Recall that we were trying to measure changes in Entropy by relating them to Specific heat

$$\Delta S = S_a - S_b = \int_a^b \frac{dQ}{T} = \int_a^b \frac{dE}{T} + \frac{pdV}{T}$$

Lets do this integral for an ideal gas

Choices: Are we keeping V const? Are we keeping E Const?

Case I : Constant V

$$dQ = dE = \frac{\partial E}{\partial T}\bigg)_V dT$$

$$\Delta S = \int_{T_a}^{T_b} \frac{1}{T'} \frac{\partial E}{\partial T'}\bigg)_V dT' = \int_{T_a}^{T_b} \frac{C_V(T')}{T'} dT'$$

There is a direct relationship between heat capacity & the change in the # of states that arises when Temp is varied

Can we solve this integral? Is $C_V(T')$ const or some function of T'?

Ia) $C_V(T') = a T^2$ (Itai's liquid gas)

$$\Delta S = \int_{T_a}^{T_b} a T' dT' = \frac{a}{2}\left[T_b^2 - T_a^2\right]$$

Ib) $C_V(T') = $ Const   (ideal gas)

$$\Delta S = \int_{T_a}^{T_b} C_V \frac{1}{T'} dT' = C_V \ln \frac{T_b}{T_a}$$

Case II   Iso thermal   E stays Constant so ideal gas & $\frac{p}{T} = \frac{\nu R}{V}$

$$\Delta S = \nu R \ln \frac{V_b}{V_a}$$

Case III   both Change

$$\Delta S = \nu \left[\int \frac{C_V dT'}{T'} + R \ln \frac{V_b}{V_a}\right]$$
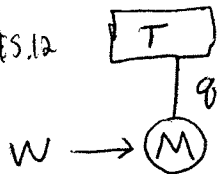
if C_V is Temp indep (ideal gas)

$$\Delta S = \nu \left[C_V \ln \frac{T_b}{T_a} + R \ln \frac{V_b}{V_a}\right]$$

Note Situation could be more complicated for materials other than ideal gas

Heat Engines   EX. (Resistor, or wheel in Liquid)
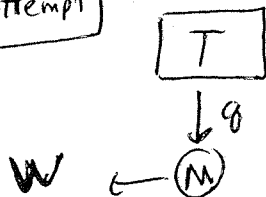
$\boxed{T}$
$|q$

$W \longrightarrow \bigcirc{M}$

$q = w$
Conservation of Energy

$\oint dQ \geq 0$ (2nd law)

Easy to do work on some device M & use it to heat a reservoir. Can we go the other way?

Rules: Keep $\bigcirc{M}$'s entropy, Temp etc. Const after each cycle
No entropy change on device that work is being done on.

1st Attempt

$\boxed{T}$
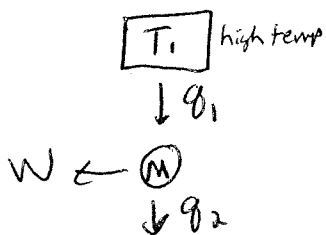$\downarrow q$

$W \longleftarrow \bigcirc{M}$

$q = w$
Consv. of Energy

$\dfrac{dQ}{T} \leq 0$ Violates 2nd law

Transferring work to heat is irreversible

2nd Attempt   what if we have another reservoir?

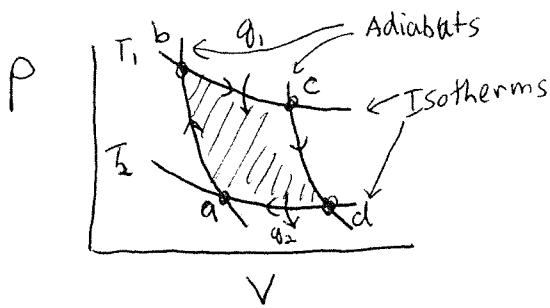$\boxed{T_1}$ high temp $q_1 = W + q_2$ Consv. of energy
$\downarrow q_1$

$W \longleftarrow \bigcirc{M}$ $-\dfrac{q_1}{T_1} + \dfrac{q_2}{T_2} \geq 0$ 2nd law
$\downarrow q_2$

$\boxed{T_2}$ Lower Temp $-\dfrac{q_1}{T_1} + \dfrac{q_1 - W}{T_2} \geq 0$ $\Rightarrow$ $\dfrac{W}{T_2} \leq q_1 \left(\dfrac{1}{T_2} - \dfrac{1}{T_1} \right)$

$$\eta \equiv \dfrac{W}{q_1} \leq \left(\dfrac{T_1 - T_2}{T_1} \right)$$
efficiency

No perfect heat energy

$\eta = 1$ if $T_2 = 0$ not possible for engines

Carnot Engine


W = area enclosed by curves

4 steps all of which are quasistatic

① Thermally insulated (adiabatic) Change V slowly until $T = T_1$

② Isothermally at $T = T_1$ Change V while System absorbs heat q_1

③ Thermally Insulated (adiabatic) Change V until $T = T_2$

④ Isothermally Change V to its initial value while releasing heat q_2

Notice: That on an S vs T diagram a Carnot cycle is simply a rectangle
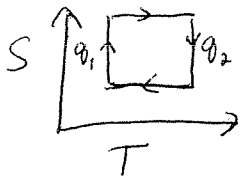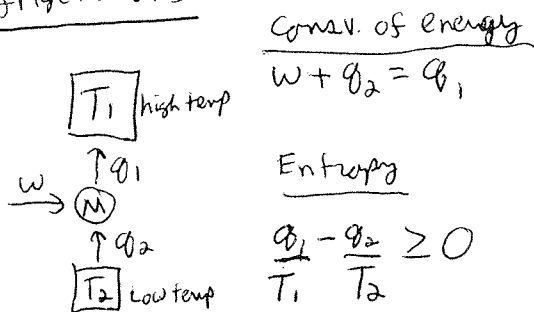

Notice: Any process can be broken up into infintesmal Carnot cycles
∴ all quasistatic processes have the same limit on their efficiency
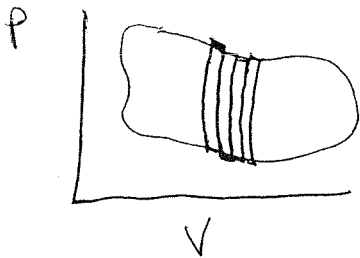
Hurricanes are examples of Carnot Engines

Refrigerators

Consv. of energy
$$W + q_2 = q_1$$

Entropy
$$\frac{q_1}{T_1} - \frac{q_2}{T_2} \geq 0$$

$$\frac{q_1}{T_1} - \frac{(q_1 - w)}{T_2} \geq 0$$

$$\frac{w}{q_1} \geq \frac{T_1 - T_2}{T_1} \quad \text{No perfect refrigerators}$$

What if we cannot measure heat capacities? Are we sunk? NO.
How do we relate changes in entropy to:

$$\alpha \equiv \frac{1}{V}\frac{\partial V}{\partial T}\Big)_P \quad \text{isobaric volume coeff of expansion} \qquad \text{or} \quad K \equiv -\frac{1}{V}\frac{\partial V}{\partial P}\Big)_T \quad \text{Isothermal Compressability}$$

Since T, S, P, V are not completely indep and are related through the fundamental thermodynamic relation:

$$dE = TdS - PdV$$

There are relationships called Maxwell Relations that we can derive.

Energy $\quad E(S,V) \qquad dE = \frac{\partial E}{\partial S}\Big)_V dS + \frac{\partial E}{\partial V}\Big)_S dV \qquad$ Since E is an Exact differential $\boxed{\text{trick 1}}$

From Fundamental relation $\quad \frac{\partial E}{\partial S}\Big)_V = T \qquad \frac{\partial E}{\partial V}\Big)_S = -P$

$$\frac{\partial^2 E}{\partial S \partial V} = \frac{\partial^2 E}{\partial V \partial S} \quad \text{or} \quad \frac{\partial}{\partial V}\Big)_S \frac{\partial E}{\partial S}\Big)_V = \frac{\partial}{\partial S}\Big)_V \frac{\partial E}{\partial V}\Big)_S \qquad \boxed{\text{trick 3}}$$

$$\boxed{\frac{\partial T}{\partial V}\Big)_S = -\frac{\partial P}{\partial S}\Big)_V} \quad \text{Maxwell relation \#1}$$

Still does not give us α or K

Legendre Transforms: get you different sets of indep variables

How do we go from $S,V \rightarrow S,P$: $\quad PdV = d(PV) - VdP \quad$ (by Chain rule)

$$dE = TdS - PdV = TdS - d(PV) + VdP$$

$$d(E + PV) = TdS + VdP$$

$\underbrace{\qquad}_{H \equiv \text{Enthalpy}}$

$dH = TdS + VdP \qquad$ Now we are back to the same place as before

$$dH = \frac{\partial H}{\partial S}\Big)_P dS + \frac{\partial H}{\partial P}\Big)_S dP \qquad \boxed{\text{Trick 1}}$$

$$\frac{\partial H}{\partial S}\Big)_P = T \qquad \frac{\partial H}{\partial P}\Big)_S = V$$

$\boxed{\text{Trick 3}}$

$$\boxed{\frac{\partial T}{\partial P}\Big)_S = \frac{\partial V}{\partial S}\Big)_P} \quad \text{maxwell relation \#2}$$

$S, V \rightarrow T, V:$ $T dS = d(TS) - S dT$

$dE = T dS - p dV = d(TS) - S dT - p dV$

$d(E - TS) = -S dT - p dV$

$\underbrace{F \equiv}_{} \quad$ Helmholtz
Free energy

$dF = -S dT - p dV$ back to same place as before
     $\boxed{\text{Trick 1}}$ & $\boxed{\text{Trick 3}}$

$$\boxed{\left.\frac{\partial S}{\partial V}\right)_T = \left.\frac{\partial P}{\partial T}\right)_V}$$ maxwell relation #3

$T, V \rightarrow T, P$ $p dV = d(pV) - V dp$

$d(E - TS) = -S dT - d(pV) + V dp$

$d(E - TS + PV) = -S dT + V dp$

$\underbrace{G \equiv}_{}$ Gibbs Free
energy   Trick 1 , Trick 3

$$\boxed{-\left.\frac{\partial S}{\partial P}\right)_T = \left.\frac{\partial V}{\partial T}\right)_P}$$ maxwell relation #4

Note: $\left.\frac{\partial V}{\partial T}\right)_P$ is related to α

& maxwell relation #4 relates it
to entropy

what about κ?   recall math trick #2

$\underset{= -\frac{1}{V}\left.\frac{\partial V}{\partial P}\right)_T}{}$

$\left.\frac{\partial V}{\partial P}\right)_T \left.\frac{\partial P}{\partial T}\right)_V \left.\frac{\partial T}{\partial V}\right)_P = -1$ or $\left.\frac{\partial V}{\partial P}\right)_T = -\left.\frac{\partial V}{\partial T}\right)_P \Big/ \left.\frac{\partial P}{\partial T}\right)_V$

both $\left.\frac{\partial V}{\partial T}\right)_P$ & $\left.\frac{\partial P}{\partial T}\right)_V$ can be related to the entropy!

Can also get relationships between different thermodynamic
quantities. Lets get relationship between C_V & C_P for any
thermal system regardless of eq of state ———

Summary   As long as we have the variables S, T, V, P

So that $E = E$(any two of the parameters S, T, V, P)   we have

$$\frac{\partial T}{\partial V}\Big)_S = -\frac{\partial P}{\partial S}\Big)_V \qquad \text{Energy} \quad E(S,V) \qquad dE = TdS - PdV$$

$$\frac{\partial T}{\partial P}\Big)_S = \frac{\partial V}{\partial S}\Big)_P \qquad \begin{array}{c} H = E + PV \\ \text{Enthalpy} \end{array} \quad H(S,P) \qquad dH = TdS + VdP$$

$$\frac{\partial S}{\partial V}\Big)_T = \frac{\partial P}{\partial T}\Big)_V \qquad \begin{array}{c} F = E - TS \\ \text{Helmholtz} \\ \text{Free energy} \end{array} \quad F(T,V) \qquad dF = -SdT - PdV$$

$$\frac{\partial S}{\partial P}\Big)_T = -\frac{\partial V}{\partial T}\Big)_P \qquad \begin{array}{c} G = E - TS + PV \\ \text{Gibbs Free} \\ \text{energy} \end{array} \quad G(T,P) \qquad dG = -SdT + VdP$$

Cuboctahedron

$$C_V = T\frac{\partial S}{\partial T}\Big)_V \qquad C_P = T\frac{\partial S}{\partial T}\Big)_P \qquad dS = \frac{\partial S}{\partial T}\Big)_P dT + \frac{\partial S}{\partial P}\Big)_T dP$$

$$\underbrace{}_{\frac{C_P}{T}}$$

$$\frac{dS}{dT} = \frac{\partial S}{\partial T}\Big)_P \frac{dT}{dT} + \frac{\partial S}{\partial P}\Big)_T \frac{dP}{dT} \quad \text{for Const } V$$

$$\frac{\partial S}{\partial T}\Big)_V = \frac{\partial S}{\partial T}\Big)_P + \frac{\partial S}{\partial P}\Big)_T \frac{\partial P}{\partial T}\Big)_V \qquad \qquad \frac{\partial S}{\partial P}\Big)_T = -\frac{\partial V}{\partial T}\Big)_P$$

$$\frac{C_V}{T} = \frac{C_P}{T} + \frac{\partial S}{\partial P}\Big)_T \frac{\partial P}{\partial T}\Big)_V \qquad \qquad \frac{\partial P}{\partial T}\Big)_V = -\frac{\partial V/\partial T\big)_P}{\partial V/\partial P\big)_T}$$

$$C_P - C_V = -T\left[\frac{\partial V}{\partial T}\Big)_P\right]^2 \frac{\partial P}{\partial V}\Big)_T$$
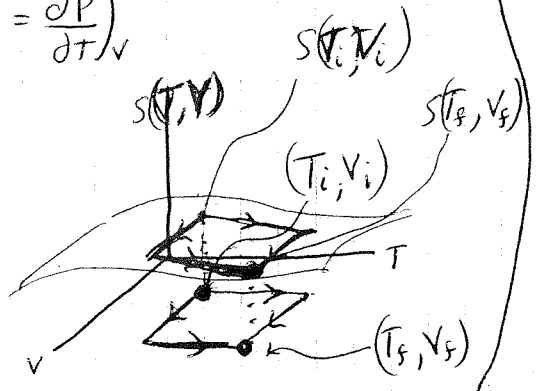
$$C_P - C_V = \frac{TV\alpha^2}{\kappa} \quad \text{regardless of Eq of state!}$$

Entropy for any thermal system:

$$dS = \underbrace{\frac{\partial S}{\partial T}\Big)_V}_{\frac{C_V}{T}} dT + \frac{\partial S}{\partial V}\Big)_T dV \qquad \frac{\partial S}{\partial V}\Big)_T = \frac{\partial P}{\partial T}\Big)_V$$

$$S(T_f, V_f) - S(T_i, V_i) = \int_{T_i}^{T_f} \frac{C_V'(T', V_i)}{T'} dT' + \int_{V_i}^{V_f} \frac{\partial P(T_0, V')}{\partial T} dV'$$

or

$$S(T_f, V_f) - S(T_i, V_i) = \int_{T_i}^{T_f} \frac{C_V'(T', V_i)}{T'} dT' + \int_{V_i}^{V_f} \frac{\partial P(T_f, V')}{\partial T} dV'$$

Aside:

If we have other variables we can write down relations for them. Lets let the # of particles N vary. with energy μ/particle

~~so we CE, Q, ...T) for~~ So variable are T, S, P, V, N, μ

$dE = TdS - PdV + \mu dN$

$dF = -SdT - PdV + \mu dN$

$dH = TdS + VdP + \mu dN$

$dG = -SdT + VdP + \mu dN$

$\left.\begin{array}{c}\end{array}\right\}$ Legendre transform $\longrightarrow$

$U' = TdS - PdV - Nd\mu$

$\Omega = -SdT - PdV - Nd\mu$

$U'' = TdS + VdP - Nd\mu$

$\underline{U''' = -SdT + VdP - Nd\mu}$

usually these are not used since N is a more common variable useful for simulations

---

Back to our simpler system where N is kept fixed.

Why define Thermodynamic Potentials F, H, G?

1) Useful for deriving Maxwell relations

2) They are minimal is System is in Equilibrium

Lets show this ~~for~~ System in Contact w/ a reservoir

E, V, T
S, P

E', V', T'
S', P'
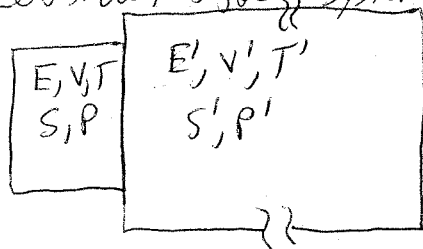
$S^{(0)} = S + S'$

$dS' = \dfrac{dE'}{T'} + \dfrac{P'dV'}{T'}$

$dS' = -\dfrac{dE}{T^\circ} + \dfrac{P^\circ dV}{T^\circ}$

$S' = -\dfrac{E}{T^\circ} - \dfrac{P^\circ V}{T^\circ} + Const$

$P \& T$ are intensive

So are $P^\circ \sim P'$ & are $T^\circ \sim T'$

$S^{(0)} = S + S' = S - \dfrac{E}{T^\circ} - \dfrac{P^\circ V}{T^\circ} + Const = Const -\dfrac{1}{T^\circ}(E - T^\circ S + P^\circ V)$

$\boxed{\text{to maximize } S^\circ \text{ we must minimize } E - T^\circ S + P^\circ V}$

recall E, S, V are variables for system T°, P° are variables for entire system or equivalently the bath or reservoir
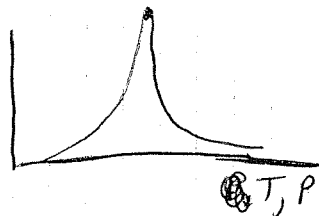
Lets see what happens under different Conditions

minimize $E - T^\circ S + P^\circ V$

Case I System is Completely isolated from reservoir &
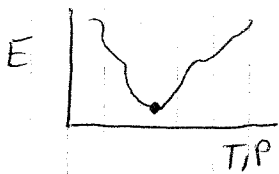
$E \& V$ are kept Constant

Then we must maximize S to

maximize S°

$\ln \Omega(E)$

T, P

Case II System is Completely isolated from reservoir &

S, V are kept Constant

Then we must minimize E to maximize S°

E

T, P

$T \& P$ not necessarily equal to $T^\circ \& P^\circ$

Since S is Const making E smaller makes E' bigger

E increases S' so S° is maximized

Case III System is allowed to exchange Volume

$\& S, P$ are held Const

$\underbrace{E}_{\substack{not \\ Const}} - \underbrace{T^\circ S}_{Const} + \underbrace{PV}_{\substack{not Const \\ due to V}}$ is minimized

E, V, T | E', V', T°
$S, P = P^\circ$ | S', P°
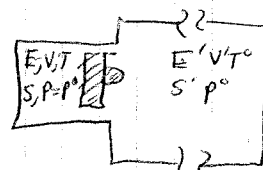
T is not necessarily equal to T°

Enthalpy $H = E + PV$ is minimized in order to maximize S°

H

V, E, T
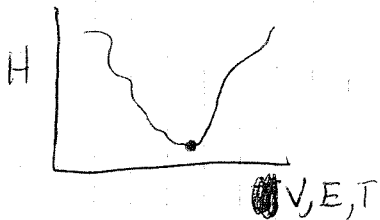
Case IV System is allowed to exchange heat $\& T, V$ are Const

$\underbrace{E}_{\substack{not \\ Const}} - \underbrace{T S}_{\substack{Const \ not \\ Const}} + \underbrace{P^\circ V}_{Const}$

$\underbrace{}_{not Const}$

E, V, S | $\sim T^\circ$
$P, T = T^\circ$ | E', V', S', P°
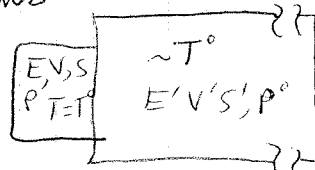
P is not necessarily equal to P°

Helmholtz $F = E - TS$ is minimized
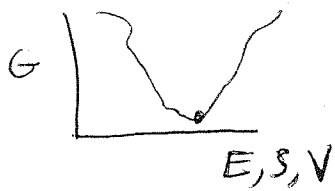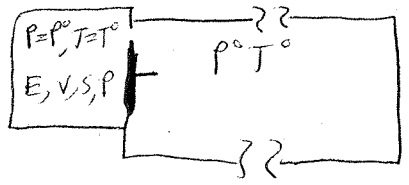free
energy

F

E, S, P
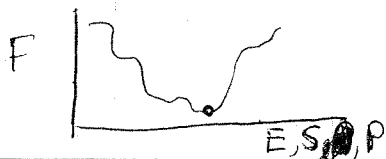
<u>Case V</u> System is allowed to exchange heat & volume w/ reservoir

$$T \& P \text{ are const}$$

Gibbs free energy $G = E - \underset{\substack{\uparrow \\ \text{const}}}{T} S + P \underset{\substack{\uparrow \\ \text{const}}}{V}$ is minimized

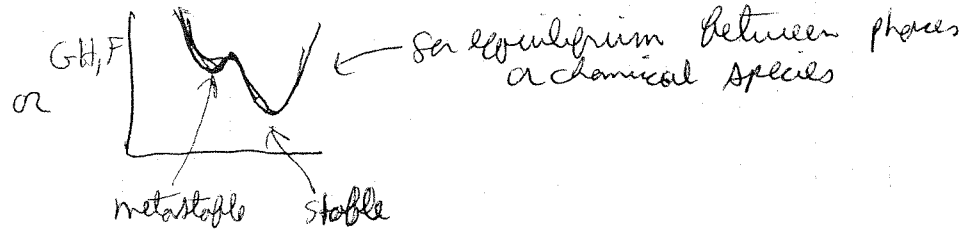$$\underset{\substack{\uparrow \\ \text{not const}}}{}$$

G vs E, S, V (curve with minimum)
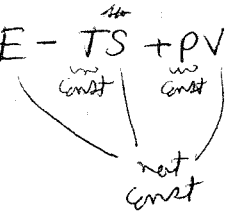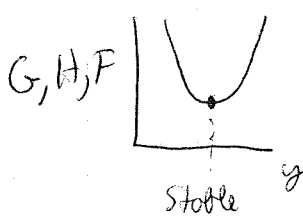
Strategy: ① determine which potential is relevant for the particular situation

② Minimize the potential in order to find equilibrium state

③ How do we determine the free energies?

Experimentally or for some cases using Stat Mech.

G, H, F (parabola) — Stable y

or G, H, F (double well) — metastable / stable — ← for equilibrium between phases or chemical species

Lets see if we can say something about systems in Equilibrium by relaxing our constraint.
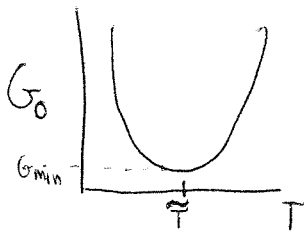
Ex: Gibbs Free Energy

— Fixed # of particles but volume & heat can be exchanged
— Reservoir w/ $T° \& P°$

Let $T \& V$ be the two independent parameters specifying state system A.

Fix V & ask how does G depend on T near G_{min}

$$\Delta T \equiv T - \tilde{T}$$

Expand $G_0 \equiv E - T°S + P°V$

$$G_0 = G_{min} + \left. \frac{\partial G_0}{\partial T} \right)_V \Delta T + \frac{1}{2} \underbrace{\left. \frac{\partial^2 G_0}{\partial T^2} \right)_V}_{\geq 0} (\Delta T)^2 + \dots$$

G_0 (curve) with G_{min} at $\tilde{T}$ vs T

Note: from first ~~observation~~ derivative

$$\frac{\partial G_0}{\partial T}\Big)_V = \frac{\partial E}{\partial T}\Big)_V - T^0\frac{\partial S}{\partial T}\Big)_V + P_0\frac{\partial V}{\partial T}\Big)_V^0 \qquad \text{for const } V \quad \frac{\partial S}{\partial T}\Big)_V = \frac{1}{T}\frac{\partial E}{\partial T}\Big)_V$$

$$\frac{\partial G_0}{\partial T}\Big)_V = \left(1 - \frac{T^0}{T}\right)\frac{\partial E}{\partial T}\Big)_V = 0$$

$$\tilde{T} = T^0 \quad \text{as we saw earlier}$$

From Second derivative $\qquad \frac{\partial^2 G_0}{\partial T^2} \geq 0$

$$\frac{\partial^2 G_0}{\partial T^2} = \frac{\partial}{\partial T}\left[\left(1 - \frac{T^0}{T}\right)\frac{\partial E}{\partial T}\Big)_V\right] = \frac{T^0}{T^2}\frac{\partial E}{\partial T}\Big)_V + \left(1 - \frac{T^0}{T}\right)\frac{\partial^2 E}{\partial T^2} \geq 0$$

$$\frac{\partial E}{\partial T}\Big)_V > 0$$

$$C_V \geq 0 \qquad \text{Lechatlier's Principle}$$

Near equilibrium any spontaneous change of a Systems parameters must bring about processes that tend to restore the system to equilibrium

Fix T & ask how G depends on V

$$G_0 - G_{min} = \frac{\partial G_0}{\partial V}\Big)_T \Delta V + \frac{1}{2}\frac{\partial^2 G}{\partial V^2}\Big)_T (\Delta V)^2 + \dots$$

Similar arguments give

$$\frac{\partial G_0}{\partial V}\Big)_T = -\tilde{P} + P^0 = 0 \qquad \text{as we saw earlier}$$

$$\frac{\partial^2 G_0}{\partial V^2}\Big)_T = -\frac{\partial P}{\partial V}\Big)_T \geq 0$$

$$K = -\frac{1}{V}\frac{\partial V}{\partial P}\Big)_T \geq 0$$

Note: From stat Mech

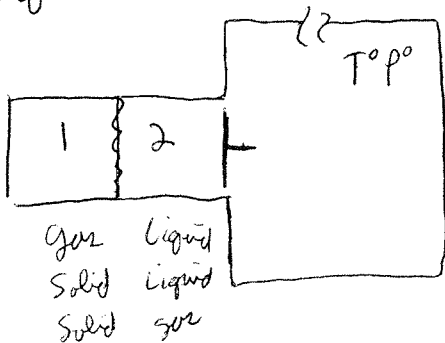$$\text{Prob} \propto \Omega = e^{S/k} = e^{(T^0 S - E - P^0 V)/kT^0} = e^{-G_0/kT^0}$$

$$P \propto e^{-\frac{1}{2}\frac{\partial^2 G}{\partial V^2}\Big)_T (\delta V)^2/kT^0} = e^{-\frac{\Delta V^2}{2VK\,kT^0}}$$

$$\overline{V^2} - \overline{V}^2 = kT^0 V K \qquad \begin{array}{l}\text{fluctuations in volume near equilibrium}\\ \text{Can get similar result for Temp fluctuations}\end{array}$$

Equilibrium between two phases & a reservoir holding T & P const

For ex: room ~~temp~~ pressure at zero °C for H_2O

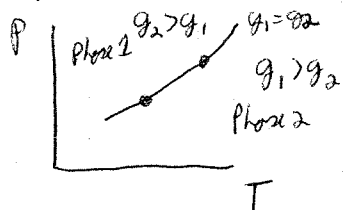$$G = v_1 g_1 + v_2 g_2 \qquad v_1 + v_2 = v = \text{const}$$

$$dv_1 = -dv_2$$

in Eq G is minimized & $dG = 0$

$$(g_1 - g_2) dv_1 = 0$$

$$g_1 = g_2$$

this way when we transfer a mole of material from state 1 to state 2 G stays constant and at a minimum

The set of points where $g_1 = g_2$ represent a phase equilibrium line

along this line $dg_1 = dg_2$ so that $g_1 = g_2$

$$dg \equiv d(\epsilon - Ts + Pv) = -s dT + v dP$$

$$-s_1 dT + v_1 dP = -s_2 dT + v_2 dP$$

$$(s_2 - s_1) dT = (v_2 - v_1) dP$$
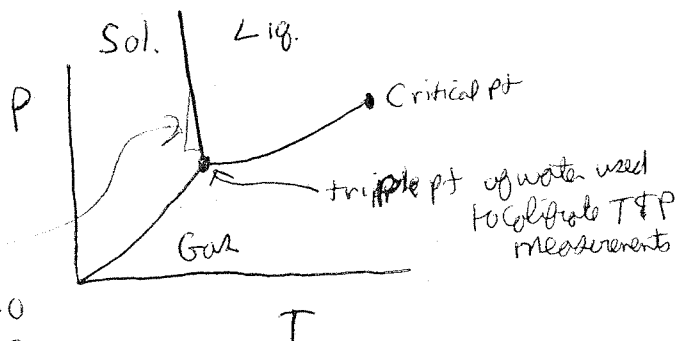
$$\boxed{\frac{dP}{dT} = \frac{\Delta S}{\Delta V}} \quad \text{Clausius Clapeyron Eq.}$$

Relates slope of phase equilibrium line w/ change in entropy & volume

$$\Delta S = S_2 - S_1 = \frac{L_{12}}{T} \qquad L_{12} \equiv \text{latent heat of transformation}$$
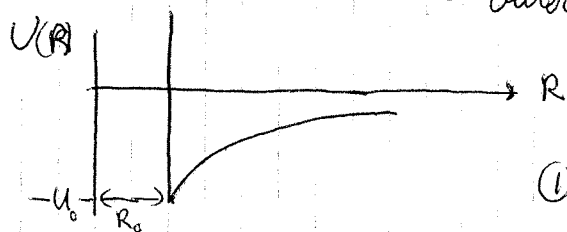
$$\frac{dP}{dT} = \frac{L_{12}}{T \Delta V}$$

For water slope is negative $\Delta S > 0$ $\Delta V < 0$

triple pt of water used to calibrate T & P measurements

Lets Analyze the Liquid gas line for a ~~Vander Waats~~ system described by the van der waals eq of state. ~ 1873

For ideal gas $PV = NkT$ assumption of no interactions

Non ideal gas: - repulsive for short distances
- attractive at long distances

What does this potential do to eq of state

① replace V by empty volume between particle
$$V \to V - Nb \qquad b = \frac{4}{3}\pi R_0^3$$

Exact derivation pg 424 of Reif

② replace P by $P + a\left(\frac{N}{V}\right)^2$ to represent extra combining force from long range attractions

$$\left(P + a\left(\frac{N}{V}\right)^2\right)\left(V - Nb\right) = NkT$$

$$\overline{V} \equiv \frac{V}{\cancel{N}v}$$

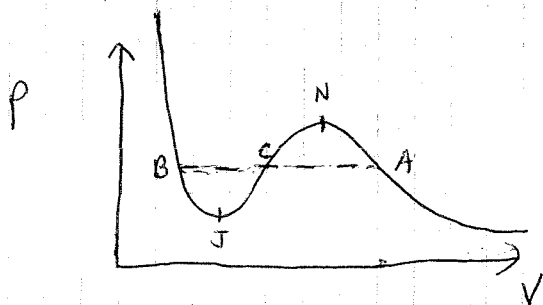$$\boxed{\left(P + \frac{a}{v^2}\right)\left(v - b\right) = RT}$$

what do PV curves look like for this cubic equation?

[Low T Case]

High P: Liquid $\frac{dP}{dV}$ is large
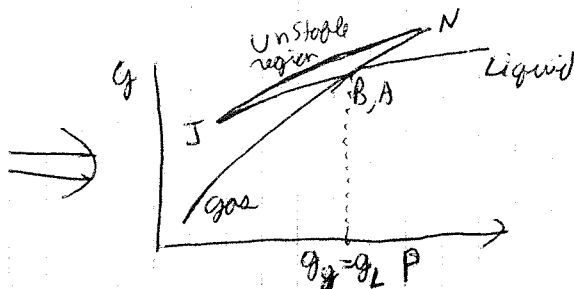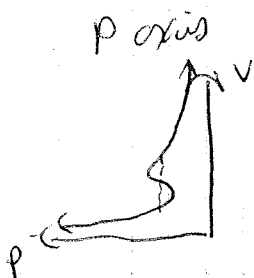
Low P: gas $\frac{dP}{dV}$ is small

intermediate P?

For Constant T
$$dg = Vdp$$
$$g - g_0 = \int_{P_0}^{P} Vdp$$

So g is just related to the area between the PV curves & the P axis

Phase transition occurs at pt A & B where
$$g_L = g_g$$