Thermodynamics 4230

Oct. 17, 2011

Lecture Set 5

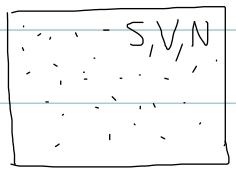
(Leo Radzihovsky)

Thermodynamic Potentials (Free energies)

- Enthalpy $H(U, p, N)$
- Helmholtz free energy $F(T, V, N)$
- Gibb's free energy $G(T, P, N)$
- Maxwell relations
- Phase transitions
- Clausius - Claperon Eqn.
- Mixtures
- Osmotic pressure

Thermodynamic Potentials

1. $U(S,V,N)$ - internal energy



→ isolated system w/ fixed S, V, N

→ state determined by maximum S

→ $dU = TdS - pdV + \mu dN$

2. $H(S,P,N)$ - Enthalpy

→ $H = U + PV$

→ fixed S, P, N

→ energy to make system in vacuum (U) + work to make room for it (PV)

→ recall C_V vs $C_p = \left.\frac{\partial H}{\partial T}\right|_p$

→ $dH = dU + pdV + Vdp = TdS + Vdp + \mu dN$

$\Rightarrow H(S, \underline{P}, N)$

$T = \left.\frac{\partial H}{\partial S}\right|_{P,N}$, $V = \left.\frac{\partial H}{\partial p}\right|_{S,N}$ } Legendre transform. cf Hamilt ↔ Lagr. $L = p\dot{q} - H$

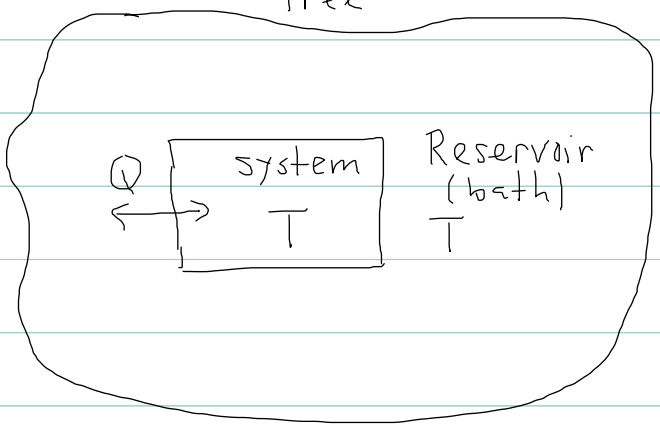
3. $F(T, V, N)$ – Helmholtz free energy

→ $F(T, V, N) = U(S, V, N) - TS$

→ fixed T, V, N

$U(S, V, N)$: energy to create isolated system

TS: heat that enters from reservoir for free



(reversible) $TdS - PdV + \mu dN$

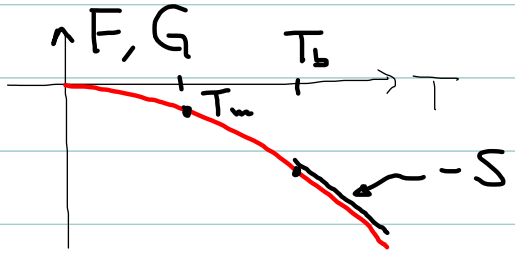
→ $dF = dU - TdS - dTS$

$= -SdT - PdV + \mu dN \Rightarrow F(T, V, N)$

minimize

$= \underbrace{Q - TdS}_{\leq 0} + W \leq W = W_{other}$ (const V)

$\Rightarrow \left.\frac{\partial F}{\partial T}\right|_{V,N} = -S, \quad \left.\frac{\partial F}{\partial V}\right|_{T,N} = -P, \quad \left.\frac{\partial F}{\partial N}\right|_{T,V} = \mu$



4. $G(T,P,N)$ – Gibb's free energy

$\rightarrow G(T,P) = F(T,V) + PV$

$= H(S,P) - TS$

$= U(S,V) + PV - TS$

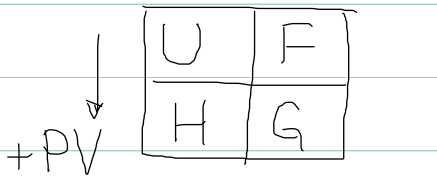
$\rightarrow dG = dU + PdV + VdP - TdS - dTS$

$= VdP - SdT + \underbrace{\mu dN} \leq W_{other}$ (const T, P)

if many species $+ \mu_1 dN_1 + \mu_2 dN_2 + \ldots$

$\Rightarrow \mu = \left.\frac{\partial G}{\partial N}\right|_{T,P}$

$\Rightarrow \underline{G = \mu N}$

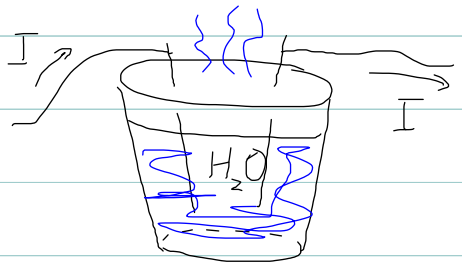


Summary:

- U – energy of syst. in isolation
- H – net energy including PV work against pressure
- F – net energy for system in contact w/ reserver @ T
- $G = U - \underbrace{TS} + \underbrace{PV}$

  heat entering from bath — work against P

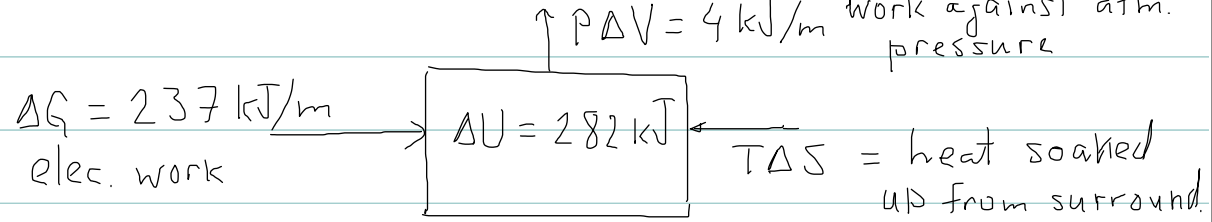
Electrolysis: separate $H_2O \rightarrow H_2 + \frac{1}{2}O_2$ via electrical current



How much energy/mole is required?

At T_{room}, done slowly @ const p, the electrical energy: $\Delta G = \Delta U + p\Delta V - T\Delta S$

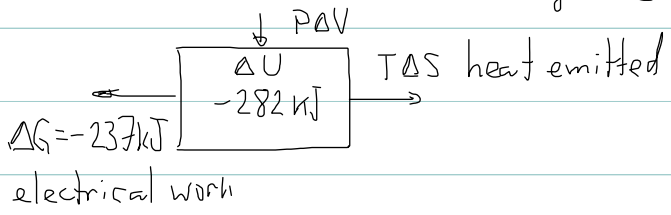
$= 282\,kJ + 4\,kJ - 49\,kJ = 237\,kJ/mol$

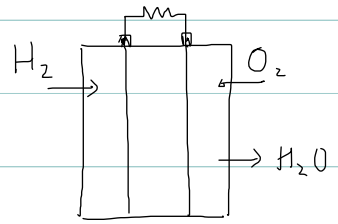


note: for isolated system (S, V, N fixed) $\Rightarrow$

$W_{elect.} = \Delta U = 282\,kJ/m$

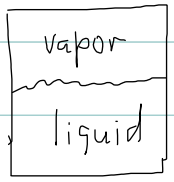
Fuel cell (battery): $\underbrace{H_2 + \frac{1}{2}O_2}_{\text{higher S}} \rightarrow H_2O$ (lower S)





(in battery no gases involved: $\Delta V \approx 0 \Rightarrow \Delta U \approx \Delta H$; $\Delta F \approx \Delta G$)

- S maximized for isolated system (fixed U, V, N):

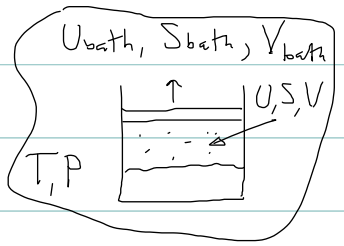


- $F = U - TS$ is minimized for system @ T - constant $\Leftrightarrow$

$S_{univ.} = S_{sys} + S_{bath}$ is maximum: $dF = \underbrace{Q - TdS}_{\leq 0} - \underbrace{P\cancel{dV}}_{\text{const } V} \leq 0$

- $G = \underbrace{U + PV}_{H} - TS$ is minimized for system @ T, p - constant $\Leftrightarrow$

$S_{universe}$ — maximized



$$dS_{univ} = dS + dS_{bath}$$

$$= dS - \frac{dU}{T} - \frac{P}{T}dV \qquad (dU_{bath} = -dU,\ dV_{bath} = -dV)$$

$$= -\frac{1}{T}(dU - TdS + pdV) = -\frac{1}{T}dG \Rightarrow \text{minimize } G$$

Why? $G = U + PV - TS$

→ If $U \downarrow$, $U_{bath} \uparrow \Rightarrow S_{bath} \uparrow$

→ If $V \downarrow$, $V_{bath} \uparrow \Rightarrow S_{bath} \uparrow$

→ $S \uparrow$

} $G \downarrow$

balance: $dS_b = \frac{dU_b}{T} + \frac{P}{T}dV_b = -\frac{dU}{T} - \frac{P}{T}dV$

at low T, ΔS_{bath} big for ΔU, ΔV; high T ΔS_{bath} small.

Maxwell relations

dU, dS, dH, dF, dG - exact differential

$\Rightarrow \frac{\partial^2 f}{\partial x \partial y} = \frac{\partial^2 f}{\partial y \partial x}$ (vanishing $\nabla \times \nabla f$, partial commute, exact)

- $dU = TdS - pdV + \mu dN$; $\frac{\partial U}{\partial S} = T$, $\frac{\partial U}{\partial V} = -p$, ...

$\Rightarrow \left.\frac{\partial T}{\partial V}\right|_{V,N} = -\left.\frac{\partial P}{\partial S}\right|_{V,N}$, $\left.\frac{\partial T}{\partial N}\right|_{S,V} = \left.\frac{\partial \mu}{\partial S}\right|_{V,N}$, ...

- $dG = -SdT + VdP + \mu dN$; $S = -\left.\frac{\partial G}{\partial T}\right|_{P,N}$, $V = \left.\frac{\partial G}{\partial P}\right|_{T,N}$, $\mu = \left.\frac{\partial G}{\partial N}\right|_{T,P}$

$-\left.\frac{\partial S}{\partial P}\right|_{T,N} = \left.\frac{\partial V}{\partial T}\right|_{P,N}$, $\left.\frac{\partial V}{\partial N}\right|_{T,P} = \left.\frac{\partial \mu}{\partial P}\right|_{T,N}$, ...

also recall: $f(x,y,z) = \text{const}$.

proof:

$0 = df = \partial_x f dx + \partial_y f dy + \partial_z f dz$

& $f(x,y,z) = c \Rightarrow z(x,y)$

$dz = \left.\frac{\partial z}{\partial x}\right|_y dx + \left.\frac{\partial z}{\partial y}\right|_x dy$

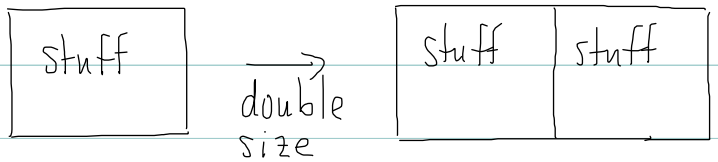
$\Rightarrow 0 = \left(\partial_x f + \partial_z f \left.\frac{\partial z}{\partial x}\right|_y\right) dx + \left(\partial_y f + \partial_z f \left.\frac{\partial z}{\partial y}\right|_x\right) dy$

$\Rightarrow \left.\frac{\partial z}{\partial x}\right|_y = -\frac{\partial_x f}{\partial_z f} = -\frac{\partial y}{\partial x} \Big/ \frac{\partial y}{\partial z}$ ✓

$\Rightarrow \left.\frac{\partial x}{\partial y}\right|_z \left.\frac{\partial y}{\partial z}\right|_x \left.\frac{\partial z}{\partial x}\right|_y = -1$

& $\left.\frac{\partial x}{\partial y}\right|_z = \frac{1}{\left.\frac{\partial y}{\partial x}\right|_z}$ ✓

Extensive vs Intensive



V, N	$\longrightarrow$	$2V, 2N$	extensive
T, P	$\longrightarrow$	T, P	intensive

Extensive: m, V, N, S, U, H, F, G

Intensive: T, ρ, n, μ

(intensive)(intensive) = (intensive)

(intensive)(extensive) = (extensive)

(extensive)(extensive) = (wrong, typically)

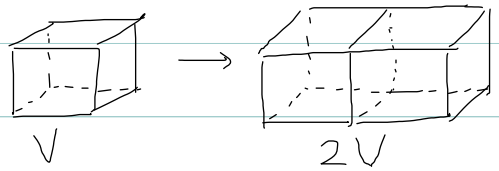
(intensive) + (intensive) = (intensive)

(extensive) + (extensive) = (extensive)

(extensive) + (intensive) = (wrong)

apple + orange

note: ignore surface effects, which are important for small syst.



, but $S \not\propto 2S$

Important relation: $\mu = \left.\frac{\partial G}{\partial N}\right|_{T,P} \Rightarrow G = \mu N$

but $\mu = \left.\frac{\partial F}{\partial N}\right|_{T,V} \not\Rightarrow F = \mu N$, why?

$G(N, P, T) = \int_{N_i}^{N} dN\, \mu(T,P)$ (N: extensive; $\mu(T,P)$: intensive)

G: extensive; P: fixed; $\mu(T,P)$: const. when T, P - const (since intensive)

but $\mu = \left.\frac{\partial U}{\partial N}\right|_{S,V} \Leftrightarrow U(S,V,N) = \int dN\, \mu(S,V,N) \not\Rightarrow U = \mu N$

(S, V: const.; $\equiv$)

$\Rightarrow G = \mu_1 N_1 + \mu_2 N_2 + \ldots$

mixture of diff. species, e.g. chem reaction solution, etc.

another derivation: $G(T,P,N) \Rightarrow G(T,P,\lambda N) = \lambda G(T,P,N)$

$\left.\frac{\partial}{\partial \lambda}\right|_{\lambda=1}$: $\Rightarrow G(T,P,N) = N \left.\frac{\partial G}{\partial N}\right|_{T,P} = N\mu$ ✓

($\left.\frac{\partial G}{\partial N}\right|_{T,P} = \mu$)

chemical reactions: e.g. $H_2O \leftrightarrow H^+ + OH^-$

H_2O: ? H^+: ? OH^-: ?

equilibrium: $0 = dG = \mu_{H_2O} dN_{H_2O} + \mu_{H^+} dN_{H^+} + \mu_{OH^-} dN_{OH^-}$

(dN_{H_2O}: -1; dN_{H^+}: 1; dN_{OH^-}: 1)

$\Rightarrow \mu_{H_2O} = \mu_{H^+} + \mu_{OH^-}$

more generally: $\nu_1 X_1 + \nu_2 X_2 + \ldots \rightarrow \nu_3 X_3 + \nu_4 X_4 + \ldots$

$\Rightarrow \nu_1 \mu_1 + \nu_2 \mu_2 + \ldots = \nu_3 \mu_3 + \nu_4 \mu_4 + \ldots$

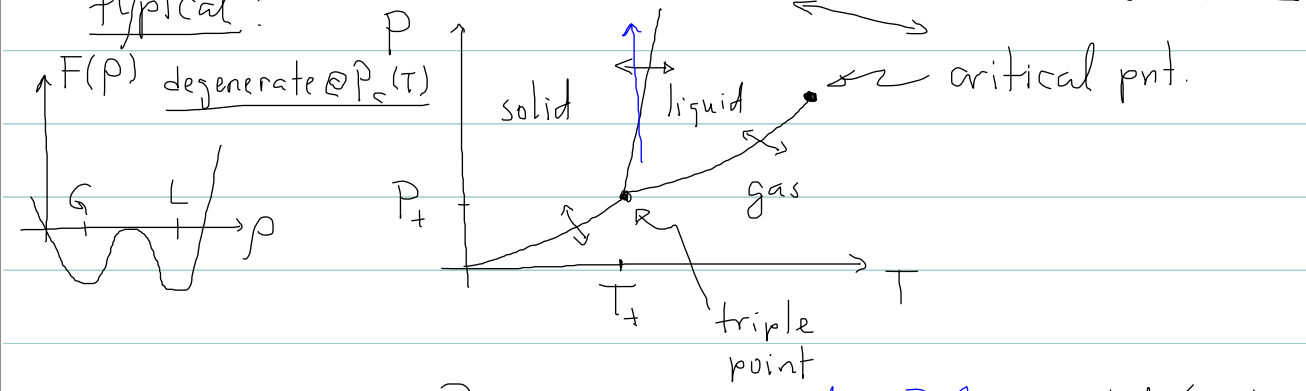
$\Rightarrow$ partial pressures & concentrations of reactance

Phase Transitions

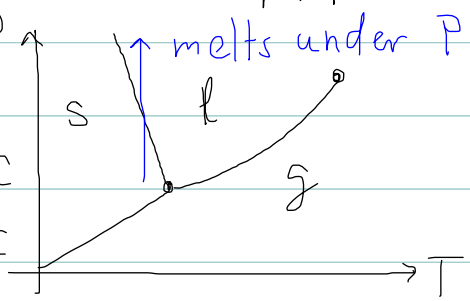
use G since usually @ fixed T, P :

Ex. gas $\leftrightarrow$ liquid $\leftrightarrow$ solid

typical:



H_2O:



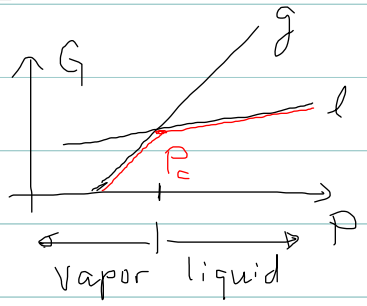
triple: 0.006 bar, 0.01 °C

critical: 221 bar, 374 °C

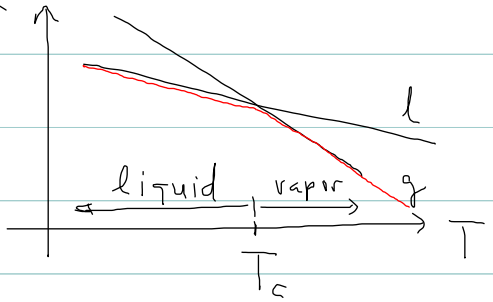
solid (ice) less dense than liquid (water)

note: (1) $\left.\frac{\partial G}{\partial P}\right|_{T,N} = V > 0 \Rightarrow$

phase w/ lower G is the stable on



(2) $\left.\frac{\partial G}{\partial T}\right|_{V,N} = -S < 0 \Rightarrow$ G



($V^{H_2O}_{solid} > V^{H_2O}_{liquid} \Rightarrow$

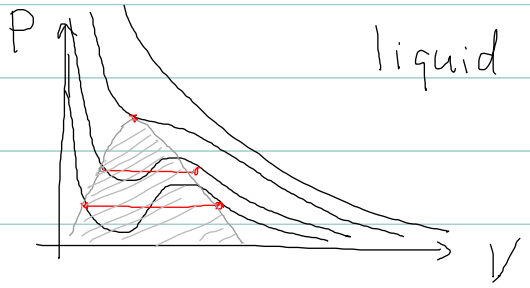
P ↗ Ice melts, since G_{water} increases slower w/ P (smaller V, high n) $\Rightarrow$ melts

van der Waals EOS:

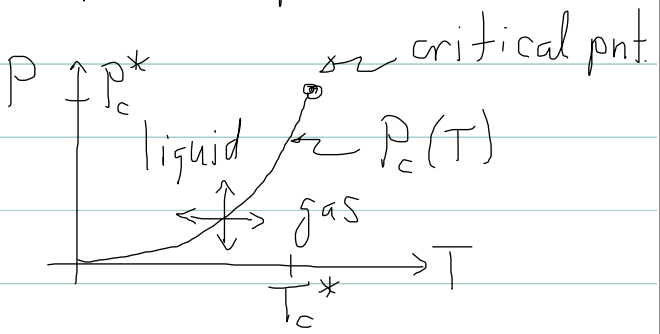
$$\left(P + \frac{aN^2}{V^2}\right)(V - Nb) = Nk_BT$$

$\frac{aN^2}{V^2}$: reduced P due to attractive interactions

Nb: excluded volume



liquid - gas phase separation



- density (V) jumps across P_c T_c

- vapor pressure $P_c(T)$ - coexistence pressure at which condensation/boiling transition takes place.

vaporization of droplet:

- self-tunes $P < P_c \rightarrow P = P_c$ as liquid evaporates

- to get $P > P_c$ need to have enclosed container & reduce volume

- under vaporization either all liquid evaporates for $P < P_c$ or $P \rightarrow P_c$.

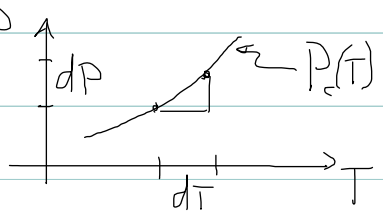
Clausius-Clapeyron Relation

phase boundary on P-T phase diagram

e.g. liquid-gas $P_c(T)$:

at $P_c(T)$: $G_\ell = G_g \iff \mu_\ell = \mu_g$ (maximizes S_{tot})

change ΔT, ΔP s.t. on $P_c(T)$



$$dG_\ell = dG_g$$

$$-S_\ell\, dT + V_\ell\, dP = -S_g\, dT + V_g\, dP$$

$$\Rightarrow (S_g - S_\ell)\, dT = (V_g - V_\ell)\, dP \Rightarrow \left.\frac{dP}{dT}\right|_{P_c} = \frac{\Delta S}{\Delta V} = \frac{L}{T\Delta V}$$

(L: latent heat)

C-C relation

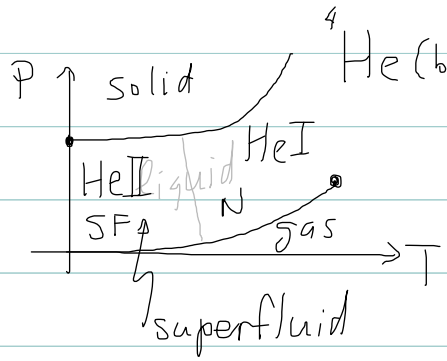
gives slope of $P_c(T)$ in terms of ΔS, ΔV

liquid – gas: $\Delta S > 0$, $\Delta V > 0 \Rightarrow \frac{dP}{dT} > 0$

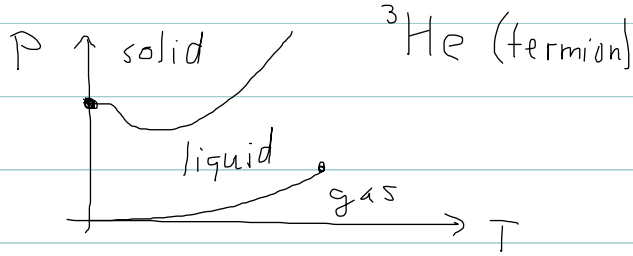
water – ice: $S_{ice} - S_{water} < 0$, $V_{ice} - V_w > 0 \Rightarrow \frac{dP}{dT} < 0$

Other Transitions

- He – only substance that remains a liquid down to T=0

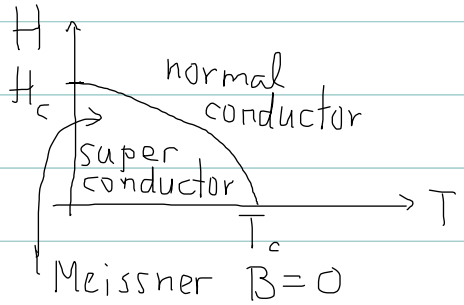


^{4}He (boson)



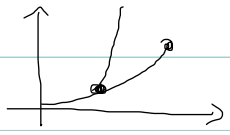
^{3}He (fermion)

- Type I S.C.

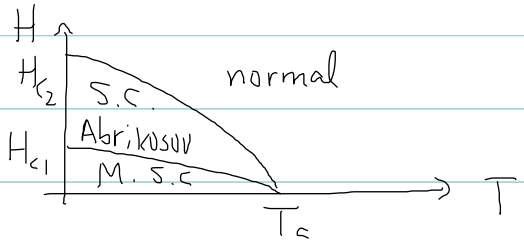


Meissner B=0

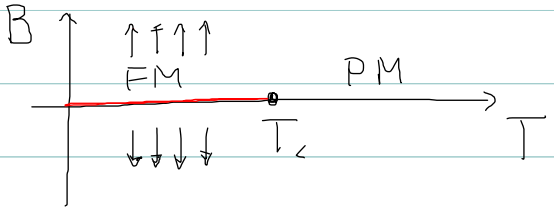
cf



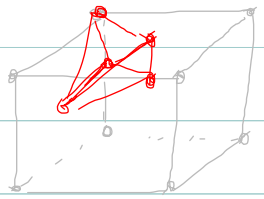
Type II S.C.



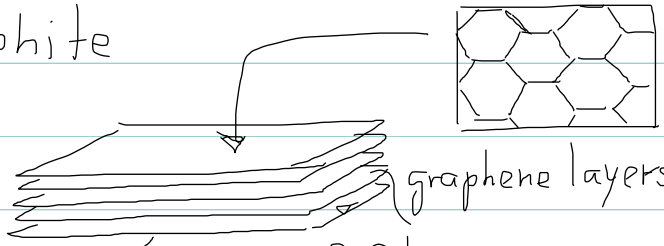
- Ferromagnet (Fe)

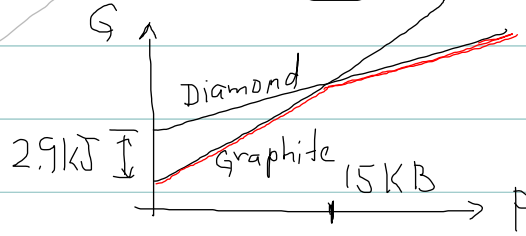


- diamond & graphite



vs


graphene layers



$\left.\frac{\partial G}{\partial P}\right|_{T,N} = V$ > for graphite

$\left.\frac{\partial G}{\partial T}\right|_{P,N} = -S \Rightarrow$ $S_{gr} > S_{diam.}$

$\Rightarrow T \nearrow \Rightarrow$ graphite

Phase transformation of mixtures

A & B molecules: $N_A + N_B = N$ ← fixed

$x \equiv \frac{N_B}{N}$ — B fraction

$1-x = \frac{N_A}{N}$ — A fraction

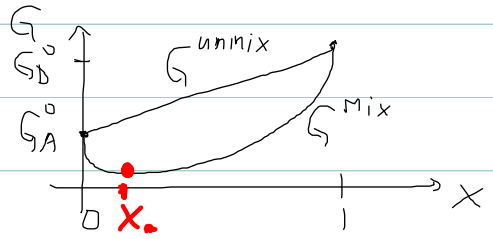
} vary x

$G_{AB}^{unmixed} = (1-x)G_A^\circ + xG_B^\circ$ — unmixed

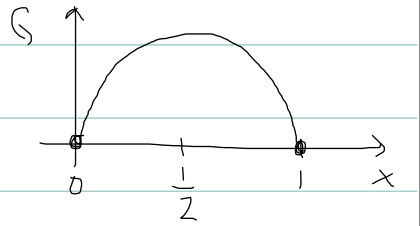
mix A & B: $\Delta S_{mix} = -k_B N[x\ln x + (1-x)\ln(1-x)]$

(see prob. 2.38 & Ising PM up/down ⇔ A & B)

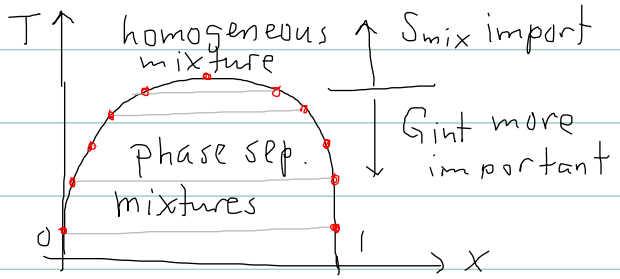
$G_0^{mix} \approx (1-x)G_A^\circ + xG_B^\circ + \underbrace{k_B T N(x\ln x + (1-x)\ln(1-x))}_{-TS}$

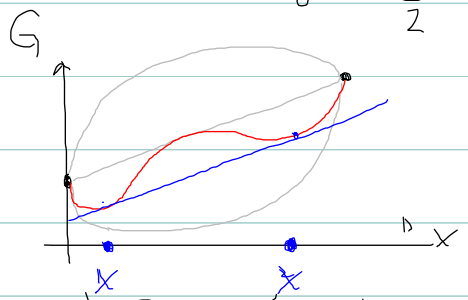


add repulsive inter. $G_{int} = V_0 x(1-x)$



$G_{int}^{Mix} = G_0^{Mix} + G_{int}$:

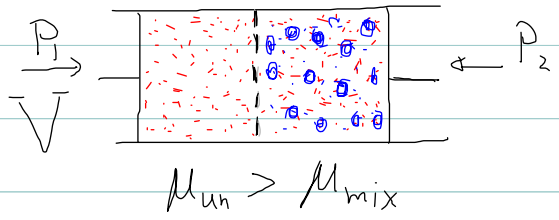




phase separates in x_1, x_2 A & B rich mixtures.

Osmotic Pressure

- solvent can go across membrane
- solute cannot



$\mu_{un} > \mu_{mix}$

e.g. membrane surrounding plant or animal cell, permeable to water & small molecules, but not large ions.

$\mu_{unmix} > \mu_{mix} \Rightarrow$ solvent moves to the right until $P_2 > P_1$ s.t. $\mu_{mix}(P_2, T) = \mu_{unmix}(P_1, T)$ and flow stops

$P_{osmotic} \equiv P_2 - P_1$ (microscopically: more from L → R than from R → L $\Leftrightarrow$ imbalanced pressure of solute)

$$P_{osm} \simeq \frac{N_B k_B T}{V}$$

can be huge: put cell inside pure water & osmotic pressure will build up (~10 Pascals) $\Rightarrow$ animal cell will burst

plant cell are rigid & use osmosis to bring water up the stem