59-240 MT #2 REVIEW - FALL 2015

L10-L14

L10 2nd Law concepts

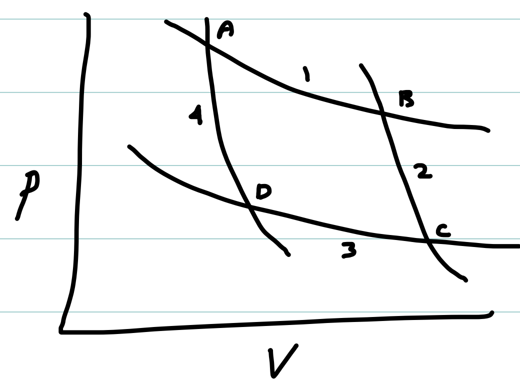
$$\Delta S_{univ} = \Delta S_{sys} + \Delta S_{sur}$$

$$\Delta S_{univ} \geq 0 \quad (\text{irrev./rev.})$$

$$dS = \frac{đq_{rev}}{T}, \qquad \Delta S = \frac{q_{rev}}{T}$$

ΔS_{sys}: $đq_{rev}$ $\quad$ ΔS_{sur}: $đq_{rev}$ or $đq$ (depends on process)

<u>CARNOT CYCLE</u>



$$\oint dS = 0 = \frac{q_h}{T_h} + \frac{q_c}{T_c} \quad \text{so:} \quad \frac{q_h}{q_c} = -\frac{T_h}{T_c}$$

<u>EFFICIENCY</u> $\varepsilon = 1 - \frac{T_c}{T_h} = \frac{|w|}{q_h}$ (rev. engine)

<u>CLAUSIUS INEQ.</u>

$$dS_{sys} \geq \frac{đq_{rev}}{T} \qquad dS_{sys} \geq 0 \text{ for isolated systems}$$

$$dS_{sur} \geq \frac{đq}{T} \qquad đq_{rev} \text{ or } đq$$

→ exp. example

(L11) ENTROPY OF PROCESSES & CHANGES

$$q_p = \Delta_{trs}H \quad ; \quad \Delta_{trs}S = \frac{\Delta_{trs}H}{T}$$

↳ exo- and endothermic processes

↳ rev: $\Delta S_{univ} = 0$; spont: $\Delta S_{univ} > 0$

↳ improbable: $\Delta S_{univ} < 0$

↳ ΔS, ΔS_{sur}, ΔS_{univ} $\quad +, 0, -$

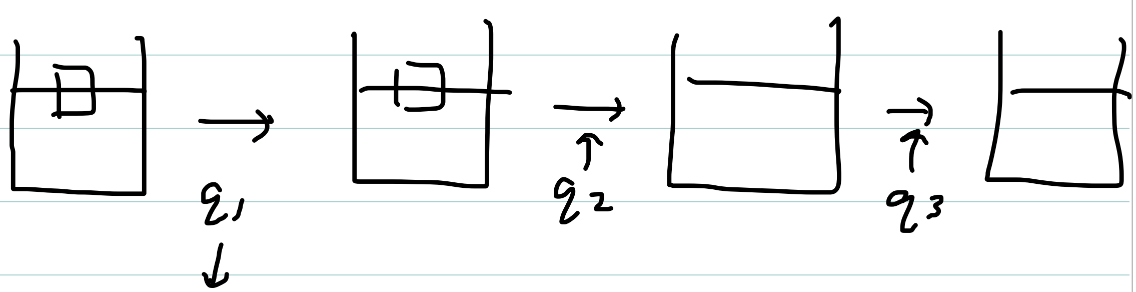
ADDITIVE ΔS

↳ const V: $\Delta S = \int_{T_i}^{T_f} \frac{đq}{T} = \int_{T_i}^{T_f} \frac{C_v dT}{T} = C_v \ln(T_f/T_i)$

↳ const p. $\Delta S = C_p \ln(T_f/T_i)$

↳ const T: $\Delta S = \frac{q_{rev}}{T} = \frac{-w_{rev}}{T} = nR\ln\left(\frac{V_f}{V_i}\right) = nR\ln\left(\frac{p_i}{p_f}\right)$

ICE CUBE:



adiabatic: $q_3 = -(q_1 + q_2)$; $T_f = T_{fus} + \frac{q_3}{C_p}$

isot. : $T_f = T_i$

MEASUREMENT of ΔS

$$S(T) = S(0) + \int_0^{T_{fus}} \frac{C_p(s)\,dT}{T} + \frac{\Delta_{fus}H}{T} + \int_{T_{fus}}^{T_{vap}} \frac{C_p(l)\,dT}{T}$$

$$+ \frac{\Delta_{vap}H}{T} + \int_{T_{vap}}^{T_f} \frac{C_p(g)\,dT}{T}$$

DEBYE: low T, $< 10K$, $C_p = \frac{1}{3} a T^3$

L12 3RD LAW + GIBBS/HELMHOLZ

$T = 0\,K$, motion ceases

↳ $S = 0\ JK^{-1}$? (indep. of arrangements)

$\Delta S \to 0$, $T \to 0$ (Nernst heat theorem)

so: $S(0) = 0\ JK^{-1}$ regarded as starting point for all pure substances

$$\Delta_r S^o = \sum_{prod} \nu S_m^o - \sum_{reac} \nu S_m^o$$

HELMHOLZ + GIBBS ENERGIES

$$dS - \frac{dq}{T} \geq 0 \quad \text{(CLAUSIUS)}$$

CONST V: $dS - \frac{dU}{T} \geq 0$

CONST p: $dS - \frac{dH}{T} \geq 0$

$dS_{U,V} \geq 0$; $dU_{S,V} \leq 0$

$dS_{H,p} \geq 0$; $dH_{S,p} \leq 0$

$A = U - TS$

$dA = dU - TdS - S\cancel{dT}^{\,0}$

$\boxed{dA_{T,V} \leq 0}$

$G = H - TS$

$dG = dH - TdS - S\cancel{dT}^{\,0}$

$\boxed{dG_{T,p} \leq 0}$

SPONT: $\Delta A, \Delta G < 0$

REV: $\Delta A, \Delta G = 0$

IMP: $\Delta A, \Delta G > 0$

ΔG: max non-EXP work

ΔA: max EXP work

$G - A = H - TS - U + TS = H - U = U + pV - U$

$\therefore G = A + pV$ OR $G = A + nRT$

(like $H = U + pV$)

(L13) 2ND LAW TOOLBOX

$dU = TdS - pdV$ $\quad\quad$ $dA = -SdT - pdV$

$dH = TdS + Vdp$ $\quad\quad$ $dG = -SdT + Vdp$

$dH = dU + d(pV)$ $\quad\quad$ $dG = dA + d(pV)$

$\Rightarrow$ derive all FET from:

$$dU = đq + đw$$

$$dS = \frac{đq_{rev}}{T} \quad\quad đw = -pdV$$

$U(S,V)$

$dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$ $\quad$ TDE

$\left(\frac{\partial U}{\partial S}\right)_V = T$; $\left(\frac{\partial U}{\partial V}\right)_S = -p$ $\quad$ ThDef

$\left(\frac{\partial}{\partial V}\left(\frac{\partial U}{\partial S}\right)_V\right)_S = \left(\frac{\partial}{\partial S}\left(\frac{\partial U}{\partial V}\right)_S\right)_V \Rightarrow$ $\quad$ ED

$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial p}{\partial S}\right)_V$ $\quad$ MR $\quad$ (4x)

PROBS: MR; IR; CR

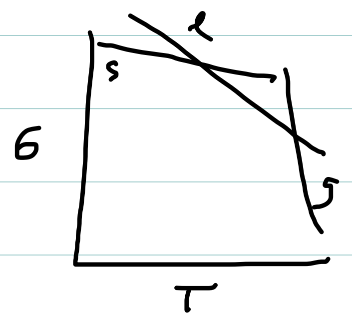
$\rightarrow$ hunt for: $(S,T)_{V,p}$ or $(T,S)_{V,p} \rightarrow C_V, C_p, q$

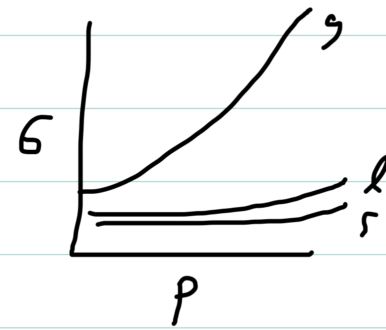
$p, V, T \rightarrow \alpha, \kappa_T$

$\left(\frac{\partial S}{\partial T}\right)_V \Rightarrow dS = \frac{đq_{rev}}{T} = \frac{C_V dT}{T}$; $\left(\frac{\partial S}{\partial T}\right)_V = \frac{C_V}{T}$ $\quad$ $\left(\frac{\partial T}{\partial S}\right)_V = \frac{T}{C_V}$

G: T and p dependence

$$\left(\frac{\partial}{\partial T}\left(\frac{G}{T}\right)\right)_p = -\frac{H}{T^2} \quad \text{(G-H eq'n)}$$





CHEMICAL POTENTIAL: $dG_m = d\mu = \left(\frac{\partial G}{\partial n}\right)_{T,p} = \left(\frac{\partial nG_m}{\partial n}\right)_{T,p}$

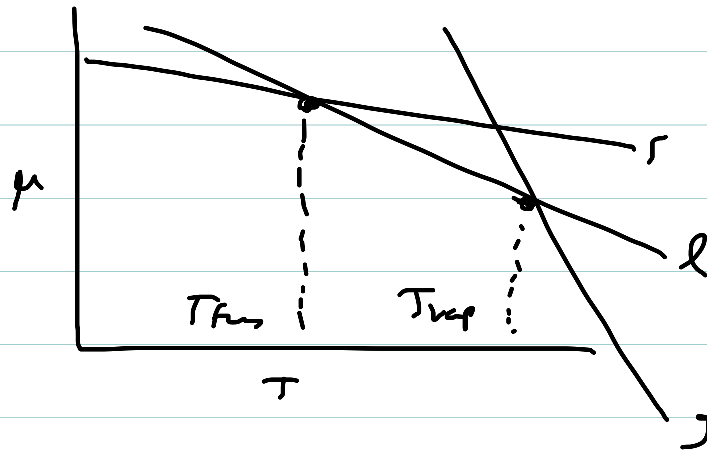
FUGACITY: $f = \phi p$; $\ln \phi = \int_0^p \left(\frac{z-1}{p}\right) dp$

$z<1$, $f<p$, $\mu<\mu^\circ$ STICK

$z>1$, $f>p$, $\mu>\mu^\circ$ REPEL

(L14) PHASE DIAGRAMS

$$\left(\frac{\partial \mu}{\partial T}\right)_p = -S_m$$



$\Delta G, \mu \Rightarrow$ SPONT! not RATE!

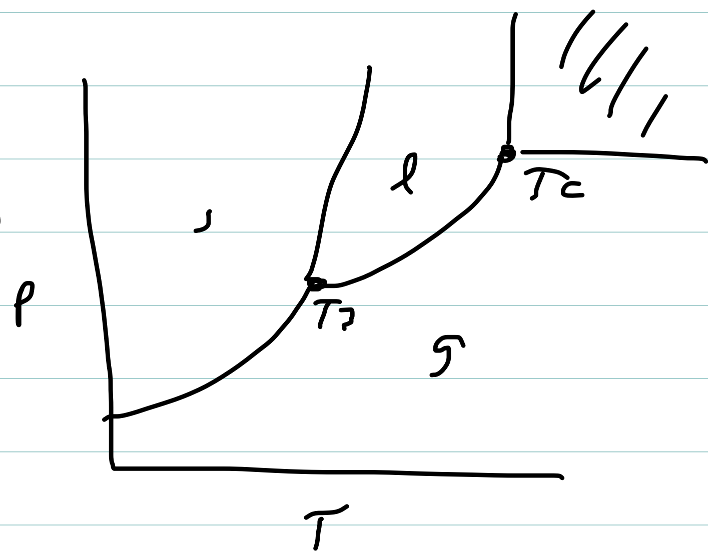
↳ metastable phases are kinetically stabilized

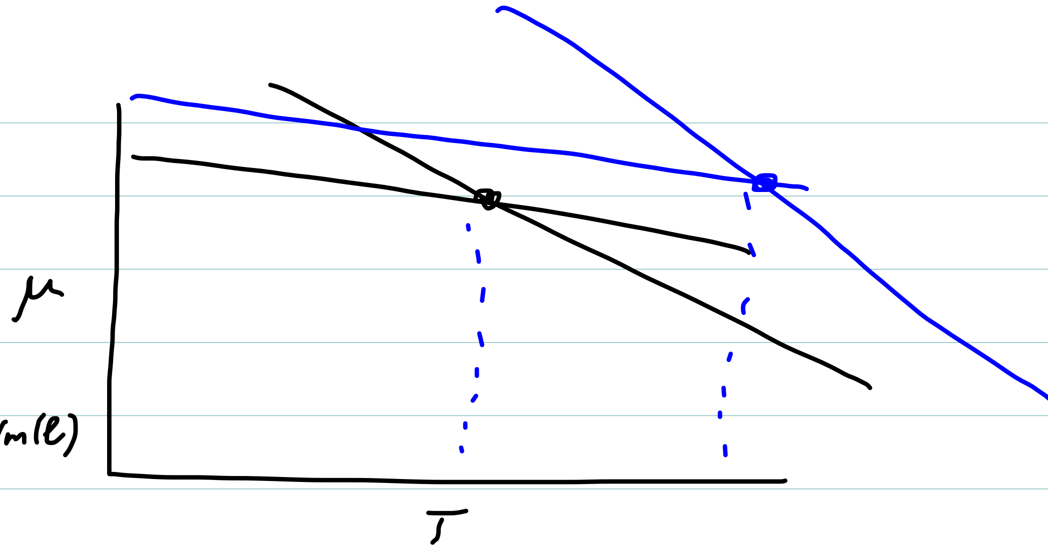
e.g., $\mu_{graphite} < \mu_{diamond}$

s/l: $V_m(s) < V_m(l)$

$\rho(s) > \rho(l)$

slope +ve





Here
$V_m(s) < V_m(\ell)$

→ freezing pt. elevation (most substances)
↳ diff for H_2O
where $V_m(s) > V_m(\ell)$
(be able to draw and explain both!)

VAPOUR PRESSURE:

$$p = p^* e^{V_m \Delta P / RT}$$

(use it!)

CLAPEYRON: $\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$

s-ℓ: $p = p^* + \frac{\Delta_{fus} H}{T \Delta_{fus} V} \ln(T/T^*)$ (also holds for s-s transitions)

ℓ-g: $p = p^* e^{-x}$ $x = \frac{\Delta_{vap} H}{R}\left(\frac{1}{T} - \frac{1}{T^*}\right)$ ← s/ℓ same
use, prove

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FORMAT:

1. mandatory
2.
3. choose 3 of 4
4.
5.
B

10 marks each
40 marks tot.