Lecture #20

Objectives

1. Be able to identify property changes on mixing
2. Be able to describe ideal Solutions in terms of the Lewis-Randell Rule
3. Be able to derive partial molar properties

1. Property changes of mixing.
   We have dealt mainly with pure fluid properties. Virtually everything in nature is a mixture. Mixture are much more complex than pure fluids. In order to understand mixtures let us define a mixing process which takes place at constant pressure and temperature. What happens when we mix two or more pure fluids at constant T and P? Understanding a constant P mixing process is easy—just mix the components in an open vessel at ambient pressure. Constant temperature is more difficult. Most mixing processes are either endothermic or exothermic. To make a mixing process isothermal you need to add or remove heat as the mixing proceeds.

   QUESTION: You go into the lab and mix 250 ml of $CHCl_3$ with 250 ml of acetone. Describe what happens, describe the process.

   The pressure is constant if done in an open container, therefore the volume will change in some way. The process will either give up heat or take in heat, but the heat transfer will probably not be fast enough to keep the process isothermal. After mixing is complete, the mixture will slowly reach thermal equilibrium with the surroundings, making the total process isothermal and isobaric.

   We define a property change on mixing as follows:

   $$\Delta\tilde{J}_{\text{mix}} = \tilde{J}(T,P,x_i) - \sum_i x_i \tilde{J}_i(T,P)$$

   where $\tilde{J}(T,P,x_i)$ is the mixture property and $\tilde{J}_i(T,P)$ are the pure fluid properties. For example, $\Delta\tilde{J}_{\text{mix}} = \Delta\tilde{V}_{\text{mix}}$ = change of volume on mixing. $\Delta\tilde{J}_{\text{mix}} = \Delta\tilde{H}_{\text{mix}}$ = enthalpy of mixing, or heat of mixing. $\Delta\tilde{H}_{\text{mix}}$ has special meaning because it corresponds to the heat that must be added or taken away in order to keep the process isothermal.

2. Ideal Solutions: The Lewis-Randall Rule.
   The Lewis-Randall ideal solution picture is appropriate when all the components of the mixture are stable liquids at the conditions of interest. Consider an ideal solution.

   (a) What would you expect $\Delta\tilde{V}^{ID}_{\text{mix}}$ to be? From microscopic arguments we see that $\Delta\tilde{V}_{\text{mix}} \neq 0$ means that there are some specific interactions between the molecules that change the volume of the mixture. For example, consider mixtures of A and B molecules of the same "size" but different dispersion interactions. A may attract or repel B, and hence introduce some volume change. Now consider molecules A and B with about the same dispersion interactions, but very different size/shapes. B may fit into the interstitial regions of fluid A, giving a $\Delta\tilde{V}_{\text{mix}} < 0$. Therefore, for an ideal solution we expect that the energy, size and shape of the molecules would be the same, and hence it is reasonable to say $\Delta\tilde{V}^{ID}_{\text{mix}} = 0$.

(b) What would you expect $\Delta \tilde{H}^{ID}_{\text{mix}}$ to be? If the energetic cross interactions between molecules A and B is stronger than or weaker than A-A or B-B interactions, then we would expect $\Delta H_{\text{mix}} \neq 0$. If the cross interactions are the same as the self-interactions then $\Delta \tilde{H}_{\text{mix}} = 0$, hence it is reasonable to say $\Delta \tilde{H}^{ID}_{\text{mix}} = 0$.

(c) What is $\Delta \tilde{U}^{IG}_{\text{mix}}$?

$$\begin{aligned} U &= H - PV \\ \Delta U_{\text{mix}} &= \Delta H_{\text{mix}} - P\Delta V_{\text{mix}} \text{ at constant pressure} \\ \Delta U^{ID}_{\text{mix}} &= \Delta H^{ID}_{\text{mix}} - P\Delta V^{ID}_{\text{mix}} \\ \Delta U^{ID}_{\text{mix}} &= 0 \end{aligned}$$

(d) What about $\Delta S^{ID}_{\text{mix}}$? We know that the mixing process produces entropy. In fact, if we mix red and blue marbles we know that we will produce entropy. We know from statistical mechanics that

$$\tilde{S} = -k \sum_i \mathcal{P}_i \ln \mathcal{P}_i$$

If we mix molecules which have the same energy, size and shape, but differ only in "color" (e.g., mixing red and blue marbles), then the corresponding change in entropy will be

$$\Delta \tilde{S}_{\text{mix}} = -R \sum_i x_i \ln x_i$$

on a per-mole basis, where x_i is the mole fraction. We therefore write

$$\Delta \tilde{S}^{ID}_{\text{mix}} = -R \sum_i x_i \ln x_i$$

(e) What is $\Delta G^{ID}_{\text{mix}}$? use $G = H - TS$, $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T\Delta S_{\text{mix}}$, and hence,

$$\Delta \tilde{G}^{ID}_{\text{mix}} = RT \sum_i x_i \ln x_i$$

(f) Likewise $\Delta \tilde{A}^{IG}_{\text{mix}}$ is given by

$$\Delta \tilde{A}^{ID}_{\text{mix}} = RT \sum_i x_i \ln x_i$$

(g) Derived properties. It is easy to show that

$$\Delta C^{ID}_{p,\text{mix}} = \Delta C^{ID}_{v,\text{mix}} = 0$$

Group activity: derive this.

3. Partial Properties (Molar and Mass).
A mixture property $\tilde{J}(T, P, x_i)$ for most fluids is not simply the mole fraction average of the pure fluid properties

$$\tilde{J}(T, P, x_i) \neq \sum_i x_i \tilde{J}_i(T, P)$$

where $J_i(T, P)$ is the pure fluid property. It turns out that it is very convenient to define a property called the partial molar property such that

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

or

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

where $\bar{J}_i$ is the partial molar property, which is a function of all the mole fractions in the mixture, i.e., it is NOT a pure fluid property. We can also have partial mass properties

$$m\tilde{J}(T,P,m_i) = \sum_i m_i \bar{J}_i(T,P,m_i)$$

$\tilde{J}(T,P,x_i)$ is a complete function, so we can write

$$d(n\tilde{J}) = n\left(\frac{\partial \tilde{J}}{\partial T}\right)_{P,n_j} dT + n\left(\frac{\partial \tilde{J}}{\partial P}\right)_{T,n_j} dP + \sum_i \left(\frac{\partial (n\tilde{J})}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i$$

at constant T and P we have

$$d(n\tilde{J}) = \sum_i \left(\frac{\partial (n\tilde{J})}{\partial n_i}\right)_{T,P,n_{j\neq i}} dn_i$$

By applying Euler's theorem on homogeneous functions we obtain

$$n\tilde{J} = \sum_i n_i \left(\frac{\partial (n\tilde{J})}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Dividing by n we get

$$\tilde{J} = \sum_i x_i \left(\frac{\partial (n\tilde{J})}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Comparing with the above definition of $\bar{J}_i$ we see that

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

Note that $\bar{J}_i$ is always defined holding T, P constant. Some examples:

$$\begin{aligned}
\bar{U}_i &= \bar{U}_i(T,P,x_i) = \left(\frac{\partial (n\tilde{U})}{\partial n_i}\right)_{T,P,n_{j\neq i}} \\
\bar{H}_i &= \left(\frac{\partial (n\tilde{H})}{\partial n_i}\right)_{T,P,n_{j\neq i}} \\
\bar{G}_i &= \left(\frac{\partial (n\tilde{G})}{\partial n_i}\right)_{T,P,n_{j\neq i}} \\
&= \mu_i
\end{aligned}$$

Note that only $\bar{G}_i$ corresponds to the chemical potential, because the natural variables for G are T, P, n_i.

From Van Ness and Abbott: "The partial property $\bar{J}_i$ is then interpreted as the value of the property of species i as is exists in solution. However, each species in a solution is an intimate part of the solution, and cannot actually have identifiable separate properties of its own. Nevertheless, we may view the definition of $\bar{J}_i$ as a formula which also defines how a solution property is *apportioned* among its constituent species, and on this basis treat partial properties as though they represent values of properties of the individual species in solution. Partial properties lend themselves completely to this interpretation, and one can always reason logically to correct conclusions from this point of view"

4. Computing partial molar properties.
While the definition

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

is perfectly valid, it is not always computationally convenient. We here devise a way to compute $\bar{J}_i$ from derivatives involving only mole fractions.

$$\bar{J}_i = \left(\frac{\partial(n\tilde{J})}{\partial n_i}\right)_{T,P,n_{j\neq i}} = n\left(\frac{\partial \tilde{J}}{\partial n_i}\right)_{T,P,n_{j\neq i}} + \tilde{J}\left(\frac{\partial n}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

but

$$\left(\frac{\partial n}{\partial n_i}\right)_{T,P,n_{j\neq i}} = 1$$

so,

$$\bar{J}_i = \tilde{J} + n\left(\frac{\partial \tilde{J}}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

Since $\tilde{J} = \tilde{J}(T, P, x_k)$

$$d\tilde{J} = \left(\frac{\partial \tilde{J}}{\partial T}\right)_{P,n_j} dT + \left(\frac{\partial \tilde{J}}{\partial P}\right)_{T,n_j} dP + \sum_k \left(\frac{\partial \tilde{J}}{\partial x_k}\right)_{T,P,n_{j\neq k}} dx_k$$

If we hold T, P constant we also know that

$$d\tilde{J} = \sum_k \left(\frac{\partial \tilde{J}}{\partial x_k}\right)_{T,P,n_{j\neq k}} dx_k$$

Divide by dn_i to get

$$\left(\frac{\partial \tilde{J}}{\partial n_i}\right) = \sum_k \left(\frac{\partial J}{\partial x_k}\right)\left(\frac{\partial x_k}{\partial n_i}\right)$$

But what is $\left(\frac{\partial x_k}{\partial n_i}\right)$?

$$\left(\frac{\partial(nx_k)}{\partial n_i}\right)_{n_{j\neq k}} = \left(\frac{\partial n_k}{\partial n_i}\right)_{n_{j\neq k}} = n\left(\frac{\partial x_k}{\partial n_i}\right)_{n_{j\neq k}} + x_k\left(\frac{\partial n}{\partial n_i}\right)_{n_{j\neq k}}$$

$$\left(\frac{\partial x_k}{\partial n_i}\right)_{n_{j\neq k}} = \frac{1}{n}\left[\left(\frac{\partial n_k}{\partial n_i}\right)_{n_{j\neq k}} - x_k\left(\frac{\partial n}{\partial n_i}\right)_{n_{j\neq k}}\right]$$

but

$$\left(\frac{\partial n}{\partial n_i}\right)_{n_{j\neq k}} = 1$$

and

$$\left(\frac{\partial n_k}{\partial n_i}\right)_{n_{j\neq k}} = \delta_{ki}$$

where δ_{ki} is the Kronecker delta,

$$\delta_{ki} = \begin{cases} 0, & k \neq i \\ 1, & k = i \end{cases}$$

Hence,

$$\left(\frac{\partial x_k}{\partial n_i}\right)_{n_{j\neq k}} = \frac{1}{n}\left(\delta_{ik} - x_k\right)$$

Use this in the above equation for $\left(\frac{\partial \tilde{J}}{\partial n_i}\right)$

$$\left(\frac{\partial \tilde{J}}{\partial n_i}\right) = \frac{1}{n}\sum_k \left(\frac{\partial \tilde{J}}{\partial x_k}\right)_{x_j} (\delta_{ik} - x_k) = \frac{1}{n}\left[\left(\frac{\partial \tilde{J}}{\partial x_i}\right)_{x_j} - \sum_k x_k \left(\frac{\partial \tilde{J}}{\partial x_k}\right)_{x_j}\right]$$

Multiply by n and put this back into

$$\bar{J}_i = \tilde{J} + n\left(\frac{\partial \tilde{J}}{\partial n_i}\right)_{T,P,n_{j\neq i}}$$

to get

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

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

$$\sum_i x_i = 1$$

If we consider this then we get

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

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

Hence, there are three different expressions for computing $\bar{J}_i$. All must give the same answer. The choice of which to use is a matter of convenience.