

Phase Equilibria in a 1-Component System

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

The **Chemical Potential** μ controls phase transitions and phase equilibria.

Equilibrium condition - at equilibrium μ must be identical throughout the system

When multiple phases are present in equilibrium, μ must be the same in all phases

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

How does μ depend on T ?

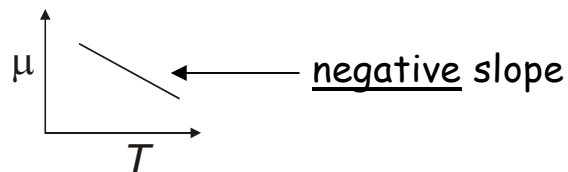
Start with Fundamental Equation for Gibbs (hence for μ)

$$dG = -SdT + Vdp \quad d\mu = -\bar{S}dT + \bar{V}dp \quad \left(\mu = \frac{G}{n} \right)$$

\bar{S} and \bar{V} are molar quantities

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -\bar{S} \quad \left(\frac{\partial \mu}{\partial p} \right)_T = \bar{V}$$

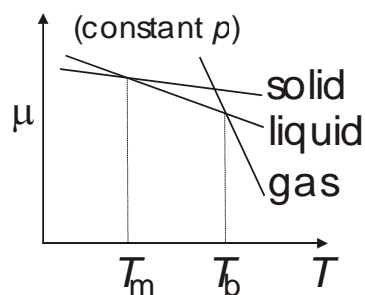
3rd Law tells us that $\bar{S} > 0 \Rightarrow \left(\frac{\partial \mu}{\partial T}\right)_p < 0$



Also we know that $\bar{S}_{\text{gas}} > \bar{S}_{\text{liquid}} > \bar{S}_{\text{solid}}$, and

$$\left(\frac{\partial \mu_{\text{gas}}}{\partial T}\right)_p = -\bar{S}_{\text{gas}}, \quad \left(\frac{\partial \mu_{\text{liq}}}{\partial T}\right)_p = -\bar{S}_{\text{liq}}, \quad \left(\frac{\partial \mu_{\text{solid}}}{\partial T}\right)_p = -\bar{S}_{\text{solid}}$$

so negative slope is steepest in gas phase, less steep in liquid phase, and least steep in solid phase.



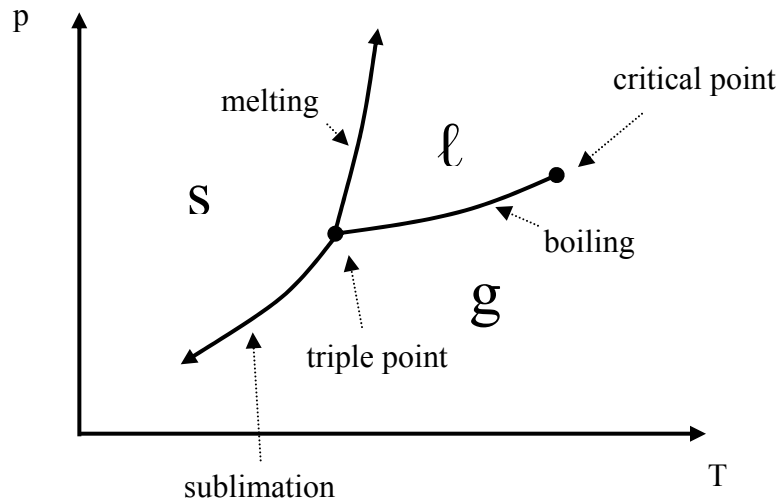
At the intersections between these curves we have

$$\mu(s, T_m) = \mu(l, T_m) \quad \mu(l, T_b) = \mu(g, T_b)$$

At the temperatures T_m and T_b , two phases coexist in equilibrium. At other temperatures only the phase with lowest μ is stable.

Phase diagrams

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



For the **melting line**, for example, solid and liquid coexist, and

$$\mu_s(T, p) = \mu_l(T, p)$$

One equation, 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 potentials 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 , $T_t = 273.16 \text{ K}$ and $p_t = 0.006 \text{ bar}$

At the **critical point** the gas-liquid line stops. Beyond the critical point on the gas-liquid line, the liquid and gas phase become indistinguishable, they merge into a single phase.

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.

Can we understand the shape (i.e. slope) of the coexistence lines?

That is, can we get an equation for $\left(\frac{dp}{dT}\right)_{\text{coexistence}}$?

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

Let α and β be two phases (e.g. α, β are ℓ, s , or g).

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

Now take $T \rightarrow T + dT$ and $p \rightarrow p + dp$, staying on the coexistence line.

So then $\mu_\alpha \rightarrow \mu_\alpha + d\mu_\alpha$ and $\mu_\beta \rightarrow \mu_\beta + d\mu_\beta$

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

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

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

Another way to write this is using $\mu = \bar{G} = \bar{H} - T\bar{S}$ so that $\mu_\alpha = \mu_\beta$ on the coexistence line implies $\bar{H}_\alpha - T\bar{S}_\alpha = \bar{H}_\beta - T\bar{S}_\beta$
 or $\Delta \bar{H}_{\alpha \rightarrow \beta} = T \Delta \bar{S}_{\alpha \rightarrow \beta}$.

Using this then we obtain the two forms of the **Clapeyron Equation** (These are always valid)

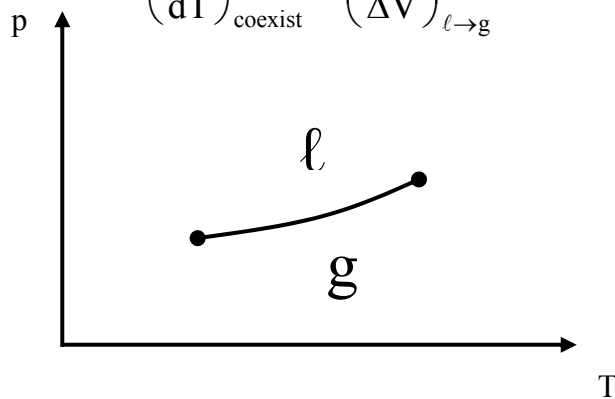
$$\boxed{\left(\frac{dp}{dT}\right)_{\text{coexist}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}}\right)_{\alpha \rightarrow \beta} \quad \text{or} \quad \left(\frac{dp}{dT}\right)_{\text{coexist}} = \left(\frac{\Delta \bar{H}}{T \Delta \bar{V}}\right)_{\alpha \rightarrow \beta}}$$

Let's now use the Clapeyron equation to understand the phase diagram.

* $\ell \rightarrow g$

$\Delta \bar{S} > 0, \quad \Delta \bar{V} \gg 0 \quad \Rightarrow \quad \left(\frac{dp}{dT}\right)_{\text{coexist}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}}\right)_{\ell \rightarrow g} > 0, \text{ but small}$

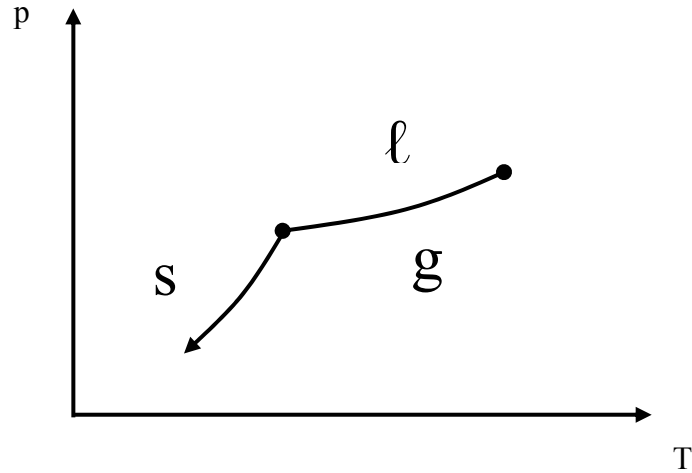
(not steep)



* $s \rightarrow g$

$$\Delta \bar{S} \gg 0, \quad \Delta \bar{V} \gg 0 \quad \Rightarrow \quad \left(\frac{dp}{dT} \right)_{\text{coexist}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{s \rightarrow g} > 0, \text{ and}$$

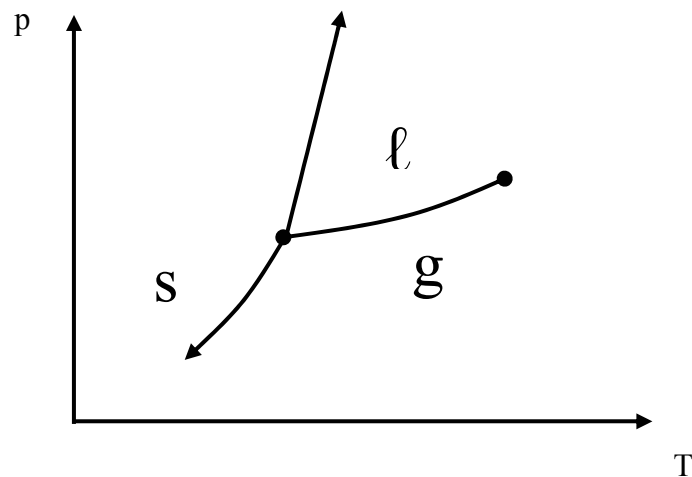
steeper than for $\ell \rightarrow g$



* $s \rightarrow \ell$

For most substances $\bar{V}_\ell \geq \bar{V}_s$ (almost equal) and $\bar{S}_\ell > \bar{S}_s$

$$\Rightarrow \left(\frac{dp}{dT} \right)_{\text{coexist}} = \left(\frac{\Delta \bar{S}}{\Delta \bar{V}} \right)_{s \rightarrow \ell} > 0, \text{ and very steep}$$



For most substances, raising the pressure above a liquid near the ℓ to s coexistence line can cause it to freeze

Except for one of the most important substances on earth: H_2O . In this case $\bar{V}_\ell < \bar{V}_s$, so that $\left(\frac{dp}{dT}\right)_{\text{coexist}} < 0$.

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

Critical Point and Supercritical Fluids

Does the $\ell \rightarrow g$ coexistence curve extend 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.

Supercritical fluids are finding remarkably practical applications.

Supercritical water ($T_c = 375\text{ }^\circ\text{C}$, $P_c = 221\text{ bar}$):

- organic molecules readily soluble

- inorganic salts nearly insoluble

- organic compounds can be oxidized to CO_2 , N_2 , mineral salts

Supercritical carbon dioxide ($T_c = 31\text{ }^\circ\text{C}$, $P_c = 75\text{ bar}$):

- reaction solvent, replaces chlorinated and volatile organic compounds

- dry cleaning solvent, replaces perchloroethylene