1st Jan 2024

- No more KTG — starting thermodynamics from Chem thermodynamics.
- Linking thermodynamics to statistical mechanics.
- Problem in every tutorial - from HW, just one.

MarKo distribution to be discussed further later.

- HW planned to be ~~out~~ every week. → to be submitted. (No grading)

○ Ideal Gas:

$$pV = nRT$$ → Derived empirically from exp (Charles', Boyle's, etc) → Experimental / Empirical equation.

○ $U = \frac{3}{2} nRT$ → KTG

○ $dU = \underbrace{TdS}_{dq} - PdV + \mu dN$ → Not seen (forget about it now) before

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

Compare

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

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

Not considering μ

$$\boxed{T \equiv \left.\frac{\partial U}{\partial S}\right|_{V,N}} \quad \boxed{p = -\left.\frac{\partial U}{\partial V}\right|_{S,N}}$$

What if we consider μdN?

μdN → Energy taken out or given by taking out or putting in molecules.

$\Rightarrow \mu$ = Chemical potential.

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

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

Once we know this, we can find T, P and μ just by taking derivatives

Why these? These are measurable quantities.

We will use the first 2 equations to do this.

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

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

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

$$\Rightarrow \ln U = \frac{2}{3} \frac{S}{NR} + f(V,N) \quad \text{(Integrating)} \qquad \text{— (I)}$$

$f(V,N)$: Const of integration.

Now, $PV = nRT$

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

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

$$\Rightarrow \frac{\partial}{\partial V}(\ln U)_{S,N} = \frac{1}{U}\left(\frac{\partial U}{\partial V}\right)_{S,N} \qquad \text{— (II)}$$

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

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

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

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

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

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

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

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

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

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

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

We are going to push dependence of N → There is new stuff there.

But physical input has been exhausted — both equations have been inputted.

Let us increase entropy of system λ times

and the same,

$$\left.\begin{array}{l} S \to \lambda S \\ V \to \lambda V \\ N \to \lambda N \end{array}\right\} \therefore U \to \lambda U \text{ (Expected)}$$

→ Extensivity

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

Using then

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

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

This needs to be λU

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

$\Rightarrow$ True if $\boxed{g(\lambda N) = \lambda^{5/3} g(N)}$

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

Fundamental relation of thermodynamics.

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

Found - goal. (2 empirical eqns, extensitivity)

Find : T, P, μ from this.

Question → Can this be derived from microscopic considerations, without empirical relations?

What if $pv = nRT$ does not ~~hold~~ 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

$F(x, y, z) \rightarrow$ Broadly, a field

In this case, it is a scalar field.

$\vec{E}(\vec{x}, \vec{y}, \vec{z}) \rightarrow$ vector field

(Certain transformation rules).

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

or notationally as, F_x, $\left(\frac{dF}{dx}\right)_{y,z}$

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,

$F(x(t), y(t))$ → Some other variable.

As $t \rightarrow t + \Delta t$, $x \rightarrow x + \Delta x$, $y \rightarrow y + \Delta y$

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,

All indep of each other.

Constant.

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

This is a relation, they can not be independent.

$\Rightarrow$ This cannot be

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.

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

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

$$= 0$$

$\Rightarrow \frac{\partial F}{\partial u_n} = 0 \quad \Rightarrow \boxed{dF = 0}$ 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 $y = \text{const} \Rightarrow dy = 0$

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

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.

4th January 2024

Last class we derived -

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

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

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

(*) 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, μ.

○ Thermodynamics → Physics that cares about Macroscopic variables

To know a system completely - we need to know all 4×10^{23} ish molecules, initial states, etc.

⇒ Thermodynamics resolves 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 >> atomic timescale.

Also,

lengthscale >> 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 → 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' states.

⇒ Conserved quantities ⇒ Due to some <u>symmetries</u> 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 coupled to each other with spring-like connections — any arbitrary motion of these can be expressed as a combination of these 3 waves → 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.

9th January 2024

⊛ Coarse ~~op~~ observation of a microscopic variables leads to macroscopic variables.

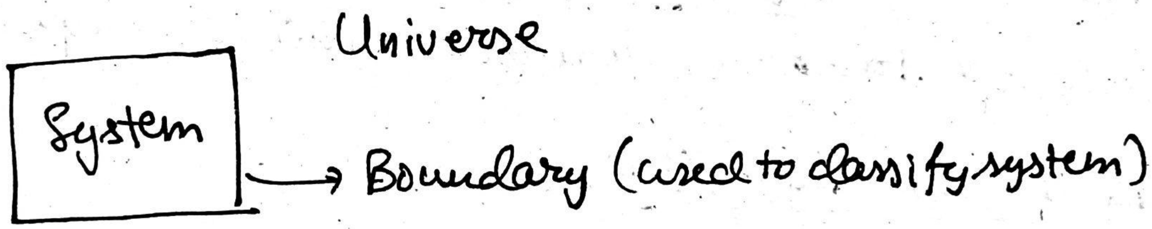
Last mode in last day's note is like a volume expansion (So?)

In his notation → Coarse graining = Observation with a least count greater than smaller modes of a system.

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

Δ Thermodynamic system —

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



Δ <u>Isolated system</u> – No exchange of matter or energy.

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

Δ <u>Open system</u> – exchange of matter and energy.

Δ <u>Closed system</u> – 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 State of a system: Macroscopic variables describe this.
↳ Equilibrium values.

(*) Always only described at equilibrium
↳ Something that is not changing with time.

Regardless of what happens in a process, thermodynamic variables are still related by thermodynamic relations.

Δ Mechanical Equilibrium –
Dictated by NLM,
$\vec{F}_N = 0$, $\vec{\tau}_N = 0$

Δ Chemical Equilibrium –
No spontaneous change in chemical composition.

Δ Thermal Equilibrium →

$\boxed{A}$ → 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)

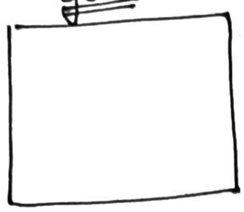
Then $\exists$ $f(x, y, z) = 0$

Equation of state → Empirical relation

⊛ Claim → (Later) the equations that relate these can be derived from microscopic physics.

o Thermal equilibrium and temperature →

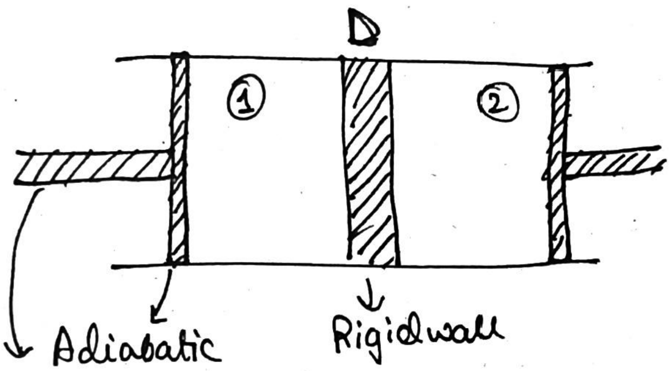
gas



→ $(P, V, m,$ composition$)$ is known

p and V can change independently

Self Note : n variables, p constraints ⇒ $n-p$ indep variables.



o D is adiabatic, ⇒ ① and ② can coexist for any (P_1, V_1) and (P_2, V_2)

o D is ~~diather~~ diathermic ⇒ (P_1, V_1) and (P_2, V_2) are not independent

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

Δ 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..

⊛ Class tests to be graded out of 10, HW out of 5.

11th 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 prev example, this means $\exists F(P_1, V_1, P_2, V_2) = 0$

↳ Holds for more complex systems

$\square$ Zeroth Law of Thermodynamics →

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)

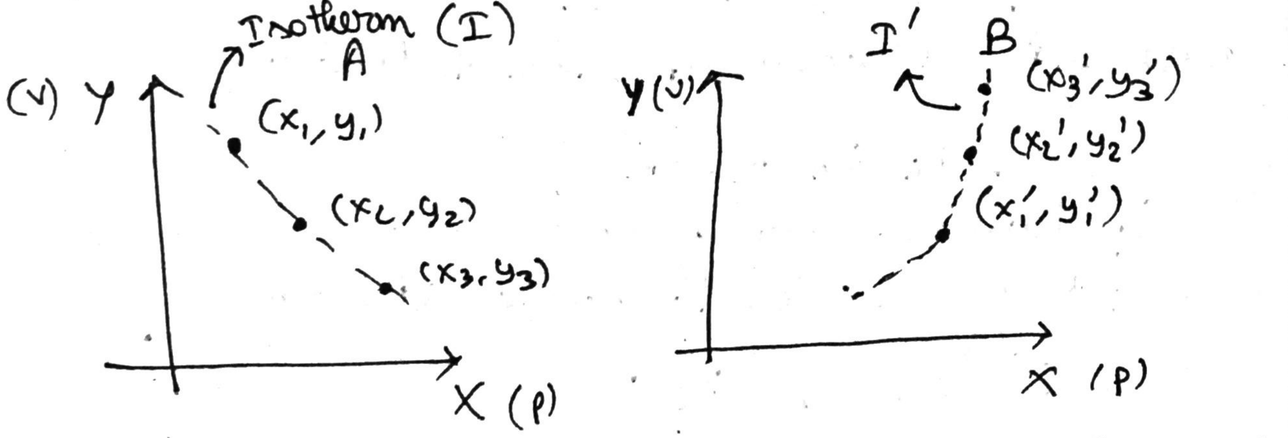
⇒ 'Suggests' that there must be a physical quantity that is same for two systems in thermal equilibrium. We are going to call this quantity 'temperature'

⊛ 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, $P_1V_1 = P_2V_2$

$\Rightarrow$ P_2V_2 held const, there are infinitely many pairs (P_1, V_1) s.t $P_1V_1 = P_2V_2$

We ~~again~~ again move $(x_2, y_2) \to (x_3, y_3)$ s.t (x_3, y_3) is in therm 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 therm 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'
$\Rightarrow$ Temperature

o A and B are two systems, there will be a function,

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

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 ~~was~~ must be,

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

Try to show that,

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

□ Heat $\rightarrow$

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

Later we accepted that this was a form of energy.

o Internal Energy : K.E + P.E $\rightarrow$ Binding, etc.

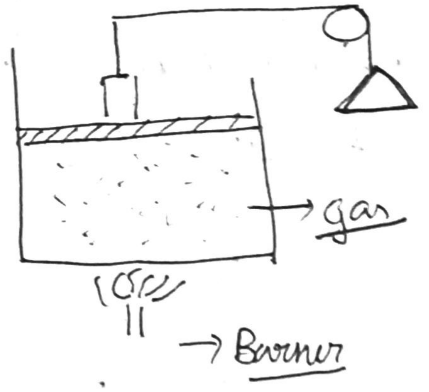
In non relativistic systems, we subtract rest energies. (mc^2)

(*) In context of thermodynamics, KE is calculated in rest frame of system.

So Internal Energy is not relativistic energy.

(*) ~~Aso~~ Also it is not related to overall motion.

16th January 2024



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

$$\underbrace{\Delta U}_{\text{Change in internal energy}} = \underbrace{\Delta Q}_{\text{Heat supplied to system}} + \Delta W$$ → Work done on/by system

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

→ $\Delta W \equiv +ve$ 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 raising piston, etc.

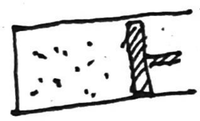
→ The same amount ΔU can be done by different combinations of ΔQ and ΔW.

Like, Money = Cash + Cheque

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

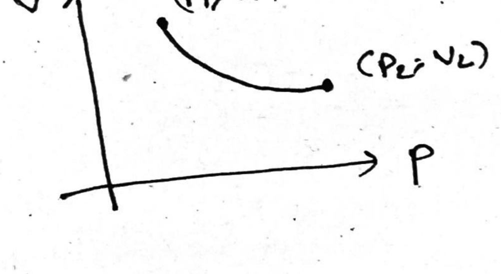
⇒ It does not matter how you reached a state (path independent)

On the other hand, ΔW is path dependant.



$$\Delta W = P\Delta V \quad (\text{from } F \cdot ds = dW)$$

In this system,

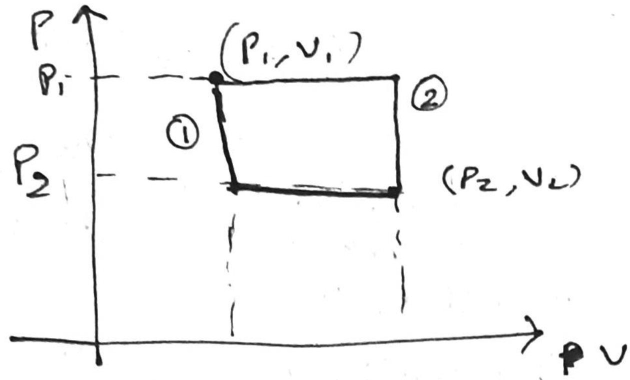


There are many paths from (P_1, V_1) to (P_2, V_2)

We imagine path 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.

(*) Note that this always has an attached <u>timescale</u>.



ΔW for this case,

$\Delta W_1 = P_2(V_2 - V_1)$

$\Delta W_2 = P_1(V_2 - V_1)$

So, $\Delta W_1 \neq \Delta W_2$

$\rightarrow$ ΔW is path dependent.

ΔQ will also change, but it will change such that ΔU remains the same.

<u>First law</u> $\rightarrow$ $dU = dQ + dW$

$\Rightarrow dU = dQ - pdV$

$\Rightarrow dQ = dU + pdV$

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,

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

(*) Isochoric process — V remains <u>constant</u>.

We define some quantity

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

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,

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

Heat capacity at constant pressure

(*) Note these are not related ~~to~~ to Idealgas systems.

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

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

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

$$PV = RT$$

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

Also,

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

Why? Since there are no interactions b/w particles of idealgas. If we bring them closer (dV), no PE changes occur. If $dT = 0$, KE is const ⇒ du is not changing.

Note that this depends on the molecular picture.

⇒ 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,

$$\boxed{C_p - C_v = R}$$

<u>Mayer's Relation</u>

☐ How do you compute this for Van der Waals gas?
(Home reading)

<u>Tutorial Begins</u>

$$dQ = du + pdv$$

$$= \left(\frac{\partial u}{\partial T}\right)_v dT + \left(\frac{\partial u}{\partial v}\right)_T dv + pdv$$

Now let us look at what happens for ideal gas.

$$dQ = C_v dT + pdV$$

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

○ <u>Adiabatic transformation of ideal gas</u> →

$$pV = RT \qquad \longrightarrow C_p - C_v$$

$$\Rightarrow pdv + vdp = RdT$$

$$\Rightarrow pdv + vdp = (C_p - C_v)dT$$

$$\Rightarrow C_v\, dT + pdv = C_p\, dT - vdp$$

LHS

As process is adiabatic; $dQ = 0$

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

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

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

and $\boxed{pdv = -C_v dT}$

Combining,

$$\frac{dp}{p} = -\frac{C_p}{C_v}\frac{dv}{V}$$

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

where $\gamma \equiv \frac{C_p}{C_v}$

$\Rightarrow \boxed{pV^{\gamma} = \text{constant}}$ for ideal adiabatic change

<u>Quasistic processes for ideal gas</u> $\rightarrow$ (Generalization)

- $\boxed{pV^{n} = \text{constant}}$

<u>Case I</u> : $n = 0$, $p = \text{constant}$ (isobaric)

<u>Case II</u> : $n = 1$, $pV = \text{constant}$ (isothermal)

<u>Case III</u> : $n = \gamma$, $\gamma = \frac{C_p}{C_v}$, $pV^{\gamma} = \text{const}$ (adiabatic)

for <u>diff value of n</u>, <u>diff processes</u>.

<u>Case IV</u> : $n \rightarrow \infty$, effect of p is negligible (isochoric)

for an ideal gas,

$$dQ = C_v dT + pdv$$

So, $\Delta Q = \int_1^2 C_v \, dT + \int_i^f p dv$

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,

$C_v = \text{constant}$? ☐ Think

Normally, we take response functions to be <u>constant</u>.

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

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

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

$= 0$ (isotherm) Substituting A

for $n \neq 1$, we get

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

- [ ] Try integrating
- [ ] Take limits of $n=0$, $n \to \infty$, $n=\gamma$ for the expression of ΔQ 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 ΔW and ΔQ for diff paths, and check that ΔU 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 $đQ$ and $đW$
for not state func

Exact differential Inexact differential.

Example : System described by (x, y)
and $df = y\,dx + x\,dy$
we want to calculate,

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

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

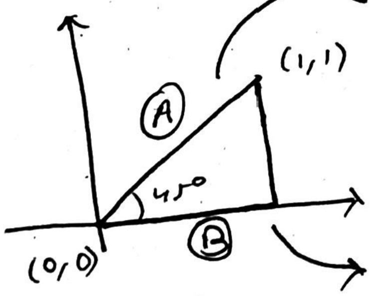
(*) Note that we do not need to care about the path taken in doing the integral.

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

(2) A quantity g s.t $dg = y\,dx$
We want to calculate,

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

Say the path,



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

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

⇒ 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 $d(f)$

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

By comparison,

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

Now, say,

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

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

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

So,

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

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

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

$$= \int_1^2 df$$

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

f only at end points.

☐ Use Stokes theorem for a closed loop to show,

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

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

Again, true in <u>general</u>.

This again shows that $đQ$ is inexact.

$$\Rightarrow \boxed{đQ = C_V dT + \left(p + \left(\frac{\partial U}{\partial V}\right)_T\right) dV} \quad \text{(Try to remember)}$$

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

In the special case of ideal gas,

$$\boxed{đQ = C_V dT + p\,dV}$$

We calculated $đQ$ for several processes,

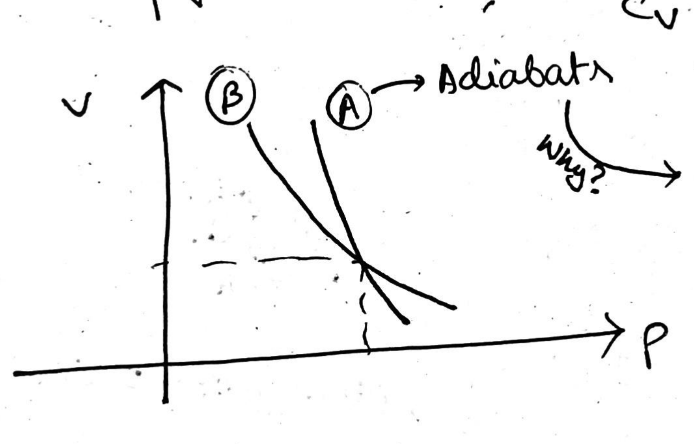
$đQ = 0$ for adiabatic process.

Isothermal,

$$pV = \text{constant}$$

Adiabatic,

$$pV^\gamma = \text{Const}, \quad \gamma = \frac{C_p}{C_V}$$



Isotherms,

$$p\,dV + V\,dp = 0$$

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

Adiabats,

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

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

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

⇒ Adiabats have <u>steeper slope</u> as compared to isotherms.

○ <u>Adiabatic lapse rate</u> →

⊛ <u>Air is bad thermal conductor</u>.

⊛ Thus, we can take approximation that expansion of air is <u>adiabatic</u>.

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

⊛ Ideal gas assumption.

So we ~~now~~ know that, $pV^{\gamma} = \text{const}$

Using ideal gas eqn,

$$\Rightarrow \cancel{p^{\gamma}} \; p^{1-\gamma} T^{\gamma} = \text{const}$$

Now taking differential (Standard Strategy)

$$\Rightarrow d\left(p^{1-\gamma} T^{\gamma}\right) = 0$$

$$\Rightarrow \frac{dp}{p} = \frac{\gamma}{\gamma - 1} \frac{dT}{T}$$

→ Easiest to take log before differentiation,

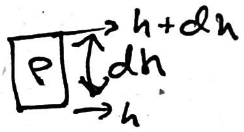
$$\ln\left(p^{1-\gamma} T^{\gamma}\right) = \ln(\text{const}) = \text{const}$$

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

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

$$\Rightarrow \frac{dp}{p} = \frac{\gamma}{\gamma-1}\frac{dT}{T}$$

Now, $dp = -\rho g\, dh$



$$\Rightarrow \frac{dp}{p} = -\frac{\rho g\, dh}{p}$$

Mass of air of 1 mol gas

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

There fore,

$$\frac{dP}{P} = -\frac{gM}{RT}\,dh$$

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

If we plugin the numbers, $\frac{dT}{dh} = 9.7°C\,/Km$

Observational $\rightarrow$ 7°C /Km.

We can apply this to many other systems.

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Observational → $7°C/Km$.

We can apply this to many other systems.

30th Jan 2024

○ 2nd Law of Thermodynamics →

When we throw a ball up, the ball comes down and has the same velocity but opp direction ⇒ It has the same K.E.
But it can have any direction ⇒ 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.

→ 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.

○ Engine :

System operating in cycles that converts heat to work.

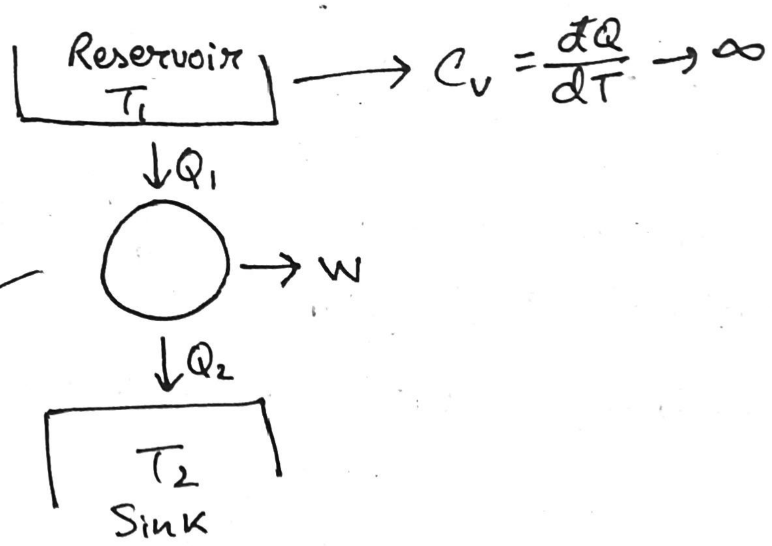
○ Heat Engine:

Q_1 → heat absorbed by system

Q_2 → 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 <u>on</u> surroundings.

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

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 ΔU increases due to it)

Note,

$$\boxed{\Delta W = -\int p\,dV}$$

as, $\Delta W = -p\Delta V$

$= -p(V_f - V_i)$

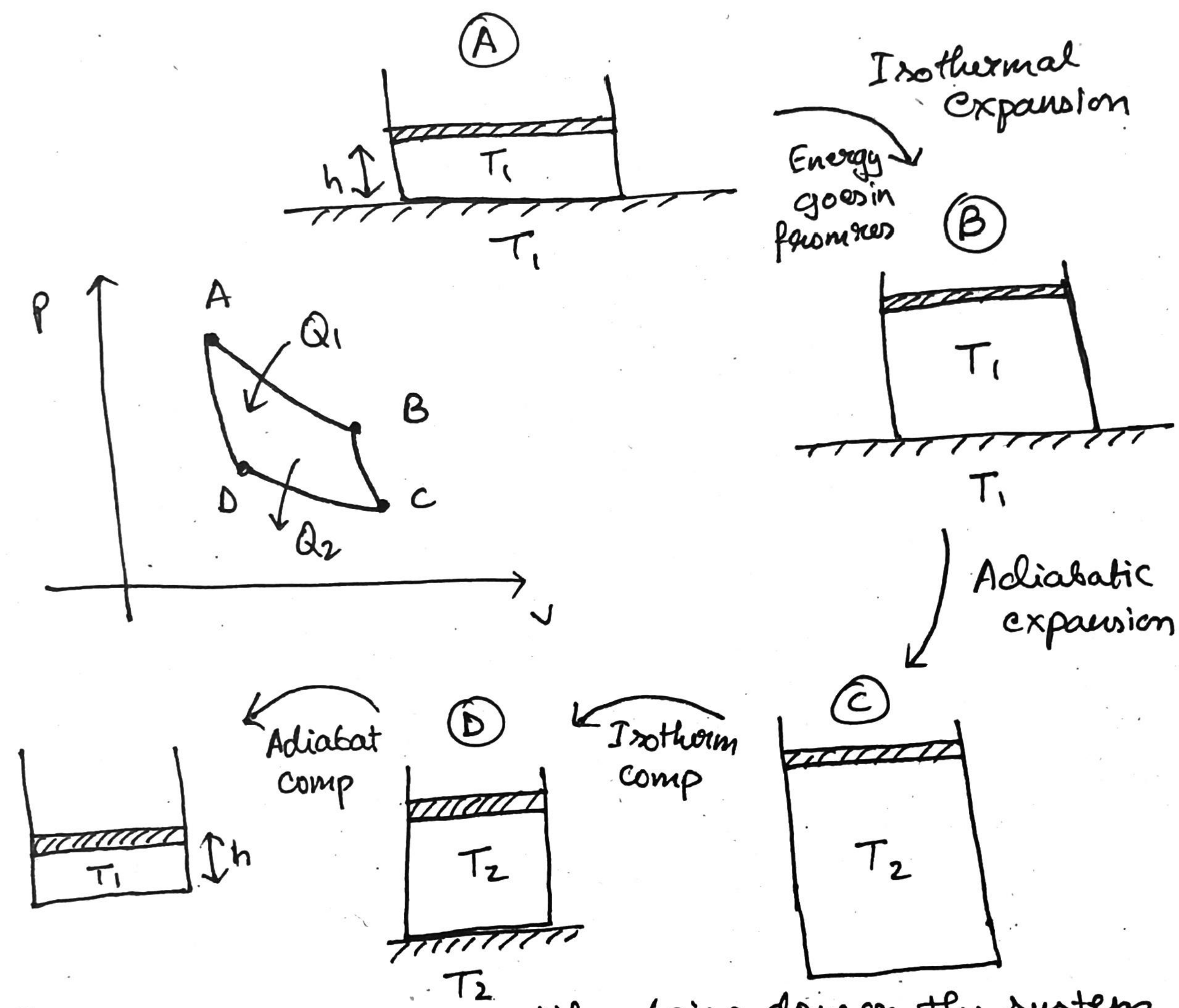
Consistent with the work convention. ← $-ve$ only if compressed, i.e work done on system.

* 2nd Law is also strictly empirical.

→ Source reservoir (T_1)

→ Sink reservoir (T_2)

* Consider ideal gas



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

$$W_{Total} = W_1 + W_2 + W_3 + W_4$$

$$Q = Q_1 - Q_2$$

We calculate these so that we can calculate η.

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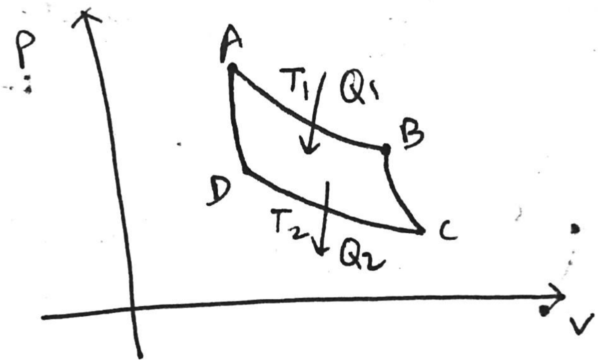
(*) If we are given two reservoirs, ~~and~~ with one being at a higher temp than the other, and we want to construct a reversible engine, it can only be done with two isotherms and two adiabats — this is the Carnot engine.

1st Feb 2024

o Heat engine:

→ Two reservoir $T_1 > T_2$
→ "Reversible" (meaning still not ~~mean~~ discussed)

Can only happen with two isotherms and two adiabats.



(*) All steps are quasistatic

(*) Note: we can also go $D \to C \to B \to A$, that is also a feature.

We begin with first law,

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

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

(*) ideal gas.

$\Rightarrow \Delta U = 0$

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

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

(2) $B \rightarrow C$: (Adiabat)

$\Delta Q = 0$

$\Rightarrow \Delta W = \Delta U$

$W_2 = -\int p\,dV$

We use $pV^{\gamma} = K$

$$\Rightarrow W_2 = -K\int \frac{dV}{V^{\gamma}} = -\frac{K}{-\gamma+1} V^{-\gamma+1}\Big|_{V_B}^{V_C}$$

$$= \frac{-K}{1-\gamma}\left(V_C^{1-\gamma} - V_B^{1-\gamma}\right)$$

$$= \frac{K}{\gamma-1}\left(\frac{V_C}{V_C^{\gamma}} - \frac{V_B}{V_B^{\gamma}}\right)$$

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

Now,

$$W_2 = \frac{K}{\gamma-1}\left(\frac{P_C V_C}{P_C V_C^{\gamma}} - \frac{P_B V_B}{P_B V_B^{\gamma}}\right)$$

$$= \frac{1}{\gamma-1}\left(P_C V_C - P_B V_B\right)$$

$$= \frac{nR}{\gamma-1}\left(T_C - T_B\right)$$

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

(3) $C \rightarrow D$: (Isothermal at T_2)

Similarly,

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

$W_3 = -Q_3$

4 $D \to A$: ~~IA~~ (Adiabatic)

$$W_4 = \frac{nR}{\gamma-1}(T_A - T_D) = \frac{nR}{\gamma-1}(T_B - T_C)$$

$$= -W_2$$

$$\therefore W = W_1 + \cancel{W_2} + W_3 + \cancel{W_4}$$

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

$$\left(\begin{array}{l} T_A = T_B = T_1 \\ T_C = T_D = T_2 \end{array}\right)$$

Now, we know that,

$$T_1 V_B^{\gamma-1} = T_2 V_C^{\gamma-1}$$

$$T_1 V_A^{\gamma-1} = T_2 V_D^{\gamma-1}$$

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

Using this,

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

(overall -ve, so system does work)

Now,

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

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

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

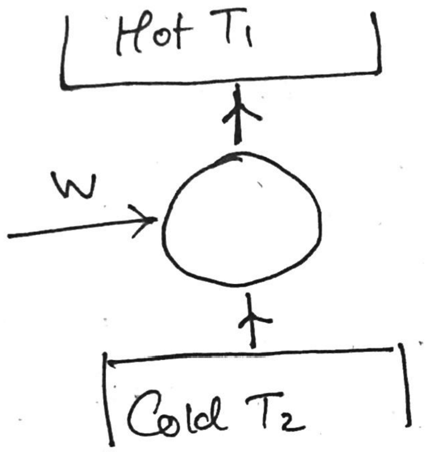
We may also write,

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

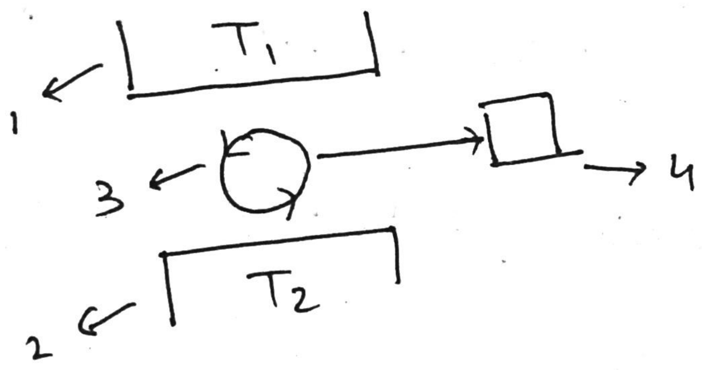
$T_1 > T_2$

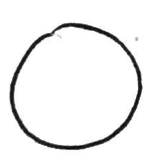
$\Rightarrow$ How do you make η large?

o Carnot Cycle as a fridgerator $\rightarrow$

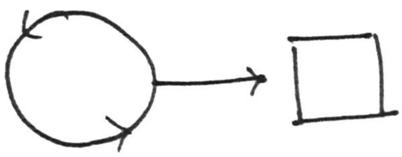


What lead us to the 4 body structure of the engine?



①  $\rightarrow$ useless.

(2)



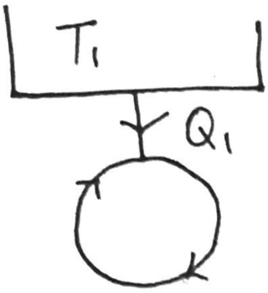
$\Delta U = 0$ (cycle)

$\Delta Q = 0$ here

$\Rightarrow \Delta W = 0$

1st Law

(3)



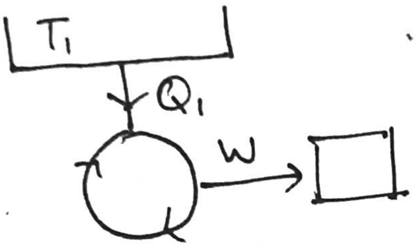
$\Delta U = 0$ (cycle)

$\Delta W = 0$ (Nothing to work on)

$\Rightarrow \Delta Q = 0$

1st Law

(4)



$\Delta U = 0.$ (cycle)

$\Rightarrow Q_1 = W$

(*) Second Law is a statement that says that this configuration <u>does not exist</u>

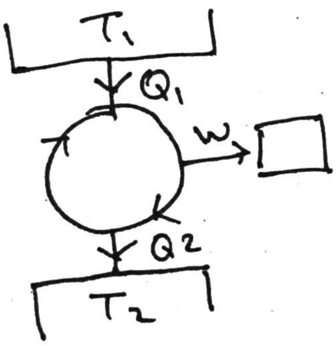
<u>This engine cannot exist</u>

How do we say this?

All experiments attempting to make this have failed.

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

(5)



This engine allows you to

(1) Be consistent with 1st Law

(2) Not violate 2nd Law.

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

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

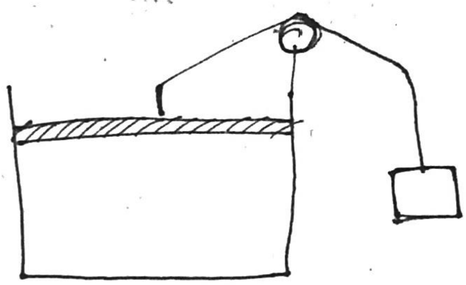
(*) Complete conversion happens in isothermal process — but that is not cyclic.

- 2nd law of thermodynamics (Clausius - Claypeyron)

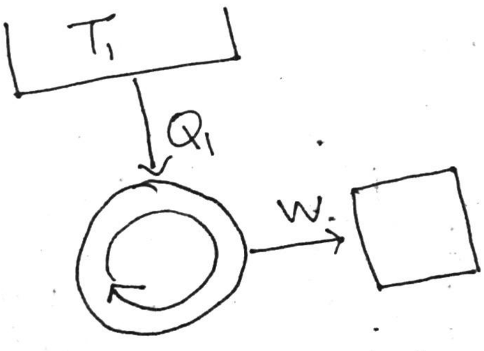
It is impossible to transfer heat from cold ~~to hot~~ body to hot body by means of a cyclic process without any effect to the surroundings.

3rd February 2023

Modelling → (the heat engine)

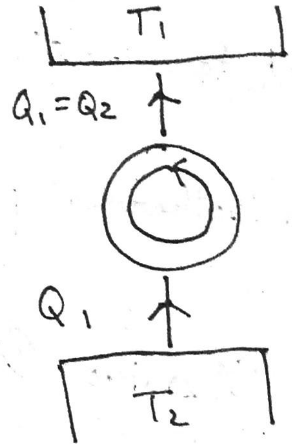


- Kelvin:



Does not exist (2nd law)

o Clausius statement:



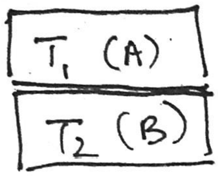
$T_1 > T_2$

Doesnotexist (2nd Law)

These statements are equivalent.

o Reversibility →

Example 1:

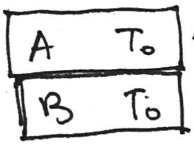


$T_1 > T_2$

Is the heat flow from T_1 to T_2 reversible,

No, it is irreversible.

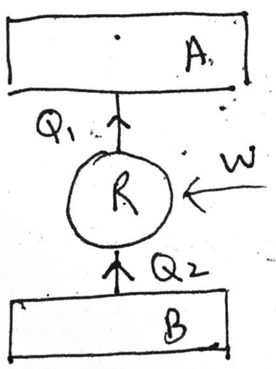
After some time,



$T_1 > T_0 > T_2$ (Q heat moved $A \to B$)

These two bodies can ~~not~~ be put back to original state.

o Use a refridgerator.



$Q_1 = Q_2 + W$

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

→ But A ~~has~~ now gets more heat than it lost.

A has W ~~extra~~ energy extra.

- Take A with another cold body C such that W 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?

→ Refridgerator worked (W)

→ C got some ~~heat~~ heat (Q)

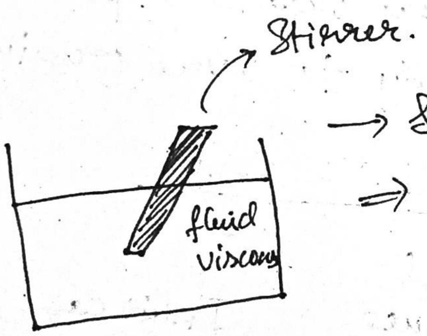
By conservation, $Q = W$.

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

(*) You can put the system to same state, but you cannot ~~convert~~ put system + surroundings to the same original state.

- Reversibility ≡ (System + Surroundings)

(*) Example 2:



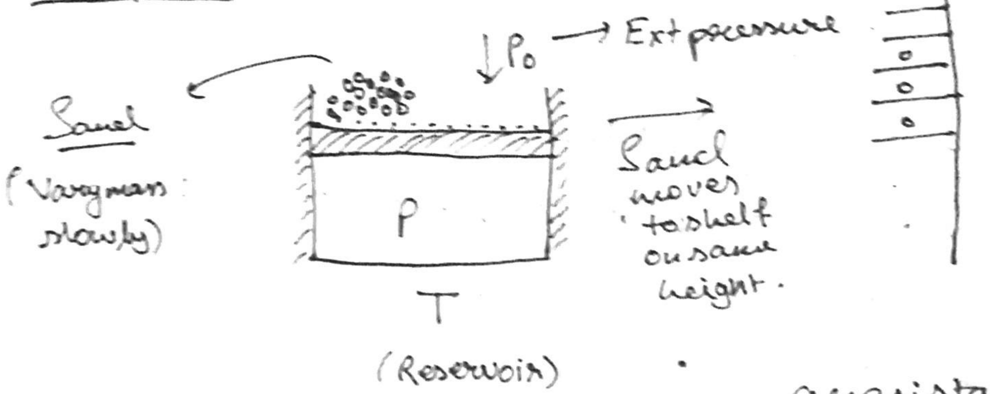
→ Stir the fluid quasistatically.

⇒ fluid will heat up.

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

→ Quasistatic process does not necessarily mean reversible.

Example 3

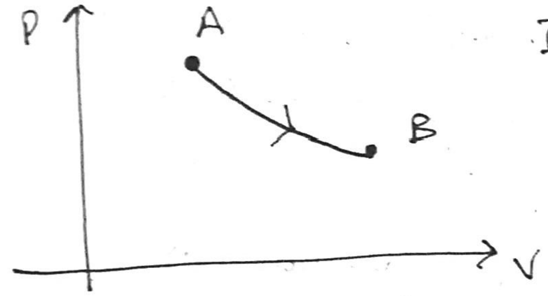


→ If we take sand off (gradually) → quasistatically., the ~~sys~~ piston moves up (taking heat from reservoir)

Work done $= \int p\,dv$

$\Delta U = 0$

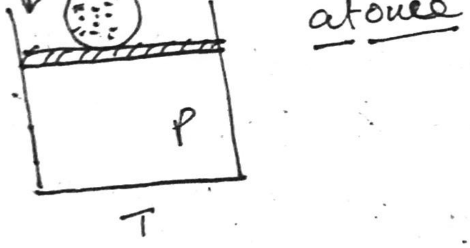
$Q = \int p\,dv$



Isothermal

→ 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.

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

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

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

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

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 is 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 quasistatic

② No dissipative forces.

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

→ Mechanical / thermal / chemical equilibrium NOT satisfied

→ Dissipative force.

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

8th Feb 2024

Clausius Inequality $\Rightarrow$

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

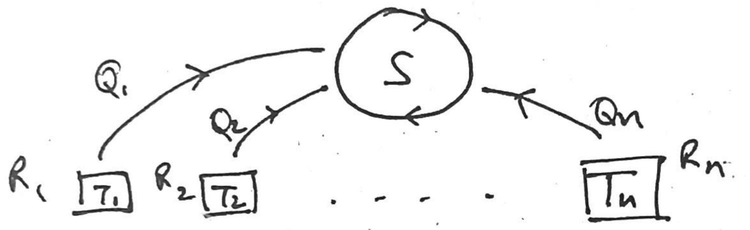
Statement $\longrightarrow$

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

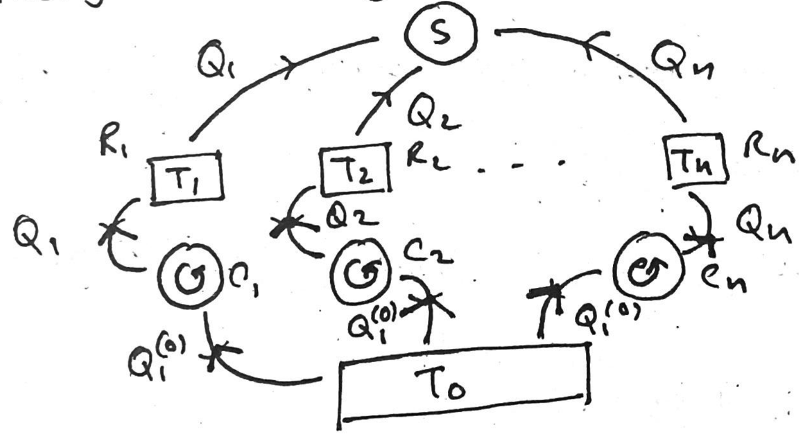
So for the carnot engine (a special subclass of this),

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

General case,



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



⊛ C_1 supplies Q_i 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 ~~cat~~ can act as heat engine as well as refridgerator.

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

② T_0 reservoir 'loses' energy

$$Q_0 = \sum_{i=1}^{N} Q_i^{(0)}$$

Now we know that for the carnot engines,

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

$$\therefore \; Q_0 = \sum_{i=1}^{N} Q_i^{(0)} = T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i}$$

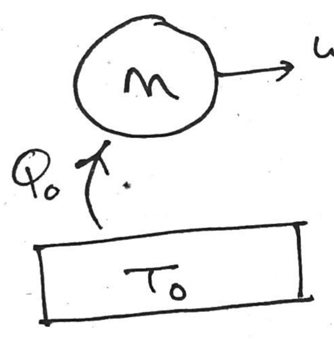
The process is cyclic for all the engines involved.
If we think of them as one engine, $\Delta U = 0$

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,

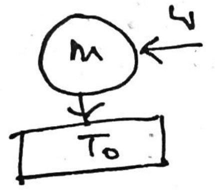


Obviously this engine cannot exist

$\Leftrightarrow$ Violates 2nd law

But this is okay if $Q_0 < 0$
Work → Heat conversion is never prohibited.

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



☑ Allowed

$$\Rightarrow Q_0 = T_0 \sum_{i=1}^{N} \frac{Q_i}{T_i} \leq 0$$

Consider S to be a reversible engine.

$\Rightarrow$ All engines / cycles are reversible.

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

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

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

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

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

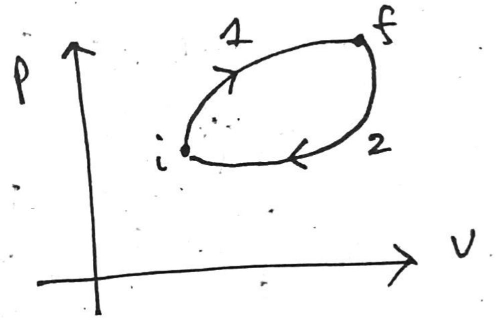
(*) equality for reversible, inequality otherwise.

This may be generalised to,

$$\oint \frac{đQ}{T} \leq 0$$

Consider a reversible cycle,

$$\oint \frac{đQ}{T} = 0$$



Now,

$$\int_i^f \frac{đQ_{rev}}{T}\bigg|_1 + \int_f^i \frac{đQ_{rev}}{T}\bigg|_2 = 0$$

$$\Rightarrow \int_i^f \frac{đQ_{rev}}{T}\bigg|_1 = + \int_i^f \frac{đQ_{rev}}{T}\bigg|_2$$

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

$\Rightarrow$ It is a state function.

<u>This will be called entropy.</u>

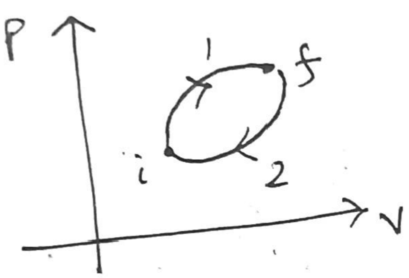
<u>9th February 2024</u>

o <u>Clausius Inequality</u> $\Rightarrow$

$$\oint \frac{đQ}{T} \leq 0$$

Eqality for reversible process

<u>Entropy:</u>



<u>Reversible:</u>

$$\int_{i1f2i} \frac{đQ_{rev}}{T} = 0$$

$$\Rightarrow \int_i^f \frac{đQ_{rev}}{T}\bigg|_1 + \int_f^i \frac{đQ_{rev}}{T}\bigg|_2 = 0$$

$$\Rightarrow \int_i^f \frac{đQ_{rev}}{T}\bigg|_1 = \int_i^f \frac{đQ_{rev}}{T}\bigg|_2$$

Does not depend on the path, clearly.

$\Rightarrow$ It is a state function.

So we define,

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

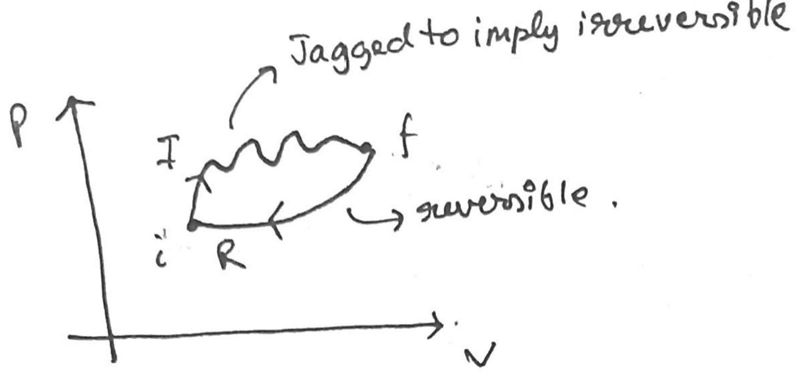
$S \equiv$ Entropy of the system.

(*) Statement of entropy is related to reversible heat transfer only.

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

it has to be $\frac{đQ_{rev}}{T}$.

Now,



Irreversible cycle → dissipation.

$$\oint \frac{đQ}{T} < 0$$

$$\Rightarrow \int_i^f \frac{đQ}{T}\Big|_I + \int_f^i \frac{đQ_{rev}}{T}\Big|_R < 0$$

$$\Rightarrow \int_i^f \frac{đQ}{T}\Big|_I < \int_i^f \frac{đQ_{rev}}{T}\Big|_R$$

$$\Rightarrow S_f - S_i > \int_i^f \frac{đQ}{T}\Big|_I$$

Words

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

∘ If isolated system $đQ = 0$ (adiabatic)

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

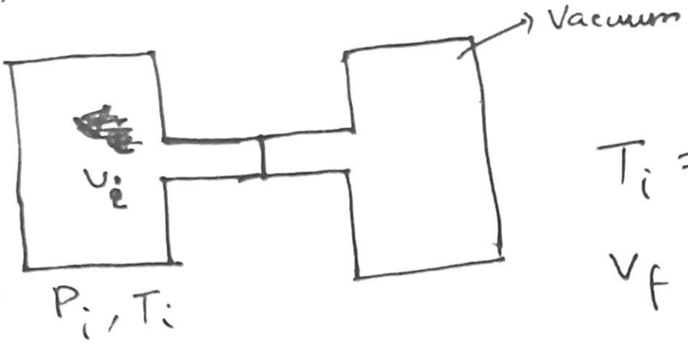
& For irreversible process,

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

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.

∘ Joule Expansion:



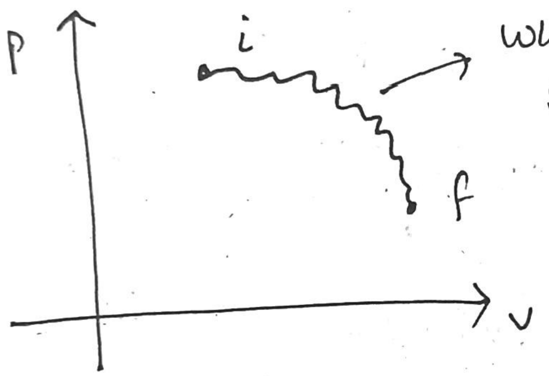
$T_i = T_f$

$V_f = 2V_i$

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

As temp / internal energy does not depend on V for ideal gas,

$$T_i = T_f$$



when barrier is opened gas expands immediately, thus irreversibly.

We want to find entropy change in this process.

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

But the path is irreversible, how do we do this?
The entropy change is a state function! It has nothing to do with ~~sys~~ 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.

$$\therefore \Delta S = \int_{V_0}^{2V_0} \frac{đQ_{rev}}{T} = \int_{V_0}^{2V_0} \frac{\cancel{du} + p\,dv}{T}$$

$$= \frac{1}{T}\int_{V_0}^{2V_0} p\,dv$$

$$= R\ln 2 > 0$$ $\therefore$ (Positive semidefinite) quantity.

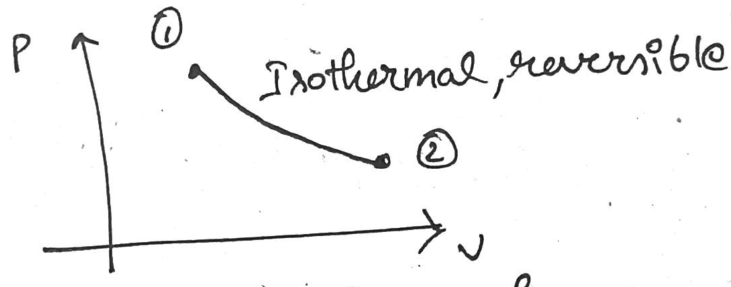
Note that here $đQ = 0$, so $\Delta S = \frac{đQ}{T} = 0$

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

o Any process of ideal gas —

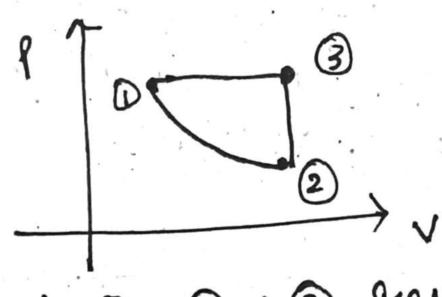
$$(P_1, V_1, T) \rightarrow (P_2, V_2, T)$$

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



We argue that this is the same for all reversible paths.
So we construct another 'reversible' path

$(P_1, V_1) \rightarrow (P_1, V_2)$ isobaric
$\downarrow$ isochoric
(P_2, V_2)



Hard to do ① → ③ → ② reversibly (req inf reservoirs)
but we donot care – we just assume it to be rev

① → ③ is not isothermal, it is isobaric

we use version of $đQ$ where p is constant.

$$\therefore\ đQ = C_V\, dT + p\, dV \quad \boxed{\checkmark}$$ we use this

$$= C_p\, dT - V dp \quad \boxed{\checkmark}$$ we use this.

$$\therefore\ \Delta S = \int \frac{đQ_{rev}}{T}$$

$$= \int C_p \frac{dT}{T} + \int C_V \frac{dT}{T}$$

$$= C_p \ln\left(\frac{T'}{T}\right) + C_V \ln\left(\frac{T}{T'}\right)$$

Show that,

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

$$\Rightarrow \Delta S = C_p \ln\left(\frac{V_2}{V_1}\right) - C_V \ln\left(\frac{V_2}{V_1}\right)$$

$$= (C_p - C_V) \ln\left(\frac{V_2}{V_1}\right)$$

$$= NR \ln\left(\frac{V_2}{V_1}\right) \qquad \text{(Ideal gas)}$$

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

(*) So, we have redefined reversibility and irreversible with respect to entropy.