Some final Considerations on Entropy

Maxwell's Relations

Don't have time to discuss, just mention - SHOULD at least know names

Already saw ENTHALPY

$$H \equiv U + PV \qquad (1)$$

Total energy needed to create a system out of nothing → includes displacing atmosphere. (Remember the Rabbit!)

Could RECOVER H → system's energy + work done by atmospheric collapse.

IF T constant — CAN EXTRACT HEAT FROM ENVIRONMENT

HELMHOLTZ FREE ENERGY $\quad F \equiv U - TS \quad$ (2)

Total energy needed to create system — heat that can be extracted from environment

IF in constant PRESSURE + TEMPERATURE

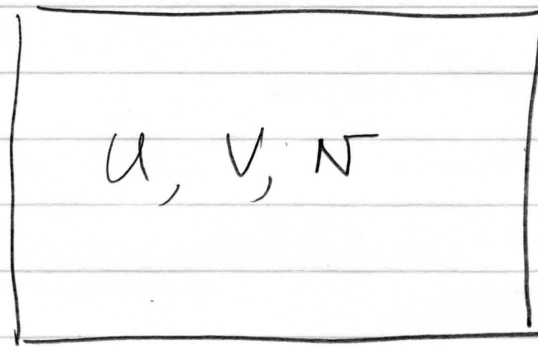
GIBBS FREE ENERGY $\quad G \equiv U - TS + PV \quad$ (3)

Heat term in

atmospheric term in (1)

$U, H, F, G \rightarrow$ THERMODYNAMIC POTENTIA

Consider Entropy of this System.



$S(U, V, N)$ — if U, V, N change by
$\Delta U, \Delta V, \Delta N$

$$\Delta S = S(U+\Delta U, V+\Delta V, N+\Delta N) - S(U, V, N)$$

Can use Taylor expansion in 3 variables

$$f(x, y, z) \rightarrow f(x+\varepsilon_x, y+\varepsilon_y, z+\varepsilon_z)$$

$$\approx f(x,y,z) + \varepsilon_x \left(\frac{\partial f}{\partial x}\right)_{y,z}(x,y,z)$$

$$+ \varepsilon_y \left(\frac{\partial f}{\partial z}\right)_{x,z}(x,y,z)$$

$$+ \varepsilon_z \left(\frac{\partial f}{\partial x}\right)_{x,y}(x,y,z)$$

KEEP ON BOARD

from Taylor expansion

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

Remember PHYSICAL SIGNIF

$$\downarrow \qquad \downarrow \qquad \downarrow$$

$$\frac{1}{T} \qquad \frac{P}{T} \qquad -\frac{\mu}{T}$$

so we can write

$$dS(U,V,N) = \frac{1}{T}dU + \frac{P}{T}dV - \frac{\mu}{T}dN$$

or

$$dU = TdS - pdV + \mu dN$$

this is called the THERMODYNAMIC IDENTITY

true for any infinitessimal change of system — as long as T, P well defined

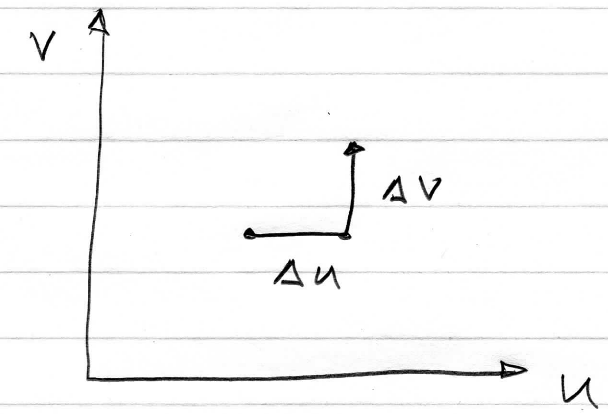
$\hookrightarrow$ QUASISTATIC

started off with $S = f(U,V,N)$

inverted to $U = f(S,N,V)$ ← 1

entropy change when U, + V change

(N fixed to make 2-D picture!)



As ~~text~~ says "memorize this"

Weeks ago we looked at QUASISTATIC PROCESSES

$$\delta W = -p\,dV$$

Compare this to $dU = T\,dS - p\,dV$ (N const)

$$\Delta U = \delta Q - \delta W$$

WORK

Clausius def of ENTROPY

small enough to maintain thermodynamic Equilibrium.

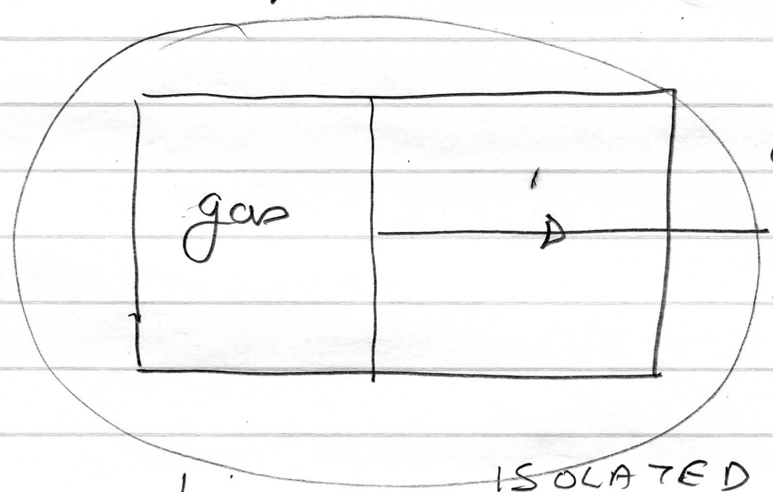
What this means is

$$\delta Q = T ds$$

change in Heat

even if WORK IS DONE

Example of QUASISTATIC PROCESS



QUASISTATIC
↓
SLOW EXPANSION

NO HEAT EXCHANGE $\rightarrow \delta Q = 0$

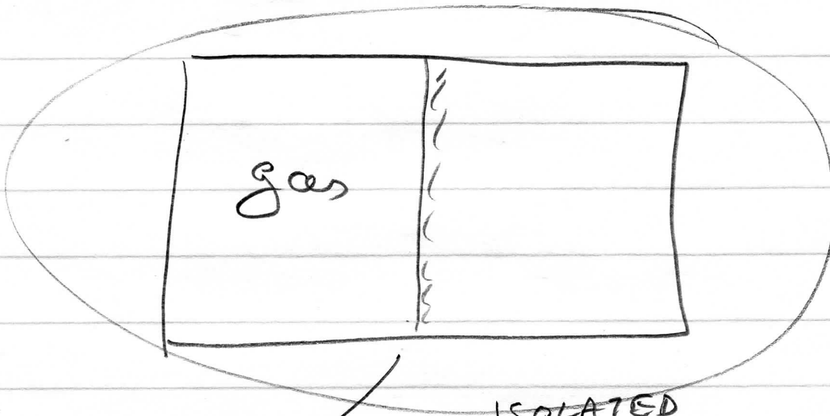
$\rightarrow T ds = 0$

QUASISTATIC ADIABATIC PROCESS $\Big\} \longrightarrow \Delta S = ds = 0$

$\delta W = -p dV$

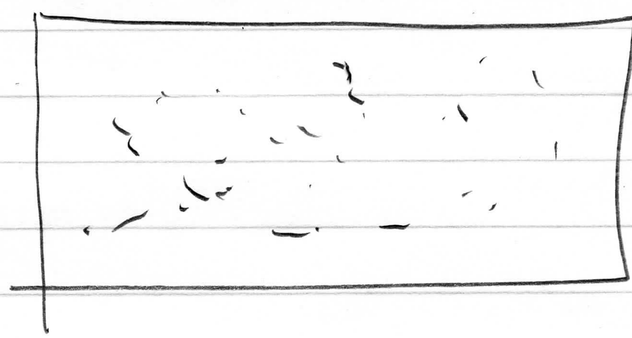
work done

COMPARE to NON-QUASISTATIC
ADIABATIC



ISOLATED

REMOVE PARTITION QUICKLY



EXPANSION

S INCREASES
BUT NO WORK DONE

gas does MAXIMUM WORK in QUASISTATIC

→ ENTROPY CHANGE IN MINIMUM

I from $S(u, V, N)$

SHOULD BE ON BOARD

$$\Rightarrow \quad dS = \left(\frac{\partial S}{\partial u}\right)_{N,V} du + \left(\frac{\partial S}{\partial V}\right)_{u,N} dV + \left(\frac{\partial S}{\partial N}\right)_{u,V} dN$$

$$dS = \frac{1}{T} du + \frac{P}{T} dV - \frac{\mu}{T} dN$$

→ know that S will MAXIMIZE

and $du = T dS - p dV + \mu dN$ — 2

$$T = \left(\frac{\partial u}{\partial S}\right)_{N,V}$$ → TEMP ⇒ Energy required to change S at fixed V, N

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

→ PRESSURE → energy required to change volume at fixed S, N.

from 2, at fixed S, V

$$\left(\frac{\partial U}{\partial N}\right)_{S,V} = \mu \qquad \text{CHEMICAL POTENTIAL}$$

energy required to change # of particles by 1 at fixed, S, V.

Could write these 3 as

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

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

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

these are examples of

MAXWELL
RELATIONS

generally for a POTENTIAL Φ depending on coordinates y_j y_k

Ⓐ →
$$\left(\frac{\partial}{\partial y_j}\left(\frac{\partial \phi}{\partial y_k}\right)_{i\neq k}\right)_{i\neq j} = \left(\frac{\partial}{\partial y_k}\left(\frac{\partial \phi}{\partial y_j}\right)_{i\neq j}\right)_{i\neq k}$$

Φ can be U, F, H, G, μ

Can derive many Maxwell Relations

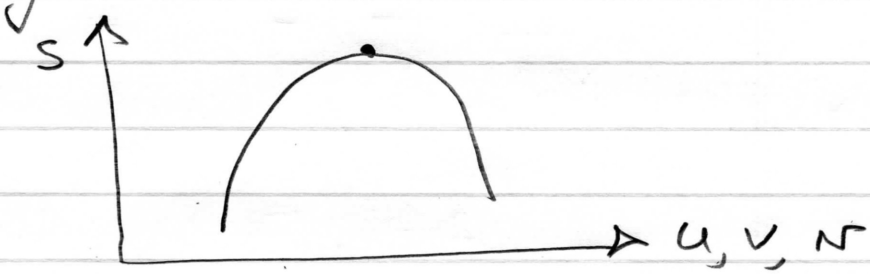
eg
$$\left(\frac{\partial T}{\partial V}\right)_{S,N} = -\left(\frac{\partial p}{\partial S}\right)_{V,N}$$

etc

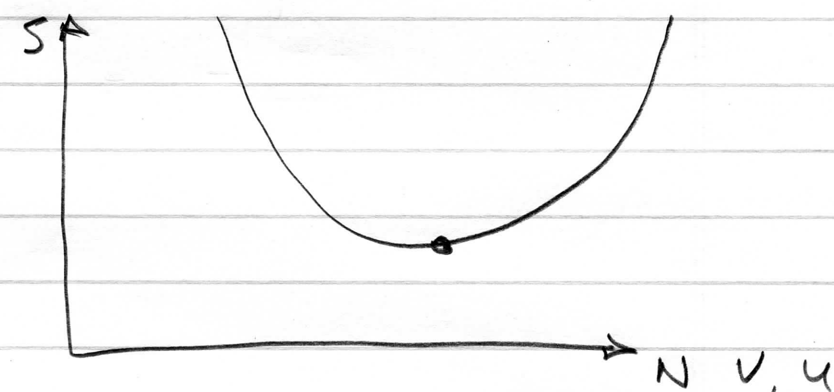
II thermodynamic STABILITY

Studied thermodynamic Equilibrium

by looking at $S \rightarrow$ MAXIMUM



Can also have $\Delta S = 0$ if MIN



Could study this using (A) for the

POTENTIALS

$\longrightarrow$ takes too long!

look at STABILITY intuitively

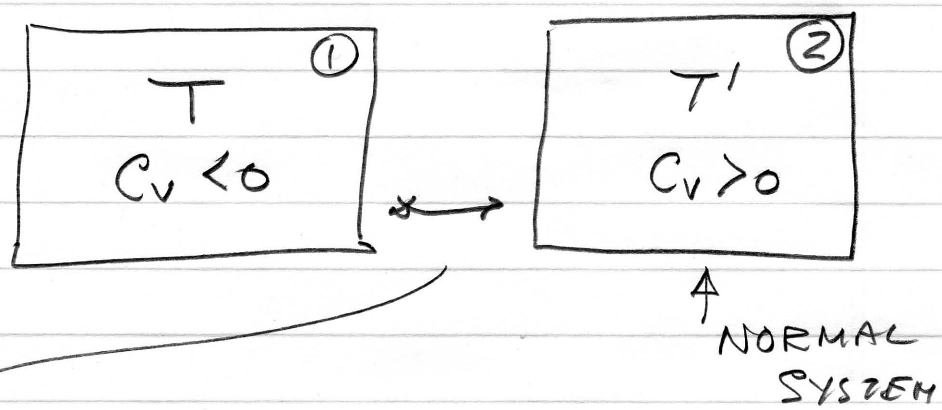
For Homogeneous Body

↳ thermoDynamic Stability

$C_V > 0, \left(\frac{\partial P}{\partial V}\right)_{T,N} < 0$

& $\left(\frac{\partial \mu}{\partial N}\right)_{U,V} > 0$ μ goes ↑ as # particles ↑

1) Imagine $C_V < 0$



Try to put in contact and bring into thermodynamic Equilibrium

↓

$T_1 = T_2$ and Constant

$T' > T$ Energy flows ② → ①

Since $C_{V,1} < 0$ → lowers T

↳ more energy ② → ①

↳ Run away catastrophe

$\Downarrow$

INSTABILITY

Conversely if $T' < T$

$C_{V,1} < 0$ → Gives energy to ②

↳ $C_{V,1} < 0$ → T① will INCREASE

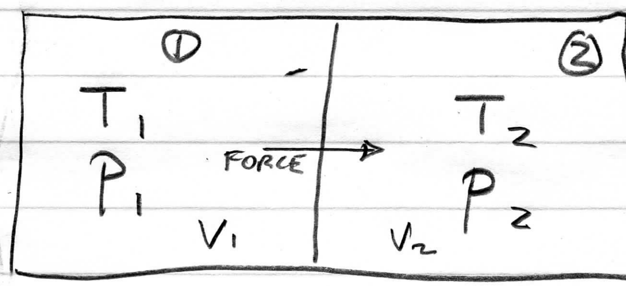
RUNAWAY ENERGY TRANSFE

2) $\left(\frac{\partial p}{\partial V}\right)_{T,N} < 0$ Bulk Modulus $= -V\left(\frac{\partial p}{\partial V}\right)_{T,N} > 0$

Suppose system has

$\left(\frac{\partial p}{\partial V}\right)_{T,N} > 0 \rightarrow V\downarrow \quad P\downarrow$

Same sort of argument



Imagine $p_1 > p_2$ so FORCE acts

to Right $\rightarrow$ & V_1 increases

$\hookrightarrow \left(\frac{\partial p}{\partial V}\right) > 0 \rightarrow$ P increases more

$\left(\frac{\partial p}{\partial V}\right) < 0$

FOR STABILITY

3) $\left(\frac{\partial \mu}{\partial N}\right) > 0$ $\Big\{ \left(\frac{\partial^2 S}{\partial N^2}\right)_{UV} < 0$

$\hookrightarrow \frac{\mu}{T} = -\left(\frac{\partial S}{\partial N}\right)_{UV}$

PARTICLES FLOW $\mu_{LARGE} \rightarrow \mu_{SMALL}$

if $\left(\frac{\partial \mu}{\partial N}\right) < 0$ 2 SYSTEMS IN CONTACT

$\mu_1 > \mu_2 \rightarrow$ PARTICLES $1 \rightarrow 2$

But $\frac{\partial \mu}{\partial N}$ $-ve$ $\rightarrow \partial\mu > 0$

Even more particles flow

INSTABILITY.