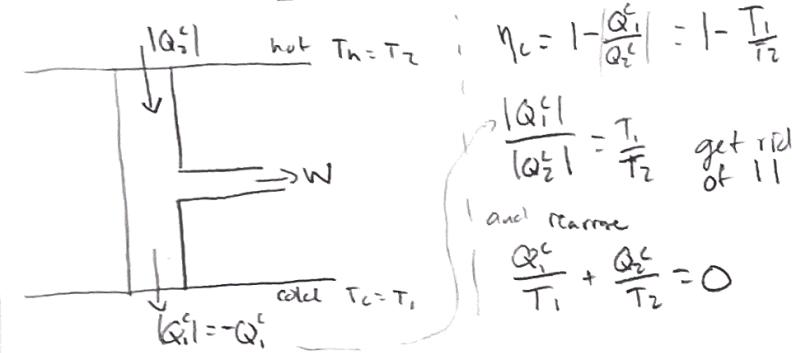


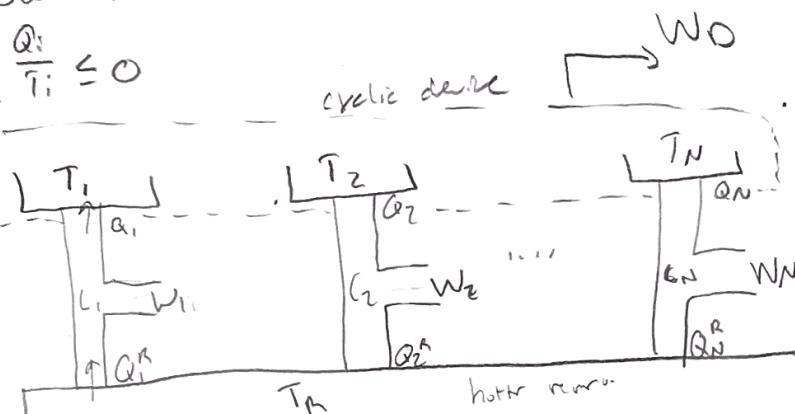
# Entropy

Consider the Carnot Engine



Now Prove

$$\sum_{i=1}^N \frac{Q_i}{T_i} \leq 0$$



Sign convention

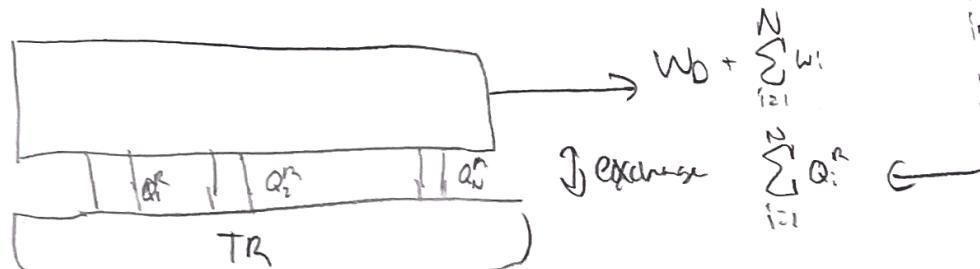
$$W_i = Q_i^R - Q_i$$

$Q > 0$  : heat flowing from  $C_i$  into top reservoir at temp  $T_i$

$W_i > 0$  : done by  $C_i$  on surroundings

$Q^R > 0$  : flowing from the hot reservoir at  $T_R$  to the Carnot device  $C_i$

Make a big black box



Then by Kelvin statement: For a cyclic device it is impossible to take heat from one reservoir and change it entirely into work  
thus!

$$\sum_{i=1}^N Q_i^R \leq 0$$

(we are allowed to do nothing or to do work on the device and transfer it entirely into heat)

↳ [Next step]  $\rightarrow \sum_{i=1}^N \frac{Q_i^R}{T_R} \leq 0$   $\rightarrow$  Heat flowing into the cycle device is power so w/ divided  $\frac{|Q_1^C|}{T_1} + \frac{|Q_2^C|}{T_2} \geq 0$  they are equal  $\rightarrow \frac{Q_1^C}{T_1} - \frac{Q_2^C}{T_2} = 0 \rightarrow \sum_{i=1}^N \frac{Q_i}{T_i} \leq 0$

For a reversible process  $\sum \frac{Q_i}{T_i} \leq 0$ ,  $Q_i^{\text{reverse}} = -Q_i^C$  running the engine in the other direction

↑ but can't be true so for a reversible proc

$$\sum_{i=1}^N \frac{Q_i}{T_i} \geq 0$$

$$\sum_{i=1}^N \frac{Q_i}{T_i} = 0$$

reversible

Entropy looking more at this reversible cyclic process



if you follow the heat or work exchanged in the susceptors and out in the middle

isothermal expand and compression



\* Justify w/ these zig zags around the cycle places

The zig zags are

$$\sum_{i=1}^N \frac{Q_i}{T_i} = 0$$

$$\lim_{N \rightarrow \infty} \sum_{i=1}^N \frac{Q_i}{T_i} = 0 \rightarrow \oint \frac{dQ}{T} = 0 = dS$$

$$dS = \frac{dQ}{T}$$

entropy

irreversibly exchanged heat

Using Entropy to get nice results

Using  $dU = \delta Q - \delta W$  and  $dU = \frac{\partial U}{\partial T}dT + \frac{\partial U}{\partial V}dV \rightarrow \delta Q = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right]dV$

This is an incorrect differential but we have an integrating factor  $\frac{1}{T}$

$\rightarrow dS = \frac{\delta Q}{T} = \frac{1}{T} \frac{\partial U}{\partial T} dT + \frac{1}{T} \left[\frac{\partial U}{\partial V} + P\right]dV$

Use the exactness test to find a new relation  $\rightarrow \frac{\partial}{\partial V} \left( \frac{1}{T} \frac{\partial U}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{1}{T} \left( \frac{\partial U}{\partial V} + P \right) \right)$

after some algebra and differentiation you get this nice result

$\rightarrow \left[ \left( \frac{\partial U}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V - P \right]$

\* You can do other nice things w/ this result, if  $U(T)$  then  $\frac{\partial U}{\partial V} = 0$  then you can reverse it and show  $U$  is independent of  $V$

Heat capacity (we will show  $C_V = T \left( \frac{\partial S}{\partial T} \right)_V$  and  $C_P = T \left( \frac{\partial S}{\partial T} \right)_P$ ) (FOR IDEAL GAS)

$$dU = \frac{\partial U}{\partial T} dT + \frac{\partial U}{\partial V} dV$$

$C_V$  we have a relation for this

$$dU = \delta Q - \delta W \rightarrow dU = C_V dT + \left[ T \left( \frac{\partial P}{\partial T} \right)_V - P \right] dV$$

From PV=nRT

$$dS = \frac{\delta Q}{T} = \frac{dU + \delta W}{T} = \frac{C_V}{T} dT + \left[ \frac{\partial P}{\partial T} - \frac{P}{T} \right] dV + \frac{P dV}{T} = \frac{C_V}{T} dT + \left( \frac{\partial P}{\partial T} \right) dV = dS$$

$$dS = \frac{\partial S}{\partial T} dT + \frac{\partial S}{\partial V} dV$$

by comparing relations then,  $\frac{\partial S}{\partial T} = \frac{C_V}{T}$  and

$$dS = \frac{C_V}{T} dT + \frac{nR}{V} dV$$

$\hookrightarrow$  [we can integrate]  $S dS = S(T, V) = \int \frac{C_V}{T} dT + g(V) = C_V \ln T + g(V)$

$S(T, V) = \int \frac{nR}{V} dV + f(T) = nR \ln V + f(T)$

(IDEAL Gas) Equation of Entropy

$\rightarrow S(T, V) = C_V \ln T + nR \ln V + A$

\* Kardas: sloppy  $\rightarrow$  use reference entropy,  $S(T_r, V_r) = C_V \ln(T_r) + nR \ln(V_r) + A_2$  and subtract them

$$S(T, V) = C_V \ln \left( \frac{T}{T_r} \right) + nR \ln \left( \frac{V}{V_r} \right) + S(T_r, V_r)$$

\* to change from  $(T, V)$  to  $T, P$  or  $PV$  easily done  
w/  $PV = nRT$

Isentropic Processes (all Isentropic processes are adiabatic)  
(and all adiabats are Iso tropic)

↳ you can show w/ previous eq of  $S(T, V)$ , if  $S$  is a constant which is what it means to be Isentropic, you get the adiabatic relation  
P.S.  $TV^{\gamma-1} = \text{const.}$

### Bulk Modulus

$$B_T = -V \left( \frac{\partial P}{\partial V} \right)_T \quad (\text{old definition})$$

Applying same logic to entropy you obtain the same result ( $B_S$ )

$$B_S = -V \left( \frac{\partial P}{\partial V} \right)_S$$


$$[ \Delta S = V \Delta P \propto \Delta V \rightarrow -V \frac{\Delta P}{\Delta V} = \text{constant} = B_S ]$$

$$\text{Also } PV^\gamma = \text{const} \rightarrow P = \frac{\text{const}}{V^\gamma}$$

$$\left( \frac{\partial P}{\partial V} \right)_S = \frac{d}{dV} \left( \frac{\text{const}}{V^\gamma} \right) = \frac{\text{const}}{PV^\gamma} \frac{d}{dV} \left( \frac{1}{V^\gamma} \right) = -\frac{\gamma P}{V} \quad \text{then} \quad B_S = -V \left( \frac{-\gamma P}{V} \right) = \gamma P$$

Getting relation in terms of  $C_V, C_P$ : Result is  $C_P = C_V + TV B_T \alpha_V^2$

$$\text{Also } ① \left( \frac{C_P}{C_V} = \frac{B_S}{B_T} \right)$$

$$② \left( \frac{\partial S}{\partial T} \right)_P = \left( \frac{\partial S}{\partial T} \right)_V + \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

got from

$$dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV \quad \text{and} \quad dV = \left( \frac{\partial V}{\partial T} \right)_P dT + \left( \frac{\partial V}{\partial P} \right)_T dP$$

$$\text{combine} \rightarrow dS = \underbrace{\left( \frac{\partial S}{\partial T} + \frac{\partial S}{\partial V} \frac{\partial V}{\partial T} \right)}_{\text{L comparison}} dT + \dots$$

$$\text{L mult by } \frac{1}{T} \quad C_P = C_V + T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

simplifying we get in terms of Bulk modulus and  $\alpha_V$

$$\left( \text{use defn} \right) \left( \frac{\partial S}{\partial V} \right)_T = \left( \frac{\partial P}{\partial T} \right)_V \quad \text{and} \quad \frac{\partial P}{\partial V} \frac{\partial V}{\partial T} \frac{\partial T}{\partial P} = -1 \rightarrow \left( \frac{\partial P}{\partial V} \right)_T = -\left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial T}{\partial P} \right)_V \rightarrow C_P = C_V - T \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P^2$$

$$\text{and } \alpha_V = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \quad \text{and} \quad B_T = -V \left( \frac{\partial P}{\partial V} \right)_T \rightarrow C_P = C_V + TV B_T \alpha_V^2$$

## Entropy and the Second Law

Second law: Entropy always increases

$$\text{thus } S_1 \leq S_2 \text{ or } S_o \leq S_f$$

Proof

( Clausius statement  
(cycle process))

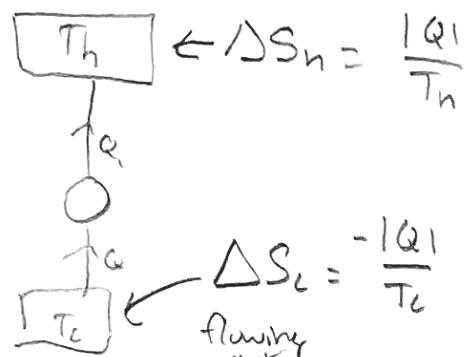
$$\sum \frac{Q_i}{T_i} \leq 0$$

$$\sum_{\text{real}} \frac{Q_i}{T_i}$$

make addit  
[so  $Q_i = 0$ ]  
just focus  
on reversible

$$+ \sum_{\text{reversible}} \frac{Q_i}{T_i} \leq 0$$

$\int \frac{dQ}{T} \rightarrow$  make reversible prob  
2 to 1 so  $S_1 - S_2 > 0$



$$\Delta S_n = \int \frac{dQ}{T} = \frac{1}{T} Q$$

Total Entropy Change

$$\Delta S = \Delta S_c + \Delta S_n = Q \left( \frac{1}{T_H} - \frac{1}{T_C} \right) < 0$$

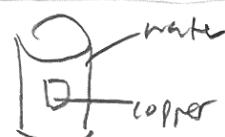
(as  $T_H > T_C$ )

Thus a non clausius machine breaks 2nd law in terms of entropy

$\Delta S = \int \frac{dQ}{T} = \int_{V_0}^{V_f} \frac{P dV}{T} = nR \int_{V_0}^{V_f} \frac{1}{V} dV = nR \ln \left( \frac{V_f}{V_0} \right)$

$dU = dQ - PdV$   
no internal energy change  $T = \text{const.}$

\* this is a reversible process while in equilibrium states, fast free expansion is not a sequence of reversible equilibrium processes. Here the end states is reversible so the  $\Delta S$  of universe is 0. Can compress back, heat flows into reservoir, back to original



$$M^w C_p^w (T_f - T_0) + M^c C_p^c (T_f - T_0) = 0 \rightarrow T_f = \frac{M^w C_p^w T_0 + M^c C_p^c T_0}{M^w C_p^w + M^c C_p^c}$$

$$\Delta S = \Delta S^c + \Delta S^w = \int \frac{dQ}{T} = \int_{T_0}^{T_f} \frac{M^c C_p^c}{T} dT + \int_{T_0}^{T_f} \frac{M^w C_p^w}{T} dT = \text{positive number}$$

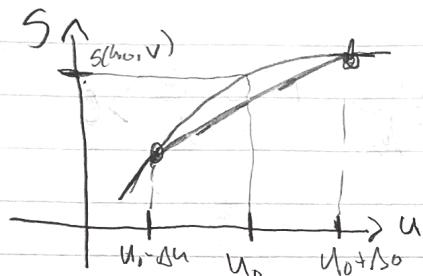
if you put  
in numbers  
 $\Delta S > 0$

□ We know entropy is extensive

$$\lambda S(u, v) = S(\lambda u, \lambda v) =$$

$$\lambda S(u, v) > S(u - \Delta u, v) + S(u + \Delta u, v)$$

otherwise:  $T > 0 \Rightarrow \left(\frac{\partial S}{\partial u}\right)_v = \frac{1}{T} > 0$ , be a concave function of  $u$



$$S(u_0 + \Delta u, v) + \frac{S(u_0 + \Delta u, v) - S(u_0 - \Delta u, v)}{2\Delta u} (\Delta u - (\Delta u - \Delta u))$$

(new equation of the line)

$$S(u_0, v) > S(u_0 - \Delta u, v) + \frac{S(u_0 + \Delta u, v) - S(u_0 - \Delta u, v)}{2\Delta u} \Delta u$$

Same thing  $\rightarrow [S(u - \Delta u, v) + S(u + \Delta u, v) < 2S(u, v)]$

$$S(u \pm \Delta u, v) = S(u, v) \pm \left(\frac{\partial S}{\partial u}\right)_v \Delta u + \frac{1}{2} \left(\frac{\partial^2 S}{\partial u^2}\right)_v (\Delta u)^2 + \dots$$

$$S(u - \Delta u, v) + S(u + \Delta u, v) - 2S(u, v) < 0$$

$$\hookrightarrow \frac{\partial^2 S}{\partial u^2} (\Delta u)^2 < 0 \rightarrow \boxed{\left(\frac{\partial^2 S}{\partial u^2}\right)_v < 0}$$

Same thing for volume:  $S(u, v - \Delta v) + S(u, v + \Delta v) < 2S(u, v)$  symmetric so

$$\boxed{\left(\frac{\partial^2 S}{\partial v^2}\right)_u < 0}$$

$$S(u + \Delta u, v - \Delta v) + S(u - \Delta u, v + \Delta v) < 2S(u, v) \quad \begin{array}{l} \text{will give the} \\ \text{same result} \end{array}$$

$$S(u - \Delta u, v - \Delta v) + S(u + \Delta u, v + \Delta v) < 2S(u, v)$$

$$S(u \pm \Delta u, v \pm \Delta v) = S(u, v) \pm \left(\frac{\partial S}{\partial u}\right)_v \Delta u + \left(\frac{\partial S}{\partial v}\right)_u \Delta v + \frac{1}{2} \left(\frac{\partial^2 S}{\partial u^2}\right)_v (\Delta u)^2 + \frac{1}{2} \left(\frac{\partial^2 S}{\partial v^2}\right)_u (\Delta v)^2 + \frac{1}{2} \left(\frac{\partial^2 S}{\partial u \partial v}\right)_{uv} \Delta u \Delta v$$

$$\hookrightarrow \left(\frac{\partial^2 S}{\partial u^2}\right)_v \Delta u^2 + 2 \left(\frac{\partial^2 S}{\partial u \partial v}\right)_{uv} \Delta u \Delta v + \left(\frac{\partial^2 S}{\partial v^2}\right)_u (\Delta v)^2 < 0 \quad \begin{array}{l} \text{for } S'' > 0 \text{ min } S'' < 0 \text{ max} \\ \& \& \end{array}$$

for 2 v:

$\frac{\partial^2 f}{\partial x^2}$	$\frac{\partial^2 f}{\partial x \partial y}$
$\frac{\partial^2 f}{\partial y \partial x}$	$\frac{\partial^2 f}{\partial y^2}$

$$= \frac{\partial^2 f}{\partial x^2} - \left(\frac{\partial^2 f}{\partial xy}\right)^2 > 0 \quad \text{then you have extremum}$$

We want!

$$f(\Delta u, \Delta v) = \text{our error}$$

$$\frac{\partial f(\Delta u, \Delta v)}{\partial \Delta u^2} = 2 \left( \frac{\partial^2 S}{\partial u^2} \right)_v \quad \text{etc., to determine}$$

$$\begin{vmatrix} 2 \left( \frac{\partial^2 S}{\partial u^2} \right)_v & 2 \frac{\partial^2 S}{\partial u \partial v} \\ 2 \frac{\partial^2 S}{\partial v \partial u} & 2 \left( \frac{\partial^2 S}{\partial v^2} \right)_u \end{vmatrix} = \left( \frac{\partial^2 S}{\partial u^2} \right)_v \left( \frac{\partial^2 S}{\partial v^2} \right)_u - \left( \frac{\partial^2 S}{\partial u \partial v} \right)^2 > 0$$

necessary only

$$\left( \frac{\partial^2 S}{\partial u^2} \right)_v < 0 \quad \text{and} \quad \left( \frac{\partial^2 S}{\partial v^2} \right)_u < 0$$

$$du = SQ - pdV = Tds - pdV \rightarrow \left( \frac{\partial S}{\partial u} \right)_V = \frac{1}{T(c_{u,V})}$$

$$\left( \frac{\partial^2 S}{\partial u^2} \right)_V = \frac{-1}{T^2(c_{u,V})} \cdot \left( \frac{\partial T}{\partial u} \right)_V, \quad \left( \frac{\partial u}{\partial T} \right)_V = c_V$$

$$\left( \frac{\partial^2 S}{\partial u^2} \right)_V = -\frac{1}{c_V T^2} < 0$$

$$c_V > 0, \quad T > 0$$

$$\left( \frac{\partial^2 S}{\partial u^2} \right)_V \left( \frac{\partial^2 S}{\partial v^2} \right)_u - \left( \frac{\partial^2 S}{\partial u \partial v} \right)^2 > 0 \Rightarrow B_+ > 0$$

$$B_+ = -\sqrt{\left( \frac{\partial^2 S}{\partial v} \right)_+} > 0$$



$\Delta V > 0 \quad \Delta P = -B_+ \frac{\Delta V}{V} < 0$   
pressure decreases and does it  
back to equilibrium

## Exact Equations



Look at this first dummy

$$\Psi(x,y) = \Psi(x, y(x)) \rightarrow \frac{\partial}{\partial x} \Psi(x,y) = \frac{\partial \Psi}{\partial x} + \frac{\partial \Psi}{\partial y} \cdot \frac{dy}{dx}$$

[Let's do]  $\frac{\partial}{\partial y} \left( \frac{\partial}{\partial x} \Psi(x,y) \right) = \frac{\partial^2}{\partial y \partial x} \Psi(x,y) = \Psi_{xy}$  or  $\frac{\partial}{\partial x} \left( \frac{\partial}{\partial y} \Psi \right) = \frac{\partial^2}{\partial x \partial y} \Psi = \Psi_{yx}$

If functions are continuous then  $\boxed{\Psi_{xy} = \Psi_{yx}}$

Exact equation:

(compare with)  $M(x,y) + N(x,y) \frac{dy}{dx} = 0$

$\underbrace{\Psi_x = M}_{\text{if}} \quad \text{then} \quad \frac{\partial}{\partial x} \Psi(x,y) = 0$

$\Psi_y = N \quad \text{then} \quad \frac{\partial}{\partial y} \Psi(x,y) = 0$

can only do this if it is exact, To tell if it is exact use the rule of  $\Psi_{xy} = \Psi_{yx}$

$\Psi_x = M \rightarrow \frac{\partial}{\partial y} M = \Psi_{xy} \leftarrow \text{should be equal}$

$\Psi_y = N \rightarrow \frac{\partial}{\partial x} N = \Psi_{yx} \leftarrow \text{equal}$

then  $\boxed{M_y = N_x}$  exactness test

ex)

$$\underbrace{2x+3}_M + \underbrace{(2y-2)}_{N} \frac{dy}{dx} = 0$$

$$M_y = 0, N_x = 0 \quad \boxed{\text{Exact}}$$

$$\Psi_x = M = 2x+3 \quad \text{and we know } \frac{\partial}{\partial x} \Psi = 0 \quad \text{or } \Psi = C$$

$$\Psi_y = N = 2y-2$$

$\boxed{\text{Integrating}} \quad \Psi = \int \Psi_x dx = \int (2x+3) dx = x^2 + 3x + h(y)$

↓ because lost functions of y

[We have a  $\Psi$  now]  $\rightarrow \begin{bmatrix} \text{so if we take} \\ \text{partial of } \Psi \text{ w.r.t. } y \\ \text{we should get } N \end{bmatrix} \rightarrow \frac{\partial}{\partial y} \Psi = N \Rightarrow \Psi_y = 0 + 0 + h'(y) = 2y-2 \rightarrow h(y) = y^2 - 2y + C_1$

$$\Psi(x,y) = x^2 + 3x + y^2 - 2y + C_1$$

$$\Psi = C$$

$$\boxed{x^2 + 3x + y^2 - 2y = C_3}$$

# Integrating factor to solve 1<sup>st</sup> order ODE

(Ex)  $(3xy + y^2) + (x^2 + xy)\frac{dy}{dx} = 0$

$M_y = 3x+2y \neq N_x = 2x+y$  let's multiply by a factor  $\mu$  to both sides  
to try to make it exact.

Let's say  $\mu(x)$ , could be  $\mu(y)$  or  $\mu(x,y)$  (more complicated)

$$M(x)(3xy + y^2) + \mu(x)(x^2 + xy)\frac{dy}{dx} = 0$$

$\frac{\partial}{\partial y}$  there should be eqn w/  $\frac{\partial}{\partial x}$   
so let's solve for  $M(x)$

$$\frac{\partial}{\partial y} : M(x)(3x+2y)$$

$$\frac{\partial}{\partial x} : \frac{\partial}{\partial x}(\mu(x))(x^2 + xy) + M(x)(2x+y)$$

has to be equal

$$\frac{\partial}{\partial x}(\mu(x))(x^2 + xy) + M(x)(2x+y) = \mu(x)(3x+2y)$$

$\hookrightarrow \mu(x)(x+y) = \mu'(x)(x^2 + xy) = \mu'(x) \cdot x(x+y) \rightarrow \mu(x) = x\mu'(x)$

$\hookrightarrow \frac{\partial \mu}{\partial x} = \frac{1}{x}\mu(x) \rightarrow \partial x \frac{1}{x} = \frac{1}{\mu(x)} d\mu \rightarrow \boxed{\mu(x) = x}$

So multiply each side by  $x$ :

$$(3x^2y + y^2x) + (x^3 + x^2y)\frac{dy}{dx} = 0$$

$$\frac{\partial}{\partial y} : 3x^2 + 2xy = 3x^2 + 2xy \stackrel{\frac{\partial}{\partial x}}{\approx}$$

exact!

Solve for this

$\Psi_y = x^3 + \frac{1}{2}x^2y^2 + h(y) =$  right hand side  
of diff eq

$x^3 + \frac{1}{2}x^2y^2 + h(y) = x^3 + x^2y$

$h(y) = 0 \Rightarrow \boxed{\text{constant} = h(y)}$

Now solve it!

$$\Psi_x = 3x^2y + xy^2 \rightarrow \Psi = x^3y + \frac{1}{2}x^2y^2 + h(y)$$

$\Psi = \dots$  Uh notes on how to do this on back,

# Solving diff eq by integration

(ex)  $\underbrace{y \cos(x) + 2x e^y}_{M(x,y)} + \underbrace{(\sin(x) + x^2 e^y - 1) \frac{dy}{dx}}_{N(x,y)} = 0$

$$M_y = \cos(x) + 2x e^y$$

exact

$$N_x = \cos(x) + 2x e^y$$

$$\Psi_x = M, \quad \Psi_y = N \quad \rightarrow \quad \frac{\partial}{\partial x} \Psi = 0 \quad ] \text{ use these relations}$$

$$\Psi_x = \underbrace{y \cos(x) + 2x e^y}_M \rightarrow \int \Psi dx = \int (y \cos(x) + 2x e^y) dx + f(y)$$

$$\hookrightarrow \boxed{\Psi = y \sin(x) + x^2 e^y + f(y)}$$

need to figure this out

if we take  $\frac{\partial}{\partial y} \Psi$  we should get **N** since it is an exact equation.

$$\frac{\partial \Psi}{\partial y} = \sin(x) + x^2 e^y + \frac{\partial f}{\partial y} = N = \sin(x) + x^2 e^y - 1 \rightarrow \frac{\partial f}{\partial y} = -1 \rightarrow f(y) = -y + C$$

$$\boxed{\Psi(x,y) = y \sin(x) + x^2 e^y - y + C} \rightarrow \frac{\partial}{\partial x} \Psi = 0 \rightarrow \Psi = C_2 \Rightarrow y \sin(x) + x^2 e^y - y + C_1 = C_2$$

$$\boxed{y \sin(x) + x^2 e^y - y = C}$$

## Exactness and differentials

$$P = \frac{nRT}{V}$$

ex)  $dP = \frac{nR}{V} dT - \frac{nRT}{V^2} dV$ , from  $P(T, V) \Rightarrow dP = \frac{\partial P}{\partial T} dT + \frac{\partial P}{\partial V} dV$   
 [is it exact] which means is the cross derivatives the same?

$\frac{\partial}{\partial V} \left( \frac{\partial P}{\partial T} \right) = \frac{\partial}{\partial T} \left( \frac{\partial P}{\partial V} \right)$  yes you can swap the partials or do it analytically.

also its when  $\text{curl } P = 0$

Consequences → if  $dA$  is exact,  $\oint dA = 0$  and  $\int_A^F = F - V$

ex)  $dA = \frac{\partial A}{\partial x} dx + \frac{\partial A}{\partial y} dy \rightarrow \int dA = \int \frac{\partial A}{\partial x} dx + \int \frac{\partial A}{\partial y} dy$

$$A = \int \frac{\partial A}{\partial x} dx + \underbrace{g(y) + h}_{\text{constants after integration}} \quad \text{and} \quad A(x, y) = \int \frac{\partial A}{\partial y} dy + \underbrace{f(x) + k}_{\text{integrating for } y \text{ putting}}$$

lets say  $dA = (ax + cxy^2)dx + (by + cx^2y)dy$  ← exact  $\frac{\partial}{\partial y}(ax + cxy^2) = \frac{\partial}{\partial x}(by + cx^2y)$   
 $= 2cxy$

Integrals now  
Integrate:  $dx$  part  $\rightarrow \int (ax + cxy^2)dx = \underbrace{\frac{1}{2}ax^2 + \frac{1}{2}cx^2y^2 + g(y) + h}_{f(x)}$   
 $dy$  part  $\rightarrow \int (by + cx^2y)dy = \underbrace{\frac{1}{2}by^2 + \frac{1}{2}cx^2y^2 + f(x) + k}_{f(y)}$

Total  $A = f(x) + f(y) + \text{cross term} = \frac{1}{2}ax^2 + \frac{1}{2}by^2 + \frac{1}{2}cx^2y^2 + h$

## Thermodynamics

$$W = \int_w s_w, Q = \int_w s_Q, \Delta U = \int_u du, \Delta H = s_Q - s_w$$

$$\hookrightarrow du = sQ - sW$$

$$\text{Work: } s_w = PdV \rightarrow dw(P, V) = \overbrace{F_p(P, V)}^0 dP + \overbrace{F_v(P, V)}^P dV : \frac{\partial}{\partial V} 0 \stackrel{?}{=} \frac{\partial}{\partial P} P \text{ no! not exact}$$

Heat:  $du = \left(\frac{\partial u}{\partial p}\right)_v dp + \left(\frac{\partial u}{\partial v}\right)_p dv \rightarrow du - sQ - sW \hookrightarrow sQ = \underbrace{du}_{\text{before}} + \underbrace{\frac{\partial w}{\partial p} dp}_{PdV}$

work  $\hookrightarrow sQ = \left(\frac{\partial u}{\partial p}\right)_v dp + \left[\frac{\partial u}{\partial v} + P\right] dV, \frac{\partial^2 u}{\partial v \partial p} \neq \frac{\partial^2 u}{\partial p \partial v} + 1 \text{ not exact}$

How is  $du$  exact though?

$$\text{Path 1: } w_1 = nRT \ln\left(\frac{V_f}{V_0}\right)$$

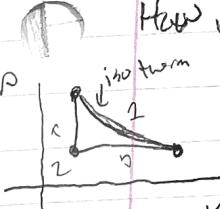
$$\text{Path 2: } w_2 = nRT \left(1 - \frac{V_0}{V_f}\right)$$

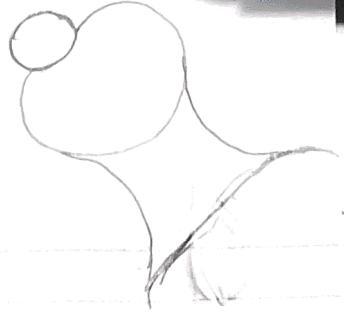
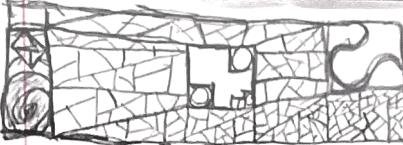
so then proves  $\Delta U_1 = 0$

$$\Delta U_2 = \Delta u_1 + \Delta u_2 = nCV \left( \frac{P_f V_0}{nR - P_0} - \frac{P_0 V_0}{nR} \right) + nC_V \left( \frac{T_f - T_0}{nR} - \frac{P_f V_0}{nR} \right) - P_f (V_f - V_0)$$

$$= -P_0 V_0 + nRT_0 - P_f V_f + P_f V_0 = 0$$

Path independent!  $\Delta u$  is exact!





## Thermodynamic Potential

not a thermodynamic potential

- $U(T, V)$  and  $P(T, V)$  are needed to have complete knowledge of equilibrium properties of a simple thermodynamic sys.

↳ What if we wanted a whole equation for everything?

(ex)  $U(S, V)$

Proof

$$dU = \underbrace{SQ - SW}_{\text{first law}} = \boxed{\underbrace{TdS - PdV}_{\text{second law}}}$$

We can transform this potential w/ a Legendre Transformation

(ex)  $dU = TdS - PdV$

$$U(S, V) \rightarrow U(S, P)$$

$$dU = TdS - d(PV) + VdP \rightarrow dU + d(PV) = TdS + VdP$$

$$= d(U + PV)$$

another thermodynamic potential  $H(S, P)$  =  $\boxed{dH = TdS + VdP}$

(ex)  $(S, V) \rightarrow (T, V)$  :  $dU = TdS - PdV = d(TS) - SdT - PdV$

$$d(U - TS) = - SdT - PdV$$

F

$$\boxed{dF(T, V) = - SdT - PdV}$$

Helmholtz free energy

(ex)  $(T, V) \rightarrow (f, P)$   $dF = - SdT - PdV = - SdT - d(PV) + VdP$

$$d(F + PV) = - SdT + VdP$$

G

$$\boxed{dG = - SdT + VdP}$$

Gibbs free energy

$$dF = - SdT - PdV$$

$$S = - \left( \frac{\partial F}{\partial T} \right)_V, P = - \left( \frac{\partial F}{\partial V} \right)_T$$

equation of state  
entropy

$$G_V = T \left( \frac{\partial S}{\partial T} \right)_V = - T \left( \frac{\partial^2 F}{\partial T^2} \right)_V, \beta_T = - V \left( \frac{\partial P}{\partial V} \right)_T = V \left( \frac{\partial^2 F}{\partial V^2} \right)_T$$

$$dV \beta_T = - \frac{\partial^2 F}{\partial V \partial T}$$

$$\left(\frac{\partial F}{\partial T}\right)_V = -S = -S \quad \frac{\partial S}{\partial V} = \frac{\partial^2 F}{\partial S \partial V}$$

### Maxwell Relations

$$dF = -SdT - PdV \rightarrow -\left(\frac{\partial S}{\partial V}\right)_T = \frac{\partial^2 F}{\partial V \partial T} = \frac{\partial^2 F}{\partial T \partial V} = -\left(\frac{\partial P}{\partial T}\right)_V \rightarrow \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$$

Properties of an ideal gas derived from Helmholtz free energy

$$F = U - TS, \quad U(T, V) = ncvT + nU_0$$

$$\rightarrow S(T, V) = ncv \ln\left(\frac{T}{T_r}\right) + nR \ln\left(\frac{V}{V_r}\right) + S(T_r, V_r)$$

$$F = ncvT \left(1 - \ln\left(\frac{T}{T_r}\right)\right) - nRT \ln\left(\frac{V}{V_r}\right) + n(U_0 - TS_r)$$

$$\rightarrow P(T, V) = -\left(\frac{\partial F}{\partial V}\right)_T = -\frac{nRT}{V} \xrightarrow{\text{only volume dependence}} -nRT \frac{1}{V} \ln\left(\frac{V}{V_r}\right) = -nRT \frac{V_r}{V} \cdot \frac{1}{V_r}$$

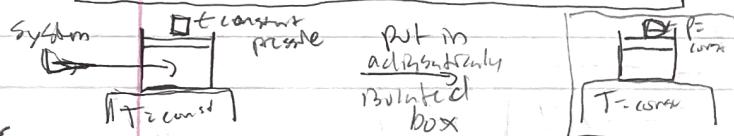
$$\rightarrow dF = -SdT - PdV, \quad S = -\left(\frac{\partial F}{\partial T}\right)_V \quad \text{should recover entropy } S_0 \\ \text{and you do.}$$

$$\rightarrow U \text{ obtained from } U = F + TS = F - T\left(\frac{\partial F}{\partial T}\right)_V = ncvT + nU_0$$

$$\hookrightarrow C_V = \left(\frac{\partial U}{\partial T}\right)_V = ncv$$

$$\hookrightarrow \beta_T = -V \left(\frac{\partial P}{\partial V}\right)_T \quad \text{etc.} \quad \frac{\partial P}{\partial V} = -P \quad \text{and} \quad \frac{\partial^2 F}{\partial V^2} = -\left(\frac{\partial P}{\partial V}\right)_T$$

### Systems in Contact w/ Reservoirs



entropy always increases

consider a sys at constant pressure & temperature

no heat exchange  $\rightarrow$  due to 2nd law the system will be at an extreme of some sort

(look at system only inside not while shaking)

$$\text{Gibbs Free Energy } G(T, P) \rightarrow G_0 = U_0 - TS_0 + PV_0 \quad (\text{initial state})$$

$$G_f = U_f - TS_f + PV_f \quad (\text{final state})$$

$$\hookrightarrow \Delta S = \frac{\Delta U + P\Delta V - \Delta G}{T} \quad (\text{second law says entropy must be } \geq 0)$$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_R \geq 0, \quad \text{where } \Delta S_R = \frac{\int_L^U \frac{\delta Q_{\text{ext}}}{T}}{T} = \frac{Q_R}{T}$$

$$\Delta S_{\text{tot}} = \frac{\Delta U + P\Delta V - \Delta G}{T} + \frac{Q_R}{T}$$

$$\Delta S_{\text{tot}} = \frac{Q - \Delta G}{T} + \frac{Q_R}{T}, \quad |Q| = |Q_R| \text{ but opposite sign, } Q = -Q_R$$

$$\Delta S_{\text{tot}} = \frac{-\Delta G}{T} \geq 0 \rightarrow \Delta G \leq 0 \quad (T=\text{const}, P=\text{const})$$

\* it does other things causing entropy to increase \*

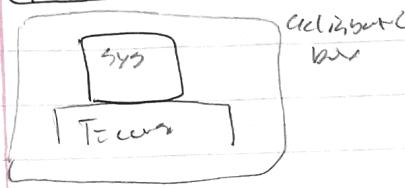
A sys w/  $V = \text{const}$  w/ a heat reservoir

$$\Delta F = \Delta U - T\Delta S \rightarrow \Delta S = \frac{\Delta U - \Delta F}{T} = \frac{Q - \Delta F}{T}$$

Volume const  
no work done  
 $V = \text{const}, V = \text{const}$

$$\Delta S_{\text{tot}} = \Delta S + \Delta S_R = \frac{Q - \Delta F}{T} + \frac{Q_R}{T} = -\frac{\Delta F}{T} \geq 0 \rightarrow \boxed{\Delta F \leq 0}$$

### Helmholtz free energy



$$\Delta S_E + \Delta S_R \geq 0$$

$$S_f + S_0 + \Delta S_n \geq 0$$

$$T(S_f - S_0) + T\Delta S_n \geq 0$$

$$+ (S_f - S_0) + Q_m \geq 0, Q = -Q_R$$

$$T(S_f - S_0) \geq Q \rightarrow U_f - U_0 = Q - W$$

$$\hookrightarrow TS_f - U_f - (TS_0 - U_0) \geq W \rightarrow F_f - F_0 \geq W$$

$$W \leq -\Delta F \quad (\text{constant temperature}) \quad (\text{max work done})$$

$\bullet$  If constant  $V$  then max work done is 0  $\rightarrow 0 \leq -\Delta F$

$$W_{\text{max}} = -\Delta F$$

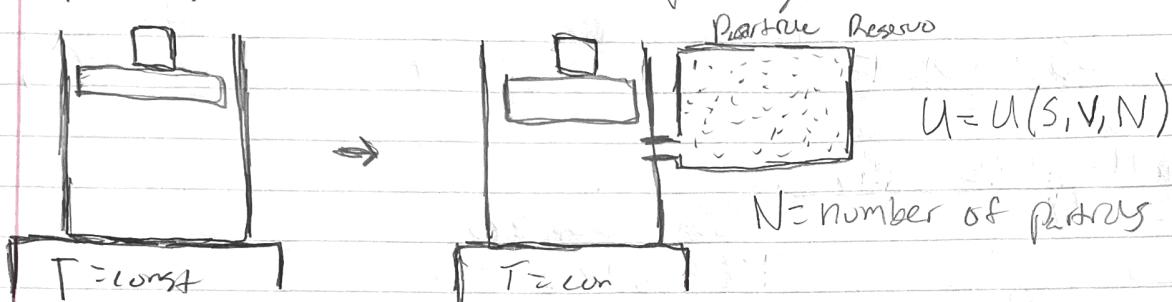
If  $V$  is a const then  $\Delta F \leq 0 \rightarrow F_f \leq F_0$

### DVT systems

Potential	Internal Energy $U(S, V)$	Enthalpy $H(S, P)$ $H = U + PV$	Helmholtz free energy $F(T, V)$ $F = U - TS$	Gibbs free energy $G(T, P)$ $G = U - TS + PV$
differential	$dU = TdS$	$dH = TdS + VdP$	$dF = -SdT - PdV$	$dG = -SdT + VdP$
Vector fields	$T = \left(\frac{\partial U}{\partial S}\right)_V, P = -\left(\frac{\partial U}{\partial V}\right)_S$	$T = \left(\frac{\partial H}{\partial S}\right)_P$ $V = \left(\frac{\partial H}{\partial P}\right)_S$	$S = \left(\frac{\partial F}{\partial T}\right)_V, P = -\left(\frac{\partial F}{\partial V}\right)_T$	$S = -\left(\frac{\partial G}{\partial T}\right)_P$ $V = \left(\frac{\partial G}{\partial P}\right)_T$
Maxwell Relations	$\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V$	$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$	$\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V$	$-\left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial V}{\partial T}\right)_P$
Properties	1st Law $\Delta U = Q - W$	For constant P pressure $\Delta H = Q$	$T = \text{const}, V = \text{const}$ $\Delta F \leq 0$	$T = \text{const}, P = \text{const}$ $\Delta G \leq 0$

## Open Systems and Chemical Potentials

Open system  $\rightarrow$  particle exchange w/ surroundings



$$U(2S, 2V, 2N) = 2U(S, V, N) \quad \text{call constant } \lambda$$

$$\left(\frac{\partial U}{\partial (2S)}\right)_{2V, 2N} \underbrace{\left(\frac{\partial (2S)}{\partial S}\right)}_S + \left(\frac{\partial U}{\partial (2V)}\right)_{2S, 2N} \underbrace{\left(\frac{\partial (2V)}{\partial V}\right)}_V + \left(\frac{\partial U}{\partial (2N)}\right)_{2S, 2V} \underbrace{\left(\frac{\partial (2N)}{\partial N}\right)}_N = U(S, V, N)$$

$$\text{for } \lambda = 1 \rightarrow \underbrace{\left(\frac{\partial U}{\partial S}\right)_{V, N} S}_{T} + \underbrace{\left(\frac{\partial U}{\partial V}\right)_{S, N} V}_{-P} + \underbrace{\left(\frac{\partial U}{\partial N}\right)_{S, V} N}_{M = \text{moo}} = U(S, V, N)$$

$$U(S, V, N) = TS - PV + \mu N \rightarrow dU = TdS - PdV + \mu dN$$

$\mu$  is a chemical potential

$$dU = \delta Q - \delta W = TdS - \underbrace{\delta W}_{PdV - \mu dN} \quad \begin{matrix} \uparrow \\ \text{more done to} \\ \text{change # of} \\ \text{particles by 1} \end{matrix}$$

hard to say

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

$$dF = \underbrace{-SdT - PdV + \mu dN}_{L_F} \quad \begin{matrix} \uparrow \\ \text{from m} \end{matrix}$$

$$G = \underbrace{U - TS + PV}_{L_G} \rightarrow dG = dF + d(PV) = -SdT + Vdp + \mu dN$$

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

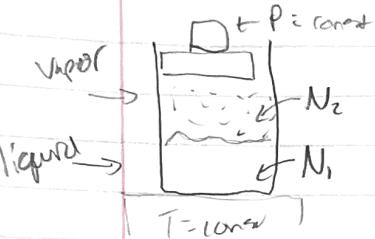
$$\mu = \mu(T, P)$$

$$G = U - TS + PV \quad \text{and} \quad U = TS - PV + \mu N \rightarrow M = \frac{G}{N}$$

intensive property  
independent of  $N$

## Phase Transitions

$V = VN$ , consider a sys of liquid + vapor in eq at given  $P + T$



$$\left. \begin{array}{l} N = N_1 + N_2 = \text{constant} \\ P + T \text{ fixed} \\ \hookrightarrow \text{sys in minimum} \\ \text{gas free energy} \end{array} \right\}$$

$$G = N_1 g_1 + N_2 g_2$$

$$G = N g_2 + N_1 (g_1 - g_2) \quad \text{for } N_1, N_2$$

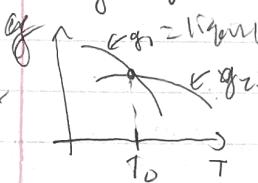
$$\text{Index 1} = \text{liquid} \quad \left. \begin{array}{l} \text{for minimum} \\ \bullet g_1 > g_2 \end{array} \right\}$$

$$\text{Index 2} = \text{vapor} \quad \left. \begin{array}{l} \hookrightarrow \text{we have} \\ \bullet g_1 < g_2 \quad \text{and } g_1 = g_2 \\ 3 \text{ things yield min} \end{array} \right\}$$

①  $g_1 > g_2 \rightarrow G$  at min for  $N_1=0$ , make  $g_1 - g_2$  pos  
so to make it  $\ominus$  min  $N_1=0$  (only vapor phase)

②  $g_1 < g_2 \rightarrow G$  at min for  $N_1=N$ ,  $N_2=0$  (only liquid)

③  $g_1 = g_2 \rightarrow G$  at min in both liquid + gas phase  $N_1+N_2=\text{const}$



$$\text{note } g_1 = g_2 \leftarrow \mu_1 = \mu_2$$

$$g_1(T, P) \neq g_2(T, P) \rightarrow P(T) \rightarrow g_1(T, P(T)) = g_2(T, P(T))$$

$$\left[ \begin{array}{l} \text{take derivs} \\ \text{thus eq} \end{array} \right] \rightarrow \left( \frac{\partial g_1}{\partial T} \right)_P + \left( \frac{\partial g_1}{\partial P} \right)_T \frac{dP}{dT} = \left( \frac{\partial g_2}{\partial T} \right)_P + \left( \frac{\partial g_2}{\partial P} \right)_T \frac{dP}{dT}$$

$$\text{w/ } dg = -SdT + VdP \text{ we see } \left( \frac{\partial g}{\partial T} \right)_P = -S \text{ and } \left( \frac{\partial g}{\partial P} \right)_T = V$$

$$\frac{dP}{dT} = \frac{S_2 - S_1}{V_2 - V_1} = \frac{Q}{T\Delta V} \quad \begin{array}{l} Q \leftarrow \text{heat need to change sys from phase} \\ 1 \text{ to } 2, \text{ has constant } T \end{array}$$

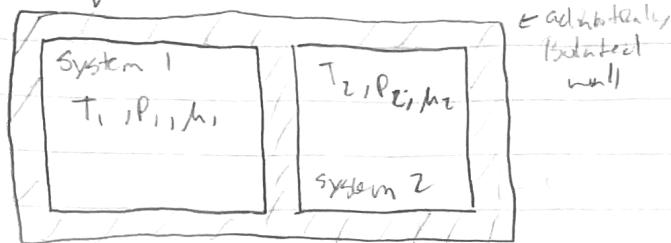
$$\Delta S = \frac{Q}{T}, \quad \begin{array}{l} \text{for water } \Delta V = \text{neg when} \\ \text{corresponds to a negative slope in} \\ \text{PT diagram.} \end{array}$$

$$\begin{array}{l} \text{only} \\ \text{per} \\ \text{partic} \\ \text{le} \\ \text{so } \frac{dN}{dV} = 0 \\ \mu = \frac{G}{N} \end{array}$$

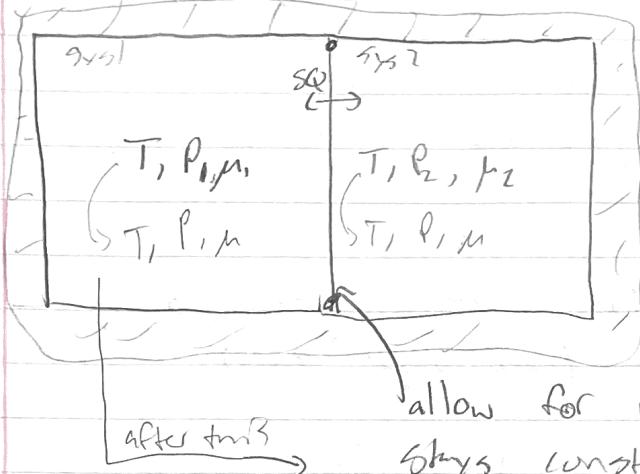
$$\mu = \mu(T, P)$$

$$g = \mu$$

# Equilibrium Conditions



allow for heat exchange only



then make it have holes to let particles through

From  $dU = TdS - PdV + \mu dN$  do for both systems

$$dS_1 = \frac{dU_1}{T_1} + \frac{P_1}{T_1} dV_1 - \frac{\mu_1}{T_1} dN_1 \quad \begin{cases} \text{use these} \\ \text{and } \rightarrow \Delta S = \Delta S_1 + \Delta S_2 \geq 0 \end{cases}$$

$$dS_2 = \frac{dU_2}{T_2} + \frac{P_2}{T_2} dV_2 - \frac{\mu_2}{T_2} dN_2 \quad \begin{cases} \text{your disregard} \\ \text{in equilibrium, no change } \Rightarrow 0 \\ dS = dS_1 + dS_2 = 0 \end{cases}$$

$$U_1 + U_2 = \text{constant} \rightarrow dU_1 = -dU_2 \quad N_1 + N_2 = \text{constant}$$

$$V_1 + V_2 = \text{constant} \rightarrow dV_1 = -dV_2 \quad \therefore dN_1 = -dN_2$$

$$\text{Now used } dS_1 \text{ and } dS_2 \Rightarrow 0 = dS = \left( \frac{1}{T_1} - \frac{1}{T_2} \right) dU_1 + \left( \frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1 - \left( \frac{\mu_1}{T_1} - \frac{\mu_2}{T_2} \right) dN_1$$

For this to be 0

$$\frac{1}{T_1} = \frac{1}{T_2}, \quad T_1 = T_2, \quad \text{then } P_1 = P_2 \quad \text{then } \mu_1 = \mu_2$$

We need vector field components to = 0