LECTURE # 26, 11-23-09

\[ \mu \text{ vs } T \text{ for different phases} \]

- Recall our derivation of

\[ d\mu = -S^*_m \, dT + V_m \, dP \]

for infinitesimal changes in \( T \) & \( P \) for a pure (single-component) system in a single phase

- It follows that

\[ (\frac{\partial \mu}{\partial T})_P = -S^*_m, \quad (\frac{\partial \mu}{\partial P})_T = V_m \]

- Recall also that \( S^*_m \) depends only weakly on \( T \) \( \leftarrow \Delta S^*_m \approx C_m \ln \frac{T_2}{T_1} \) within a single phase

- And \( S^*_m \) jumps by \( \Delta H/T \) upon each change of phase: \( \Delta H_{\text{fus}}/T_{\text{fus}} \) & \( \Delta H_{\text{vap}}/T_{\text{vap}} \) both \( > 0 \)

\[ \Rightarrow S^*_m \text{ sol} < S^*_m \text{ eq} < S^*_m \text{ gas} \]

- Consistent with above observations, we have

\[ \begin{align*}
\text{sol.} & \quad \text{eq.} & \quad \text{gas} \\
0 & \quad T_{\text{fus}} & \quad T_{\text{vap}} \\
0 & \quad T_m & \quad T_b
\end{align*} \]
And from \( \frac{\partial \mu}{\partial T} \big|_p = -S_m \) it follows that

![Graph Fig. 8.1](image)

**NOTE:** curves are slightly concave downwards, because \( S_m \) increases slightly with \( T \) in each phase.

**NOTE ALSO:** \( (\mu \text{ vs } T) \)-slope \( \leftrightarrow -S_m \) is smallest for sol. and largest for gas.

\[ \text{Increase in } T \Rightarrow \text{switch from sol. \( \rightarrow \) liq.} \]

\[ \text{followed by switch from liq. \( \rightarrow \) gas} \]

in order for \( M \leftrightarrow G_m \) to be minimum.

Two-phase coexistence at \( T_m \), and at \( T_b \).

\[ \frac{\partial \mu}{\partial P} \big|_T = +V_m > 0 \Rightarrow \text{all of above } \mu \text{ vs } T \]

curves are translated upwards as pressure is increased.
**Fig. 8.2:** left

- **EACH SHIFT UPWARD OF \( \mu \) vs \( T \)**
- **IS EQUAL TO**
- \( (\Delta P)V_m \) **FOR THAT PHASE**

\[ T_m, T'_m, T_b, T'_b \]

- **Dashed curves show \( \mu \) vs \( T \)**
- **for each phase at higher pressure**

\[ \text{sol.} - \text{liq.} - \text{gas} \]

- **Freezing/melting (\( T_m \)) and boiling (\( T_b \)) temperatures are higher at higher pressure because \( V_m^{\text{gas}} > V_m^{\text{liq}} > V_m^{\text{sol}} \)**
  - (hence freezing & boiling point elevations)

- **For a very few substances -- notably, water --**
  - \( V_m^{\text{liq}} < V_m^{\text{sol}} \) \( \implies \) **freezing point depression**
  - (see Fig. 8.2: right)

\[ \rightarrow \text{If pressure is decreased enough, i.e.,} \]

- \( \mu \) \( \text{gas} \) vs \( T \) curve **displaced sufficiently downward**, it will cross the \( \mu \) \( \text{sol} \) vs \( T \) curve before (at lower temperature than) it crosses the \( \mu \) \( \text{liq} \) vs \( T \) curve, \( \implies \) **"sublime"** (vaporize)

**SOLID WILL "SUBLIME" (VAPORIZE)**

**INSTEAD OF MELT**
At a somewhat higher pressure than that above, we have a three-phase coexistence.

We can collect all of the above results into a $P$ vs $T$ phase diagram: