The Thermodynamics of Vapor-Liquid Equilibrium for Dummies

I. Introduction

Consider we have a multi-component system at vapor-liquid equilibrium. The following three conditions define thermodynamic equilibrium. First, we have thermal equilibrium, equating the temperature in the two phases,

$$T^V = T^L . \tag{1}$$

Second, we have mechanical equilibrium, equating the pressure in the two phases,

$$P^V = P^L . \tag{2}$$

Third, we have chemical equilibrium, equating the chemical species of each comonent in the two phases,

$$\mu_\alpha^V = \mu_\alpha^L \qquad \text{for } \alpha = 1 \text{ to } N_c, \tag{3}$$

where N_c is the number of components in the mixture.

II. Equilibrium Expression in terms of Gibbs free energies

For the practical evaluation of equation (3), one typically rewrites the equations in terms of fugacities. Let us derive this alternative statement. The chemical potential of component α in phase ϕ, μ_α^ϕ, is defined as

$$\mu_\alpha^\phi \equiv \left(\frac{\partial N^\phi \underline{G}^\phi}{\partial N_\alpha^\phi} \right)_{T,P,N_{\beta\neq\alpha}} \tag{4}$$

where $\underline{G}^\phi$ is the molar Gibbs free energy of the mixture of phase ϕ, N^ϕ is the total number of moles in phase ϕ, and N_α^ϕ is the number of moles of component α in phase ϕ. As a result of this definition, the molar Gibbs free energy of the mixture is given by

$$\underline{G}^\phi = \sum_{\alpha=1}^{N_c} x_\alpha^\phi \mu_\alpha^\phi \tag{5}$$

One typically proceeds by writing the molar Gibbs free energy of the mixture as a sum of an ideal mixture (IM) component and an excess (XS) component,

$$\underline{G}^{\phi} = \underline{G}^{\phi,IM} + \underline{G}^{\phi,XS} \quad , \tag{6}$$

where the excess term, by definition, includes everything that isn't included in the ideal mixture. The molar Gibbs free energy of an ideal mixture is defined as

$$\underline{G}^{\phi,IM} \equiv RT\sum_{\alpha=1}^{N_C} x_{\alpha}^{\phi}\ln\left(x_{\alpha}^{\phi}\right). \tag{7}$$

As a consequence of this definition, the excess molar Gibbs free energy of a mixture must be

$$\underline{G}^{\phi,XS} = \underline{G}^{\phi} - \underline{G}^{\phi,IM} = \underline{G}^{\phi} - RT\sum_{\alpha=1}^{N_C} x_{\alpha}^{\phi}\ln\left(x_{\alpha}^{\phi}\right). \tag{8}$$

The definitions of the mixture properties also defined the partial molar Gibbs free energy of an ideal mixture as

$$\overline{G}_{\alpha}^{\phi,IM} \equiv \underline{G}_{\alpha}^{\phi} + RT\ln\left(x_{\alpha}^{\phi}\right), \tag{9}$$

where $\underline{G}_{\alpha}^{\phi}$ is the molar Gibbs free energy of componenat α in the pure state. The partial molar excess Gibbs free energy of a mixture is

$$\overline{G}_{\alpha}^{\phi,XS} \equiv \mu_{\alpha}^{\phi} - \underline{G}_{\alpha}^{\phi} - RT\ln\left(x_{\alpha}^{\phi}\right). \tag{10}$$

As a result of equations (9) and (10), we see that we have an expression for the chemical potential in terms of ideal mixture and excess terms, which is analogous to the expression for the molar Gibbs free energy of the mixture in equation (6), namely

$$\mu_{\alpha}^{\phi} = \overline{G}_{\alpha}^{\phi,IM} + \overline{G}_{\alpha}^{\phi,XS} = \underline{G}_{\alpha}^{\phi} + RT\ln\left(x_{\alpha}^{\phi}\right) + \overline{G}_{\alpha}^{\phi,XS}. \tag{11}$$

So, we can rewrite the statement of chemical equilibrium, equation (3), as

$$\underline{G}_{\alpha}^{V} + RT\ln\left(x_{\alpha}^{V}\right) + \overline{G}_{\alpha}^{V,XS} = \underline{G}_{\alpha}^{L} + RT\ln\left(x_{\alpha}^{L}\right) + \overline{G}_{\alpha}^{L,XS} \qquad \text{for } \alpha = 1 \text{ to } N_c. \tag{12}$$

This expression, while useful in the purposes of making a continuous derivation, is not practically employed.

III. Equilibrium Expression in terms of fugacities

In phase ϕ of the pure component α, we define a fugacity, f_α^ϕ, as

$$f_\alpha^\phi \equiv P \exp\left(\frac{\underline{G}_\alpha^\phi - \underline{G}_\alpha^{IG}}{RT}\right) , \tag{13}$$

where $\underline{G}_\alpha^{IG}$ is the molar Gibbs free energy of pure alpha as an ideal gas, where the pressure is equal to zero. When we have an equation of state, the evaluation of the pure component fugacity involves evaluating the following integral

$$f_\alpha^\phi \equiv P \exp\left(\frac{1}{RT}\int_0^P \left(\underline{V}_\alpha^\phi(P) - \frac{RT}{P}\right) dP\right) . \tag{14}$$

We can also define a fugacity coefficient as

$$\varphi_\alpha^\phi \equiv \frac{f_\alpha^\phi}{P} , \tag{15}$$

For single-component vapor-liquid equilibrium, equation (12) becomes

$$\underline{G}_\alpha^V = \underline{G}_\alpha^L \tag{16}$$

By performing the same operations on both sides of equation (16), we could also write this as

$$P \exp\left(\frac{\underline{G}_\alpha^V - \underline{G}_\alpha^{IG}}{RT}\right) = P \exp\left(\frac{\underline{G}_\alpha^L - \underline{G}_\alpha^{IG}}{RT}\right) . \tag{17}$$

We see that equation (17) contains the fugacities, so that an alternative expression for single component vapor-liquid equilibrium is

$$f_\alpha^V = f_\alpha^L . \tag{18}$$

Equation (18) is frequently used for the calculation of single-component vapor liquid equilibrium.

For a given T, one guesses P. One evaluates the integral in equation (14) for both phases. If the two fugacities are equal, one guessed a good P. Otherwise, one needs to guess a new value of P following some methodical iterative procedure. One can also do this given P and iterating over T.

We are interested in multi-component vapor-liquid equilibrium. In the multi-component case, the fugacity of component α in a mixture in phase ϕ, $\bar{f}_{\alpha}^{\phi}$, is defined as

$$\bar{f}_{\alpha}^{\phi} \equiv x_{\alpha}^{\phi} P \exp\left(\frac{\mu_{\alpha}^{\phi} - \bar{G}_{\alpha}^{\phi,IGM}}{RT}\right) = x_{\alpha}^{\phi} P \exp\left(\frac{\bar{G}_{\alpha}^{\phi,XS}}{RT}\right) . \tag{19}$$

where IGM indicates an ideal gas mixture. When we have an equation of state, the evaluation of the pure component fugacity involves evaluating the following integral

$$\bar{f}_{\alpha}^{\phi} \equiv P \exp\left(\frac{1}{RT}\int_{0}^{P}\left(\bar{V}_{\alpha}^{\phi}(P) - \bar{V}_{\alpha}^{\phi,IGM}(P)\right)dP\right) . \tag{20}$$

We can also define a fugacity coefficient in a mixture as

$$\bar{\varphi}_{\alpha}^{\phi} \equiv \frac{\bar{f}_{\alpha}^{\phi}}{x_{\alpha}^{\phi} P} , \tag{21}$$

Using equation (9), we have a definition for the partial molar Gibbs free energy of component α in an ideal gas mixture

$$\bar{G}_{\alpha}^{\phi,IGM} \equiv \underline{G}_{\alpha}^{\phi,IG} + RT\ln\left(x_{\alpha}^{\phi}\right) \tag{22}$$

it can be shown by direct comparison of equation (19) and equation (3) that another expression for the chemial equilibrium condition is that the mixture fugacities are equal in each phase for each component

$$\bar{f}_{\alpha}^{V} = \bar{f}_{\alpha}^{L} \qquad \text{for } \alpha = 1 \text{ to } N_c, \tag{23}$$

Equation (23) is used for the calculation of multi-component vapor liquid equilibrium, where equations of state are available for both the liquid and vapor phases.

To work this problem one needs to be given two of the four quantities, T, P, the composition of the vapor phase, or the composition of the liquid phase. For example if we know the temperature and liquid composition, we must guess the pressure and vapor composition. We evaluate the integrals in equation (20). If the fugaciitiess are equal, one guessed a good P and $\left\{x_{\alpha}^{V}\right\}$. Otherwise, one needs to guess new values, following some methodical iterative procedure.

IV. Equilibrium Expression in terms of activities

The problem with fugacities is frequently we do not have a good equation of state for the liquid mixture. Thus we are unable to evaluate the right-hand side of equation (23). Therefore, we introduce the concept of the activity. The activity of component α in a mixture in phase ϕ, a_α^ϕ, is defined as the ratio of the fugacity of component a in a mixture to that in the pure component, at the same T and P.

$$a_\alpha^\phi \equiv \frac{\bar{f}_\alpha^\phi}{f_\alpha^\phi} \tag{24}$$

We also can define an acitivity coefficient, γ_α^ϕ,

$$a_\alpha^\phi \equiv x_\alpha^\phi \gamma_\alpha^\phi \tag{25}$$

Models for activity coefficient exist. With such a model, one can compute the right-hand side of equation (23).

$$\bar{f}_\alpha^\phi \equiv x_\alpha^\phi \gamma_\alpha^\phi f_\alpha^\phi \tag{26}$$

Note that one still requires the equation of state for the pure component liquid.

V. An Example

system: two component vapor-liquid equilibrium.
given: temperature and liquid composition
unknown: pressure and vapor composition

V.A. pure component vapor phase

V.A.1. Peng-Robinson equation of state for component β

$$P = \frac{RT}{\underline{V} - b_\beta} - \frac{a_\beta(T)}{\underline{V}\left(\underline{V} + b_\beta\right) + b_\beta\left(\underline{V} - b_\beta\right)} \tag{27}$$

$$a_\beta(T) = 0.45724 \frac{R^2 T_{c,\beta}^2}{P_{c,\beta}} \alpha_\beta(T) \tag{28}$$

$$\alpha_\beta(T) = \left[1 + \kappa_\beta\left(1 - \sqrt{\frac{T}{T_{c,\beta}}}\right)\right]^2 \tag{29}$$

$$\kappa_\beta = 0.37464 + 1.54226\omega_\beta - 0.26992{\omega_\beta}^2 \tag{30}$$

where ω_β is the acentricity factor of component β.

$$b_\beta = 0.07780 \frac{RT_{c,\beta}}{P_{c,\beta}} \tag{31}$$

V.A.2. pure component fugacity, vapor phase. We don’t need this.

$$\ln\left(\frac{f_\alpha^V}{P}\right) = \left(Z_\alpha^V - 1\right) - \ln\left(Z_\alpha^V - B_\alpha\right) - \frac{A_\alpha}{2\sqrt{2}B_\alpha} \ln\left(\frac{Z_\alpha^V + \left(1 + \sqrt{2}\right) B_\alpha}{Z_\alpha^V + \left(1 - \sqrt{2}\right) B_\alpha}\right) \tag{32}$$

where the compressibility is given as

$$Z_\alpha^V = \frac{\underline{V}_\alpha^V P}{RT} \tag{33}$$

$$A_\alpha = \frac{a_\alpha P}{RT} \tag{34}$$

$$B_\alpha = \frac{b_\alpha P}{RT} \tag{35}$$

V.B. mixture component vapor phase

V.B.1. Peng-Robinson equation of state with mixing rules

$$P = \frac{RT}{\underline{V} - b_{mix}} - \frac{a_{mix}(T)}{\underline{V}\left(\underline{V} + b_{mix}\right) + b_{mix}\left(\underline{V} - b_{mix}\right)} \tag{36}$$

$$a_{mix}(T) = \sum_{\alpha=1}^{N_C}\sum_{\beta=1}^{N_C} x_\alpha^V x_\beta^V \sqrt{a_\alpha a_\beta}\left(1 - k_{\alpha\beta}\right) \tag{37}$$

where $k_{\alpha\beta}$ is the binary interaction parameter and is 0 for $\alpha=\beta$. If you don't know it, assume it is zero.

$$b_{mix} = \sum_{\alpha=1}^{N_C} x_\alpha^V b_\alpha \tag{38}$$

V.B.2. component in mixture fugacity, vapor phase

$$\begin{aligned}\ln\left(\frac{\bar{f}_\alpha^V}{x_\alpha^V P}\right) &= \frac{B_\alpha}{B_{nix}}\left(Z_{mix}^V - 1\right) - \ln\left(Z_{mix}^V - B_{mix}\right) \\ &- \frac{A_{mix}}{2\sqrt{2}B_{mix}}\left[\frac{2\sum_{\beta=1}^{N_C} x_\beta^V A_\beta}{A_{mix}} - \frac{B_\alpha}{B_{nix}}\right]\ln\left(\frac{Z_{mix}^V + \left(1+\sqrt{2}\right) B_{mix}}{Z_{mix}^V - \left(1-\sqrt{2}\right) B_{mix}}\right)\end{aligned} \tag{39}$$

where the compressibility is given as

$$Z_{mix}^V = \frac{\underline{V}_{mix}^V P}{RT} \tag{40}$$

$$A_{mix} = \frac{a_{mix}P}{RT} \tag{41}$$

$$B_{mix} = \frac{b_{mix}P}{RT} \tag{42}$$

V.C. pure component liquid phase

V.C.1. Peng-Robinson equation of state for component β

Same as for the pure component vapor phase. Equations (27) to (31).

V.C.2. pure component liquid phase fugacities

Same as equations (32) to (35) replacing V with L.

$$\ln\left(\frac{f_\alpha^L}{P}\right) = \left(Z_\alpha^L - 1\right) - \ln\left(Z_\alpha^L - B_\alpha\right) - \frac{A_\alpha}{2\sqrt{2}B_\alpha}\ln\left(\frac{Z_\alpha^L + \left(1+\sqrt{2}\right)B_\alpha}{Z_\alpha^L + \left(1-\sqrt{2}\right)B_\alpha}\right) \tag{43}$$

$$Z_\alpha^L = \frac{\underline{V}_\alpha^L P}{RT} \tag{44}$$

V.D. mixture liquid phase

Use an activity coefficient model.

$$\bar{f}_\alpha^L \equiv x_\alpha^L \gamma_\alpha^L f_\alpha^L \tag{26}$$

For example, the Wilson activity coefficient model for binary mixtures. (Note the rest of this document is not limited to binary mixtures.) Only the Wilson model.

$$\ln\left(\gamma_\alpha^L\right) \equiv -\ln\left(x_\alpha^L + \Lambda_{\alpha\beta}x_\beta^L\right) + x_\beta^L\left(\frac{\Lambda_{\alpha\beta}}{x_\alpha^L + \Lambda_{\alpha\beta}x_\beta^L} - \frac{\Lambda_{\beta\alpha}}{x_\beta^L + \Lambda_{\beta\alpha}x_\alpha^L}\right) \tag{45}$$