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# PENG-ROBINSON VLE CALCULATION PROCEDURE INCLUDING SOME BACKGROUND by Paul Paslay, P.E. #44278

This is a summary of some of the details concerning the computer program procedure for making vapor-liquid equilibrium calculations. The input to the program is given in terms of the composition of the entire flow (the feed). That is, the amounts of the individual oil and vapor are not specified in the program input. The procedure determines how much of the whole flow is liquid and how much is vapor as well as the chemical composition of each. The procedure assumes two mixtures are present. One is liquid and one is vapor. The usual chemical equilibrium condition is used to find the proportion of the liquid and the vapor.

Begin by considering a *single* mixture, liquid or vapor. Let the fixed mass of mixture contain N components and,

P, V, T	= total pressure, volume and temperature of the mixture, respectively
$n_i$	= number of moles of $i^{\text{th}}$ component in the mixture
$S = S(P, V, T, n_j)$	= entropy of mixture, $n_j = n_1, n_2, \dots, N$
$U = U(P, V, T, n_j)$	= internal energy of mixture, $n_j = n_1, n_2, \dots, N$
$H = U + P \cdot V$	= enthalpy of mixture, $n_j = n_1, n_2, \dots, N$
$F = H - T \cdot S$	= Gibbs free energy or thermodynamic potential of mixture, $n_j = n_1, n_2, \dots, N$
$A = U - T \cdot S$	= Helmholtz free energy or work function of mixture, $n_j = n_1, n_2, \dots, N$

In the above definitions, the equation of state,  $f(P, V, T, n_i) = 0$ , may be used to eliminate P, V or T from the functions H, S, U, F and A. Also recall that for any reversible thermodynamic change,

$$dU = T \cdot dS - P \cdot dV \quad 1$$

For a constant mass system undergoing differential change under reversible conditions at constant temperature and pressure,

$$dF = dU - T \cdot dS + P \cdot dV = -(\text{maximum obtainable work}) + P \cdot dV \quad 2$$

where (maximum obtainable work) is the reversible work associated with the change. The decrease in Gibbs free energy equals the maximum obtainable work less the work done by the expansion of the system at constant pressure. That is, any change in a system at equilibrium at constant temperature and pressure is such that the free energy remains constant.

In general, for a variable mass system undergoing differential changes, the combination of the definition of the free energy in the form,  $F(T, P, n_j)$ , and Equation 1 may be written as,

$$dF = -S \cdot dT + V \cdot dP + \sum_N \left( \frac{\partial F}{\partial n_i} \right)_{T, P, n_j} \cdot dn_i \quad 3$$

where the partial derivative is taken holding temperature, pressure and all of the component moles but  $n_i$  constant. These partial derivatives are defined in the chemical literature as,

$$\mu_I = \text{chemical potential of } I^{\text{th}} \text{ component} \equiv \left. \frac{\partial F}{\partial n_I} \right|_{T,P,n_j}$$

4

Now, for a change of the mixture at constant temperature and pressure,  $dF_I$  for the  $I^{\text{th}}$  component is defined as,

$$dF_I = \mu_I \cdot dn_I \quad \left( \text{i.e. } dF = \sum_I dF_I \right) \quad 5$$

To help fix ideas, for an ideal gas,

$$\mu_I - \tilde{\mu}_I = R \cdot T \cdot \ln(P_I) = R \cdot T \cdot \ln(n_I \cdot P) \quad 6$$

where  $\tilde{\mu}_I$  is the value for a reference state and  $P_I$  is the partial pressure of the  $I^{\text{th}}$  component. This result has been extended for a real gas or liquid to the form,

$$\mu_I - \mu^{\circ}_I \equiv R \cdot T \cdot \ln(f_I) \quad 7$$

where  $f_I$  is named the fugacity for the  $I^{\text{th}}$  component. Equation 7 is valid for any component, liquid or vapor. The fugacity for each component can be found from the equation of state of the mixture expressed in terms of its components. The reference state is chosen so that  $\mu^{\circ}_I = -R \cdot T \cdot \ln(n_I \cdot P)$  and then,

$$\mu_I = R \cdot T \cdot \ln\left(\frac{f_I}{n_I \cdot P}\right) \quad 8$$

This reference state infers that  $\mu_I \rightarrow 0$  as  $P \rightarrow 0$  since real gas behavior approaches ideal gas behavior as the pressure is reduced to low values compared to the critical pressure. Equation 5 may be written as,

$$dF_I = R \cdot T \cdot \ln\left(\frac{f_I}{n_I \cdot P}\right) \cdot dn_I \quad 9$$

Now, consider a vapor mixture and a liquid mixture in thermodynamic equilibrium. They are each composed of the same  $N$  components. The total mass is fixed. Let a superscripted  $V$  refer to the vapor part of the mixture and a superscripted  $L$  refer to the liquid part of the mixture. Also, define  $dn_I$  as the change in the number of moles of substance  $I$  in the vapor phase. Therefore, the change in the number of moles of substance  $I$  in the liquid phase is  $-dn_I$ . The expression for the change of Gibbs free energy for the combined vapor and liquid mixture can be deduced as,

$$dF = dF^V + dF^L = -(S^V + S^L) dT + (V^V + V^L) dP + \sum_N \left( \left. \frac{\partial F^V}{\partial n_I} \right|_{T,P,n_j} - \left. \frac{\partial F^L}{\partial n_I} \right|_{T,P,n_j} \right) \cdot dn_I \quad 10$$

or

$$dF = - (S^V + S^L) dT + (V^V + V^L) dP + \sum_N (\mu_1^V - \mu_1^L) dn_1$$

11

It is a fundamental assumption of chemical thermodynamics that, when a two phase mixture is at equilibrium at a constant temperature and constant pressure,

$$dF = 0 \quad \text{for arbitrary changes } dn_I, I = 1, 2, \dots, N \quad 12$$

Equations 11 and 12 then give the equilibrium conditions as,

$$\mu_1^V = \mu_1^L \quad \text{for } I = 1, 2, \dots, N \quad 13$$

or

$$\frac{f_1^V}{n_1^V} = \frac{f_1^L}{n_1^L} \quad \text{for } I = 1, 2, \dots, N \quad 14$$

Now, for the vapor and liquid combined system, define,

$$\begin{aligned} \beta &= \text{vapor mole fraction of liquid and vapor together} \\ &= \frac{(\text{total moles of vapor})}{(\text{total moles of liquid}) + (\text{total moles of vapor})} \end{aligned}$$

$$y_I = \text{mole fraction for } I^{\text{th}} \text{ component in vapor} = \frac{(\text{moles of } I^{\text{th}} \text{ component in vapor})}{(\text{total moles of vapor})}$$

$$x_I = \text{mole fraction for } I^{\text{th}} \text{ component in liquid} = \frac{(\text{moles of } I^{\text{th}} \text{ component in liquid})}{(\text{total moles of liquid})}$$

$$\begin{aligned} z_I &= \text{mole fraction for } I^{\text{th}} \text{ component in combined composition} \\ &= \frac{(\text{total moles of } I^{\text{th}} \text{ component in liquid}) + (\text{total moles of } I^{\text{th}} \text{ component in vapor})}{(\text{total moles of liquid}) + (\text{total moles of vapor})} \end{aligned}$$

$$\phi_I^V = \frac{f_1^V}{y_I \cdot P} = \text{vapor phase fugacity coefficient for } I^{\text{th}} \text{ component}$$

$$\phi_I^L = \frac{f_1^L}{x_I \cdot P} = \text{liquid phase fugacity coefficient for } I^{\text{th}} \text{ component}$$

When a calculation is performed with the VLE option, the  $z_I$  are specified  $\left( \sum_N z_I = 1 \right)$  and the  $2 \cdot N + 1$  unknowns are  $y_I$ ,  $x_I$  and  $\beta$ . The equations that determine the unknowns are,

$$\beta \cdot y_I + (1 - \beta) \cdot x_I = z_I \quad I = 1 \text{ through } N \quad \text{mass balance} \quad 15$$

$$y_I \cdot \phi_I^V = x_I \cdot \phi_I^L \quad I = 1 \text{ through } N \quad \text{vapor-liquid equilibrium } (f_I^V = f_I^L) \quad 16$$

$$\sum_N y_I = 1 \quad \text{by definition} \quad 17$$

Satisfaction of these equations ensures that,

$$\sum_N x_I = 1 \quad 18$$

In order to find  $\phi_I^V$  and  $\phi_I^L$  the equations of state must be used for the vapor phase as well as for the liquid phase. The Peng-Robinson equation of state for VLE these calculations is described. The Peng-Robinson equation of state is,

$$P = \frac{R \cdot T}{v - b} - \frac{a}{v^2 + u \cdot b \cdot v + w \cdot b^2} \quad 19$$

with,

$R$  = ideal gas constant

$v$  = specific volume

$u$  = 2

$w$  = -1

$a, b$  = values found as described below

The values for the parameters  $a$  and  $b$  are found separately for the vapor phase and the liquid phase using the same formulation. The formulation is given below,

$$b_I = 0.07780 \cdot R \cdot \frac{T_{C_I}}{P_{C_I}} \quad 20$$

$$a_I = a_{C_I} \cdot \alpha_I \quad 21$$

$$a_{C_I} = 0.45724 \cdot R^2 \cdot \frac{T_{C_I}^2}{P_{C_I}} \quad 22$$

$$\alpha_I = \left[ 1 + f(\omega_I) \cdot \left( 1 - \sqrt{\frac{T}{T_{C_I}}} \right) \right]^2 \quad 23$$

$$f(\omega_I) = 0.37464 + 1.54226 \cdot \omega_I - 0.26992 \cdot \omega_I^2 \quad 24$$

$\omega_I$  = Pitzer's acentric factor for  $I^{\text{th}}$  component

$$a_{IJ} = \sqrt{a_I \cdot a_J}$$

then,

$$a = \sum_{I=1}^N \sum_{J=1}^N y_I \cdot y_J \cdot (1 - \bar{k}_{IJ}) a_{IJ} \quad 26$$

$$b = \sum_{I=1}^N y_I \cdot b_I \quad 27$$

where the set,  $\bar{k}_{IJ}$ , gives the Peng-Robinson binary interaction parameters.

An alternative to Equation 19 is obtained by eliminating  $v$  in favor of the compressibility factor,  $Z$ , where,

$$Z = \frac{P \cdot v}{R \cdot T} \quad 28$$

The result is a cubic equation in  $Z$  for the Peng-Robinson equation as follows,

$$Z^3 - (1 + B^* - u \cdot B^*) Z^2 + (A^* + w \cdot B^{*2} - u \cdot B^* - u \cdot B^{*2}) Z - A^* \cdot B^* - w \cdot B^{*2} - w \cdot B^{*3} = 0 \quad 29$$

with,

$$A^* = \frac{a \cdot P}{R^2 \cdot T^2} \quad 30$$

$$B^* = \frac{b \cdot P}{R \cdot T} \quad 31$$

Now, for a single substance, Equation 29 will yield three roots. Since the coefficients of the equation are real, they are either 1.) one real root and two complex roots that are complex conjugates or 2.) three real roots. If there is only one real root the substance exists in a single phase. If there are three real roots, the minimum valued root corresponds to the liquid phase and the maximum valued root corresponds to the vapor phase. In the three root case with a specified temperature, the value of the pressure that yields a solution in chemical equilibrium for the vapor and liquid roots is the vapor pressure for the single substance at that temperature.

For a mixture with two phases, there are two sets of roots corresponding to the vapor and liquid phases. Chemical equilibrium must be found between these phases. The sets of roots must be evaluated individually to determine the appropriate choices. For each set, when there is only one real root, it is chosen. When there are three real roots for the liquid phase, the minimum valued root of this set is chosen. When there are three real roots for the vapor phase, the maximum valued root of this set is chosen. Chemical equilibrium calculations are made for the two chosen roots.

The logarithm of the fugacity coefficient for the Peng-Robinson equation of state for a single mixture is given by,

$$\begin{aligned} \ln(\phi_K) &= \frac{1}{R \cdot T} \cdot \int_0^P \left( \frac{\partial}{\partial n_K} \left[ \left( \frac{\partial F}{\partial P} \right)_{T,n} \right]_{P,T,n_K} - \frac{R \cdot T}{P} \right) \cdot dP \\ &= \frac{b_K}{b} \cdot (Z-1) - \ln(Z-B^*) - \frac{A^*}{2 \cdot \sqrt{2} \cdot B^*} \cdot \left[ \frac{2 \cdot \sum_{I=1}^N x_I \cdot a_{IK} \cdot (1 - \bar{k}_{IK})}{a} - \frac{b_K}{b} \right] \cdot \ln \left( \frac{Z + (\sqrt{2} + 1) B^*}{Z - (\sqrt{2} - 1) B^*} \right) \end{aligned} \quad 32$$

The objective of the chemical equilibrium calculations in the two phase case is to find values of  $\beta$  as well as  $x_I$  and  $y_I$  ( $I = 1, 2, \dots, N$ ) that satisfy Equations 15, 16 and 17 for the specified values of temperature and total pressure. The calculation procedure usually involves much iteration that requires the determination of the Peng-Robinson parameters for each step.

A suitable validation calculation for the procedure is based on the following condition, derived from Equations 15, 16 and 17,

$$\sum_{I=1}^{I=N} \frac{z_I \cdot (K_I - 1)}{(K_I - 1) \cdot \beta + 1} = 0 \quad 33$$

where,

$$K_I = \frac{\phi_I^L}{\phi_I^V} \quad 34$$

The calculation procedure may be started with the following approximation for the distribution coefficients,

$$K_I = \frac{P_{CI}}{P} \cdot e^{\left[ 5.37 \cdot (1 + \omega_I) \left( 1 - \frac{T_{CI}}{T} \right) \right]} \quad 35$$

where  $P_{CI}$  and  $T_{CI}$  are the critical pressure and critical temperature for the  $I^{\text{th}}$  component. These values are used with the specified values of  $z_I$  in Equation 33 to find  $\beta$ . A root-finding algorithm is used to find  $\beta$ . When  $\beta$  is found, the compositions of the liquid and the vapor phases may be found using,

$$x_I = \frac{z_I}{1 + \beta \cdot (K_I - 1)} \quad 36$$

$$y_I = \frac{z_I \cdot K_I}{1 + \beta \cdot (K_I - 1)} \quad 37$$

Improved values for the distribution coefficients can be found by calculating fugacity coefficients for these distributions and a new value for  $\beta$  can be found using Equation 33. This iterative process is continued until successive values of  $\beta$  differ by less than a specified amount (typically  $1 \cdot 10^{-6}$ ).

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