Phase Equilibria in a One-Component System I

Goal: Understand the general phenomenology of phase transitions and phase coexistence conditions for a single component system.

The Chemical Potential $\mu$ controls phase transitions and phase equilibria, as well as equilibrium in chemical reactions.

For example, consider two phases (liquid and solid) of water at a fixed $(T, p)$.

If $\mu_s(T, p) = \mu_l(T, p)$ then... liquid water and ice coexist
If $\mu_s(T, p) > \mu_l(T, p)$ then... the water is in the liquid phase
If $\mu_s(T, p) < \mu_l(T, p)$ then... the water is in the solid phase

Phase diagrams

Describe the phase properties as a function of state variables, for example in terms of $(T, p)$. 

![Phase diagram of water](image)
For the **melting line**, for example, solid and liquid coexist, and

\[ \mu_s(T, p) = \mu_l(T, p) \]

One equation \([\mu_s(T, p) = \mu_l(T, p)]\), two variables \((T, p)\). This means that coexistence of two phases is described by \(T(p)\) or \(p(T)\). e.g. a line in the \((T, p)\) phase diagram.

At the **triple point**, the chemical potential of all three phases are the same… solid, liquid and gas coexist.

\[ \mu_s(T, p) = \mu_l(T, p) = \mu_g(T, p) \]

Two equations, two variables. This defines a unique point \((T_t, p_t)\) in the \((T, p)\) phase diagram.

For \(H_2O\), \(T_t = 273.16\) K and \(p_t = 0.006\) bar

(Recall the definition of the temperature scale in Lecture # 2)

In the **single phase (planar) regions** of the diagram, one of the chemical potentials is lower than the other two. \(T\) and \(p\) can be changed independently without changing phases.

The above cases are summarized by a **phase rule** for a one component system:

\[ F = 3 - p \]

Where \(F\) is the number of independent variables (also called the number of degrees of freedom) and \(p\) is the number of phases that coexist. This is a specific case of the "Gibbs' Phase Rule" which will be presented in more detail next week.
Can we understand the shape (i.e. slope) of the coexistence lines? For example, can we get an equation for \(\frac{dP}{dT}\)\text{coexistence}?

**Goal**: to be able to predict, using state functions, phase transitions and equilibria.

Let \(\alpha\) and \(\beta\) be two phases (e.g. \(\alpha, \beta\) are l, s, or g).

On a coexistence curve, \(\mu_\alpha(T, p) = \mu_\beta(T, p)\)

Now take \(T \to T + dT\) and \(p \to p + dp\), staying on the coexistence line.

So then \(\mu_\alpha \to \mu_\alpha + d\mu_\alpha\) and \(\mu_\beta \to \mu_\beta + d\mu_\beta\)

AND \(d\mu_\alpha = d\mu_\beta\)

But since \(d\mu = d\overline{G} = -\overline{S}dV + \overline{V}dp\), having \(d\mu_\alpha = d\mu_\beta\) implies that \(-\overline{S}_\alpha dT + \overline{V}_\alpha dp = \overline{S}_\beta dT + \overline{V}_\beta dp\) on the coexistence line.

That means \(\left(\frac{dp}{dT}\right)_{\text{coexist}} = \left[\frac{\overline{S}_\beta - \overline{S}_\alpha}{\overline{V}_\beta - \overline{V}_\alpha}\right] = \left(\frac{\Delta \overline{S}}{\Delta \overline{V}}\right)_{\alpha \to \beta}\)

Another way to write this is using \(\mu = \overline{G} = \overline{H} - T\overline{S}\) so that \(\mu_\alpha = \mu_\beta\) on the coexistence line implies \(\overline{H}_\alpha - T\overline{S}_\alpha = \overline{H}_\beta - T\overline{S}_\beta\) or \(\Delta \overline{H}_{\alpha \to \beta} = T\Delta \overline{S}_{\alpha \to \beta}\). Using this then we obtain the two forms of the **Clapeyron Equation** (These are always valid)

\[
\left(\frac{dp}{dT}\right)_{\text{coexist}} = \left(\frac{\Delta \overline{S}}{\Delta \overline{V}}\right)_{\alpha \to \beta} \quad \text{or} \quad \left(\frac{dp}{dT}\right)_{\text{coexist}} = \left(\frac{\Delta \overline{H}}{T\Delta \overline{V}}\right)_{\alpha \to \beta}
\]
Let's now use the Clapeyron equation to obtain a qualitative understanding of the phase diagram.

- \( l \rightarrow g \)

\[
\Delta S > 0, \quad \Delta V \gg 0 \quad \Rightarrow \quad \left( \frac{dp}{dT} \right)_{\text{coexist}} \left( \frac{\Delta S}{\Delta V} \right)_{l \rightarrow g} > 0, \text{ but small (not steep)}
\]

- \( s \rightarrow g \)

\[
\Delta S \gg 0, \quad \Delta V \gg 0 \quad \Rightarrow \quad \left( \frac{dp}{dT} \right)_{\text{coexist}} \left( \frac{\Delta S}{\Delta V} \right)_{s \rightarrow g} > 0, \text{ and steeper than for } l \rightarrow g
\]
• $s \rightarrow l$

For most substances $V_l \geq V_s$ (almost equal) and $\overline{S}_l > \overline{S}_s$

$$\Rightarrow \left( \frac{dp}{dT} \right)_{\text{coexist}} = \left( \frac{\Delta \overline{S}}{\Delta V} \right)_{s \rightarrow l} > 0,$$

and very steep

\[
\begin{align*}
\text{For most substances, raising the pressure above a liquid near the liq} \\
\text{to s coexistence line can cause it to freeze}
\end{align*}
\]

Except for one of the most important substances on earth: H$_2$O. In this case $\overline{V}_l < \overline{V}_s$, so that $\left( \frac{dp}{dT} \right)_{\text{coexist}} < 0$

Thus increasing the pressure above ice can cause it to melt, and the bottom of the ocean is not ice, but liquid water at 4°C.

Interestingly enough, silicon shows similar behavior (at much higher temperatures).

**Critical Point and Supercritical Fluids**

Does $l \rightarrow g$ coexistence curve extend to indefinitely high $T$ and $P$?

NO - it stops at critical point $(T_c, P_c)$
Above \((T_c, P_c)\), \(l\) and \(g\) become indistinguishable: single fluid phase for all \(T > T_c, P > P_c\).

Supercritical fluids are finding remarkably practical applications.

Supercritical water \((T_c = 375 \degree C, P_c = 221\) bar\):
- organic molecules readily soluble
- inorganic salts nearly insoluble
- organic compounds oxidized to \(CO_2, N_2,\) mineral salts

Supercritical carbon dioxide \((T_c = 31 \degree C, P_c = 75\) bar\):
- reaction solvent, replaces chlorinated and volatile organic compounds
- dry cleaning solvent, replaces perchloroethylene