

CHAPTER III



EQUATIONS OF STATE FOR PHASE EQUILIBRIUM COMPUTATIONS

An equation of State is an algebraic relation between pressure, temperature and molar volume of a pure substance by theoretical or semitheoretical relations. In functional form this relation is

$$f(P, V, T) = 0 \quad (3.1)$$

Equations of state may be applied to gases and liquids. For multicomponent systems, mixing rules are needed for combining pure species constant.

From a practical point of view, the usefulness of a reliable equation exceeds by far the mere description of the P-V-T behavior, for it leads directly to departures from ideal-gas value of thermodynamic properties such as enthalpy, entropy, and free energy. As a result, fugacity, vapor pressure, and phase equilibrium in fluid mixtures can all be derived.

3.1 CLASSIFICATION

Pure component equations of state in current use which have adaptations for prediction of mixture properties and vapor-liquid equilibrium behavior may be assigned to four general

classifications. [10]



1. The Van der Waals Family

The first and most numerous of these is the Van der Waals (VdW) family which began with the original Van der Waals equation over a century ago.

$$P = \frac{RT}{(V - b)} - \frac{a}{V^2} \quad (3.2)$$

or

$$Z = \frac{V}{(V - b)} - \frac{a}{RTV} \quad (3.3)$$

The basic ideas of van der Waals concerning the importance of separating repulsion effects caused by molecular size from cohesive effects of molecular attraction and the validity of a continuous equation connecting both liquid and vapor states have remained important considerations in all subsequent equation of state development. His equation provided the basis for the first theory of corresponding states and the first guidelines for a method of extending a pure component equation to mixtures. The Van der Waals repulsion and attraction terms were derived from elementary molecular considerations and the fact that such a simple equation gave such a remarkably good qualitative description of the overall P-V-T behavior of vapors and liquids produced an immediate effort to make it also quantitatively correct. This effort continues to the present day.

2. The Benedict-Webb-Rubin Family

It is appropriate to call the second group the Benedict-Webb-Rubin(BWR) family after the original equation of that name which was developed in the 1940's, although it descended from several precursors which began in the early 1900's. The earliest of these was the equation of Keyes in 1917. He attempted to improve the Van der Waals repulsion contribution and his ideas were continued by Beattie and Bridgeman in the 1920's. They devised an improvement to Keyes' equation designed to correct the repulsion term for effects of molecular aggregation and to remodel the attraction term based on the fact that intermolecular attraction in simple molecules is related to their polarizability. The final result differed significantly from the Van der Waals form and although it was better at low or moderate densities, it was a disaster at high densities and in the liquid region. The isothermal derivative of pressure with volume at these conditions had the wrong sign. The BWR equation remedied this empirically by adding the exponential term $e^{-\gamma\rho^2}$ to the Beattie-Bridgeman equation with the constant chosen to equate the fugacities of saturated vapor and liquid states. Historically, the first pure component equation of state which could predict vapor-liquid equilibrium conditions quantitatively was developed by Kammerlingh Onnes in 1901. The original BWR equation was the first to predict vapor-liquid equilibria in mixtures accurately. He owed this success to the Kammerlingh Onnes idea of forcing the equation for pure components to predict correct vapor pressures at low pressure and to equate equilibrium phase fugacities at higher pressure and this idea has

been essential in all subsequent development of equations of state suitable for vapor liquid equilibrium predictions. Like the Van der Waals family, the Benedict-Webb-Rubin family has many members with further modifications and variations still being introduced today.

3. Reference Fluid Equations

In recent times, with the development of new experimental techniques to furnish extremely precise P-V-T data over wide ranges of pressure and temperature and the increasing accessibility of large computers, a third type of equation of state has arisen which is called a reference equation. In these equations, there is generally no consideration given to developing a simple analytical form suitable for representing any other components or mixtures. Some of these may contain thirty or more constants and are practical only in the form of computer card decks or tapes. Rather than a traditional equation of state, it should be regarded as a compact representation of a mass of single component P-V-T data in a form suitable for accurate differentiation to obtain thermodynamic properties in computer operations. Although each of these equations applies only to a single pure component, they are exceptionally important to the computation of multi-component phase equilibrium properties because they provide the very precise description of the pure reference fluid properties needed by modern corresponding states theories of mixtures.

4. Augmented Rigid Body Equations

The fourth general type in this classification consists of equations which begin with rigid body equations of state and are followed by successive terms to account for contributions of molecular attraction. The rigid bodies interact only an infinite repulsion at their points of contact. It has been known for many years that the form and numerical value of the repulsion term in the Van der Waals equation is incorrect. However it is only recently that simple analytical equations have been developed to give accurate representation of the computer calculated data on the behavior of hard spheres. The equation of Carnahan and Starling for hard spheres, when followed by terms to give the contribution at molecular attraction, generate the newest family of equations of state.

Although these are at present more in a development stage than in widespread use, they can be extended to high density mixtures and have the advantage of a theoretically based composition dependence, as shown by Mansoori, Carnahan, Starling and Leland [13] for hard sphere mixtures. As a consequence, these equations offer considerable promise for vapor-liquid equilibrium computations in the future.

3.2 APPLICATION OF AN EQUATION OF STATE TO MIXTURES

Extending a pure component equation of state to mixtures requires expressing its constants as functions of composition. For vapor-liquid equilibrium computations this must be done in a manner which predicts the actual composition dependence of the mixture with sufficient accuracy to permit the differentiation of mixture properties with respect to either composition or moles of the individual components, (eq.2.5), as this procedure is required to determine fugacities of individual components in the vapor and liquid mixtures.

For a member of the Van der Waals family of equations, there are some theoretical guidelines to the composition dependence of its constants. Any pure fluid, k , whose properties can be expressed as a sum of contributions of the interactions between pairs of type k molecules with a pair potential in the form :

$$u(r) = \sum_{kk} \epsilon_{kk} f\left(\frac{r}{\sigma_{kk}}\right) \quad (3.4)$$

has a dimensionless equation of state in the form :

$$z = f_k\left(\frac{\epsilon_{kk}}{kT}, \rho \sigma_{kk}^3\right) \quad (3.5)$$

With this description one can develop an optimal extension of the function in Equation (3.5) to mixtures of molecules which obey this equation of state function in their pure states. The result for mixtures is :

$$Z = f_k \left(\frac{\bar{\epsilon}}{kT}, \rho \bar{\sigma}^3 \right) \quad (3.6)$$

where for n components :

$$\bar{\epsilon} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \epsilon_{ij} \sigma_{ij}^3 \quad (3.7)$$

$$\bar{\sigma} = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sigma_{ij}^3 \quad (3.8)$$

Equations (3.7) and (3.8) are called the Van der Waals 1-fluid mixing rules because they predict mixture properties from an equation of state function for a single fluid in the form of Equation (3.2) and because the parameters ϵ_{ij} and σ_{ij}^3 can be related to Van der Waals type "a" and "b" parameters in any two parameter equation of state. This can be shown by applying the critical criteria

$$\left(\frac{\partial P}{\partial V} \right)_T = 0 \quad (3.9)$$

and

$$\left(\frac{\partial^2 P}{\partial V^2} \right)_T = 0 \quad (3.10)$$

to Equation (3.5). When this is done, one finds that both ϵ and the ratio of the "a" to the "b" parameter are equal respectively to universal proportionality constants multiplied by T_c . Furthermore both σ^3 and "b" parameter are equal to constants times $\frac{V_c}{c}$.



The various proportionality constants are the same for all fluids obeying Equation (3.4) exactly. Eliminating the critical constants from these relationships shows that "a" is proportional to $\epsilon\sigma^3$ and these relationships shows that "a" is proportional to $\epsilon\sigma^3$ and that "b" is proportional to σ^3 for all fluids described by the two parameter equation at state. By relating ϵ and σ^3 in this manner to the equation at state parameters, Equation (3.7) and (3.8) give the following result for a mixture of n component.

$$a_{\text{mix}} = \sum_i \sum_j x_i x_j a_{ij} \quad (3.11)$$

$$b_{\text{mix}} = \sum_i \sum_j x_i x_j b_{ij} \quad (3.12)$$

When the proportionality constants are the same for all fluids, they cancel from each side of Equation (3.7) and (3.8) in this operation and do not appear in the mixing rules in Equation (3.11) and (3.12).

It is important to point out that these theoretically derived mixing rules are a consequence of obedience to a two parameter equation of state and do not depend in any specific way on Van der Waal's equation at all in order to derive them. Furthermore, the existence of these theoretically based rules still does not mean that the equations of state in the Van der Waals family in the form of equation (3.3) can be extended to mixtures in a completely satisfactory manner.