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

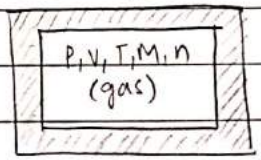
→ ThermoD - internal change in system; Macroscopic properties (P, V, T, M, n) due to use of Heat.
[Kinetic Theory of Gases - molecular microscopic level]

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

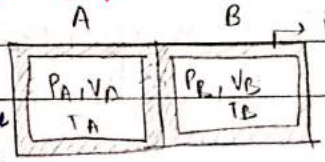
non conducting, ↳ insulating



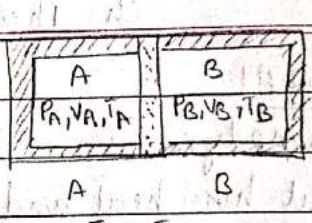
→ Hence, there will be no exchange of heat, ($\Delta q = 0$) and the system will be adiabatic

* 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 $T_A \neq T_B$

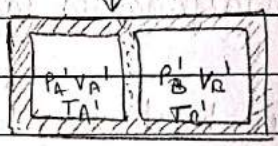


▨ Non conducting boundary - adiabatic
▥ conducting boundary - dithermic



$T_A > T_B$

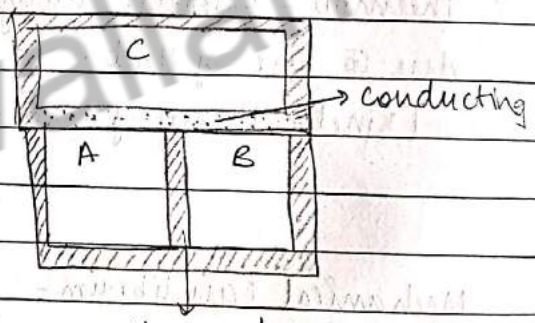
- Initially $T_A \neq T_B$ and $T_A > T_B$ so KE of particles of A > B.
- Moves faster and transfers heat as KE
- Then $T_A' = T_B'$ and the system now stays in this state of conditions till $t = \infty$ from $t =$ Thermal eqb



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 blw A and C & B & C are conducting so after time 't' $T_A' = T_C'$, $T_B = T_C'$
- when the boundary blw A & B is made conducting at that instant, it is seen that there is no ΔT exchange blw A' and B' $\therefore T_A' = T_B'$

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

VIDEO #2

INTERNAL ENERGY

The total energy possessed by a body = KE + PE + Internal Energy

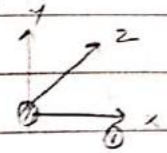
KE → motion of body

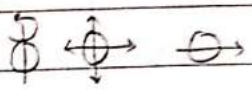
PE → Gravitational + Electrostatic, etc PE of body

Internal Energy → Molecular level Energies

→ Internal Energy accounts for molecular level of energies :-

* KE of molecules (due to $\vec{v}$ in different axes)
* PE of molecules (due to Force of attractions)
* Vibrational | Rotational | Translational KE
  ↓ considered significant only @ High T





—for ideal gas—

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

So, **Total Energy of body = Internal Energy**
(E) (U)

For ideal gas :- No force of attraction blw particles, so no PE created due to it.

∴ TE of ideal gas = KE of gas = IE

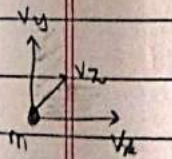
↓ linear ↓ rotatory ↓ vibration

Ideal gas

Monoatomic

eg He, Ne, Ag, Xe, Kr, Rn

E = U = KE



spin $\frac{1}{2}I\omega^2$

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

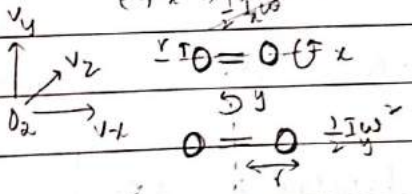
• Vibration later

DOF = 3

(3 independent terms)

Diatomic

eg - O_2, N_2, H_2, etc



(as $r_x = 0$) $\frac{1}{2}I_x\omega_x^2 \to 0$

$\frac{1}{2}I\theta = 0$ ∀ x

$\frac{1}{2}I\omega_y^2$

$\frac{1}{2}I_z\omega_z^2$

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

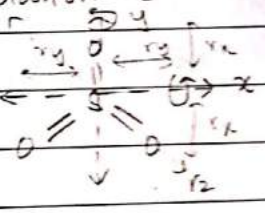
DOF = 5

Polyatomic

eg SO_2, SO_3, CH_4, NH_3, etc

Translational = 3

Rotation = 3



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

DOF = 6

For linear stuff eg - H - Be - H, $I_x \approx 0$ ($r_x = 0$)

∴ 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 (k) 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)

∪ monoatomic mole = $\frac{f}{2}kT$ = KE of molc

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

∴ Internal Energy 'U' (1 mole) = $\frac{f}{2}RT$

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 molᶜ

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

Q) Find KE of 1 molᶜ of He at 300K

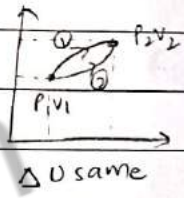
$KE = U = f \times \frac{1}{2}KT = 3 \times \frac{1}{2}KT = \frac{3}{2}KT$

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

diff eqn both sides

$dU = n\left(\frac{f}{2}R\right)dT$ (as 'n', 'R' = constant can't diff)

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

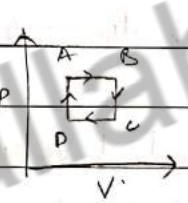


★ $\Delta U = U_f - U_i$ (doesn't depend on path)

$\therefore$ cyclic process $\Delta U = 0$

★ for constant temperature $\Delta T = 0$

or, $\Delta U = 0$



[Internal Energy is function of T]

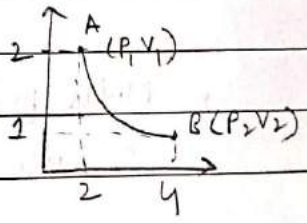
Q) Find ΔU in the case where a gas changes from state A to B

$P_1V_1 = 2 \times 2 = 4$

$P_2V_2 = 1 \times 4 = 4$

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

$\therefore \Delta T = 0$ or $\Delta U = 0$



Video #3 - Specific Heat Capacity

Heat → Energy exchange b/w system and surroundings

→ 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

$$C = \frac{Q}{m\Delta T}$$

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

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

$C_{isothermal} = \infty$
$C_{adiabatic} = 0$

① At constant volume

$$C_v = \frac{Q}{m\Delta T}$$

1g gas → Temp 1°C ↑ (@ const Vol^m)
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 ~~C_p, C_p~~ C_P, c_p (Molar specific Heat capacity, gram specific heat capacity)

C_p = Molar mass c_p

C_v = Molar mass c_v

For any gas $C_p - C_v = R$ "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 $(C_p - C_v) = R$

$$C_p - C_v = \frac{R}{28}$$

$Q_v = nC_v\Delta T$ $C_v = \frac{f}{2}R$ $C_p = \left(\frac{f}{2}+1\right)R$ $\gamma = \frac{C_p}{C_v}$

$Q_p = nC_p\Delta T$

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

f	$C_v = f/2R$	$C_p = C_v + R$	$\gamma = \frac{C_p}{C_v}$	$C_p - C_v = R$
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)	$C_v = 6R$	$C_p = 4R$	$\gamma = \frac{4}{3} = 1.33$	

$\gamma_{mono} > \gamma_{di} > \gamma_{poly}$

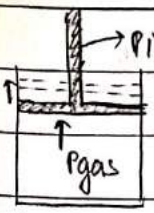
1.66 1.4 1.33

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

Video #4 - Work done in thermodynamics

Work - Mechanical way of transfer of energy.

Work done = $P\Delta V$ (P: pressure, ΔV: change in volume)

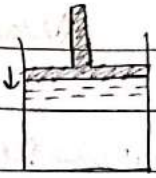


i) If gas expands - work done by gas

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

$W = +ve$

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 ($P = 1 atm$), when it expands 0.5L

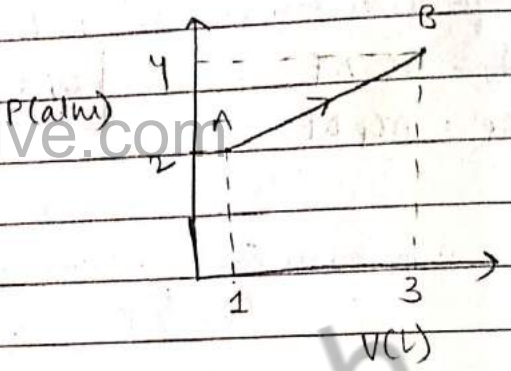
$W = P\Delta V = 1atm\ (0.5L)$

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

$= 0.5 \times 101.3 J$

$= 50.65 J$

Q) Find the work done?

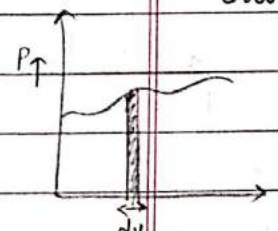


$W = P\Delta V$

$= ?$

but pressure is not constant

$W = P\Delta V$ (instantaneous P constant)

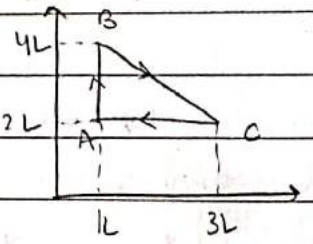


$dW = PdV$

$\int dW = \int PdV \Rightarrow \boxed{W = \int PdV}$

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

Q) Find the work done b/w ABC



→ work done = path function

$\therefore W$ = 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)

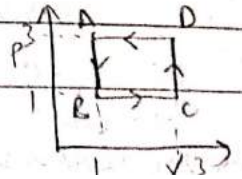
Total $= 4 atm\text{-}L = 4 \times 101.3 J = 405.2 J$

→ Here, $\Delta U = 0$ (cyclic)

Shortcut in physics for 'W' done

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

Q) W = ? anticlockwise



$\therefore W = -(\text{area}) = (-4 atm\text{-}L)$

Video #5 - First Law of ThermoDynamics

(Law of conservation of Energy)

$\Delta U = \Delta q \mp \Delta W$ → 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)

$Q = w + \Delta U$ → 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)

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

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

→ w
- by system = (+ve)
- on system = (-ve)

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

$\Delta U = nC_V\Delta T$

↳ 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]

$\Delta T = 100\,K$

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

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

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

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

$Q = Q_p = nC_p\Delta T$

$= n\left(\frac{f}{2}+1\right)R\ \Delta T$

$= 1 \times \left[\frac{3}{2}+1\right] 2 \times 100$

$= \frac{5}{2} \times 2 \times 100 = 500$ cal

$\therefore W = 200$ cal

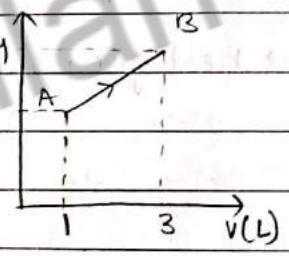
Q) In an isothermal process, 50J of heat is given to an ideal gas. Find W & ΔU

Ans: T- constant ; $Q = W + \Delta U = W + \cancel{nC_V\Delta T}^{0}$

$Q = 50J = W$

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

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

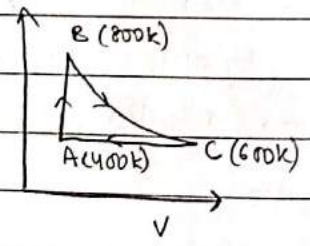


W_{AB} = area = 6 atm-L = 606 J

$Q = W + \Delta U$

$= 606 + 200 = 806$ J

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)

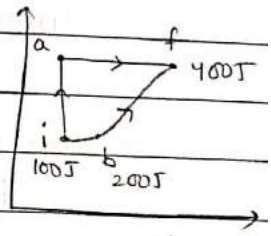
$\Delta U_{AB} = nC_V\Delta T = n\frac{f}{2}R\Delta T = 1 \times \frac{5}{2} \times 2 \times 400 = 400J = +1000R$

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

$\Delta U_{CA} = \cancel{-200 \times 5} = -500R$

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

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

$\therefore Q_{ib} = 150J$

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

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

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

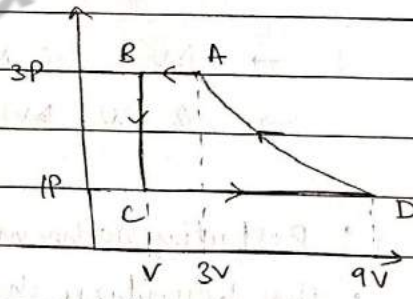
$500 = \cancel{W_{ia}}^{0} + W_{af} + U_{if} = 200 + U_{if}$

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

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

JEE 2011 Q)

Process		Options
a)	A → B (t, q, r)	p) U increases
b)	B → C (q, r)	q) U decreases
c)	C → D (p, s)	r) Q is lost
d)	D → 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 → B ($3P \times 2V = 6PV$) (work = -ve)

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 → 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

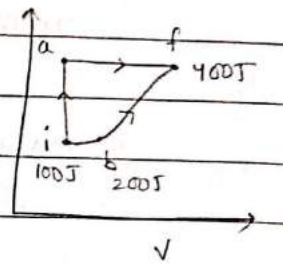
- C → D (volume ↑ $\therefore W = +ve$)

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

- D → A (volume ↓, $W = -ve$), $P_1V_1 = P_2V_2 = 9PV$ (Isothermal) $U \rightarrow$ 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

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

$\therefore Q_{ib} = 150J$

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

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

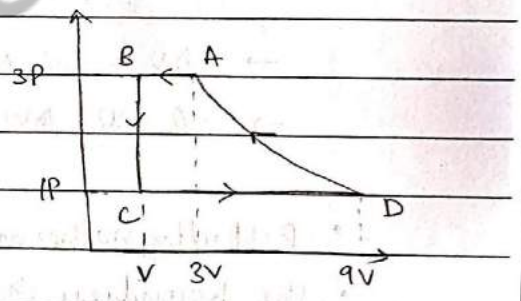
$300 = U_{if} = U_{iaf}$

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

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

JEE2011 Q)

Process		Options
a) A → B	(t, q, r)	p) U increases
b) B → C	(q, r)	q) U decreases
c) C → D	(p, s)	r) Q is lost
d) D → 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 → B ($3Px - 2V = -6PV$) (work = -ve)

No. of moles in all points is equal

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

→ $PV \downarrow \therefore T \downarrow$ ($PV = kT$)

W = compress (-ve)

$Q = nC_p\Delta T$ $U = nC_v\Delta T$

or, U - decrease

$Q = U + W = -ve$

- B → 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 → 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 → 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 ($\Delta Q = 0$)	Isothermal ($\Delta T = 0$)
→ gas of 'n' moles $T_1 \longrightarrow T_2$ $W = \frac{nR(T_2 - T_1)}{\gamma - 1}$	$W = nRT \log_e \frac{V_2}{V_1}$

TYPES OF PROCESSES

① **Isothermal Process** -

- Constant Temperature, $\Delta T = 0$

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

  → $\Delta U = nC_v \Delta T$ ∴ 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

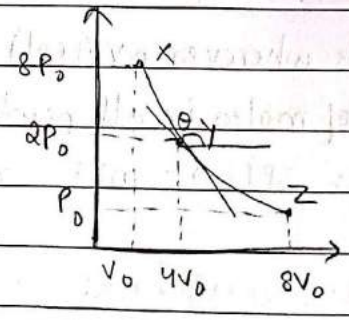
$PV = \text{constant}$

$d(PV) = 0$

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

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

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



∴ 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 $P_1 \to P_2$

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

$$\Rightarrow W = nRT \int_{V_1}^{V_2} \frac{1}{V} dV = nRT \log_e \frac{V_2}{V_1} = 2.302 \times nRT \log_{10} \frac{V_2}{V_1}$$

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 / no Exchange, $\Delta Q = 0$ ideal gas: PV^γ = constant
- Perfectly adiabatic, very fast

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

Ex: Tyre if burst ⇝ cools
- As bursting is quick process
- Upon bursting work done by the gas → +ve

$Q^{\nearrow 0} = W + \Delta U$

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

- Perfectly insulated wall

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

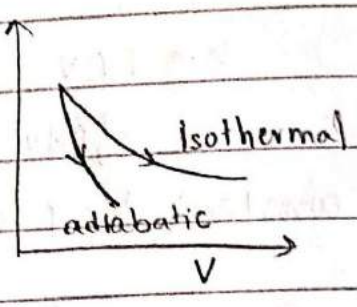
so, $\frac{nRT}{V} V^\gamma = \text{constant}$

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

- $PV^{\gamma} = \text{constant}$

$P\left(\frac{nRT}{P}\right)^{\gamma} = \text{constant}$

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



- Slope of adiabatic curve, steeper than isothermal graph

$(PV) = k \rightarrow$ isothermal

$PV^{\gamma} = k \rightarrow$ adiabatic

$d(PV^{\gamma}) = 0$

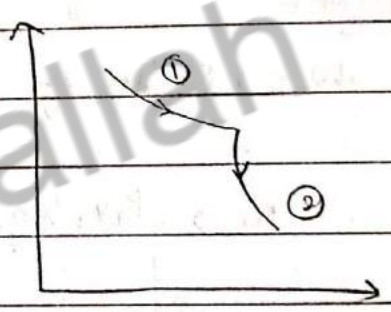
$P\,dV^{\gamma} dV + V^{\gamma} dP = 0$

$P\gamma V^{\gamma-1} dV + V^{\gamma} dP = 0$

$V^{\gamma} dP = -P\gamma V^{\gamma-1} dV$

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

$\left(\frac{dP}{dV}\right)_{adi} = -\gamma\left(\frac{P}{V}\right)$



① - isothermal

② - Adiabatic

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

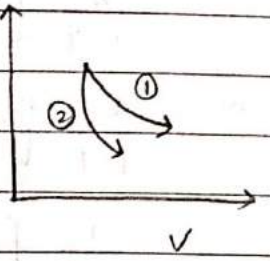
Q) JEE 2002 If ① and ② are P|V slopes of an adiabatic process, such that slope$_2$ > slope$_1$. What are the gases?

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,

$\gamma_m > \gamma_{di}$

$\therefore$ slope$_m$ > slope$_{di}$ $\therefore$ 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 $\Rightarrow$ $\frac{nRT}{V} V^\gamma$ = const $\Rightarrow$ $TV^{\gamma-1}$ = constant

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

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

$\frac{V_1^{\gamma-1}}{V_1^{\gamma-1}} = \frac{a}{32^{\gamma-1}}$ $\Rightarrow$ $32^{\gamma-1} = a = 32^{\frac{7}{5}-1} = 32^{2/5} = 2^2 = 4$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

$T_1 \longrightarrow V_1\ (5.6)$

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

$$T_1V_1^{\gamma-1} = T_2\left(\frac{V_1}{8}\right)^{\gamma-1}$$

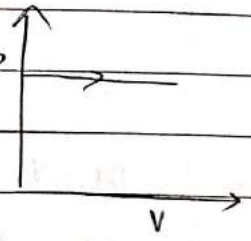
$\Rightarrow 4T_1 = T_2$

$$W = \frac{nR(T_2-T_1)}{\gamma-1} = \frac{0.125\times R(4T_1-T_1)}{\frac{2}{3}} = \frac{1}{4}\times\frac{R}{2}\times 3T_1\times 3$$
$$= \frac{9}{8}RT_1$$

③ **Isobaric Process** - $(\Delta P = 0)$

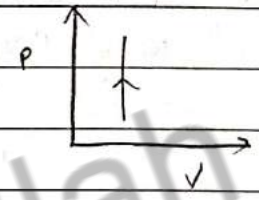
→ Constant pressure - P

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



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

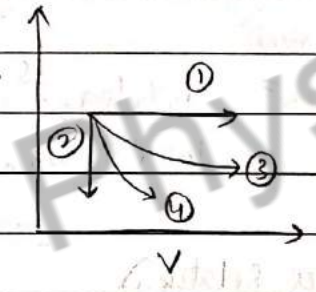
④ **Isochoric Process** - $(\Delta V = 0)$



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

$$Q = W + \Delta U$$

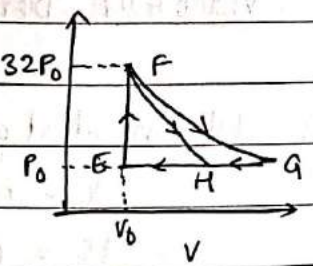
$\boxed{Q = \Delta U}$ all heat used to ↑ Internal E.



① - Isobaric
② - Isochoric
③ - Isothermal
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, F→H, F→G, E→F



List I (Process)	List II (work done)
p) G→E	$160P_0V_0\log_e 2$
q) G→H	$56P_0V_0$
r) F→H	$24P_0V_0$
s) F→G	$31P_0V_0$

1) GF is isothermal curve

work in GE is PΔV, but V_2 = not given, from GF $P_1V_1 = P_2V_2$

$32P_0V_0 = P_0\cdot(32V_0)$

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

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^γ = constant $\gamma = \frac{5}{3}$

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

$$\text{or, } 32 = x^{5/3}$$

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

$$\text{or, } V_2 = 8V_0$$

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

3) F → H is adiabatic

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

4) F → G is isothermal

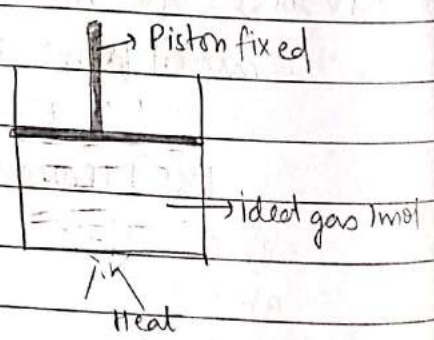
$$W = nRT \log_e \frac{V_2}{V_1} = P_1V_1 \log_e \frac{V_2}{V_1} = 32P_0V_0 \log_e \frac{32V_0}{V_0}$$

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

$$= 160 P_0V_0 \log_e 2$$

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

case I - Let an ideal gas be heated at constant 'V'



$$Q = nC_V\Delta T$$

$$dQ = nC_V dT$$

$$= 1 \times C_V dT$$

$$W = \int P dV = 0 \quad (\Delta V = 0)$$

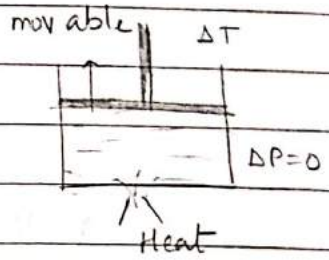
$$Q = W + \Delta U$$

$$dQ = dW + du$$

$$C_V dT = 0 + du$$

$$du = C_V dT$$

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



$$Q = nC_p\Delta T$$
$$= C_p\Delta T$$
$$dw = PdV$$
$$dQ = du + dw$$
$$C_pdT = du + PdV$$

For ideal gas, ΔU only dependent on ΔT and nothing else $\therefore dU = C_vdT$

$$C_pdT = C_vdT + PdV$$

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

$PdV + V\cancel{dP}^{0} = RdT$

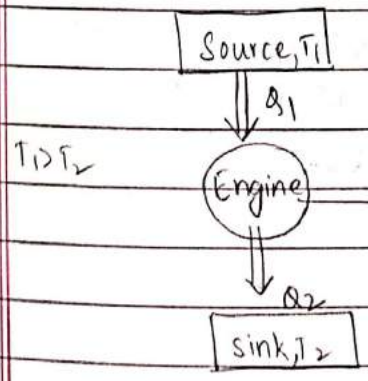
$\Delta P = 0 \quad \therefore PdV = RdT$

$$C_pdT = C_vdT + RdT$$
$$C_p = C_v + R$$
$$C_p - C_v = R$$

Video #08 – 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)

Heat Engine -
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 % $= \frac{\text{Work done}}{\text{Heat supplied}} \times 100$

$$Q_1 = w + Q_2$$
$$Q_1 - Q_2 = w$$
$$= \frac{w}{Q_1} \times 100$$
$$\text{or, } \frac{Q_1 - Q_2}{Q_1} \times 100$$

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

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

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

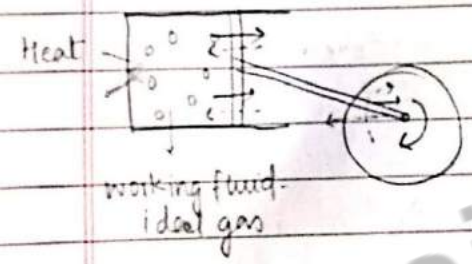
→ $\eta = 100\%$ or, 1 only if $Q_2 = 0$, ie heat can't be fully extracted for work

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

But not possible

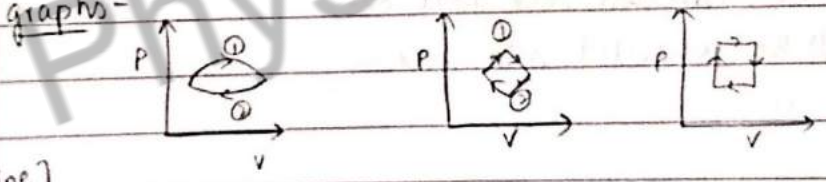
→ There has to be little wastage of heat ($Q_2 \neq 0$)

Working of Engine -

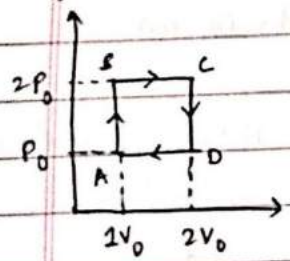


→ When the gas expands, piston moves out and work done to move front
→ Then due to inertia, rod moved back and gas compresses
→ one cycle completed (1 exp + 1 comp)

graphs -



[Heat Engine]



	ΔU	W	Q
A→B	$\oplus \frac{3}{2} RT_0$	0	$\frac{3}{2} RT_0$
B→C	$\oplus \frac{3}{2} R 2T_0$	$2P_0V_0$ $(2RT_0)$	$\frac{7}{2} RT_0$
C→D	$\frac{3}{2} R(-2T_0)$	0	$-3RT_0$
D→A	$\frac{3}{2} R(-T_0)$	$P_0(-V_0) = -RT_0$	$-2.5RT_0$

B to D - heat extracted → Q_1 → Heat gain by engine to work (W)

Heat loss after work (W) → Q_2 → D to A heat rejected

RT_0 - work (W)

1 mole monoatomic gas

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

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

then $2P_0 \cdot 2V_0 = nRT$ ~~or, $x = \frac{1}{2}\left(\frac{V_0}{2}\right)$~~

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

$2T_1 = T_2$

At A - $P_0V_0T_0$ B - $P_0V_0 2T_0$ C - $2P_0 2V_0 4T_0$ D = $P_0, 2V_0, 2T_0$

Net ΔU in 1 cycle = 0

work done = RT_0 → forward exp - return comp

Q lost total = $-5.5RT_0$ as work = RT_0 and total = 0

Thermodynamics - 09

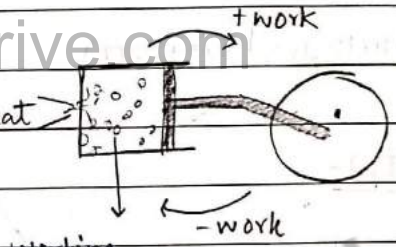
Carnot's Engine

- Carnot's Heat Engine
- Working, graph
- Derivation of $\eta = 1 - \frac{T_2}{T_1}$ with depth
- Refigerator
- 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



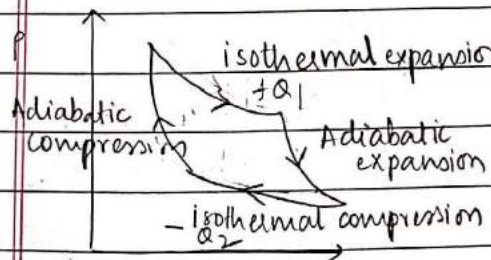
Working fluid → ideal gas, net work +ve

1 complete cycle → one stroke

Carnot's Engine - Hypothetical engine

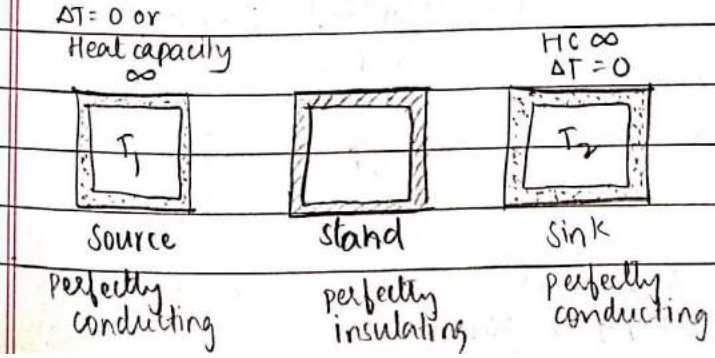
↓

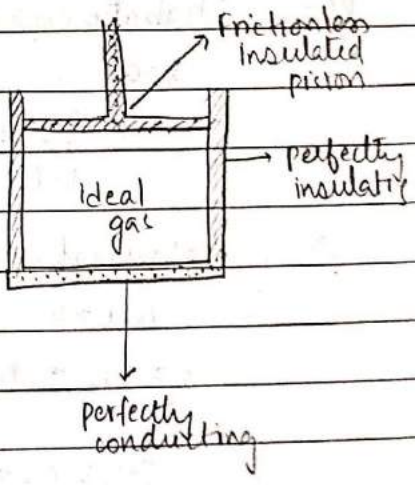
Most effective engine → Revessible Engine → η = max of any such engine which works b/w same two temp T_1 & T_2



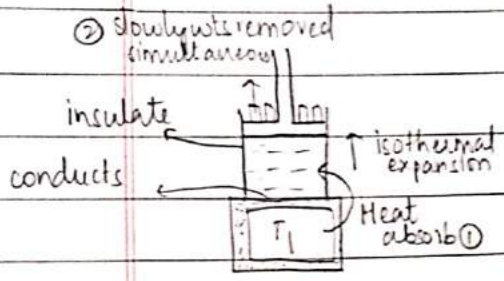
$$\eta = 1 - \frac{Q_2}{Q_1} = 1 - \frac{T_2}{T_1}$$

STROKE OF CARNOT'S ENGINE

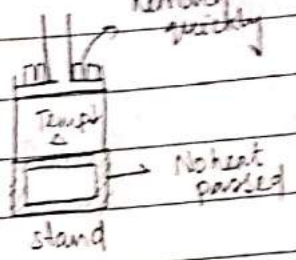




Step 1-



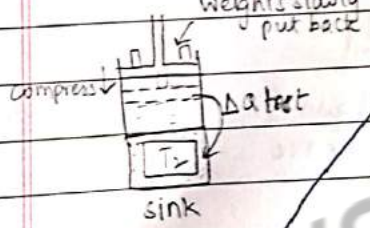
Step 2-



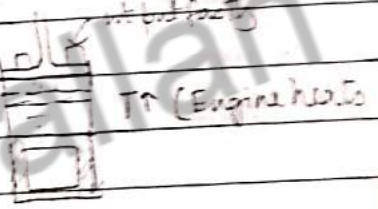
$P_1 V_1 T_1$ —— +ve work ——→ $P_2 V_2 T_1$

(isothermal expansion) (adiabatic expansion)

Step 3-



Step 4-



+ve work

-ve work

$P_3 V_3 T_2$ ←—— -ve work ——— $P_4 V_4 T_2$

(isothermal compression) (adiabatic compression)

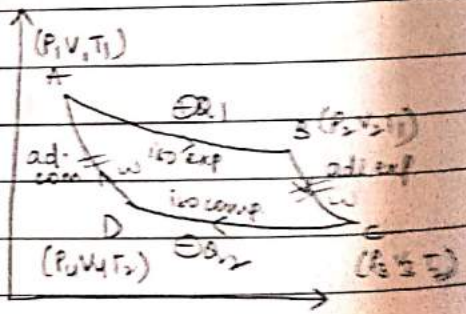
AB- Isothermal expansion

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

$\Delta Q = w + \Delta U \quad (\Delta U \to 0)$

$\Delta Q = w$

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



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

$\Delta U = 0$

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

Total $\Delta U = 0$

Total $w = w_1 + w_2 + w_3 + w_4 = w_{net}$ $\quad (w_2 = -w_4)$

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

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

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

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

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

$$P_1P_2P_3P_4 \times V_1V_2^\gamma V_3V_4^\gamma = P_1P_2P_3P_4 \times V_1^\gamma V_2 V_3^\gamma V_4$$

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

$(\gamma-1)\sqrt{\ }$ →

$$V_2V_4 = V_3V_1$$

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

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

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

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

Q1) 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

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

$$\Rightarrow 1 - \frac{500}{500} = \frac{w}{10^4} \Rightarrow \frac{10^4}{5} = w \Rightarrow 0.2 \times 10^4 \Rightarrow 2000J$$

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

$$\eta = \frac{1}{6} = 1 - \frac{T_2}{T_1} \qquad \eta' = \frac{1}{3} = 1 - \frac{(T_2 - 65)}{T_1}$$

$$\frac{T_2}{T_1} = \frac{5}{6} \qquad \frac{2}{3} = \frac{T_2 - 65}{T_1} \quad \frac{2T_2 - 130}{2T_1} = \frac{4}{6}$$

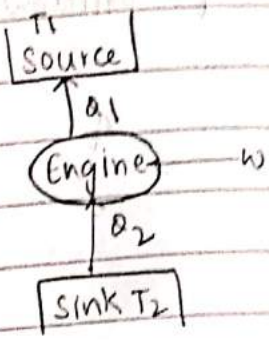
$2T_2 - 130 = T_2$

$T_2 = 130$

or, $T_1 = \frac{T_2 \times 6}{5} = \frac{130 \times 6}{5} = 156$

solve, $T_2 = 52$

REFRIGERATOR



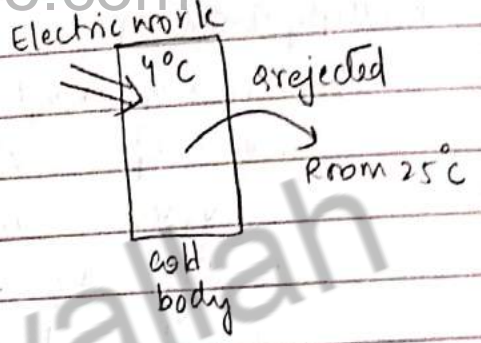
"Reverse Heat Engine"

→ 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

$Q_1 = W + Q_2$

$T_1 > T_2$



→ Removing heat from cold To hot body is a <u>non-spontaneous process</u>, 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 refigerator $T = -3°C$, 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 $= Q_1$

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

$Q_1 - Q_2 = W = 10 - 9 = 1\,J$ $\therefore \frac{W}{Q_1} = \frac{10}{9} - 1 = \frac{10-9}{9} = \frac{1}{9}$ $\therefore Q_1 = 9$

<u>Coefficient of Performance</u>

Heat Rejected should be ↑,

Work done ↓

$$K = \frac{Q_2}{W} = \frac{Q_2}{Q_1 - Q_2}$$

$$K = \frac{T_2}{T_1 - T_2}$$

For work done in a Polytropic Process

Any process in which PV^{α} = 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 ⇒ $W = \int P\,dV$ $\qquad P = \frac{K}{V^{\alpha}}$

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

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

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

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

Heat capacity

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

$$nC_{Poly}\Delta T = \frac{nR\Delta T}{(1-\alpha)} + nC_V\Delta T \qquad \frac{C_P}{C_V} = \gamma \Rightarrow C_P = \gamma \cdot C_V$$

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

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

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