EQUATION OF STATE FROM MULTIPROPERTY ANALYSIS— GENERAL DEVELOPMENT

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A multiproperty analysis method for simultaneously utilizing data for several thermodynamic properties in equation of state development is presented. Current problems in the use of equations of state which give evidence of the need for multiproperty analysis are discussed. Pertinent thermodynamic and statistical considerations are presented in developing the mathematical framework for multiproperty analysis. Test calculations are included for illustrative purposes and to substantiate the practical value of multiproperty analysis.

Many significant problems associated with the use of equations of state are related to the traditional reliance on pure-component pressure-volume-temperature (PVT) data for equation of state development. It is proposed that a number of these problems can be solved by utilizing multicomponent, multiproperty thermodynamic data in establishing the equations.

The most fundamental problem is that equations of state developed from PVT data, while often accurate in reproducing PVT properties, generally are less reliable for predicting phase behavior and thermodynamic properties. Ellington and Eakin (1) have pointed out that if the uncertainty in PVT data are of the order of one percent, the uncertainty in thermodynamic properties obtained by differentiation generally will be of the order of 10 percent. If a second differention is involved, the uncertainty in the derived property may approach 100 percent. In addition, equations of state developed from pure-component data are often restricted to use with lower molecular weight compounds. This limitation occurs because vapor phase data for heavier materials are scarce in the literature and experimentally impractical to obtain. Finally, the pure-component PVT approach cannot make use of the wealth of experimental mixture data that are available and which could be used as additional criteria for defining equations of state.

Until recently, attempts have been made to solve these problems individually. Martin (2), Opfell, Pings, and Sage (3), Hust and McCarty (4), and others have proposed conceptual methods for use of multiproperty data, but effective reduction to practice, particularly with regard to mixtures, has not been reported. Eakin and Ellington (5), Simon and Briggs (6), and Opfell, Pings, and Sage (3) have used mixture PVT data in equation development with some success, but did not solve the problems associated with predicting phase equilibria and thermodynamic properties nor the limitations with regard to heavy components. Starling (7) has reported some success in treating heavy components through use of phase equilibria data for mixtures containing high molecular weight hydrocarbons. Multicomponent phase equilibria data were also utilized by Chao and Seader (8) for determining solubility parameters and liquid fugacity coefficients of components which, in the pure state, are normally gases under the conditions of interest. Phase equilibria was then predicted using Hildebrand's regular solution equation (9) for the liquid and the Redlich-Kwong (10) equation for the vapor. Orye and Prausnitz (11) have made use of binary phase equilibria data to obtain parameters for use in the Wilson equation (12). Multicomponent phase equilibria were then predicted using the Wilson equation for the liquid and the virial equation for the vapor. However, use of the Wilson equation requires binary data for the ½n (n−1) component pairs in an n-component system and this quantity of data is seldom available for systems containing more than four components. Thus some progress has been made in attacking various aspects of current problems in equation of state development but each attempt lacks generality.

It has been pointed out by Starling and

Wolfe (13), however, that there is a unified approach by which all of these problems are treated. Specifically, simultaneous use of all available thermodynamic information, including data for both mixtures and pure components, is proposed as a basis for establishing equations of state. A statistical method is presented in this paper which can utilize PVT, phase equilibria, and any other thermodynamic property data which can be related through an equation of state. This would include enthalpy, specific heats, and Joule-Thomson coefficients as well as infinite dilution K-values (14) and thermodynamic data obtained by differential techniques, such as heats and volumes of mixing (15, 16) and partial molal volumes (17).

Prototype test calculations, in which PVT and enthalpy data are utilized simultaneously, are presented in this paper to demonstrate the practical value of multiproperty analysis in equation of state development. These calculations were made to study the proposed methods, rather than to obtain a final equation of state relation. Subsequent work, in which multiproperty analysis has been utilized to develop an accurate and self-consistent equation of state for fluids, will be published in the near future.

THERMODYNAMIC CONSIDERATIONS

It can be shown that the state of a homogeneous phase containing C components is fixed by specification of C+1 intensive variables (18). Furthermore a convenient choice for these variables (19) is temperature, T, molar density, ρ , and component mole fractions, x_i, $i=1,2...(C-1)$. The concept of an equation of state, then, asserts that all thermodynamic properties may be expressed as functions of these variables. Of course, thermodynamics cannot predict the mathematical form of the equation; this is usually determined by experiment and relevance to molecular theory. Theoretical forms of equations of state provide sound starting points for development, but ultimate recourse must be to empiricism based on experimental evidence of behavior. It is with respect to choosing the types of thermodynamic data which are analyzed that the most significant improvements can be made in equation of state development.

The equation of state concept is general and, if it is to be applied in general, there is no logical reason for preferring the use of one type of experimental data over another. In fact, valuable information about behavior with respect to changes in the intensive variables (and, therefore, information about the form of the equation itself) is lost by ignoring different types of data. Specific heat, enthalpy, and Joule-Thomson coefficient data, for example, give information regarding temperature effects. Component chemical potentials (or fugacities) obtained from phase data provide the significance of composition effects, as do other experimental partial molal properties. It seems, then, that the simultaneous use of all of these properties in developing an equation should yield a much more general result than use of a single property.

The mathematical form of an equation of state which will be suited to this approach will require considerable effort to determine. Certainly, it should conform to theoretical considerations as much as possible and be analytically differentiable with respect to all intensive variables. The determination of equation parameters will, in general, require the use of large amounts of data. Mathematical treatment of these data can be effectively established only through the use of statistical methods.

STATISTICAL APPROACH

For an assumed form of an equation of state as a function of temperature, density, composition, and parameters, the statistical problem of interest is to determine the parameter set which best describes all thermodynamic behavior. The method chosen is to seek that set of parameters which minimizes the relative difference between experimental and computed thermodynamic properties. Arguments in favor of this choice are given in the following analysis.

It is assumed that the experimental values of a thermodynamic property, R, are normally distributed. Denoting the expected value and variance of the experimental value of R by μ (R) and σ^2(R), the probability distribution of the experimental value of R, $\underline{P}$(R), is Eq. 1

$$\underline{P}(R) = [2\pi\sigma^2(R)]^{-\frac{1}{2}} \exp\{-\frac{[R-\mu(R)]^2}{2\sigma^2(R)}\}$$

Consideration is now given to the probability distribution of a set of data. To distinguish different properties the subscript notation, R_j, is used, where R_1 could be pressure, R_2 enthalpy, etc. To set apart the thermodynamic states of the systems considered, the notation R_{jk} is used, where "k" refers to a fixed set of values of the defining intensive variables. Thus, for properties such as pressure or enthalpy, which apply to a single phase, "k" corresponds to a fixed phase temperature (T_k), molar density (ρ_k), and component mole fractions (x_{ik}, i 1,2,...C). On the other hand, for properties such as vapor-liquid equilibrium ratios or component K-values in a two-phase system, "k" refers to fixed values of T_k along with vapor and liquid densities (ρ_{kv} and ρ_{kl}) as well as compositions of the coexisting phases (x_{ikv} and x_{ikl}). If it is assumed that Equation 1 is valid and that probabilities are independent, then the probability distribution of a set of experimental thermodynamic property values, $\underline{P}\{R_{jk}\}$, is given by

$$\begin{aligned}\underline{P}\{R_{jk}\} &= \pi_j \pi_k \underline{P}(R_{jk}) \\ &= \pi_j \pi_k [2\pi\sigma^2(R_{jk})]^{-\frac{1}{2}} \\ &\quad \exp\left(-\sum_j \sum_k \frac{[R_{jk}-\mu(R_{jk})^2]}{2\sigma^2(R_{jk})}\right)\end{aligned} \qquad \text{Eq. 2}$$

The value of Equation 2 is that it provides a rigorous mathematical framework for the estimation of equation-of-state parameters. The concept (20) to be applied is that maximization of the likelihood of occurrence of the set of thermodynamic data $\{R_{jk}\}$ corresponds to maximization of the probability distribution function $\underline{P}\{R_{jk}\}$.

Formulating this approach requires the additional assumption that the equation of state will yield the true value of the thermodynamic property in question. The true value of the property is denoted by

$$(R_{jk})_{true} = \eta_{jk}(\{r\}_{jk}, \{A\}) \qquad \text{Eq. 3}$$

where the functional form of η_{jk} is provided by the equation of state. In Equation 23, the notation $\{r_{jk}\}$ is used to indicate the set of intensive variables characteristic of the jth property in the kth state. $\{A\}$ is used to denote the set of equation-of-state parameters to be considered. If, for example, unlike interaction parameters are assumed to be functions of pure component parameters and the nth parameter for the mth component is denoted by A_{mn}, then $\{A\} = \{A_{mn}\}$. For simplicity, this is the only case considered, although the method may be applied to unlike interaction parameters. If parameters in the true equation of state were known exactly, expected values of thermodynamic properties would be given by

$$\mu(R_{jk}) = \eta_{jk} \qquad \text{Eq. 4}$$

For many properties it may be assumed that standard deviations of the data are proportional to the expected values; *i.e.,*

$$\sigma(R_{jk}) = \beta_j \eta_{jk} \qquad \text{Eq. 5}$$

where β_j is the constant of proportionality for the jth property.

The use in Equation 3 of estimated values of equation parameters, $\bar{A}_{mn}$, yields estimated expected values $\bar{\eta}_{jk}$ and standard deviations $\bar{\sigma}$ (R_{jk}). If these estimated values are substituted into Equation 2 for $\underline{P}\{R_{jk}\}$, an estimated probability distribution is obtained. Maximization of the resulting function for $\underline{P}\{R_{jk}\}$ with respect to the $\bar{A}_{mn}$ then yields the best estimates for the parameters. When experimental data are very accurate, it is not unreasonable to assume that standard deviations of the data are proportional to the experimental values. Thus

$$\sigma(R_{jk}) = \beta_j R_{jk} \qquad \text{Eq. 6}$$

Use of Equation 6 simplifies the analysis considerably. The form of $\underline{P}\{R_{jk}\}$ becomes

$$\begin{aligned}\underline{P}\{R_{jk}\} &= \{\pi_j \pi_k [2\pi\beta_j^2 R_{jk}^2]^{-\frac{1}{2}}\}\cdot \\ &\quad \exp\{-\tfrac{1}{2} \sum_j \frac{1}{\beta_j^2} \sum_k [1-\frac{\bar{\eta}_{jk}}{R_{jk}}]^2\}\end{aligned} \qquad \text{Eq. 7}$$

Maximization of $\underline{P}\{R_{jk}\}$ is then equivalent to minimization of the function

$$Q^* = \sum_j \frac{1}{\beta_j^2} \sum_k [1 - \frac{\bar{\eta}_{jk}}{R_{jk}}]^2 \qquad \text{Eq. 8}$$

Differences in the values of β_j are a measure of accuracy differences in experimental data for different properties. If the relative errors can be estimated, then

$$W_j = (\frac{\beta_1}{\beta_j})^2 \qquad \text{Eq. 9}$$

can be estimated and the minimization of Q^* in Equation 8 is equivalent to minimization of

$$Q = \sum_j W_j \sum_k [1 - \frac{\bar{\eta}_{jk}}{R_{jk}}]^2 \qquad \text{Eq. 10}$$

Thus, the W_j have the role of weighting functions in the analysis. The condition for a minimum function Q in Equation 10 is given by

$$\sum_n \sum_m \delta\,\bar{A}_{mn} \{\sum_j W_j \sum_k [1 - \frac{\bar{\eta}_{jk}}{R_{jk}}] \frac{1}{R_{jk}} \frac{\partial\bar{\eta}_{jk}}{\partial\bar{A}_{mn}}\} = 0 \qquad \text{Eq. 11}$$

In the absence of constraints such as critical conditions of pure components, etc., variations in the $\bar{A}_{mn}$, denoted by $\sigma\,\bar{A}_{mn}$, are independent and the quantities within the brackets in Equation 11 are all identically zero; thus

$$\sum_n \sum_m \delta\bar{A}_{mn} \sum_j W_j \sum_k [1 - \frac{\bar{\eta}_{jk}}{R_{jk}}] \frac{1}{R_{jk}} \frac{\partial\bar{\eta}_{jk}}{\partial\bar{A}_{mn}} \qquad \text{Eq. 12}$$

$$= 0$$

The relations represented by Equation 12 are the "normal equations" of the regression analysis. These must be solved simultaneously for estimation of equation parameters $\bar{A}_{mn}$. It should be noted that if constraining conditions are considered, usual methods, such as use of Lagrangian multipliers, may be applied to determining the $\bar{A}_{mn}$.

For any realistic equation of state, the normal equations are non-linear. Searching techniques, such as steepest descent, may be used (6). However, since the equation of state is analytic, a linearization technique (20) is usually acceptable. Simplest is the Gauss-Newton method (21) using the truncation of the Taylor's series expansion of $\bar{\eta}_{jk}$ which is linear in the $\bar{A}_{mno}$ and zero order approximations for the derivatives. The approximating function may then be written as

$$\bar{\eta}_{jk} = \bar{\eta}_{jk}(\bar{A}_o) + \sum_s \sum_r \left[\frac{\partial\,\eta_{jk}}{\partial\,\bar{A}_{rs}} \quad (\bar{A}_{rs} - \bar{A}_{rso}) \right] \qquad \text{Eq. 13}$$

where $\bar{A}_{rso}$ are guessed values for the $\bar{A}_{rs}$. The normal equations then become a set of equations which are linear in the correction terms ($\bar{A}_{rs} - \bar{A}_{rso}$).

$$\sum_j W_j \sum_k \frac{1}{R^2_{jk}} [\frac{\partial\bar{\eta}_{jk}}{\partial\bar{A}_{mn}}]_o \sum_s \sum_r [\frac{\partial\,\bar{\eta}_{jk}}{\partial\,\bar{A}_{rs}}]_o (\bar{A}_{rs} - \bar{A}_{rso}) \qquad \text{Eq. 14}$$

$$= \sum_j W_j \sum_k \frac{1}{R_{jk}} [1 - \frac{\eta_{jk}}{R_{jk}}]_o [\frac{\partial\,\bar{\eta}_{jk}}{\partial\,\bar{A}_{mn}}]_o$$

The set of simultaneous equations represented by Equation 14 can be solved by matrix methods. Of course the values for the $\bar{A}_{rs}$ obtained in this manner are only approximate because the truncated Taylor's expansion is accurate only in the limit as the $\bar{A}_{rso}$ approach the $\bar{A}_{rs}$. It is therefore necessary to treat the approximate values of $\bar{A}_{rs}$ as new guessed values in a second iteration. In principle, this iterative procedure can be continued until the correction terms ($\bar{A}_{rs} - \bar{A}_{rso}$) become arbitrarily small.

It is convenient to represent the relations of Equation 14 in matrix form

$$AB = C \qquad \text{Eq. 15}$$

The elements of the square matrix A are

$$A_{gh} = \sum_j W_j \sum_k \frac{1}{R^2_{jk}} [\frac{\partial\,\bar{\eta}_{jk}}{\partial\,\bar{A}_{mn}}]_o \; [\frac{\partial\,\bar{\eta}_{jk}}{\partial\,\bar{A}_{mn}}]_o \qquad \text{Eq. 16}$$

and the elements of the column matrices B and C are

$$B_h = (\bar{A}_{rs} - \bar{A}_{rso}) \qquad \text{Eq. 17}$$

$$C_g = \sum_j W_j \sum_k \frac{1}{R_{jk}} [1 - \frac{\bar{\eta}_{jk}}{R_{jk}}]_o [\frac{\partial\,\bar{\eta}_{jk}}{\partial\,\bar{A}_{mn}}]_o \qquad \text{Eq. 18}$$

where

$$g = M\ (m-1) + n \qquad \text{Eq. 19}$$

$$h = M\ (r-1\_ + s \qquad \text{Eq. 20}$$

and M is the number of parameters to be determined in the pure component equation of state. The solution of Equation 15 is then

$$B = A^{-1}C \qquad \text{Eq. 21}$$

where A^{-1}_{gh} is the inverse of A. The elements of the inverse matrix, A^{-1}_{gh} are related to estimates of the generalized covariances by the following equations,

$$\overline{\text{Cov}}\ (\bar{A}_{mn}, \bar{A}_{rs}) = (\beta_1)^2 A^{-1}_{gh} \qquad \text{Eq. 22}$$

$$\overline{\text{Var}}\ (\bar{A}_{mn}, \bar{A}_{mn}) = (\bar{\beta}_1)^2\ A_{gg}^{-1} \qquad \text{Eq. 23}$$

where $\bar{\beta}_1 = \frac{1}{(N-U)} \sum_j w_j \sum_k [\ 1 - \frac{\bar{\eta}_{jk}}{R_{jk}}]^2$ **Eq. 24**

where N is the total number of data treated and U is the number of parameters estimated in the regression calculation. Estimates of the relative errors in the properties other than R_1 may be obtained using Equation 9 in the form

$$\bar{\beta}_j = \frac{\bar{\beta}_1}{(w_j)^{\frac{1}{2}}} \qquad \text{Eq. 25}$$

Consideration must be given to the assignment of relative errors in the treatment of multiproperty data. This weighing is important because proper statistical weighting must insure least bias in estimated parameters. Several methods can be used for assigning values to the weighting functions given in Equation 9, including: (a) direct estimation of the relative uncertainty, β_j, in Equation 6, through knowledge of errors in the pertinent dependent variables, (b) indirect estimation of β_j through regression on individual properties, (c) indirect estimation of β_j through regression on multiproperty data. In applications of the third method, constraining conditions would commonly be imposed.

Regardless of the equation of state forms to be studied, the treatment of multiproperty data leads to large computer storage requirements. For this reason, programs treating individual properties should be developed and proven before combining to treat multiproperty data. To this end, regression programs for PVT and enthalpy data were developed separately and then combined to treat these two types of thermodynamic data simultaneously. Calculations discussed in the next section were made with these programs to demonstrate the feasibility and practical value of equation of state development from multiproperty analysis.

TEST CALCULATIONS

To substantiate the practical value of multiproperty analysis in equation of state development, prototype computations were made using PVT and enthalpy data. It should be emphasized that the computations presented here were made to study the proposed methods, rather than to obtain a final equation of state relation. In these calculations, methane was chosen as the prototype fluid and the BWR equation (22) was chosen as the prototype equation of state. The BWR expression for pressure is

$$\begin{aligned} P = {} & RT\rho + (B_oRT - A_o - \frac{C_o}{T^2})\rho^2 \qquad \text{Eq. 26} \\ & + (bRT - a)\rho^3 + a\alpha\ \rho^6 \\ & + \frac{c}{T^2}\ \rho^3(1+\gamma\rho^2)\exp(-\gamma\rho^2) \end{aligned}$$

while the BWR expression for the isothermal enthalpy correction is

$$\begin{aligned} H-H^\circ = {} & (B_oRT - 2A_o - \frac{4C_o}{T^2})\rho \qquad \text{Eq. 27} \\ & + \tfrac{1}{2}(2bRT - 3a)\rho^2 + \frac{6}{5}\ a\alpha\ \rho^5 \\ & + \frac{c}{T^2}\ \rho^2\ [3(\frac{1 - \exp(-\gamma\rho^2)}{\gamma\rho^2}) \\ & - \tfrac{1}{2}\exp(-\gamma\rho^2) + \gamma\rho^2\exp(-\gamma\rho^2)\ ] \end{aligned}$$

Values of the eight BWR parameters for methane reported by Benedict, Webb, and Rubin (22) are: B = 0.682401, A_o = 6995.25, C_o = 275763 x 10^8, b = 0.867325, a = 2984.12, α = 0.511172, c = 498106 x 10^3, γ = 1.53961. The units for these parameters correspond to pressure in psia, temperature in °R and density in lb-mole/cu ft. The value of the gas constant consistent with these parameter values is R = 10.7335.

Regression calculations were made using (a) only PVT data, (b) only enthalpy data, and (c) PVT and enthalpy data simultaneously. The data utilized were the PVT data of Hoover (23) and Vennix (24) at −99.7°F and the enthalpy data of Jones, *et al*, (25) at −100.0°F. Hoover's data were used for pressures below 700 psia. Vennix' data were used for higher pressures. In these calculations, an arbitrary choice was made to perform regression with respect to the parameter C_0. Original (22) values were used for the remaining BWR parameters. When volumetric (PVT) data alone were used in the regression calculations, the function Q(V) was minimized,

$$Q(V) = \sum_{k=1}^{NP} [1 - \frac{ZC_k}{ZE_k}]^2 \quad \text{Eq. 28}$$

In this relation, NP is the number of PVT data points, and ZE_k and ZC_k are, respectively, the experimental and calculated compressibility factors for the kth PVT data point. The corresponding function, Q(H), which was minimized when enthalpy data alone were considered is

$$Q(H) = \sum_{m=1}^{NHP} [1 - \frac{(HC - H^\circ)_m}{(HE - H^\circ)_m}]^2 \quad \text{Eq. 29}$$

NHP is the number of enthalpy data points, H° is zero pressure enthalpy and $(HE - H^\circ)_m$ and $(HC - H^\circ)_m$ are, respectively, the experimental and calculated enthalpy corrections for the mth data point. When PVT and enthalpy data were treated simultaneously in the regression calculations, the function Q(V + H) was minimized.

$$Q(V + H) = Q(V) + WQ(H), \quad \text{Eq. 30}$$

where W is the weighting function defined in Equation 9. Density values used in calculating the enthalpy correction, Equation 27, were determined by trial and error using the BWR expression for the pressure, Equation 26. The results of minimizing Q(V), Q(H), and Q(V + H) are summarized in Table 1. The statistical estimate of C_0 for each calculation is given, along with the calculated estimate of the standard deviation in C_0, $\bar{\sigma}$ (C_0). The estimated standard deviations of the data (Equations 24 and 25) are given as $\bar{\beta}(z)$ and $\bar{\beta}$ (H). Average deviations of calculated compressiblity factors and enthalpy corrections from the experimental values also are given in Table 1. Deviations at the individual pressures of the data are given in Tables 2 and 3. In these tables, C_0 (BWR) is the original coefficient, C_0 (V) is the coefficient determined from PVT data, C_0(H) is the coefficient determined from enthalpy data, and C_0 (V + H) is the coefficient determined from simultaneous treatment of PVT and enthalpy data with $W = 1.0$.

Certain practical benefits of multiproperty analysis are demonstrated by the following illustrative problem. Suppose the objective is to determine a value of C_0 such that the calculated enthalpy correction is, on the average, within 2.7 percent of the experimental data at −100°F. At the same time, it is required that compressibility factors calculated using the experimental density data at −99.7°F deviate from the experimental values by no more than 0.7 percent on the average. Using the original coefficient, C_0 (BWR), it may be noted from Tables 2 and 3 that neither of the above criteria are satisfied when C_0 (BWR) is used. The traditional regression approach using only PVT data to determine C_0 (V), as may be noted in Table 2, gave a low resultant average deviation of calculated compressibility factors from the experimental values of 0.52 percent. However, the average deviation of calculated enthalpy corrections from experimental values is 3.30 percent. Regression on the enthalpy data alone to determine C_0 (H) yields an improved description of enthalpy behavior compared with results using PVT data, as noted by the average deviation of 2.86 percent in Table 3. However, calculated compressibility factors using C_0 (H) deviate from the experimental values by an average amount of 2.11 percent.

Finally, multiproperty analysis was applied. Because the problem (as stated) requires average enthalpy deviations to be less than 2.7 percent, regression calculations using a number of different weighting functions could have been carried out. Standard deviations estimated from regression on PVT and enthalpy data individually were $\bar{\beta}(Z) = 0.92$ percent and $\bar{\beta}(H) = 3.58$ percent, so that Equation 9 in the form

$$W = \left[\frac{\bar{\beta}(Z)}{\bar{\beta}(H)}\right]^2 \quad \text{Eq. 31}$$

yields a value for W of 0.00676. But when regression calculations were made with various W, the criteria of the problem were satisfied for all values of the weighting function over the approximate range $0.6 \leq W < 1.2$. These data are summarized

TABLE 1. *Summary of results of regression calculations.*

Weighting function	Parameter estimates		Std. dev. (%)		Avg. dev. (%)	
	$C_0 \times 10^{-3}$	$\bar{\sigma}(C_0) \times 10^{-3}$	$\bar{\beta}(z)$	$\bar{\beta}(H)$	z	H-H°
0.0000[a]	283553	582	0.92	—	0.52	3.30
0.0676	283331	597	0.95	3.64	0.50	3.21
0.1000	283230	653	1.04	3.29	0.49	3.17
0.2500	282803	839	1.36	2.72	0.46	2.92
0.5000	282227	1056	1.75	2.47	0.43	2.76
0.7500	281727	1213	2.06	2.38	0.52	2.66
1.0000	281225	1348	2.34	2.34	0.65	2.65
10.0000	277137	2450	6.81	2.16	1.72	2.75
100.0000	275708	2983	22.01	2.20	2.11	2.86
[b]	275708	4964		3.58	2.11	2.86

[a] This calculation minimized Q(V) in Equation 28.

[b] This calculation minimized Q(H) in Equation 29.

TABLE 2. *Deviations of calculated methane compressibility factors from experimental values at —99.7°F.*

Pressure, psia	Deviations (%)			
	C_0 (BWR)	C_0 (V)	C_0 (H)	C_0 (V+H)[a]
148	—0.17	—0.10	—0.17	—0.12
194	—0.02	0.08	—0.02	0.05
252	—0.01	0.12	—0.01	0.08
308	—0.17	0.00	—0.17	—0.05
347	—0.35	—0.15	—0.35	—0.21
406	—0.43	0.17	—0.43	—0.25
454	—0.29	0.03	—0.29	—0.07
503	—0.05	0.32	—0.05	0.21
769	—1.39	—0.11	—1.40	—0.49
797	—1.45	0.08	—1.46	—0.38
862	—2.19	0.44	—2.21	—0.34
870	—2.36	0.45	—2.38	—0.39
894	—2.65	0.61	—2.68	—0.37
912	—2.91	0.64	—2.94	—0.42
958	—3.25	0.80	—3.27	—0.41
1013	—3.51	0.86	—3.54	—0.45
1136	—4.79	0.83	—3.82	—0.55
1420	—4.56	—0.07	—4.60	—1.41
1742	—5.30	—1.16	—5.33	—2.40
2149	—7.07	—3.35	—7.09	—4.46
Avg. dev. (%)	2.16	0.52	2.11	0.65

[a] Weighting function of unity used for determination of C_0(V+H).

TABLE 3. *Deviations of calculated methane enthalpy corrections from experimental values at —100°F.*

Pressure, psia	Deviations (%)			
	C_0 (BWR)	C_0 (H)	C_0 (V)	C_0 (V+H)[a]
100	—1.08	—1.06	—2.39	—2.02
200	—4.72	—4.71	—6.28	—5.89
300	—5.35	—5.34	—6.98	—6.47
400	—3.84	—3.82	—5.62	—5.07
500	—2.74	—2.72	—4.70	—4.13
600	—1.39	—1.38	—3.69	—3.05
700	2.05	2.10	—0.98	—0.05
800	4.87	4.94	—0.68	1.10
900	5.99	6.08	—1.72	0.61
1000	3.21	3.27	—1.56	—0.18
1200	0.95	0.99	—2.30	—1.35
1500	—0.35	—0.32	—3.05	—2.27
2000	—0.48	—0.45	—2.90	—2.19
Avg. dev. (%)	2.82	2.86	3.30	2.65

[a] Weighting function of unity used for determintion of C_0(V+H).

in Table 1. The optimal value of W is somewhere between 0.75 and 1.0. The discrepancy between the optimum W and the W expected from Equation 9, as well as the unusual behavior displayed in Table 1, are as yet unexplained.

This illustrative problem demonstrates that when use of single property data for determining equation-of-state parameters leads to unacceptable calculations of other properties, regression with multiproperty data can yield an equation which is sufficiently accurate for predicting the properties in question. Further, this problem demonstrates that constraints, such as those considered, can be utilized to determine the range of permissible values of weighting functions.

There are a number of advantages of multiproperty analysis that cannot be shown with the simplified calculations presented here. Multiproperty analysis obviously can be quite valuable in testing proposed new equation of state forms to insure self consistency in prediction of differing types of thermodynamic behavior. In addition, appropriate modifications of the temperature, density, and composition dependence of an equation of state can be discerned from multiproperty analysis. In this regard, analysis of volumetric and enthalpy data are being used to find modifications of the BWR equation which yield improved predictions of thermodynamic behavior at low temperatures. Further, the use of multiproperty data in nonlinear regression analysis can improve the convergence characteristics of the required iterative solutions. It has been observed, for example, that regression calculations using enthalpy data alone often tend to oscillate or even diverge. These oscillations have been damped by the simultaneous use of PVT and enthalpy data. These and other practical advantages of multiproperty analysis will be discussed in more detail when the results of subsequent studies are presented.

NOMENCLATURE

A_{mn}	Equation of state parameter
A, B, C	Matrices of normal equations
A_o, B_o, C_o, b, a, c	Parameters in BWR equation
H	Enthalpy
H°	Enthalpy of ideal gas
HE	Experimental enthalpy
HC	Calculated enthalpy
$\underline{P}$(R)	Probability distribution function for R
P	Pressure
Q	Regression function
Q*	Regression function
R	Denotes a thermodynamic property, also Universal Gas Constant
R_{jk}	Values of jth property in kth state
T	Absolute temperature
W_j	Statistical weighting function
x_i	Mole fraction of ith component in a mixture
Z	Compressibility factor
ZE	Experimental compressibility factor
ZC	Calculated compressibility factor

Greek Alphabet

α	Parameter in BWR equation
β_j	Relative standard deviation
γ	Parameter in BWR equation
η (R)	Equation of state expression for property R
ρ	Molar density
σ^2(R)	Variance of property R
	Standard deviation
μ (R)	Expected value of property R

Other

Σ	Summation
π	Product
{ }	Mathematical set

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