

MODERN METHODS OF EQUATION OF STATE DEVELOPMENT

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Recent advances in methods of equation of state development are discussed with attention to theoretical and practical aspects. Methods for obtaining thermodynamically consistent prediction of all fluid properties by use of multiproperty data to develop the equation are considered. Examples of equations of state which predict both vapor and liquid behavior are given.

The advances made in recent years in methods of equation of state development may prove to be among the most significant in the history of the equation of state. Improved methods of empirical equation of state development have been made possible by a clearer understanding of (a) the statistical problems involved, (b) use of data other than PVT data, and (c) use of theoretical relations to suggest the temperature-, density-, and composition-dependence of the equation of state. Elucidation of the statistical problems involved in equation of state correlation has led to development of the method of multiproperty analysis. Study of thermodynamic data other than PVT data has shown the need for use of additional data in equation of state development. Recent advances in the statistical-mechanical theory of fluids have suggested the temperature- and density-dependence of the equation of state, while the molecular theory of corresponding states has pointed out ways of generalizing the equation of state for pure fluids. For mixtures, the virial equation of state from statistical mechanics, together with the corresponding states principle, has indicated the composition-dependence of the mixture equation of state. Molecular models for the critical region have suggested methods for incorporating the so-called critical-region scaling laws into the equation of state.

STATISTICAL METHODOLOGY

A useful recent advance in the statistical methodology for determining equation of state parameters is the method of multiproperty analysis (1), in which all thermodynamic data can be utilized to determine equation of state parameters. Multiproperty analysis was developed to eliminate certain problems associated with the traditional

use of PVT data alone to determine equation of state parameters.

Traditional method

In the traditional method of equation of state development, where PVT data alone are used to determine the parameters in the assumed mathematical relation for the equation of state, inaccuracies in correlation arise. All correlation methods for the physical properties of real systems are faced with two inescapable problems, i.e., (a) errors in the mathematical model used to describe the behavior of the system, and (b) errors in the data used to determine the parameters in the model. Errors in the data refer to systematic and random errors that occur with all experimental measurements. Errors in the model stem from lack of knowledge of the true mathematical model for the behavior of the system to be described. Here, in discussing the problem of data error, it is assumed that reasonable equation of state models are available.

For equations of state which are intended to describe both the gas and liquid phases, the pressure expressed as a function of temperature and molar density, as indicated in Equation 1, is usually taken as the response variable for least squares determination of the parameters in the equation of state.

$$P = P(T, \rho) \quad \text{Eq. 1}$$

The resultant equation of state is then used to calculate derived properties, such as vapor pressure, enthalpy, entropy, specific heats, and other thermodynamic properties. Unfortunately, these derived properties require the computation of derivatives of the pressure, as exemplified by the relations for the enthalpy and constant-volume heat capacity given in Equations 2 and 3,

$$H = H^0 + \frac{1}{\rho} (P - \rho RT) + \int_0^{\rho} \frac{1}{\rho^2} [P - T \left(\frac{\partial P}{\partial T} \right)_{\rho}] d\rho \quad \text{Eq. 2}$$

$$C_V = C_V^0 - \int_0^{\rho} \frac{T}{\rho^2} \left(\frac{\partial^2 P}{\partial T^2} \right)_{\rho} d\rho \quad \text{Eq. 3}$$

where H^0 and C^0 are ideal gas properties. The calculation of derivatives involved in these relations will be of lower accuracy than the PVT data from which they are derived, especially in the liquid region. In the liquid phase, the relative error in the calculated first derivative is at least ten times the relative error in the density, while the relative error in the second derivative is at least 100 times that in the density (2). Because most reported density data which are considered to be reliable have relative errors between 10^{-2} and 10^{-3} , it is obvious that the traditional method of equation of state development from PVT data alone cannot yield highly accurate predictions of derived properties. This problem can be circumvented for measurable properties, such as the enthalpy and heat capacity, by correlation of these properties individually. But, such an approach leaves the prediction of properties which cannot be measured experimentally, e.g., entropy and chemical potential, as unanswered problems. It is believed that multiproperty analysis provides a method for attacking these problems in a unified way.

Multiproperty analysis

The strategy of multiproperty analysis is to use more detailed information in correlation development than is supplied by a single property. For example, if the vapor phase can be described accurately, which is possible using accurate PVT and calorimetric data, then vapor pressure data are valuable for assuring the accuracy of the predicted Gibbs free energy of the liquid. By virtue of the Clausius-Clapeyron equation, the accuracy of the enthalpy of vaporization and the liquid entropy is enhanced. Data on velocity of sound also are valuable because of the relationship of velocity of sound to adiabatic compressibility, and because velocity of sound can be measured quite accurately in some regions where other properties cannot be measured easily. The problem of properly describing the composition-dependence of mixture properties can be attacked by using not only PVT and calorimetric data for mixtures, but also data

for excess properties and for mixture vapor-liquid equilibrium.

To develop the framework of multiproperty analysis, it is assumed that the experimental values of each property considered are normally distributed. Assuming that the experimental data are independent, the total probability distribution function for all of the different types of data is then the product of the probability distribution functions for each individual measurement. Thus a rigorous mathematical framework for estimation of correlation model parameters is provided. The concept of maximum likelihood is based on the assumption that maximization of the likelihood of occurrence of the combined set of data corresponds to maximization of the total probability distribution function.

In the special case in which the experimental data for individual properties are subject to relative error, maximization of the total probability distribution function corresponds to minimization of the function Q given in Equation 4,

$$Q = \sum_j \sum_k \frac{1}{\beta_{jk}^2} \left[1 - \frac{\bar{\eta}_{jk}}{R_{jk}} \right]^2 \quad \text{Eq. 4}$$

where R_{jk} is the experimental value of the j_{th} type of data at the k_{th} data point, $\bar{\eta}$ is the calculated value of the property, and β_{jk} is the relative error in the measured property. Differentiation of Q with respect to the parameters in the correlation yields (upon setting these relations equal to zero) the so-called normal equations of regression. In general, normal equations are nonlinear and must be solved by iterative methods which are, in part, dependent upon the selection of the response variables involved.

Selection of response variables

Selection of the appropriate dependent or response variables for the statistical analysis can be quite important in equation of state correlation. As a matter of convenience, the pressure or the compressibility factor often has been chosen as the response variable in the traditional use of PVT data for equation of state development. However, for the calculation of derived properties at a given temperature-pressure condition, it is necessary to calculate density from the pressure equation. This procedure yields errors in derived properties which are

proportional to the errors in calculated density, according to the relation given in Equation 5 for propagation of error.

$$\sigma^2(R) = \left(\frac{\partial R}{\partial \rho} \right)^2 \sigma^2(\rho) \quad \text{Eq. 5}$$

Thus, a statistical analysis method which improves the accuracy of predicted densities simultaneously improves the accuracy of derived properties. It has been found (3) that in the liquid range the accuracy of predicted densities can be improved considerably by using density, rather than pressure or compressibility factor, as the response variable in regression on PVT data.

As a general rule, the response variable used in regression analysis should be the variable which is subject to greatest uncertainty. In PVT measurements it is density which is subject to much greater relative error than is either the temperature or the pressure, and density is the appropriate variable because the response variable in regions where the isothermal derivative of pressure with respect to density is large. With regard to other data, there also are various choices possible for response variables. For example, in utilizing vapor pressure data, one might choose to minimize the difference between calculated liquid and vapor fugacities along the vapor pressure curve, or one might elect to minimize the difference between experimental and calculated vapor pressures. Because vapor pressure is directly measurable, it is the more appropriate response variable. However, the saturated fugacities along the vapor pressure curve were used successfully as response variables in early applications of multiproperty analysis using vapor pressure data (4). Similarly, in the use of mixture vapor-liquid equilibrium data, one can choose to minimize the difference between experimental and calculated vapor-liquid equilibrium ratios, or K values, as has been done to date in the applications of multiproperty analysis (4). On the other hand, minimization of the difference between experimental and predicted phase compositions would be more appropriate because it is the phase compositions which are the directly measured quantities.

CORRELATION METHODOLOGY

Methods for determining the tempera-

ture, density, and composition-dependence of equation of state correlations, together with methods for generalization of equation of state correlations, should now be discussed. Recent advances in the molecular theory of fluids have provided valuable information which can be used in empirical equation of state development. Of course, one cannot hope to develop empirical equations of state of high accuracy without careful observation of the behavior of the fluids under consideration. For this reason, both theoretical and empirical justification for equation of state relations are discussed simultaneously in the following summaries.

Density-dependence

The compressibility factors of most empirical equations of state can be expressed as the sum of a temperature-independent term and a temperature-dependent term, as indicated in Equation 6.

$$Z(T, \rho) = Z_R(\rho) + Z_A(T, \rho) \quad \text{Eq. 6}$$

The classic example of this type of relation in van der Waals equation (Eq. 7), which is based on the molecular model of a hard sphere in a uniform, attractive potential field.

$$Z = \frac{v}{(v-b)} - \frac{1}{T} \left(\frac{a}{Rv} \right) \quad \text{Eq. 7}$$

In van der Waals equation, a is the uniform, attractive potential, and b is the molar volume occupied by the rigid spheres. Equation 7 is essentially correct for this molecular model except that the first term describes the equation of state of rigid spheres in only one dimension. Although the equation of state of rigid spheres in three dimensions is not known exactly, molecular dynamics calculations (5) have indicated which analytical relations for the hard sphere equation of state are the most accurate. Equation 8, which is based on the hard-sphere virial series (6), represents the molecular dynamics calculations with extreme accuracy up to densities where the molecular dynamics calculations indicate a fluid-solid transition (5).

$$Z_R = \frac{1+y+y^2-y^3}{(1-y)^3} \quad \text{Eq. 8}$$

where $y = b/4v$.

Thus, Equation 8 can be substituted for the temperature-independent part of the compressibility factor in Equation 6. This substitution (7) has been found to improve

considerably the prediction of gas phase densities and enthalpies for the van der Waals and Redlich-Kwong equations so modified. The hard-sphere equation of state (Eq. 8) is finding considerable use in both the equilibrium and nonequilibrium theories based on van der Waals ideas and also as the reference fluid in perturbation equation of state calculations. In these applications, the hard-sphere diameter is usually treated as temperature-dependent. Because the temperature dependence of the hard-sphere diameter has not yet been sufficiently well defined in a nonarbitrary manner, the full potential for applications of the hard-sphere equation of state has not yet been realized.

Temperature dependence

Perturbation theory (8) indicates that the equation of state for the compressibility factor should be an expansion in reciprocal temperature, as indicated in Equation 9.

$$Z = Z_R + \frac{1}{T} + \frac{2}{T^2} + \dots \text{Eq. 9}$$

Equation 9 has been useful in empirical equation of state development efforts because available PVT data cannot be used to define analytically the temperature-dependence of the pressure beyond the linear term in Equation 10.

$$P(T, \rho) = B(\rho) + A(\rho)T + C(T, \rho) \text{Eq. 10}$$

PVT data for nonpolar fluids indicate (9) that the isochoric derivative of pressure with respect to temperature is negative at high and low densities and positive at densities between ρ_c and $1.8\rho_c$, but this information is not sufficiently accurate to define the appropriate analytical relation for $C(T, \rho)$. However, by virtue of the relation given in Equation 11, the second derivative of pressure with respect to temperature at constant density can be studied by examining the density dependence of the constant-volume heat capacity (10).

$$\left(\frac{\partial^2 P}{\partial T^2} \right)_\rho = - \frac{\rho^2}{T} \left(\frac{\partial C}{\partial \rho} \right)_T \text{Eq. 11}$$

Benedict et al. approximated $C(T, \rho)$ in Equation 10 by the relation given in Equation 12.

$$C(T, \rho) = \frac{\rho^2}{T^2} f(\rho) \text{Eq. 12}$$

The function $f(\rho)$ is negative at $\rho = 0$,

passes through a region of positive values between ρ_c and $1.8\rho_c$ and then reduces asymptotically to the zero density-constant value as the density increases. However, it has been found repeatedly that the Benedict-Webb-Rubin (BWR) equation of state is capable of fairly accurate predictions only up to densities of about 1.8 times the critical density; the analytical form of the BWR equation is incorrect at high densities and corresponding low temperatures.

Equation generalization

From a practical point of view, after an equation of state for the pressure as a function of temperature and density has been discerned, the most important next step is to generalize the equation for fluids other than those considered in its development. For the special case of monatomic fluids, the molecular theory of corresponding states has been proven to provide an accurate generalization. For the polyatomic fluids, which are of more practical interest, a modified form of corresponding states can be derived in which reduced properties are expressed by relations of the type given in Equation 13 for the reduced pressure.

$$P^* = \frac{P}{T_C v_C} = P_0^* \left(\frac{T}{T_C}, \frac{v}{v_C} \right) + \omega P_1^* \left(\frac{T}{T_C}, \frac{v}{v_C} \right) \text{Eq. 13}$$

In Equation 13, P_0^* is the reduced pressure of a monatomic fluid, while ωP_1^* is a correction for the asymmetry of polyatomic molecules. The factor ω is roughly proportional to the Pitzer acentric factor (12). This relation is valuable because it allows generalization of an empirical equation on a semi-empirical basis. Generalization of this type is discussed below (APPLICATIONS).

Composition dependence

The most successful basis for estimating composition dependence of empirical equations of state has been the statistical-mechanical virial equation, which rigorously expresses the composition dependence of the virial coefficients (13). The composition dependence used in the original BWR equation (14) was based on these ideas, but implicitly ignored deviations from the geometric-mean rule for the attractive intermolecular potential energy between unlike molecules (13). For empirical equation of state development these deviations from the geometric mean can be taken into account, in an empirical way, by

use of relations such as those derived by Prausnitz (15) for the Redlich-Kwong equation and by Bishnoi and Robinson (16) for the BWR equation. Use of these relations for the composition-dependence of a modified BWR equation is summarized below (APPLICATIONS).

Critical region behavior

The critical region has always been difficult to describe by analytical equations of state. Obviously, thermodynamic properties, such as the constant-pressure heat capacity, which become infinite at the critical point cannot be described accurately in the region about the critical point by using an analytical equation of state. It has been found that non-analytical relations based on the so-called scaling-law behavior, introduced recently in the theory of the critical region, more accurately describe critical-region behavior than do analytical equations (17). The scaling-law relations are now being incorporated into equations of state for description of broad ranges of fluid behavior, and additional applications can be expected in the future.

APPLICATIONS

A number of the important factors discussed above have been taken into account in the recent development of a modified form of the BWR equation (18). It was first determined that the temperature-dependence of the BWR equation could be modified for improved prediction of enthalpy behavior. The resultant modified BWR equation is given in Equation 14.

$$\begin{aligned}
 P = & \rho RT \\
 & + \left(A_1 RT - A_2 - \frac{A_3}{T^2} + \frac{A_4}{T^3} - \frac{A_5}{T^4} \right) \rho^2 \\
 & + \left(A_6 RT - A_7 - \frac{A_8}{T} \right) \rho^3 \\
 & + A_9 \left(A_7 + \frac{A_8}{T} \right) \rho^4 \\
 & + \frac{A_{10} \rho^3}{T^2} (1 + A_{11} \rho^2) \exp(-A_{11} \rho^2)
 \end{aligned} \quad \text{Eq. 14}$$

The terms involving the parameters A_4 , A_5 , and A_9 constitute the modifications to the original BWR equation (11). The modified BWR equation was then general-

ized according to the modified corresponding states concepts. It was determined (18) that the reduced parameters for the normal paraffin hydrocarbons, methane through normal heptane, could be expressed as functions of the acentric factor, as shown in Equations 15 and 16,

$$\frac{\left(\rho_{c,i} \right)^{S_m} A_{m,i}}{\left(R \right)^m \left(T_{c,i} \right)^{\phi_m}} = B_m + C_m \omega_i, \quad \text{Eq. 15}$$

for $m = 1-4, 6-11$

$$\frac{\left(\rho_{c,i} \right)^{S_m} A_{m,i}}{\left(R \right)^m \left(T_{c,i} \right)^{\phi_m}} = B_m + C_m \omega_i \exp(-3.8 \omega_i), \quad \text{Eq. 16}$$

for $m = 5$

where

$T_{c,i}$ and $\rho_{c,i}$ are the critical temperature and density of the i th component; ω_i is the characterization parameter of equation 13 for the i th component;

$$\begin{aligned}
 S_1 = 1, S_2 = 1, S_3 = 2, \\
 S_4 = 6, 10, 11; S_5 = 3, S_6 = 9, S_7 = 0, S_8 = 1, 5, 9, 11; S_9 = 1, \\
 S_{10} = 2, 5, 7, 8, 10; S_{11} = 0, S_{12} = 1, 7, 9, 10; S_{13} = 1, S_{14} = 2, 7; \\
 S_{15} = 2, S_{16} = 3, S_{17} = 4, S_{18} = 5.
 \end{aligned}$$

The generalized parameters B_m and C_m appearing in these equations were determined by multiproperty analysis, simultaneously using density, enthalpy, and vapor pressure data for the first seven normal paraffin hydrocarbons (18). Using these generalized parameter values, the characterization parameter ω_i was estimated from vapor pressure data for other fluids, including non-hydrocarbons, olefinic, naphthenic, and aromatic hydrocarbons. For 23 pure fluids, densities were predicted with an average absolute deviation from experimental values of 1.38% for 971 data points. Enthalpy departures were predicted with an average absolute deviation from experimental values of 1.74 Btu/lb for 620 data points. Saturated liquid and vapor fugacities along the vapor pressure curve were predicted within 1.08% for 663 data points.

For application to mixtures, the composition-dependence of parameters given in Equations 17 and 18 was utilized,

$$A_m = \left[\sum_i x_i A_{m,i}^{1/\alpha} \right]^{\alpha_m}, \quad \text{Eq. 17}$$

$m = 1, 6 - 11$

$$A_m = \sum_i \sum_j x_i x_j (A_{mi} A_{mj})^{1/2} (1 - k_{ij})^{\beta_m},$$

Eq. 18

$$m = 2 - 5$$

where

x_i is the mole fraction of the i th component and summations range over number of components in the mixture.

These relations are based on concepts summarized above in (CORRELATION METHODOLOGY). The interaction parameter k_{ij} for binary pairs was determined from binary vapor-liquid equilibrium data (19). It was found that the resultant mixture equation of state is capable of predicting mixture densities within 1.16% for 14 mixtures and capable of predicting mixture enthalpies within 2.2 Btu/lb for 23 mixtures, including a ten-component natural gas mixture. Vapor liquid equilibrium predictions using the mixture equation of state were studied utilizing vapor-liquid equilibrium data for 41 systems, including a ten-component natural gas-LNG system and a 15-component absorber system. In general, it was found that predicted vapor and liquid compositions were within the larger of 5% or 0.0005 of the experimental mole fractions. Further discussion of the development of this correlation has been presented in the literature (19). A computer program for utilizing this correlation in engineering calculations also is available (20).

CONCLUSIONS

Advances in both statistical methodology and correlation methodology have contributed importantly to recent improvements in equation of state development methods. Statistical methodology has been improved through the use of multiproperty analysis. Correlation methodology has been improved by taking into account the density, temperature, and composition-dependence implied by recent results in the molecular theory of fluids. Molecular theory also has been valuable in equation of state generalization, and has given a clearer understanding of the critical region. Although not all individual advances made in equation of state development have been simultaneously incorporated in a correlation study, recent studies do indicate that a high degree of success for future equations of state is possible by utilizing these techniques, to-

gether with the always important careful scrutiny of experimental behavior.

NOMENCLATURE

A, B, C,	Equation of state functions
$A_m, B_m, C_m, D_m,$	Parameters in modified BWR equation
E_m, a, b, c, d	
a_i, a_e	Perturbation equation of state functions
b	Rigid-sphere molar covolume
C_v	Constant-volume heat capacity
C_v^0	Constant-volume heat capacity of ideal gas
$f(\rho)$	Function of molar density
H	Enthalpy
H^0	Enthalpy of ideal gas
k_{ij}	Interaction parameter
P	Pressure
P_0^*	Reduced pressure
P_i^*	Reduced pressure of monatomic fluid
P^*	Reduced pressure with correction for asymmetry
Q	Regression function
R	Denotes a thermodynamic property, also Universal Gas Constant
R_{jk}	Values of j th property in k th state
T	Absolute temperature
T_c	Critical temperature
v	Molar volume
v_c	Critical molar volume
x_i	Mole fraction of i th component in a mixture
y	Reduced density
Z	Compressibility factor
Z_{R}	Hard sphere fluid compressibility factor contribution
Z_A	Perturbation compressibility factor contribution
<i>Greek Alphabet</i>	
α	Parameter in modified BWR equation
β_{jk}	Relative standard deviation of j th data type at k th data point
γ	Parameter in modified BWR equation
(R)	Equation of state expression for property R
ρ	Molar density
ρ_c	Critical molar density
$\sigma^2(R)$	Variance of property R
ω_1	Characterization parameter for i th component

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