

CHAPTER II

EQUATIONS OF STATE

2.1 General Equation Of State (EOS).

An analytical expression relating the pressure to the temperature and volume is called “equation of state.” A good equation of state is perhaps the best method for handling a large amount of P-V-T data. More importantly, it provides a most efficient and versatile means of expressing various thermodynamic functions in terms of P-V-T data. The importance and necessity of an accurate equation of state is reflected by the appearance of numerous such equations in literature. Despite the abundance of such equations of state, none has proven completely satisfactory for all areas of interest in scientific and engineering applications.

2.1.1 Ideal Gas Equation.

The earliest equation of state[1] may be the ideal gas law which results from Boyle’s and Charles’ laws:

$$PV = RT \qquad (2-1)$$

This equation does not adequately describe the volumetric behavior of gases except at very low pressure. Consequently, many attempts have been made to develop a equation of state for the real fluids.

2.1.2 Van der Waals Equation Of State.

In 1873, van der Waals derived the first equation of state that was capable of expressing the continuity from gaseous to liquid states:

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

or

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

Though not accurate, this equation deserves special mention because of its enormous contribution to the corresponding states principle and to the later development of similar equations of state. The parameter "a" is assumed to account for the attractive force between molecules, and the parameter "b", known as co-volume, is considered to reflect the volume of molecules. In this case the only information needed in applying Equation (2-2) are the critical properties.

The van der Waals equation of state predicts the critical compressibility factor $Z_c = 0.375$. This value is considerably higher than those of real fluids. For instance, the Z_c 's of hydrocarbons are all less than 0.29. Only a small number of gases, mostly quantum gases, have Z_c 's slightly greater 0.3.

2.1.3 Redlich-Kwong Equation of State and Its Modifications.

As did most of the previous investigators, Redlich and Kwong modified the pressure correction term a/V^2 as follows:

$$P = \frac{RT}{V-b} - \frac{a/T^{0.5}}{V(V+b)} \quad (2-12)$$

Equation (2-12), generally known as the RK equation, is believed to be the first simple equation of state that found a successful industrial application, e.g., by Chao and Seader in their well-known vapor liquid equilibrium correlation. Even though the theoretical basis of $b = 0.26V_c$ is not well justified, the improvement was so remarkable that a great many investigators have since attempted to make further improvement in the equation of state with varying degrees of success.

2.1.4 Other Equations of State.

Other remarkable equations of state include those of Hirshfelder et al. and of Martin and Hou. Hirshfelder et al. developed a generalized set of equations of state based on the critical temperature, critical pressure, critical compressibility factor and the Riedel's parameter.

Martin and Hou developed an accurate equation of state by analyzing the P-V-T behavior in a comprehensive and systematic way. Despite its high accuracy the Martin-Hou equation as well as the modified version by Martin failed to gain widespread use mainly because of its complexity and lack of information for mixture

application. Nevertheless Martin-Hou's contribution in P-V-T analysis has been well recognize.

Shah, Bienkowski, and Cochran (1994)[10], Equations of state (EOS) are used to describe phase equilibrium, calculate physical properties such as pressure and molar volume of substances at different temperatures, and predict thermodynamic properties such as specific heat, isothermal compressibility, and enthalpy. EOSs based only on pure fluids and binary mixtures are very valuable tools in predicting the complex behavior of multicomponent mixtures. These equations are widely used in the chemical and petroleum industries to model and predict phase equilibrium and in process design and economic evaluation calculations. Different equations of state predict these properties with different degrees of accuracy and require vastly different amounts of resources for proper application.

2.2 Cubic Equation of State.

In general, an equation of state is developed first for pure substances, the extended to mixtures through the use of mixing rules for combining the pure component parameters. Conflict between accuracy and simplicity is a big dilemma in the development of an equation of state. Despite the wide use of high-speed computers, simplicity is still highly desired for easy and unequivocal applications of the equation to complex problems. However, no "simple equation of state" has proven to be sufficiently accurate for the P-V-T representation of real fluids over the entire vapor and liquid regions. It is generally meant by "simple equation of state" that the equation has two or three adjustable parameters and is in cubic form with respect to molar volume or compressibility factor.

For process calculations particularly in petroleum and cryogenic technology, cubic equations of state have proved to be extremely useful. They are simple and can be solved with a straightforward algebraic procedure, so that they lead to robust computer programs for the prediction of thermodynamic data and to relatively short computing times. They contain only a small number of adaptable parameters which can easily be related to the critical properties, so that the equations lend themselves well for generalization and application to mixtures. At least one of the parameters must be treated as an empirical function of temperature, but such a function can also be generalized. Comparisons have shown (Oellrich et al., 1977) that thermodynamic computation procedures with generalized cubic equations of state are on the more expensive procedures using extended virial equations.

However, the very fact that these equations are cubic in volume also imparts to them their main characteristic weakness: their failure to give a good account of the volume at the critical point and at temperatures and pressures immediately above the critical. In that region the pressures changes not as a third-order function but as a fifth-order function of volume (Levelt Sengers, 1976) so that the cubic equation of state is fundamentally inadequate. Fortunately, for technical reasons of flow stability and process control it would be extremely unattractive to run a chemical process at or immediately above the critical point of one of its fluids: process designers avoid such conditions. The prediction of phase equilibrium can of course suffer from said inadequacy, but in many cases this leads to only minor errors since the calculated fugacity is much less seriously affected than the calculated volume itself (Harmens, 1975). So the shortcomings of the cubic equation are not always experienced as

particularly troublesome. The various cubic equations of state also differ as to the extent and the severity of their supercritical unreliability.

From the various cubic equations of state and associated procedures for parameter evaluation, two have acquired wide popularity: the Redlich-Kwong-Soave (Soave, 1972) and the Peng-Robinson (1976) procedure. They employ different two-parameter equations of state, but the treatment of the parameters is very similar. In both cases the repulsion parameter is kept constant at its critical point value, while the attraction parameter contains a generalized function of temperature, fitted to the vapor pressure. For superheated vapors that subcritical temperature function is simply extrapolated above the critical temperature.

Edmister and Lee (1984), Most of the simple equations that evolved from the van der Waals' equation are in cubic form, the simplest form for representing P-V-T relations of both vapor and liquid phases. But the simple equations are not accurate enough for the many P-V-T representations, and a more complex form of equation such as Benedict-Webb-Rubin equation is required to describe accurately the P-V-T relations of real fluids. However, simple equations of state have found extremely valuable applications in phase equilibrium predictions, as demonstrated by Soave and by Peng and Robinson in their modifications of the Redlich-Kwong equation of state.

Cubic equations of state, which are the industry standard, model the repulsive forces incorrectly resulting in inaccuracies in representing thermodynamic properties, especially in the supercritical fluid and condensed-phase regions. Cubic equations are widely accepted in the petroleum and chemical industries because of their simplicity and reasonable accuracy.

Van der Waals (vdW) proposed the first cubic equation of state in 1873. In most cubic equations of state, the contribution to the pressure due to repulsive forces between molecules is given by the van der Waals repulsive term:

$$P_{rep} = \frac{RT}{(V - b)} \quad (2-13)$$

It was based on the assumption that only collisions between a pair of molecules occur in dilute gases. As a result, four times the volume of one molecule was not available to any other molecule. While this assumption is true for dilute gases, it is no longer valid at higher densities. The Redlich-Kwong equation of state (Redlich and Kwong, 1949) was considerably superior to other equations of state available at that time.

The RK equation retained the van der Waals P_{rep} term, a practice followed in all the popular cubic equations of state. Soave (1972) introduced a temperature dependence in the parameter of the RK equation (SRK) and let it be a function of the acentric factor of the fluid. Peng and Robinson (PR) proposed an equation of state in 1976 which offer better liquid density predictions than the Soave equation of state.

Tang, H. (1987), The most widely used equation of state for calculating phase equilibria is the Redlich-Kwong two-constant equation of state. Since its two constants a and b are determined by the critical parameters T_c and P_c , it can also be regarded as a two-parameter equation. Soave proposed an improved form of this equation by introducing a third parameter, the eccentricity factor ω , which increases its accuracy significantly. Using the same principle, Peng and Robinson proposed a new type of equation, similar to the Soave equation, containing the critical generalized compressibility factor 0.307, which is closer to that of a real fluid, thereby further

improving the accuracy of calculation. This type of equation is known as a cubic equation. Since its roots can be determined analytically, it is suitable for phase-equilibrium calculations.

In all these equations, the constants a and b are functions of the critical temperature T_c and the critical pressure P_c , or of the eccentricity factor ω , while the critical compressibility factor is the same for all components.

Although a EOS has inherent limitations, cubic equations enjoy wide popularity for industrial applications because of their simplicity and capacities. A well-known two-parameter EOS is the Redlich-Kwong (RK) equation (1949). There have been several attempts to improve the RK EOS either by changing the temperature function, the volume function, or by improving the mixing rule. Probably the best known modifications of the RK EOS were presented by Soave (SRK, 1972) and Peng and Robinson (PR, 1976)

The ability of predicting vapor pressure and vapor-liquid equilibrium (VLE) from any EOS is controlled by the selection of an appropriate α function and an appropriate mixing rule (Twu et al., 1991)[14]. On the other hand, the accuracy of calculating volumetric properties is controlled by the volume function. The PR EOS is good example of a EOS using a different volume function than the RK EOS. It improves the calculation of liquid density for mid-range hydrocarbons relative to RK EOS. For example the liquid density calculation is better for n-hexane, but worse for methane. One of the inherent limitations of a two-parameter EOS is that the resulting critical compressibility factor predicted by the EOS is constant for all components. As a

result, the predicted saturated liquid densities and critical volumes differ considerably from their experimental values

2.3 Noncubic Equation Of State.

Cubic equations of state[12] have found wide application for process design, especially VLE calculations, as they offer a good balance of simplicity and accuracy. Their weak point is in general their low accuracy in PVT calculations (which does not affect their good accuracy in VLE calculations, due to an error cancelation between the two phases).

The need of a more accurate description of the PVT behavior of pure compounds and their mixtures becomes important in particular conditions, such as those found in supercritical fluid extraction.

Simple cubic EOS's have been rendered sophisticated by many Authors in order to overcome that weak point, but it has become evident that their accuracy cannot go beyond a certain limit; it is enough to compare the values of the critical compressibility given by any cubic EOS with the experimental ones: typical calculated values are too high by more than 10% and such an error is maintained over all the critical area.

Up to now the need for more accurate PVT data has found a solution in the development of accurate but complicated equations, with many adjustable parameters, whose determination requires the availability of plentiful accurate experimental data,

not available usually; their application is thus restricted to a handful of well studied substances.

It is still desirable to have an equation of state with a limited number of adjustable parameters and a better accuracy than it can be attained by a cubic EOS. Yet, such an EOS could not be expected to provide the very high accuracies reached by the more specialized multi-parameter equations, accuracies which are not necessary for process design purposes.

The proposed equation of state is based on the same philosophy of all van der Waals-type equations, i.e. it includes two contributions to the total pressure: a repulsive one, connected to the molecules' finite volume and an attractive one expressing the molecular interactions.

Shah, Bienkowski, and Cochran (1994)[10]'s goal is to develop a new equation of state that retains desirable features of the popular cubic equations of state with improved accuracy. They proposed to improve accuracy by using a form of the repulsive term with better accuracy than the van der Waals form, which leads to an equation of state that can be solved efficiently and has roots that can be unequivocally identified. They chose to test forms for the repulsive contribution that lead to an equation of state which is quartic in volume. Kubic (1986b) proposed the first quartic equation of state and extended it to mixtures(1986a). Soave (1990) has also proposed a quartic equation of state for pure fluids.