Chapter 8: Phase Diagrams

Phase Diagrams

- Pure substances
  Phases: uniform with respect to composition and state of aggregation on both microscopic and macroscopic length scale
- Solids, liquids and gases
- Solids: many different phases (crystal structures)

What determines which phase is thermodynamically most stable?

Key quantity $\mu = G_m$ at particular $T, P$ : lowest $\mu$ defines stable phase
  $\rightarrow$ phases can coexist in thermodynamic equilibrium $\mu_I = \mu_{II}$

For pure substances

$$d\mu = -S_m dT + V_m dP$$

$\mu$ decreases with increasing $T$ ($S_m > 0$)

$\mu$ increases with $V_m > 0$

$$S_{\text{solid}} < S_{\text{liquid}} < S_{\text{gas}}$$

$$V_{\text{solid}} \approx V_{\text{liquid}} < V_{\text{gas}}$$

$$\Delta S_{\text{heating}} = \int \frac{C_p}{T}, \quad \Delta S_{\text{phase trans}} = \frac{\Delta H_{\text{phase}}}{T_{\text{phase}}}$$
Situation A: 3 phases at different $T$
Situation B: 2 phases $(s + g)$
A or B depends on pressure (B: low pressure)

Happens at very particular $P, T : P_{\text{triple}}, T_{\text{triple}}$

Dependence of $\mu$ on $P$

$$d \mu = -S_m dT + V_m dP$$

$$\left( \frac{\partial \mu}{\partial P} \right)_T = V_m \quad V_m^{\text{gas}} \gg V_m^{\text{solid/liquid}}$$
$T^{P_2}_{vap} > T^{P_1}_{vap}$ if $P_2 > P_1$ (eg. Pressure cooker, cook in the mountains changes boiling temperature)

Solid – liquid

Usually $V^\text{liquid}_m > V^\text{solid}_m$ → with the exception of water, where $V^\text{Ice}_m > V^\text{water}_m$, since $\rho^\text{Ice}_m < \rho^\text{water}_m$. Ice floats on water, if reversed lakes would freeze solid.

With increasing $P$ benzene becomes solid, however with ice as $P$ increases, ice becomes liquid water.
Calculating $\Delta H_{\text{sublimation}}$

<table>
<thead>
<tr>
<th>Phase Transformation</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>solid $\rightarrow$ gas</td>
<td>$\Delta H_{\text{sub}}$</td>
</tr>
<tr>
<td>solid $\rightarrow$ liquid</td>
<td>$\Delta H_{\text{fus}}$</td>
</tr>
<tr>
<td>liquid $\rightarrow$ gas</td>
<td>$\Delta H_{\text{vap}}$</td>
</tr>
</tbody>
</table>

Changes in $\Delta H$ due to change in $P \rightarrow$ vanishes in limit

At the triple point:

$$
\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}
$$

$$
\Delta H_{\text{sub}} > \Delta H_{\text{fus}} \text{ or } \Delta H_{\text{vap}}
$$

Clapeyron Equation

Describes $P - T$ coexistence curve:

Phases equilibrium $\alpha$ and $\beta$

$$
\mu_\alpha = \mu_\beta
$$

$$
d \mu_\alpha = d \mu_\beta
$$

$$
-S_{\alpha,m}dT + V_{\alpha,m}dP = -S_{\beta,m}dT + V_{\beta,m}dP
$$

$$
(S_{\beta,m} - S_{\alpha,m})dT = (V_{\beta,m} - V_{\alpha,m})dP
$$

$$
\Delta S^m_{\alpha \rightarrow \beta}dT = \Delta V^m_{\alpha \rightarrow \beta}dP
$$

Take the limit...

$$
\left( \frac{\partial P}{\partial T} \right)_{\text{coexistence curve}} = \frac{\Delta S^m_m}{\Delta V^m_m}
$$

either $\alpha \rightarrow \beta$ or $\beta \rightarrow \alpha$

$$
\Delta S_{\text{phase}}^m = \frac{\Delta H_{\text{phase}}^m}{T_{\text{phase}}}
$$

a) Solid – liquid coexistence:
\[
\left( \frac{\partial P}{\partial T} \right)_{\text{coexistence curve}} = \frac{\Delta S_m}{\Delta V_m} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}} \Delta V_m} \quad \Delta V_m = V_{\text{solid}} - V_{\text{liquid}} \quad V_m = \frac{m}{\rho}
\]

→ calculate slope of \( \left( \frac{\partial P}{\partial T} \right)_{\text{coexistence curve}} \)

\[
\frac{\Delta P}{\Delta T} = \frac{\Delta H_{\text{fus}}}{T_{\text{fus}} \Delta V_m}
\]

Melt under high pressure

\[ T_{\text{melt}} (\text{high } P) \neq T_{\text{melt}} (\text{low } P) \]

b) Solid – gas or liquid – gas coexistence:

\[
\left( \frac{\partial P}{\partial T} \right)_{\text{coexistence curve}} = \frac{\Delta H_{\text{trans}}}{T_{\text{trans}} \Delta V_m} \quad \Delta V_m = V_{\text{gas}} - V_{\text{solid/liquid}} \approx V_{\text{gas}}
\]

\[
\left( \frac{\partial P}{\partial T} \right)_{\text{coexistence curve}} = \frac{\Delta H_{\text{trans}} P}{T_{\text{trans}} RT_{\text{trans}}} \quad V_{\text{gas}} = \frac{V}{n} = \frac{RT}{P}
\]

\[
\left( \frac{\partial P}{\partial T} \right)_{\text{coexistence curve}} = \Delta H \frac{P}{RT^2} \quad \text{(The usual sloppy derivation follows)}
\]

\[
\frac{dP}{P} = \frac{\Delta H}{R} \frac{dT}{T^2} \quad \text{(is exact differential...)}
\]

\[
\int_{P_i}^{P_f} \frac{dP}{P} = \int_{T_i}^{T_f} \frac{\Delta H}{R} \frac{dT}{T^2} \quad \text{assume } \Delta H \text{ constant}
\]

\[
\ln P_f - \ln P_i = \frac{\Delta H}{R} \left( \frac{1}{T_f} - \frac{1}{T_i} \right)
\]

\[
\ln \left( \frac{P_f}{P_i} \right) = \ln \left( \frac{P_f}{P_o} \right) - \frac{\Delta H}{R} \left( \frac{1}{T_f} - \frac{1}{T_i} \right) \quad \Delta H = \Delta H_{\text{vap}} \text{ or } \Delta H_{\text{sub}}
\]

\[
\frac{dP}{dT} : l \rightarrow g \text{ (flat)} > \frac{dP}{dT} : s \rightarrow g \text{ (steep)}
\]

True for every substance
Example 8.2 in book

All kinds of things to calculate with Clapeyron

Vapour Pressure of Benzene

Change in Vapour pressure with respect to \( T \) can be calculated with solid/liquid – gas coexistence curve

100% humidity in bath \( P_{H_2O} = P^* \) (Vapour P of H\(_2\)O)