% up to densities of 0.9 mole/cu. ft. in the temperature range from the critical temperature up to 460°F. The maximum deviations occurred at the highest pressures along the isotherms close to the critical isotherm.

The equation fits the vapor-pressure data from —10°F. to the critical temperature with an average deviation of 0.57% and predicts a saturated liquid density in that temperature range with an average deviation of about 2.5%. A more detailed comparison of the properties of the saturated liquid are presented in Table 2.

### VAPOR-LIQUID EQUILIBRIA IN THE CARBON DIOXIDE—PROPANE SYSTEM

Poettmann and Katz (*11*) studied the phase behavior of the carbon dioxide–propane system, and more recently Reamer, Sage, and Lacey (*12*) repeated their study. Fair agreement was realized between the two sets of data, but as it is believed that the more recent work is more accurate, it has been selected as a basis for comparison with the predicted vapor-liquid equilibria. The comparison was made through the predicted and observed vaporization ratios, commonly called $K$ values. The observed $K$ value was calculated from the equation

$$K_j\,(obs) = \frac{y_j}{x_j} \qquad (2)$$

At equilibrium the fugacities of any component in the liquid and vapor phases are equal; so Equation (2) may be changed thus:

$$K_j\,(calc) = \frac{f^L{}_j/x_j}{f^G{}_j/y_j} \qquad (3)$$

The fugacity coefficient $f_j/x_j$ varies much less rapidly with the composition than the fugacity itself, and so it is convenient to use Equation (3) to calculate the predicted values.

It is assumed that the $P$-$V$-$T$ properties and vapor-liquid equilibria of any mixture of carbon dioxide and propane can be repre-

TABLE 1.—VALUES OF THE CONSTANTS FOR CARBON DIOXIDE

| | A | B |
|---|---|---|
| $A_o$ | 10322.8 | 9488.04 |
| $B_o$ | 0.799496 | 0.719000 |
| $C_o$ | $1.69301\times10^9$ | $1.80146\times10^9$ |
| $a$ | 8264.46 | 8264.46 |
| $b$ | 1.05820 | 1.05820 |
| $c$ | $2.91971\times10^9$ | $2.91971\times10^9$ |
| $\alpha$ | 0.348000 | 0.348000 |
| $\gamma$ | 1.38400 | 1.38400 |

Set $A$ is to be used for the calculation of vapor pressures and for pressures in the gaseous phase up to 280°F. Set $B$ is to be used for the calculation of pressures in the gaseous phase above 280°F.

TABLE 2.—THE PROPERTIES OF SATURATED LIQUID CARBON DIOXIDE

| Temp., °F. | Vapor pressure, lb./sq. in. abs. Calc. | Vapor pressure, lb./sq. in. abs. Obs. | Deviation, % | Liquid density, lb. moles/cu. ft. Calc. | Liquid density, lb. moles/cu. ft. Obs. | Deviation, % |
|---|---|---|---|---|---|---|
| 85.0 | 1034.5 | 1032.2 | −0.220 | 0.893 | 0.888 | −0.563 |
| 80.0 | 970.6 | 969.4 | −0.124 | 0.972 | 0.983 | −1.170 |
| 50.0 | 652.7 | 652.9 | +0.031 | 1.179 | 1.224 | −3.676 |
| 20.0 | 417.7 | 422.0 | +1.109 | 1.300 | 1.339 | −2.913 |
| −10.0 | 255.0 | 257.6 | +1.010 | 1.395 | 1.437 | −2.923 |

Critical Properties

| | Calculated | Observed |
|---|---|---|
| Critical temperature, °R. | 549.0 | 547.5 |
| Critical pressure, lb./sq. in. abs. | 1,093.2 | 1,069.9 |
| Critical density, lb. mole/cu. ft. | 0.685 | 0.664 |

sented by Equation (1). The parameters of this equation are functions of the composition and the individual constants of the pure components and they may be calculated by the relationships suggested by Benedict, Webb, and Rubin(*6*). These relationships are given as being most suitable for hydrocarbons but, though they have some basis in fact, they are largely empirical. It is conceivable that a more suitable method of determining these parameters for gases other than hydrocarbons might be found, but no attempt was made in this study. The determination of the fugacity coefficient for each component was begun by obtaining by trial, liquid and vapor densities which would represent several pressures for the range covered by the isotherm under investigation. This was done for the pure components where possible and for several intermediate compositions. The purpose was to obtain a scale of compositions by which fugacity coefficients might be interpolated to any other intermediate composition. By use of the values of the density so determined, fugacity coefficients for both phases were calculated from Equation (4) at their respective pressures and compositions.

$$
\begin{aligned}
RT \ln f_j/x_j &= RT \ln RTd \\
&+ \Big[ (B_o + B_{oj})\, RT - 2\, (A_o A_{oj})^{1/2} - 2\, (C_o C_{oj})^{1/2} T^{-2} \Big] d + \frac{3}{2} \Big[ (b^2 b_j)^{1/3} RT - (a^2 a_j)^{1/3} \Big] d^2 + \frac{3}{5} \Big[ a(\alpha^2 \alpha_j)^{1/3} \\
&+ \alpha\, (a^2 a_j)^{1/3} \Big] d^5 + \frac{3d^2}{T^2} (c^2 c_j)^{1/3} \Big[ (\frac{1 - e^{-\gamma d^2}}{\gamma d^2}) - \frac{1}{2} e^{-\gamma d^2} \Big] - \frac{2d^2}{T^2} c \\
&\left( \frac{\gamma_j}{\gamma} \right)^{1/2} \Big[ \frac{1 - e^{-\gamma d^2}}{\gamma d^2} - e^{-\gamma d^2} - \frac{1}{2} \gamma d^2 e^{-\gamma d_2} \Big] \qquad (4)
\end{aligned}
$$

The fugacity coefficients in both phases were plotted against pressure, with composition as a further parameter. From this plot it was possible to evaluate the fugacity coefficients at pressures and compositions corresponding to any

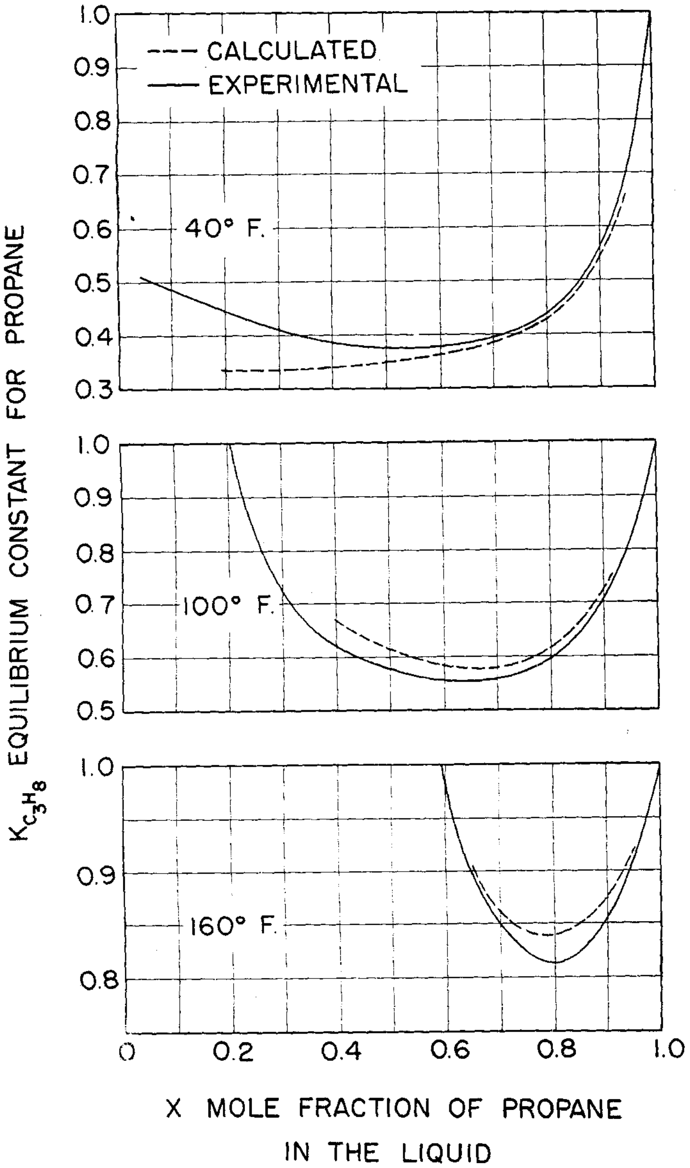

Fig. 4. Calculated and observed values of *K* for propane.

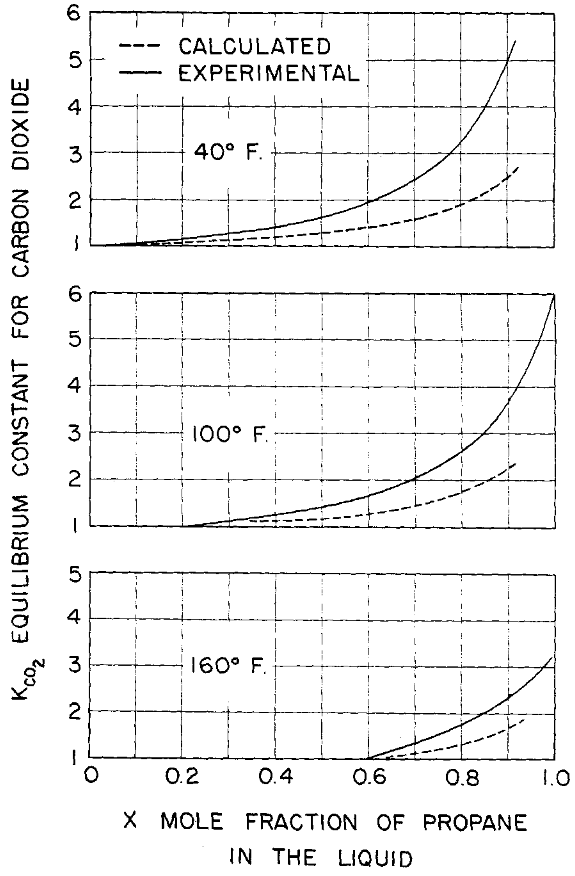

Fig. 5. Calculated and observed values of *K* for carbon dioxide.

given state of the system. The predicted $K$ values were then calculated for three temperatures, 40°, 100°, and 160°F.

The graphical comparison of the observed and predicted $K$ values given in Figures 4 and 5 shows that they differ markedly for carbon dioxide but less so for propane. As might be expected, the deviations are greatest at the lowest temperature. It is evident that this method gives calculated $K$ values for this system which are outside the limits of experimental accuracy.

Benedict, Webb, and Rubin(*6*) point out that to be strictly correct the fugacity coefficients should be evaluated at the calculated equilibrium composition and not at the observed equilibrium composition; however, this calculation is a lengthy trial-and-error procedure and was not carried out in this study. They further point out that the error introduced by this assumption is small if calculated $K$ values are close to the observed $K$ values. This certainly was not the case for carbon dioxide, and so it is expected that the values will have an appreciable error, though nowhere nearly sufficient to account for the deviations observed.

## DISCUSSION

The deviation found between the observed and calculated $K$ values in the propane–carbon dioxide system is believed to be due to the method of expressing the dependence of the parameters of the equation on composition for a mixture. The authors of the equation(*6*) point out that the way they suggest is the most suitable for hydrocarbons and in such systems the method works extremely satisfactorily. It also works in some cases outside the hydrocarbons(*13*) but in others(*15*), including this work, it is not so successful.

The reason for the lack of success in certain cases is thought to be caused by the increased interaction of the molecules of the components in the liquid phase. For the systems in which the equation works successfully, the components have been either hydrocarbons or isosteric molecules, and in neither case would one expect much interaction in the liquid phase. In any case the interaction would be similar in both types of cases and it is satisfactorily represented by the suggested method of combining the individual parameters. When one or more of the components is dissimilar in chemical character from the others, however, then added interactions come into play, which are not accounted for by the present method, and one would hardly expect the equation as it stands to work successfully.

This does not mean however that the equation must be limited to very special cases. Presumably the interactions of molecules in the liquid phase can be classified into various types and if that is the case, then the possibility exists that a suitable method of combining the parameters appropriate to each type of interaction might be found. A good review of the various semitheoretical and empirical ways of combining the parameters which have been used is given by Beattie(*1*).

Another alternative which has been suggested by Benedict(*2*) for systems consisting of a gas, such as carbon dioxide and the hydrocarbons, is to correct one of the parameters, such as $C_o$, for the mixture to bring the oberved and calculated $K$ values into agreement. It is hoped that this correction can then be generalized, so that it may be predicted for all the hydrocarbons. This method might obviously be extended so that the correction could cover a much wider range of gases, but owing to the extreme complexity of the interactions in the liquid phase this may not be possible. Stotler and Benedict(*15*) found that they could not correlate the liquid-vapor equilibria for the methane-nitrogen system using the original method, but by a suitable adjustment of the parameter $A_o$ for the mixture a good agreement was obtained, indicating the feasibility of the foregoing method.

If either of the two methods discussed above can be made to work satisfactorily, then obviously the utility of the Benedict equation of state is greatly increased. Even with the assistance of electronic digital computors, to have to study each system individually would be extremely inconvenient, and it is considered that a thorough investigation of the preceding methods would be profitable.

## SUMMARY

The Benedict equation of state has been applied to the prediction of the volumetric and phase behavior of carbon dioxide. Two sets of constants are presented; the first set predicts the vapor pressure and volumetric behavior in the temperature range from —10° up to 280°F.; the second set predicts the volumetric behavior for temperatures between 280° and 460°F.

The resulting equation fits the $P$-$V$-$T$ data with an over-all deviation in the dependent pressure variable of 0.32% up to densities of 0.9 lb. mole/cu.ft. in the temperature range considered. The vapor pressures are represented with an average deviation of 0.57% in the temperature range from —10°F. to the critical temperature, and the critical properties are adequately represented.

In the binary system of carbon dioxide and propane predicted and observed $K$ values are compared at 40°, 100°, and 160°F. The agreement is poor and deviations greater than 100% are found for carbon dioxide at the lowest temperature. In general the deviations are less for propane than for carbon dioxide. These deviations are believed to be due to the method of expressing the dependence of the parameters of the equation on composition.

## NOTATION

$A_o, B_o, C_o, a, b, c, d, \alpha, \gamma$ = coefficients for the Benedict equation of state
$P$ = pressure, lb./sq. inch abs.
$R$ = universal gas constant, (lb./sq.in.) (cu.ft.) / (lb. mole(°R.)
$T$ = absolute temperature, °R.
$V$ = molal volume, cu.ft./lb. mole
$K$ = vaporization ratio

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