# CHAPTER V
# EQUATIONS OF STATE

## 5.1 INTRODUCTION

An equation of state is an algebraic relation between pressure( P ). temperature ( T ), and molar volume ( V ) which may be expressed by mathematic as follow:

$$f(P,V,T) = 0 \qquad (5\text{-}1)$$

An equation of state may be solved for any one of three quantities P, V, or T as a function of the other two. For instance V = V(T, P). By itself, a suitable PVT equation of state can be used to evaluate many important properties of pure substances and mixtures, including the following:

- Densities of liquid and vapor phases
- Vapor pressure
- Critical properties of mixture
- Vapor-liquid equilibrium relations
- Deviation of enthapy from ideality
- Deviation of entropy from ideality

At present no one equation of state exists that equally suitable for all these properties of any large variety of substances, but many useful results of limited scope have been achieved.

Equations of state remain an active field of research, primarily in these areas:

1. Highly accurate equations with many constants for important pure substances or mixtures such as air, water, ammonia, carbon dioxide, light hydrocarbon and cryogenic fluids.

2. Complex equations or computer algorithms for mixtures encountered in the nature gas and petroleum industries.

3. Simpler equations, such as cubics, that may be adequate for making the repeated calculations for phase equilibrium and deviation functions for process design of multistage separation of mixtures.

## 5.2 CUBIC EQUATIONS OF STATE

Cubic equation can be used to represent behavior both vapor and liquid phases but in the critical region, none of the cubic equations is satisfactory. It can be expressed by the equation .

$$P = \frac{RT}{V-b} - \frac{a}{V^2 + ubV + wb^2} \quad (5\text{-}2)$$

An equivalent from equation (5-2) is

$$Z^3 - \left(1 + B^* - uB^*\right)Z^2 + \left(A^* + wB^{*2} - uB^* - uB^{*2}\right)Z - A^*B^* - wB^{*2} - wB^{*3} = 0 \quad (5\text{-}3)$$

where $$A^* = \frac{aP}{R^2T^2} \quad (5\text{-}4)$$

$$B^* = \frac{bP}{RT} \quad (5\text{-}5)$$

$u, w, a, b$ are constants for cubic equations

### 5.2.1 Root of cubic equations

When equation (5-3) is solved. It have three positive real roots, the larged one is vapor, the smallest one is liquid and the intermediate one without physical significance. The larged and the smallest root of cubic equations are used for calculating thermodynamic properties of gases and liquids.

**5.2.2 Redlich-Kwong (1949) equation**

Two constants of Redlich-Kwong equation have been determined to be one of the most useful equations which has been proposed following Van der Waal's work. From equation (5-2) . The constants of Redlich-Kwong equation are as follows:

$$u = 1 \qquad w = 0$$

$$a = \frac{0.42748 R^2 Tc^{2.5}}{Pc Tc^{0.5}} \tag{5-6}$$

$$b = \frac{0.08664 RTc}{Pc} \tag{5-7}$$

For mixtures, a mixing rule is applied to Redlich-Kwong equation as follows:

$$a = \sum_i \sum_j y_i y_j a_{ij} \tag{5-8}$$

$$b = \sum_i y_i b_i \tag{5-9}$$

$$a_{ij} = \frac{0.42748 R^2 Tc_{ij}^{2.5}}{Pc_{ij} T^{0.5}} \tag{5-10}$$

$$b_i = \frac{0.08664 RTc_i}{Pc_i} \tag{5-11}$$

where

$$Tc_{ij} = \left(Tc_i Tc_j\right)^{0.5} \left(1 - k_{ij}\right) \tag{5-12}$$

$$Pc_{ii} = \frac{Zc_{ij} RTc_{ij}}{Vc_{ij}} \tag{5-13}$$

$$Zc_{ij} = \frac{Zc_i + Zc_j}{2} \tag{5-14}$$

$$Vc_{ij} = \left( \frac{Vc_i^{\,0.3333} + Vc_j^{\,0.3333}}{2} \right) \tag{5-15}$$

### 5.2.3 Soave (1972) equation

Soave proposed a modification to the Redlich-Kwong equation which introduced a third parameter, acentric factor, and a temperature dependency into the cohesive energy to account for the effect of nonsphericity on fluid PVT properties.

From equation (5-2) . The constants of Soave equation as follows:

$$u = 1 \quad , \quad w = 0$$

$$a = \frac{0.42748 R^2 Tc^2}{Pc}\left[1 + fw\left(1 - Tr^{0.5}\right)\right]^2 \tag{5-16}$$

$$b = \frac{0.08664 RTc}{Pc} \tag{5-17}$$

where

$$fw = 0.48 + 1.57\omega - 0.176\omega^2 \tag{5-18}$$

For mixtures, a mixing rule is introduced to Soave equation as follows:

$$a = \sum_i \sum_j y_i y_j \left(a_i a_j\right)^{0.5}\left(1 - k_{ij}\right) \tag{5-19}$$

$$b = \sum_i y_i b_i \tag{5-20}$$

where

$$b_i = \frac{0.08664 RTc_i}{Pc_i} \tag{5-21}$$

$$a_i = ac_i \alpha_i \tag{5-22}$$

$$ac_i = \frac{0.42748 R^2 Tc_i^2}{Pc_i} \tag{5-23}$$

$$\alpha_i^{0.5} = 1 + m_i\left(1 - Tr_i^{0.5}\right) \tag{5-24}$$

$$m_i = 0.48 + 1.57\omega_i - 0.176\omega_i^2 \tag{5-25}$$

### 5.2.4 Peng-Robinson (1976) equation

This equation of state was developed using the same basis as Soave equation. From equation 3-2 . The constants of Soave equation are as follows:

$$u = 2 \quad , \quad w = -1$$

$$a = \frac{0.45724 R^2 Tc^2}{Pc}\left[1 + fw\left(1 - Tr^{0.5}\right)\right]^2 \tag{5-26}$$

$$b = \frac{0.07780 RTc}{Pc} \tag{5-27}$$

where

$$fw = 0.37464 + 1.5422\omega - 0.26992\omega^2 \tag{5-28}$$

For mixtures, a mixing rule is introduced to Peng-Robinson equation as follows:

$$a = \sum_i \sum_j y_i y_j \left(a_i a_j\right)^{0.5} \left(1 - k_{ij}\right) \tag{5-29}$$

$$b = \sum_i y_i b_i \tag{5-30}$$

where

$$b_i = \frac{0.07780 R Tc_i}{Pc_i} \tag{5-31}$$

$$a_i = ac_i \alpha_i \tag{5-32}$$

$$ac_i = \frac{0.45724 R^2 Tc_i^{\,2}}{Pc_i} \tag{5-33}$$

$$\alpha_i^{\,0.5} = 1 + m_i\left(1 - Tr_i^{\,0.5}\right) \tag{5-34}$$

$$m_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^{\,2} \tag{5-35}$$

## 5.3 APPLICABILITY OF CUBIC EQUATION

For nonpolar molecules, cubic equation can predict the properties of gases and liquids accurately in subcritical region. Redlich-Kwong equation is not satisfactory for liquid phase, therefore it can not use for calculating vapor-liquid equilibria. Vapor-liquid equilibria calculation uses Soave and Peng-Robinson equation. In mixture, interaction parameter ( $k_{ij}$ ) for hydrocarbon pairs is taken as zero that is assume no chemical interaction between molecules.