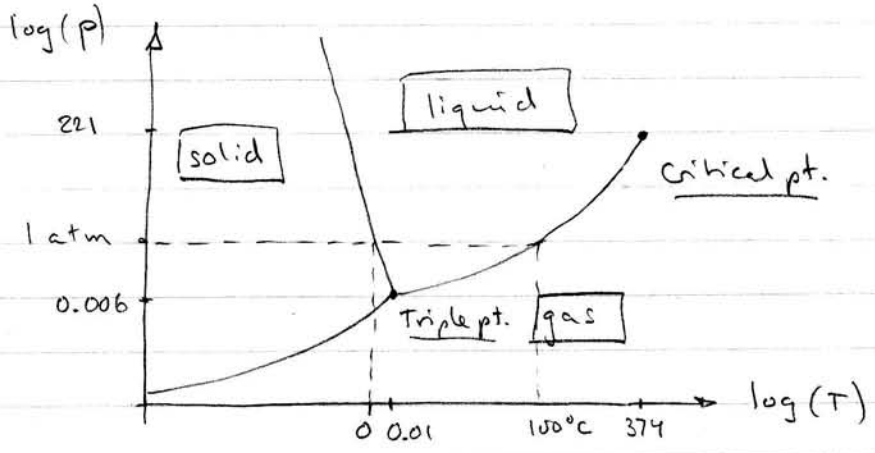
Lecture 20 - Phase transformations

Phase = macroscopic region in which physical properties are homogeneous

Ex: gas vs. liquid vs. solid
superfluid (superconducting) vs. normal
ferromagnet vs. paramagnet
crystallographic phases in solids (ex: ice)
alloy phases (ex: Fe + C, steel)
etc...

Different phases will be favored depending on certain parameters
Ex: for gas / liquid / solid phase, will depend on P, T

Can plot this on a phase diagram:
Ex: H_2O

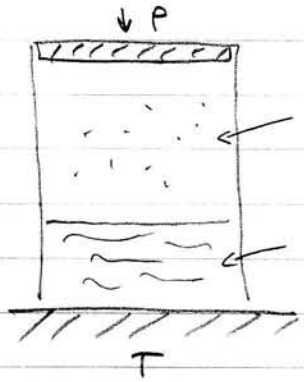


Lines = phase boundaries where 2 phases coexist
"coexistence line"
Triple pt. = pt. where all 3 phases coexist
Critical pt. = pt. where gas and liquid are indistinguishable
density of gas and liquid are the same

Note that p, T are convenient parameters for phases of a substance like water, for other phase diagrams other parameters may be more appropriate (ex: ferromagnetism : B-field and T
ex: alloys : T and % of one component etc.)

Look at behavior along a phase boundary, where 2 phases are in equilibrium. For gas/liquid/solid p, T are appropriate parameters so $G = G(T, p)$ is the right thermodynamic potential and G is minimized

Phase boundaries equivalent to:



$$G = \sum_i \mu_i N_i$$

$$= \mu_1 N_1 + \mu_2 N_2$$

$N_{tot} = N_1 + N_2$ fixed

$$dG = 0 = \mu_1 dN_1 + \mu_2 dN_2 = (\mu_1 - \mu_2) dN_1$$

$$dN_2 = -dN_1$$

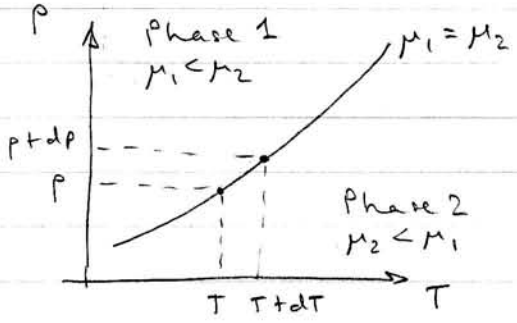
$\therefore \boxed{\mu_1(T,p) = \mu_2(T,p)}$ on phase boundary

Expected! Along phase boundary phase 1 + 2 are in
- thermal equilibrium $T_1 = T_2 = T$
- mechanical equil. $p_1 = p_2 = p$
- diffusive equil. $\mu_1 = \mu_2$ { gas molecules can join liquid phase and vice versa

Note that on phase boundary

$$G = N_1\mu_1 + N_2\mu_2 = (N_1 + N_2)\mu_1 = N_{tot}\mu_1$$

G is independent of N_1 or N_2 so any amount of phase 1 or 2 can coexist. (as long as $N_1 + N_2 = N_{tot}$)



In phase 1 : $\mu_1 < \mu_2$
(favors increasing N_1 over N_2)
In phase 2 : $\mu_2 < \mu_1$

At some P, T on phase boundary $\mu_1(T,P) = \mu_2(T,P)$
Make a small change dT and find dP such that we stay on boundary:

$$\mu_1 + d\mu_1 = \mu_2 + d\mu_2 \qquad \therefore \quad d\mu_1 = d\mu_2$$

$$d\mu_1 = \left(\frac{\partial \mu_1}{\partial T}\right)_P dT + \left(\frac{\partial \mu_1}{\partial P}\right)_T dP = \left(\frac{\partial \mu_2}{\partial T}\right)_P dT + \left(\frac{\partial \mu_2}{\partial P}\right)_T dP$$

However, note that $G_1 = N_1\mu_1$, $G_2 = N_2\mu_2$

and $dG_1 = -S_1\,dT + V_1\,dP = \left(\frac{\partial G_1}{\partial T}\right)_{P,N_1} dT + \left(\frac{\partial G_1}{\partial P}\right)_{T,N_1} dP$ for constant N_1

and similarly for G_2.

So, $\left(\frac{\partial \mu_1}{\partial T}\right)_P = \frac{1}{N_1}\left(\frac{\partial G_1}{\partial T}\right)_{P,N_1} = \frac{-S_1}{N_1} \equiv -s_1$ "entropy per particle"

$$\left(\frac{\partial \mu_1}{\partial P}\right)_T = \frac{1}{N_1}\left(\frac{\partial G_1}{\partial P}\right)_{T,N_1} = \frac{V_1}{N_1} \equiv v_1 \qquad \text{"volume per particle"}$$

Similarly for μ_2, so:

$$d\mu_1 = -s_1\,dT + v_1\,dp = -s_2\,dT + v_1\,dp = d\mu_2$$

$$\boxed{\left.\frac{dp}{dT}\right|_{\text{phase boundary}} = \frac{s_2 - s_1}{v_2 - v_1}}$$

Clausius-Clapeyron equation

s, v could be per particle or per mole, it doesn't matter

What does this say? Look at H_2O phase diagram

Liquid-gas boundary:

$$\left.\frac{dp}{dT}\right|_{l\leftrightarrow g} = \frac{s_g - s_l}{v_g - v_l} > 0$$

Makes sense: $v_g \gg v_l$ and $s_g > s_l$ (gas has more entropy)

Solid-liquid boundary:

$$\left.\frac{dp}{dT}\right|_{s\leftrightarrow l} = \frac{s_l - s_s}{v_l - v_s} < 0$$

$s_l \geq s_s$ (as expected)

But $v_l < v_s$. H_2O is unusual, expands upon freezing

(For most materials, $v_l > v_s$ and $\frac{dp}{dt} > 0$)

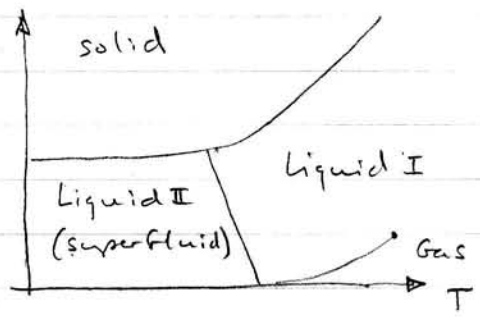
Critical pt:

$$\left.\frac{dp}{dT}\right|_{c.p.} = \frac{s_g - s_l}{v_g - v_l} \to \infty$$

$v_g = v_l$ densities of water vapor and liquid are the same

phases become indistinguishable

Another Ex: ^4He



phase boundary between solid ^4He and superfluid ^4He is almost horizontal

$\therefore \quad S_{\ell II} \approx S_s$

In most materials solid is more ordered so $S_s < S_\ell$ but superfluid phase is a Bose-Einstein condensate (roughly) which is low entropy!

For some phase transitions $\Delta S = 0$ identically

Types of phase transitions:

First order - S, V discontinuous across transition

(called "first order" because S, V are first derivatives of G)

Ex: gas/solid/liquid except at critical pt.

Second order - S, V continuous across transition

(now usually called "continuous")

Ex: ferromagnetism, critical pt.

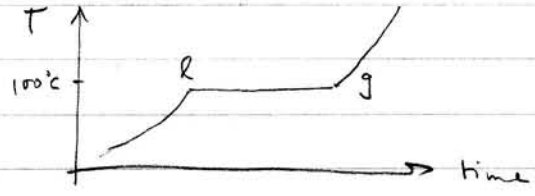
Latent heat

For 1st order transitions, crossing phase boundary requires change in entropy ΔS

At constant T, this corresponds to heat $Q = T\Delta S = L$ called "latent heat"

Ex: for liquid ↔ gas, L is the heat that must be added to transfer one molecule reversibly from liquid to gas

When you bring water to a boil, just below 100°C heat is put into H_2O not to change T, but solely to change its phase



Ex: conversely liquid → solid L is released

Write Clausius-Clapeyron eq'n as $\boxed{\frac{dp}{dt} = \frac{L}{T\Delta V}}$

On coexistence line:

$$\mu_1 = \mu_2 \qquad \therefore \quad \frac{G_1}{N_1} = \frac{H_1 - TS_1}{N_1} = \frac{H_2 - TS_2}{N_2}$$

$$\therefore \quad h_1 - Ts_1 = h_2 - Ts_2$$

$$h_2 - h_1 = T(s_2 - s_1) = T\Delta s = L$$

so $L = \Delta h$ = enthalpy difference between phases

Can get this from heat capacity at constant pressure:

$$C_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial U}{\partial T}\right)_p + p\left(\frac{\partial V}{\partial T}\right)_p = \left(\frac{\partial}{\partial T}(U + pV)\right)_p$$

$$= \left(\frac{\partial H}{\partial T}\right)_p$$

or $H = \int C_p \, dT$ and $\Delta H = \int (C_{p2} - C_{p1}) \, dT$

Vapor pressure equation

Consider liquid → gas transition

$V_g \gg V_\ell$ so $\Delta V \approx V_g = \frac{V_g}{N_g N_A}$ v_g = volume per mole

Using the ideal gas law $\Delta V \approx \frac{N_A k_B T}{p} = RT$

∴ on coexistence line: $\frac{dp}{dt} = \frac{L}{RT^2} p$

$$\int \frac{dp}{p} = \int \frac{L \, dT}{RT^2}$$

Assume L = const. = L_0 (turns out to be a pretty good approx.)

$$\therefore \int \frac{dp}{p} = L_0 \int \frac{dT}{RT^2} \Rightarrow \ln p = \frac{-L}{RT} + \text{const.}$$

$$\boxed{p = p_0 e^{-L/RT}}$$ vapor pressure vs. T

So p increases rapidly with T ⇒ this is the phase boundary line in the phase diagram for H_2O

For water, this equation works pretty well over 8 orders of magnitude!