

$$P_0 = 4 \times 10^5 \text{ Pa}$$

$$T = 300 \text{ K}$$

$$G = U - TS + PV$$

$$dG = dU - (T dN_L + S dT) + d(P \frac{N T}{P})$$

$$= d(\frac{N P_0}{P}) - N k_B dT - N k_B dV$$

$$\Delta G = - \int_{0.006}^{0.012} \frac{N k_B}{V} dV \approx -1729 \text{ J}$$

$$2. \Delta \mu = \mu_g - \mu_l = ?$$

$$\mu = \frac{dG}{dN} = \frac{6.1 \text{ kJ}}{\text{mol}}$$

$$\mu = \frac{-1729 \text{ J}}{1 \text{ mol} \cdot 0.02 \times 10^{-23} \text{ mol}} \approx -2.87 \text{ eV}$$

$$3. \text{ Excluded volume/particle, } b = 1.8 \times 10^{-28} \text{ m}^3 \quad S = N k_B \ln(V - Nb) + f(T, N)$$

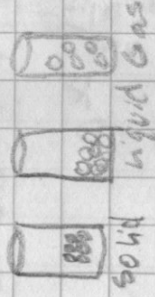
$$dG = dU - S dT + P dV$$

$$= d(\frac{N P_0}{P} - N k_B T) - S dT + P dV \approx -1750.8 \text{ J}$$

$$\int dG = \int_{0.006}^{0.012} \frac{N k_B}{V - Nb} dV \approx -1750.8 \text{ J}$$

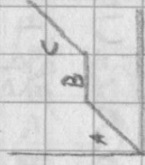
$$4. \Delta \mu = \frac{\Delta G}{N} = \frac{-1750.8 \text{ J}}{N_A} \approx -2.907 \times 10^{-21} \text{ J}$$

Lecture 9: Phase Transitions



Latent heat:

T



There is a phase transition at T_B .

represent w/ L

$$L = \Delta U + P \Delta V = Q$$

Enthalpy:

$$H = U + PV$$

$$\frac{H}{N} = \frac{U}{N} + P \frac{V}{N}$$

At the phase transition temperature,

$$L = \Delta H = T \Delta S$$

where the change is b/w the 2 phases

$$\Delta S = \int \frac{dQ}{T} = \frac{Q}{T}$$

$$G = \mu_G(p, T) N_G + \mu_L(p, T) N_L$$

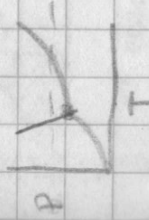
$$G = U + P V - T S$$

$$\Delta G = \Delta U + P \Delta V - T \Delta S$$

$$\Delta G = 0 = \Delta H - T \Delta S$$

$$\Delta H = T \Delta S = L$$

Mapping Phase Boundaries:



Plot the chemical potential as we change temperature (P const).

$$\mu = \frac{U}{N} + P \frac{V}{N} - T \frac{S}{N}$$

$$G = \mu N$$

	U	V	S
Solid	low	low	low
Liquid	middle	middle	middle
Gas	high	high	high



classical-dipole approximation

Lin approx of the phase transition line.

$$\frac{d\mu}{dT} = \frac{dG}{dT} = \frac{dU}{dT} = 0$$

$$\text{Fundamental Rel: } dS = \frac{1}{T} dU + P \frac{dV}{T} - \frac{\mu}{T} dN$$

Always true for quasistatic processes. "F" = ma for quasistatic thermo

HW8: Gibbs Free energy

1) $n = 1 \text{ mole}$ $p = 10^6 \text{ Pa}$ $T = 300 \text{ K}$

1. $\frac{dG}{dV} = ?$ fixed temp

$G = U - TS + pV$

$\frac{dG}{dV} = 0$ $U = \frac{NkT}{2}$ $p(V(T, T_1)) = 0$

$dU = p dV + NkT$

$dG = dU - T dS + p dV + V dp$

$p dV = 0$

2.

$pV = nRT$

$V = \frac{nRT}{p} \approx 0.0025 \text{ m}^3$

3. For ideal gases 1) U depends only on U, T
For a gas that obeys (1)

$\frac{dG}{dV} = \frac{dU}{dV} - T \frac{dS}{dV} + p$

$\frac{dG}{dV} = -T Nk \left(\frac{1}{V - Nb} \right) + p$

2) $dS(U, V) = \left(\frac{dS(U, V)}{dU} \right) dU + \left(\frac{dS(U, V)}{dV} \right) dV$

In eq: $T dS = dU + p dV$

1. $\left(\frac{dS(U, V)}{dV} \right) \Rightarrow T dS = p dV$

2. $\frac{dU}{dS} = T$ $3. \frac{dU}{dV} = p$

5. $\frac{dF}{dT} \Rightarrow dF = dU - T dS - S dT$
 $= dU - \left(\frac{1}{T} dU + \frac{p}{T} dV \right) T - S dT$
 $= -S dT$

6. Gibbs: $G = U - TS + pV$
 $\left(\frac{dG}{dT} \right)_p \Rightarrow dG = dU - T dS - S dT + p dV + V dp$
 $= dU - T \left(\frac{1}{T} dU + \frac{p}{T} dV \right) - S dT + p dV + V dp$

7. $\frac{dG}{dp} \Rightarrow$

$dG = dU - T dS + p dV + V dp$
 $= dU - p dV + p dV + V dp - T dS = dU + V dp - T dS = V dp$

$\left(\frac{dG}{dp} \right)_T = V$

$\frac{dG}{dV} = \frac{dU}{dV} - T \frac{dS}{dV} + p = -T \frac{p}{T} + p = 0$

$\frac{dG}{dV} = \frac{dU}{dV} - T \frac{dS}{dV} + p dV + V dp$

$dG = p dV$

$\left[\frac{dG}{dV} = 0 \right]^{2/m^3}$

$\frac{dG}{dV}$ is minimized @ T, p, n

2) S takes form $Nk \ln(V)$

$S = Nk \ln(V - Nb) \approx 8 \times 10^{-29} \text{ m}^3, V_{eq} = ?$

$V = \frac{Nk}{p} + Nb$

$\approx 0.00254 \text{ m}^3$

4. Helmholtz free energy

$F(T, V) = U - TS$

$\left(\frac{dF(T, V)}{dV} \right)_T \Rightarrow dF = dU - S dT - T dS$

$dF = dU - T dS$

$dF = dU - \left(\frac{1}{T} dU + \frac{p}{T} dV \right) T$

$= dU - dU - p dV$

$\left(\frac{dF}{dV} \right)_T = -p$

$\left[\frac{dG}{dT} = -S \right]$