Phase Equilibrium: Conditions for Equilibrium (CfE)

Phase Diagrams: Conditions for Equilibrium (CfE)

- Write down the conditions for equilibrium for: a pure single phase system, a pure multi-phase system, and a multi-phase mixture
- Explain how energetic and entropic effects balance at equilibrium
- Use the Clapeyron equation and/or the Clausius-Clapeyron equation to relate T and P for pure species phase equilibrium
- Use the Antoine equation to relate T and P for pure species phase equilibrium
- Explain the relationship between the Clausius-Clapeyron equation and the Antoine equation
- Write exact differentials for extensive properties in terms of \( m+2 \) independent variables for mixtures of \( m \) species
- Define and explain the difference between the terms: pure species property, total solution property, and partial molar property
- Calculate total solution properties from partial molar properties
- Calculate partial molar properties
  - using graphical methods
  - using equations of state
  - using the Gibbs-Duhem equation
- Explain the origin of enthalpy, entropy, and volume changes due to mixing
- Calculate the enthalpy of solution from the enthalpy of mixing and vice versa
- Explain why the chemical potential is the relevant property for determining solution equilibrium

CfE: Gibbs Free Energy (Balancing Energy and Entropy)

Gibbs Free Energy (Balancing Energy and Entropy)

We spoke at the beginning of the course about the fact that equilibrium requires:

\[ T_v = T_L \rightarrow \text{thermal equilibrium} \]
\[ P_v = P_L \rightarrow \text{mechanical equilibrium} \]

What else?!
Our discussion of entropy suggests that our other condition(s) for equilibrium should be related to minimizing entropy; however, that is difficult to quantify because we need to examine the entire universe in order to do so. Instead, let's start with the first law for the closed system above (where a pure-species vapor and liquid are in equilibrium):

\[ dU = \delta Q + \delta W \]
\[ dU = \delta Q - PdV \]

Since we must have mechanical equilibrium, we know that \( P = P_v = P_L \) so that \( dP = 0 \).

Because of this we can subtract \( VdP \) from this equation without changing anything, so

\[ dU = \delta Q - PdV - VdP = \delta Q - d(PV) \]

Rearranging and using the definition of enthalpy:

\[ dU + d(PV) = dH = \delta Q \]

Now invoking the second law, we know that a real process satisfies:

\[ dS \geq \frac{\delta Q}{T} \]

Rearranging and using our result from above:

\[ TdS \geq \delta Q = dH \text{ so that } TdS \geq dH \]

Rearranging:

\[ dH - TdS \leq 0 \]

Recalling the definition of the Gibbs free energy \( (G) \), we write

\[ G \equiv H - TS \]

so that

\[ dG = dH - d(TS) = dH - TdS - SdT \]

Once again, equilibrium requires that \( T = T_v = T_L \) so that \( dT = 0 \), and

\[ dG = dH - TdS \]

Combining with earlier result, we find that a useful condition for equilibrium is that

\[ dG \leq 0 \]

**NOTE:**

While one might be tempted to presume that equilibrium between vapor and liquid would not be possible, due to the fact that the entropy of a vapor is higher than that of a liquid (so why wouldn't it all become vapor?!), this is not true. The fact that it requires energy from outside the system to change the liquid into a vapor means that the increase in entropy of our system would be offset by a decrease in entropy of the surroundings.

**USEFUL:**

The Gibbs free energy simplifies equilibrium considerations because it allows us to only consider the system rather than the universe. It does this by explicitly accounting for entropy changes in the system and energy interactions with the surroundings.

**OUTCOME:**

Explain how energetic and entropic effects balance at equilibrium.
**Equilibrium: Two (pure) Phases**

We have shown that the criteria for equilibrium is:
\[ dG \leq 0 \]

For a mixture of two phases we can write:
\[ G = n_i g_i + n_v g_v \]

so that
\[ dG = n_i d g_i + g_i d n_i + n_v d g_v + g_v d n_v \]

Since we are assuming thermal equilibrium (constant \( T \)) and mechanical equilibrium (constant \( P \)), the state postulate says that \( g \) is fixed so that \( d g_i = d g_v = 0 \), so
\[ dG = g_i d n_i + g_v d n_v \]

At equilibrium the rate of change of material *from* one phase must be balanced by the rate of change of material *to* that phase, so that \( d n_v = -d n_i \) and
\[ dG = (g_i - g_v) d n_v \leq 0 \]

Once we reach equilibrium the inequality takes on the value of zero, so
\[ g_i = g_v \]

**OUTCOME:**

*Write down the conditions for equilibrium for: a pure single phase system, a pure multi-phase system, and a multi-phase mixture*

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**Clapeyron Equation**

Taking the criteria for phase equilibrium as our starting point:
\[ g_i = g_v \]

We can write:
\[ d g_i = d g_v \]

Using one of our fundamental property relations, for phase "k"
\[ d g_k = v_i d P - s_i d T \]

so
\[ v_i d P - s_i d T = v_i d P - s_i d T \]

\[ \frac{dP}{dT} = \frac{s_i}{v_i} \]

Recalling that we could also write
\[ g_k = h_k - T s_k \]

we have
\[ h_i - T s_i = h_v - T s_v \]
\[ s_i - s_v = \frac{h_i}{T} \]

combining we get
DEFINITION:
The Clapeyron equation relates the phase equilibrium pressure (often called $P_{sat}$) to the temperature for any combination of phases:

$$\frac{dP}{dT} = \frac{h_f-h_v}{T(v_f+v_v)}$$

OUTCOME:
Use the Clapeyron equation and/or the Clausius-Clapeyron equation to relate $T$ and $P$ for pure species phase equilibrium

CfE: Clausius-Clapeyron Equation

Clausius-Clapeyron Equation

Starting from the Clapeyron Equation:

$$\frac{dP}{dT} = \frac{h_f-h_v}{T(v_f+v_v)}$$

We can note that, in general:

$$(v_f-v_v) \approx -v_v$$

Taking $v_v$ from the ideal gas law ($v_v = \frac{RT}{P}$), and combining

$$\frac{dP}{dT} = \frac{h_f-h_v}{T(v_f+v_v)} = \frac{-P(h_f-h_v)}{RT^2} = \frac{P(h_f-h_l)}{RT^2} = \frac{\Delta h_v}{RT^2}$$

rearranging and integrating

$$\int \frac{dP}{P} = \int \frac{\Delta h_v}{R} \frac{dT}{T^2}$$

$$\ln P = \frac{\Delta h_v}{R} \frac{1}{T} + \text{Const}$$

NOTE:
This suggests that a plot of saturation pressure, $P_{sat}$ versus $\frac{1}{T}$ should yield a straight line. This is close to correct for most materials.

Perhaps a more useful way to use this equation is to know the saturation pressure at a particular temperature (say, the normal boiling point ... i.e., $P_{sat} = 1\text{bar}$):

$$\ln \frac{P_2}{P_1} = \frac{\Delta h_v}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

DEFINITION:
The Clausius-Clapeyron equation is a special case of the Clapeyron equation that assumes ideal gas behavior for the vapor and exploits the fact that the specific volume of a vapor is substantially larger than that of a liquid.

OUTCOME:
Use the Clapeyron equation and/or the Clausius-Clapeyron equation to relate $T$ and $P$ for pure species phase equilibrium

CfE: Antoine Equation
Antoine Equation
Since the Clausius-Clapeyron equation assumes ideal gas behavior for the vapor it is not strictly accurate for all fluids.
An empirical relation is often used that exploits the same general form of equation ...

**DEFINITION:**
The Antoine Equation is an empirical relation for the saturation pressure as a function of temperature that is loosely based on the Clausius-Clapeyron relation.

\[
\ln P = A - \frac{b}{c + T}
\]

**NOTE:**
The units on this equation make no sense, so we need to be careful with the constants A, B, and C.

**OUTCOME:**
Use the Antoine equation to relate \( T \) and \( P \) for pure species phase equilibrium

**OUTCOME:**
Explain the relationship between the Clausius-Clapeyron equation and the Antoine equation

**TEST:**
Use the Antoine equation to prove that the normal boiling point of water (which is pretty non-ideal) is 100°C.

CfE: Mixture Properties

**Mixing: One Phase**
We know from experience that:

In other words, since the interactions between molecules of A-A and B-B differs from the interaction between A-B, we get:
but we know that
\[ n_{\text{mixture}} = n_A + n_B \]
Combining these, we can show that the intensive property \( v \) gives
\[ v = v_{\text{mixture}} = x_A v_A + x_B v_B \]

**NOTE:**
This is actually quite general. That is, typically the mixture properties (either extensive or intensive) are **not** simply the sum (or weighted average) of the individual pure component properties.

Recall that, by the state postulate, we can write (note that we will now drop the subscript "mixture"):
\[ v = F(P, T) \]
We know that this works for a single phase pure component (we have a common example, \( P_v = RT \)). We can also write
\[ V = F(P, T, n) \]
which we also have experience with (\( PV = nRT \)). It turns out that for multiple components, the **Duhem relation** tells us that we can write
\[ V = F(P, T, n_1, n_2, n_3, \ldots, n_m) \]
Therefore, following the same procedure that we used for fundamental property relations, we can write
\[ dV = \left( \frac{\partial V}{\partial P} \right)_{T,n_i} dP + \left( \frac{\partial V}{\partial T} \right)_{P,n_i} dT + \sum_{j} \left( \frac{\partial V}{\partial n_j} \right)_{P,T,n_{\neq i}} dn_j \]

**OUTCOME:**
Write exact differentials for extensive properties in terms of \( m+2 \) independent variables for mixtures of \( m \) species

since at equilibrium we have \( dP = dT = 0 \), we can reduce this to
\[ dV = \sum_j \left( \frac{\partial V}{\partial n_j} \right)_{P,T,n_{\neq j}} dn_j \]

**DEFINITION:**
We define the **partial molar properties** as being
\[ \bar{V}_j = \sum_j \left( \frac{\partial V}{\partial n_j} \right)_{P,T,n_{\neq j}} dn_j \]
which we can think of as the contribution of species \( j \) to the mixture property.

We can rewrite our expression for \( dV \) then as
\[ d\bar{V} = \sum_j \bar{V}_j dn_j \]
Integrating this (and noting that the constant of integration is zero -- we will simply accept this for now):
\[ \bar{V} = \sum_j \bar{V}_j n_j \]
dividing by \( n_{\text{tot}} \) we can also write:
\[ v = \sum_j \bar{V}_j x_j \]
Just to be sure that we have our nomenclature right ...
**DEFINITION:**
We define the **total solution properties** as being the mixture properties which we will denote \( v_{\text{mixture}} \) or simple \( v \) (with specific volume as an example).

**DEFINITION:**
We define the **pure component properties** as being the properties of the individual components when they are not in a mixture and will denote it as \( v_i \).

**DEFINITION:**
We define the **partial molar properties** as being
\[
\bar{V}_j = \left( \frac{\partial V}{\partial n_j} \right)_{P,T,n_{\neq j}}
\]
which we can think of as the contribution of species \( j \) to the mixture property.

**OUTCOME:**
Define and explain the difference between the terms: pure species property, total solution property, and partial molar property.

CfE: Relations for Partial Molar Properties

**Partial Molar Property Relations**

Recall that:
\[ H = U + PV \]

If we take the derivative of both sides with respect to the number of moles of species \( j \):
\[
\left( \frac{\partial H}{\partial n_j} \right)_{P,T,n_{\neq j}} = \left( \frac{\partial U}{\partial n_j} \right)_{P,T,n_{\neq j}} + P \left( \frac{\partial V}{\partial n_j} \right)_{P,T,n_{\neq j}}
\]

since \( P \) is a constant
\[
\left( \frac{\partial H}{\partial n_j} \right)_{P,T,n_{\neq j}} = \left( \frac{\partial U}{\partial n_j} \right)_{P,T,n_{\neq j}} + P \left( \frac{\partial V}{\partial n_j} \right)_{P,T,n_{\neq j}}
\]

using the definition of partial molar properties, we note
\[
\bar{H}_i = \bar{U}_i + P \bar{V}_i
\]

**NOTE:**
This procedure works for any of the derived property definitions (i.e., \( G \) or \( A \) also).

Using the Duhem relation, we know that we can write a total differential for \( G \) in terms of \( T, P, \) and \( n_j \) as follows:
\[
dG = \left( \frac{\partial G}{\partial P} \right)_{T,n_i} dP + \left( \frac{\partial G}{\partial T} \right)_{P,n_i} dT + \sum \left( \frac{\partial G}{\partial n_j} \right)_{P,T,n_{\neq j}} dn_j
\]

From analysis of pure substance systems, we already had written
\[
dG = -SdT + VdP
\]
so we can combine these to get (recognize that we have invoked the definition of the partial molar \( \bar{G}_i \)):
Recalling from our Maxwell relations, we showed that
\[ -S = \left( \frac{\partial G}{\partial T} \right)_p \]
\[ V = \left( \frac{\partial G}{\partial P} \right)_T \]
Taking the derivative with respect to the number of moles of species \( j \) for these relations:
\[ -\left( \frac{\partial S}{\partial n_j} \right)_p = \left( \frac{\partial G}{\partial n_j} \right)_p \]
\[ \left( \frac{\partial V}{\partial n_j} \right)_p = \left( \frac{\partial G}{\partial n_j} \right)_T \]
Invoking the definition of the partial molar Gibbs free energy, and taking either the derivative with respect to \( T \) or \( P \) of that expression we get:
\[ \left( \frac{\partial G}{\partial T} \right)_P = \left( \frac{\partial G}{\partial n_j} \right)_P \]
\[ \left( \frac{\partial G}{\partial P} \right)_T = \left( \frac{\partial G}{\partial n_j} \right)_T \]
Noting that the right hand sides of the top equations in the last two groups are the same (as are the bottom two), we can write:
\[ -\tilde{S}_i = \left( \frac{\partial G_i}{\partial T} \right)_P \]
\[ \tilde{V}_i = \left( \frac{\partial G_i}{\partial P} \right)_T \]

**NOTE:**
The Maxwell relations (and all other fundamental property relations) can be re-written in terms of partial molar properties. This second expression in particular is of utility in calculations as it relates \( \tilde{G}_i \) to measurable properties.

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CfE: Calculating Partial Molar Properties: Gibbs-Duhem Relation

**Calculating Partial Molar Properties: Gibbs-Duhem Relation**
Noting that the partial molar volumes, \( \tilde{V}_i \), may be summed to yield the total solution (extensive) volume:
\[ V = \sum \tilde{n}_i \tilde{V}_i \]
Taking the derivative of both sides:
\[ dV = d\left( \sum \tilde{n}_i \tilde{V}_i \right) = \sum_i (\tilde{V}_i d\tilde{n}_i + \tilde{n}_i d\tilde{V}_i) \]
recall that, from the definition of partial molar properties:
\[ dV = \sum_i \tilde{V}_i d\tilde{n}_i \]
so this can be eliminated from our equation to give the Gibbs-Duhem relation:
\[ \sum_i \tilde{n}_i d\tilde{V}_i = 0 \]

**DEFINITION:**
The *Gibbs-Duhem* equation relates the partial molar property values of one of the components in a mixture to that of the other species. This makes sense since the reason that we do not use the
pure component specific volumes \((\tilde{V}_i \neq v_i)\) is specifically because the interaction \(a-a\) is different from \(a-b\) (but it should not be different from \(b-a\)).

Using the Gibbs-Duhem relation for a binary mixture goes as follows:

\[
d\tilde{V}_a n_a + d\tilde{V}_b n_b = 0
\]

if we divide both sides by \(dx_a\) and \(n_{tot} = (n_a + n_b)\),

\[
x_a \frac{d\tilde{V}_a}{dx_a} + x_b \frac{d\tilde{V}_b}{dx_a} = 0
\]

if we note that \(x_b = 1 - x_a\) we can rearrange and integrate to get

\[
\tilde{V}_b = \int \tilde{d}\tilde{V}_b = -\int \left( \frac{2a}{\tilde{V}_a} \frac{d\tilde{V}_a}{dx_a} \right) dx_a
\]

**NOTE:**
If we know an expression for \(\tilde{V}_a\) (or at least how the slope changes with \(x_a\)), we can evaluate this integral to get \(\tilde{V}_b\).

**OUTCOME:**
Calculate partial molar properties using the Gibbs-Duhem equation

**TEST YOURSELF:**
If the partial molar volume of component "a" in an a-b mixture is known to be given by:

\[
\tilde{V}_a = 50x_a + 150x_b + 30x_ax_b
\]

determine \(\tilde{V}_b\) using the Gibbs-Duhem equation.

CfE: Calculating Partial Molar Properties: Equations of State

**Calculating Partial Molar Properties: EOS**

Another method of calculating partial molar properties is to use equations of state.

If we have a mixture that is well described by a volume-explicit virial equation of state, so that:

\[
z = \frac{V}{RT} = 1 + B_{mix} P
\]

**NOTE:**
Here \(v\) is the "total solution property", so it represents the specific volume of the actual mixture of the fluids.

If we assume that we have a binary mixture of materials "1" and "2", we have discussed in the past that \(B_{mix}\) is related to binary interactions between molecules of types 1 and 2:

\[
v = \frac{RT}{p} + y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22}
\]

We know that, in order to calculate a partial molar property, we need to start with an extensive property, so we multiply by \(n_{tot} = n_1 + n_2\), so

\[
V = n_{tot} v = (n_1 + n_2) \frac{RT}{P} + \frac{n_1^2 B_{11} + 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)^2}
\]

Taking the derivative with respect to \(n_1\) ill give us \(\tilde{V}_1\) so

\[
\tilde{V}_1 = \left( \frac{\partial V}{\partial n_1} \right)_{P,T,n_2} = \frac{RT}{P} + \frac{2n_1 B_{11} + 2n_2 B_{12}}{(n_1 + n_2)^2} \cdot \frac{n_1^2 B_{11} - 2n_1 n_2 B_{12} + n_2^2 B_{22}}{(n_1 + n_2)^2}
\]
which we can simplify to
\[ \tilde{\nu}_1 = \frac{RT}{P} + 2y_1B_{11} + 2y_2B_{12} - B_{mix} \]

**NOTE:**
We can then calculate \( \tilde{\nu}_2 \) either following the same procedure of the Gibbs-Duhem equation.

**OUTCOME:**
Calculate partial molar properties using equations of state (and mixing relations)

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CfE: Calculating Partial Molar Properties: Graphical Methods

**Calculating Partial Molar Properties: Graphical Methods**

Start with the summation equation for partial molar properties:
\[ \nu = \sum_j x_j \tilde{\nu}_j \]

For a binary mixture this gives:
\[ \nu = x_1 \tilde{\nu}_1 + x_2 \tilde{\nu}_2 = x_1 \tilde{\nu}_1 + (1-x_1) \tilde{\nu}_2 \]

Taking the derivative with respect to \( x_1 \) of both sides:
\[ \frac{d\nu}{dx_1} = \tilde{\nu}_1 - \tilde{\nu}_2 \]

Multiplying both sides by \( x_1 \) and then adding and subtracting \( x_2 \tilde{\nu}_2 \) gives:
\[ x_1 \frac{d\nu}{dx_1} = x_1 \tilde{\nu}_1 - x_1 \tilde{\nu}_2 + (x_2 \tilde{\nu}_2 - x_2 \tilde{\nu}_2) = (x_1 \tilde{\nu}_1 + x_2 \tilde{\nu}_2) - (x_2 \tilde{\nu}_2 - x_2 \tilde{\nu}_2) = \nu - \tilde{\nu}_2 \]

When we rearrange this, we note that \( \nu \) versus \( x_1 \) gives a straight line:
\[ \nu = \tilde{\nu}_2 + x_1 \frac{d\nu}{dx_1} \]

**NOTE:**
The slope of this line will be the local slope (often called the tangent line) of the \( \nu \) curve, and the intercept of the line will be \( \tilde{\nu}_2 \).

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**PROCEDURE:**
At the desired concentration \( (y_a \) value) go up to the \( \nu \) curve (black). Draw a tangent line. Follow the tangent line to the \( y \)-intercept to
get $\tilde{V}_b$. Note that you go to an "a" concentration to get a "b" partial molar quantity. Also, note that the $\tilde{V}_a$ and $\tilde{V}_b$ curves are shown for display purposes only, they are not typically known.

**NOTE:**
Using this procedure at $y_a = 1$ will yield the "infinite dilution" value for $\tilde{V}_b$ ($\tilde{V}_b^\infty$, that is the value of $\tilde{V}_b$ where $y_b = 0$).

**OUTCOME:**
Calculate partial molar properties using graphical methods.

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**Property Changes upon Mixing**

As discussed previously, mixtures do not simply exhibit the weighted average properties of their component parts. We have spent the last several sets of notes showing exactly how to calculate the contribution of each of the components to the mixture. That is, we have recognized that:

$$V \neq \sum n_i \tilde{V}_i$$

Instead:

$$V = \sum n_i \tilde{V}_i$$

so that, in general:

$$\tilde{V}_i \neq \tilde{V}_i$$

Besides the methods previously discussed, a typical way to experimentally handle this fact is to define property changes of mixing, such as the $\Delta V_{\text{mix}}$, as:

$$\Delta V_{\text{mix}} = V - \sum n_i \tilde{V}_i$$

That is, $\Delta V_{\text{mix}}$ specifically accounts for the difference between the naive assumption (that mixtures yield the weighted average) and reality. Another way to write this is

$$\Delta V_{\text{mix}} = \sum n_i (\tilde{V}_i - \tilde{V}_i')$$

or graphically, the $\Delta V_{\text{mix}}$ (or $\Delta V_{\text{mix}}$ if we speak in terms of intensive rather than extensive volume):

![Graphical representation of property changes upon mixing](image)
NOTE:
The value of $\Delta V_{\text{mix}}$ (or $\Delta V_{\text{mix}}$) goes to zero at the two endpoints (pure component solutions), and varies in magnitude as concentration varies.

When $\Delta V_{\text{mix}}$ is measured experimentally, it is typically tabulated for the mixture in question, so that it may be used to determine the total solution property by rearranging its definition:

$$V = \sum n_i V_i + \Delta V_{\text{mix}}$$

NOTE:
One should note that the property changes are measured per unit mass/mole or mixture/solution. Also, a particularly useful property change that one can find tabulated is $\Delta H_{\text{mix}}$.

OUTCOME:
Explain the origin of enthalpy, entropy, and volume changes due to mixing.

CfE: $\Delta H_{\text{mix}}$ vs. $\Delta H_{\text{sol}}$

$\Delta H_{\text{mix}}$ vs. $\Delta H_{\text{sol}}$

Sometimes the tabulated values of property changes upon mixing and reported in terms of a change per unit mass/mole solvent rather than per solution.

DEFINITION:
The $\Delta H_{\text{sol}}$ or "delta H of solution" is measured as the enthalpy change when 1 mol of solute is mixed with a specified amount of solvent (rather than solution).

This definition leads to a simple relationship between $\Delta H_{\text{mix}}$ and $\Delta H_{\text{sol}}$. That is:

$$\Delta H_{\text{sol}} = \frac{\Delta H_{\text{mix}}}{x_{\text{solute}}}$$

or:

$$\Delta H_{\text{mix}} = x_{\text{solute}} \Delta H_{\text{sol}}$$

where $x_{\text{solute}}$ is the mole fraction of the solute (dissolved or minor component).

OUTCOME:
Calculate the enthalpy of solution from the enthalpy of mixing and vice versa.

NOTE:
Typically, one can find tabulated values of $\Delta H_{\text{mix}}$ and $\Delta V_{\text{mix}}$, but not other properties. This is due to the fact that often the $\Delta S_{\text{mix}}$ is assumed to be given by the ideal gas result. That is $\Delta S_{\text{mix}} = -\sum_i n_i R \ln(y_i)$. By combining the tabulated values with this result for $\Delta S_{\text{mix}}$, one can calculate most other mixing values.
NOTE:
This expression for $\Delta S_{\text{mix}}$ will be true for "regular" solutions. We will discuss deviations from this behavior in the next section.

CfE: Phase Equilibrium for Mixtures

Phase Equilibrium for Mixtures
We have shown that, for pure components, equilibrium is given when:
\[ dG = 0 \]
or
\[ g_L = g_v \]
For a mixture of multiple components (and at least two phases) we can start at the same place:
\[ dG = 0 = dG_L + dG_v = [-SdT + VdP + \sum \tilde{G}_i d_{n_i}]_L + [-SdT + VdP + \sum \tilde{G}_i d_{n_i}]_v \]
Since we are again assuming mechanical and thermal equilibrium, we have
\[ T_L = T_v \text{ and } P_L = P_v \] so that
\[ dT_L = dT_v = 0 \text{ and } dP_L = dP_v = 0 \]
this simplifies our $dG$ expression to
\[ dG = 0 = \left[ \sum \tilde{G}_i d_{n_i} \right]_L + \left[ \sum \tilde{G}_i d_{n_i} \right]_v \]
At the microscopic scale, the rate of change of material from one phase must be balanced by the rate of change of material to that phase for each component, so that $d_{n_v} = -d_{n_L}$ and
\[ dG = 0 = \sum [\tilde{G}_{i_L} - \tilde{G}_{i_v}] d_{n_L} \]
This is true when the partial molar Gibbs free energy of each component is equal across the phases. That is
\[ \tilde{G}_{i_L} = \tilde{G}_{i_v} \]

**DEFINITION:**
Differences in the partial molar Gibbs free energy create a potential for the material to change phase. Thus, this quantity is often called the chemical potential or species, $i$, and denoted as $\mu_i$.
\[ \mu_i = \tilde{G}_i \]
so we can write our phase equilibrium condition (for mixtures) as
\[ \mu_{i_L} = \mu_{i_v} \]

**OUTCOME:**
Explain why the chemical potential is the relevant property for determining solution equilibrium