Lecture 24

Objectives:

1. Be able to use two different methods to compute partial molar properties.
2. Be able to derive the generalized Gibbs-Duhem Equation from partial molar properties.
3. Be able to define fugacity and fugacity coefficients.
4. Be able to compute fugacities and fugacity coefficients from an equation of state.
5. Be able to numerically solve for vapor-liquid phase equilibrium for a pure fluid.

1. Example of computing partial molar properties. Compute $\bar{H}_i$ given the binary correlation

$$\tilde{H} = x_1 \tilde{H}_1 + x_2 \tilde{H}_2 + Ax_1 x_2$$

Recall that

$$\bar{J}_i = \tilde{J} + \left( \frac{\partial \tilde{J}}{\partial x_i} \right)_{x_j \neq i} - \sum_k x_k \left( \frac{\partial \tilde{J}}{\partial x_k} \right)_{x_j \neq k}$$

The above definition of $\bar{J}_i$ does not take into consideration that the $x_i$ are not all independent, but are related by

$$\sum_i x_i = 1$$

If we consider this then we get

$$\tilde{J}_i = \bar{J} - \sum_{k \neq i} x_k \left( \frac{\partial \tilde{J}}{\partial x_k} \right)_{T,P,x_j \neq i,k}$$

Both of these expressions are used in texts and both give the same answer. Which you use is a matter of convenience.

Using the first equation we get:

$$\begin{align*}
\tilde{H}_1 &= \tilde{H} + \tilde{H}_1 + Ax_2 - x_1 \tilde{H}_1 - Ax_1 x_2 - x_2 \tilde{H}_2 - Ax_1 x_2 \\
&= x_1 \tilde{H}_1 + x_2 \tilde{H}_2 + Ax_1 x_2 + \tilde{H}_1 + Ax_2 - x_1 \tilde{H}_1 - Ax_1 x_2 - x_2 \tilde{H}_2 - Ax_1 x_2 \\
&= \tilde{H}_1 + Ax_2 - Ax_1 x_2 \\
&= \tilde{H}_1 + Ax_2 - A(1 - x_2)x_2 \\
&= \tilde{H}_1 + Ax_2 - Ax_2 + Ax_2^2 \\
\tilde{H}_1 &= \tilde{H}_1 + Ax_2^2
\end{align*}$$

Using the second equation we substitute $x_1 = 1 - x_2$ to get:

$$\begin{align*}
\tilde{H}_1 &= \tilde{H} - x_2 \frac{d}{dx_2} \left[ (1 - x_2) \tilde{H}_1 + x_2 \tilde{H}_2 + A(x_2 - x_2^2) \right] \\
&= (1 - x_2) \tilde{H}_1 + x_2 \tilde{H}_2 + A(x_2 - x_2^2) - x_2 \left[ \tilde{H}_2 - \tilde{H}_1 + A(1 - 2x_2) \right] \\
&= \tilde{H}_1 + Ax_2^2
\end{align*}$$
Which is exactly the same as obtained with the first equation. Question: When would you use one over the other?

2. Gibbs-Duhem Equation.
Any molar property $\tilde{J}$ can be written in terms of a partial molar property, $\bar{J}_i$ as

$$n\tilde{J}(T, P, x_i) = \sum_i n_i\bar{J}_i(T, P, n_i)$$

Then,

$$d(n\tilde{J}) = \sum_i \bar{J}_i(T, P, n_i)dn_i + \sum_i n_id\bar{J}_i(T, P, n_i)$$

but since $n\tilde{J} = J(T, P, n_i)$ we can also write

$$d(n\tilde{J}) = \left(\frac{\partial(n\tilde{J})}{\partial T}\right)_{P,n_j}dT + \left(\frac{\partial(n\tilde{J})}{\partial P}\right)_{T,n_j}dP + \sum_{i=1}^C \left(\frac{\partial(n\tilde{J})}{\partial n_i}\right)_{T,P,n_j\neq i}dn_i$$

$$= n\left(\frac{\partial \tilde{J}}{\partial T}\right)_{P,n_j}dT + n\left(\frac{\partial \tilde{J}}{\partial P}\right)_{T,n_j}dP + \sum_{i=1}^C \bar{J}_idn_i$$

Where we have used the definition of the partial molar property,

$$\bar{J}_i = \frac{\partial(n\tilde{J})}{\partial n_i}_{T,P,n_j\neq i}$$

If we subtract the top equation for $d(n\tilde{J})$ from the bottom equation we get,

$$-n\left(\frac{\partial \tilde{J}}{\partial T}\right)_{P,n_j}dT - n\left(\frac{\partial \tilde{J}}{\partial P}\right)_{T,n_j}dP + \sum_{i=1}^C n_i\bar{J}_i = 0$$

dividing by $n$ gives,

$$-\left(\frac{\partial \tilde{J}}{\partial T}\right)_{P,n_j}dT - \left(\frac{\partial \tilde{J}}{\partial P}\right)_{T,n_j}dP + \sum_{i=1}^C x_i\bar{J}_i = 0$$

This is the generalized Gibbs-Duhem equation. This can be used to evaluate thermodynamic models for thermodynamic consistency. It also can be used to test experimental data for consistency, and do minimizing the amount of experimental data needed for evaluating thermodynamic properties of mixtures.

3. Fugacity and fugacity coefficients.
What are the conditions for phase equilibrium? $T^\alpha = T^\beta$, $P^\alpha = P^\beta$, $\mu^\alpha_i = \mu^\beta_i$ for $i = 1$, number of components. If we can calculate $\bar{G}_i$ then we can calculate $\mu_i$ (they are the same). Unfortunately, we don’t often have correlations for $\mu_i$. Engineers have developed an auxiliary function called the fugacity, that is more convenient than the chemical potential to compute, but plays the same sort of role. Here are two “derivations” of $f$, the fugacity.
Define \( f \) to have the same units as pressure. For a pure fluid at constant \( T \) we may write

\[
d\tilde{G} = \tilde{V} dP
\]  

(1)

for an ideal gas we have

\[
d\tilde{G}' = \frac{RT}{P} dP = RT d \ln P
\]  

(2)

This leads us to define a function that is like the pressure such that for a real fluid

\[
d\tilde{G} = RT d \ln f
\]  

(3)

We require that for an ideal gas \( f = P \), and also that

\[
\lim_{P \to 0} \left( \frac{f}{P} \right) = 1
\]

This leads to a method of computing \( f \) from \( PV T \) properties. Let \( \phi = f/P \) be the fugacity coefficient. Then

\[
\ln \phi = -\frac{1}{RT} \int_0^P \left( \frac{RT}{P} - \tilde{V} \right) dP = -\frac{1}{RT} \int_0^P \Delta \tilde{V}' dP
\]

We can find an alternate expression for \( \phi \) by subtracting Eq. (3) from Eq. (2):

\[
\begin{align*}
d\tilde{G} - d\tilde{G}' &= RT d \ln f - RT d \ln P = RT d \ln \frac{f}{P} = RT d \ln \phi \\
d \left( \tilde{G} - \tilde{G}' \right) &= RT d \ln \phi \\
\tilde{G} - \tilde{G}' &= -\Delta G' = RT \ln \phi \\
\phi &= \exp \left( \frac{-\Delta G'}{RT} \right)
\end{align*}
\]

For mixtures we define \( \hat{f}_i \) as the fugacity of \( i \) in a mixture. The definitions are

\[
d\tilde{G}_i = RT d \ln \hat{f}_i
\]

\[
\hat{\phi}_i = \frac{\hat{f}_i}{x_i P}
\]

\[
\lim_{P \to 0} \hat{\phi}_i = 1
\]

We have three separate notational cases: (1) Pure fluids: \( f_i, \phi_i = f_i/P \). (2) Total mixture properties: \( f, \phi = f/P \). (3) Components in mixture (analogous to partial properties): \( \hat{f}_i, \hat{\phi}_i = \hat{f}_i/(x_i P) \). Note that we use a circumflex (\( \hat{\text{~}} \)) to represent the mixture properties, because they are like partial properties, but they have slightly different definitions.
Alternate route to the fugacity. Define the fugacity for a pure fluid as

\[ \mu = \mu^0 + RT \ln f \]

where \( \mu^0 = \mu^0(T) \) and is the temperature dependent part of the ideal gas chemical potential. (Note that when \( P \to 0 \) \( f \to P = RT/\tilde{V} \)). Now note that

\[ \mu^\alpha = \mu^\beta \]

\[ \mu^\alpha + RT \ln f^\alpha = \mu^\beta + RT \ln f^\beta \]

but \( \mu^0 = \mu^0(T) \) so,

\[ RT \ln f^\alpha = RT \ln f^\beta \implies f^\alpha = f^\beta \]

So, \( f \) is like \( \mu \) in specifying phase (and chemical) equilibrium. For a mixture,

\[ \mu_i = \mu^0_i + RT \ln \hat{f}_i \]

So the same sort of argument holds for \( \hat{f}_i \) being analogous to \( \mu_i \) in a mixture.

4. Relation to partial properties.

The fugacity of component \( i \) in a mixture, \( \hat{f}_i \), is not the partial property of the mixture fugacity, \( f \). But it can be shown that

\[ \ln \frac{\hat{f}_i}{x_i} = \left( \frac{\partial(n \ln f)}{\partial n_i} \right)_{T,P,n_j \neq i} \]

I.e., \( \ln \frac{\hat{f}_i}{x_i} \) is the partial property (not molar) to \( \ln f \). The usual definition also holds:

\[ \ln f = \sum_i x_i \ln \frac{\hat{f}_i}{x_i} \]

It can also be shown the \( \ln \hat{\phi}_i \) is the partial property to \( \ln \phi \), i.e.,

\[ \ln \hat{\phi}_i = \left( \frac{\partial(n \ln \phi)}{\partial n_i} \right)_{T,P,n_j \neq i} \]

and

\[ \ln \phi = \sum_i x_i \ln \hat{\phi}_i \]

There are many important relationships for these quantities and other thermodynamic properties. See a standard text.
5. Computing \( f, \hat{f} \) from an equation of state.

The fugacity coefficient of a mixture can be calculated from

\[
RT \ln \phi = \int_0^P \left( \tilde{V} - \frac{RT}{P} \right) dP
\]

We can then compute \( \hat{\phi}_i \) or \( \hat{f}_i \) from the partial property relations presented. But, most EOS are pressure explicit (i.e., \( P \) as a function of \( \tilde{V}, T \)), so the above integral equation is not very useful. We can transform the above equation to the following form:

\[
\ln \phi = z - 1 - \ln z - \frac{1}{RT} \int_{-\infty}^{\tilde{V}} \left( \frac{P}{\tilde{V}} - \frac{RT}{\tilde{V}} \right) d\tilde{V}
\]

We can compute \( \ln \hat{\phi}_i \) from the above equation and making use of the method of computing partial molar properties.

\[
\ln \hat{\phi}_i = \ln \phi + \left( \frac{\partial \ln \phi}{\partial x_i} \right)_{x_j \neq i} \sum_k x_k \left( \frac{\partial \ln \phi}{\partial x_k} \right)_{x_j \neq k}
\]

6. Computing phase equilibrium for pure fluids.

The procedure for computing VLE from an equation of state is as follows: (1) Guess an initial value for the equilibrium pressure \( P \). (2) Compute \( \tilde{V} \) for the vapor and liquid (use a cubic EOS solver or find the roots some other way). (3) Compute \( \phi \) for each phase to see if they are equal in liquid and vapor branch, or see if \( \ln(\phi_l/\phi_v) = 0 \). (4) Iterate.

You could use a bisection method to approximate the root, or more sophisticated method such as Netwon-Raphson. A quick and dirty way to do this is to use a spreadsheet.

7. Define activity coefficients.

The activity coefficient \( \gamma_i \), is defined in the following relation:

\[
\hat{f}_i = x_i \gamma_i f_i
\]

Note that \( \gamma_i \) relates the fugacity of component \( i \) in the mixture to the pure component fugacity of \( i \) at the same temperature and pressure. We can write

\[
\gamma_i = \frac{\hat{f}_i}{x_i f_i}
\]

The activity coefficient can also be defined in terms of the chemical potential. For an ideal mixture we know that

\[
\mu_i = \mu^*_i(T, P) + RT \ln x_i
\]

where \( \mu^*_i(T, P) \) the chemical potential of the pure fluid at the same \( T, P \) of the mixtures, and is a function of temperature and pressure only. The activity coefficient is the correction of the above formula to real mixtures:

\[
\mu_i = \mu^*_i(T, P) + RT \ln \gamma_i x_i
\]

Thus, \( \gamma_i \) can be seen as a correction factor for ideal mixtures. Note that \( G^{ex} \) is given by

\[
G^{ex} = RT \sum_i x_i \ln \gamma_i
\]
8. Define activity. The activity coefficient gets its name from the activity, $a_i$,

$$a_i = x_i \gamma_i.$$ 

But this equation is only true if the fluid is at a pressure of 1 bar. This is because the rigorous definition of the activity is

$$a_i = \frac{\hat{f}_i}{f_i^0},$$

where $f_i^0$ is the fugacity of pure $i$ at the same temperature as the mixture, but at a standard pressure of 1 bar. Note that the standard pressure used to be defined as 1 atm, but now by convention is 1 bar. For liquids at moderate pressure the difference between 1 bar and the pressure of the system has a negligible effect on the properties.

9. When would you use the fugacity, and fugacity coefficients and when would you use the activity coefficients? Fugacity is used mainly for gases or for liquids that can be described by an EOS. Activity coefficients are used to describe liquid mixtures, especially highly non-ideal mixtures.