Ch- Thermodynamics

Video #1

→ Thermodynamics - Heat, Motion

→ About how heat and work are interconverted

→ Thermodynamics law: 1, 2, 0

→ Earlier heat was considered as a fluid named caloric, which possessed heat properties, and the molecules are self repellant and go away from hot to cold body

→ Now: property which transfers from hot to cold body

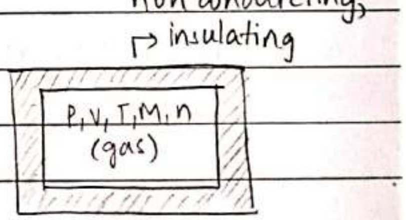
→ ThermoD - internal change in system ; Macroscopic properties (P, V, T, M, n) due to use of Heat.

[Kinetic Theory of Gases - molecular microscopic level]

Mechanical Equilibrium -

$F_{net} = 0$, $a_{COM} = 0$, $\tau_{net} = 0$, $\alpha_{COM} = 0$

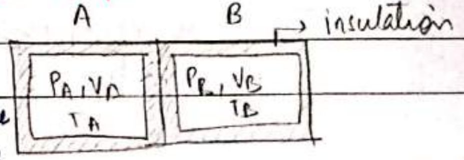
Thermal Equilibrium - System macroscopic properties like P, V, T, M, n become constant



→ Let there be a gas w/ P, V, T, M, n which is insulated from all sides by a non conducting material

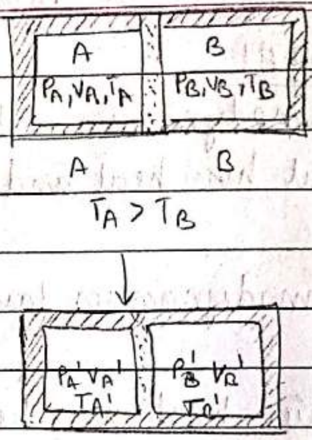
→ Hence, there will be no exchange of heat, ($\Delta q = 0$) and the system will be adiabatic

* If the state and properties of a system remain the same; then the system is in thermal equilibrium [Temp of 2 bodies need not be the same!



2 bodies A, B are separated by non conducting boundary, there will be NO Q exchange and the system will have same state ∴ In TEq^b even tho $T_A \neq T_B$

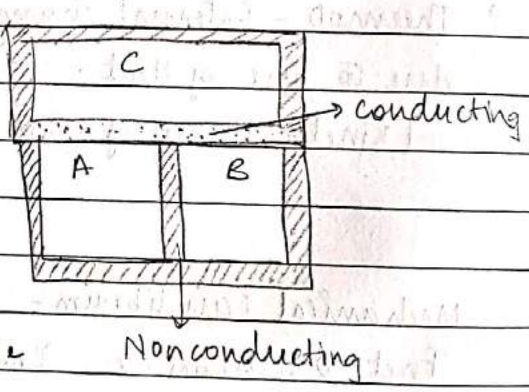
▨ Non conducting boundary - adiabatic
⬚ conducting boundary - dithermic



- Initially $T_A \neq T_B$ and $T_A > T_B$ so KE of particles of A > B.
- Moves faster and transfers heat as KE
- Then $T_A' = T_B'$ and the system now stays in this state of conditions till $t = \infty$ from t = Thermal eqb

99%. Thermal eqb = $T_A = T_B$
1%. " = Macroscopic properties of body stay same

ZEROTH LAW OF THERMOD

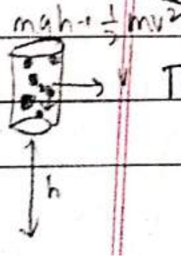


- At beginning $T_A \neq T_B \neq T_C$
- The boundary b/w A and C (&) B & C are conducting so after time 't'
  $T_A' = T_C'$, $T_B' = T_C'$
- when the boundary b/w A & B is made conducting at that instant, it is seen that there is no Q exchange b/w 'A' and 'B'
  ∴ $T_A' = T_B'$

∴ If 2 bodies are in thermal eqb w/ the same body, then they are at TE w/ each other.

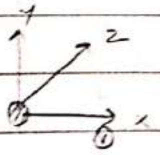
Video#2

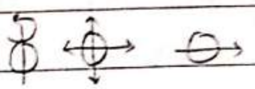
INTERNAL ENERGY



$$\text{The total energy possessed by a body} = \underbrace{KE}_{\text{motion of body}} + \overbrace{PE}^{\text{Gravitational + Electrostatic, etc PE of body}} + \underbrace{\text{Internal Energy}}_{\text{Molecular level Energies}}$$

→ Internal Energy accounts for molecular level of energies :-
- KE of molecules (due to V in different axes)
- PE of molecules (due to Force of attractions)
- Vibrational | Rotational | translational KE
  considered significant only @ High T





Our considerations are for a body whose KE = PE = 0 [at rest and not @ height] —for ideal gas-

so, $\boxed{\text{Total Energy of body} = \text{Internal Energy}}$
(E) (U)

For ideal gas :- No force of attraction b/w particles, so no PE created due to it

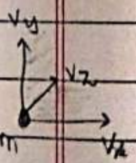
$\boxed{\therefore \text{TE of ideal gas} = \text{KE of gas} = \text{IE}}$
linear rotatory vibration

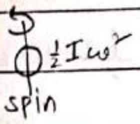
Ideal gas

Monoatomic

eg He, Ne, Ar, Xe, Kr, Rn

$\boxed{E = U = KE}$





$U = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \cancel{\frac{1}{2}I\omega^2} \to 0$ (as $I \approx 0$)

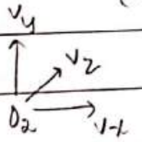
• Vibration later

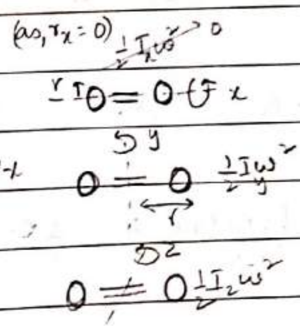
$\boxed{DOF = 3}$

(3 independent terms)

Diatomic

eg - O_2, N_2, H_2, etc





$\therefore U = \frac{1}{2}mv_x^2 + \frac{1}{2}mv_y^2 + \frac{1}{2}mv_z^2 + \frac{1}{2}I_y\omega^2 + \frac{1}{2}I_z\omega^2$

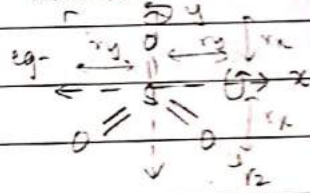
$\boxed{DOF = 5}$

Polyatomic

eg SO_2, SO_3, CH_4, NH_3, etc

Translational = 3
Rotation = 3

eg-



$U = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) + \frac{1}{2}I(\omega_x^2 + \omega_y^2 + \omega_z^2)$

$\boxed{DOF = 6}$

For linear stuff eg-
Cl - Be - Cl, $I_x \approx 0$ ($r_x = 0$)
$\therefore DOF = 5$

Degree of freedom - No of independent terms in the expression of KE (doesn't depend on each other at all)

* At High temp vibration terms are also added (+2) for each gas

LAW OF EQUIPARTITION OF ENERGY

Lay man lang: The total KE/IE of the body is divided equally among the each element of degree of freedom

eg: IE = 90J for monoatomic gas ∴ $\frac{1}{2}mv_x^2 = \frac{1}{2}mv_y^2 = \frac{1}{2}mv_z^2 = 30J$

Def. The avg KE associated w/ each degree of freedom is $\frac{1}{2}kT$ where ⓚ is Boltzman's constant, T = absolute Temp.

$$k \text{ (Boltzman constant)} = \frac{R \text{ (gas constant)}}{N_A \text{ (Avogadro No } N_A)}$$

$$k = \frac{8.314}{6.023 \times 10^{23}}$$

- Average KE associated w/ each DOF of a monoatomic gas = $\frac{1}{2}kT$

(UE) for all the gas = $\frac{3}{2}kT$

(for mono, f=3)

U monoatomic mole = $\frac{f}{2}kT$ = KE of mol^c

KE mol = U mole = $\frac{f}{2}kT \times N = \frac{f}{2}RT$; U_n moles = $\frac{f}{2}RT \times n$

$$\boxed{\therefore \text{Internal Energy } \underset{1 \text{ mole}}{`U'} = \frac{f}{2}RT}$$

Summary

- E_1 molecule for 1 DOF = $\frac{1}{2}kT$
- E_1 molecule = $\frac{f}{2}kT$
- E_1 mole = $\frac{f}{2}kT \times N_A = \frac{f}{2}RT$
- E_n mole | U_n mole = $n \times \frac{f}{2}RT$

Q) Find KE of 2 moles of H_2 at 300K

diatomic gas, $KE = U = \frac{f}{2}kT$ for 1 mol^c

$KE = \frac{f}{2}kT \times N_A \times 2$ for 'n' moles $= n\frac{f}{2}RT = 2 \times \frac{5}{2} \times RT = 5RT$

Q) Find KE of 1 mol^c of He at 300K

$KE = U = f \times \frac{1}{2}kT = 3 \times \frac{1}{2}kT = \frac{3}{2}kT$

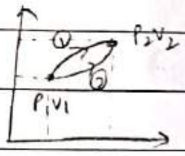
✱ $U = KE = n \cdot \frac{f}{2}RT$ (1mole) [Internal Energy is state fun depends on state NOT Path]

differentiating both sides

$dU = n\left(\frac{f}{2}R\right)dT$ (as 'n', 'R' = constant cant diff)

$$\boxed{\Delta U = n\left(\frac{f}{2}R\right)\Delta T}$$

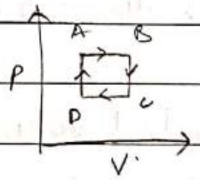
$\Delta U = nC_V\Delta T$



ΔU same

✱ $\Delta U = U_f - U_i$ (doesnt depend on path)

∴ cyclic process $\Delta U = 0$



✱ for constant temperature $\Delta T = 0$

or, $\Delta U = 0$

[Internal Energy is function of T]

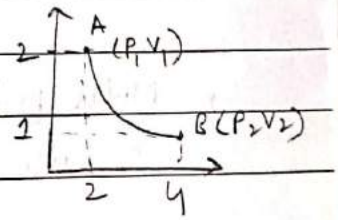
Q) Find ΔU in the case where a gas changes from state A to B

$P_1V_1 = 2 \times 2 = 4$

$P_2V_2 = 1 \times 4 = 4$

as $P_1V_1 = P_2V_2$, Boyle's law is obeyed

∴ $\Delta T = 0$ or $\Delta U = 0$



Video #3 – Specific Heat Capacity

Heat → Energy exchange b/w system and surrounding

→ Form of transfer of energy (when there is temp diff)

→ Symbol (Q), unit → Joule, common unit: calorie

$$\boxed{1\,cal = 4.182\,J}$$

→ Heat given to the system (+ve)
Heat given by the system (-ve)

Specific Heat capacities of Gases

$$\boxed{c = \frac{Q}{m\Delta T}}$$

Temp needed to raise temp of unit mass by unit °temp

Process
(i) Isothermal, T = constant
$\Delta T = 0$
(ii) Adiabatic process, $\Delta q = 0$

$c_{isoteermal} = \infty$
$c_{adiabatic} = 0$

① At constant volume

$c_v = \frac{Q}{m\Delta T}$ 1g gas ⟶ Temp 1°C↑ (@ const Volᵐ)

$c_v = J/g°C$

② At constant pressure

$c_p = \frac{Q}{m\Delta T}$ $c_p = J/g°C$

→ Molar specific Heat capacity - MSHC of gas = Amount of heat needed to raise the temperature of 1 mole of substance by 1°C

→ Relation b/w ~~Cp, cp~~ Cp, cp (Molar specific Heat capacity, gram specific heatcapacity

$$\boxed{C_p = \text{Molar mass } c_p}$$
$$\boxed{C_v = \text{Molarmass } c_v}$$

For any gas $\boxed{C_p - C_v = R}$ "capital"

Q) For N_2 the value of $C_p - C_v$ = gram specific

(a) 14R (b) $\frac{R}{14}$ (c) 28R [✓ (d)] $\frac{R}{28}$

$C_p - C_v = R$ Molar mass $(c_p - c_v) = R$

$$\boxed{c_p - c_v = \frac{R}{28}}$$

$Q_v = nC_v\Delta T$

$Q_p = nC_p\Delta T$

$\boxed{C_v = \frac{f}{2}R}$ ∴ $\boxed{C_p = \left(\frac{f}{2}+1\right)R}$ $\boxed{\gamma = \frac{C_p}{C_v}}$

f = 3, 5, 6 (for mono di, tri atomic)

f	$C_v = f/2 R$	$C_p = C_v + R$	$\gamma = \frac{C_p}{C_v}$	$C_p - C_v = R$
Monoatomic (3)	$C_v = \frac{3}{2}R$	$C_p = \frac{5}{2}R$	$\gamma = \frac{5}{3} = 1.66$	
Diatomic (5)	$C_v = \frac{5}{2}R$	$C_p = \frac{7}{2}R$	$\gamma = \frac{7}{5} = 1.4$	
Triatomic/Poly (6)	$C_v = 6R$	$C_p = 4R$	$\gamma = \frac{4}{3} = 1.33$	

$$\boxed{\begin{matrix}\gamma_{mono} > \gamma_{di} > \gamma_{poly}\\ 1.66 \quad 1.4 \quad 1.33\end{matrix}}$$

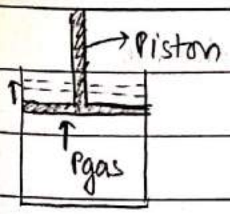
$$\boxed{\gamma = 1 + \frac{2}{f}}$$

Video #4 - Work done in thermodynamics

Work - Mechanical way of transfer of energy.

$$\text{Work done} = P\Delta V$$

P → pressure, ΔV → change in vol^m

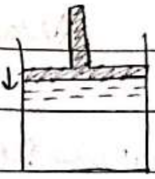


i) If gas expands - work done by gas

$\Delta V = V_f - V_i = +ve$

$W = +ve$

in chemistry reverse signs



ii) If gas compresses, work done on gas (system)

$W = P\Delta V$ $(V_i > V_f)$

$= -ve$

gas Expansion is having +ve work!

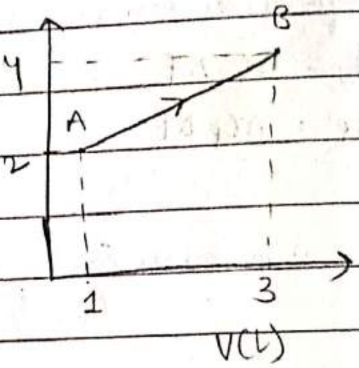
Q) Find the work done by a gas ($P = 1atm$), when it expands 0.5L

$W = P\Delta V = 1atm\,(0.5L)$

$= 0.5\ atm\text{-}L$

$= 0.5 \times 101.3J$

$= 50.65J$

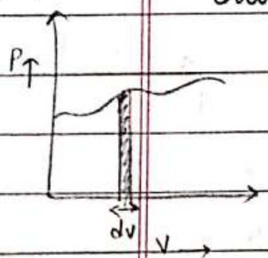


Q) Find the work done?

$W = P\Delta V$

$= ?$

but pressure is not constant

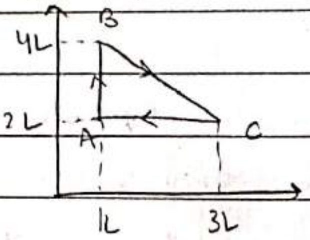


$w = P\Delta V$ (in strip - P constant)

$dW = P\,dv$

$\int dw = \int P\,dv \Rightarrow \boxed{W = \int P\,dV}$

$\boxed{\text{Here work = area under graph}} = \oplus 6\ atm\text{-}L$ (gas expand)



Q) Find the work done b/w ABC

→ work done = path function

∴ W = Area under AB + BC + AC

$W_{AB} = 0$ (vol^m same $\Delta V = 0$)

W_{BC} = area of trapezium $= \frac{1}{2}(2)(4+2) = \oplus 6\ atm\text{-}L$

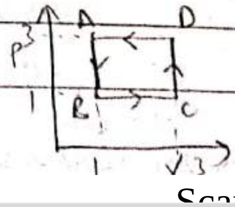
W_{CA} = area of rectangle $= \frac{1}{2}(2)(2) = \ominus 2\ atm\ L$ (vol^m less| gas contracted)

Total $= 4atm\text{-}L = 4 \times 101.3J = 405.2\ J$

→ Here, $\Delta U = 0$ (cyclic)

Shortcut in physics for 'w' done

$\boxed{W = \pm \text{Area of cycle}}$ → +ve if clockwise, → -ve if anticlockwise



Q) $w = ?$ anticlockwise

∴ $w = -(\text{area}) = (-4atm\text{-}L)$

Video #5 - First Law of ThermoDynamics
(Law of conservation of Energy)

$$\boxed{\Delta U = \Delta q \mp \Delta W} \rightarrow \text{work done by the system}$$

ΔU ↓ Change in Internal Energy

Δq ↳ Heat given to the system

$dE/dU = dq \mp dw$

INTERNAL ENERGY

Total energy = Internal Energy (when KE/PE of body = 0)

$$\boxed{Q = W + \Delta U} \rightarrow \text{Increase in Internal Energy of system}$$

Q ↙ Heat given to the system

W ↓ Work done by system

→ Heat given used to increase 'U' or do work

→ Q ⟨ given to system (+ve)
  ⟨ given by system (-ve)

$$\boxed{Q = nC\Delta T}$$
- $Q_V = nC_V\Delta T$, $C_V \rightarrow \frac{f}{2}R$
- $Q_P = nC_P\Delta T$, $C_P \rightarrow \left(\frac{f}{2}+1\right)R$

$R = 8.314\ J/mol\,k,\ 2\ cal/mol\,k$

→ W ⟨ by system = (+ve)
  ⟨ on system - (-ve)

$$\Delta U = n\left(\frac{f}{2}kT\right)N_A = n\underbrace{\frac{f}{2}R}_{C_V}\Delta T$$

$$\boxed{\Delta U = nC_V\Delta T}$$
↳ state function, work in cyclic = 0, path independent

Q) 1 mole of O_2 is heated from 25°c → 125°c at constant volume. Find (i) Q (ii) ΔU (iii) w [Given, O_2 is diatomic, f = 5, R = 2 cal/mol]

$\Delta T = 100k$

$\Delta U = nC_V\Delta T = 1 \times \left(\frac{f}{2}R\right)\Delta T = 1 \times \frac{5}{2} \times 2 \times 100 = 500\ cal$

$\Delta W = 0\ (\Delta V = 0)$

$\Delta Q = 500\ cal = \Delta U$

Q) Above question w/ constant pressure and 1 mole 'He'

$U = nC_v\Delta T$
$= n\frac{f}{2}R\Delta T$
$= 1\times\frac{3}{2}\times 2\times 100 = 300$ cal

$Q = Q_p = nC_p\Delta T$
$= n\left(\frac{f}{2}+1\right)R\,\Delta T$
$= 1\times\left[\frac{3}{2}+1\right]2\times 100$
$= \frac{5}{\cancel{2}}\times\cancel{2}\times 100 = 500$ cal

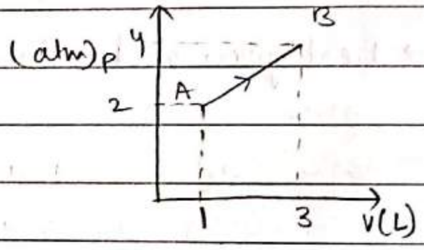
$\therefore W = 200$ cal

Q) In an isothermal process, 50J of heat is given to an ideal gas. Find W & ΔU

Ans: T- constant ; $Q = W + \Delta U = W + \cancelto{0}{nC_v\Delta T}$
$Q = 50J = W$

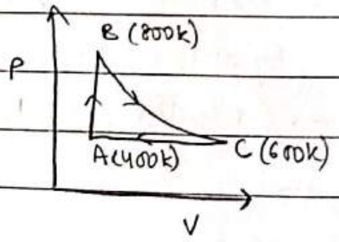
Or all the energy provided in isothermal process used to due work

Q) Find $W_{AB} = ?$ if $\Delta U = +200J$, $Q = ?$



$W_{AB} =$ area $= 6$ atm-L $= ⊕606J$
$Q = W + \Delta U$
$= 606 + 200 = 806J$

JEE MAINS 2014 Q) 1 mole diatomic gas has following path then -



(a) $\Delta U_{ABCA} = 250R$
(b) $\Delta U_{CA} = 750R$
(c) $\Delta U_{AB} = -350R$
~~(d)~~ $\Delta U_{BC} = -500R$

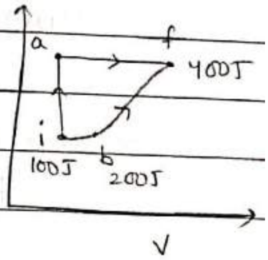
sol^n. $W_{ABCA} =$ area $=$ ⊕ , but $U = 0$ (cycle)

$\Delta U_{AB} = nC_v\Delta T = n\frac{f}{2}R\Delta T = 1\times\frac{5}{\cancel{2}}\times\cancel{2}\times 400 = 4000J = +1000R$

$\Delta U_{BC} = n\frac{f}{2}R\Delta T = -5\times 200 = -1000J = -500R$
$\Delta U_{CA} =$ ~~200×5~~ $= -500R$

52:41

JEE Advance Q) Find $\frac{Q_{bf}}{Q_{ib}}$ if $U_i = 100J$, $U_b = 200J$, $Q_{iaf} = +500J$,
$W_{af} = +200J$, $W_{ib} = +50J$, $W_{bf} = +100J$



(a) 1 ~~(b) 2~~ (c) 3 (d) 4

$U_{ib} = U_b - U_i = +100J$, $W_{ib} = 50J$

$\therefore Q_{ib} = 150J$

$Q_{iaf} = W_{iaf} + U_{if}$

$500 = \overset{0}{\cancel{W_{ia}}} + W_{af} + U_{if} = 200 + U_{If}$

$300 = U_{If} = U_{iaf}$

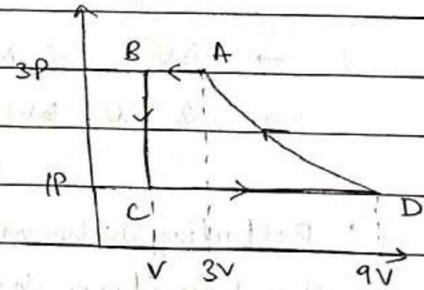
$300 = U_f - U_i \Rightarrow U_f = U_i + 300 = 400J$

ib	bf
$\Delta U = 100J$	$\Delta U = 200J$
$W_{ib} = 50J$	$W = 100J$ (give
$Q = 150J$	$Q = 300J$

Ratio $= \frac{300}{150} = \underline{\underline{2}}$

JEE2011 Q) **Process** **Options**

a) $A \longrightarrow B$ (t, q, r) p) U increases
b) $B \longrightarrow C$ (q, r) q) U decreases
c) $C \longrightarrow D$ (p, s) r) Q is lost
d) $D \longrightarrow A$ (t, r) s) Q is gained
t) work is done on system



→ t) Work is wherever ΔV (-ent) → a) ~~c)~~ d)
expand by

$A \rightarrow B$ (work = -ve)
$3P \times -2V = -6PV$

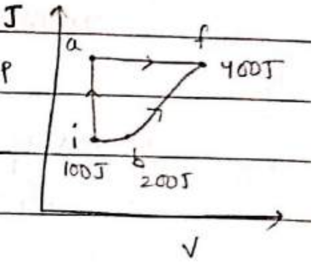
No. of moles in all points is equal

- A: $3P(3V) = nRT \Rightarrow \frac{9PV}{RT} = n$
- B: $3P(V) = nRT \Rightarrow \frac{3PV}{RT} = n$

→ W = compress (-ve)
$Q = nC_p\Delta T$ $U = nC_v\Delta T$
$PV\downarrow \therefore T\downarrow$ ($PV = kT$)
or, U - decrease
$Q = U + W = -ve$

- $B \longrightarrow C$ (volume same $\therefore W = 0$)
  $P_1V_1 = 3PV$ $P_2V_2 = PV$
  $\therefore P_1V_1\downarrow$ or, $T\downarrow$ $\therefore U$ = decreases , $\therefore Q$ = decrease
- $C \rightarrow D$ (volume ↑ $\therefore W = +ve$)
  $P_1V_1 = PV$ $P_2V_2 = 9PV$ or, $PV\uparrow \therefore T\uparrow$ [$U\uparrow$, $Q = U + W = +ve$]
- $D \rightarrow A$ (volume ↓ , $W = -ve$) , $P_1V_1 = P_2V_2 = 9PV$ (Isothermal) U → constant
  $Q = W + \Delta U = -ve$ (lost)

JEE Advance Q) Find $\frac{Q_{bf}}{Q_{ib}}$ if $U_i = 100J$, $U_b = 200J$, $Q_{iaf} = {}^{+}500J$,
$W_{af} = +200J$, $W_{ib} = +50J$, $W_{bf} = +100J$



(a) 1 ~~(b) 2~~ (c) 3 (d) 4

$U_{ib} = U_b - U_i = +100J$, $W_{ib} = 50J$

$\therefore Q_{ib} = 150J$

$Q_{iaf} = W_{iaf} + U_{if}$

$500 = \overset{0}{\cancel{W_{ia}}} + W_{af} + U_{if} = 200 + U_{if}$

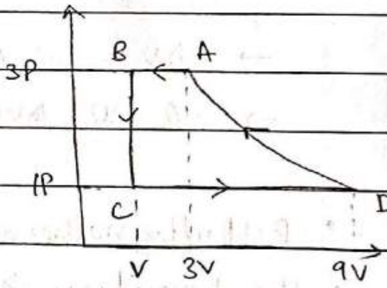
$300 = U_{if} = U_{iaf}$

$300 = U_f - U_i \Rightarrow U_f = U_i + 300 = 400J$

ib	bf
$\Delta U = 100J$	$\Delta U = 200J$
$w_{ib} = 50J$	$W = 100J$ (given)
$Q = 150J$	$Q = 300J$
Ratio $= \frac{300}{150} = 2$	

JEE2011 Q)

Process		Options
a) $A \longrightarrow B$	(t, q, r)	p) U increases
b) $B \longrightarrow C$	(q, r)	q) U decreases
c) $C \longrightarrow D$	(p, s)	r) Q is lost
d) $D \longrightarrow A$	(t, r)	s) Q is gained
		t) work is done on system



→ t) work is wherever ΔV (tent) → a) ~~c)~~ d) expand by

$A \rightarrow B$ (work = −ve) $3P \times -2V = -6PV$

No. of moles in all points is equal

- A: $3P(3V) = nRT \Rightarrow \frac{9PV}{RT} = n$
- B: $3P(V) = nRT \Rightarrow \frac{3PV}{RT} = n$

→ W = compress (−ve)
$Q = nC_p\Delta T$ $U = nC_v\Delta T$
$PV\downarrow \therefore T\downarrow$ $(PV = kT)$
or, U − decrease
$Q = U + W = -ve$

- $B \longrightarrow C$ (volume same $\therefore W = 0$)

$P_1V_1 = 3PV$ $P_2V_2 = PV$

$\therefore P_1V_1\downarrow$ or, $T\downarrow$ $\therefore U =$ decreases, $\therefore Q =$ decrease

- $C \longrightarrow D$ (volume ↑ $\therefore W = +ve$)

$P_1V_1 = PV$ $P_2V_2 = 9PV$ or, $PV\uparrow \therefore T\uparrow$ [$U\uparrow$, $Q = U + W = +ve$]

- $D \rightarrow A$ (volume ↓, $W = -ve$), $P_1V_1 = P_2V_2 = 9PV$ (Isothermal) $U \rightarrow$ constant
$Q = W + \Delta U = -ve$ (lost)

Video #6

Summary:

Adiabatic process $(\Delta Q = 0)$

→ gas of 'n' moles

$T_1 \longrightarrow T_2$

$$\boxed{w = \frac{nR(T_2 - T_1)}{\gamma - 1}}$$

Isothermal $(\Delta T = 0)$

$$\boxed{w = nRT \log_e \frac{V_2}{V_1}}$$

TYPES OF PROCESSES

① Isothermal Process -

- Constant Temperature, $\Delta T = 0$

ideal gas : $P \propto \frac{1}{V} \Rightarrow PV = \text{constant}$ $[P_1V_1 = P_2V_2]$

→ $\Delta U = nC_v \Delta T$ ∴ Isothermal process $\Delta U = 0$

→ $Q = \Delta U + \Delta W$ ∴ Isothermal process $\boxed{Q = W}$

(Heat used to do work, not increase temperature)

- Perfectly isothermal process - very slow
- The boundary should be perfectly conducting / diathermic
- Slope of P-V graph

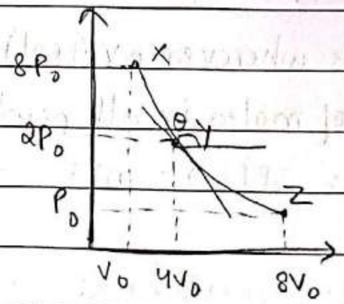
$PV = \text{constant}$

$d(PV) = 0$

$V\,dP + P\,dV = 0$

$P\,dV = -V\,dP$

$\frac{-P}{V} = \frac{dP}{dV}$



∴ Slope of P/V graph in isoT. process $\boxed{\left(\frac{dP}{dV}\right)_{iso} = \frac{-P}{V}}$ -ve sign as slope -ve

eg- Find slope at Y :- $\left(\frac{dP}{dV}\right)_Y = \frac{-P}{V} = \frac{-2P_0}{4P_0} = \frac{-P_0}{2V_0}$

work done in Isothermal process (by the gas)

$W = P\Delta V$ if $P =$ constant

$W = \int P dV$ if $P =$ not constant

At constant temp an ideal gas expands from V_1 to V_2 and $P_1 \rightarrow P_2$

$$W = \int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$\Rightarrow W = nRT \int_{V_1}^{V_2} \frac{1}{V} dV = nRT \log_e \frac{V_2}{V_1} = 2.303 \times nRT \log_{10} \frac{V_2}{V_1}$$

Formulae:-

$$W = nRT \log_e \frac{V_2}{V_1} = 2.303 \times nRT \log_{10} \frac{V_2}{V_1} = 2.303 \times nRT \log_{10} \frac{P_1}{P_2}$$

$(P_1V_1 = P_2V_2)$

$$W \Rightarrow P_1V_1 \log_e \frac{V_2}{V_1} = P_2V_2 \log_e \frac{V_2}{V_1} \quad [P_1V_1 = P_2V_2 = nRT]$$

$$\Rightarrow P_1V_1 \log_e \frac{P_1}{P_2} = P_2V_2 \log_e \frac{P_1}{P_2}$$

all in above are also equal to Q ($Q = W$ as $\Delta U = 0$)

② Adiabatic process

- constant heat energy) noExchange, $\Delta Q = 0$
- Perfectly adiabatic, very fast

ideal gas: $PV^{\gamma} =$ constant

$\boxed{P_1V_1^{\gamma} = P_2V_2^{\gamma}}$ $\gamma = \frac{C_P}{C_V}$

Ex: Tyre if burst ⇝ cools

- As bursting is quick process
- Upon bursting workdone = by the gas → +ve

$-\Delta U = W \rightarrow \Delta U \downarrow\downarrow$ or $\Delta T \downarrow$

$$\overset{0}{\cancel{Q}} = W + \Delta U$$

or, $\boxed{-\Delta U = W}$

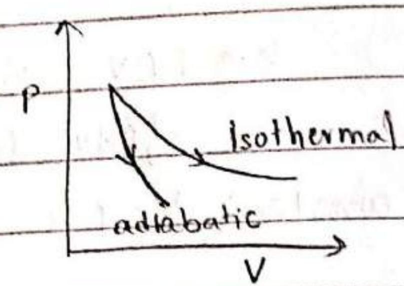
- Perfectly insulated wall

For adiabatic process: $\boxed{PV^{\gamma} = \text{constant}}$

so, $\frac{nRT}{V} V^{\gamma} = $ constant

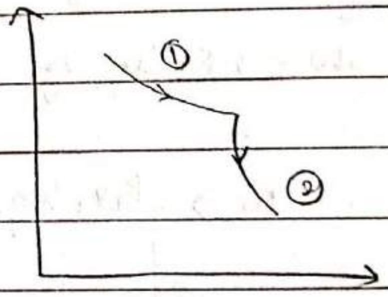
$$\boxed{TV^{\gamma - 1} = \text{constant}}$$

- $$PV^{\gamma} = \text{constant}$$
$$P\left(\frac{nRT}{P}\right)^{\gamma} = \text{constant}$$
$$\boxed{P^{1-\gamma}T^{\gamma} = \text{constant}}$$



- Slope of adiabatic curve, steeper than isothermal graph

$$(PV) = k \rightarrow \text{isothermal}$$
$$PV^{\gamma} = k \rightarrow \text{adiabatic}$$
$$d(PV^{\gamma}) = 0$$
$$P\,dV^{\gamma}\,dV + V^{\gamma}dP = 0$$
$$P\gamma V^{\gamma-1}dV + V^{\gamma}dP = 0$$
$$V^{\gamma}dP = -P\gamma \cancel{V}^{\gamma-1}dV$$
$$\cancel{V^{\gamma}}\frac{dP}{dV} = \frac{-P\gamma \cancel{V^{\gamma}}\,\cancel{dV}}{V}$$
$$\left(\frac{dP}{dV}\right)_{adi} = -\gamma\left(\frac{P}{V}\right)$$



① - isothermal
② - Adiabatic

Or, $\left(\frac{dP}{dV}\right)_{adiabatic} = \gamma\left(\frac{dP}{dV}\right)_{iso}$ [slope adi = γ × slope iso]

$$\gamma = 1 + \frac{2}{f}$$

$\gamma_m = 1.67$
$\gamma_d = 1.4$
$\gamma_p = 1.33$

$$\gamma_m > \gamma_d > \gamma_p$$

∴ slope of mono > di > poly for adiabatic process - PV.

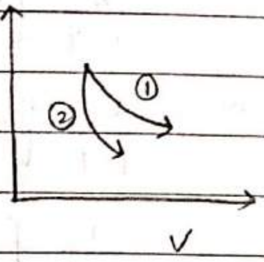
Q) JEE 2002 If ① and ② are P|V slopes of an adiabatic process, such that slope$_2$ > slope$_1$. What are the gases?

a) He O_2

b) O_2 He

c) He Ar

d) O_2 N_2



slope of adiabatic process $\frac{\Delta P}{\Delta V}$ depends on γ directly,

$\gamma_m > \gamma_{di}$

∴ slope$_m$ > slope$_{di}$ ∴ gas 2 = mono, gas 1 = di

Q) JEE 2010 Diatomic ideal gas is compressed adiabatically to $\frac{1}{32}$ of its initial volume. If initial temp of gas is T_i & final temp is aT_i, the value of a is :-

a) 1 b) 2 c) 3 d) 4

PV^γ = constant ⇒ $\frac{nRT}{V}V^\gamma$ = const ⇒ $TV^{\gamma-1}$ = constant

$V_1 \longrightarrow V_2 = \left(\frac{V_1}{32}\right)$

$\cancel{T_i} V_1^{\gamma-1} = a\cancel{T_i}\left(\frac{V_1}{32}\right)^{\gamma-1}$

$\cancel{V_1^{\gamma-1}} = a\frac{\cancel{V_1^{\gamma-1}}}{32^{\gamma-1}}$ ⇒ $32^{\gamma-1} = a = 32^{\cancel{1}+\frac{2}{f}-\cancel{1}} = 32^{2/5} = 2^2 = 4$

Work done in adiabatic process

$P_1, V_1, T_1 \longrightarrow P_2, V_2, T_2$

$w = \int P dV$

$= \int \frac{nRT}{V} dV$ → not useful as T not constant

but, $PV^\gamma = k$ or, $P = \frac{k}{V^\gamma}$

$w = \int_{V_1}^{V_2} \frac{k}{V^\gamma} dV = k\int_{V_1}^{V_2} \frac{1}{V^\gamma} dV = k\int_{V_1}^{V} V^{-\gamma} dV$

$= k\left(\frac{V^{-\gamma-1}}{-\gamma-1}\right)_{V_1}^{V_2}$ → PTO

$$W = k\left[\frac{V^{-\gamma+1}}{-\gamma+1}\right]_{V_1}^{V_2}$$

$$= \frac{k}{1-\gamma}\left[V^{1-\gamma}\right]_{V_1}^{V_2}$$

$$W = \frac{k}{1-\gamma}\left[V_2^{1-\gamma} - V_1^{1-\gamma}\right] \qquad k = P_1V_1^{\gamma} = P_2V_2^{\gamma}$$

$$= \frac{1}{1-\gamma}\left[P_2V_2^{\gamma}\cdot V_2^{1-\gamma} - P_1V_1^{\gamma} + V_1^{-\gamma+1}\right] = \frac{1}{1-\gamma}\left[P_2V_2 - P_1V_1\right]$$

$$\boxed{W = \frac{P_2V_2 - P_1V_1}{1-\gamma} = \frac{nR(T_2-T_1)}{1-\gamma}}$$

Or, $-\Delta U = W \therefore \Delta U = -W$

$$\boxed{\Delta U = \frac{P_2V_2 - P_1V_1}{\gamma-1} = \frac{nR(T_2-T_1)}{\gamma-1}}$$

Q) 2011 5.6L of He at STP adiabatically compressed to 0.7L. Taking initial temp to be T_1, work done in process is

✓ a) $\frac{9}{8}RT_1$ b) $\frac{3}{2}RT_1$ c) $\frac{15}{8}RT_1$ d) $\frac{9}{2}RT_1$

No. of moles 'n' $= \frac{5.6}{22.4} = \frac{1}{4}$ moles

$V_1 = 5.6L \quad V_2 = 0.7L \quad T_1$

$W = \int PdV = P\int \frac{K}{V^{\gamma}}dV$

~~$W = \frac{K}{1-\gamma}\left[V_2^{+1-\gamma} - V_1^{1-\gamma}\right]$~~

~~$= \frac{K}{1-\gamma}\left[0.7^{1-\gamma} - 5.6^{1-\gamma}\right]$~~

$W = \frac{nR(T_2-T_1)}{\gamma-1}$

$TV^{\gamma-1}$ = constant

$T_1 \rightarrow V_1\ (5.6)$

$T_2 \rightarrow V_2\ (0.7) = \frac{1}{8}V_1 = \frac{V_1}{8}$

$T_1\cancel{V_1^{\gamma-1}} = T_2\left(\frac{\cancel{V_1}}{8}\right)^{\gamma-1}$

$\Rightarrow 4T_1 = T_2$

Date
Page

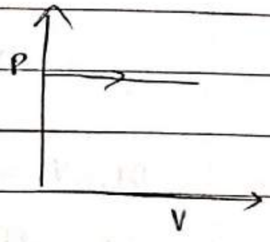
$$W = \frac{nR(T_2-T_1)}{\gamma-1} = \frac{0.25 \times R(4T_1-T_1)}{\frac{2}{3}} = \frac{1}{4}\times\frac{R}{2}\times 3T_1 \times 3$$

$$= \frac{9}{8}RT_1$$

③ Isobaric Process - $(\Delta P = 0)$

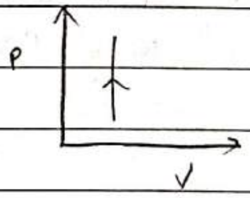
→ constant pressure - P

$$W = \int_{V_1}^{V_2} P\,dV = P\int_{V_1}^{V_2} dV = P(V_2-V_1) = P\Delta V$$



$\boxed{W = P\Delta V}$ $\qquad Q = \Delta U + P\Delta V$

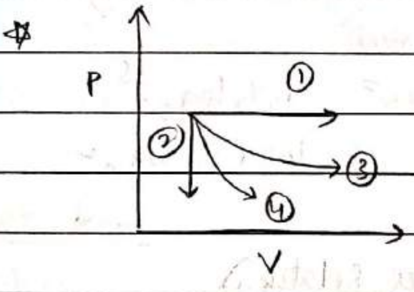
④ Isochoric Process - $(\Delta V = 0)$



$W = \int P\,dV = 0$

$Q = W + \Delta U$

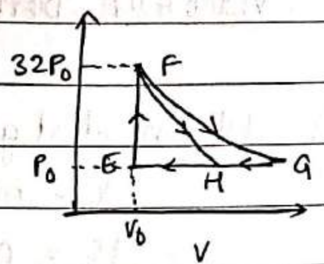
$\boxed{Q = \Delta U}$ all heat used to ↑ Internal E.



① - Isobaric
② - Isochoric
③ - I-sothermal
④ - Adiabatic

JEE Adv 2017 Q)
1:28:11

JEE Adv 2013) one mole of monoatomic ideal gas, is moved from G→E, G→H, ~~H~~F→H, F→G, E→F



List 1 (Process)	List II (work done)
p) G→E	$160 P_0V_0 \log_e 2$
q) G→H	$36 P_0V_0$
r) F→H	$24 P_0V_0$
s) F→G	$31 P_0V_0$

1) GF is isothermal curve

work in GE is $P\Delta V$, but V_2 = not given, from GF $P_1V_1 = P_2V_2$

$32P_0V_0 = P_0 \cdot \underline{(32V_0)}$

$\therefore$ Work $= P_0 \times \overset{(V_2-V_1)}{31V_0} = 31P_0V_0$

2) G→H is also isobaric

$\therefore W = P\Delta V$ but V_2 = not given

we found $V_1 = 32V_0$

→ as FH is adiabatic curve $PV^{\gamma} = \text{constant}$ $\gamma = \frac{5}{3}$

$$32P_0 V_0^{5/3} = P_0 \cancel{8}(xV_0)^{5/3}$$

Or, $32 = x^{5/3}$

$32^{3/5} = x = 8$

Or, $V_2 = 8V_0$

$\therefore$ work $= P\Delta V = P_0(32V_0 - 8V_0) = P_0 \times 24V_0 = 24P_0V_0$

3) F→H is adiabatic

$$w = \frac{P_2V_2 - P_1V_1}{\gamma - 1} = \frac{(P_0 \times 8V_0) - (32P_0V_0)}{\frac{2}{f}} = \frac{\overset{12}{\cancel{24}}P_0V_0 \times 3}{\cancel{2}} = 36P_0V_0$$

4) F→G is isothermal

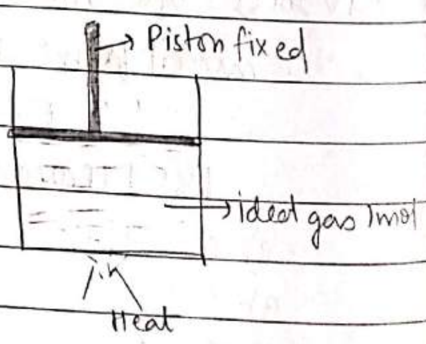
$$w = nRT \log_e \frac{v_2}{v_1} = P_1V_1 \log_e \frac{v_2}{v_1} = 32P_0V_0 \log_e \frac{32\cancel{V_0}}{\cancel{V_0}}$$

$$= 32P_0V_0 \log_e 2^5$$

$$= 160\, P_0V_0 \log_e 2$$

<u>Video #07</u> Derivation of $C_P - C_V = R$ (Mayer's Relation)

<u>case1</u> - Let an ideal gas be heated at constant 'V'



$Q = nC_V\Delta T$

$dQ = nC_VdT$

$= 1 \times C_V dT$

$w = \int PdV = 0$ $(\Delta V = 0)$

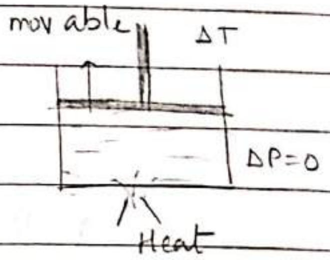
$Q = w + \Delta U$

$dQ = dw + du$

$C_VdT = 0 + du$

$du = C_VdT$

<u>Case 2</u> - the pressure is kept fixed now, volume can change such that the same ΔT occurs.



$Q = nC_p \Delta T$

$= C_p \Delta T$

$dw = PdV$

$dQ = du + dw$

$C_p dT = du + PdV$ For ideal gas, ΔU only dependent on ΔT and <u>nothing else</u> $\therefore dU = C_v dT$

$C_p dT = C_v dT + PdV$

(now, $PV = nRT$ | $PV = RT$)

$PdV + \overset{0}{\cancel{V\delta P}} = R\delta T$

$\Delta P = 0 \therefore PdV = R\delta T$

$C_p dT = C_v dT + RdT$

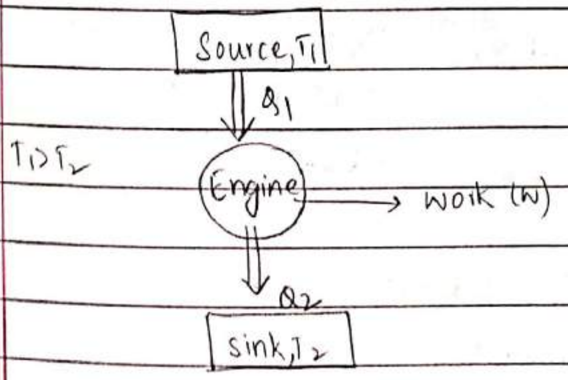
$C_p = C_v + R$

$C_p - C_v = R$

<u>Video #08</u> - Second law of Thermodynamics
(About spontainity of a process)

① All work can be converted into heat but,
② All heat can't be converted into work (used in engine)

<u>Heat Engine</u> -
Makes work from heat (petroleum ignited, to convert into work)



- Source provides some heat Q_1, out of which is some is used to do work W, and other residual energy Q_2 is sent to sink.
- Temp source T_1 > Temp sink T_2
- Efficiency $\eta = \frac{\text{Work done}}{\text{Heat supplied}} \times 100$

$= \frac{W}{Q_1} \times 100$

or, $\frac{Q_1 - Q_2}{Q_1} \times 100$

$Q_1 = W + Q_2$

$Q_1 - Q_2 = W$

or, efficiency $\eta = \frac{Q_1 - Q_2}{Q_1} = 1 - \frac{Q_2}{Q_1}$

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

$$\eta\% = \frac{W}{Q_1} \times 100 = \frac{Q_1 - Q_2}{Q_1} \times 100 = \left(1 - \frac{Q_2}{Q_1}\right) \times 100$$

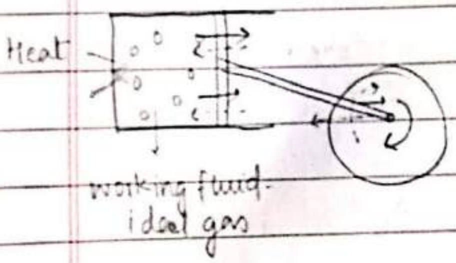
→ $\eta = 100\%$ or, 1 only if $Q_2 = 0$, ie heat can't be fully extracted for work

→ For $Q_2 = 0$ the source can be at any T and sink ~~can~~ will be not needed

But not possible

→ There has to be little wastage of heat ($Q_2 \neq 0$)

Working of Engine -

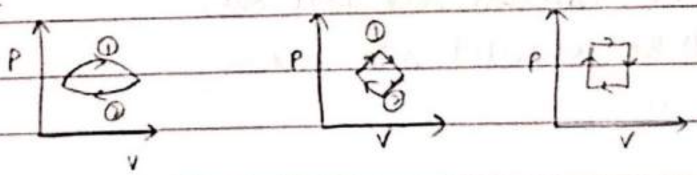


→ When the gas expands, piston moves out and work done to move front

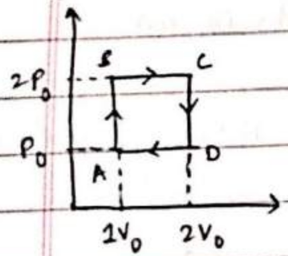
→ Then due to inertia, rod moved back and gas compresses

→ one cycle completed (1 exp + 1 comp)

graphs-



[Heat Engine]



	ΔU	W	Q	
A→B	$\oplus \frac{3}{2}RT_0$	0	$\frac{3}{2}RT_0$	} Heat gain by engine to work (W) → Q_1 → B to D - heat extracted
B→C	$\oplus \frac{3}{2}R2T_0$	$2P_0V_0$ $(2RT_0)$	$\cancel{7}5RT_0$	
C→D	$\frac{3}{2}R(-2T_0)$	0	$-3RT_0$	} Heat loss after work (W) → Q_2 → D to B heat rejected
D→A	$\frac{3}{2}R(-T_0)$	$P_0(-V_0) = -RT_0$	$-2.5RT_0$	

$\underbrace{}$ ↳ RT_0 - work (W)

1mole monoatomic gas

A→B $\quad \Delta U = nC_v\Delta T = n\left(\frac{f}{2}R\right)\Delta T = \frac{3}{2}R\Delta T$

PV = nRT always $\quad \therefore P_0V_0 = nRT$

then $2P_0 \, 2V_0 = nRT$ ~~or, x = ½ (V₀/2)~~

$$\frac{nRT_1}{P_0} = \frac{nRT_2}{2P_0} \quad (V_0 \text{ same})$$

$$2T_1 = T_2$$

At A - $P_0 V_0 T_0$ $\quad$ B - $P_0 V_0 2T_0$ $\quad$ C - $2P_0 2V_0 4T_0$ $\quad$ D = $P_0, 2V_0, 2T_0$

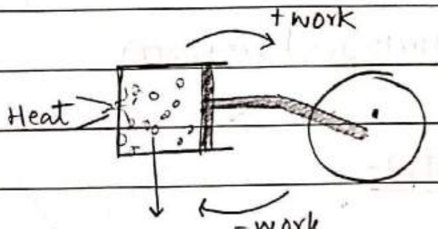
$\boxed{\text{Net } \Delta U \text{ in 1 cycle} = 0}$ $\quad$ $\boxed{\text{work done} = RT_0}$ < forward exp - return comp $\quad$ Q lost total = $-5.5RT_0$

as work = RT_0 and total = 6.5

Thermodynamics - 09

Carnot's Engine

- Carnot's Heat Engine
- working graph
- Derivation of $\eta = 1 - \frac{T_2}{T_1}$ with depth
- Refrigerator
- Numericals



→ All heat given (Q_1) not coverted into doing work (w)

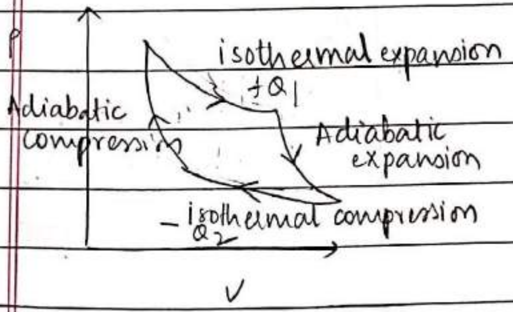
→ That's why residue Q → heats the engine up.

→ Going front - absorbs Q, back - rejects

working fluid
↓
ideal gas
net work +ve

1 complete cycle
↓
one stroke

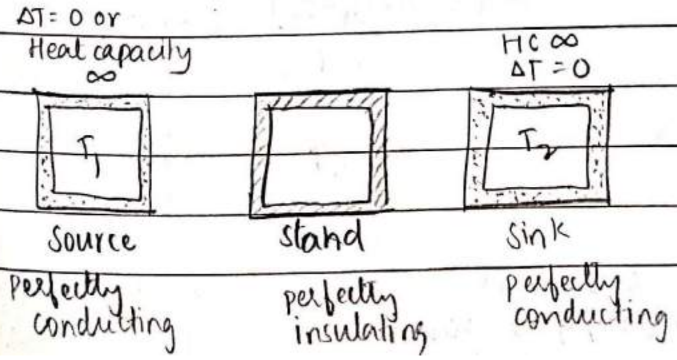
Carnot's Engine - Hypothetical engine
↓
Most effective engine → Reversible Engine → η = max of any such engine which works b/w same Two temp T_1 & T_2

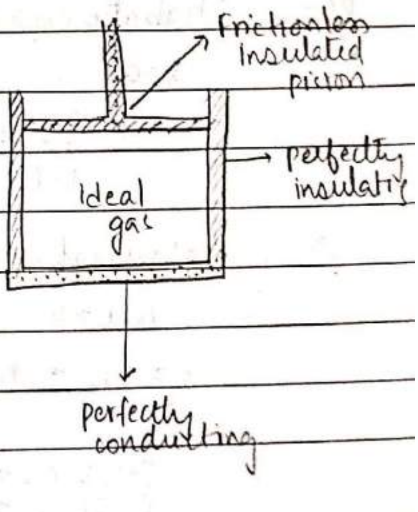


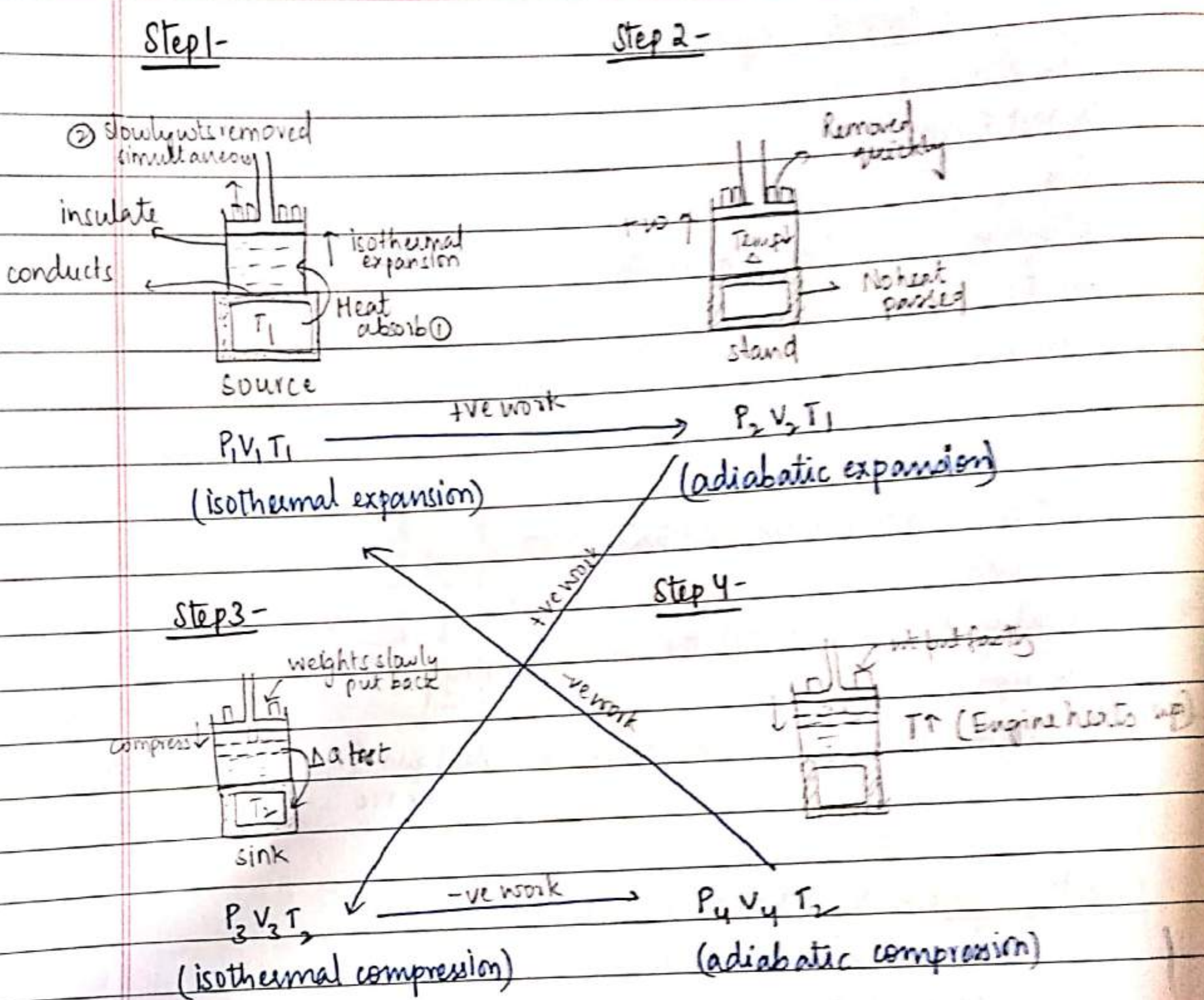
$$\boxed{\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}}$$

↓

STROKE OF CARNOT'S ENGINE







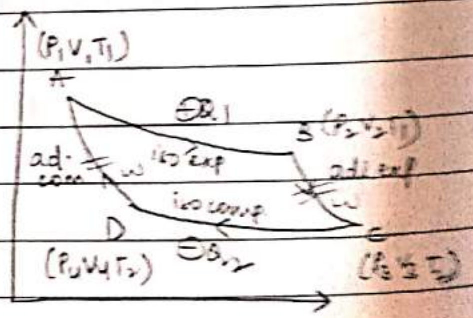
AB- Isothermal expansion

$\Delta T = 0 \quad \Delta U = 0$

$\Delta Q = w + \cancel{\Delta U}^{0}$

$\Delta Q = w$

$Q_1 = w_1 = nRT_1 \log_e \frac{V_2}{V_1}$



BC- Adiabatic expansion

$Q = 0$

$w_2 = \frac{nR(T_2 - T_1)}{1-\gamma} = -\Delta U$

DA- Adiabatic comp

$Q = 0$

$w_4 = \frac{nR(T_1 - T_2)}{1-\gamma} = -\Delta U$

CD- Isothermal compression

$\Delta U = 0$

$Q_2 = w_3 = nRT_2 \log \frac{V_4}{V_3}$

$(w_2 = -w_4)$

Total $\Delta U = 0$

Total $w = w_1 + \cancel{w_2} + w_3 + \cancel{w_4} = w_{net}$

$$\boxed{\frac{Q_2}{Q_1} = \frac{T_2}{T_1}}$$

η = Efficiency = $\dfrac{w_{net}}{Q_1}$

$$\eta = \frac{nRT_1 \log_e V_2/V_1 + nRT_2 \log_e V_4/V_3}{nRT_1 \log_e V_2/\cancel{V_1}}$$

$$= 1 + \frac{\log_e V_4/V_3 \times T_2}{\log_e V_2/V_1 \times T_1}$$

now, $P_1V_1 = P_2V_2$ — ①
$P_2V_2^{\gamma} = P_3V_3^{\gamma}$ — ②
$P_3V_3 = P_4V_4$ — ③
$P_4V_4^{\gamma} = P_1V_1^{\gamma}$ — ④

multiply ①×②×③×④

$$\cancel{P_1P_2P_3P_4} \times V_1V_2^{\gamma}V_3V_4^{\gamma} = \cancel{P_1P_2P_3P_4} \times V_1^{\gamma}V_2V_3^{\gamma}V_4$$

$$V_2^{\gamma-1}V_4^{\gamma-1} = V_3^{\gamma-1}V_1^{\gamma-1}$$

$\sqrt[\gamma-1]{} \rightarrow$ $\quad V_2V_4 = V_3V_1$

$$\frac{V_2}{V_1} = \frac{V_3}{V_4} \Rightarrow \eta = 1 + \frac{T_2}{T_1} \times \frac{\log_e \frac{V_4}{V_3}}{\log_e \frac{V_2}{V_1}}$$

$$\left[\text{but, } \frac{V_2}{V_1} = \frac{V_3}{V_4} \text{ or, } \frac{V_2}{V_1} = \left(\frac{V_4}{V_3}\right)^{-1}\right]$$

$$\Rightarrow \eta = 1 + \frac{T_2}{T_1} \times \frac{\log_e\left(\frac{V_3}{V_4}\right)^{-1}}{\log_e\left(\frac{V_2}{V_1}\right)}$$

$$= 1 - \frac{T_2}{T_1}\,\frac{\cancel{\log_e V_3/V_4}}{\cancel{\log_e V_2/V_1}} \Rightarrow \boxed{1 - \frac{T_2}{T_1} = \eta}$$

1Q) Source has T = 227°c, Sink = 127°c, Heat absorbed from source = 10^4 J
work done per cycle

a) 1000J [✓ b) 2000J] c) 3000J d) 4000J

$$\eta \Rightarrow 1 - \frac{T_2}{T_1} = \frac{w}{Q_1}$$

$$\Rightarrow 1 - \frac{\cancel{4}00}{\cancel{5}00} = \frac{w}{10^4} \Rightarrow \frac{10^4}{5} = w \Rightarrow 0.2\times10^4 \Rightarrow 2000J$$

Q2) The $\eta = \frac{1}{6}$. If sink Temperature is reduced by 65°c, $\eta = \frac{1}{3}$. calculate actual sink temperature a) 48°c b) 49°c c) 51°c [✓ d) 52°c]

$$\eta = \frac{1}{6} = 1 - \frac{T_2}{T_1} \qquad \frac{T_2}{T_1} = \frac{5}{6}$$

$$\eta' = \frac{1}{3} = 1 - \frac{(T_2 - 65)}{T_1}$$

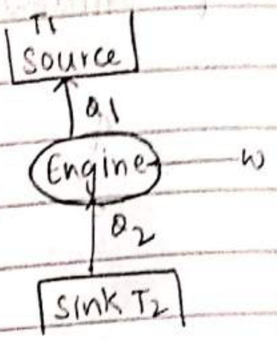
$$\frac{2}{3} = \frac{T_2 - 65}{T_1} \qquad \frac{2T_2 - 130}{2T_1} = \frac{4}{6}$$

$2T_2 - 130 = T_2$
$T_2 = 130$
or, $T_1 = \dfrac{T_2 \times 6}{5} = \dfrac{\overset{26}{\cancel{130}} \times 6}{\cancel{5}} = 156$

→ solve, $T_2 = 52$

REFRIGERATOR

"Reverse Heat Engine"

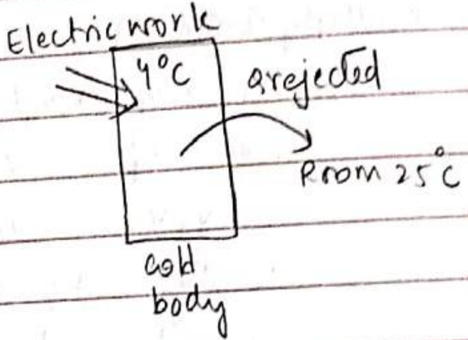


$Q_1 = w + Q_2$

$T_1 > T_2$

→ It uses electrical energy (to do work) and extracts heat from cold body (fridge = sink)

→ Moves this heat to engine which uses energy and Removes total energy to surroundings ($Q_2 > Q_1$) → Room/source



→ Removing heat from cold to hot body is a non-spontaneous process, Hence needs excess electrical work

→ Every thing else is same w/ carnot

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

Q) If inside refrigerator T = −3°c, Room Temp = 27°c, How much heat is rejected to room per second if 1J of Electrical Energy is given to refrigerator per second?

a) 4J b) 7J [✓ c) 9J] d) 13J

Heat rejected = Q_1

$$\frac{T_2}{T_1} = \frac{Q_2}{Q_1} \Rightarrow \frac{Q_1}{Q_2} = \frac{T_1}{T_2} \times \cancel{Q_2} = \frac{300}{270} \cancel{\times 1} = \frac{10}{9}$$

$$Q_1 - Q_2 = w = 10 - 9 = 1\,J \qquad \therefore \frac{w}{Q_1} = \frac{10}{9} - 1 = \frac{10-9}{9} = \frac{1}{9} \quad \boxed{Q_1 = 9}$$

coefficient of Performance

Heat Rejected should be ↑,

Work done ↓

$$\boxed{K = \frac{Q_2}{w} = \frac{Q_2}{Q_1 - Q_2}} \qquad \boxed{k = \frac{T_2}{T_1 - T_2}}$$

For work done in a Polytropic Process

Any process in which $PV^{\alpha} = \text{constant}$ (α = anything)

→ $\alpha = \gamma$, PV^{γ} = constant or adiabatic

→ $\alpha = 1$, PV = constant or isothermal

→ $\alpha = 0$, $PV^{0} = P$ = constant or isobaric

Now work done ⇒ $W = \int P\,dV$ $\quad P = \frac{K}{V^{\alpha}}$

$$W = \int_{V_1}^{V_2} \frac{K}{V^{\alpha}}\,dV$$

$$= K\int_{V_2}^{V_2} V^{-\alpha}\,dV = K\left\{\frac{V^{-\alpha+1}}{-\alpha+1}\right)_{V_1}^{V_2} = K\left(\frac{V^{1-\alpha}}{1\cancel{+}\alpha}\right)_{V_1}^{V_2}$$

$$W = K\left(\frac{V_2^{1-\alpha} - V_1^{1-\alpha}}{1 \mp \alpha}\right) \qquad K = P_1V_1^{\alpha} = P_2V_2^{\alpha}$$

$$W = \frac{nR(T_2 - T_1)}{1-\alpha} = \frac{P_2V_2 - P_1V_1}{1-\alpha} \qquad \therefore W = \frac{nR\Delta T}{1 \alpha}$$

Heat capacity

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

$$\cancel{n} C_{poly} \cancel{\Delta T} = \frac{\cancel{n} R \cancel{\Delta T}}{(1-\alpha)} + \cancel{n} C_V \cancel{\Delta T} \qquad \frac{C_P}{C_V} = \gamma \Rightarrow C_P = \gamma \cdot C_V$$

$$\cancel{7C_V}\ C_{Poly} = \frac{R}{1-\alpha} + C_V$$

$$\boxed{\therefore\ C_{Poly} = \frac{R}{1-\alpha} + C_V}$$

$$C_V = \left(\frac{f}{2}R\right)$$