5.60 Thermodynamics & Kinetics
Spring 2008

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 $\mu_s(T, p) = \mu_\ell(T, p)$ then... liquid water and ice coexist

If $\mu_s(T, p) > \mu_\ell(T, p)$ then... the water is in the liquid phase

If $\mu_s(T, p) < \mu_\ell(T, p)$ then... the water is in the solid phase
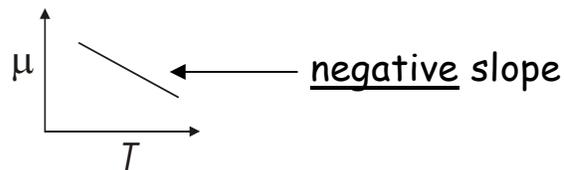
How does μ depend on T?

Start with Fundamental Equation for Gibbs (hence for μ)

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

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

$$\left(\frac{\partial \mu}{\partial T} \right)_p = -\bar{S} \qquad \left(\frac{\partial \mu}{\partial p} \right)_T = \bar{V}$$
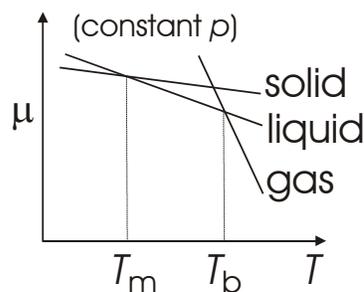
3rd Law tells us that $\bar{S} > 0 \quad \Rightarrow \quad \left(\dfrac{\partial \mu}{\partial T}\right)_p < 0$

μ ←   negative slope

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

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

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

$$\mu(s, T_m) = \mu(\ell, T_m) \qquad\qquad \mu(\ell, T_b) = \mu(g, T_b)$$

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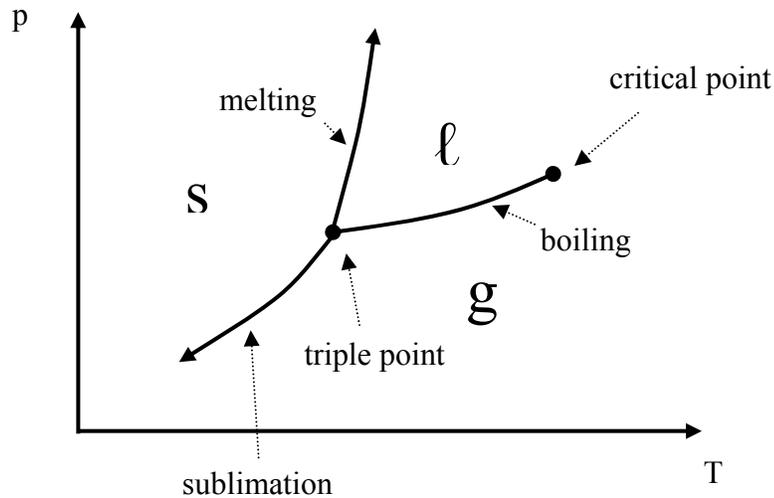
For the **melting line,** for example, solid and liquid coexist, and

$$\mu_s(T, p) = \mu_\ell(T, p)$$

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.

$$\mu_s(T, p) = \mu_\ell(T, p) = \mu_g(T, p)$$

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

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:

$$\boxed{F = 3 - p}$$

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 $\left(\dfrac{dp}{dT}\right)_{coexistence}$?

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 $p \rightarrow p + dp$, <u>staying on the coexistence line.</u>

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 $d\mu = d\overline{G} = -\overline{S}\,dT + \overline{V}\,dp$, 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 $\quad \left(\dfrac{dp}{dT}\right)_{coexist} = \left[\dfrac{\overline{S}_\beta - \overline{S}_\alpha}{\overline{V}_\beta - \overline{V}_\alpha}\right] = \left(\dfrac{\Delta\overline{S}}{\Delta\overline{V}}\right)_{\alpha\to\beta}$

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

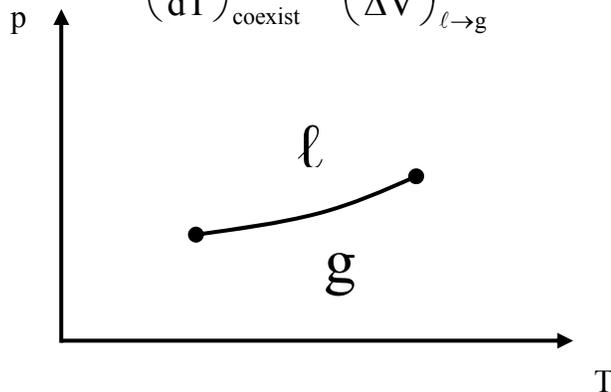Using this then we obtain the two forms of the **Clapeyron Equation** (These are <u>always</u> valid)

$$\left(\dfrac{dp}{dT}\right)_{coexist} = \left(\dfrac{\Delta\overline{S}}{\Delta\overline{V}}\right)_{\alpha\to\beta} \qquad \text{or} \qquad \left(\dfrac{dp}{dT}\right)_{coexist} = \left(\dfrac{\Delta\overline{H}}{T\Delta\overline{V}}\right)_{\alpha\to\beta}$$

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

✿ $\ell \to g$

$\Delta\overline{S} > 0,\quad \Delta\overline{V} \gg 0 \qquad \Rightarrow \qquad \left(\dfrac{dp}{dT}\right)_{coexist} = \left(\dfrac{\Delta\overline{S}}{\Delta\overline{V}}\right)_{\ell\to g} > 0$, but small
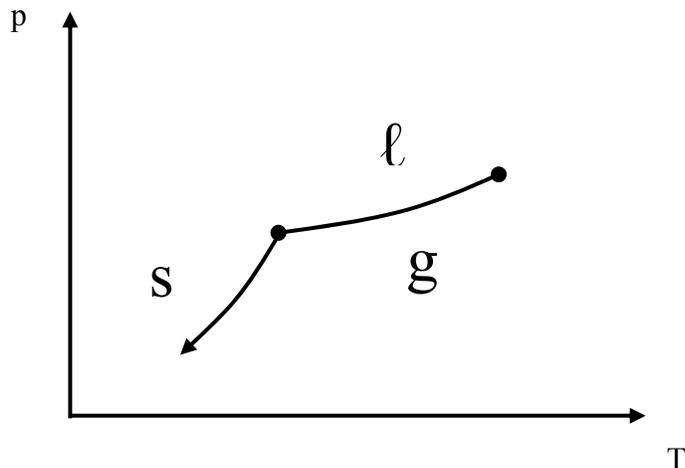
(not steep)

❀   s → g

$$\Delta \overline{S} \gg 0, \qquad \Delta \overline{V} \gg 0 \qquad \Rightarrow \qquad \left(\frac{dp}{dT}\right)_{coexist} = \left(\frac{\Delta \overline{S}}{\Delta \overline{V}}\right)_{s \to g} > 0, \text{ and}$$
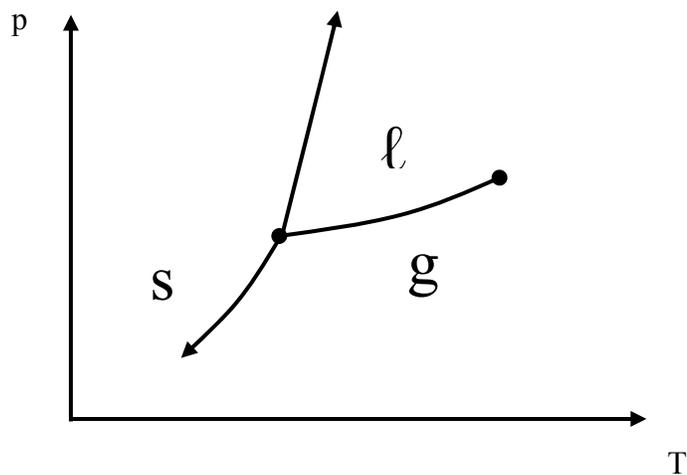
steeper than for $\ell \to g$

❀   s → ℓ

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

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

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 $\overline{V}_\ell < \overline{V}_s$, so that $\left(\dfrac{dp}{dT}\right)_{coexist} < 0$.

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

Critical Point and Supercritical Fluids

Does the ℓ → 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 °C, P_c = 221 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 °C, P_c = 75 bar):

     reaction solvent, replaces chlorinated and volatile organic compounds

     dry cleaning solvent, replaces perchloroethylene