

## CHAPTER III



### THEORY

Multicomponent mixture is composed of more than one chemical species. The thermodynamic properties of mixtures, particularly liquid mixtures, are usefully expressed in relation to the properties of the pure constituent chemical species. These relations require the definition of thermodynamic properties such as partial molar property, property changes of mixing and excess property. In addition, the prediction of thermodynamic properties for mixtures can use the most commonly encountered equations of state such as a modified Redlich-Kwong, Peng-Robinson, Peng-Robinson-Stryjek-Vera and the extended Peng-Robinson-Stryjek-Vera: Peng-Robinson-Stryjek-Vera2.

#### 3.1 Density

Density is defined as the mass per unit volume and usually is expressed in units of kilograms per cubic meter in SI, and pounds per cubic foot in the American Engineering System. The Greek symbol  $\rho$  (rho) is used by engineers to represent density.

The density of a substance is not constant; in fact, density varies with both temperature and pressure. As a rule, liquid and solid densities do not change very much as temperature and pressure change. This characteristic is called being a 'weak function' of temperature and pressure. Although for highly accurate work one may need tabulated data for liquids and solids as a function of temperature and pressure (Snider, 1984).

Gases, however, are different. Gases show large changes in density as either the temperature or pressure changes. That is as the temperature increases, the density decreases, and as the pressure increases, the density increases. The density of a mixture of substances varies with the composition of the mixture.

### 3.2 Specific Volume and Molar Volume

Specific volume is the volume occupied by a unit mass of a substance; i.e., volume per mass, normally given in units of cubic meter per kilograms in SI and cubic foot per pound in the American Engineering System. Note that specific volume is simply the inverse of density:

The term molar volume refers to the volume occupied by a mole of substance, and is reported in units of cubic meter per mole or cubic foot per mole.

$$v = \frac{1}{\rho} \quad (3.1)$$

From the relation between density ( $\rho$ ) and specific volume ( $v$ ), equation 3.1, therefore the volume any gas depend on temperature, pressure and composition present. If the composition is kept constant, at a specific temperature the volume increases when the pressure decreases and at a specific pressure the volume increases when the temperature increases.

### 3.3 Partial Molar Properties

In general, any mixture extensive property  $M_t$  can be expressed as a function of the two intensive properties temperature and pressure and the number of moles of the individual components as

$$M_t = M_t(T, P, n_1, n_2, \dots) \quad (3.2)$$

where

$$M_t = nM \quad (3.3)$$

For example,  $M$  can represent any of the molar properties  $V$ ,  $H$ ,  $U$ ,  $S$ ,  $A$ , or  $G$ ; it can also represent such properties as the compressibility factor  $Z$ , the thermal compressibility  $\kappa$ , the volume expansion coefficient  $\beta$ , and density  $\rho$ .

In view of the functional dependence of  $M_t$ , total differential gives

$$dM_t = \left[ \frac{\partial M_t}{\partial T} \right]_{P, n_i} dT + \left[ \frac{\partial M_t}{\partial P} \right]_{T, n_i} dP + \sum_{i=1}^c \left[ \frac{\partial M_t}{\partial n_i} \right]_{T, P, n_j} dn_i \quad (3.4)$$

The partial molar properties of component 'i' in a mixture, partial derivative with respect to  $n_i$  at constant P, T, and  $n_j$  is denoted as follows

$$\bar{M}_i = \left[ \frac{\partial M_t}{\partial n_i} \right]_{T,P,n_j} \quad (3.5)$$

Substitution into equation (3.4) gives an expression for the total differential of any

$$dM_t = \left[ \frac{\partial M_t}{\partial T} \right]_{P,n_i} dT + \left[ \frac{\partial M_t}{\partial P} \right]_{P,n_i} dP + \sum_{i=1}^c \bar{M}_i dn_i \quad (3.6)$$

extensive function for a homogeneous fluid.

At constant temperature and pressure, equation (3.6) can be integrated to give

$$M_t = \sum_{i=1}^c n_i \bar{M}_i \quad (3.7)$$

Upon division by n, this becomes

$$M = \sum_{i=1}^c x_i \bar{M}_i \quad (3.8)$$

As an example of the characteristics of partial properties, consider it to be the molar volume. Then,

$$V = \sum_{i=1}^c x_i \bar{V}_i \quad (3.9)$$

where, by definition of partial molar volume,

$$\bar{V}_i = \left[ \frac{\partial V_t}{\partial n_i} \right]_{T,P,n_j} \quad (3.10)$$

The partial molar properties are very useful in analyzing the dependence of mixture properties provides the basis for deriving many useful thermodynamic relations such as the property changes on mixing, the fugacity of a component in a mixture, the excess properties, the solution theories, the Gibbs – Duhem equation, etc.

### 3.4 Volume Changes of Mixing

For general mixing, the volume of the mixture is not equal to the sum of the volumes of the components. If the mixture have 'c' components that are mixed at

constant temperature and pressure, volume changes of mixing will be the difference between the mixture volume and the volume of the components.

By definition of volume changes of mixing,  $\Delta V_{\text{mix}}$

$$\begin{aligned}\Delta V_{\text{mix}} &= V_t - V_{t,\text{pure}} \\ &= \sum_{i=1}^c n_i (\bar{V}_i - V_i) \\ &= \sum_{i=1}^c n_i \bar{V}_i - \sum_{i=1}^c n_i V_i\end{aligned}\quad (3.11)$$

Then division by  $n$ , we obtained

$$\Delta V_{\text{mix}} = \sum_{i=1}^c x_i (\bar{V}_i - V_i) \quad (3.12)$$

Volume changes of mixing is functions of temperature, pressure and composition.

### 3.5 Excess Molar Volume

For a mixture, at constant temperature  $T$  and Pressure  $P$ , the excess molar volume  $V^E$  is defined as the difference between an actual molar volume value  $V_{\text{mix}}$  and the value calculated molar volume for an ideal solution  $V_i$ , as follows:

$$V^E = V_{\text{mix}} - \sum_{i=1}^c x_i V_i \quad (3.13)$$

### 3.6 Equations of State

Equations of state are widely used in the prediction of thermodynamic properties of pure fluid and mixtures. The term equation of state is used to describe an empirically-derived function which provides a relation between pressure, density, temperature and (for a mixture) composition; such a relation provides a prescription for the calculation of all of the configurational and residual thermodynamic properties of the system within some domain of applicability. Consequently, equation of state method may be used to

determine equilibrium conditions as well as other properties. Many equations of state can represent adequately the properties of the gas phase, some are applied only to the liquid, but the most important category of equation of state models contains those that may be applied in the same form to both gaseous and liquid phases. There are no equations of state applicable simultaneously to solid, liquid and gas.

Equation of state can be used to evaluate many important properties of pure substances and mixtures, including the following (Stanley, 1985):

1. Densities of liquid and vapor phases
2. Vapor pressure
3. Critical properties of mixtures
4. Vapor-liquid equilibrium relations
5. Deviation of enthalpy from ideality
6. Deviation of entropy from ideality
7. Fugacity coefficient

Today the development of equations of state remains an active field of research, primarily in areas of (Assael et al., 1995):

1. Highly-accurate equations, often with many constants, for important pure substances such as water, ammonia, carbon dioxide etc.
2. Accurate equation of state models for specific such as those encountered in the natural gas and petroleum industries.
3. Simple equations of state that combine satisfactory predictive capabilities with the computational efficiency required for detailed simulations of chemical processing operations such as multistage separation processes for mixtures.
4. Models for complex systems such as electrolytes, polymers, coal liquids, and highly polar substances.

### 3.6.1 Cubic Equations of State

Equations of state that are explicit in pressure and of the third degree in volume are among the most successful of the simpler forms.

The following cubic equations of state will be described further in this section:

1. A modified Redlich-Kwong equation of state
2. Peng – Robinson equation of state
3. Peng – Robinson-Stryjek-Vera equation of state
4. Peng – Robinson-Stryjek-Vera 2 equation of state

#### 3.6.1.1 A modified Redlich-Kwong Equation of State

The modification of the Redlich-Kwong equation (MRK equation) involved  $\alpha$  function which is a monotonic function of  $T$ , as well as a linear function of  $\omega$ . A simplified version of the Fuller equation of state (1976) was chosen as a compromise after investigating several other possibilities. The form of the equation is presented as follows, (Lee et al., 1992):

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + 1.5b)} \quad (3.14)$$

or

$$Z^3 - (1 - 0.5B)Z^2 + (A - 1.5B(1 + B))Z - AB = 0 \quad (3.15)$$

where

$$a\alpha = \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - k_{ij}) \sqrt{(a_i \alpha_i)(a_j \alpha_j)} \quad (3.16)$$

$$b = \sum_{i=1}^n x_i b_i \quad (3.17)$$

and

$$a_i = a_c \alpha_i \quad (3.18)$$

$$a_c = 0.43164 \frac{(RT_i^c)^2}{P_i^c} \quad b_i = 0.07635 \frac{RT_i^c}{P_i^c} \quad (3.19)$$

$$\alpha_i = \exp(\beta_i(1 - \sqrt{T_{r,i}})) \quad \text{for } T_{r,i} > 1 \quad (3.20)$$

$$\alpha_i = 1 + \beta_i(1 - \sqrt{T_{r,i}}) \quad \text{for } T_{r,i} \leq 1 \quad (3.21)$$

$$\beta_i = 0.965 + \omega \left( 1.45 + \frac{1.6}{\sqrt{T_{r,i}}} \right) \quad (3.22)$$

### 3.6.1.2 Peng–Robinson (PR) Equation of State

The Peng and Robinson is today probably the most widely used equations of state, requires only the critical constants and the acentric factor for its application to a pure fluid. This equation usually permit VLE calculations to be made with acceptable accuracy.

Single phase properties such as enthalpy and entropy may also be acceptable but liquid densities are usually rather poor. This poor performance is essentially due to the fact that the equations are really oversimplifications of the P-V-T surface which have been forced to fit vapor pressure data without any constraints on the densities of the co-existing phases. These equations perform best for light hydrocarbons and other small non-polar molecules but reasonable results may be obtained for more complicated substances including polar molecules. Reliable results should not be expected for systems with hydrogen bonding or other forms of molecular association (Assael et al., 1995). The equation is summarized as follows:

$$P = \frac{RT}{V_m - b} - \frac{a\alpha}{V_m(V_m + b) + b(V_m - b)} \quad (3.23)$$

or

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (3.24)$$

where

$$A = \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - k_{ij}) \sqrt{A_i A_j} \quad (3.25)$$

$$B = \sum_{i=1}^n x_i B_i \quad (3.26)$$

$$a\alpha = \sum_{i=1}^n \sum_{j=1}^n x_i x_j (1 - k_{ij}) \sqrt{(a_i \alpha_i)(a_j \alpha_j)} \quad (3.27)$$

$$b = \sum_{i=1}^n x_i b_i \quad (3.28)$$

and

$$A_i = 0.45724\alpha_i \frac{P_{r,i}}{T_{r,i}^2} \quad B_i = 0.07780 \frac{P_{r,i}}{T_{r,i}} \quad (3.29)$$

$$a_i = 0.45724 \frac{(RT_i^c)^2}{P_i^c} \quad b_i = 0.07780 \frac{RT_i^c}{P_i^c} \quad (3.30)$$

$$\alpha_i = \left[ 1 + n_i (1 - \sqrt{T_{r,i}}) \right]^2 \quad (3.31)$$

$$n_i = 0.37464 + 1.54226\omega_i - 0.26992\omega_i^2 \quad (3.32)$$

### 3.6.1.3 Peng-Robinson-Stryjek-Vera (PRSV) Equation of State

Peng-Robinson equation of state has been modified by Stryjek and Vera in 1986. This cubic equation of state called the Peng-Robinson-Stryjek-Vera (PRSV) equation, which reproduces well the vapor pressure data of pure compounds and calculates vapor-liquid equilibria of systems. In addition, the equation also was used to calculate excess molar volumes of mixtures (Djordjevic' et al., 1994). A major improvement is obtained with the following simple expression for  $\kappa_i$  and  $\kappa_{ij}$ , equation (3.39) being an adjustable parameter characteristic of each pure compound. The equation is summarized as follows (Stryjek and Vera, 1994):

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \quad (3.33)$$

or

$$Z^3 + Z^2 \left( \frac{bP}{RT} - 1 \right) + Z \left( \frac{aP}{(RT)^2} - 3 \left( \frac{bP}{RT} \right)^2 - 2 \frac{bP}{RT} \right) + \left( \frac{bP}{RT} \right)^3 + \left( \frac{bP}{RT} \right)^2 - \frac{abP^2}{(RT)^3} = 0 \quad (3.34)$$

where

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{(a_i a_j)} (1 - k_{ij}) \quad (3.35)$$

$$b = \sum_{i=1}^n x_i b_i \quad (3.36)$$

and

$$a_i = 0.457235 \left( \frac{(RT_i^c)^2}{P_i^c} \right) \alpha_i \quad b_i = 0.077796 \frac{RT_i^c}{P_i^c} \quad (3.37)$$



$$\alpha_i = [1 + \kappa_i (1 - T_{r,i}^{0.5})]^2 \quad (3.38)$$

$$\kappa_i = \kappa_{0i} + \kappa_{1i} (1 + T_{r,i}^{0.5}) (0.7 - T_{r,i}) \quad (3.39)$$

$$\kappa_{0i} = 0.378893 + 1.4897153\omega_i - 0.17131848\omega_i^2 + 0.0196554\omega_i^3 \quad (3.40)$$

### 3.6.1.4 Peng-Robinson-Stryjek-Vera 2 (PRSV2) Equation of State

An extended version of the PRSV equation, called PRSV2, was proposed by Stryjek and Vera (1986d) for the reproduction of accurate data of vapor pressure of pure compounds and may be used for vapor-liquid equilibria calculations over a wide temperature range with the aid of simple mixing rules. The equation has three pure compound adjustable parameters. The equation is presented as follows:

$$P = \frac{RT}{V_m - b} - \frac{a}{V_m(V_m + b) + b(V_m - b)} \quad (3.41)$$

or

$$Z^3 + Z^2 \left( \frac{bP}{RT} - 1 \right) + Z \left( \frac{aP}{(RT)^2} - 3 \left( \frac{bP}{RT} \right)^2 - 2 \frac{bP}{RT} \right) + \left( \frac{bP}{RT} \right)^3 + \left( \frac{bP}{RT} \right)^2 - \frac{abP^2}{(RT)^3} = 0 \quad (3.42)$$

where

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j \sqrt{(a_i a_j)} (1 - k_{ij}) \quad (3.43)$$

$$b = \sum_{i=1}^n x_i b_i \quad (3.44)$$

and

$$a_i = 0.457235 \left( \frac{(RT_i^c)^2}{P_i^c} \right) \alpha_i \quad b_i = 0.077796 \frac{RT_i^c}{P_i^c} \quad (3.45)$$

$$\alpha_i = [1 + \kappa (1 - T_{r,i}^{0.5})]^2 \quad (3.46)$$

$$\kappa = \kappa_{0i} + [\kappa_{1i} + \kappa_{2,i} (\kappa_{3,i} - T_{r,i})] (1 - T_{r,i}^{0.5}) (1 + T_{r,i}^{0.5}) (0.7 - T_{r,i}) \quad (3.47)$$

$$\kappa_{0i} = 0.378893 + 1.4897153\omega_i - 0.17131848\omega_i^2 + 0.0196554\omega_i^3 \quad (3.48)$$

### 3.6.2 Mixing Rules for Cubic Equations of State

In general, an equation of state is developed first for pure substances, and then extended to mixtures through the use of mixing rules for combining the pure component parameters.

The following are the mixing rules, equations (3.49) and (3.50) and the conventional one binary parameter, equation (3.51) for equations of state:

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij} \quad (3.49)$$

$$b = \sum_{i=1}^n x_i b_i \quad (3.50)$$

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (3.51)$$

Where  $a$ ,  $b$  are parameters of equation of state and  $k_{ij}$  is binary interaction parameter of molecule  $i$  and  $j$ .

### 3.6.3 Binary Interaction Parameter

The binary interaction parameter ( $k_{ij}$ ) which appears in equations (3.16), (3.25), (3.35) and (3.43) is defined as parameter which involve interaction of molecule '  $i$  ' and '  $j$  '. The values of parameters are usually obtained from experimental data such as equilibrium data on binary mixtures. By assumption,  $k_{ij}$  are independent of composition and by definition,  $k_{ij} = 0$  if  $i = j$ ; otherwise, it is a small quantity, values of which are found by reduction of experimental data with the equation of state.