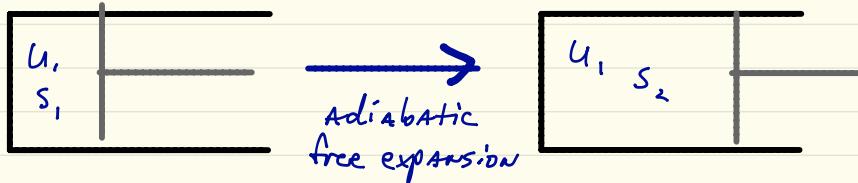
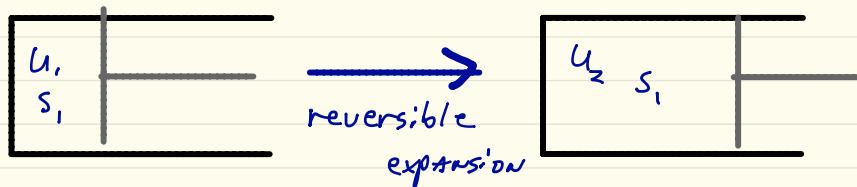


Lecture 5

Energy minimum principle



No heat or work, $\Delta U = 0$, ΔS maximized



No heat, $\Delta S = 0$, $\Delta U = dW$ minimized

Intuitively, system expands to minimize U . Can we prove it?

From our postulates, $dS = 0$ and $d^2S \leq 0$ @ equilibrium with respect to any **internal variables**. What about dU and d^2U ?

Write $dS = \left(\frac{\partial S}{\partial u}\right)_x du + \left(\frac{\partial S}{\partial x}\right)_u dx$ \times an internal DOF

$$dS = 0 \rightarrow \left(\frac{\partial U}{\partial x}\right)_S = -\frac{\left(\frac{\partial S}{\partial x}\right)_u}{\left(\frac{\partial S}{\partial u}\right)_x} = -T_{eq} \left(\frac{\partial S}{\partial x}\right)_u = 0$$

Shows energy is an extremum @ equilibrium

maximum or minimum?

Let $(\frac{\partial U}{\partial X})_S = "P"$ P is a function of $U + X$

$$dP = \left(\frac{\partial P}{\partial U}\right)_X dU + \left(\frac{\partial P}{\partial X}\right)_U dX$$

$$\left(\frac{\partial P}{\partial X}\right)_S = \left(\frac{\partial P}{\partial U}\right)_X \cancel{\left(\frac{\partial U}{\partial X}\right)_S}^0 + \left(\frac{\partial P}{\partial X}\right)_U \cancel{\left(\frac{\partial X}{\partial X}\right)_S}^1$$

$$\left(\frac{\partial P}{\partial X}\right)_S = \left(\frac{\partial P}{\partial X}\right)_U \quad \begin{matrix} \text{derivatives same @ const} \\ S+U \end{matrix}$$

$$\left(\frac{\partial P}{\partial X}\right)_U = \left[\frac{\partial}{\partial X} \left(\frac{\partial U}{\partial X} \right)_S \right]_U$$

$$= \left[\frac{\partial}{\partial X} \left\{ -T_{eq} \left(\frac{\partial S}{\partial X} \right)_U \right\} \right]_U \quad \text{from above}$$

$$= -T_{eq} \underbrace{\left(\frac{\partial^2 S}{\partial X^2} \right)_U}_{}.$$

≤ 0 @ equilibrium

$$\left(\frac{\partial P}{\partial X}\right)_U = \left(\frac{\partial^2 U}{\partial X^2}\right)_S \geq 0 @ \text{equilibrium}$$

Energy minimum principle - when a constraint is relaxed at constant S , the system relaxes to the state of minimum energy

From this the same conditions on equilibrium can be found, $T_1 = T_2, \dots$

(3)

This by itself isn't so useful, but it leads to useful stuff.

A basic problem is that the extensive variables, especially S , aren't so convenient as independent variables. T, P — those are nice to measure & control.

Legendre transform provides way to do this change of variables

Given a function $Y = Y(x)$ fundamental eq
 $p = \frac{dY}{dx}$ intensive variable

Legendre transform $\psi(p) = Y - px$

contains all the same information as the original function. Legendre transform on ψ recovers Y .

Can apply to multi-dimensional functions in same way.

(As an aside, Hamiltonian mechanics, which use positions & momenta as variables, is a Legendre transform on the Lagrangian mechanics of positions & velocities.)

$$\begin{aligned} y &= mx + b \\ b &= y - mx \\ &= y - \left(\frac{\partial f}{\partial x}\right)x \end{aligned} \quad \left. \begin{array}{l} \text{intercept} \\ \text{of} \\ \text{tangent} \\ \text{line} \end{array} \right\}$$

Example $Y = \frac{1}{4} X^2$

$$p = \frac{dY}{dX} = \frac{1}{2} X$$

$$\psi(p) = Y - pX = p^2 - p(2p) = -p^2$$

p , slope

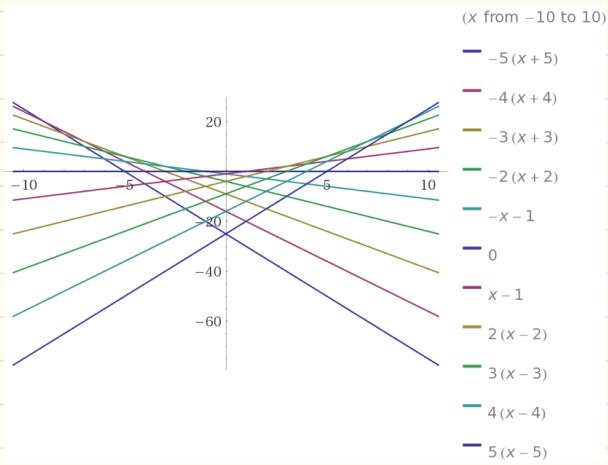
-2
-1
0
1
2

$\psi(p)$, intercept

-4
-2
0
-2
-4

family of lines
whose tangents
define Y

$$Y = \frac{1}{4} X^2$$



plot

$p x - p^2$ where $p = \{-5, -4, -3, -2, -1, 0, 1, 2, 3, 4, 5\}$

4

Enthalpy $H \equiv H(S, V, N)$ Legendre transform V

$$H = U - \left(\frac{\partial U}{\partial V}\right)_{S, N} V$$

$$H = U + PV$$

$$dH = dU + d(PV)$$

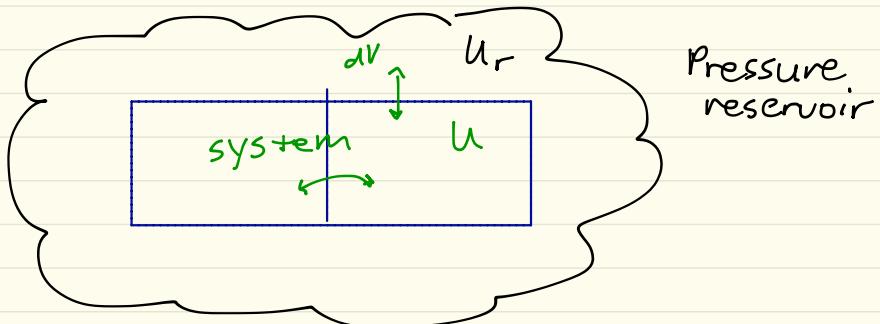
$$= TdS - PdV + \sum_i \mu_i dN_i + PdV + VdP$$

$$dH = TdS + VdP + \sum_i \mu_i dN_i$$

Enthalpy is a state function and is a natural function of S, P, N

$$H = H(S, P, N_i)$$

$$\left(\frac{\partial H}{\partial S}\right)_{P, N_i} = T \quad \left(\frac{\partial H}{\partial P}\right)_{S, N_i} = V \quad \left(\frac{\partial H}{\partial N_j}\right)_{S, P, V, i \neq j} = \mu_j$$



Assume the reservoir much much bigger than the system, so P_r invariant to small changes in volume

(5)

Relax some constraint on system so it goes to a new equilibrium.

$$dU_{\text{tot}} = dU + dU_r = 0 \quad @ \text{constant } S$$

System + reservoir only exchange volume, so

$$\begin{aligned} dU_r &= -P_r dV_r \\ dV_r &= -dV \quad dU_{\text{tot}} = dU + P_r dV \\ &= d(U + P_r dV) \quad (\text{const } P_r = P) \\ &= dH \end{aligned}$$

$dH = 0$ @ equilibrium at constant pressure.

Further, $d^2H = d^2(U + PV)$

$$\begin{aligned} &= d^2U + P \underset{\substack{\rightarrow 0 \\ \text{tot}}}{d^2V} \quad U \text{ an independent variable, so its} \\ &\quad \text{2nd derivative with other internal variables vanishes} \\ d^2H &= d^2U \underset{\substack{\rightarrow 0 \\ \text{tot}}}{} > 0 \end{aligned}$$

Like U , H is minimized @ equilibrium over the set of states with $P = P_r$.

$$H = U + PV$$

H is the internal energy of a system, including the energy to make "space" for it in the environment

Recall Euler equation $U = TS - PV + \sum \mu N$

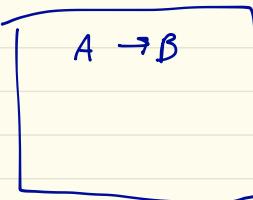
Combining, $H = TS - \sum \mu N$

5.5

$$H_A = U_A + PV_A$$

$$H_B = U_B + PV_B$$

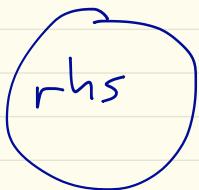
$$H_S - H_A = \Delta U + W$$



$$\begin{matrix} U_A & S_A & V_A & P_A \end{matrix}$$

$$\begin{matrix} U_B & S_B & V_B & P_B \end{matrix}$$

$$dQ = TdS$$



$$dW = -PdV$$



$$dU + dQ + dW = 0$$

If system + rws @ same P, $dW^{\text{rws}} = PdV$ systems

$$dU + PdV + dQ = 0$$

$$d(U + PV) + dQ = 0$$

$$dH = -dQ_{\text{rhs}} = dQ_{\text{sys}}$$

H is heat flow @ const P

If $dS = 0 \rightarrow dH = 0$

H minimized @ const P + S.

From definition of heat capacity,

$$C_p = \frac{1}{N} \left(\frac{\partial S}{\partial T} \right)_{p,N} = \frac{1}{N} \left(\frac{\partial H}{\partial T} \right)_{n,p} = \frac{1}{N} \left(\frac{\partial q_{as}}{\partial T} \right)_p$$

$$dH = \partial q_{as}$$

Enthalpy is thus heat flow at constant pressure and when system experiences only PV work. Common situation, which makes enthalpy useful.

Enthalpy of an ideal gas?

$$U = cNRT \quad H = U + PV = cNRT + NRT \\ = (c+1)NRT$$

enthalpy of an ideal gas is a natural, exclusive function of T (as is its derivatives).

Could, with difficulty, convert into $H(S, P, N)$, using S expression of ideal gas.

$$C_{p,ig} = \left(\frac{\partial H_{ig}}{\partial T} \right)_{n,p} = (c+1)R = C_{v,ig} + R$$

State functions have the property that cross-derivatives are equal:

$$df = \underbrace{\left(\frac{\partial f}{\partial x}\right)_y dx}_{A(x,y)} + \underbrace{\left(\frac{\partial f}{\partial y}\right)_x dy}_{B(x,y)}$$

$$\left(\frac{\partial A}{\partial y}\right)_x = \left(\frac{\partial B}{\partial x}\right)_y$$

because order of differentiation doesn't matter

Basis of so-called "Maxwell relations"

$$dH = TdS + VdP + \sum_i \mu_i dN_i$$

$$\left(\frac{\partial T}{\partial P}\right)_{S,N} = \left(\frac{\partial V}{\partial S}\right)_{P,N}$$

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

$$\left(\frac{\partial V}{\partial N}\right)_{S,P} = \left(\frac{\partial \mu}{\partial P}\right)_{S,N}$$

We'll use these when we apply enthalpy

Helmholtz potential

$U \equiv U(S, V, N)$ Legendre transform S

$$F = U - \left(\frac{\partial U}{\partial S}\right)_{V, N} S$$

$$F = U - TS$$

$$dF = dU - d(TS)$$

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

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

F is a natural function of T, V, N , $F(T, V, N)$

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

Euler relation gives

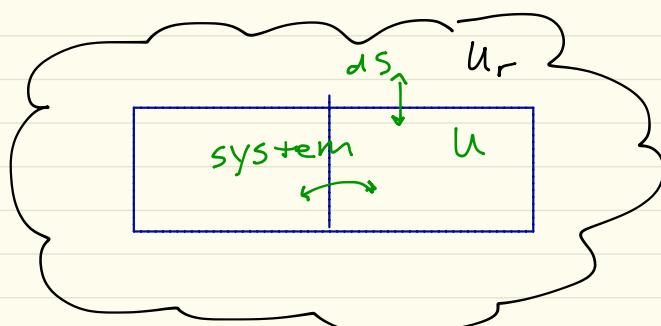
$$F = -PV + \sum \mu N$$

$$\left(\frac{\partial S}{\partial V}\right)_{N, T} = \left(\frac{\partial P}{\partial T}\right)_{N, V}$$

Maxwell relations

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

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



Assume the reservoir much much bigger than the system, so T_r invariant to small changes in entropy.

Relax some constraint on system so it goes to a new equilibrium.

$$dU_{\text{tot}} = dU + dU_r = 0 \quad @ \text{constant } S$$

System + reservoir only exchange heat, so

$$dU_r = T_r dS_r$$

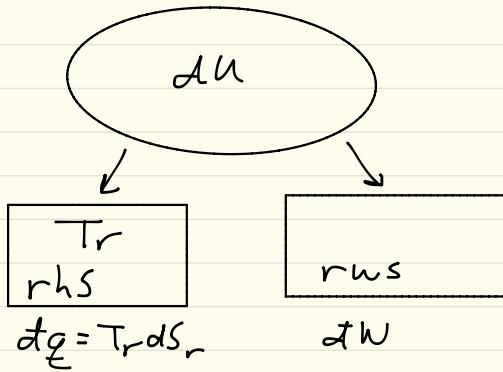
$$\begin{aligned} dS_r &= -dS \quad dU_{\text{tot}} = dU + T_r dS_r \\ &= d(U - T_r dS) \quad (\text{const } T_r = T) \\ &= dF \end{aligned}$$

$dF = 0$ @ equilibrium at constant temperature

Also, $\partial^2 F > 0$ @ equilibrium

Helmholtz potential minimized @ equilibrium over manifold of states with $T = T_r$.

reversible
work
theorem



$$dU + \delta q + dW = 0 \quad dS + dS_r = 0$$

$$dU - Tr dS = - dW \rightarrow \boxed{dF = - dW}$$

F is thus the "free energy," the maximum amount of work extractable in contact with a thermal reservoir.

Helmholtz free energy of an ideal gas?

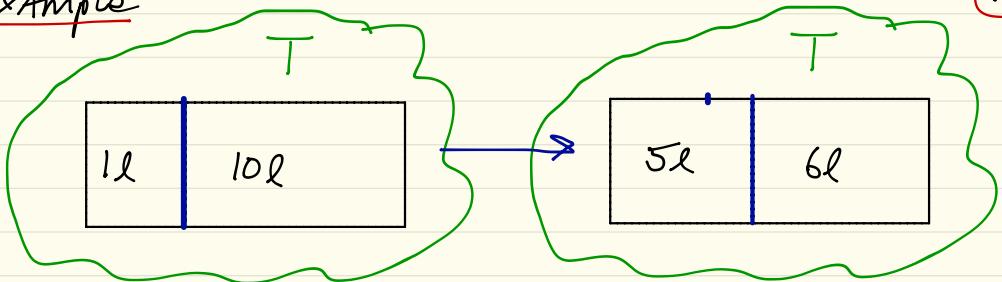
$$F = U - TS = cNRT - TS(T, V, N)$$

$$S(T, V, N) = cNR \ln \frac{T}{T_0} + NR \ln \frac{V}{V_0} \frac{N_0}{N} + Ns_0$$

$$\begin{aligned} F &= cNRT - TNs_0 + NRT \ln \left\{ \left(\frac{T}{T_0} \right)^c \left(\frac{V}{V_0} \right) \left(\frac{N_0}{N} \right) \right\} \\ &= \left(\frac{NT}{N_0 T_0} \right) \left(cN_0 RT_0 - N_0 T_0 s_0 \right) + NRT \ln \dots \end{aligned}$$

$$\boxed{F_{ig} = NRT \left\{ \frac{F_0}{N_0 RT_0} + \ln \left\{ \left(\frac{T}{T_0} \right)^c \left(\frac{V}{V_0} \right) \left(\frac{N_0}{N} \right) \right\} \right\}}$$

11

example

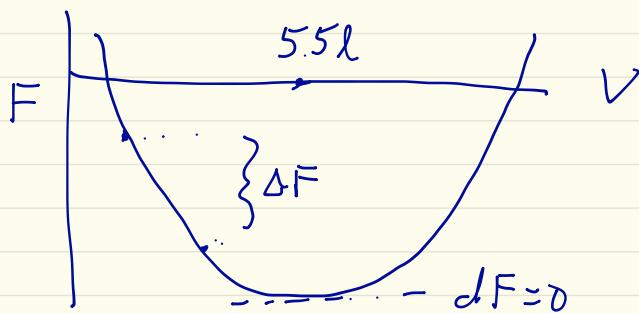
1 mole in each chamber, ideal gases

$$\text{@ constant } T, N, \quad F = \text{const} - NRT \ln \left(\frac{V}{V_0} \right)$$

$$\Delta F = -NRT \left\{ \ln \frac{5}{V_0} + \ln \frac{6}{V_0} - \ln \frac{1}{V_0} - \ln \frac{10}{V_0} \right\} = -NRT \ln 3$$

$\text{@ } 273K$

Free energy $\downarrow \rightarrow$ w done



F always defined. Useful properties across processes in which T, V constants,

Gibbs potential

$$U \equiv U(S, V, N)$$

Legendre transform S and V

$$G = U - \left(\frac{\partial U}{\partial S}\right)_{V, N} S - \left(\frac{\partial U}{\partial V}\right)_{S, N} V$$

$$G = U - TS + PV$$

$$dG = dU - d(TS) + d(PV)$$

$$= TdS - PdV - TdS - SdT + PdV + VdP + \sum_i \mu_i dN_i$$

$$dG = -SdT + VdP + \sum_i \mu_i dN_i$$

G is a natural function of T, P, N

$$\left(\frac{\partial G}{\partial T}\right)_{P, N} = -S \quad \left(\frac{\partial G}{\partial P}\right)_{T, N} = V \quad \left(\frac{\partial G}{\partial \mu_i}\right)_{T, P} = \mu_i$$

Euler relation gives

$$G = \sum_i \mu_i N_i$$

For a single component system, the molar Gibbs energy is μ .

$$G/N = \mu \quad \frac{G}{N} = \sum_i \mu_i dX_i$$

For this reason μ is often called molar Gibbs energy and μ_i partial molar Gibbs energy.

Gibbs energy is minimized at equilibrium for a system in communication with a constant T and P reservoir. Corresponds to maximum work that can be extracted at constant T + P.

Most widely applied to problems in chemical equilibria. We will return to this.

Maxwell relations

$$-\left(\frac{\partial S}{\partial P}\right)_{T,N} = \left(\frac{\partial U}{\partial T}\right)_{P,N}$$

$$-\left(\frac{\partial S}{\partial N_i}\right)_{T,P} = \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N}$$

$$\left(\frac{\partial V}{\partial N_j}\right)_{P,T} = \left(\frac{\partial \mu_i}{\partial P}\right)_{N,T}$$

Can derive important relationship between G and H:

$$G = H - TS \rightarrow \frac{G}{T} = \frac{H}{T} - S$$

$$\begin{aligned}\left(\frac{\partial(G/T)}{\partial T}\right)_{P,V} &= \frac{\partial(H/T)}{\partial T} - \left(\frac{\partial S}{\partial T}\right) \\ &= -\frac{H}{T^2} + \underbrace{\frac{1}{T}\left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial S}{\partial T}\right)_P}_{= 0!}\end{aligned}$$

$$\left(\frac{\partial(G/T)}{\partial T}\right)_{P,V} = -\frac{H}{T^2}$$

Similarly,

$$\left(\frac{\partial(F/T)}{\partial T}\right)_{P,V} = -\frac{U}{T^2}$$

Gibbs-Helmholtz relation
T-dependence of G
related to H!

Very commonly used
relation in chemical
systems.

everything potential (A for all es)

$U = U(S, V, N)$ Legendre transform S, V, N

$$A = U - \left(\frac{\partial U}{\partial S}\right)S - \left(\frac{\partial U}{\partial V}\right)V - \left(\frac{\partial U}{\partial N}\right)_N$$

$$= U - TS + PV - \mu N \quad \downarrow \quad \text{Given Euler form of } U$$

$$= 0 !!$$

A is a natural function of T, P, μ

$$dA = -SdT + VdP - Nd\mu = 0$$

Gibbs-Duhem relation recovered !!

See, it all hangs together...

Susceptibilities

First derivatives of $S, H \rightarrow$ intensive thermo properties

Second " " " " \rightarrow material properties

The second derivatives of G have special significance at constant N :

$$\left(\frac{\partial^2 g}{\partial T^2} \right)_{P,N} = - \left(\frac{\partial S}{\partial T} \right)_{P,N} = - \frac{C_p}{T} \quad \text{heat capacity!}$$

$$\left(\frac{\partial^2 S}{\partial P^2} \right)_{T,N} = \left(\frac{\partial V}{\partial P} \right)_{T,N} = -V K_T \quad \text{isothermal compressibility!}$$

$$\left(\frac{\partial^2 g}{\partial T \partial P} \right)_N = \left(\frac{\partial V}{\partial T} \right)_{P,N} = V \alpha \quad \text{coefficient of thermal expansion!}$$

These 3 form a "complete set". All 1st derivatives @ constant N can be expressed in terms of these.

coefficient of thermal expansion

$$\alpha = \frac{1}{V} \left(\frac{dV}{dT} \right)_{P,V}$$

fractional increase in volume
with T ($\equiv dV/V$)

ideal gas $\alpha = \frac{1}{T} > 0$

isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{dV}{dP} \right)_T$$

fractional decrease in volume
with P ($\equiv dV/V$)

ideal gas $\kappa_T = 1/P > 0$

constant pressure heat capacity

$$C_p = \frac{T}{N} \left(\frac{dS}{dT} \right)_P = \frac{1}{N} \left(\frac{\partial S}{\partial T} \right)_P$$

$$\begin{aligned} \text{ideal gas } S(T, P, N) &= cNR \ln\left(\frac{T}{T_0}\right) + NR \ln\left[\frac{RT}{P} \cdot \frac{P_0}{RT_0}\right] + \text{const} \\ &= (c+1)NR \ln\left(\frac{T}{T_0}\right) + NR \ln\left(\frac{P_0}{P}\right) + \text{const} \end{aligned}$$

$$\frac{T}{N} \left(\frac{dS}{dT} \right)_P = \frac{T}{N} (c+1)NR \cdot \frac{1}{T} = \underline{(c+1)R} > 0$$

Constant volume heat capacity

$$C_v = \frac{1}{N} \left(\frac{dS}{dT} \right)_v = \frac{1}{N} \left(\frac{dq}{dT} \right)_v \text{ ideal gts } C_v = cR$$

All other susceptibilities can be related to these 3

Example

vdW coefficient of isothermal compressibility

$$\kappa_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left(\frac{\partial V}{\partial P} \right)_T$$

$$P = \frac{RT}{V-b} - \frac{a}{V^2} \rightarrow \left(\frac{\partial P}{\partial V} \right)_T = -\frac{RT}{(V-b)^2} + \frac{2a}{V^3}$$

$$\rightarrow V \left(\frac{\partial P}{\partial V} \right)_T = \frac{2a}{V^2} - \frac{RTV}{(V-b)^2}$$

$$\kappa_T = \frac{1}{\frac{RTV}{(V-b)^2} - \frac{2a}{V^2}} = \frac{V^2(V-b)^2}{RTV^3 - 2a(V-b)^2}$$

Fun, fun... is this always > 0 ? NO!

Reflects regions of instability. We'll return to this.