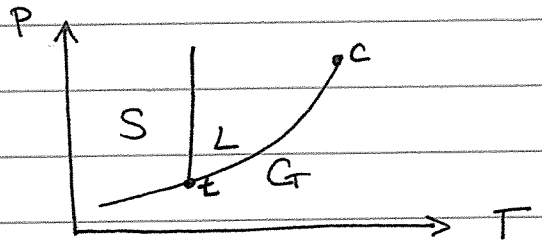
Phase Equilibria

A brief review of phase diagrams:



← The standard solid-liquid-gas behavior of most substances.

Water looks a bit different. The slope of the S/L coexistence line goes to the upper left.

t = the triple point where all 3 phases coexist

at this <u>one</u> point there are <u>no</u> thermodynamic "degrees of freedom" (P & T have been specified).

In the solid, liquid & gas regions there are 2 degrees of freedom (we can change P or T without changing phase)

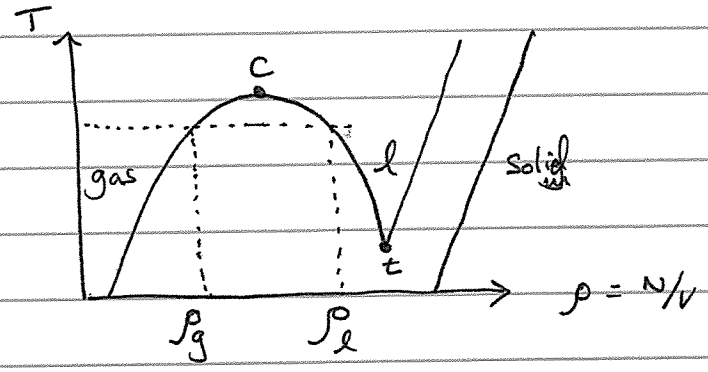
Along a <u>coexistence line</u> between 2 phases, we say there is <u>one</u> degree of freedom (if we change P, we must also change T to stay on the line).

The Gibbs phase rule: $f = 3 - p$

f = degrees of freedom; p = # of coexisting phases

Critical Points

Another way of viewing the same phase diagram



← An "orthobaric" density plot

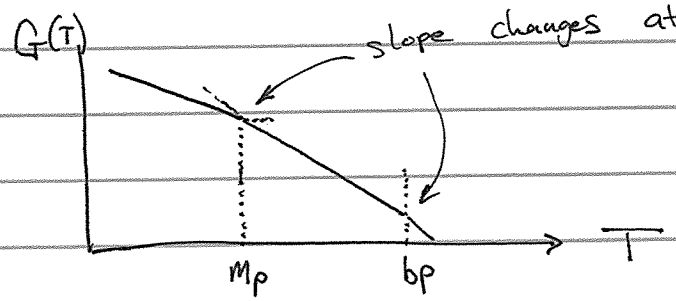
At any temperature, we can read across to the densities of the liquid & gas that are at equilibrium

Note that the densities of these coalesce at the critical point.

At the critical point, all sorts of strange things happen:

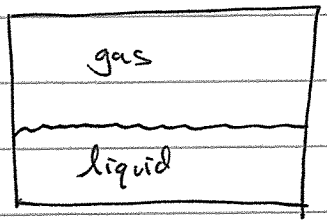
1) Density fluctuations occur at all length scales, so
2) incoming light is scattered (critical opalescence)
3) $\Delta S_{vaporization} = \frac{\Delta H_{vap}}{T}$ and both $\to 0$ at the critical point.

The Gibbs Free energy is closely tied to the phase diagram



G itself is continuous, but $\frac{\partial G}{\partial T}$ is discontinuous

Chemical Potentials



← if we're at the boiling point these phases are in equilibrium

$$G = G^l + G^g$$

if n moles of molecules move from one phase to the other:

$$dG = \left(\frac{\partial G^l}{\partial n^l}\right) dn^l + \left(\frac{\partial G}{\partial n^g}\right) dn^g$$

but, $dn^l = -dn^g$

$$\therefore \quad dG = \left[\left(\frac{\partial G}{\partial n^g}\right)_{P,T} - \left(\frac{\partial G}{\partial n^l}\right)_{P,T}\right] dn^g$$

$$dG = \left[\mu_g - \mu_l\right] dn^g$$

(μ_g, μ_l ← chemical potentials)

At equilibrium $dG = 0$, but dn^g isn't zero because molecules are constantly shuttling back & forth, so

$$\mu_g = \mu_l \quad \text{at equilibrium coexistence}$$

In general $\mu_\alpha \equiv \left(\frac{\partial G}{\partial n_\alpha}\right)_{T,P}$

$$\mu_\alpha(T,P) = \mu_\beta(T,P) \quad \text{at equilibrium}$$

Take derivatives of both sides:

$$\left(\frac{\partial \mu_\alpha}{\partial T}\right)_P dT + \left(\frac{\partial \mu_\alpha}{\partial P}\right)_T dP = \left(\frac{\partial \mu_\beta}{\partial T}\right)_P dT + \left(\frac{\partial \mu_\beta}{\partial P}\right)_T dP$$

remember that μ_α is just the Gibbs free energy/mole, so:

$$\left(\frac{\partial \mu_\alpha}{\partial P}\right)_T = \frac{1}{n_\alpha}\left(\frac{\partial G_\alpha}{\partial P}\right)_T = \frac{1}{n_\alpha} V_\alpha = \text{molar volume of } \alpha$$

$$\left(\frac{\partial \mu_\alpha}{\partial T}\right)_P = \frac{1}{n_\alpha}\left(\frac{\partial G_\alpha}{\partial T}\right)_P = \frac{1}{n_\alpha}\left(-S_\alpha\right) = \text{molar entropy of } \alpha$$

So we have: (molar quantities)

$$V_\alpha\, dP - S_\alpha\, dT = V_\beta\, dP - S_\beta\, dT$$

$$\therefore \frac{dP}{dT} = \frac{S_\beta - S_\alpha}{V_\beta - V_\alpha} = \frac{\Delta S}{\Delta V}$$

Now, at equilibrium, $\Delta G = \Delta H - T\Delta S = 0$, so $\Delta S = \frac{\Delta H}{T}$

$$\therefore \frac{dP}{dT} = \frac{\Delta H_{vap}}{T\Delta V}$$

$\frac{dP}{dT}$: change in pressure as we move along the vapor-liquid coexistence line

This is called the Clapeyron equation and gives us the slope of l-line in the phase diagram

---

There's a cool modification of this:

$$\Delta V = V_g - V_l \leftarrow \text{molar volumes}$$

V_g: much larger than V_l

$$\therefore \frac{dP}{dT} \approx \frac{\Delta H_{vap}}{T V_g} \leftarrow V_g \approx \frac{n_g RT}{n_g P} = \frac{RT}{P}$$

$$\therefore \frac{1}{P}\frac{dP}{dT} = \frac{\Delta H_{vap}}{RT^2} \Rightarrow \boxed{\frac{d\ln P}{dT} = \frac{\Delta H_{vap}}{RT^2}}$$

Clausius-Clapeyron!

The integrated form of Clausius-Clapeyron:

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

← relationship between vapor pressures P_1 & P_2 at 2 different temperatures

↑ super important in industrial processes & distillation....

Chemical potentials & Statistical Mechanics

Some more details on μ:

$$\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P} = \left(\frac{\partial A}{\partial n}\right)_{T,V}$$

but: ← Partition function

$$A = -k_B T \ln Q$$

$$\mu = -k_B T \left(\frac{\partial \ln Q}{\partial n}\right) = -RT \left(\frac{\partial \ln Q}{\partial N}\right)$$

But: $Q = \frac{q^N}{N!}$ ← molecular P.f

$$\ln Q = N \ln q - N \ln N + N$$

$$\frac{\partial \ln Q}{\partial N} = \ln q - \ln N - 1 + 1 = \ln \frac{q}{N}$$

$$\therefore \quad \mu = -RT \ln\left(\frac{q}{N}\right)$$

for an ideal gas, $q = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$

$$\frac{q}{N} = \frac{q}{V} \cdot \frac{V}{N} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} \frac{RT}{P}$$

$$\mu = -RT \ln\left[\frac{q}{V}\frac{k_B T}{P}\right]$$

$$\mu = -RT \ln\left(\frac{q}{V} k_B T\right) + RT \ln P$$

$$\mu(T,P) = \mu_o(T) + RT \ln \frac{P}{P_o}$$

← deviations from standard state

$\mu_o(T)$ ⇐ standard state chemical potential

(using a molecular partition function at standard conditions)