Thermodynamics

44 : <u>Internal Energy</u>

Total Energy of gas molecules in the form of translational, rotational, & vibrational energy

<u>Change in internal energy</u>

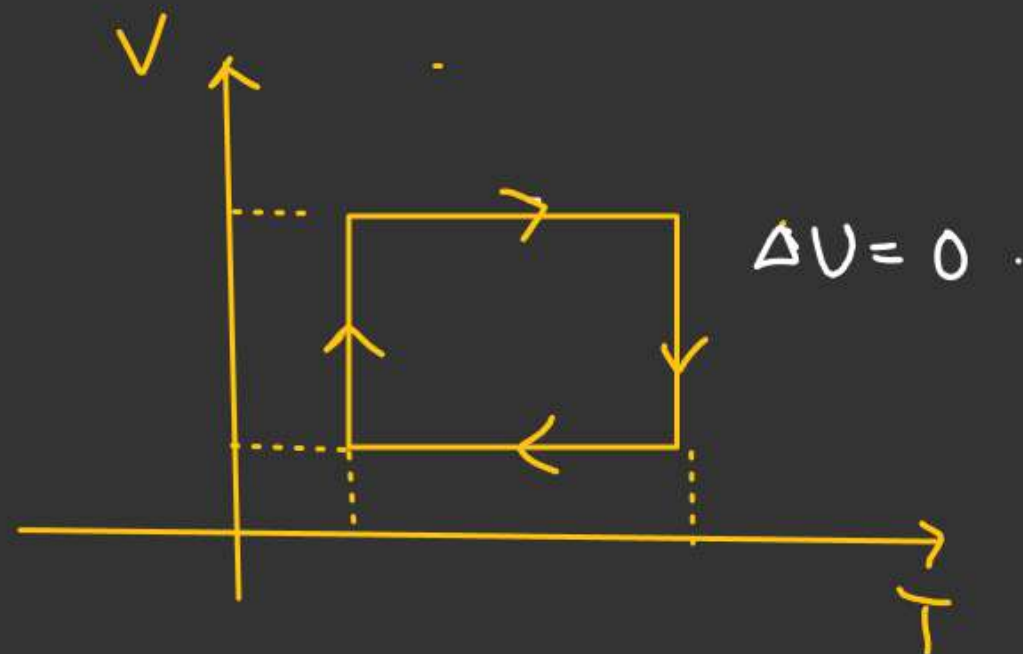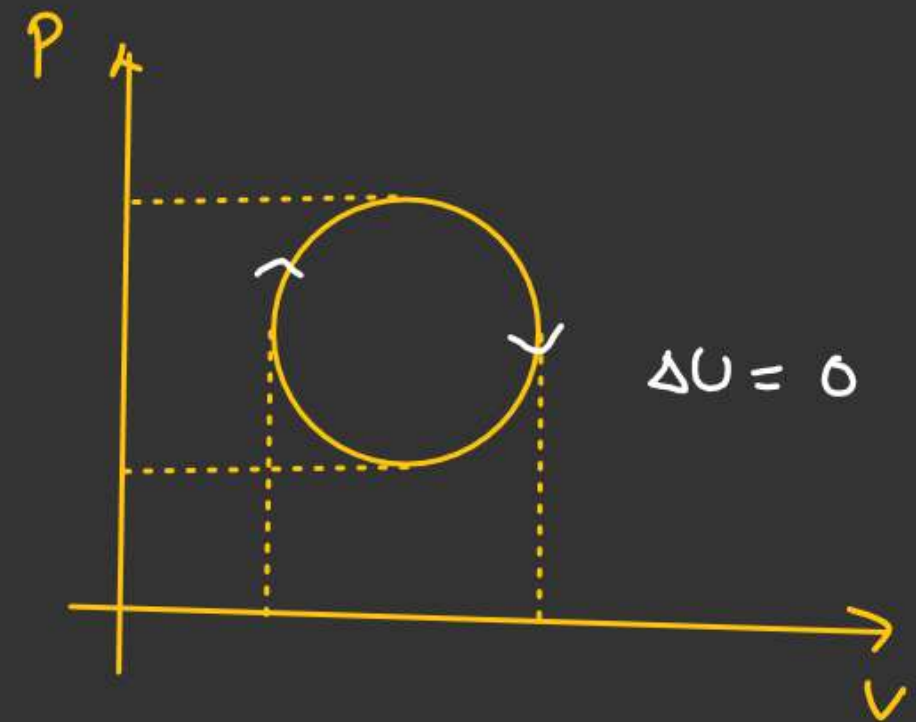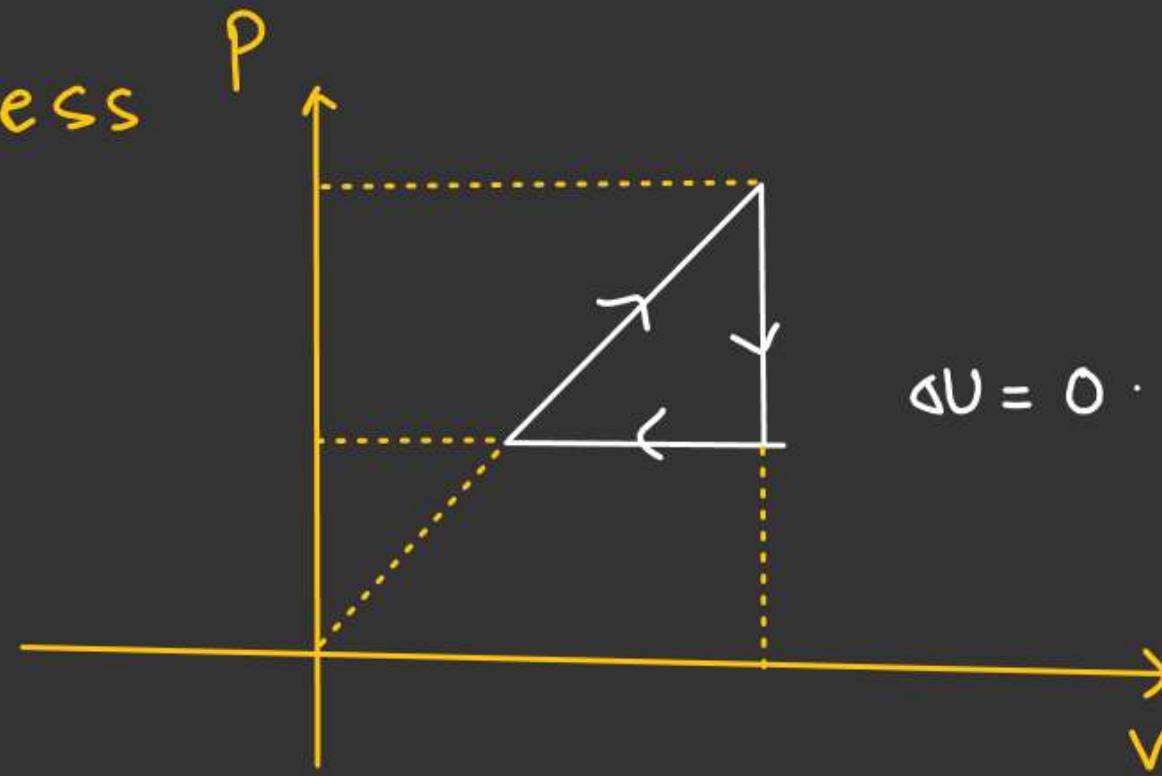$\Delta U \longrightarrow$ state function

$$\Delta U_{I} = \Delta U_{II} = \Delta U_{III}$$

I

II

III

U_1

U_2

Thermodynamics

Ex. For Cyclic Process

$$\boxed{\Delta U = 0}$$
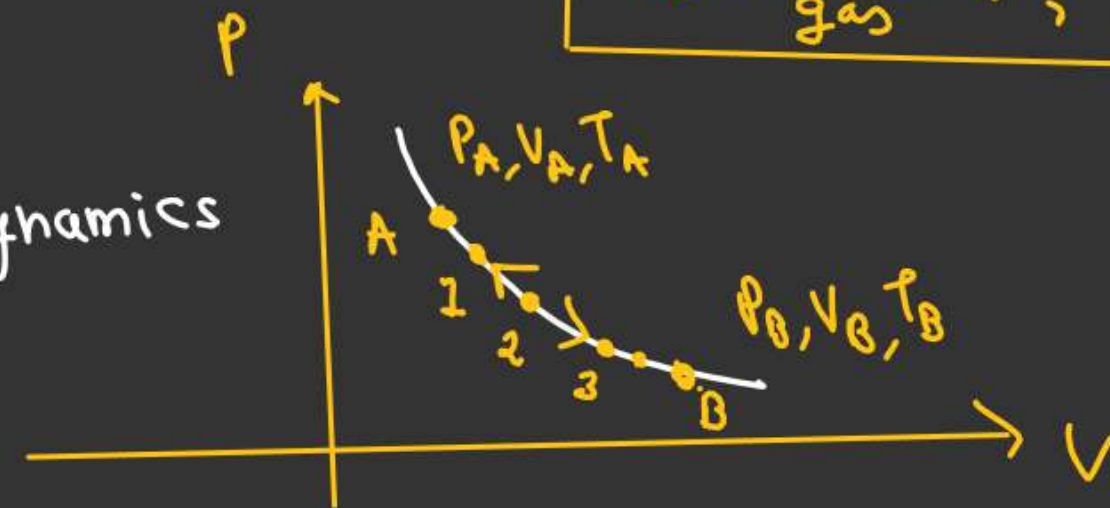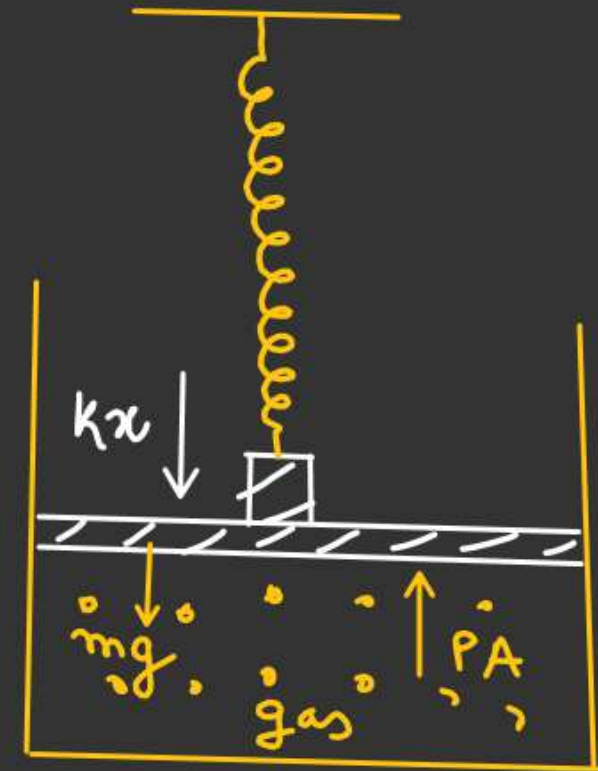

$\Delta U = 0$

$\Delta U = 0$

$\Delta U = 0$

Reversible process

- System is in equlibrium with Surrounding.

- Only possible when process occur very slowly.

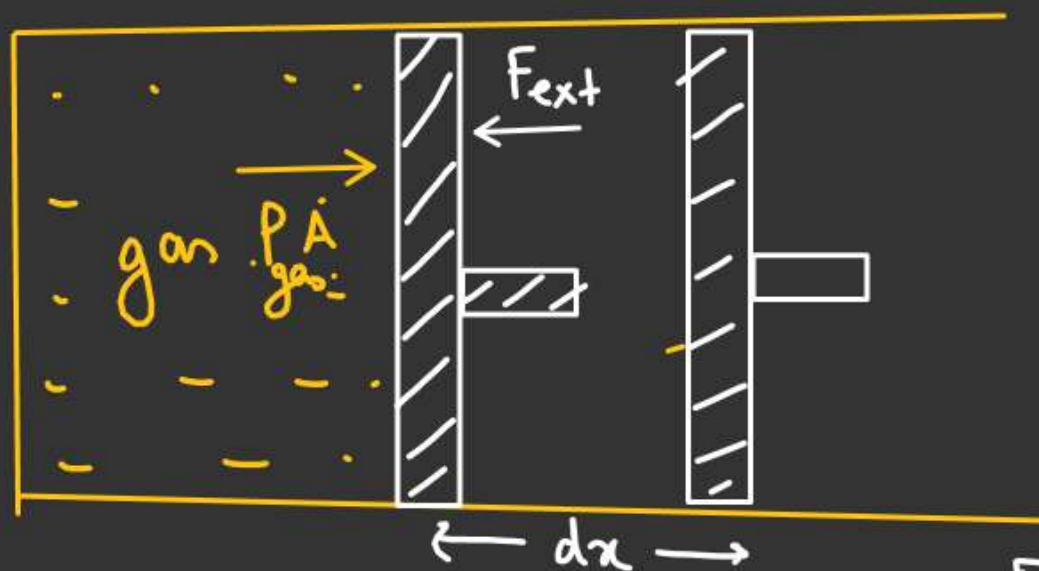- For reversible process always force balance on piston.

$$PA = mg + Kx$$

$$\boxed{P = \frac{mg}{A} + \frac{Kx}{A}}$$

- In Reversible process all the thermodynamics variables can reachived.

Thermodynamics

☆☆. Thermodynamic work (Reversible process)

$$\int dW_{gas} = \int P_{gas} \cdot A \, dx$$

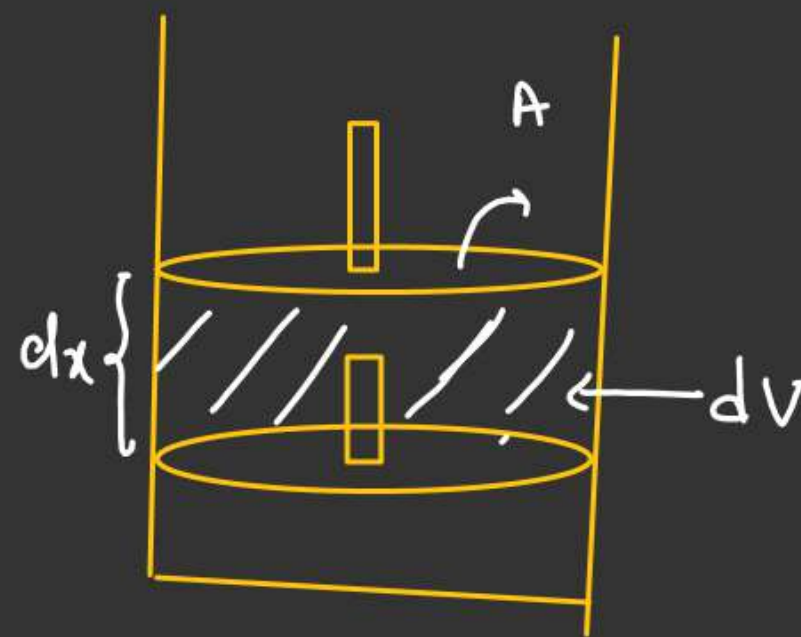$$\boxed{W_{gas} = \int P_{gas} \, dV}$$

$A \, dx = dV$

↓

Cross sectional area of piston

For piston to move very slowly

$$F_{ext} = P_{gas} A$$

$$\int dW_{ext\,agent} = -f_{ext} \cdot dx = -\int P_{gas} A \, dx$$

$$W_{ext\,agent} = -\int P_{gas} \, dV$$

Thermodynamics

$$W = \int_{V_i}^{V_f} P \cdot dV$$

$$P = f(V)$$

$P = C$ only for Isobaric.

$W_{\text{by the gas}} = +ve$

$W_{\text{on the gas}} = -ve$

$W_{\text{on the gas}} \longrightarrow$ Volume decreases (Compressional work)

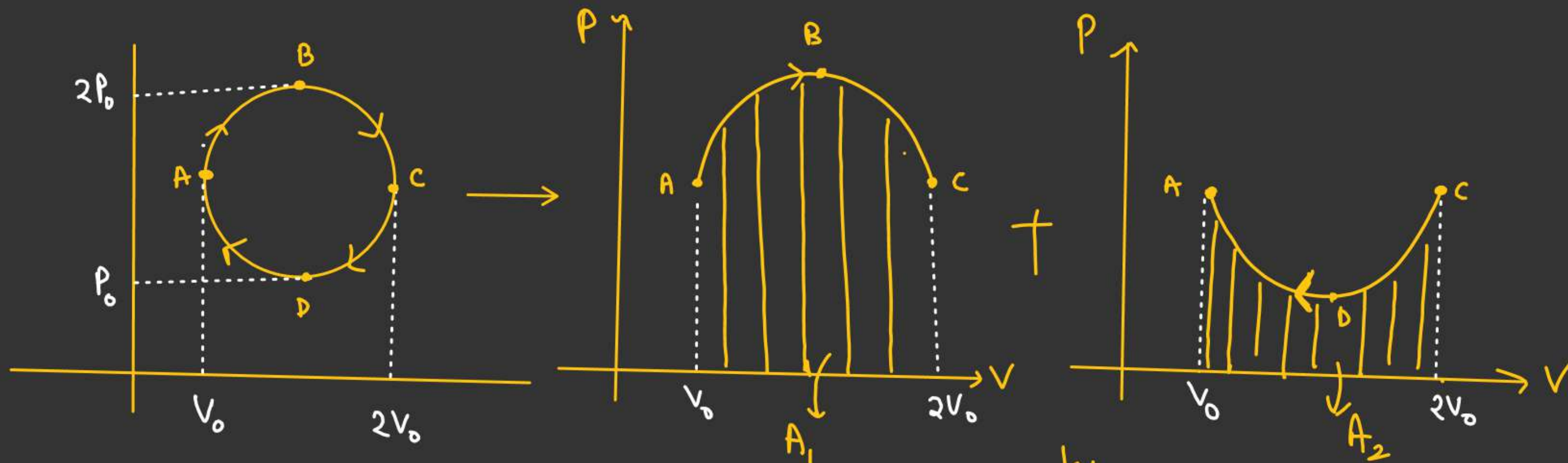$W_{\text{by the gas}} \longrightarrow$ Volume increases (Expansional work done)

Area under curve $= \int_{V_i}^{V_f} P \cdot dV$

Thermodynamics

Thermodynamic work done in Cyclic process

$$(W_{ABC}) = +A_1$$
$\underset{\text{By the gas.}}{\downarrow}$

$$W_{CDA} = \ominus A_2$$

If Cycle is clockwise $\underset{\text{on the gas.}}{}$ ✓

$$A_1 > A_2 \Rightarrow W_{net} > 0 \Rightarrow \text{By the gas.}$$

If Cycle in anticlockwise

$$W_{net} = (-A_1 + A_2) \Rightarrow A_1 > A_2 \Rightarrow \underset{\text{on the gas.}}{W_{net} = -ve}$$

$$W_{net} = W_{ABC} + W_{CDA}$$

$$= (A_1 - A_2)$$

$\hookrightarrow$ Area of Cycle

Thermodynamics

Q& / Thermodynamic work done in Cyclic process

P axis with values $2P_0$, $\frac{3P_0}{2}$, P_0; points A, B, C, D on circle; V axis with V_0, $2V_0$

① W_{net} = Area of Ellipse.

$$= \pi ab. = + \frac{\pi P_0 V_0}{4} \; J.$$

$$2a = V_0 \implies a_0 = \frac{V_0}{2}$$

$$2b = P_0 \implies b = \frac{P_0}{2}$$

② $\underline{W_{compressional}}$ = $\begin{pmatrix} \text{Area of} \\ \text{Rectangle} \end{pmatrix} - \frac{1}{2}\begin{pmatrix} \text{Area of} \\ \text{Ellipse} \end{pmatrix}$
   ↳ On the gas.

$$- \left[\frac{3P_0 V_0}{2} - \frac{1}{2}\left(\frac{\pi P_0 V_0}{4} \right) \right]$$

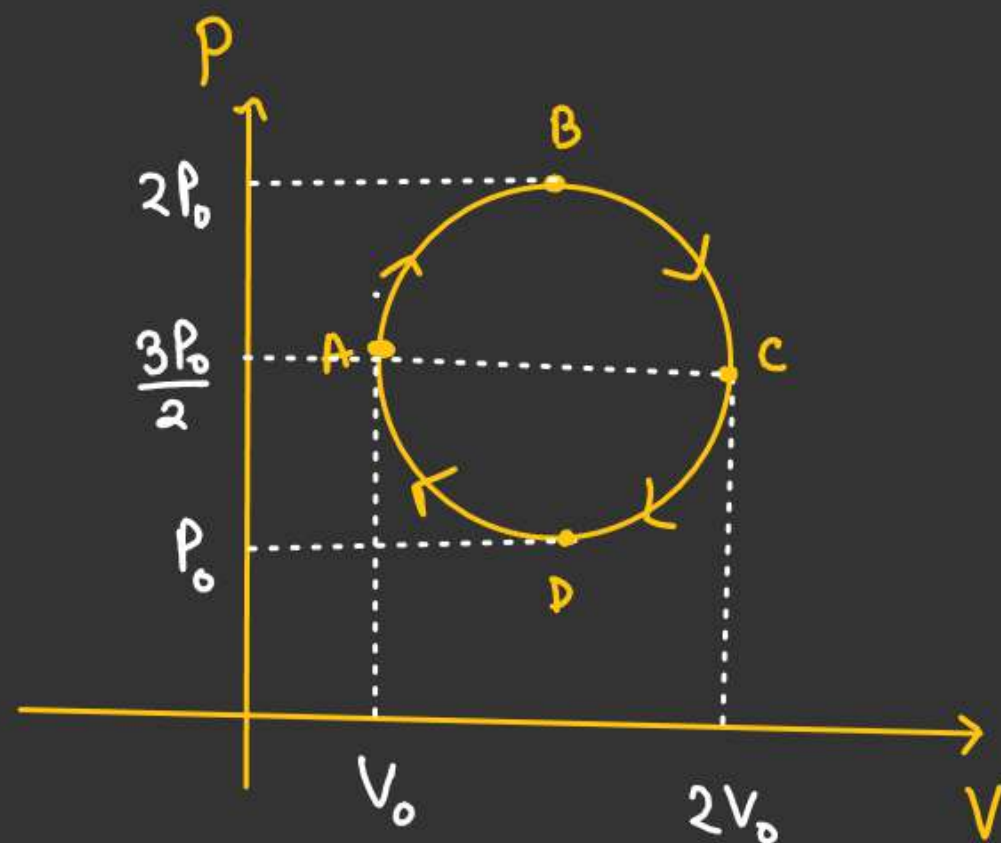$$- \left[\left(\frac{3 P_0 V_0}{2} - \frac{\pi P_0 V_0}{8} \right) \right] J.$$

Find

1) W_{net} = ?

2) $W_{compressional}$ = ?

3) $W_{expansional}$ = ?
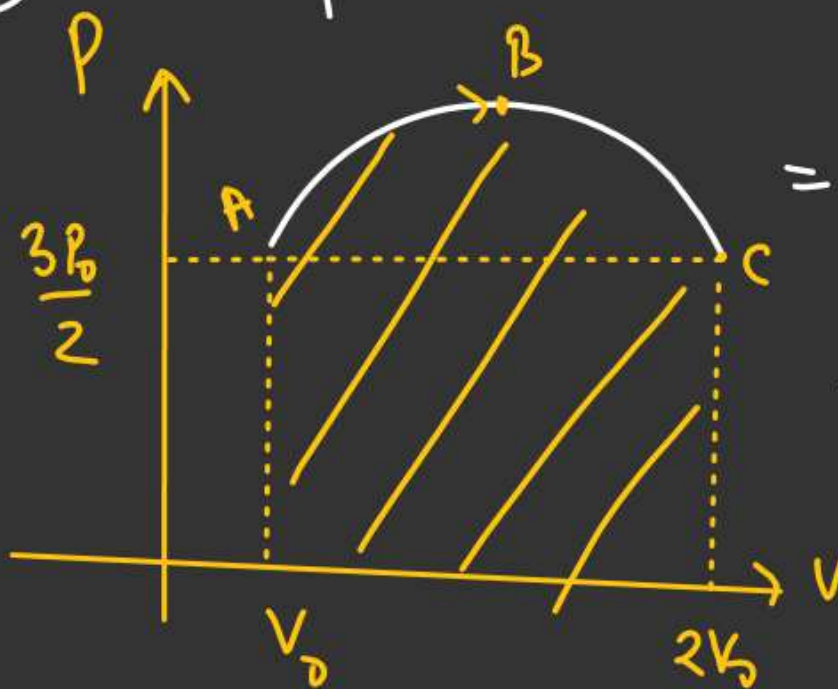
Thermodynamics

Thermodynamic work done in Cyclic process

&& /.

P

$2P_0$ .... B

$\frac{3P_0}{2}$ ..... A C

P_0 ....

D

V_0 $\quad$ $2V_0$ $\quad$ V

③ $W_{expansional} = \frac{1}{2}(\text{Area of Ellipse}) + \text{Area of Rectangle}$

P

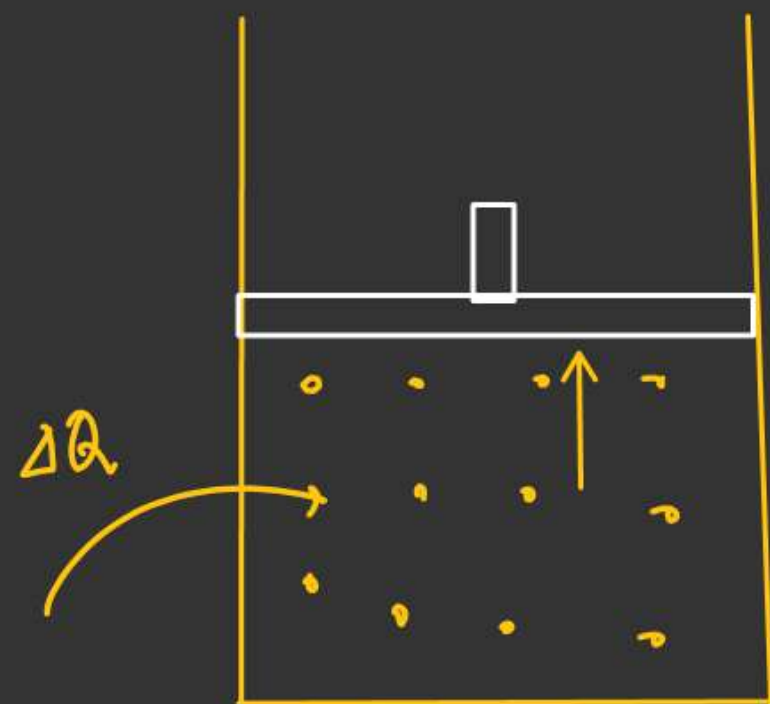$\frac{3P_0}{2}$ ...... A .... B C

V_0 $\quad$ $2V_0$ $\quad$ V

$= \frac{1}{2}\left(\frac{\pi P_0 V_0}{4}\right) + \left(\frac{3P_0 V_0}{2}\right)$

$= \left(\pi \frac{P_0 V_0}{8} + \frac{3P_0 V_0}{2}\right) J.$

Find

1) $W_{net} = ?$

2) $W_{compressional} = ?$

3) $W_{expansional} = ?$

Thermodynamics

1st Law of thermodynamics (Based on energy conservation)

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

Change in
internal
Energy

work done.

ΔQ

$\Delta Q_{given} = +ve$

$\Delta Q_{released} = -ve$

$\Delta W_{on\ the\ gas} = -ve$

$\Delta W_{by\ the\ gas} = +ve$

Thermodynamics

Thermodynamics process

Isobaric $(P = C)$

$\rightarrow$ Molar heat Capacity.

$$C = \frac{1}{n}\left(\frac{dQ}{dT}\right)$$

$\downarrow$

Heat given to raise the temp of 1 mol of gas by $1°C$.

At Constant pressure

$$C \rightarrow C_p$$

$$C_p = \frac{1}{n}\frac{(dQ)}{dT} \rightarrow \text{at Constant pressure.}$$

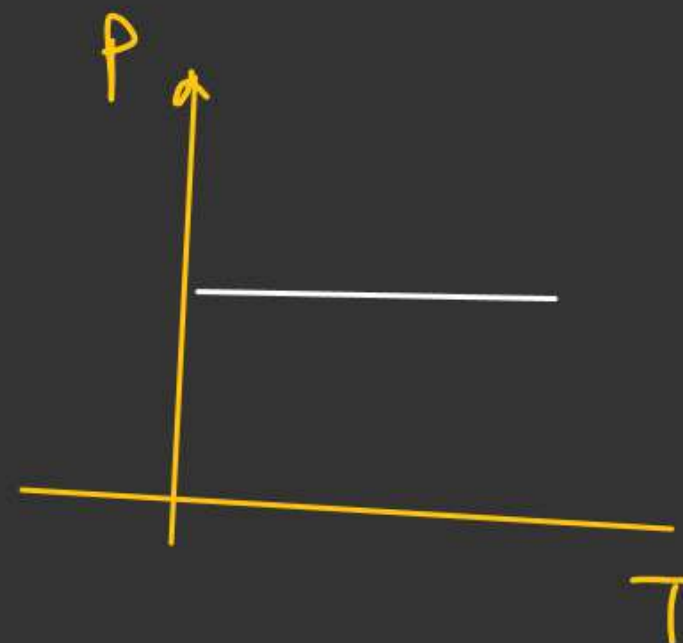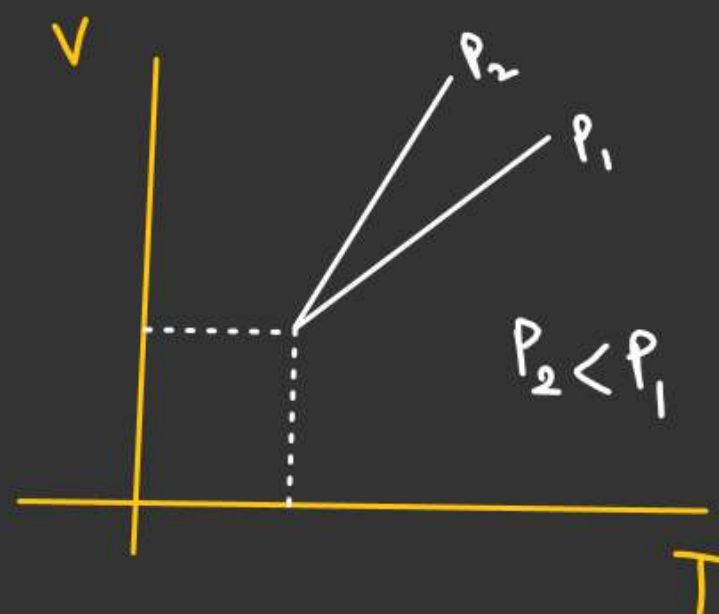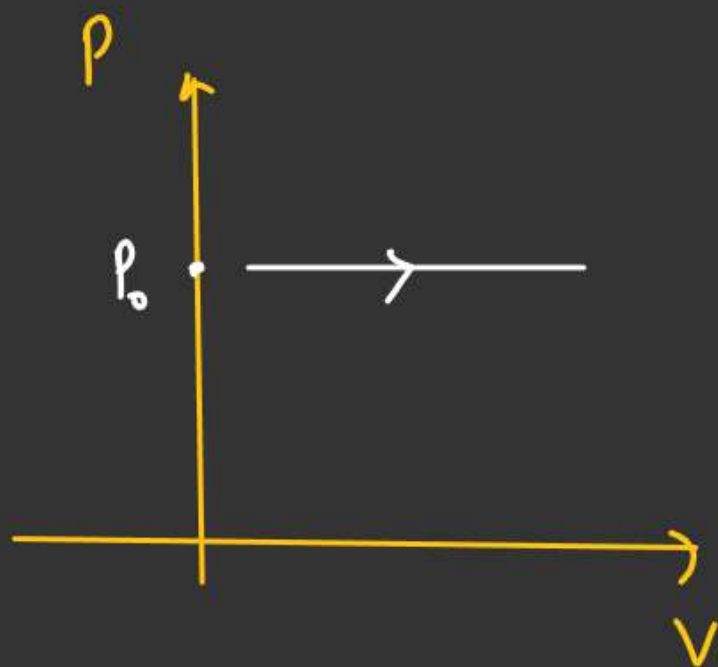$\rightarrow$ ## Work done.

$$P = C$$

$$\int_0^W dW = P\int_{V_i}^{V_f} dV$$

$$\boxed{W = P(V_f - V_i)}$$

$$PV_i = nRT_i$$

$$PV_f = nRT_f$$

$$\boxed{W = nR(T_f - T_i)}$$

Thermodynamics

P

P_0 •————————→

V

V

P_2

P_1

$P_2 < P_1$

T

P

T

$PV = nRT$

$V = \left(\dfrac{nR}{P}\right)T$

$y = m\,x$

$m = \left(\dfrac{nR}{P}\right)$

Thermodynamics

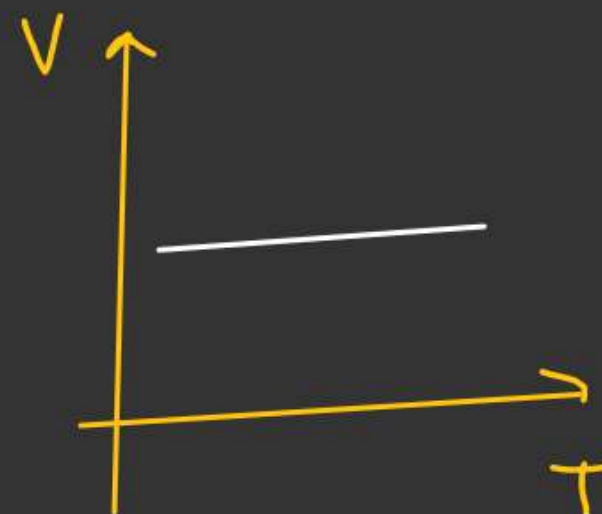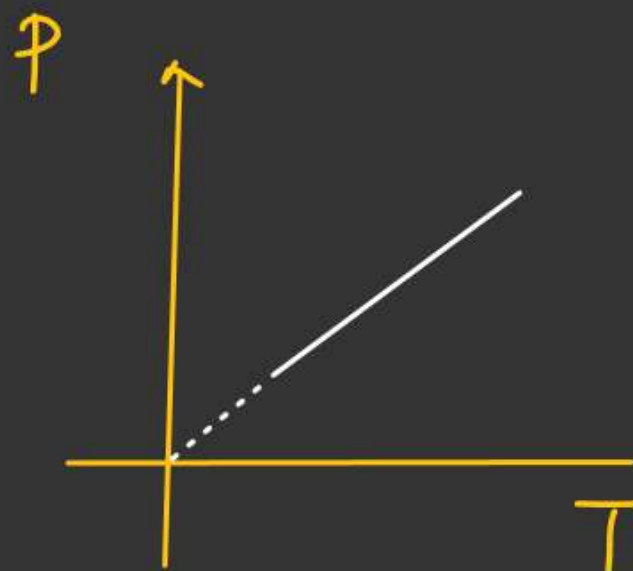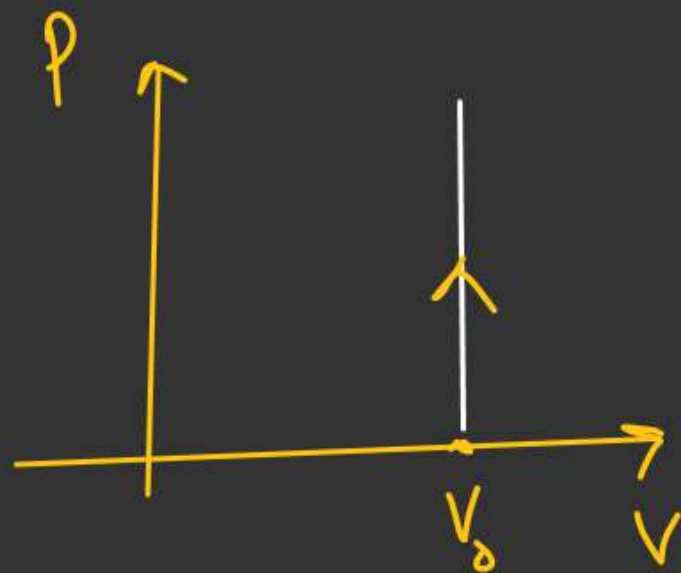**14.** ## Isochoric $(V = c)$

→ Molar heat Capacity.

At Constant volume.

$$C \to C_V = \frac{1}{n} \frac{(dQ)}{dT}$$

$$PV = nRT$$
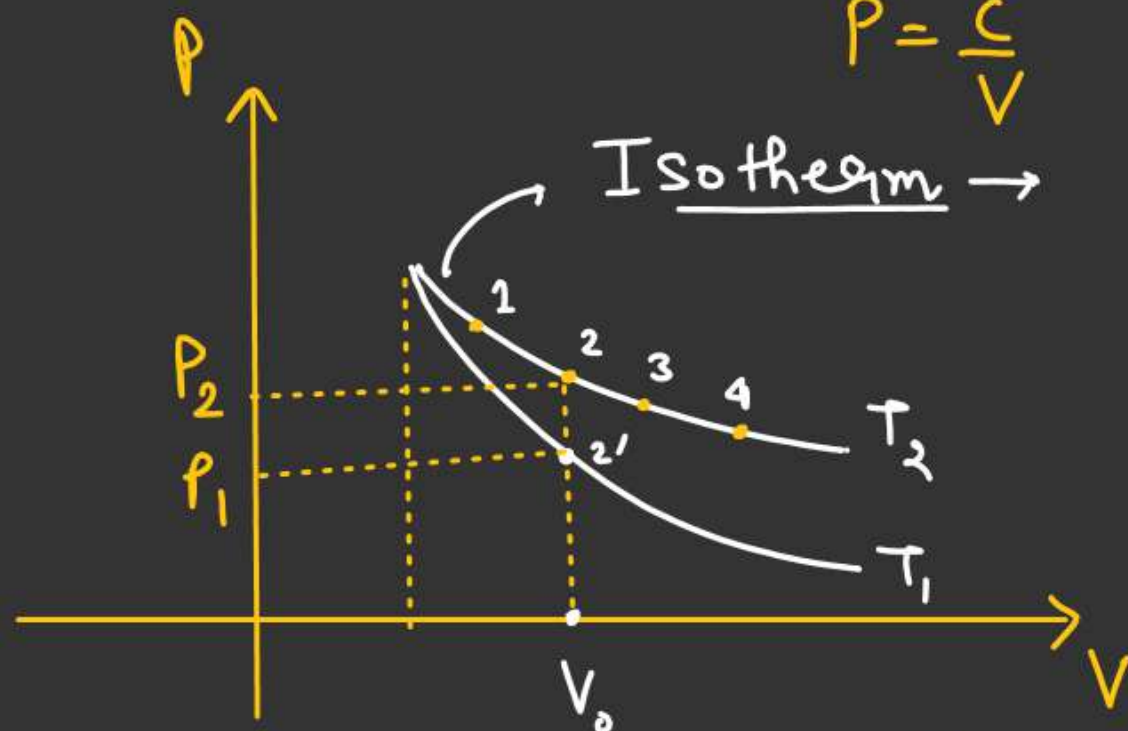$$P = \left(\frac{nR}{V}\right)T$$

→ **Work** $= 0$

Isothermal

P-V Curve

$$PV = nRT$$

$$P = \frac{(nRT)}{V} \rightarrow C$$

$$P = \frac{C}{V}$$

Isotherm → locus of all the points.
at same temp.

$$T_1 = T_2 = T_3 = T_4 = T_2$$

$$T_2 > T_1 \implies \text{Higher isotherms are at higher temp.}$$

$$P_2 V_0 = nRT_2$$

$$P_1 V_0 = nRT_1$$

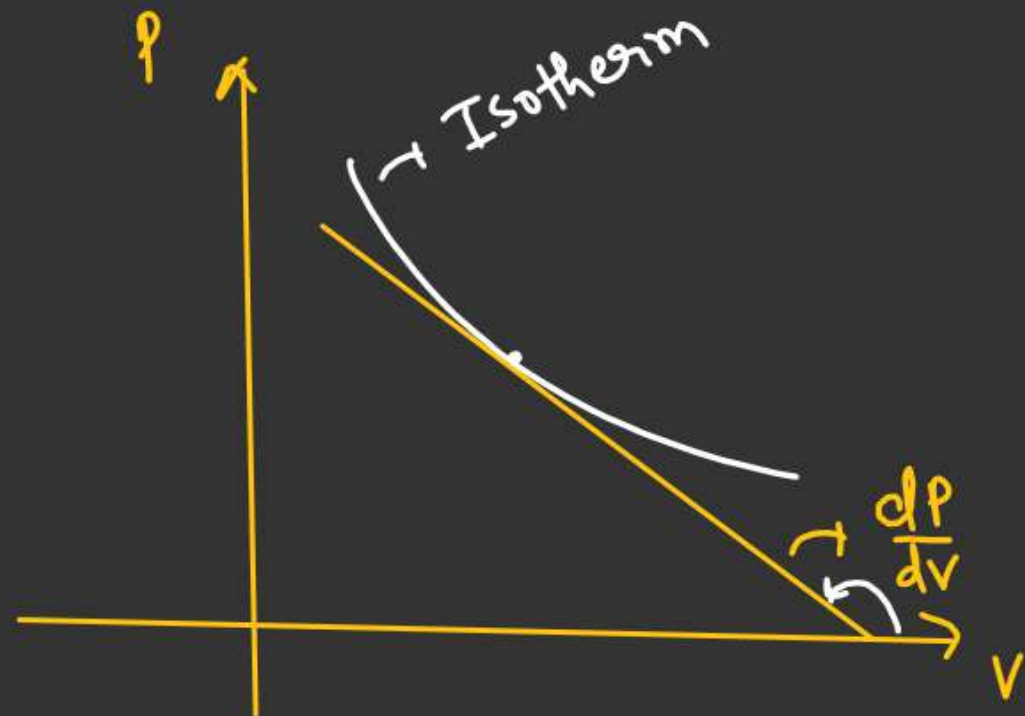$$\frac{P_2}{P_1} = \frac{T_2}{T_1}$$

$$P_2 > P_1$$

$$T_2 > T_1$$

Thermodynamics

44.

Slope of isotherm

$$P = nRT$$

Actually the diagram shows P vs V curve labeled "← Isotherm" with tangent line slope $\frac{dP}{dV}$.

$$\boxed{\text{Slope of isotherm} = -\left(\frac{P}{V}\right)}$$

$$PV = nRT$$

$$\frac{d}{dV}(PV) = \frac{d}{dV}(nRT)$$

$$P \cdot \frac{d}{dV}(V) + V\left(\frac{dP}{dV}\right) = 0$$

$$P + V\left(\frac{dP}{dV}\right) = 0$$

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

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

Bulk Modulus.

$$B = \frac{-dP}{\left(\frac{dV}{V}\right)} \quad \begin{array}{l}\rightarrow \text{Volumetric Stress} \\ \rightarrow \text{Volumetric Strain}\end{array}$$

$$B_{\text{isothermal}} = -V\left(\frac{dP}{dV}\right)$$

$$= P.$$

$$\boxed{B_{\text{isothermal}} = P.}$$

Thermodynamics

Work done in isothermal

$$P_i, V_i \, T \longrightarrow P_f, V_f, T$$

$$\int_0^W dw = \int_{V_i}^{V_f} P \, dv$$

$$PV = nRT$$

$$P = \left(\frac{nRT}{V}\right)$$

$$W = nRT \int_{V_i}^{V_f} \frac{dv}{V}$$

$$P_i V_i = nRT$$

$$P_f V_f = nRT$$

$$\frac{P_i}{P_f} = \left(\frac{V_f}{V_i}\right)$$

$$\boxed{\begin{array}{l} W = nRT \ln\left(\dfrac{V_f}{V_i}\right) \\[4mm] W = nRT \ln\left(\dfrac{P_i}{P_f}\right) \end{array}}$$