



CHAPTER III

THEORY

3.1 Basic knowledge in thermodynamics

One method for representing the PVT behavior of fluid are the use of empirical equation of state, exemplified by the class of polynomial equation that are cubic in molar volume. The simplest useful polynomial equation of state are cubic. There has been extensive progress made in recent years in research towards the development of analytic statistical-mechanical equation of state applicable for process design calculation. However, cubic equation of state is still widely used in chemical engineering practice for the calculation and prediction of fluids and fluid mixtures.

These equation of state are generally modification of the Van der Waals equation of state:

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Extensive researches on equations of state have indicated that the Van der Waals equation of state is not accurate enough for the prediction of properties of compressed gases and liquids. This deficiency of the Van der Waals equation of state has initiated a great deal of research on the development of other equations of state.

3.1.1 Generic-Redlich-Kwong equation of state

A cubic equation of state be explicit in pressure and that it yield steep isothermal for small value of V , then algebraic arguments lead to an expression of the form:

$$P = \frac{RT}{v-b} - \frac{\theta[v-\eta]}{[v-b][v^2 + \delta v + \epsilon]} \quad 3-1)$$

Where each of the five parameters b , θ , ϵ , δ , and η can be depended upon temperature and composition.

Equation 3-1) may be considered a generalization of the Van der Waals equation, to which it reduces as the simplest nontrivial special case . Thus for $\eta = b$, $\delta = \epsilon = 0$ and $\theta = \text{constant} = a$, we obtain :

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

Which is the Van der Waals equation.

We define the Generic -Redlich-Kwong equation of state.

$$P = \frac{RT}{v-b} - \frac{\theta}{v[v+b]} \quad 3-2)$$

Equation 3-2) is obtained from eq. 1) by the assignments $\delta = \eta = b$ and $\epsilon = 0$; parameters θ is function of T .

$$\theta = \frac{a}{T^{1/2}} \quad 3-3)$$

Parameter a and b are constant.

Equation 3-2) may be written to display more explicitly its cubic nature.

$$V^3 - \frac{RT}{P}V^2 - \left(b^2 + \frac{bRT}{P} - \frac{\theta}{P}\right)V - \frac{b\theta}{P} = 0 \quad 3-4)$$

There are many ways to solve this equation of state. The two most often used are the classical derivative conditions on the critical isotherm :

$$\left(\frac{\partial P}{\partial V}\right)_{T,cr} = 0 \quad 3-5a)$$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T,cr} = 0 \quad 3-5b)$$

Equation 3-5) when applied to a cubic equation yield the equivalent requirement that the equation gives three equals roots for the volume at the critical state, i.e.,

$$(V - V_c)^3 = 0$$

or
$$V^3 - 3V_cV^2 + V_c^2V - V_c^3 = 0 \quad 3-6)$$

At the critical state, the generic Redlich-Kwong may be written as

$$V^3 - \frac{RT_c}{P_c}V^2 - \left(b_c^2 + \frac{b_cRT_c}{P_c} - \frac{\theta_c}{P_c}\right)V - \frac{b_c\theta_c}{P_c} = 0 \quad 3-7)$$

Here T_c and P_c are the usual critical properties; since b and θ may depend upon T , the subscripts on these quantities indicate that they are evaluated at the critical temperature.

Comparison of coefficients of V in Eq. 3-6) and 3-7) yields three equation relating the five quantities P_c , V_c , T_c , b_c and θ_c :

$$\frac{RT_c}{P_c} = 3V_c \quad 3-8)$$

$$b_c^2 + \frac{b_c RT_c}{P_c} - \frac{\theta_c}{P_c} = -3V_c^2 \quad 3-9)$$

$$\frac{b_c \theta_c}{P_c} = V_c^3 \quad 3-10)$$

By Eq.3-8) $V_c = \frac{RT_c}{P_c} \quad 3-11)$

and thus, by Eq. 3-10) $\theta_c = \frac{1}{27} \frac{R^3 T_c^3}{b_c P_c^2} \quad 3-12)$

Substitution of Eq.3-11) and 3-12) into Eq. 3-9) yields on rearrangement the cubic equation

$$\hat{b}_c^3 + \hat{b}_c^2 + \frac{1}{3} \hat{b}_c - \frac{1}{27} = 0 \quad 3-13)$$

When $\hat{b}_c = \frac{b_c P_c}{RT_c}$. Equation 3-14) has but one real root given by.

$$\hat{b}_c = 0.08664 \quad 3-14a)$$

$$b_c = 0.08664 \frac{RT_c}{P_c} \quad 3-14b)$$

Substitution of Equation 3-15b) into 3-12) gives

$$\theta_c = 0.42748 \frac{R^2 T_c^2}{P_c} \quad 3-15a)$$

Also $\theta = \frac{a}{T^{1/2}}$, and Equation 3-15a) yields

$$a_c = 0.42748 \frac{R^2 T_c^{3/2}}{P_c} \quad 3-15b)$$

3.1.2 Soave-Redlich-Kwong equation of state

Most modifications of Redlich-Kwong equation incorporate, in addition to T_c and P_c , a third corresponding states parameter, usually the acentric factor ω : One such modifications is that of Soave who retain the original expression for b ,

$$b = b_c = 0.08664 \frac{RT_c}{P_c}$$

but replaces the original expression for a ,
from eq 3-3) and 3-11)

$$a = a' f(T)$$

$$a = a' f(T_c)$$

So

$$a = a_c \frac{f(T)}{f(T_c)} \quad 3-16)$$

$$\alpha = \frac{f(T)}{f(T_c)} \quad 3-17)$$

$$a = a_c \alpha \quad 3-18)$$

When

$$\alpha = \left[1 + (0.480 + 1.57\omega - 0.176\omega^2) \left(1 - t_r^{1/2} \right) \right]^2 \quad 3-19)$$

For SRK equation of state

$$b = \Omega_b \frac{RT_c}{P_c} \quad 3-20)$$

$$a = a_c \left[1 + (0.480 + 1.57\omega - 0.176\omega^2) \left(1 - t_r^{1/2} \right) \right]^2 \quad 3-21)$$

$$a_c = \Omega_a \frac{R^2 T_c^2}{P_c} \quad (3-22)$$

From Eq. 3-17) may be written to cubic equation of state

$$Z^3 - Z^2 + Z(A - B - B^2) - AB = 0 \quad (3-23)$$

When $Z = \frac{PV}{RT}$

$$A = \frac{aP}{RT^2}$$

$$B = \frac{bP}{RT}$$

From Eq.3-20) and 3-23):

$$A = 0.4274 \left[\frac{P_r}{T_r^2} \right] \alpha \quad (3-24)$$

$$B = 0.08664 \frac{P_r}{T_r} \quad (3-25)$$

3.1.3 Peng-Robinson equation of state

Peng-Robinson equation of state can be expression of the form:

$$P = \frac{RT}{v-b} - \frac{a}{v[v+b] + b[v-b]} \quad (3-26)$$

When $a = a' f(T)$

From equation 3-26) may be written to cubic equation of state :

$$Z - (1-B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad 3-27)$$

When $Z = \frac{PV}{RT} \quad 3-28)$

$$A = \frac{aP}{RT^2} \quad 3-29)$$

$$B = \frac{bP}{RT} \quad 3-30)$$

The classical derivative condition on the critical isotherm be used to solve this equation.

At critical, $\left(\frac{\partial P}{\partial V}\right)_{T:Cr} = 0$

$$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T:Cr} = 0$$

Compare the coefficient of v^n in equation 3-6) and 3-27) i.e.,

$$3v_c = 1 - B \quad 3-31)$$

$$3v_c^2 = A - 3B^2 - 2B \quad 3-32)$$

$$v_c^3 = AB - B^2 - B^3 \quad 3-33)$$

Combine equation 3-29), 3-30) and 3-31), 3-32) :

$$3v_c = 1 - \frac{bP_c}{RT_c} \quad 3-34)$$

$$3v_c^2 = \frac{a_c P_c}{R^2 T_c^2} - \frac{3b_c^2 P_c^2}{R^2 T_c^2} - \frac{2b_c P_c}{RT_c} \quad 3-35)$$

$$v_c^3 = \frac{a_c P_c}{R^2 T_c^2} \frac{b P_c}{RT_c} - \frac{b^2 P_c^2}{R^2 T_c^2} - \frac{b^3 P_c^3}{R^3 T_c^3} \quad 3-36)$$

$$a_c = \left[v_c^3 + \frac{b^2 P_c^2}{R^2 T_c^2} + \frac{b^3 P_c^3}{R^3 T_c^3} \right] \frac{R^3 T_c^3}{b_c P_c^2} \quad 3-37)$$

Combine equation 3-35) and 3-37) :

At critical temperature,

$$a(T_c) = 0.45724 \frac{R^2 T_c^2}{P_c} \quad 3-38)$$

$$b(T_c) = 0.07780 \frac{RT_c}{P_c} \quad 3-39)$$

At other temperature ,

$$a_c = \frac{f(T)}{f(T_c)}$$

$$a = a_c \alpha$$

At $T=T_c$,

$$\alpha = 1$$

α is a function of $T_r = T/T_c$ and ω :

$$\alpha^{0.5} = 1 + m(1 - T_r^{0.5}) \quad 3-40)$$

$$m = 0.37464 + 1.54226 \omega - 0.26992 \omega^2 \quad 3-41)$$

So for equation of state :

$$a = a_c \left[1 + (0.37464 + 1.54226 \omega - 0.26992 \omega^2)(1 - T_r^{0.5}) \right]^2 \quad 3-42)$$

$$b = b_c = 0.07780 \frac{RT_c}{P_c} \quad 3-43)$$

3.2 Cubic equation of state for mixtures

Application of empirical equations of state to mixtures is usually done through mixing rules for the equation of state parameters. Only a few type of mixing rules have gained general acceptance for use with cubic equation of state; most of them may be considered special cases of the quadratic mixing rule

$$P = \sum_i \sum_j X_i X_j P_{ij} \quad (3-44)$$

Here, the unsubscripted symbol P represents the value of parameter for a mixture.

The double subscripts parameters are of two type :

1. If $j=i$, then $P_{ij} = P_{ii} = P_i$
2. If $j \neq i$, then P_{ij} represents interactions between unlike chemical species, and is called an interaction parameter

Interaction parameters (P_{ij}) are independent of composition. They are related to the pure-fluid parameters P_i and P_j by empirical recipes called combination rules :

1. Arithmetic-mean combination rule

$$P_{ij} = \frac{1}{2}(P_{ii} + P_{jj}) = \frac{1}{2}(P_i + P_j) \quad (3-45)$$

Then
$$P = \sum_i X_i P_i \quad (3-46)$$

2. Geometric-mean combination rule

$$P_{ij} = (P_{ii} P_{jj})^{1/2} = (P_i P_j)^{1/2} = (P_{ii} P_{jj})^{1/2} = (P_i P_j)^{1/2} \quad (3-47)$$

Then
$$P = \left(\sum_i X_i P_i^{1/2} \right)^2 \quad (3-48)$$

3. Combination rule that modified from geometric-mean combination rule by adding interaction parameter l_{ij} .

$$P_{ij} = (1 - l_{ij})(P_i P_j)^{1/2} \quad 3-49)$$

$l_{ij} = 0$ when $j=i$ and l_{ij} is a small value.

For equation of state that are generally modifications of the van der Waals equation of state,

$$P = \frac{RT}{v-b} - \frac{a}{v^2}$$

According to the van der Waals, the extension of this equation of state to mixtures requires replacement of a and b by the following compositions-dependent expression :

$$a = \sum_i \sum_j X_i X_j a_{ij} \quad 3-50)$$

$$b = \sum_i \sum_j X_i X_j b_{ij} \quad 3-51)$$

In this equation, a_{ij} and b_{ij} ($i = j$) are parameters corresponding to pure component (i) while a_{ij} and b_{ij} ($i \neq j$) are called the unlike - interaction parameters. It is customary to relate the unlike - interaction parameters to the pure - component parameters by the following expression :

$$a = (1 - k_{ij})(a_{ii} a_{jj})^{1/2} \quad 3-52)$$

$$b_{ij} = (b_{ii} + b_{jj})/2 \quad 3-53)$$

Van Der Waals mixing rules is used in this research for a , b in cubic equation of state by the following expression :

$$a = \sum_i \sum_j X_i X_j (a_i a_j)^{0.5} (1 - k_{ij}) \quad 3-54)$$

$$b = \sum_i X_i b_i \quad 3-55)$$

3.3 Phase equilibrium from equation of state

For multicomponent mixtures, Analytical computational procedures must be applied with thermodynamic properties represented preferably by algebraic equations. Because mixtures properties depend on temperature, pressure, and phase composition, these equation tend to be complex. Nevertheless the equation presented in the following are widely used for computing phase equilibrium, enthalpy and densities of mixtures over wide range of conditions.

1. Fugacity—a Basis for Phase Equilibrium

For each phase in a multiphase, multicomponent system, the Gibbs free energy is given functionally as

$$G = G\{T, P, n_1, n_2, \dots, n_c\}$$

Where n=moles and subscripts refer to species. The total differential of G is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P, nj} \left(\frac{\partial G}{\partial P}\right)_{T, nj} dP + \sum \left(\frac{\partial G}{\partial n_i}\right)_{P, T, nj} dn_i \quad 3-56)$$

where $j \neq i$. From classical thermodynamics

$$\left(\frac{\partial G}{\partial T}\right)_{P, nj} = -S \quad 3-57)$$

and

$$\left(\frac{\partial G}{\partial P}\right)_{P, nj} = V \quad 3-58)$$

Where S=entropy and V=volume. Defining the chemical potential, μ , of species i as

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{P, T, nj} \quad 3-59)$$

and substituting into (3-56), we have

$$dG = SdT + VdP + \sum u_i dn_i \quad 3-60)$$

When (3-60) is applied to a closed system consisting of two phases in equilibrium at uniform temperature and pressure, where each phase is an open system capable of mass transfer with another phase

$$dG_{system} = \sum [\sum u_i^{(k)} - dn_i^{(k)}] = 0 \quad 3-61)$$

Where the superscript (k) refers to each of phase. Conservation of moles of each species requires that

$$dn_i^{(1)} = \sum dn_i^{(k)}$$

which, upon substitution into (3-61), gives

$$\sum [\sum (u_i^{(k)} - u_i^{(1)}) dn_i^{(k)}] = 0 \quad 3-62)$$

With $dn_i^{(1)}$ eliminated in (3-62), each $dn_i^{(k)}$ terms can be varied independently of any other $dn_i^{(k)}$ terms. But this requires that each coefficient of $dn_i^{(k)}$ in (3-62) be zero. Therefore.

$$\mu_i^{(1)} = \mu_i^{(2)} = \mu_i^{(3)} = \dots \mu_i^{(p)} \quad 3-63)$$

Thus, the chemical potentials of any species in a multicomponent system are identical in all phases at physical equilibrium.

Chemical potential cannot be expressed as an absolute quantity, and the numerical values of chemical potential are difficult to relate to more easily understood physical quantities. Furthermore, the chemical potential approaches an infinite negative value as pressure approaches zero. For these reasons, the

chemical potential is not directly useful for phase equilibrium calculations. Instead, fugacity, as defined below, is employed as a surrogate.

Equation (3-59) restated in terms of chemical potential is

$$\left(\frac{\partial \mu_i}{\partial P}\right)_{(T)} = \bar{v}_i \quad 3-64)$$

where \bar{v}_i = partial molal volume. For a pure substance that behaves as an ideal gas, $\bar{v}_i = RT/P$, and (3-64) can be integrated to give

$$\mu_i = RT \ln P + C_1 \{T\} \quad 3-65)$$

Where C_1 depends on T.

Unfortunately, (3-65) does not describe real multicomponent gas or liquid behavior. However, (3-65) was rescued by G.M. Lewis, who in 1901 invented the fugacity f , a pseudo pressure, which, when used in place of pressure in (3-65), preserves the functional form of the equation. Thus, for a component in a mixture

$$f_i = C_2 \{T\} \exp(\mu_i / RT) \quad 3-66)$$

where C_2 is related to C_1 .

Regardless of the value of C_1 , it is shown in Prausnitz that, at physical equilibrium, (3-63) can be replaced with

$$f_i^{(1)} = f_i^{(2)} = \dots \quad 3-67)$$

For a pure, ideal gas, fugacity is equal to the pressure and, for a component in an ideal gas mixture, it is equal to its partial pressure, $P_i = y_i P$.

Because of the close relationship between fugacity and pressure, it is convenient to define their ratio for a pure substance as

$$v_i^o = f_i^o / P \quad 3-68)$$

where v_i° is the pure species fugacity coefficient and f_i° is the pure species fugacity. The fugacity concept was extended to mixtures by Lewis and Randall and used to formulate the ideal solution rule

$$f_{iv} = y_i f_i^\circ v \quad 3-69)$$

$$f_{iL} = x_i f_i^\circ \quad 3-70)$$

where subscripts V and L refer, respectively, to the vapor and liquid phases. Ideal liquid solutions occur when molecular diameters are equal, chemical interactions are absent, and intermolecular forces between like and unlike molecules are equal. These same requirements apply to the gas phase, where at low pressures molecules are not in close proximity and an ideal gas solution is closely approximated.

It is convenient to represent the departure from both types of ideality (ideal gas law and ideal gas solution) by defining the following mixture fugacity coefficients.

$$\phi_{iv} = \frac{f_{iv}}{y_i P} \quad 3-71)$$

$$\phi_{iL} = \frac{f_{iL}}{x_i P} \quad 3-72)$$

At a given temperature, the ratio of the fugacity of a component in a mixture to its fugacity in some standard state is termed the activity. If the standard state is selected as the pure species at the same pressure and phase condition as the mixture, then

$$a_i = \frac{f_i}{f_i^\circ} \quad 3-73)$$

For an ideal solution, substitution of (3-69) and (3-70) into (3-73) shows that $a_{iv} = y_i$ and $a_{iL} = x_i$

To represent departure of activity from mole fraction when solutions are non ideal, activity coefficients based on concentrations in mole fractions are commonly used



$$\gamma_{iv} = \frac{a_{iv}}{y_i} \quad 3-74)$$

$$\gamma_{iL} = \frac{a_{iL}}{x_i} \quad 3-75)$$

For ideal solution, $\gamma_{iv} = 1.0$ and $\gamma_{iL} = 1.0$

3.4 Summary

The two constant equation of Generic-Redliche-Kwong is empirical relationships which is applicable over a wide range of pressure. The GRK equation is particularly attractive because it contains only two constant and these can be determined directly from the critical temperature, T_c and critical pressure, P_c . Furthermore, the GRK equation has an accuracy that compares quite favorably with more complex equation of state in vapor region and it has the ability to approximate the liquid region when the two constant Van der Waals equation can fail badly in this respect. This GRK equation of state is suitable for the vapor phase and unsuitable for liquid phase. The major difficulty with the GRK equation is its failure to predict vapor pressure and other liquid phase thermodynamic properties accurately for a wide range of molecular shape.

SRK is the most modification of Redliche Kwong equation by Soave (1972) who retains the original expression for b , but replace the original expression for a , in addition to T_c and P_c , a third corresponding state parameter, usually the acentric factor ω ; these improves the performance of the equation for nonsimple fluid. Modification of Redliche Kwong by adding of ω as a third constant greatly improves its ability to predict vapor pressure and other liquid phase thermodynamic.

PR equation is a new two constant equation of state that modified by Peng and Robinson in 1976. Parameter expresses in term of P_c , T_c , ω , like SRK. The model is likely to improve prediction of liquid density and phase equilibrium in the critical region. These equations can application to all calculation of all fluid properties both liquid and gas in natural process.