Physics 301 Fall 2014

# Lec #6 Chemical Thermodynamics (Ch 5)

## Helmholtz Free Energy (F)

$U(S,V,N)$ $S$ hard to control experimentally, so replace $S \to T$ by Legendre transformation.

$$F \equiv U - TS$$

$$dF = dU - d(TS) = \cancel{TdS} - pdV + \mu dN - \cancel{TdS} - SdT$$

$$= -pdV - SdT + \mu dN$$

$$= \underbrace{\left(\frac{\partial F}{\partial V}\right)_{T,N}}_{-p} dV + \underbrace{\left(\frac{\partial F}{\partial T}\right)_{V,N}}_{-S} dT + \underbrace{\left(\frac{\partial F}{\partial N}\right)_{V,T}}_{\mu(T,V,N)} dN$$

so

For a system in environment at <u>constant $T$</u>, heat $Q = T\Delta S$ comes "for free".

<u>at constant $T$</u>, $\Delta T = 0$ so

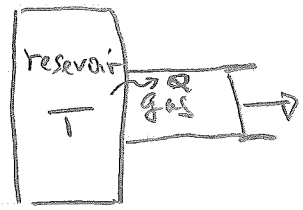
$$\Delta F = \Delta U - T\Delta S = Q + W - T\Delta S$$

and since $Q \leq T\Delta S$ (= for reversible)

so $\boxed{\Delta F \leq W}$

more general than $\Delta F \leq -p\Delta V$ since $W$ can be other than mechanical work

<u>Example</u> Expansion of ideal gas at constant T




$\Delta V = V_f - V_i$

$$S = k \ln\left[ f(N)\, V^N U^{3N/2} \right] = Nk \ln V + \text{const}$$

$$\Delta S = Nk \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta F = \overset{0}{\overset{\shortparallel}{\Delta U}} - T\Delta S = -NkT \ln\left(\frac{V_f}{V_i}\right)$$

or from computing mechanical work -

$$W = -\int p\, dV = -\int_{V_i}^{V_f} NkT \frac{dV}{V} = -NkT \ln\left(\frac{V_f}{V_i}\right) = \Delta F$$

Heat comes from reservoir,

$$Q = T\Delta S = +NkT \ln\left(\frac{V_f}{V_i}\right)$$

$$\Delta F = W = \overset{0}{\overset{\shortparallel}{\left[Q - T\Delta S\right]}} + W$$

So work done <u>by</u> expansion $= -W = -\Delta F$,
whereas $\Delta U = 0$.

note at constant T, $\frac{\Delta P}{P} = \frac{\Delta V}{V}$

F simply related to partition function Z

$$F = -kT \ln Z \qquad (6.56)$$

So good starting point to calculate various thermodynamic quantities

## Extensive, Intensive Quantities

**Extensive** – proportional to size of system
additive like volume.

**Intensive** are unchanged with scaling (say doubling) system.

Extensive : $V, N, S, U, H, F$, mass
Intensive : $T, P, \mu$, density

$\underline{V} \times$ density $=$ mass or $P\underline{V} = \underline{N}kT$
(extensive) x (intensive) = extensive intensive * extensive = intensive * extensive

extensive x extensive is neither (typically an error)

$\underline{F} = \underline{U} - T\underline{S}$ is extensive

# Gibbs free energy (G)

Chemical reactions occur at constant T, P.

Make Legendre transformation to replace $V \to p$ in $F(T,V,N)$

$F = U - TS$ Helmholtz free energy

$G = U + pV - TS = F + pV$ Gibbs free energy

$$dG = dF + d(pV)$$

$$= -pdV - SdT + \mu dN + pdV + Vdp$$

$$= Vdp - SdT + \mu dN$$

$$= \left(\frac{\partial G}{\partial p}\right)_{T,N} dp + \left(\frac{\partial G}{\partial T}\right)_{p,N} dT + \left(\frac{\partial G}{\partial N}\right)_{p,T} dN$$

So $G(T,P,N)$ depends on one extensive quantity $N$. Scaling size of system $T, P$ unchanged. $\Delta G \propto \Delta N$

$$G = \mu(T(\lambda), P(\lambda))\, N$$

So chemical potential is Gibbs free energy per molecule.

$$dG = \left(\frac{\partial \mu}{\partial p}\right) N dp + \left(\frac{\partial \mu}{\partial T}\right) N dT + \mu dN$$

Whereas, $\left(\frac{\partial F}{\partial N}\right)_{V,T} = \mu(V,T,N)$

changing $N$ at fixed $V$ changes density. Generally, <u>F doesn't scale with density</u> since it depends separately on $V, N$.

<u>Thermodynamic identities</u>

$U(S,V,N)$: $dU = TdS - pdV + \mu dN$
$H(S,P,N)$: $dH = TdS + Vdp + \mu dN$
$F(T,V,N)$: $dF = -SdT - pdV + \mu dN$
$G(T,P,N)$: $dG = -SdT + Vdp + \mu dN$

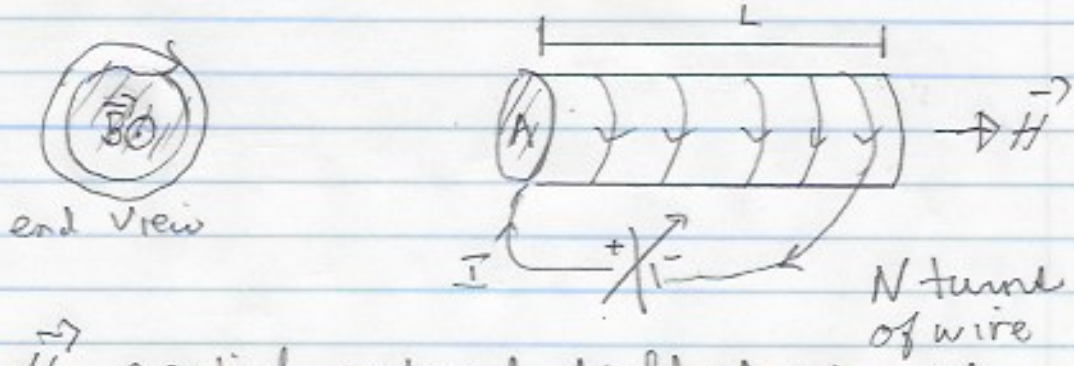
so, for example $\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$

and $\frac{\partial \mu}{\partial P} = \frac{1}{N}\frac{\partial G}{\partial P} = \frac{V}{N}$

$\longrightarrow -TS$

| | | |
|---|---|---|
| $\downarrow$ | $U$ | $F$ |
| $+PV$ | $H$ | $G$ |

Example (5.17) Paramagnetic Solid inside Solenoid.
What is enthalpy, Gibbs free energy?
Refer to Mandl, Statistical Physics



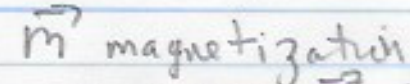

$\vec{H}$ applied external field of solenoid
$\vec{B}$ total field inside paramagnet.

$$\vec{B} = \mu_0 \left( \vec{H} + \frac{\vec{M}}{V} \right) \qquad V = LA \text{ volume}$$

$\vec{M}$ magnetization of sample
$\mu_0 = 4\pi \times 10^{-7}\ N/A^2$ permeability of free space
$\vec{H}, \vec{B}, \vec{M}$ all along solenoid axis direction

Ampere's law applied to solenoid gives H

outside, $H = 0$




$\leftarrow \frac{N}{L}$ wires / length

inside, $H = \text{const}$

$$\oint_{\text{dotted box}} \vec{H} \cdot d\ell = H \Delta x = \left( \frac{N}{L} \Delta x \right) I \qquad \boxed{H = \frac{N}{L} I}$$

Work done by battery is $W = \int (\mathcal{E} I)\, dt$
emf $\mathcal{E}$ is

$$\mathcal{E} = \frac{d\Phi_B}{dt} = NA \frac{dB}{dt}$$

differential work

$$dw = (\mathcal{E} I)dt = \left(NA \frac{dB}{dt}\right)\left(\frac{HL}{N}\right) dt$$

$$dw = VH\,dB \qquad \text{then } B = \mu_0\left(H + \frac{M}{V}\right) \text{ gives}$$

$$dw = VH\mu_0\left(dH + \frac{dM}{V}\right)$$

integrate to get total work

$$W = \underbrace{V\mu_0 \tfrac{1}{2} H^2}_{\text{external}} + \underbrace{\int \mu_0 H\,dM}_{\text{sample, like "}-\int p\,dV\text{"}}$$

Internal energy of sample:

$$\Delta U = Q + \mu_0 H \Delta M = T\Delta S + \mu_0 H \Delta M$$

<u>In analogy to mechanical enthalpy</u> $H_{mech} = U + PV$
<u>magnetic enthalpy</u>

enthalpy function $H_B = U \underbrace{- \mu_0 HM}_{\text{potential energy of sample with } \vec{m} \text{ placed inside field } \vec{H}}$

includes this potential energy

then

$$\Delta H_B = \Delta U - \mu_0 \Delta H M - \mu_0 H \Delta M$$

$$= T\Delta S - \mu_0 M \Delta H \qquad \underline{\text{enthalpy}}$$

Gibbs: $G_m = H_m - TS$

$$\Delta G_m = -S\Delta T - \mu_0 M \Delta H \qquad \underline{\text{Gibbs}}$$

## Why Free Energies are Useful

$$\boxed{\text{System in environment } \Delta S_{TOT} \text{ max when free energies are minimum.}}$$

Case 1: Environment maintains system at const $T, V, N$

$$F = U - TS \xrightarrow{\text{const } T} \Delta F = \Delta U - T\Delta S$$

$$\Delta S_{TOT} = \underset{\text{env.}}{\Delta S_e} + \underset{\text{system}}{\Delta S_s} \qquad U_{TOT} = U_e + U_s = \text{const.}$$

$$\Delta S_e = \frac{1}{T}\Delta U_e = -\frac{1}{T}\Delta U_s$$ and @ const. V, first identity

$$\Delta S_{TOT} = -\frac{1}{T}\Delta U_s + \Delta S_s = -\frac{1}{T}\left(\Delta U_s - T\Delta S_s\right) = -\frac{1}{T}\Delta F_s$$

Case 2: Environment maintains system at const. $T, P, N$

$$V_{TOT} = V_s + V_e = \text{const.}$$
$$U_{TOT} = U_s + U_e = \text{const.}$$

$$G = U + PV - TS \xrightarrow{\text{const } T, P} \Delta G = \Delta U + p\Delta V - S\Delta T$$

first identity $$\Delta S_e = \frac{1}{T}\Delta U_e + \frac{P}{T}\Delta V_e = -\frac{1}{T}\left(\Delta U_s + \frac{P}{T}\Delta V_s\right)$$

$$\Delta S_{TOT} = -\frac{1}{T}\left(\Delta U_s + \frac{P}{T}\Delta V_s\right) + \Delta S_s$$

$$= -\frac{1}{T}\left(\Delta U_s + p\Delta V_s - T\Delta S_s\right) = -\frac{1}{T}\Delta G_s$$

Example (5.2) Fixing of ammonia @ room temp. and atmospheric pressure

Compute $\Delta G$ from $\Delta G = \Delta H - T\Delta S$

$$N_2 + 3H_2 \rightarrow 2NH_3$$

| | | | | |
|---|---|---|---|---|
| $\Delta H$ (kJ) | 0 | 0 | $\rightarrow$ | $2(-46.11)$ |
| $S$ (J/K) | 191.61 | $+3(130.68)$ | $\rightarrow$ | $2(192.45)$ |

enthalpy

$\Delta H_{fi} = -92.2$ kJ/mole energy released

Q= $T\Delta S_{fi} = 298K\left[2(192.45) - 191.61 - 3(130.68)\right]$ J/K

$= -59.23$ kJ this heat will raise the Temperature

$\Delta G_{fi} = \Delta H - T\Delta S = -32.99$ kJ

in agreement with table $-32.9$ kJ

not spontaneous for T>464K

Combustion of ammonia.

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$$

then 2N0+O_2 -> 2N0_2

$\Delta H$ $4(-46.11) + 0 \rightarrow 4(\underline{90.4}) - 6(241.8)$

Not in table

$\Delta H_{fi} = -904.8$ kJ exothermic reaction energy released

ΔG_fi = - 955.6 = ΔH_fi - Q

Q=+50.8 ΔS>0 spontaneous for all T

First step in Ostwald Process, needs heat and catalyst. I don't know why.

Gibbs from https://en.wikipedia.org/wiki/Standard_Gibbs_free_energy_of_formation
Enthalpy from https://en.wikipedia.org/wiki/Standard_enthalpy_of_formation

so the numbers I have are:

| | NH3 gas | 02 | NO | H2O(gas) |
|---|---|---|---|---|
| Delta_H : | -46.1 | 0 | 90.4 | -241.8 |
| Delta_G: | -16.4 | 0 | 87.6 | -228.6 |

4NH3 + O2 -> 4NO + 6H2O

Delta_H_fi = 4*(90.4)+6*(-241.8)- 4*(-46.1) = - 904.8
Delta_G_fi = 4*(87.6)+6*(-228.6)- 4*(-16.4) = - 955.6

Q = Delta_H_fi - Delta_G_fi = -904.8 -(- 955.6) = +50.8

Example (5.6, 5.7) metabolism of glucose

$$C_6H_{12}O_6 + 6O_2 \rightarrow 6CO_2 + 6H_2O$$

| | $\Delta H$ kJ | $\Delta G$ kJ | S (J/K) |
|---|---|---|---|
| glucose | -1273 | -910 | 212 |
| $O_2(g)$ | 0 | 0 | 205 |
| $CO_2(g)$ | -393.5 | -394.4 | 214 |
| $H_2O(l)$ | -285.8 | -237.1 | 70 |

$\Delta H_{fi} = -2803$ kJ

$\Delta G_{fi} = -2879$ kJ

maximum work at room T, P $= -\Delta G = 2879$ kJ

$\Delta G - \Delta H = -T\Delta S = -79$ kJ

so $Q = T\Delta S = +79$ kJ <u>heat absorbed</u>

$\Delta S_{fi} = +292$ J/K entropy increase due to heat absorbed

notice that change in enthalpy does not include heat absorbed Q

metabolism of glucose produces 38 ATP molecules. Muscle uses ATP

$ATP \rightarrow ADP +$ phosphate ($PO_4^{-3e}$ ion)

phosphoric acid $H_3PO_4$

catalyzed by myosin which contracts muscle filament

force $= 4\,pN = 4 \times 10^{-12}\,N$ pico-Newtons

distance $= 11\,nm = 11 \times 10^{-9}\,m$ nano-meters

Work done $44 \times 10^{-21}\,J$

Thermodynamic efficiency:

$$\epsilon = \frac{38\,(44 \times 10^{-21}\,J/\#)(6 \times 10^{23}\,\#/mol)}{\text{max work } \Delta G_fi = 2879 \times 10^{3}\,J}$$

$$= \frac{38(44)\,6}{29} \times 10^{-3} = 0.35 = \underline{\underline{35\%}}$$

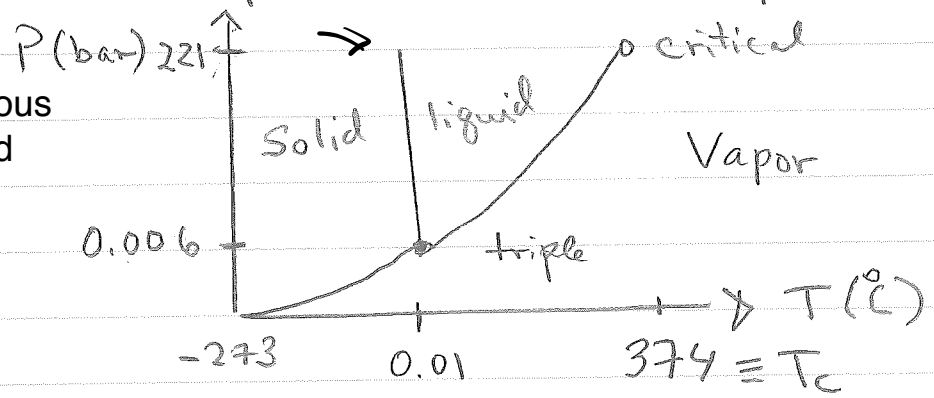
The rest of the energy is waste heat. So we sweat!

<u>Phase transformations</u>, pure substance

phase - spatially homogeneous with boundary.

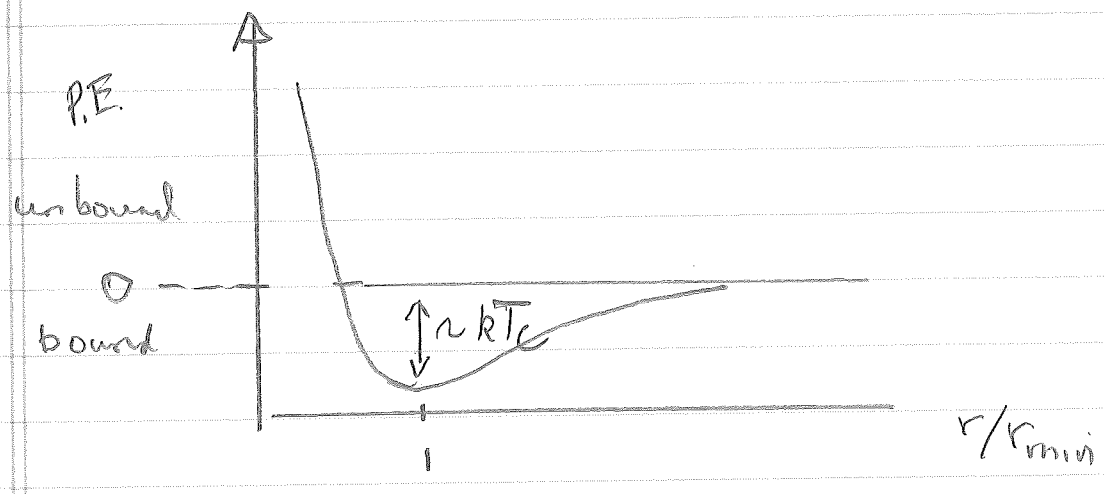
<u>sketch</u> of phase diagram for water.
Lines correspond to co-existent phases

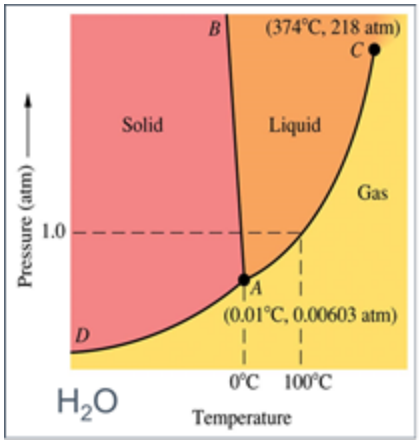
water has anomalous slope of solid/liquid

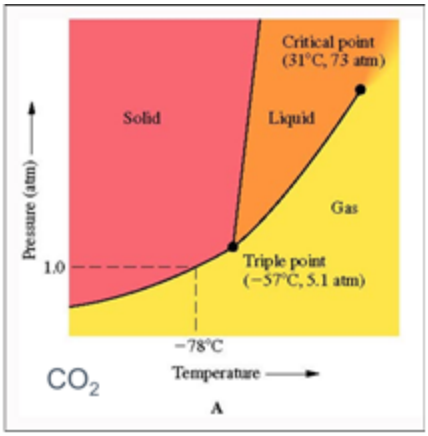



Along vaporization curve (t → c)
liquid density decreases, vapor density increases

Inter-molecular potential energy (PE) curve






water has anomalous slope of solid/liquid

<u>Latent heat</u> heat Q required for phase transformation at constant T, P. fusion or vaporization. Consider vaporization,

$$L_{vap} = Q = \Delta U + P\Delta V \overset{\text{const. } P}{=} \Delta(U+PV) = \Delta H$$

change in enthalpy

also, $Q = T\Delta S$ so

$$L_{vap} = T(S_{vap} - S_{liq})$$

L is Temperature dependent Water @ 100°C

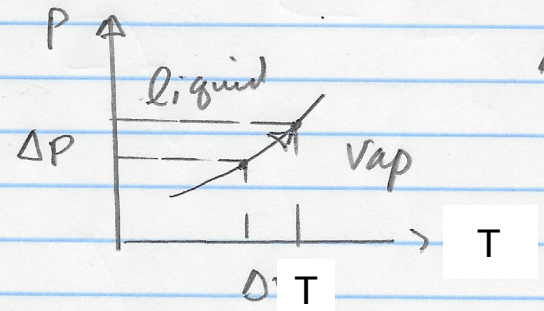
$L_{vap} = 2257$ kJ/kg $= 0.42$ eV/molecule

<u>Phase boundary defined by</u>

$$\Delta G = 0 = \left(\frac{\partial G}{\partial N_{vap}}\right)_{T,P} \Delta N_{vap} + \left(\frac{\partial G}{\partial N_{liq}}\right)_{TP} \overset{-\Delta N_{vap}}{\overset{\shortparallel}{\Delta N_{liq}}}$$

$$= \Delta N_{vap}(\mu_{vap} - \mu_{liq}) \Rightarrow$$ chemical potential equal

Consider change along boundary




$\Delta G_{liq} = \Delta G_{vap}$

= G along boundary

* Clausius-Capeyron relation

$$-S_l \Delta T + V_l \Delta P = -S_v \Delta T + V_v \Delta P$$

$$* \quad \frac{dP}{dT} = \frac{S_v - S_l}{V_v - V_l} = \frac{L_{vap}}{T}\left(\frac{1}{\Delta V}\right)_{\text{vapor-liquid}}$$

## Simplest model ideal gas

$$V = \frac{NkT}{P}$$ then ignoring volume of liquid,

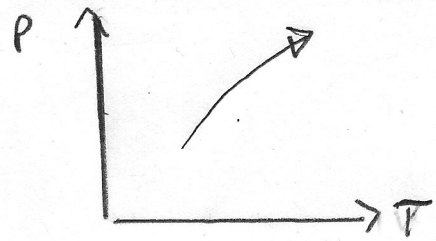
$$\Delta V = V_{vapor}$$

$$\frac{dP}{dT} = \frac{L_v}{T}\left(\frac{1}{V}\right) = \frac{L_v}{T}\left(\frac{P}{NkT}\right) = \frac{L_v}{Nk}\frac{P}{T^2}$$

$$\frac{dP}{P} = \frac{L_v}{Nk}\frac{dT}{T^2}$$ take $L_v$ constant and integrate

$$\ln P = -\left(\frac{L_v}{NkT}\right) + \text{const}$$

$$P_{vap}(T) = \frac{P_0}{\exp\left(\frac{-L_v}{NkT_0}\right)} \exp\left(-\frac{L_v}{NkT}\right)$$




no critical point

realistic gas

$L_v(T)$

Next simplest model Van der Waals has critical point