**Week 9**

**Outline**
- Phase Transitions
- Clausius - Clapeyron Equations
- One - Component Phase Diagrams

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**Phase Transitions**

\[
\text{Solid} \xrightarrow{\text{freezing}} \text{Liquid} \xrightarrow{\text{Vaporization}} \text{Gas} \xrightarrow{\text{Condensation}} \text{Liquid} \xrightarrow{\text{freezing}} \text{Solid}
\]

For a one component system at equilibrium between 2 phases (const. \( T \& P \))

\[
de G_{T,P} = 0 \implies \mu_\text{Phase I} = \mu_\text{Phase II}
\]

Since the chemical potentials at equilibrium

\[
\left( \frac{dP}{dT} \right)_\text{equilibrium} = \frac{\Delta \overline{S}_\phi}{\Delta V_\phi}
\]

(derived from \( d\mu = -\overline{S}dT + \overline{V}dP \))

\[
* \left( \frac{d\mu}{dT} \right) \text{ is useful for HW 44 } *
\]

Since equilibrium phase change is a reversible process

\[
\Delta \overline{S}_\phi = \frac{\Delta H_\phi}{T}
\]

\[
\implies \left( \frac{dP}{dT} \right)_{\text{Phase Change}} = \frac{\Delta H_\phi}{T \Delta V_\phi}
\]

\[
\text{* Note } \Delta H_{\text{Sublimation}} = \Delta H_{\text{Melting}} + \Delta H_{\text{Vaporization}} \text{ } \text{ What?}
\]
For Ideal gas:

\[ \frac{d \ln P}{dT} = \frac{\Delta H^0}{RT^2} \]

Only for

\[ \ln \left( \frac{P_2}{P_1} \right) = \frac{\Delta H^0}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right) \]

Note: \( K_{eq} = \left( \frac{a_{gas}}{a_{soln}} \right) = \left( \frac{P_0}{1} \right) \)

Clausius-Clapeyron Eq. useful for #1 \# 46 & 49

One-Component Phase Diagram

Gibbs Phase Rule: \( f = C - P + 2 \)

One-Component System \( C = 1 \)

\[ \Rightarrow f = 3 - P \]

1 Phase \( \Rightarrow f = 2 \), \( T \) and \( P \) Covary \( \Rightarrow \) Plane

2 Phases \( \Rightarrow f = 1 \), Only \( T \) or \( P \) Varies \( \Rightarrow \) Line

3 Phases \( \Rightarrow f = 0 \), \( T \) and \( P \) fixed \( \Rightarrow \) Point
Planes \((f=2)\)

See solid, liquid, gas planes. Both \(P\) and \(T\) are free.

Lines \((f=1)\)

1. Solid \(\leftrightarrow\) liquid \(\left(\frac{dP}{dT}\right)_S = \frac{\Delta H_{\text{melt}}}{T \Delta V_{\text{melt}}}\)

2. Liquid \(\leftrightarrow\) gas \(\left(\frac{dlnP}{dT}\right)_l = \frac{\Delta H_{\text{vap}}}{RT^2}\)

3. Solid \(\leftrightarrow\) gas \(\left(\frac{dlnP}{dT}\right)_s = \frac{\Delta H_{\text{sub}}}{RT^2}\)

Clausius-Clapeyron

\(P\) and \(T\) are dependent on each other.

Points \((f=0)\)

Critical Point Both \(P\) and \(T\) are fixed
Outline

* Multicomponent Phase Behavior
* Ideal and Real Solutions
* Thermodynamic Relations of Liquid Mixtures

Multicomponent Phase Behavior

Still using $f = C - P + 2$

Where $f =$ degrees of freedom
$P_i =$ number of phases existing simultaneously
$C =$ number of components

For multicomponent systems $C \neq 1$

Phase diagrams of multicomponent (m.c.) systems are more complex... (See supplemental video)

Important roles on phase diagram

* Melting points of individual components
* Melting ranges of the mixed components
* Eutectic Point (if it exists!)

Ideal and Real Solutions

Ideal solutions assume all molecular interactions are equal! $\Delta H_{\text{mix}} = 0$

An ideal solution is one that follows Raoult's Law

$P_i = \chi_i P_i^*$

Where: $P_i =$ vapor pressure above liquid of component $i$
$\chi_i =$ mole fraction of component $i$
$P_i^* =$ vapor pressure of the pure component $i$
Real Solutions obey Raoult's Law in highly dilute Conditions.

All Solutions have the following:

\[ P_i^{vapor} = a_i^{(l)} P_i^{*} \]  \( \uparrow \) pressure of component i (pure)

\[ a_i^{(l)} \]  \( \uparrow \) activity of component i

For ideal conditions \( a_i^{(l)} = x_i \)  \( \downarrow \) mole fraction

For Real Solutions \( a_i^{(l)} = \gamma_i^{(l)} x_i \)

\( \gamma_i^{(l)} \) activity coefficient

Thermodynamic Relations of Liquid mixtures

Assume equilibrium \( H_i^{(l)} = H_i^{(v)} \)

\[ H_i^{(l)}(T, P, x_i^{(l)}) = H_i^{(l)}(T) + RT \ln \gamma_i^{(l)} x_i \quad \text{(Ideal)} \]

\[ \cdots \quad + RT \ln (\gamma_i^{(l)} x_i) \quad \text{(Real)} \]

Mixing of two solutions under const. \( T, P \):

\[ \Delta H_{mix} = 0 \]

\[ \Delta V_{mix} = V_{mixture} = \sum_i V_i \ \text{(before mixing)} = 0 \]

\[ \Delta S_{mix} = - \sum_i n_i R \ln \gamma_i \]

\[ \Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix} = \sum_i n_i R T \ln \gamma_i \]

\[ \Delta U_{mix} = \Delta H_{mix} - \Delta (PV)_{mix} = 0 \]

\[ \Delta A_{mix} = \Delta U_{mix} - T \Delta S_{mix} = \sum_i n_i R T \ln \gamma_i \]