

⊗ Nomore KTG — starting thermodynamics from Chem thermodynamics.

⊗ Linking thermodynamics to statistical mechanics.

⊗ Problem in every tutorial - from HW, just one.

Mark distribution to be discussed further later.

⊗ HW planned to be over every week. → to be submitted. (No grading)

○ Ideal Gas:

$$\textcircled{O} \quad U = \frac{3}{2} nRT$$

$pV = nRT \rightarrow$  Derived empirically

from exp (Charles', Boyle's, etc)

→ Experimental / Empirical equation.

↳ KTG

$$\textcircled{O} \quad dU = T dS - P dV + \cancel{\mu dN} \quad \begin{array}{l} \text{not seen (forget about it)} \\ \text{before} \end{array}$$

→ Combination of 1st law and 2nd law, in a sense.

$$\Rightarrow U = U(S, V, N)$$

$$\Rightarrow dU = \left. \frac{\partial U}{\partial S} \right|_{V, N} dS + \left. \frac{\partial U}{\partial V} \right|_{S, N} dV$$

Not considering  $\mu$

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

$$P = - \left. \frac{\partial U}{\partial V} \right|_{S, N}$$

What if we consider  $\mu dN$ ?

$\mu dN \rightarrow$  Energy taken out or given by taking out or putting in molecules.

→  $\mu$  = Chemical potential.

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

Goal's We wish to find  $U = U(V, S, N)$  for ideal gas.

Once we know this, we can find  $T$ ,  $P$ , and  $\mu$  just by taking derivatives

Why then? These are measurable quantities.

We will use the first 2 equations to do this.

$$U = \frac{3}{2} nRT \Rightarrow T = \frac{2U}{3nR}$$

$$\left(\frac{\partial U}{\partial S}\right)_{V,N} = T = \frac{2U}{3nR}$$

$$\Rightarrow \frac{\partial U}{U} = \frac{2}{3} \cdot \frac{1}{nR} \cdot dS$$

$$\Rightarrow \ln U = \frac{2}{3} \cdot \frac{S}{nR} \quad (\text{Integrating}) \\ + f(V, N) \xrightarrow{\text{Const of integration.}}$$

$$\text{Now, } PV = nRT$$

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

$$\left(\frac{\partial U}{\partial V}\right)_{S,N} = -P = -\frac{nRT}{V} = -\frac{2}{3} \frac{U}{V}$$

$$\Rightarrow \frac{\partial}{\partial V} (\ln U)_{S,N} = \frac{1}{U} \left(\frac{\partial U}{\partial V}\right)_{S,N} \quad \text{--- (I)}$$

$$\Rightarrow \frac{\partial}{\partial V} (\ln U)_{S,N} = \frac{\partial}{\partial V} \left( \frac{2}{3} \frac{S}{nR} + f(V, N) \right), \text{ from (I)}$$

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

$$\Rightarrow \frac{1}{U} \left(\frac{\partial U}{\partial V}\right)_{S,N} = \left(\frac{\partial f}{\partial V}\right)_{S,N} \quad (\text{from (I)})$$

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

$$\Rightarrow -\frac{2}{3} \frac{U}{V} = U \left(\frac{\partial f}{\partial V}\right)_{S,N}$$

$$\Rightarrow \left(\frac{\partial f}{\partial V}\right)_N = -\frac{2}{3} \cdot \frac{1}{V}$$

$$\Rightarrow f = -\frac{2}{3} \ln V + g(N)$$

$$\therefore \ln U = \frac{2}{3} \frac{S}{nR} + \left(-\frac{2}{3}\right) \ln V + g(N)$$

We may just write it as  $\ln(g(N))$  (const.)

$$\boxed{\ln U = \frac{2}{3} \frac{S}{nR} - \frac{2}{3} \ln V + \ln(g(N))}$$

(\*) → Using only  $PV = nRT$ ,  $U = \frac{3}{2}nRT$

We are going to push dependence of  $N \rightarrow$  There is new stuff there.

But physical input has been exhausted — 6th equations have been inputted.

Let us increase entropy of system 2 times

and the same,  $S \rightarrow 2S$   
 $V \rightarrow 2V$   
 $N \rightarrow 2N$

$\boxed{U \rightarrow 2U \text{ (Expected)}}$

→ Extensivity

$$\rightarrow U = g(N) V^{-2/3} \exp\left(\frac{2S}{3NR}\right)$$

Using this

$$U \rightarrow g(2N) (2N)^{-2/3} \exp\left(\frac{2 \cdot 2S}{3 \cdot 2NR}\right)$$

$$\Rightarrow U \rightarrow g(2N) (2N)^{-2/3} \exp\left(\frac{2S}{3NR}\right)$$

This needs to be  $2U$

$$2^{-\frac{2}{3}} = 1 \Rightarrow x = \frac{5}{3}$$

$$\rightarrow \text{True if } g(2N) = 2^{5/3} g(N)$$

$$\Rightarrow \boxed{g(N) = k \cdot N^{5/3}}$$

Fundamental relation of thermodynamics

$$\Rightarrow \boxed{U = k N \left(\frac{V}{N}\right)^{-2/3} \exp\left(\frac{2}{3} \frac{S}{nR}\right)}$$

Found - goal. (2 empirical eqns, extensivity)

Find :  $T, P, g$  from this.

Question → Can this be derived from microscopic considerations, without empirical relations?  
What if  $PV = nRT$  does not hold — some other system.

This is the goal of statistical mechanics → to derive this from fundamental physics.  
→ This will be derived later in course.

### Tutorial Class begins

$F(x, y, z)$  → Broadly, a field

In this case, it is a scalar field.

$\vec{E}(x, y, z)$  → vector field

(certain transformation rules).

$$\frac{\partial F}{\partial x} = \lim_{h \rightarrow 0} \frac{F(x+h, y, z) - F(x, y, z)}{h}$$

or, notationally as,  $F_x$ ,  $\left(\frac{\partial F}{\partial x}\right)_{y, z}$   
all other variables are fixed.

$$\frac{\partial^2 F}{\partial x \partial y} = \frac{\partial^2 F}{\partial y \partial x} \rightarrow \text{partial derivatives commute.}$$

Sometimes,  $\rightarrow$  some other variable.

$$F(x(t), y(t))$$

$$\text{A} \rightarrow t \rightarrow t + \Delta t, x \rightarrow x + \Delta x, y \rightarrow y + \Delta y$$

So, under this change, the new field is,

$$F(x + \Delta x, y + \Delta y) = F(x, y) + \left(\frac{\partial F}{\partial x}\right)_y \Delta x + \left(\frac{\partial F}{\partial y}\right)_x \Delta y$$

$$\Rightarrow \Delta F = \frac{\partial F}{\partial x} \Delta x + \frac{\partial F}{\partial y} \Delta y$$

Or in some other way,

$$\frac{dF}{dt} = \left( \frac{\partial F}{\partial x} \right)_y \frac{dx}{dt} + \left( \frac{\partial F}{\partial y} \right)_x \frac{dy}{dt}$$

If  $x$  and  $y$  had some other variable dependence, it would be  $\frac{\partial F}{\partial t_1}$  and  $\frac{\partial F}{\partial t_2}$ .

Consider,  $\begin{array}{l} \text{All independent of each other.} \\ \text{Constant} \end{array}$

$$F(x_1, \dots, x_n) = C$$

$\Rightarrow$  This cannot be  $\begin{array}{l} \text{This is a relation,} \\ \text{they cannot be independent.} \end{array}$

but,  $x_1, \dots, x_n$  are functions of independent variables

$$u_1, \dots, u_n$$

In terms of this new variable,

$$F(u_1, \dots, u_n) = C$$

$$dF = \frac{\partial F}{\partial u_1} du_1 + \dots + \frac{\partial F}{\partial u_n} du_n$$

$u_1, \dots, u_n$  are independent variables.

$$\text{So, } F(u_1 + \Delta u_1, u_2, \dots, u_n) = C$$

$$\Rightarrow \frac{\partial F}{\partial u_1} = \lim_{\Delta u_1 \rightarrow 0} \frac{F(u_1 + \Delta u_1, u_2, \dots, u_n) - F(u_1, \dots, u_n)}{\Delta u_1}$$

$$\Rightarrow \frac{\partial F}{\partial u_n} = 0 \quad \Rightarrow \boxed{\frac{\partial F}{\partial u_i} = 0} \quad \rightarrow \text{Essentially saying this in a convoluted way.}$$
$$\Rightarrow \frac{\partial F}{\partial x_1} dx_1 + \frac{\partial F}{\partial x_n} dx_n = 0$$

Consider,

$$F(x, y, z) = 0$$

$$\Rightarrow dF = \left(\frac{\partial F}{\partial x}\right)dx + \left(\frac{\partial F}{\partial y}\right)dy + \left(\frac{\partial F}{\partial z}\right)dz = 0.$$

take  $y = \text{const} \Rightarrow dy = 0$

$$\Rightarrow \boxed{\left(\frac{\partial z}{\partial x}\right)_y = -\frac{\left(\frac{\partial F}{\partial x}\right)}{\left(\frac{\partial F}{\partial z}\right)}}$$

Similarly,

$$\boxed{\left(\frac{\partial y}{\partial z}\right)_x = -\frac{\frac{\partial F}{\partial z}}{\frac{\partial F}{\partial y}}}$$

$$\boxed{\left(\frac{\partial x}{\partial y}\right)_z = -\frac{\frac{\partial F}{\partial y}}{\frac{\partial F}{\partial x}}}$$

$$\Rightarrow \boxed{\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1}$$

Used later in course.

Exact, inexact differentials

Lagrange multipliers to optimize functions.

Last class we derived -

4<sup>th</sup> January 2024

$$U = KN \left( \frac{V}{N} \right)^{-2/3} \exp \left( \frac{2}{3} \frac{S}{NR} \right)$$
$$= f(N, V, S)$$

If  $V \rightarrow \lambda V$ ,  $S \rightarrow \lambda S$ ,  $N \rightarrow \lambda N$ ,

then  $\frac{V}{N} \rightarrow \frac{V}{N}$ ,  $\frac{S}{N} \rightarrow \frac{S}{N}$ , only  $N \rightarrow \lambda N$ .

(\*) If we are given another  $U = f(N, V, S)$  for another system, we should be able to tell if it is correct or not, and calculate  $T, P, \mu$ .

O Thermodynamics  $\rightarrow$  Physics that cares about Macroscopic variables

To know a system completely - we need to know all  $N \times 10^{23}$  molecules, initial states, etc.

$\Rightarrow$  Thermodynamics reduces this into a few effective variables, not  $10^{23}$  something variables.

Just like GTR reduces to NLM / N's theory of gravitation

But this works / is useful for when we have the timescale of measurement is much larger than atomic timescale.

timescale  $\gg$  atomic timescale.

Also,

lengthscale  $\gg$  Intermolecular distance.

So based on timescale and length scale, we worry about the effective DOF, not the fundamental DOF

Finding these effective DOF is essential to good application.

Equilibrium  $\rightarrow$  The system does not change parameters in scales used.

What are good choices to guide the selection of DOF of a system at equilibrium?

→ Constant quantities in an 'Equilibrium' state.

⇒ Conserved quantities  $\Rightarrow$  Due to some symmetries of the system.

∅ Other quantities may also emerge, which are good descriptors of the system.

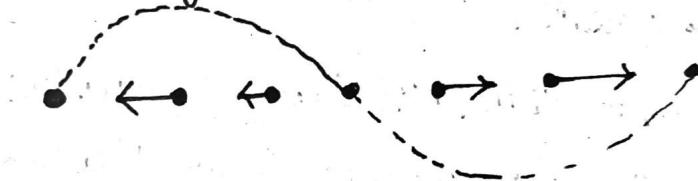
∅ Emergence of macroscopic variables:

Let us consider a system of nine atoms.

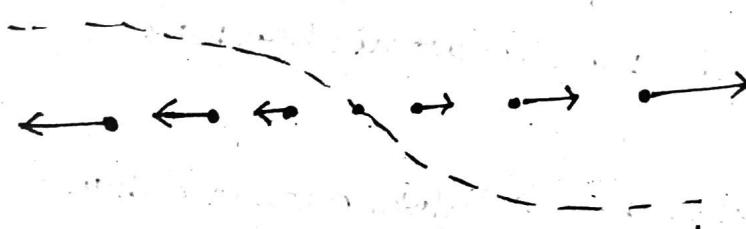


Wave has the amplitude proportional to the distance these atoms move

Or something like,



Or,



9 particles in a system  $\Leftrightarrow$  coupled to each other with spring-like connections — any arbitrary motion of these can be expressed as a combination of these 3 waves  $\rightarrow$  normal modes

⊗ But this depends on the resolution (scales) that we use to measure this system.

If it is large, we may resolve only the third one.

⇒ Your observation scale determines the mode that you observe.

⇒ System will be effectively described by that mode.

⇒ That is the only DOF that is effective

This is akin to the "Emergence" of Thermodynamic Variables.

9<sup>th</sup> January 2024

④ Coarse op observation of a microscopic variables leads to macroscopic variables.

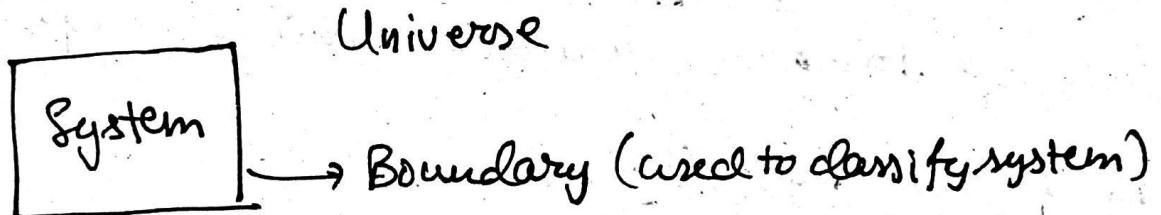
Last mode in last day's note is like a volume expansion (So?)

In his notation  $\rightarrow$  Coarse graining = Observation with a least count greater than smallest modes of a system.

This is how the last mode leads to a macroscopic quantity like volume (length)

A Thermodynamic System -

Take a part of the universe that you want to study.



A Isolated system - No exchange of matter or energy.

⑤ In the context of thermodynamics we do not consider mass and energy equivalent.

A Open system - Exchange of matter and energy.

A Closed system - Allows energy exchange, but not matter.

## Exchange of energy -

Heating the system

WORK



Relation of these two: 1st Law

Δ Adiabatic wall — No exchange of heat energy.

↳ Another way of saying 'thermally isolated'?

Δ Diathermic wall → Allow energy transfer.

Δ A State of a system; Macroscopic variables describe this. ↳ Equilibrium values

✳ Always only described at equilibrium. ↳ Something that is

Regardless of what happens in a process, thermodynamic variables are still related by thermodynamic relations. ↳ not changing with time.

Δ Mechanical Equilibrium —

Dictated by NLM,

$$\vec{F}_N = 0, \vec{\gamma}_N = 0$$

Δ Chemical Equilibrium —

No spontaneous change in chemical composition.

Δ  →



diathermic

Allow a system to evolve.  
No change in properties.

If we have all three eqs, it is called thermodynamic equilibrium.

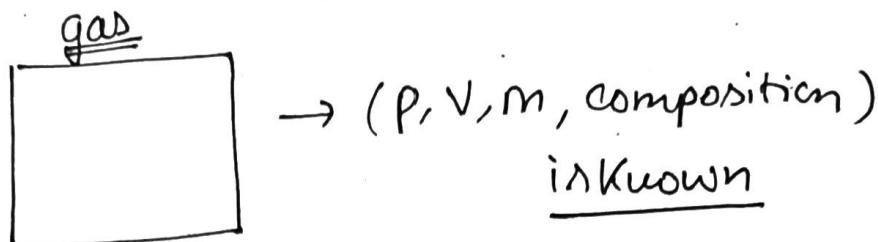
Macroscopic variables -  $(x, y, z)$  (Say)

Then  $\exists f(x, y, z) = 0$

Equation of state  $\rightarrow$  Empirical relation

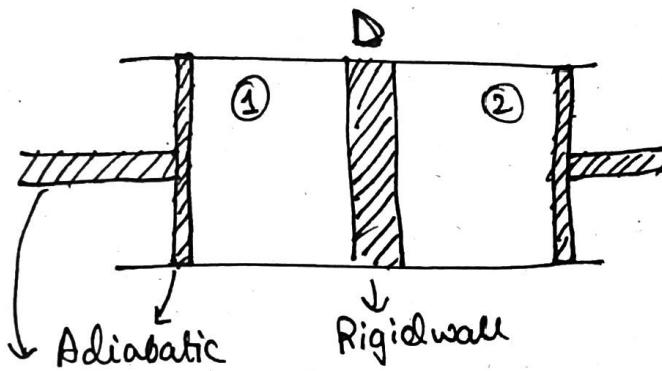
⊗ Claim  $\rightarrow$  (Later) the equations that relate these can be derived from microscopic physics.

○ Thermal equilibrium and temperature  $\rightarrow$



p and V can change independently

Self Note : n variables, p constraints,  $\Rightarrow$  n-p independent variables.



○ D is adiabatic,  $\Rightarrow$  ① and ② can coexist for any  $(P_1, V_1)$  and  $(P_2, V_2)$

○ D is ~~diathermic~~ diathermic  $\Rightarrow (P_1, V_1)$  and  $(P_2, V_2)$  are not independent

$\Rightarrow \exists$  a function  $f(P_1, V_1, P_2, V_2) = 0$

△ Thermal eq is a state achieved by two or more systems characterised by restricted state of parameters on having been separated by a diathermic wall.

⊗ Temp defined & next class ..

④ Class test to be graded out of 10,  
HW out of 5.

11<sup>th</sup> January 2024

## Thermal Equilibrium:

- System connected to its surroundings by a diathermic wall
  - Wait (Associated timescale)
  - Thermal equilibrium

Based on this logic, we will create laws of equilibrium thermodynamics

→ When these laws are violated, we will say that the system is not in equilibrium.

In particular, this means  $\exists F(p_1, v_1, p_2, v_2) = 0$

↳ Holds for more

## □ Zeroth Law of Thermodynamics → complex systems

If systems A and B are separately / individually in thermal equilibrium with system C, then ~~they are in~~  
A and B are also in thermal equilibrium.

(Found empirically - from experience)

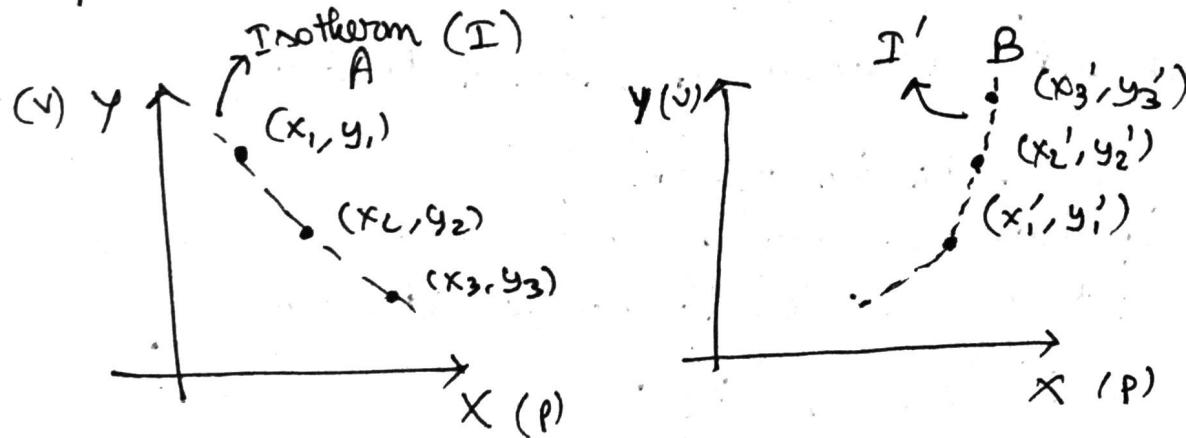
⇒ 'Suggests' that there must be a physical quantity that is same for two systems in thermal equilibrium.  
We are going to call this quantity 'temperature'

④ This idea of equilibrium can be generalised -  
any system that exchanges something akin to energy (chemical eq, mechanical eq)

⇒ Temperature ( $T$ )

$$\left. \begin{array}{l} T_A = T_C \\ T_B = T_C \end{array} \right\} \Rightarrow T_A = T_B$$

Two systems, where the system is described by two independent variables  $x$  and  $y$ . (could be anything -  $P$  and  $V$  for gas)



$A$  and  $B$  are connected by are in thermal equilibrium

Make  $(x_1, y_1)$  to  $(x_2, y_2)$  but still in thermal equilibrium with  $(x_1', y_1')$

Self Note: Think in terms of  $P$  and  $V$ .

In thermal eq of ideal gas,  $P_1 V_1 = P_2 V_2$ .

$\Rightarrow P_2 V_2$  held const, there are infinitely many pairs

$$(P_1, V_1) \text{ s.t } P_1 V_1 = P_2 V_2$$

We again move  $(x_2, y_2) \rightarrow (x_3, y_3)$  &  $(x_3, y_3)$

is in thermal eq. with  $(x_1', y_1')$

$\Rightarrow (x_1, y_1), (x_2, y_2), (x_3, y_3)$  are all in thermal eq with each other. (By zeroth law - as they are individually in thermal eq with  $(x_1', y_1')$ )

⊗ Locus of all points that represents states at which a system is in thermal equilibrium with one state of another system.

Note that we can also take states  $(x_2', y_2'), (x_3', y_3')$  which are in thermal equilibrium with each other.

$\rightarrow$  All points on  $I$  and  $I'$  are in thermal equilibrium

$\Rightarrow$  They are conjugate isotherms

We can construct any such isotherm pairs.

Formally, common properties of  $I$  and  $I'$   
⇒ Temperature

○ A and B are two systems, there will be interaction,

$$F_1(x_A, y_A, x_B, y_B) = 0$$

if they are in thermal equilibrium.

Say B and C are in thermal equilibrium,

$$F_2(x_B, y_B, x_C, y_C) = 0$$

By Zeroth law, there must be,

$$F_3(x_A, y_A, x_C, y_C) = 0$$

Try to show that,

$$\begin{aligned} f_1(x_A, y_A) &= f_2(x_B, y_B) = f_3(x_C, y_C) \\ &= \theta \rightarrow \underline{\text{Temperature}} \end{aligned}$$

□ Heat →

people originally thought of this as a fluid,  
some ~~calorif.~~ caloric fluid.

Later we accepted that this was a form of energy.

○ Internal Energy :  $K.E + (\bar{P}.E)$  → Binding, etc.

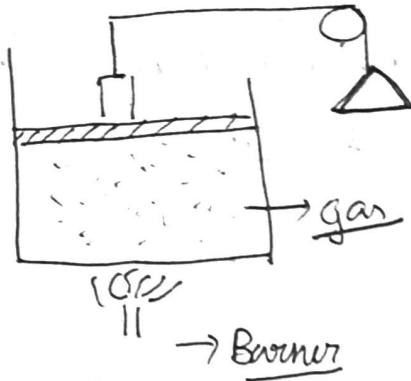
In <sup>non</sup> relativistic systems, we subtract rest energies,  
 $(mc^2)$

⊗ In context of thermodynamics, KE is  
calculated in rest frame of system.

So Internal Energy is not relativistic energy.

⊗ Also it is not related to overall motion.

16<sup>th</sup> January 2024



The piston can work on gas, and vice-versa.

(CPV)  
→ Burner

$$\Delta U = \Delta Q + \Delta W \rightarrow \text{Work done by system}$$

Change in internal energy  
Heat supplied to system

→  $\Delta Q = +ve$  when added to the system

→  $\Delta W = +ve$  when work is done on the system by surroundings

This is the 1st Law of thermodynamics:

⊗ This has no physics other than energy conservation.

NOW,

$$\Delta Q = \Delta U + (-\Delta W)$$

Some heat energy increases internal energy of system  
Some heat energy does work by moving piston, etc.

→ The same amount  $\Delta U$  can be done by different combinations of  $\Delta Q$  and  $\Delta W$ .

Like, Money = Cash + Cheque

This tells you that  $U$  is a state function (Example of exact differential)

⇒ It does not matter how you reached a state (path independent)

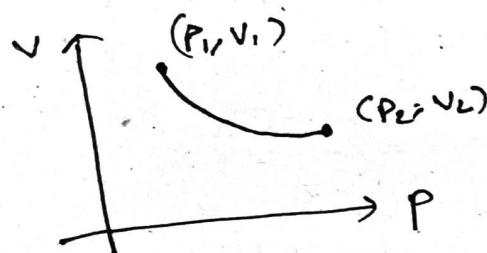
On the other hand,  $\Delta W$  is path dependant.



$$\Delta W = P \Delta V$$

(from  $F = dS - \partial V$ )

In this system,

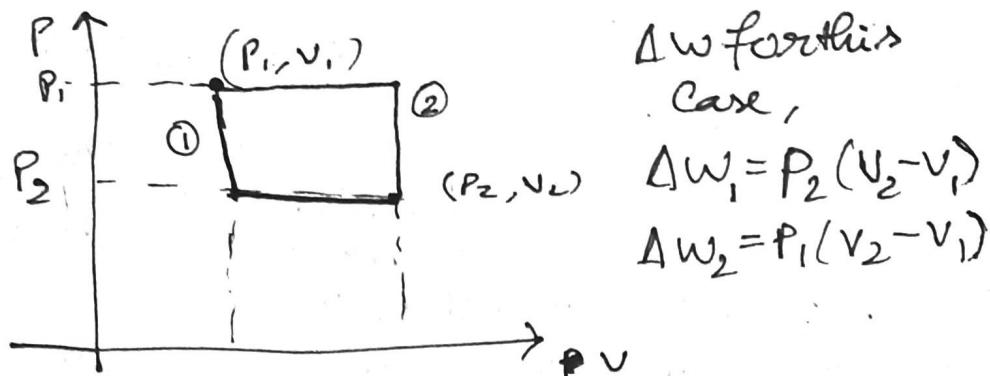


There are many paths from  $(P_1, V_1)$  to  $(P_2, V_2)$

We imagine paths where the points are in equilibrium (as  $P$  and  $V$  need to be well defined)

This way of moving from  $(P_1, V_1)$  to  $(P_2, V_2)$  is a quasistatic process — every intermediate point is well defined thermodynamic equilibrium states.

$\otimes$  Note that this always has an attached timescale.



$$\text{So, } \Delta w_1 \neq \Delta w_2$$

$\rightarrow \Delta w$  is path dependent.

$\Delta Q$  will also change, but it will change such that  $\Delta u$  remains the same.

First law  $\rightarrow du = dQ + dw$

$$\Rightarrow du = dQ - pdV$$

$$\Rightarrow dQ = du + pdV$$

Internal energy,

$$u = u(T, V)$$

$$\therefore du = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(\frac{\partial u}{\partial V}\right)_T dV$$

This allows us to write,

$$dQ = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(P + \left(\frac{\partial u}{\partial V}\right)_T\right) dV$$

$\otimes$  Isochoric process —  $V$  remains constant.

We define some quantity

$$C_V = \left( \frac{dQ}{dT} \right)_V = \left( \frac{\partial U}{\partial T} \right)_V$$



Response function: To see how system responds when we do something.  
(Easy to measure in lab)

Heat capacity at constant volume.

In a similar way,

$$C_P = \left( \frac{dQ}{dT} \right)_P = \left( \frac{\partial U}{\partial T} \right)_V + \left\{ P + \left( \frac{\partial U}{\partial V} \right)_T \right\} \left( \frac{\partial V}{\partial T} \right)_P$$

Heat capacity at constant pressure

~~Note~~ Note there are not related to ideal gas systems.

$$C_P = C_V + \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P$$

$$\rightarrow C_P - C_V = \left[ P + \left( \frac{\partial U}{\partial V} \right)_T \right] \left( \frac{\partial V}{\partial T} \right)_P \rightarrow \text{True in general}$$

Now we consider the case of ideal gas → (Diff for diff system)

$$PV = RT$$

$$\Rightarrow P \left( \frac{\partial V}{\partial T} \right)_P = R$$

Also,

$$\left( \frac{\partial U}{\partial V} \right)_T = 0 \quad (\text{Ideal gas})$$

Why? Since there are no interactions b/w particles of ideal gas.

If we bring them closer ( $dV$ ), no PE changes occur.

If  $dT = 0$ , KE is const  $\Rightarrow dU$  is not changing

Note that this depends on the molecular picture.

$\Rightarrow$  for the first law itself,  $\left( \frac{\partial U}{\partial V} \right)_T = 0$  is not trivial, until we commit to the microscopic picture.

So, for ideal gas,

$$C_p - C_v = R$$

Mayer's Relation

- How do you compute this for Vander Waals gas?  
(Home reading)

Tutorial Begins

$$dQ = dU + pdV$$

$$= \left(\frac{\partial U}{\partial T}\right)_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + pdV$$

Now let us look at what happens for ideal gas.

$$dQ = C_V dT + pdV$$

$$(As \left(\frac{\partial U}{\partial V}\right)_T = 0)$$

o Adiabatic transformation of ideal gas →

$$PV = RT \rightarrow C_p - C_v$$

$$\Rightarrow pdV + Vdp = RdT$$

$$\Rightarrow pdV + Vdp = (C_p - C_v)dT$$

$$\xrightarrow{LHS} \Rightarrow C_v dT + pdV = C_p dT - Vdp$$

As process is adiabatic;  $dQ = 0$

$$\Rightarrow C_v dT + pdV = 0$$

$$\therefore C_p dT - Vdp = 0$$

$$\Rightarrow \boxed{Vdp = C_p dT}$$

$$\text{and } \boxed{pdV = -C_v dT}$$

Combining,

$$\frac{dP}{P} = - \frac{C_P}{C_V} \frac{dv}{v}$$

$\Rightarrow$  Integrate it  $\Rightarrow \ln P = -\gamma \ln V + \ln C$

$$\text{Where } \gamma = \frac{C_P}{C_V}$$

$$\Rightarrow \boxed{PV^\gamma = \text{constant}}$$

for ideal adiabatic change

Quasi static processes for ideal gas  $\rightarrow$  (Generalization)

$$o \boxed{PV^n = \text{constant}}$$

Case I :  $n=0$ ,  $P = \text{constant}$  (isobaric)

Case II :  $n=1$ ,  $PV = \text{constant}$  (isothermal)

Case III :  $n=\gamma$ ,  $\gamma = \frac{C_P}{C_V}$ ,  $PV^\gamma = \text{constant}$  (adiabatic)

for diff value of n, diff processes.

Case IV :  $n \rightarrow \infty$ , effect of  $P$  is negligible (isochoric)

for an ideal gas,

$$dQ = C_V dT + PdV$$

$$\text{So, } \Delta Q = \int_i^f C_V dT + \int_i^f PdV$$

How does  $P$  change with  $V$ ? we use  $PV^n = C$

$$\rightarrow \Delta Q = C_V(T_f - T_i) + \int_i^f \frac{A}{V^n} dV$$

 Taken as temp independent,  
but that may not be right

for Ideal Gas,

$$C_V = \text{constant} ? \square \text{ Think}$$

Normally, we take response functions to be constant.

We do it for  $n=1$  (Special case) (most common)

$$\Delta Q = C_V(T_f - T_i) + \int_i^f \frac{A}{V^n} dV$$

$$= C_V(T_f - T_i) + RT_i \ln\left(\frac{V_f}{V_i}\right)$$

for  $n \neq 1$ , we get  
 $\stackrel{t}{=} 0$  (isothermal)  $\rightarrow$  substituting A

$$\Delta Q = C_V(T_f - T_i) + R \left( \frac{T_i - T_f}{n-1} \right)$$

□ Try integrating

□ Take limits of  $n=0, n \rightarrow \infty, n=\infty$

for the expression of  $\Delta Q$  given later.

We do Adiabatic,

$$\Delta Q = C_V(T_f - T_i) + R \left( \frac{T_i - T_f}{\gamma-1} \right)$$

$$= C_V(T_f - T_i) + \frac{(C_p - C_v)(T_i - T_f)}{\frac{C_p - C_v}{C_v}}$$

$$= 0$$

\* General formulae for moving from one state to another quasistatically -

□ Now calculate  $\Delta W$  and  $\Delta Q$  for diff paths, and check that  $\Delta U$  is a state function.

## O First Law of Thermodynamics → We continue.

18th January 2024

$$dU = dQ + dW$$

→ U is a state function, Q and W are not

To distinguish state functions and path functions,  
we write  $dU$  for state, and  $dQ$  and  $dW$   
for not state func

Exact differential

Inexact differential.

Example : System described by  $(x, y)$

$$\text{and } df = y dx + x dy$$

We want to calculate,



$$\Delta f = \int_{(0,0)}^{(1,1)} df = \int_{(0,0)}^{(1,1)} d(xy) = (xy) \Big|_{(0,0)}^{(1,1)}$$

$$= (1)(1) - (0)(0) = 1$$

① Note that we do not need to care about the path taken.  
in doing the integral.

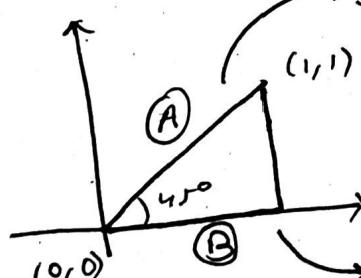
The change of the function does not depend upon the path taken.

② A quantity  $g \rightarrow f dg = y dx$

We want to calculate,

$$\Delta g = \int_{(0,0)}^{(1,1)} y dx \quad \rightarrow \text{We cannot proceed unless we know the } \underline{\text{path}}.$$

Say the path,



$$y = x \Rightarrow \Delta g = \int_{(0,0)}^{(1,1)} x dx = \frac{1}{2} \quad (\text{path A})$$

$$\Delta g = \int_{(0,0)}^{(1,0)} (0) dx + \int_{(1,0)}^{(1,1)} y \cdot (0) = 0 \quad (\text{path B})$$

$\Rightarrow$  The quantity depends on the path.

Putting it mathematically,

$F_1(x, y) dx + F_2(x, y) dy$  is exact if  
it can be written as some  $d(f)$

$$\therefore df = \left(\frac{\partial f}{\partial x}\right)dx + \left(\frac{\partial f}{\partial y}\right)dy$$

By comparison,

$$F_1 = \frac{\partial f}{\partial x}, F_2 = \frac{\partial f}{\partial y}$$

Now, say,

$$\vec{F} = \vec{i} f$$

$$\Rightarrow (F_1 \hat{i} + F_2 \hat{j}) = \left(\frac{\partial f}{\partial x} \hat{i} + \frac{\partial f}{\partial y} \hat{j}\right)$$

So most forces that are expressed as gradient of a scalar have exact differential structure.

So,

$$\int_1^2 F_1(x, y) dx + F_2(x, y) dy$$

$$= \int_1^2 \vec{F} \cdot d\vec{r}$$

$$= \int_1^2 (\vec{i} \cdot f) d\vec{r}$$

$$= \int_1^2 df$$

$$= f(2) - f(1)$$

f only at endpoints.

□ Use Stokes theorem for a closed loop to show,

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y} \quad \text{or} \quad \frac{\partial F_2}{\partial x} = \frac{\partial F_1}{\partial y} \quad \text{then it is } \underline{\text{exact}}$$

$$dQ = \left(\frac{\partial u}{\partial T}\right)_V dT + \left(p + \left(\frac{\partial u}{\partial V}\right)_T\right) dV$$

Again, true in general.

This again shows that  $dQ$  is exact.

$$\Rightarrow dQ = C_V dT + \left(p + \left(\frac{\partial u}{\partial V}\right)_T\right) dV \quad (\text{try to remember})$$

$$C_V = \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial u}{\partial T}\right)_V$$

In the special case of ideal gas,

$$dQ = C_V dT + p dV$$

We calculated  $dQ$  for several processes.

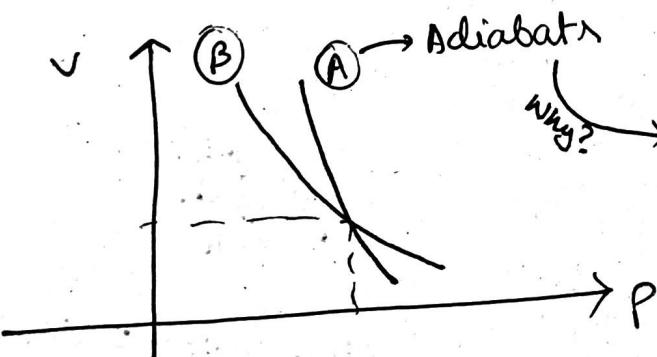
$$dQ = 0 \quad \text{for adiabatic process.}$$

Isothermal,

$$pV = \text{constant}$$

Adiabatic,

$$pV^\gamma = \text{const}, \quad \gamma = \frac{C_P}{C_V}$$



$$\text{Isotherm, } p dV + p V dp = 0$$

$$\Rightarrow \frac{dp}{dV} = -\frac{p}{V}$$

Adiabatic,

$$\gamma p dV^{\gamma-1} dV + V^\gamma dp = 0$$

$$\Rightarrow \frac{dp}{dV} = -\gamma \frac{p}{V}$$

$\frac{dp}{dV}$  is slope of graph.  $\gamma > 1$  (as  $C_P > C_V$ )

$\Rightarrow$  Adiabats have steeper slope as compared to isotherms.

## 0 A diabatic lapse rate →

\* Air is bad thermal conductor.

Thus, we can take approximation that expansion of air is adiabatic.

We want to find out how temp changes as we go up the atmosphere.

\* Ideal gas assumption.

So we know that,  $PV^\gamma = \text{const}$

Using ideal gaseqn,

$$\Rightarrow P^{1-\gamma} \propto T^\gamma = \text{const}$$

Now taking differential (Standard Strategy)

$$\Rightarrow d(P^{1-\gamma} T^\gamma) = 0$$

$$\Rightarrow \frac{dP}{P} = \frac{\gamma}{\gamma-1} \frac{dT}{T}$$

→ Easiest to take log before differentiation.

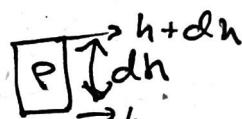
$$\ln(P^{1-\gamma} T^\gamma) = \ln(\text{const}) = \text{const}$$

$$\Rightarrow (1-\gamma) \ln P + \gamma \ln T = \text{const}$$

$$\Rightarrow (1-\gamma) \frac{dP}{P} + (\gamma) \frac{dT}{T} = 0$$

$$\Rightarrow \frac{dP}{P} = \frac{\gamma}{\gamma-1} \frac{dT}{T}$$

Now,  $dP = -Pg dh$



$$\Rightarrow \frac{dP}{P} = - \frac{Pg dh}{P}$$

Now,  $PV = RT \Rightarrow P \left( \frac{m}{\rho} \right) = RT$

Mass of air of 1 m<sup>3</sup> gas

Therefore,

$$\frac{dp}{P} = - \frac{gM}{RT} dh$$

$$\therefore \boxed{\frac{dT}{dh} = - \frac{\gamma-1}{\gamma} \frac{gM}{R}}$$

If we plugin the numbers,  $\frac{dT}{dh} = 9.7^\circ C / km$   
Observational  $\rightarrow 7^\circ C / km$ .

We can apply this to many other systems.

Therefore,

$$\frac{dp}{P} = - \frac{gM}{RT} dh$$

$$\boxed{\frac{dT}{dh} = - \frac{\gamma-1}{\gamma} \frac{gM}{R}}$$

If we plugin the numbers,

$$\frac{dT}{dh} = 9.7^\circ C / Km$$

Observational  $\rightarrow 7^\circ C / Km$

We can apply this to many other systems.

-----  
30<sup>th</sup> Jan 2024

### o 2nd Law of Thermodynamics $\rightarrow$

When we throw a ball up, the ball comes down and has the same velocity but opp direction  $\Rightarrow$  It has the same K.E.

But it can have any direction  $\Rightarrow$  It does not violate Energy conservation that way.

So energy conservation does not give us enough info to fix dynamics of a system.

So, similarly, the first law does not tell us what processes can happen, and what cannot happen.

$\rightarrow$  We need the 2nd law to tell us what is feasible and what is not feasible.

⊗ A amount of heat energy can never be converted completely to work.

### o Engine :

System operating in cycles that converts heat to work.

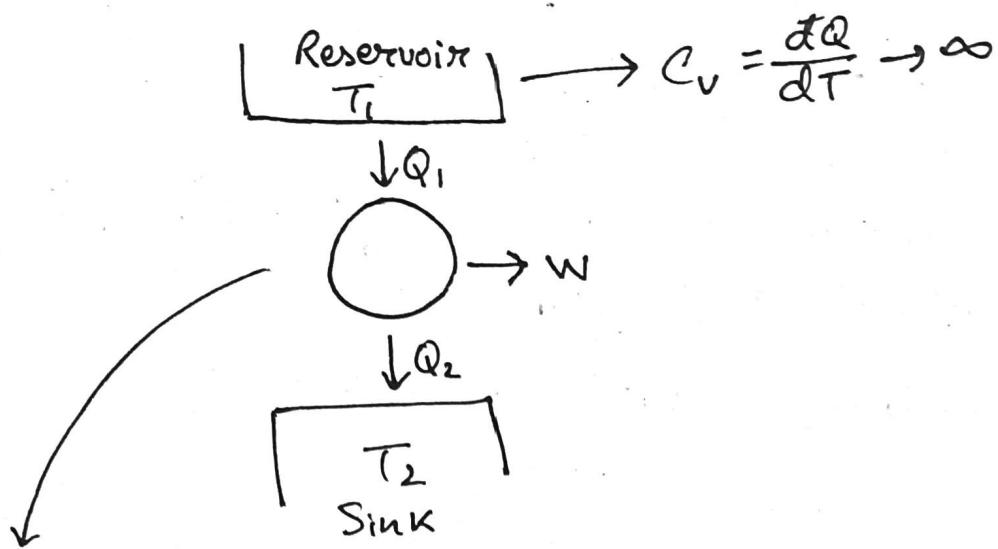
### o Heat Engine :

$Q_1 \rightarrow$  heat absorbed by system

$Q_2 \rightarrow$  heat rejected by system.

$W \rightarrow$  work done by engine.

We can think of such an engine as,



After one complete cycle, the system comes back to its original state  $\Rightarrow \Delta U = 0$  for each cycle.

$$\Delta U = \Delta Q + \Delta W$$

$$\Rightarrow (Q_1 - Q_2) + W = 0$$

$$\Rightarrow W = -(Q_1 - Q_2)$$

(\*)  $W$  is -ve if  $Q_1 > Q_2 \Rightarrow$  System works on surroundings.

$$\eta = \frac{|W|}{Q_1} = 1 - \frac{Q_2}{Q_1} < 1$$

Why can I not make an engine with only one reservoir?

O Convention (follow whatever you like)  $\rightarrow$

$$\Delta U = \Delta Q + \Delta W$$

$\Delta Q \equiv$  +ve for addition of heat energy to system.

$\Delta W \equiv$  +ve for work done on the system.

i.e., +ve if  $\Delta U$  increases due to it)

Note,

$$\Delta W = \int p dV$$

$$\text{or, } \Delta W = -P\Delta V$$

$$= -P(V_f - V_i)$$

Consistent ←  
with the work  
convention.

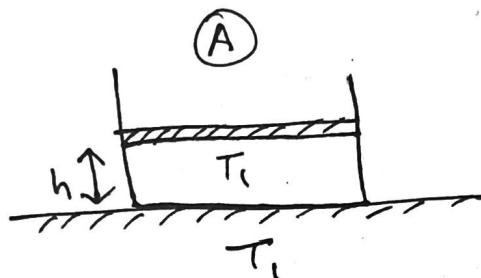
↓  
-ve only if compressed, i.e  
work done on system.

⊗ 2nd Law is also strictly empirical.

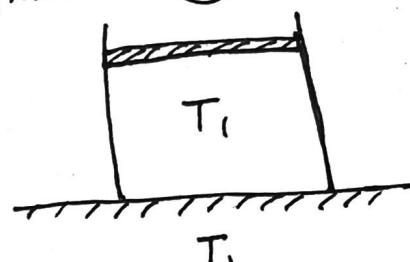
→ Source reservoir ( $T_1$ )

⊗ Consider ideal gas

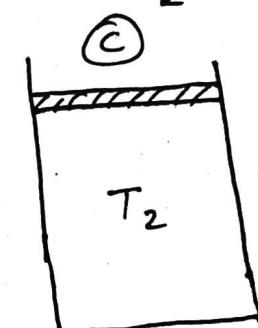
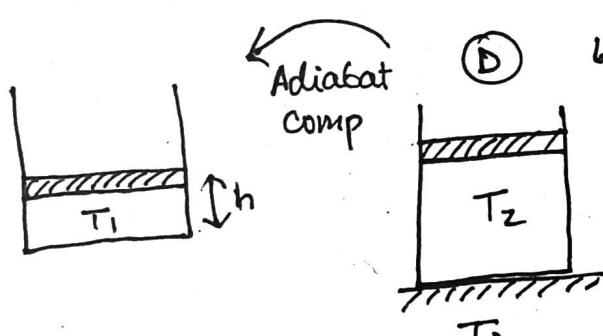
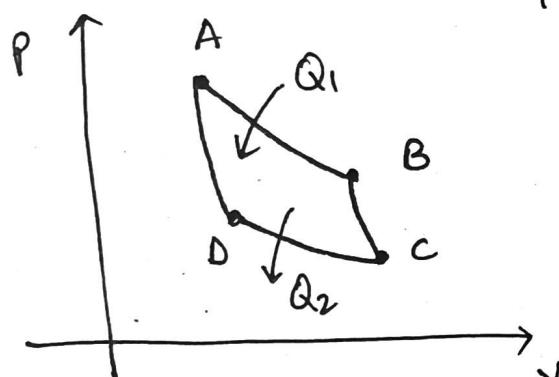
→ Sink reservoir ( $T_2$ )



Isothermal expansion  
Energy goes in form of  
gas



Adiabatic expansion



⊗ Every step, work is either being done on the system  
or by the system.

$$W_{\text{Total}} = W_1 + W_2 + W_3 + W_n$$

$$Q = Q_1 - Q_2$$

We calculate here so that we can calculate  $\eta$ .

- \* If we are given two reservoirs, ~~and~~<sup>one</sup> with one being at a higher temp than the other, and we want to construct a reversible engine, it can only be done with two isotherms and two adiabats — this is the Carnot engine.

$$Q = Q_1 - Q_2$$

We calculate these so that we can calculate  $\eta$ .

- ✳ If we are given two reservoirs, ~~and~~ with one being at a higher temp than the other, and we want to construct a reversible engine, it can only be done with two isotherms and two adiabats — this is the Carnot engine.
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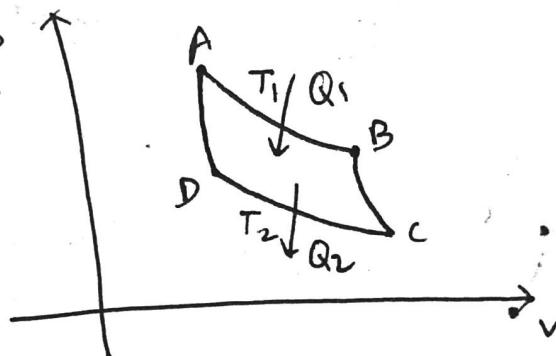
18 Feb 2024

### Heat engine:

→ Two reservoirs  $T_1 > T_2$

→ "Reversible" (meaning still not ~~means~~ discussed)

Can only happen with two isotherms and two adiabats.



✳ All steps are quasi-static

- ✳ Note: we can also go  $D \rightarrow C \rightarrow B \rightarrow A$ , that is also a feature.

We begin with first law:

$$\Delta U = \Delta Q + \Delta W ; \quad \Delta W = - \int p dV$$

- ①  $A \rightarrow B$  : (Isothermal expansion at temp  $T_1$ )

✳ ideal gas.

$$\Rightarrow \Delta U = 0$$

$$\therefore \Delta Q = -\Delta W = - \int p dV$$

$$\Rightarrow Q_1 = nRT_1 \ln\left(\frac{V_B}{V_A}\right) \quad (+ve, \text{ heat goes into system})$$

② B → C : (Adiabat)

$$\Delta Q = 0$$

$$\Rightarrow \Delta W = \Delta U$$

$$W_2 = - \int p dV$$

$$\text{We use } PV^\gamma = K$$

$$\begin{aligned} \Rightarrow W_2 &= -K \int \frac{dV}{V^\gamma} = -\frac{K}{\gamma-1} V^{\gamma-1} \Big|_{V_B}^{V_C} \\ &= \frac{-K}{\gamma-1} \left( V_C^{1-\gamma} - V_B^{1-\gamma} \right) \\ &= \frac{K}{\gamma-1} \left( \frac{V_C}{V_C^\gamma} - \frac{V_B}{V_B^\gamma} \right) \end{aligned}$$

$$\text{Now, } P_C V_C^\gamma = P_B V_B^\gamma = K$$

Now,

$$\begin{aligned} W_2 &= \frac{K}{\gamma-1} \left( \frac{P_C V_C}{P_C V_C^\gamma} - \frac{P_B V_B}{P_B V_B^\gamma} \right) \\ &= \frac{1}{\gamma-1} (P_C V_C - P_B V_B) \\ &= \frac{\gamma n R}{\gamma-1} (T_C - T_B) \end{aligned}$$

Since  $T_B > T_C \Rightarrow W_2 < 0 \Rightarrow \text{Work done by system.}$

③ C → D : (Isothermal at  $T_2$ )

Similarly,

$$Q_3 = nRT_2 \ln\left(\frac{V_D}{V_C}\right)$$

$$W_3 = -Q_3$$

④ D  $\rightarrow$  A: ~~(Isobaric)~~ (Adiabatic)

$$W_h = \frac{nR}{r-1} (T_A - T_D) = \frac{nR}{r-1} (T_B - T_C)$$
$$= -W_2$$

$$\therefore W = W_1 + W_2 + W_3 + W_h$$

$$= -nRT_1 \ln\left(\frac{V_B}{V_A}\right) - nRT_2 \ln\left(\frac{V_B}{V_C}\right)$$

$$\begin{cases} T_A = T_B = T_1 \\ T_C = T_D = T_2 \end{cases}$$

Now, we know that,

$$T_1 V_B^{r-1} = T_2 V_C^{r-1}$$

$$T_1 V_A^{r-1} = T_2 V_D^{r-1}$$

$$\Rightarrow \frac{V_B}{V_A} = \frac{V_C}{V_D}$$

Using this,

$$W = -nR \ln\left(\frac{V_B}{V_A}\right) (T_1 - T_2)$$

(Overall -ve, so system does work)

Now,

$$\eta = \frac{|W|}{Q_1} = -nR \ln\left(\frac{V_B}{V_A}\right) \frac{(T_1 - T_2)}{\dot{Q}}$$

$$\Rightarrow \eta = \frac{-nR \ln\left(\frac{V_B}{V_A}\right) (T_1 - T_2)}{-nR \ln\left(\frac{V_B}{V_A}\right) T_1}$$

$$\Rightarrow \eta = 1 - \frac{T_2}{T_1} < 1$$

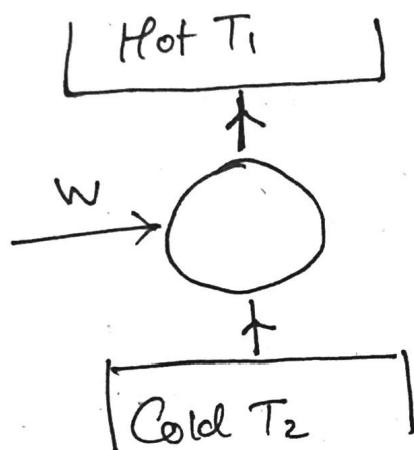
We may also write,

$$\eta = 1 - \frac{|Q_3|}{Q_1}$$

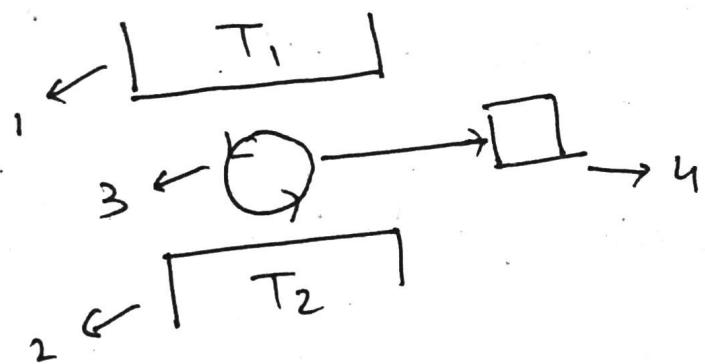
$T_1, T_2$

$\Rightarrow$  How do you make  $\eta$  large?

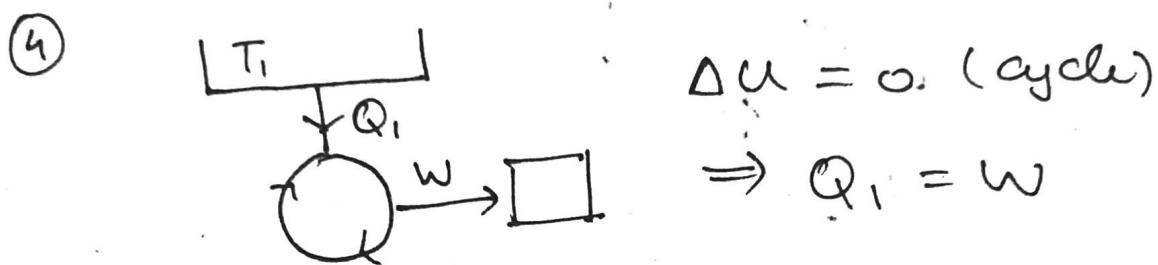
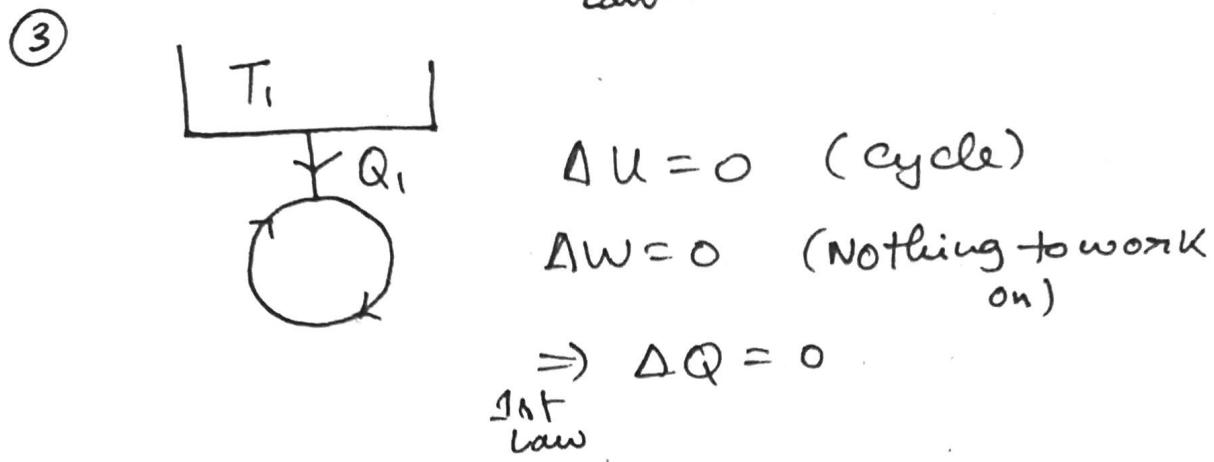
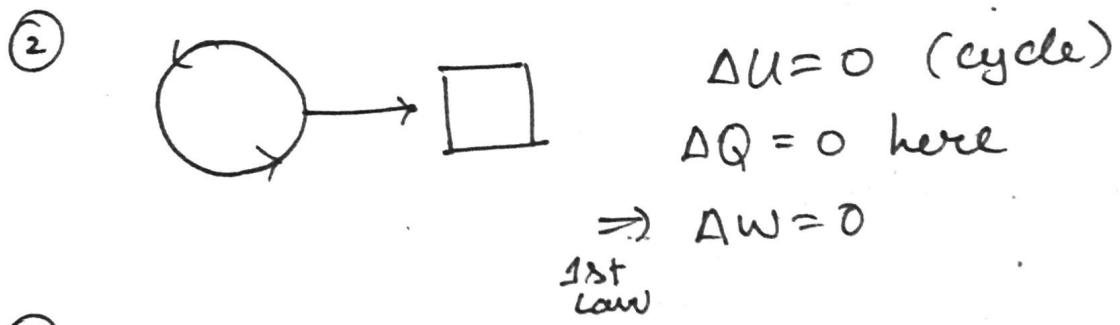
○ Carnot Cycle as refrigerator  $\rightarrow$



What lead us to the  $n$  body structure of the engine?



①  $\rightarrow$  useless.

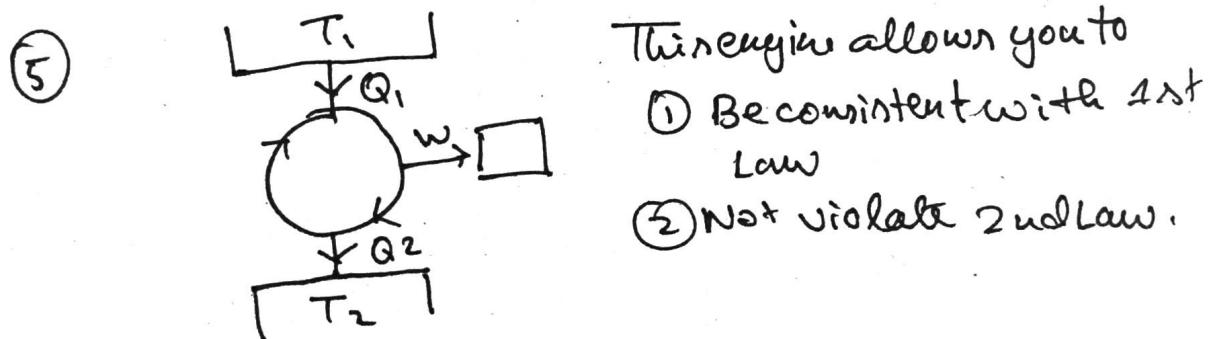


✗ Second Law is a statement that says that this configuration does not exist

This engine cannot exist

How do we say this?  
 All experiments attempting to make this have failed.

So we add another ingredient to make an engine that works.



## o 2nd law of thermodynamics → (Kelvin - Planck)

No cyclic process is possible whose sole result is  
complete conversion of heat to work.

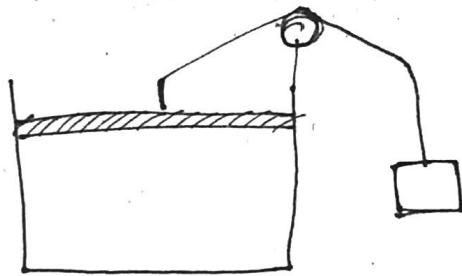
\* Complete conversion happens in isothermal process —  
but that is not cyclic.

## o 2nd law of thermodynamics (Clausius - Clapeyron)

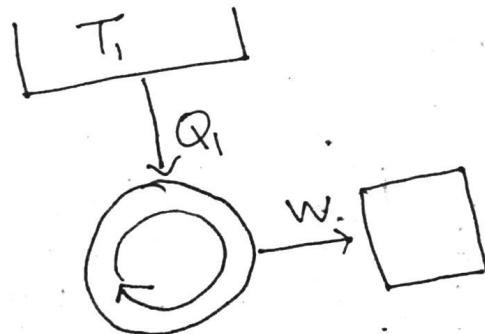
It is impossible to transfer heat from cold ~~to hot~~  
body to hot body by means of a cyclic process without  
any effect to the surroundings.

3rd February 2023

## Modelling → (the heat engine)

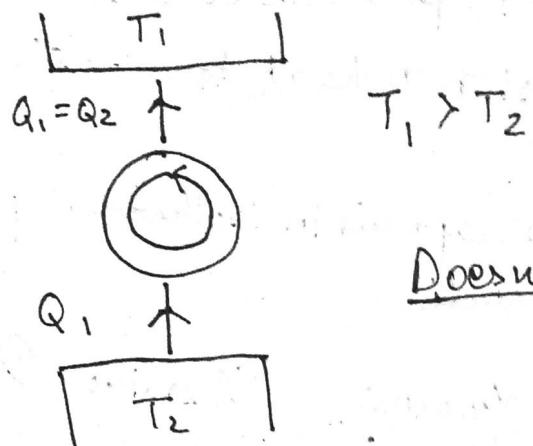


## o Kelvin:



Does not exist (2nd law)

o Clausius statement:

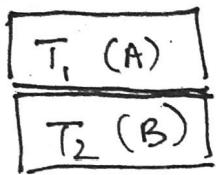


Does not exist (2nd Law)

These statements are equivalent.

o Reversibility →

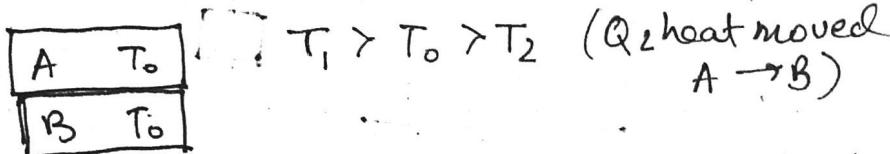
④ Example 1:



$$T_1 > T_2$$

Is the heat flow from  $T_1$  to  $T_2$  reversible?  
No, if it is irreversible.

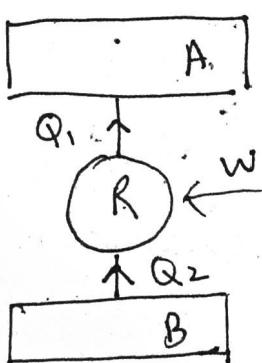
After some time,



$$T_1 > T_0 > T_2 \quad (\text{Q}_2 \text{ heat moved } A \rightarrow B)$$

These two bodies can't be put back to original state.

o Use a refrigerator.



$$Q_1 = Q_2 + w$$

→ State of B is now exactly what you started with.

→ But A is now getting more heat than it lost.

A has ~~w~~ extra energy extra.

- Take A with another cold body C such that  $W_{\text{energy}}$  is taken out.

→ Now A is back to the original state.

So the statement of reversibility does not state that we cannot put them back.

But what else has happened?

→ Refrigerator worked ( $W$ )

→ C got some heat ( $Q$ )

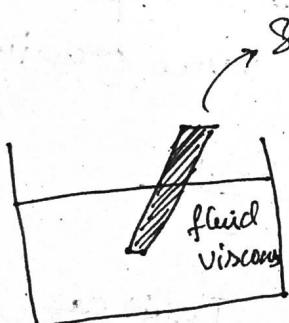
By conservation,  $Q = W$ .

To bring the surroundings back to original condition, we would need to convert  $Q$  to  $W$  completely — 2nd law prohibits this.

- \* You can't put the system to same state, but you cannot convert system + surroundings to the same original state.

- Reversibility  $\equiv$  (System + Surroundings)

- \* Example 2:



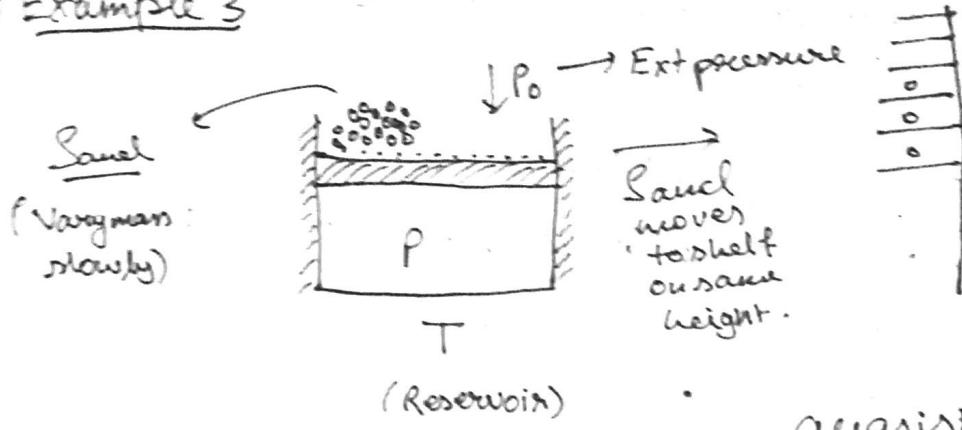
→ Stir the fluid quasistatically:

→ fluid will heat up.

To bring system back to original state, the heat has to be extracted and converted completely to work — prohibited by 2nd law

→ Quasistatic process does not necessarily mean reversible.

### Example 3

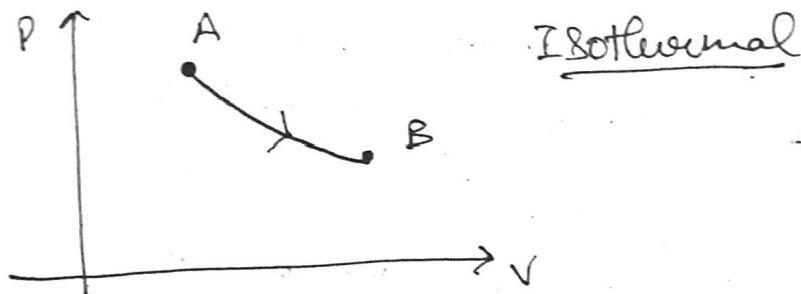


→ If we take sand off (gradually), the system moves up (taking heat from reservoir) quasistatically.

$$\text{Work done} = \int pdv$$

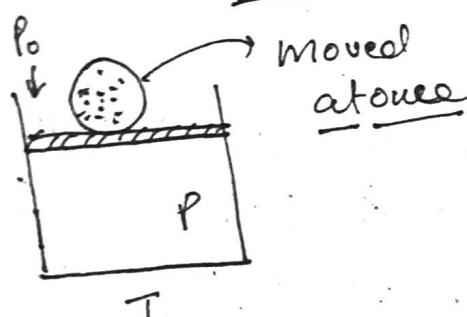
$$\Delta U = 0$$

$$Q = \int pdv$$



→ If we move sand from shelf to on piston, the system goes back quasistatically to same original state (A)

Quasistatic reversible



In this case, the gas will go to state B non-quasi- statically ..

But system goes A → B.

$$\begin{aligned}\text{Work done by gas} &= \int F \cdot dx \\ &= P_0 A (x_f - x_i) \\ &= P_0 (V_f - V_i)\end{aligned}$$

Heat taken from reservoir,  $Q_1 = P_0(V_f - V_i)$

Now put the weight (mass) at top of the piston.

$W = (mg + P \cdot A) \Delta x$  = heat that goes to reservoir.

So, extra heat goes to the reservoir =  $mg \Delta x$

But notice that we had to take the mass from  $x_i$  to  $x_f$  before we can put it on the piston at state B.

This extra heat is precisely what the amount of work we did against the gravitational force.

To put the system back to original state, we would have to extract  $mg \Delta x$  heat from reservoir and convert it completely to work — prohibited by 2nd law.

So,

Reversible →

- ① Must be quasi-static
- ② No dissipative forces.

Typically all irreversible processes, one of the following ~~two~~ must be true

- Mechanical / Thermal / Chemical equilibrium NOT satisfied
- Dissipative force.

HW: Convince yourself that Joule's free expansion is irreversible.

8<sup>th</sup> Feb 2024

## Claudius Inequality $\rightarrow$

- A thermodynamic system performs a complete cycle. To do that, it interacts with reservoirs  $R_1, \dots, R_n$  with temp  $T_1, \dots, T_n$  and exchange heat  $Q_1, \dots, Q_n$ .
- Convention  $\rightarrow Q \equiv +ve$ , heat goes into system.

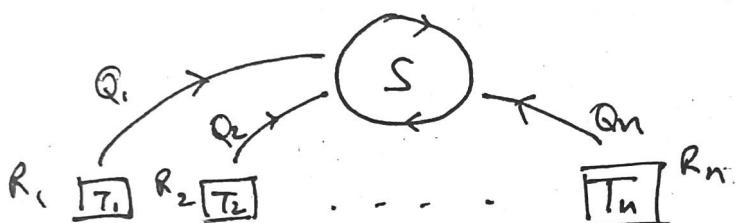
Statement  $\rightarrow$

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

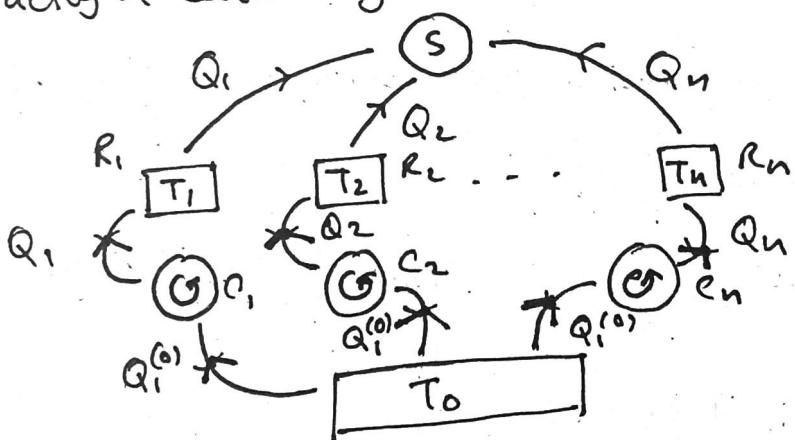
So for the carnot engine (a special subclass of this),

$$\frac{Q_1}{T_1} + \frac{Q_2}{T_2} = 0$$

General case,



We introduce a reservoir with arbitrary temp  $T_0$ , and exactly  $n$  carnot engines.



\*  $C_1$  supplies  $Q_1$  heat to  $R_1$ , the same heat that it ~~loses to~~ loses to  $S$ , and so on to  $n$ .

\* Note that this is possible due to the fact that

Carnot engines are reversible and can act as heat engine as well as refrigerator.

① Same  $R_1, \dots, R_n$  goes back to same state

②  $T_0$  reservoir loses energy

$$Q_o = \sum_{i=1}^N Q_i^{(0)}$$

Now we know that for the car engines,

$$\frac{Q_c^{(0)}}{Q_i} = \frac{T_0}{T_i}$$

$$\therefore Q_o = \sum_{i=1}^N Q_i^{(0)} = T_0 \sum_{i=1}^N \frac{Q_i}{T_i}$$

This occurs in cyclic for all the engines involved.

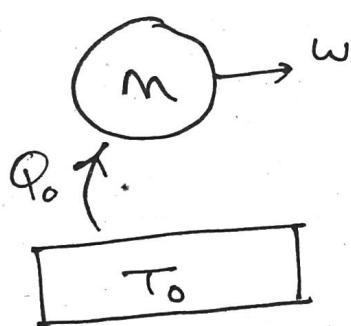
If we think of them as one engine,  $\Delta U = 0$ .

$$\text{Now, } \Delta U = \Delta Q + \Delta W$$

$$\Rightarrow -\Delta Q = \Delta W$$

$$\Rightarrow \Delta W = -T_0 \sum_{i=1}^N \frac{Q_i}{T_i} \rightarrow \text{Work done.}$$

Combining the engines,

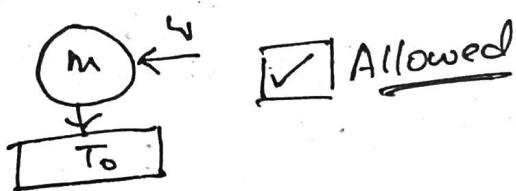


Obviously this engine  
cannot exist

$\Leftrightarrow$  Violates 2nd law

i.e., if work is done  
on system and  
heat is given to  
 $T_0$  reservoir.

But this is okay if  $Q_o < 0$   
work  $\rightarrow$  heat conversion is  
never prohibited.



$$\Rightarrow Q_o = T_0 \sum_{i=1}^N \frac{Q_i}{T_i} \leq 0$$

Consider S to be a reversible engine.

$\Rightarrow$  All engines / cycles are reversible.

Replace  $Q_i \rightarrow -Q_i$  (reverse the process)

$$\therefore T_0 \sum_{i=1}^N \frac{Q_i}{T_i} \geq 0$$

This can only be consistent if  $T_0 \sum_{i=1}^N \frac{Q_i}{T_i} = 0$

$$\Rightarrow \boxed{\text{for reversible } \sum_{i=1}^N \frac{Q_i}{T_i} = 0}$$

$$\Rightarrow \boxed{\text{for a cyclic process, } \sum_{i=1}^N \frac{Q_i}{T_i} \leq 0}$$

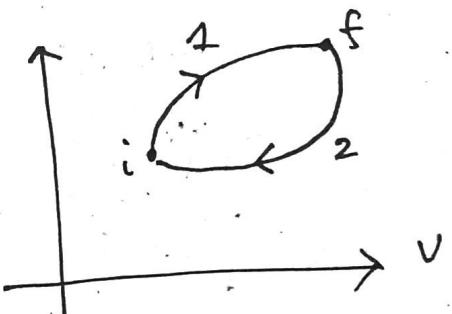
⊗ equality for reversible, inequality otherwise.

This may be generalised to,

$$\oint \frac{dQ}{T} \leq 0$$

Consider a reversible cycle,

$$\oint \frac{dQ}{T} = 0$$



Now,

$$\left[ \int_i^f \frac{dQ_{rev}}{T} \right]_1 + \left[ \int_i^f \frac{dQ_{rev}}{T} \right]_2 = 0$$

$$\Rightarrow \left[ \int_i^f \frac{dQ_{rev}}{T} \right]_1 = - \left[ \int_i^f \frac{dQ_{rev}}{T} \right]_2$$

$\Rightarrow \frac{dQ_{rev}}{T}$  does not depend on path

$\Rightarrow I+$  is a state function.

This will be called entropy.

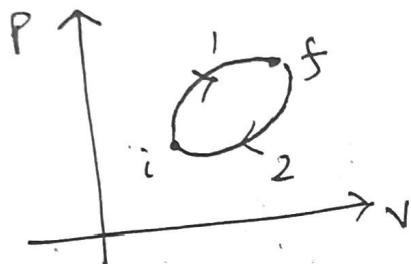
Clausius Inequality  $\rightarrow$

9th February 2024

$$\oint \frac{dQ}{T} \leq 0$$

Inequality for reversible process

Entropy:



Reversible?

$$\int_{i \rightarrow f} \frac{dQ_{rev.}}{T} = 0$$

$$\Rightarrow \int_i^f \left| \frac{dQ_{rev.}}{T} \right|_1 + \int_f^i \left| \frac{dQ_{rev.}}{T} \right|_2 = 0$$

$$\Rightarrow \int_i^f \left| \frac{dQ_{rev.}}{T} \right|_1 = \int_i^f \left| \frac{dQ_{rev.}}{T} \right|_2$$

Does not depend on the path, clearly.

$\Rightarrow I+$  is a state function.

So we define,

$$\int_1^2 \frac{dQ_{rev.}}{T} = \int_1^2 dS \equiv S_2 - S_1$$

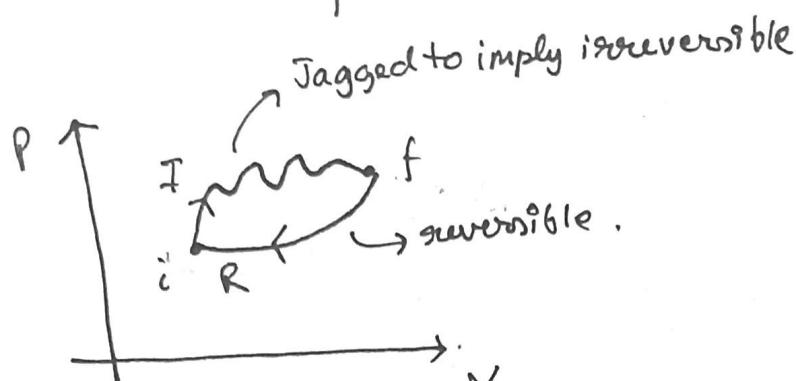
$S \equiv$  Entropy of the system.

Statement of entropy is related to reversible heat transfer only.

$\Rightarrow \frac{dQ}{T}$  is not strictly correct,

it has to be  $\frac{dQ_{rev}}{T}$ .

Now,



Irreversible cycle  $\rightarrow$  dissipation.

$$\oint \frac{dQ}{T} < 0$$

$$\Rightarrow \int\limits_i^f \frac{dQ}{T} \Big|_I + \int\limits_f^i \frac{dQ_{rev}}{T} \Big|_R < 0$$

$$\Rightarrow \int\limits_i^f \frac{dQ}{T} \Big|_I < \int\limits_i^f \frac{dQ_{rev}}{T} \Big|_R$$

$$\Rightarrow S_f - S_i > \int\limits_i^f \frac{dQ_{\cancel{rev}}}{T} \Big|_I$$

$$\Rightarrow \Delta S \geq \frac{dQ}{T}$$

o If isolated system  $dQ = 0$  (adiabatic)

$$S(f) > S(i)$$

For irreversible processes,

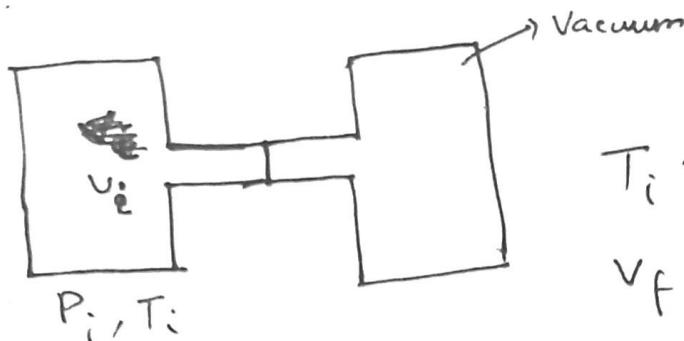
$$S(f) > S(i)$$

Reversible process,  $S(f) = S(i)$  (Isentropic)

Entropy is an extensive parameter - if we scale system in contact with reservoir at temp T, the heat it exchanges with the reservoir also scales. T remains same.

$\Rightarrow$  Entropy is extensive.

### 0 Joule Expansion:



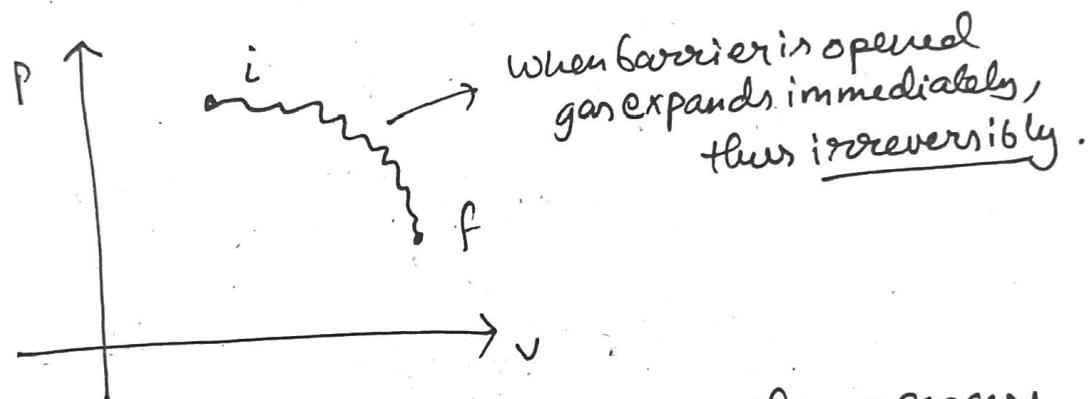
$$T_i = T_f$$

$$V_f = 2V_i$$

$$P_f = \frac{1}{2}P_i$$

$\Delta$  temp/internal energy does not depend on  $V$  for ideal gas,

$$T_i = T_f$$



We want to find entropy change in this process.

$$\Delta S = S_2 - S_1 = \int \frac{dQ_{rev}}{T}$$

But the path is irreversible, how do we do this?

The entropy change is a state function!  $\Rightarrow$  It has nothing to do with ~~the~~ path. We may construct any hypothetical path which is reversible and calculate entropy change for that path - it is going to be the same for any path.

① S is state function - allows you to take any rev path.

②  $dS$  is defined for any reversible path.

We choose isotherm here.

$$\begin{aligned}\therefore \Delta S &= \int_{V_0}^{2V_0} \frac{dQ_{rev}}{T} = \int_{V_0}^{2V_0} \frac{\cancel{dT} + pdV}{T} \\ &= \frac{1}{T} \int_{V_0}^{2V_0} pdV \\ &= R \ln 2 > 0. \quad (\text{Positive semidefinite quantity})\end{aligned}$$

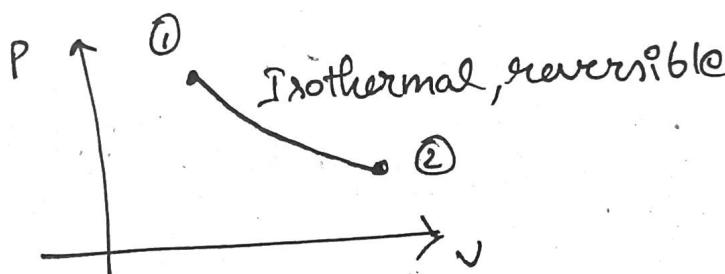
Note that here  $dQ = 0$ , so  $\Delta S = \frac{dQ}{T} = 0$

But that is, not reversible, do not be fooled by this. It must be

Any process of ideal gas -

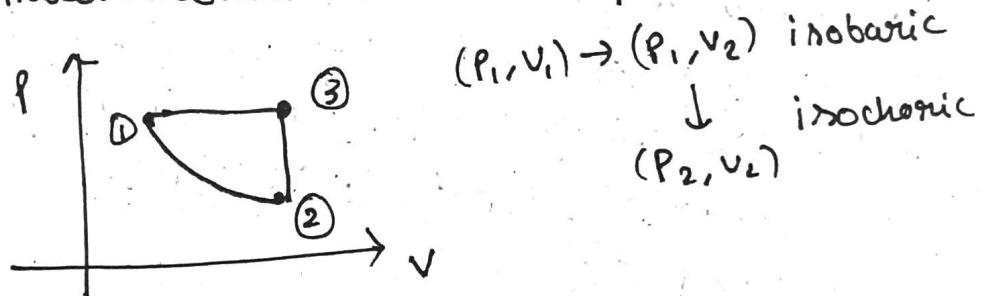
$$(P_1, V_1, T) \rightarrow (P_2, V_2, T)$$

$$\Delta S = NR \ln \left( \frac{V_2}{V_1} \right) \rightarrow \boxed{\text{Check}}$$



We argue that this is the same for all reversible paths.

So we construct another 'reversible' path



Hard to do ① → ③ → ② reversibly (req inf reservoir)  
but we don't care - we just assume it to be rev

① → ③ is not isothermal, it is isobaric

We use version of  $dQ$  where  $p$  is constant.

$$\begin{aligned}\therefore dQ &= C_V dT + p dV \quad \checkmark \text{ we use this} \\ &= C_p dT - V dp \quad \checkmark \text{ we use this.}\end{aligned}$$

$$\begin{aligned}\therefore \Delta S &= \int \frac{dQ_{\text{rev}}}{T} \\ &= \int C_p \frac{dT}{T} + \int C_V \frac{dT}{T} \\ &= C_p \ln\left(\frac{T'}{T}\right) + C_V \ln\left(\frac{T'}{T}\right)\end{aligned}$$

Show that,

$$\frac{T'}{T} = \frac{V_2}{V_1}$$

$$\begin{aligned}\Rightarrow \Delta S &= C_p \ln\left(\frac{V_2}{V_1}\right) - C_V \ln\left(\frac{V_2}{V_1}\right) \\ &= (C_p - C_V) \ln\left(\frac{V_2}{V_1}\right) \\ &= N R \ln\left(\frac{V_2}{V_1}\right) \quad (\text{Ideal gas})\end{aligned}$$

We can construct entropy some other way too —  
we demand that  $dS$  is a state variable with the  
formula — axiomatically like Carnot.

\* So, we have redefined reversibility and irreversibility  
with respect to entropy.

20<sup>th</sup> February

### Clausius inequality →

$$\oint \frac{dQ}{T} \leq 0$$

→ Equality holds for reversible processes.

⊗  $\int_i^f \frac{dQ_{rev}}{T} \Big|_1 = \int_i^f \frac{dQ_{rev}}{T} \Big|_2$

This allows us to introduce a state function —

$$dS = \frac{dQ_{rev}}{T}$$

$$\Rightarrow S_f - S_i = \Delta S = \int \frac{dQ_{rev}}{T}$$

↑  
Entropy (State fn.)

⊗  $S(f) - S(i) > \int_i^f \frac{dQ_{irrev}}{T}$

$$\Rightarrow \Delta S \geq \frac{dQ}{T}$$

□ Clarify this step.

o Process adiabatic →

$$S(f) \geq S(i)$$

(2nd Law entropic version)

1. Here we note that this is limited to adiabatic processes only — but that is not entirely true. It is equivalent to all other versions of the statement.

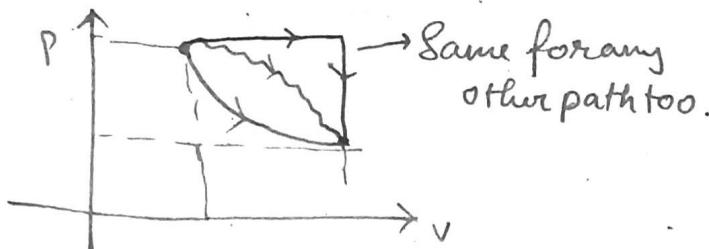
⊗ We can always consider a process adiabatic if we consider system + surroundings.

Calculations of entropy ~~case~~ → change →

① Joule's Free Expansion →

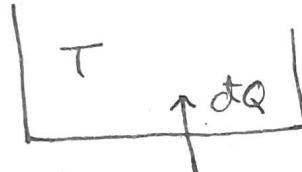
→ Process is irreversible  $(P_0, V_0, T_0) \rightarrow (\frac{P_0}{2}, 2V_0, T_0)$

→ Consider hypothetical "isothermal process".



Connect same initial and final state.

② Entropy change of a reservoir →



\* Marker for reservoir's internal energy -

\* If you add water to the ocean, the height of ocean remains unchanged, but the amount of water does change.

$$\Delta S = \int \frac{dQ_{rev}}{T}$$

$$\text{or } dS = \frac{dQ_{rev}}{T} = \frac{dQ}{T}$$

$T$  is the only marker of the reservoir (only state func)  
so it does not matter if the heat was transferred reversibly or irreversibly.

### ③ Reservoir ( $T_R$ ) and small system ( $T_S$ )

$$\Delta S_{\text{system}} = \int \frac{dQ_{\text{rev}}}{T} \quad (T_R > T_S, \text{say})$$

$$dQ = C dT \Rightarrow C \equiv \frac{dQ}{dT} \quad (\text{polytropic process})$$

$$\therefore \Delta S_{\text{system}} = \int_{T_S}^{T_R} \frac{CdT}{T} = C \ln \left( \frac{T_R}{T_S} \right)$$

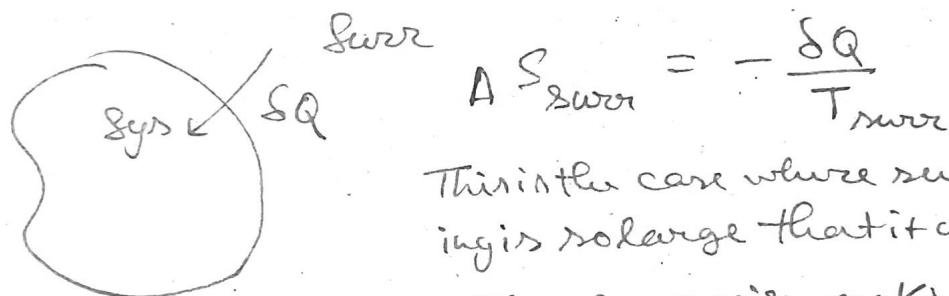
$$\Delta S_{\text{reservoir}} = \int \frac{dQ}{T_R} = \frac{\Delta Q}{T_R} = \frac{C(T_S - T_R)}{T_R}$$

Now, we add these,

$$\Delta S_{\text{universe}} = \Delta S_{\text{reservoir}} + \Delta S_{\text{system}} \rightarrow ?$$

We will find that it is +ve.

o Principle of entropy increase →



This is the case where surroundings is so large that it acts like a reservoir, making this true.

$$\Delta S_{\text{sys}} \geq \frac{\delta Q}{T_{\text{sys}}} \rightarrow \text{Ansatz eing.}$$

$$\therefore \Delta S_{\text{univ}} = \Delta S_{\text{sys}} + \Delta S_{\text{sur}}$$

$$\geq \frac{\delta Q}{T_{\text{sys}}} - \frac{\delta Q}{T_{\text{sur}}}$$

$$= \delta Q \left( \frac{1}{T_{\text{sys}}} - \frac{1}{T_{\text{sur}}} \right) \geq 0$$

as  $T_{\text{sur}} > T_{\text{sys}}$

## Internal Energy for Ideal and Van der Waals gas →

④ We have used thus far the fact that  $\left(\frac{\partial U}{\partial V}\right)_T = 0$  for ideal gas as experimental fact. Now we derive it.

$$dQ = \left(\frac{\partial U}{\partial T}\right)_V dT + \left[P + \left(\frac{\partial U}{\partial V}\right)_T\right] dV$$

(1st law of thermodynamics)

$$\Rightarrow \frac{dQ}{T} = dS = \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V dT + \left[\frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T}\right] dV$$

(2nd law added) → State function.

RHS must be exact differential.

•  $M(x, y) dx + N(x, y) dy$  is exact if  $\frac{\partial M}{\partial y}|_x = \frac{\partial N}{\partial x}|_y$

$$\left[\frac{\partial}{\partial V} \left\{ \frac{1}{T} \left(\frac{\partial U}{\partial T}\right)_V \right\}\right]_T = \left[ \frac{\partial}{\partial T} \left\{ \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} \right\} \right]_V$$

Then  $dS$  is an exact differential.

$$\Rightarrow \frac{1}{T} \frac{\partial^2 U}{\partial T \partial V} = \frac{1}{T} \frac{\partial^2 U}{\partial V \partial T} - \frac{1}{T^2} \left(\frac{\partial U}{\partial V}\right)_T + \left[\frac{\partial}{\partial T} \left(\frac{P}{T}\right)\right]_V$$

Cancel

$$\Rightarrow \left(\frac{\partial U}{\partial V}\right)_T = T^2 \left[\frac{\partial}{\partial T} \left(\frac{P}{T}\right)\right]_V$$

$$= T \left(\frac{\partial P}{\partial T}\right)_V - P$$

$$\Rightarrow \boxed{\frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} = \left(\frac{\partial P}{\partial T}\right)_V}$$

IMP  $\begin{matrix} * \\ \equiv \end{matrix}$  (No assumption of system)

Take entropy expression,  $\left(\frac{\partial S}{\partial V}\right)_T = 0 + \left(\frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T}\right)$

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

One of Maxwell's equations.

o Idealgas  $\rightarrow$

$$P = \frac{nRT}{V} \Rightarrow \left(\frac{\partial P}{\partial T}\right)_V = \frac{nR}{V}$$

$$\therefore \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} = \frac{nR}{V}$$

$$\Rightarrow \frac{1}{T} \left(\frac{\partial U}{\partial V}\right)_T + \frac{P}{T} = \frac{P}{T} \quad (\text{for IG})$$

$\Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T = 0}$

Idealgas internal energy does not depend on volume.

$$\Rightarrow U = f(T) = \frac{3}{2} nRT \xrightarrow{\substack{\text{Thermodynamics} \\ \text{cannot tell} \\ \text{you - } kT^2 \text{ does.}}}$$

o van der Waals gas  $\rightarrow$

□ Do calculation yourself.

$$\Rightarrow \boxed{\left(\frac{\partial U}{\partial V}\right)_T = \frac{n^2 a}{V^2}}$$

Integrating,

$$U = g(T) - \frac{n^2 a}{V}$$

$\downarrow$   
Thermodynamics  
cannot calculate this

$$du = dQ + dw$$

$$\Rightarrow dQ = du - dw$$

→ Reversible geostatic (hydrostatic) pressure

$$d\omega = -pdV$$

Now,

$$\delta Q_{\text{rev}} = T \delta S \Rightarrow \delta S = \frac{1}{T} \delta Q_{\text{rev}}$$

Read

lead about this that makes it Q-ray exact differential.

( side comment -  
exam ques )

$$\therefore TdS = dU + pdV$$

We may think this only for reversible processes. — but that is  
not the case.

$$TdS = dU + PdV$$

↓                      ↓                      →  
 Exact (state)          Exact (state)          Exact (state)

If we change,  $(S_1, U_1, V_1) \rightarrow (S_2, U_2, V_2)$ , it does not depend on the process/path, as this is a change in state variables only.

$\Rightarrow$  This expression is true in general.

\* Note that  $d\text{w} = -pdV$  can be done when we have assumed quasi-static process.

$$TdS = C_V dT + \nu dP$$

Ideal gas.

$$\Rightarrow TdS = C_P dT - \nu dP$$

$$\text{Now, } PV = RT \Rightarrow \nu dP + \nu dV = R dT$$

$$\therefore TdS = (C_P \nu dP + C_V \nu dV) \frac{1}{R}$$

\* We can use these formulae to calculate change in entropy.

Always pick the path along which integration is the easiest.

$$\therefore S_2 - S_1 = C_P \ln\left(\frac{V_2}{V_1}\right) + C_V \ln\left(\frac{P_2}{P_1}\right)$$

$$(P_1, V_1) \rightarrow (P_2, V_2)$$

$$\Rightarrow S_2 - S_1 = C_V \ln\left(\frac{P_2}{P_1}\right) + \gamma C_V \ln\left(\frac{V_2}{V_1}\right)$$

$$= C_V \ln\left(\frac{P_2 V_2^\gamma}{P_1 V_1^\gamma}\right)$$

Entropy change for Van der Waals gas  $\rightarrow$

$$S_2 - S_1 = \int \frac{dT}{T} Q + \underbrace{\frac{1}{T} \left( P + \left( \frac{\partial U}{\partial V} \right)_T \right) dV}_{\text{probably wrong}}$$

$$\Rightarrow U = U_0 + \nu T - \nu^2 \frac{a}{V^2}$$

↓  
Cannot be derived  
in thermodynamics.

$$\Rightarrow \left( \frac{\partial u}{\partial v} \right)_T = \frac{n^2 a}{v^2}$$

$$P + \left( \frac{\partial u}{\partial v} \right)_T = \frac{nRT}{v-nb} - \frac{n^2 a}{v^2} + \frac{n^2 a}{v^2}$$

$$= \frac{nRT}{v-nb}$$

$$\frac{dQ}{T} = C_V \frac{dT}{T} + \frac{nR\gamma}{(v-nb)^{\gamma}} dv$$

$$\Rightarrow \frac{dQ}{T} = C_V \frac{dT}{T} + \frac{nR}{(v-nb)} dv$$

$$\therefore S_2 - S_1 = \int \frac{dQ}{T}$$

$$= C_V \ln \left( \frac{T_2}{T_1} \right) + R \ln \left( \frac{v_2 - nb}{v_1 - nb} \right)$$

On the ~~not~~ change,  $(T_1, v_1) \rightarrow (T_2, v_2)$

$$\text{In isothermal: } S_2 - S_1 = R \ln \left( \frac{v_2 - b}{v_1 - b} \right)$$

\* You can also calculate this by calculating total heat exchanged and dividing that by T.

HW: Calculate dW, calculate du,

calculate dQ.

$$\therefore dQ = TdS$$

$$\Rightarrow C_p = T \left( \frac{\partial S}{\partial T} \right)_p$$

$$\Rightarrow C_v = T \left( \frac{\partial S}{\partial T} \right)_v$$

Now,

$$S = S(V, T)$$

$$\Rightarrow dS = \left( \frac{\partial S}{\partial V} \right)_T dV + \left( \frac{\partial S}{\partial T} \right)_V dT$$

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

$$\Rightarrow C_p - C_v = T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P$$

Now using maxwell equation,

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

$$\Rightarrow C_p - C_v = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P$$

True in general

Ideal gas,  $PV = nRT$

$$\Rightarrow C_p - C_v = \frac{nR}{V} \cdot \frac{nR}{P} T \\ = nR$$

\* In older derivation, we had to assume  $U$  is not a function of  $V$ . — so 2nd law input required.

$$\therefore dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\therefore \left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

Using maxwell eqn again

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

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P}$$

*using that - 1 pd formulae*

*another one of Maxwell's equations.*

$$\therefore dS = \left(\frac{\partial S}{\partial T}\right)_V dT + \left(\frac{\partial S}{\partial V}\right)_T dV$$

$$\therefore \left(\frac{\partial S}{\partial P}\right)_T = \left(\frac{\partial S}{\partial V}\right)_T \left(\frac{\partial V}{\partial P}\right)_T$$

Using Maxwell eqn again

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

$$\Rightarrow \boxed{\left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P}$$

Using that - 1 PD formulae

another one of Maxwell's equations.

29<sup>th</sup> Feb 2024

Energy dimensions  $\rightarrow U - PV + TS \rightarrow$  Infinite possibilities of constructing these.

But there are only specific constructions that are useful.

$$\rightarrow \text{Enthalpy} = H = U + PV$$

$$\rightarrow \text{Helmholtz free energy} = A(\text{chem}) = F = U - TS$$

$$\rightarrow \text{Gibbs free energy} = G = H - TS$$

$$\rightarrow \text{Internal energy} = U$$

These are combinations of 8 total variables (out of inf possible)

Then why these 4?

- First law: Energy conservation.
  - Second law: Entropy increases for natural processes
- Question: Will the processes in which entropy increases, necessarily happen?

The ~~ans~~ answer to this is dictated by thermodynamic potentials like  $H, F, G$ .

$\Rightarrow$  Thermodynamic potentials minimized at eq.

Which one of the potentials is relevant? It depends on the processes that we study.

Thus these determine if the processes can happen or not.

$$0 \quad dU = TdS - pdV$$

$$\Rightarrow U = U(S, V)$$

$$\therefore dU = \left(\frac{\partial U}{\partial S}\right)_V dS + \left(\frac{\partial U}{\partial V}\right)_S dV$$

$$\Rightarrow T = \left(\frac{\partial U}{\partial S}\right)_V, \quad P = -\left(\frac{\partial U}{\partial V}\right)_S$$

$$\Rightarrow \boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V} \quad \text{RHS becomes equal.}$$

One of Maxwell's relations

Now,

$$\frac{\partial}{\partial T} = -\left(\frac{\partial S}{\partial V}\right)_U \quad \text{using}$$

$$\left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x \left(\frac{\partial z}{\partial x}\right)_y = -1$$

Isochoric process:  $dU = TdS = \delta Q$

$$C_V = \left(\frac{\delta Q}{\delta T}\right)_V = \left(\frac{\delta U}{\delta T}\right)_V = T \left(\frac{\delta S}{\delta T}\right)_V$$

o Enthalpy:  $H = U + PV$

$$dH = dU + PdV + VdP$$

$$\Rightarrow dH = TdS - PdV + PdV + VdP$$

$$\Rightarrow \boxed{dH = TdS + VdP}$$

$$\Rightarrow H = H(S, P)$$

$$\therefore dH = \left(\frac{\partial H}{\partial S}\right)_P dS + \left(\frac{\partial H}{\partial P}\right)_S dP$$

Comparing,

$$T = \left(\frac{\partial H}{\partial S}\right)_P, \quad V = \left(\frac{\partial H}{\partial P}\right)_S$$

Using same method,

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P}$$

2nd Maxwell's relation

o Isobaric process: (most chem experiments)

$$dH = TdS = \delta Q = C_P dT$$

$$C_P = \left(\frac{\delta Q}{\delta T}\right)_P = \left(\frac{\delta H}{\delta T}\right)_P = T \left(\frac{\delta S}{\delta T}\right)_P$$

$$\Delta H = \int_{T_1}^{T_2} C_P dT$$

## Ostwald-Helmholtz free energy -

$$F = U - TS$$

$$\rightarrow dF = -SdT - pdV$$

$$F = F(T, V)$$

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

In Stat mech, we will derive expression for  $F$  for microscopic physios.

You get the third Maxwell relation from this, same method,

$$\boxed{\left(\frac{\partial p}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}$$

Consider a system going  $i \rightarrow f$ , s.t. system's temp is constant.

External condition (like ext press in Chem)

In practice, it is like it is in touch with a reservoir.

$$\int_i^f \frac{dQ}{T} \leq S_f - S_i$$

$$\Rightarrow \int_i^f dQ \leq T(S_f - S_i)$$

$$\Rightarrow \Delta Q \leq TS_f - TS_i$$

Q Question: work done by the system?

$$\Delta U = \Delta Q + \Delta W \xrightarrow{\text{Sign}}$$

$$\Delta U = \Delta Q - \mu \Delta V$$

$$\Rightarrow \Delta U + |\Delta W| \leq TS_f - TS_i$$

$$\Rightarrow U_f - U_i + |\Delta W| \leq TS_f - TS_i$$

$$\Rightarrow |\Delta W| \leq [U_i - TS_i] - [U_f - TS_f]$$

$$\Rightarrow |\Delta W| \leq F_i - F_f = -\Delta F$$

$\Delta W$  for isothermal process has upper limit  $\rightarrow$  decrease in Helmholtz free energy.

7th March 2024

Thermo dynamic systems find their equilibrium points at minimizations of thermodynamic potentials

(\*) The thermo dynamic potentials are related by Legendre transformations:

Using  $dU = TdS - pdV$  and each of the thermodynamic potentials, we can derive all of Maxwell's relations.

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

$$c_V \equiv \left(\frac{\partial Q}{\partial T}\right)_V = \left(\frac{\partial U}{\partial T}\right)_V = T \left(\frac{\partial S}{\partial T}\right)_V$$

$H = U + PV \rightarrow$  Thermo pots are func. of only stat variables.

$$\Rightarrow dH = TdS + Vdp$$

$$\left(\frac{\partial T}{\partial P}\right)_S = \left(\frac{\partial V}{\partial S}\right)_P$$

$$c_P \equiv \left(\frac{\partial Q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P = T \left(\frac{\partial S}{\partial T}\right)_P$$

$$F = U - TS \rightarrow \text{Helmholtz free energy.}$$

$$\Rightarrow dF = -SdT - pdV \quad (\text{A in chem})$$

$$\Rightarrow \left(\frac{\partial F}{\partial V}\right)_T = + \left(\frac{\partial P}{\partial T}\right)_{p,V} \quad \text{Arbeiter 'work'}$$

when  $dT=0$  (isothermal),  $dF = -pdV \rightarrow$  work done.

$$\Rightarrow \Delta F = - \int pdV$$

(Isothermal)

Used a lot in physics.

\* Calculation of internal states — important in Stat Mech. It is similar to how quantum mechanical states are fixed for fixed dimension.

$$G = H - TS \rightarrow \text{Gibbs free energy.}$$

$$\Rightarrow dG = -SdT + VdP$$

$$\Rightarrow \left(\frac{\partial S}{\partial P}\right)_T = - \left(\frac{\partial V}{\partial T}\right)_P$$

Good for isothermal and isobaric

Helmholtz free energy →

Consider work done by the system →

$$\Delta U = \Delta Q \rightarrow \Delta W$$

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

$$\text{Clausius} \rightarrow \int_i^f \frac{dQ}{T} \leq S_f - S_i$$

We take isothermal change from i to f.

$$\Delta Q = \int_i^f dQ \leq T(S_f - S_i)$$

$$\Rightarrow \Delta Q = \Delta U + \Delta W \leq T(S_f - S_i)$$

$$\Rightarrow U_f - U_i + \Delta W \leq T(S_f - S_i)$$

$$\Rightarrow \Delta W \leq [U_i - TS_i] - [U_f - TS_f]$$

$$\Rightarrow \boxed{\Delta W \leq -\Delta F}$$

Equality holds for reversible processes.

In the isothermal process, the work done by system can't be max change in Helmholtz free energy.

$\downarrow$   
(reduction)

$$U = (F) + (TS)$$

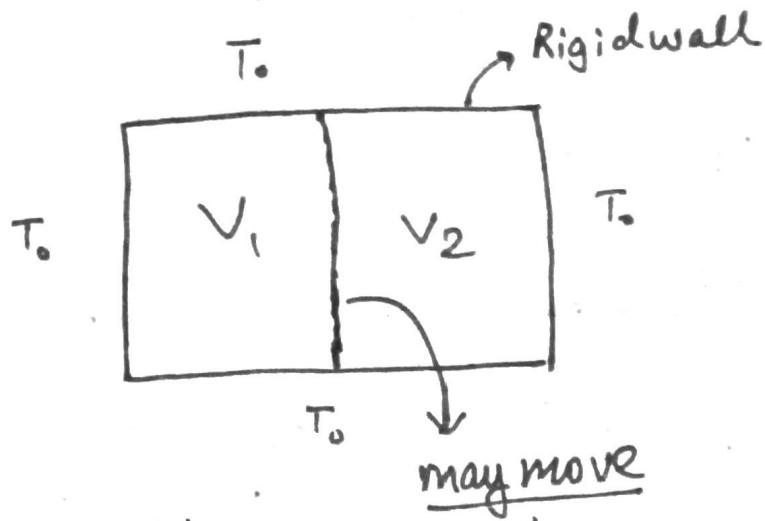
↓

accessible to      Not accessible  
U to do work      to do work  
                        ↓  
                        Under  
                        isothermal  
                        process.

Consider isothermal and isochoric process.

$$0 \leq -\Delta F \Rightarrow F_f \leq F_i$$

Why? Let us take an example.



$$V = V_1 + V_2$$

moves such the pressure on  
RHS and LHS are same.

How do we know this?

Using  $F_f \leq F_i$ , every step we take here (every movement of the wall),  $F$  is reduced so, like SHO   $\rightarrow F$  is minimized.

$$F = F_1(V, T) + F_2(V_2, T)$$

$$\Rightarrow \delta F = \left( \frac{\partial F_1}{\partial V_1} \right)_T \delta V_1 + \left( \frac{\partial F_2}{\partial V_2} \right)_T \delta V_2$$

$$V = V_1 + V_2 = \text{constant}$$

$$\Rightarrow \delta V_1 = -\delta V_2$$

$$\therefore \left[ \left( \frac{\partial F_1}{\partial V_1} \right)_T - \left( \frac{\partial F_2}{\partial V_2} \right)_T \right] \delta V_1 = \delta F = 0$$

minima  
(extremized)

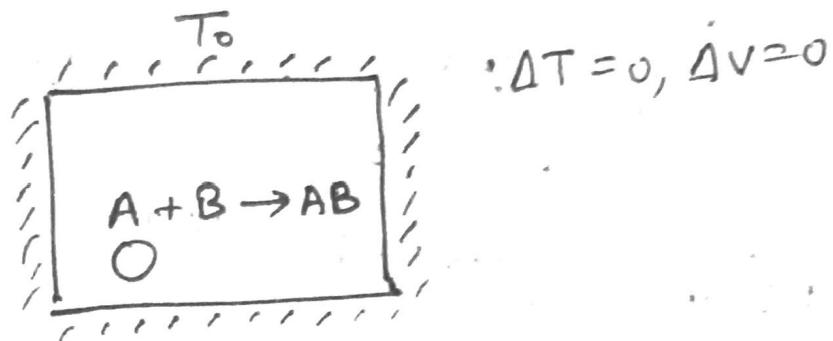
This can only hold if,

$$\left(\frac{\partial F_1}{\partial V_1}\right)_T = \left(\frac{\partial F_2}{\partial V_2}\right)_T \quad (\text{As } S_V \text{; arbitrary})$$

$$\Rightarrow P_1 = P_2 \quad (\text{Using Maxwell's relation})$$

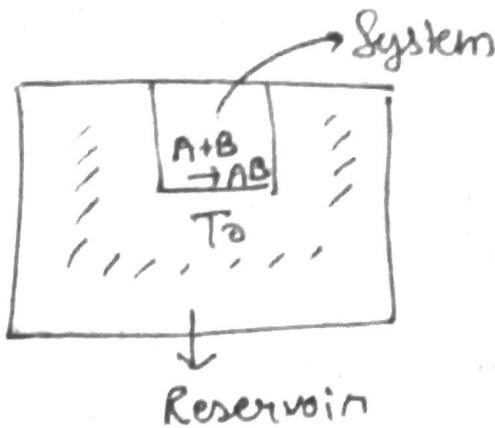
Therefore,  $F$  is minimized: (This argument says extremized, but we can show that it is minimized)  $\square$  How?

Similarly, if we take a chem reaction in isochoric + isothermal conditions,



Reaction will continue till  $F$  is minimized.

$$\delta G = -SdT + Vdp$$



$$\Delta T = 0, \Delta V = 0$$

Some reaction

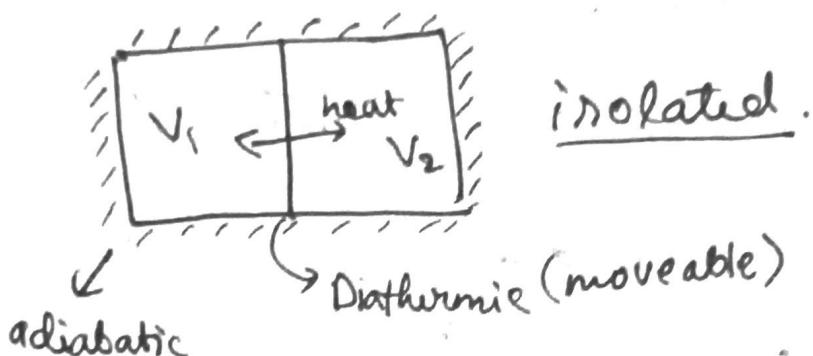
(chemical, ice melting  
etc)

inside system — that is,

where the heat energy is used.

Here  $F$  is minimized.

o Mechanical Equilibrium  $\rightarrow$



At equilibrium,  $S$  is maximum.

$\Rightarrow dS = 0$  at equilibrium.

Also,

$$U_1 + U_2 = U = \text{constant} \Rightarrow dU_1 = -dU_2$$

$$V_1 + V_2 = V = \text{constant} \Rightarrow dV_1 = -dV_2$$

$$\therefore dS = \left( \frac{\partial S_1}{\partial V_1} \right)_{U_1} dV_1 + \left( \frac{\partial S_1}{\partial U_1} \right)_{V_1} dU_1$$

$$+ \left( \frac{\partial S_2}{\partial V_2} \right)_{U_2} dV_2 + \left( \frac{\partial S_2}{\partial U_2} \right)_{V_2} dU_2$$

$$\Rightarrow dS = \left[ \left( \frac{\partial S_1}{\partial V_1} \right)_{U_1} - \left( \frac{\partial S_2}{\partial V_2} \right)_{U_2} \right] dV_1$$

$$+ \left[ \left( \frac{\partial S_1}{\partial u_1} \right)_{V_1} - \left( \frac{\partial S_2}{\partial u_2} \right)_{V_2} \right] du_1$$

$$\Rightarrow dS = du_1 \left( \frac{1}{T_1} - \frac{1}{T_2} \right) + \left( \frac{P_1}{T_1} - \frac{P_2}{T_2} \right) dV_1$$

$= 0$  As  $S$  is maximum.

$$\therefore \frac{1}{T_1} - \frac{1}{T_2} \Rightarrow \boxed{T_1 = T_2}$$

$$\frac{P_1}{T_1} - \frac{P_2}{T_2} \Rightarrow \boxed{P_1 = P_2} \rightarrow \begin{array}{l} \text{Conditions req} \\ \text{for system to be in} \\ \text{thermo dynamic} \\ \text{equilibrium.} \end{array}$$

□ Verify that second order change of  $S$  is  $-ve$  — i.e., it is a maximum.

## ○ Thermo dynamic relations with heat capacities:

$$S = S(T, V)$$

$$\Rightarrow dS = \left( \frac{\partial S}{\partial T} \right)_V dT + \left( \frac{\partial S}{\partial V} \right)_T dV$$

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

~~$c_p$~~

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

$$\Rightarrow c_P - c_V = T \left( \frac{\partial S}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \xrightarrow{\text{Maxwell}} \underbrace{\left( \frac{\partial V}{\partial T} \right)_P \left( \frac{\partial P}{\partial T} \right)_V}_{\text{Easily measurable quantities.}}$$

(observables)

Using any equation of state we may derive  $C_p - C_v$  using this.

Using the three derivative multiplied = -1 formula,

$$C_p - C_v = -T \left( \frac{\partial V}{\partial P} \right)_T \left( \frac{\partial P}{\partial T} \right)_V \quad \{$$

$$C_p - C_v = -T \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P \quad \}$$

for normal materials,  $\left( \frac{\partial P}{\partial V} \right) = -ve$

$$C_p > C_v \quad \text{usually.}$$

Now,

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

$$\Rightarrow \frac{\partial}{\partial T} \left[ \left( \frac{\partial S}{\partial V} \right)_T \right] = \left( \frac{\partial^2 P}{\partial T^2} \right)_V$$

$$\Rightarrow \frac{\partial}{\partial V} \left[ \left( \frac{\partial S}{\partial T} \right)_V \right] = \left( \frac{\partial^2 P}{\partial T^2} \right)_V$$

$$\Rightarrow \boxed{\left( \frac{\partial C_V}{\partial V} \right)_T = T \left( \frac{\partial^2 P}{\partial T^2} \right)_V}$$

These are general and can be used with any eqn of state.

$$\left( \frac{\partial C_p}{\partial P} \right)_T = -T \left( \frac{\partial^2 V}{\partial T^2} \right)_P$$

Same method  
of derivation.

0 TdS equations →

$$S = S(T, V)$$

$$\Rightarrow TdS = T \left( \frac{\partial S}{\partial T} \right)_V dT + T \left( \frac{\partial S}{\partial V} \right)_T dV$$

$$\Rightarrow TdS = C_V dT + T \left( \frac{\partial P}{\partial T} \right)_V dV$$

$$\Rightarrow TdS = C_V dT - T \left( \frac{\partial P}{\partial V} \right)_T \left( \frac{\partial V}{\partial T} \right)_P dV$$

$$\Rightarrow TdS = C_V dT + T \alpha E_T dV$$

$$\alpha = \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P \text{ Vol exp. coefficient.}$$

$$E_T = -V \left( \frac{\partial P}{\partial V} \right)_T \text{ isothermal elasticity.}$$

1st TdS equation

(There are 2 other)

2nd TdS equation:

$$TdS = C_p dT - TV ddp$$

3rd TdS equation:

$$TdS = C_V \left( \frac{\partial T}{\partial P} \right)_V dp + C_P \left( \frac{\partial T}{\partial V} \right)_P dV$$

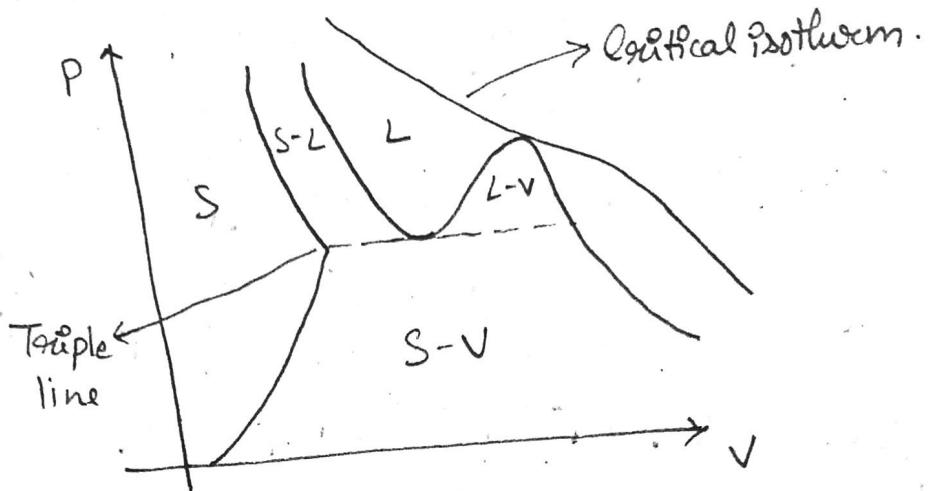
2 1/2 weeks of no classes.

Next tutorial will have 2 problems.

12<sup>th</sup> March 2024

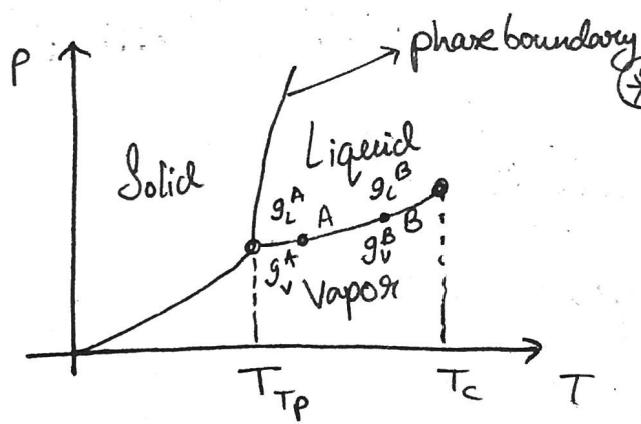
Let us imagine a hydrostatic system described by  $(P, V, T)$ . It describes a 3D surface with the constraint of the equation of state — ~~so~~ but this constraint depends on the phase of the system.

Plot →



In physics we see  $P \text{ vs. } T$  graphs.

Corresponding  $P-T$  diagram,



\* Here, the nice thing is that each phase has a separate area, unlike the previous one.

Note: These are for standard liquid — not water.

Goal of condensed matter — predict phase plot from underlying physics..

There is some sort of interplay b/w thermal energy and some other energy at phase boundaries.

What does a curve on the P-T diagram mean?

At every point on the curve, two phases coexist at that temp and pressure. at equilibrium.

Constant ~~volume~~<sup>pressure</sup> and Constant temperature →

$$\delta Q = -SdT + Vdp$$

Gibbs free energy is minimized.

$$G = m_L g_L + m_V g_V \rightarrow \text{Free energy per unit mass.}$$

$\downarrow$        $\downarrow$   
Mass of liq    Mass of vapor

$$M = \cancel{m_L} + m_V = \text{constant.}$$

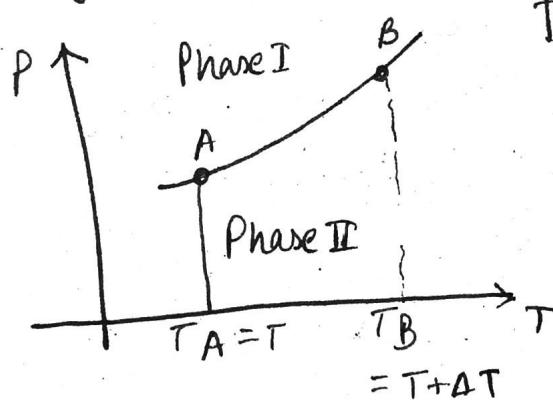
$$\rightarrow \delta G = d(m_L) g_L + d(m_V) g_V = 0$$

Using this,

$$g_L = g_V$$

All points on the curve are eq points, but the lines are where two phases coexist.

Take a P-T diagram,



for equilibrium,

$$g_1^A = g_2^A$$

and,

$$g_1^B = g_2^B$$

$$\Rightarrow g_1^B - g_1^A = g_2^B - g_2^A$$

as  $Q = (P, T, m_1, m_V)$  and  $g = g(P, T)$ ,

this is not just  $\partial = 0$ , i.e.,  $g_1^A \neq g_1^B$

$$\Rightarrow dg_1 = dg_2$$

$$\Rightarrow \left( \frac{\partial g_1}{\partial P} \right)_T dP + \left( \frac{\partial g_1}{\partial T} \right)_P dT = dg_1$$

$$\Rightarrow v_1 dP - s_1 dT = dg_1 \quad (\text{Maxwell})$$

Similarly,

$$dg_2 = v_2 dP - s_2 dT$$

$$\Rightarrow v_1 dP - s_1 dT = v_2 dP - s_2 dT$$

$$\Rightarrow \frac{dP}{dT} = \frac{s_2 - s_1}{v_2 - v_1} = \frac{\frac{\Delta S}{\Delta N}}{\frac{\Delta Q}{T \Delta V}} = \frac{\Delta Q}{T \Delta V} \quad \begin{matrix} \text{infinitesimal change despite} \\ \text{being } \Delta \end{matrix}$$

$$\Rightarrow \boxed{\frac{dP}{dT} = \frac{\Delta Q}{T(\Delta V)}} \quad \text{Clausius - Clapeyron equation.}$$

Slope of P-T graph

Change in  
specific vol going  
from one phase  
to another.

Depending on this,  
slope may be +ve  
or -ve

$$T \left( \frac{\partial S}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V \quad (\text{Maxwell eqn}).$$

$$\Rightarrow \left( \frac{\partial Q}{\partial V} \right)_T = T \left( \frac{\partial P}{\partial T} \right)_V$$

During evaporation,

$$\delta Q = L dm$$

↳ Latent heat for evaporation.

$$dV = (v_{\text{vap}} - v_{\text{liq}}) dm$$

→ Specific volumes.

$$\therefore \frac{\delta Q}{dV} = \frac{L}{v_{\text{vap}} - v_{\text{liq}}} = T \frac{\partial P}{\partial T}$$

Something about Gibbs F.E change being discontinuous at phase change.