


# Thermodynamics

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# Calculation of work in diff. processes →

## (A) Isothermal Process → (Ideal gas)

$$T = \text{const.}$$

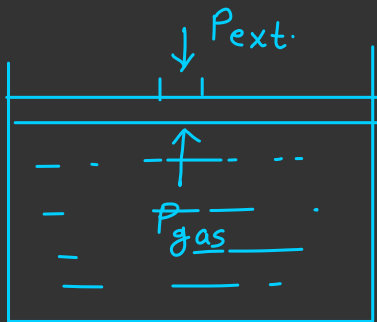
$$PV = \text{const.}$$

$$P_1 V_1 = P_2 V_2 = nRT$$

$$\Delta T = 0 \Rightarrow \Delta U = \Delta H = 0$$

$$q = -w$$

## (i) Reversible isothermal Process →



$$P_{\text{ext.}} = P_{\text{gas}} \pm dp$$

$\therefore dp$  is very small

$$\therefore P_{\text{gas}} \pm dp \approx P_{\text{gas}}$$

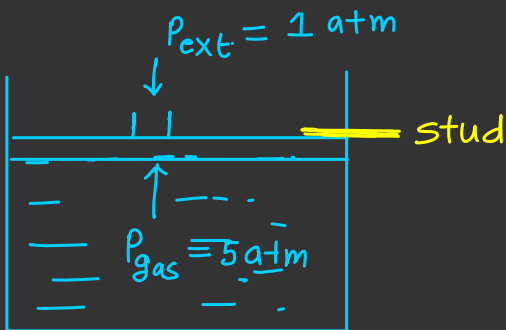
$$\therefore P_{\text{ext.}} \approx P_{\text{gas}} = \frac{nRT}{V}$$

$$W = - \int_{V_1}^{V_2} P_{\text{ext.}} \cdot dV$$

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

$$\begin{aligned}
 W &= -nRT \ln \frac{V_2}{V_1} = -2.303 nRT \log_{10} \frac{V_2}{V_1} \\
 &= -nRT \ln \frac{P_1}{P_2} = -P_1 V_1 \ln \frac{V_2}{V_1} \\
 &= -P_1 V_1 \ln \frac{P_1}{P_2} = -P_2 V_2 \ln \frac{V_2}{V_1} \\
 &= -P_2 V_2 \ln \frac{P_1}{P_2}
 \end{aligned}$$

(ii) Irreversible isothermal Process →

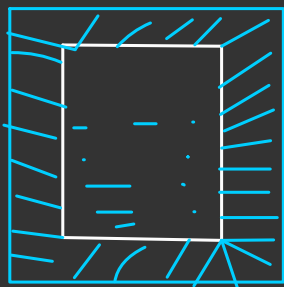


$$\begin{aligned}
 P_{\text{ext.}} &= \text{Const.} \\
 W &= - \int_{V_1}^{V_2} P_{\text{ext.}} \cdot dV \\
 &= -P_{\text{ext.}} \int_{V_1}^{V_2} dV
 \end{aligned}$$

$$W = -P_{\text{ext.}} (V_2 - V_1)$$

### (iii) Free expansion (Expansion in vacuum) $\rightarrow$

When a gas is allowed to expand against zero external pressure then it is called free expansion. It is an Irr. Process.



Insulated  
evacuated closed  
container

$$P_{\text{ext}} = 0$$

$$\Rightarrow w = 0$$

Isothermal free expansion

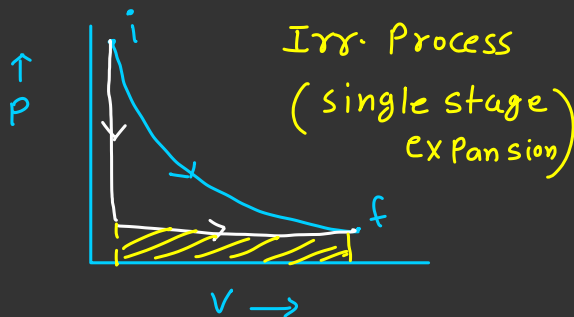
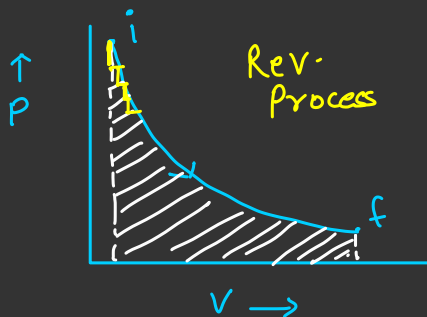
$$\Rightarrow \Delta U, \Delta H = 0$$

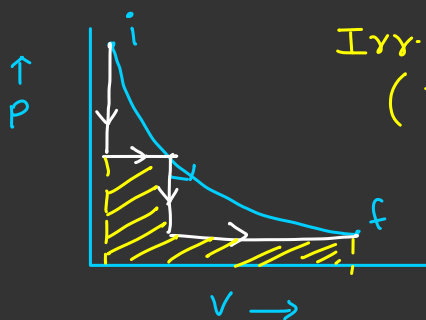
$$q = 0$$

Comparison b/w magnitude of work done in  
Rev. and Irr. Processes  $\rightarrow$

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### (i) Expansion $\rightarrow$

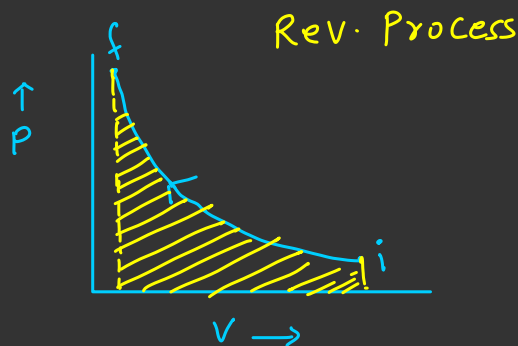




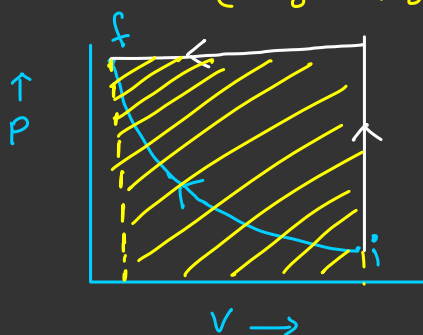
Irr. Process  
(Two stage expansion)

$$|w|_{\text{Rev.}} > |w|_{\text{Irr.}} \rightarrow \text{Expansion}$$

(ii) compression  $\rightarrow$



Rev. Process



Irr. Process  
(single stage comp.)

$$|w|_{\text{Irr.}} > |w|_{\text{rev.}} \rightarrow \text{Compression}$$

**Illustration - 2** Five mole of an ideal gas at 293 K are expanded isothermally from an initial pressure 0.4 kPa to a final pressure of 0.1 kPa against a constant external pressure of 0.1 kPa. (a) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$ .  
(b) Calculate the corresponding value of  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  if the above process is carried out reversibly.

Sol<sup>n</sup>  $n = 5, T = 293 \text{ K}$

$$P_1 = 0.4 \text{ kPa} \quad , \quad P_2 = 0.1 \text{ kPa}$$

(a) Irr. isothermal Process

$$\Delta U = \Delta H = 0$$

$$\begin{aligned} W &= -P_{\text{ext.}} (V_2 - V_1) \\ &= -P_{\text{ext.}} \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right) \\ &= -0.1 \times 5 \times 8.314 \times 293 \left( \frac{1}{0.1} - \frac{1}{0.4} \right) \\ &\quad \text{Joule} \end{aligned}$$

$$q = -W$$

(b) Rev. isothermal Process  $\rightarrow$

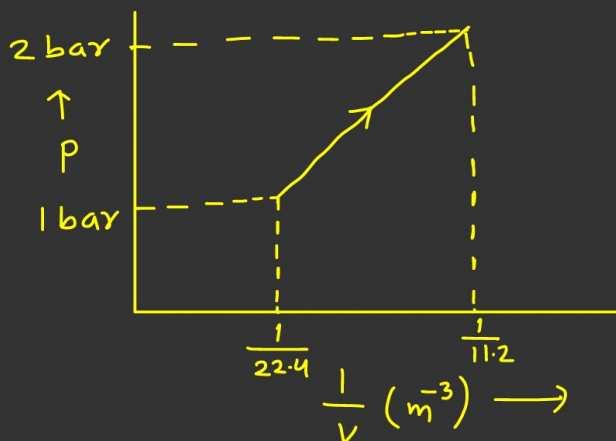
$$\Delta U = \Delta H = 0$$

$$\begin{aligned} W &= -nRT \ln \frac{P_1}{P_2} \\ &= -5 \times 8.314 \times 293 \ln \frac{0.4}{0.1} \quad \text{J} \end{aligned}$$

$$q = -W$$

Q.

calculate  $\Delta U, \Delta H, q, w$  for a given amount of an ideal gas — (process is carried out reversibly)



$$[\ln 2 = 0.7]$$

Sol<sup>n</sup>

Rev. Isothermal Process ( $p_1 v_1 = p_2 v_2$ )

$$w = -p_1 v_1 \ln \frac{v_2}{v_1}$$
$$= -1 \times 22.4 \ln \frac{11.2}{22.4}$$

$$= 22.4 \times 0.7 = 15.68 \text{ bar-m}^3$$

$$= 15.68 \times 10^5 \frac{\text{N}}{\text{m}^2} \times \text{m}^3$$

$$= 1568 \text{ kJ}$$

$$\Delta U = \Delta H = 0$$

$$q = -w = -1568 \text{ kJ}$$

## (B) Isobaric Process $\rightarrow$

$$w = - \int_{V_1}^{V_2} p_{\text{ext.}} \cdot dV$$

Rev. isobaric Process  $\Rightarrow p_{\text{ext.}} = p_{\text{gas}}$

$$w = -p \int_{V_1}^{V_2} dV$$

$$\begin{aligned} w &= -p(V_2 - V_1) = -nR(T_2 - T_1) \\ &= -p\Delta V = -nR\Delta T \end{aligned}$$

$$q = \Delta U - w$$

$$q_p = n c_{V,m} \Delta T - (-nR\Delta T)$$

$$= n\Delta T (c_{V,m} + R)$$

$$= n\Delta T \cdot c_{p,m} = \Delta H$$

## (C) Isochoric Process $\rightarrow$

$$V = \text{const.} \Rightarrow \Delta V = 0$$

$$w = 0$$

$$q_V = \Delta U - w = \Delta U - 0 = \Delta U$$



(D) Adiabatic Process  $\rightarrow$

$$q = 0$$

$$\Delta U = w$$

$$\int dU = \int dw$$

$$\int n C_{V,m} dT = \int -P_{\text{ext}} \cdot dV$$

(i) Rev. adiabatic Process —

$$\int_{T_1}^{T_2} \frac{\cancel{nR}}{\gamma-1} dT = - \int_{V_1}^{V_2} \frac{\cancel{nR}T}{V} \cdot dV$$

$$\frac{1}{\gamma-1} \int_{T_1}^{T_2} \frac{dT}{T} = - \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\frac{1}{\gamma-1} \ln \frac{T_2}{T_1} = \ln \frac{V_1}{V_2}$$

$$\ln \frac{T_2}{T_1} = \ln \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$T_1 \cdot V_1^{\gamma-1} = T_2 \cdot V_2^{\gamma-1}$$

or

$$TV^{\gamma-1} = \text{const.}$$

$$P_1^{1-\gamma} \cdot T_1^{\gamma} = P_2^{1-\gamma} \cdot T_2^{\gamma}$$

or

$$P^{1-\gamma} \cdot T^{\gamma} = \text{const.}$$

$$P_1 V_1^{\gamma} = P_2 V_2^{\gamma} \quad \text{or} \quad PV^{\gamma} = \text{const.}$$

(ii) Irr. adiabatic Process  $\rightarrow$

$$\int_{T_1}^{T_2} n C_{V,m} dT = \int_{V_1}^{V_2} -P_{\text{ext}} \cdot dV$$

$$\frac{nR}{\gamma-1} (T_2 - T_1) = -P_{\text{ext}} (V_2 - V_1)$$

$$\frac{\cancel{nR}}{\gamma-1} (T_2 - T_1) = -P_{\text{ext}} \left( \frac{\cancel{nR} T_2}{P_2} - \frac{\cancel{nR} T_1}{P_1} \right)$$

$$\frac{T_2 - T_1}{\gamma-1} = -P_{\text{ext}} \left( \frac{T_2}{P_2} - \frac{T_1}{P_1} \right)$$

Q. one mole of a nonlinear triatomic ideal gas is expanded irreversibly adiabatically at 300 K from 16 atm to 1 atm.

calculate  $q$ ,  $\Delta U$ ,  $w$ ,  $\Delta H = ?$

Sol<sup>n</sup>  $\rightarrow$   $P_1 = 16 \text{ atm}$ ,  $P_2 = 1 \text{ atm} = P_{\text{ext}}$

$$n = 1, \quad \gamma = 4/3$$

$$T_1 = 300 \text{ K}$$

$$q = 0$$

$$\frac{T_2 - T_1}{\gamma - 1} = -P_{\text{ext}} \left( \frac{T_2}{P_2} - \frac{T_1}{P_1} \right)$$

$$T_2 = 230 \text{ K}$$

$$\begin{aligned} w = \Delta U &= n C_{V,m} (T_2 - T_1) \\ &= 1 \times 3R (230 - 300) \end{aligned}$$

$$\begin{aligned} \Delta H &= n C_{P,m} (T_2 - T_1) \\ &= 1 \times 4R (230 - 300) \end{aligned}$$

(ii) Calculate  $q$ ,  $\Delta U$ ,  $\Delta H$ ,  $w$  if Process is carried out reversibly.

$$\begin{aligned} q &= 0 \\ P_1^{1-\gamma} \cdot T_1^\gamma &= P_2^{1-\gamma} \cdot T_2^\gamma \\ T_2 &= T_1 \left( \frac{P_1}{P_2} \right)^{\frac{1-\gamma}{\gamma}} \\ &= 300 \left( \frac{16}{1} \right)^{-1/4} = 150 \text{ K} \end{aligned}$$

$$\begin{aligned} W &= \Delta U = n C_{V,m} (T_2 - T_1) \\ &= 1 \times 3R (150 - 300) \end{aligned}$$

$$\Delta H = 1 \times 4R (150 - 300)$$

(E) Polytropic Process  $\rightarrow$

$$PV^x = \text{const.}, \quad TV^{x-1} = \text{const.}$$

$$P^{1-x} \cdot T^x = \text{const.}$$

$$(0 \leq x \leq \infty)$$

if  $x = 0 \Rightarrow P = \text{const.} \Rightarrow \text{Isobaric Process}$

$$\kappa = 1 \Rightarrow P V = \text{const.} \Rightarrow \text{Isothermal Process}$$

$$\kappa = \gamma \Rightarrow P V^\gamma = \text{const.} \Rightarrow \text{adiabatic process}$$

$$\kappa = \infty \Rightarrow V = \text{const.} \Rightarrow \text{Isochoric Process}$$

$$W = - \int_{V_1}^{V_2} P_{\text{ext}} \cdot dV$$

$$W = - \int_{V_1}^{V_2} P \cdot dV$$

$$P V^\kappa = K$$

$$P_1 V_1^\kappa = P_2 V_2^\kappa = K$$

$$= - \int_{V_1}^{V_2} K V^{-\kappa} dV = \frac{-K}{-\kappa+1} \left[ V_2^{-\kappa+1} - V_1^{-\kappa+1} \right]$$

$$W = \frac{P_2 V_2 - P_1 V_1}{\kappa - 1} = \frac{n R (T_2 - T_1)}{\kappa - 1} \quad *$$

Calculation of heat capacity for polytropic Process  $\rightarrow$

$$q = \Delta U - W$$

$$n \cdot C_{m, \Delta T} = n C_{V, m} \Delta T - \frac{n R \Delta T}{\kappa - 1}$$

molar  
heat  
capacity of ideal gas

$$C_m = C_{V,m} - \frac{R}{\gamma - 1}$$

Q. For a system containing an ideal mono-atomic gas undergoes a process in which ratio of  $P$  to  $V$  is equal to 1. Calculate molar heat capacity for the process.

$$\begin{aligned} \text{Sol}^n \quad \frac{P}{V} = 1 &\Rightarrow P V^{-1} = 1 \\ \gamma &= -1 \end{aligned}$$

$$\begin{aligned} C_m &= C_{V,m} - \frac{R}{\gamma - 1} \\ &= \frac{3}{2} R - \frac{R}{-2} \Rightarrow 2R \end{aligned}$$

Q. A Diatomic ideal gas undergoes a process in which  $PT^2 = \text{const.}$ , find the molar heat capacity for that process?

Sol<sup>n</sup> →

$$p T^2 = \text{const.}$$

$$p^{1-x} \cdot T^x = \text{const.} \Rightarrow p \cdot T^{\frac{x}{1-x}} = \text{const.}$$

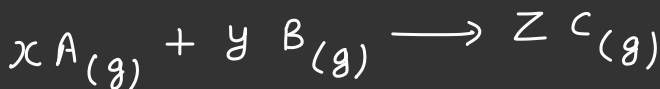
$$\frac{x}{1-x} = 2 \Rightarrow x = \frac{2}{3}$$

$$C_m = C_{V,m} - \frac{R}{x-1}$$

$$= \frac{5}{2} R - \frac{R \times 3}{-1} = \frac{11}{2} R$$

(F) work done in chemical Rx<sup>n</sup>/ phase transformation in open vessel/ closed vessel at const. temp. →

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$$\Delta V = z (V_m)_C - \left[ x (V_m)_A + y (V_m)_B \right]$$

$$(V_m)_A = (V_m)_B = (V_m)_C = V_m$$

$$\Delta V = V_m (z - x - y) = V_m \cdot \Delta n_g$$

$$= \frac{RT}{P} \cdot \Delta n_g$$

$$w = -\int p_{\text{ext}} \cdot dV = -p_{\text{ext}} \Delta V$$

In case of open container  $\Rightarrow p_{\text{ext}} = p_{\text{gas}} = p$

$$w = -\cancel{p} \cdot \frac{RT}{\cancel{p}} \cdot \Delta n_g$$

$$w = -\Delta n_g \cdot RT$$

24. 130 g of Zn is dissolved in dilute sulphuric acid in an open beaker. Find the work done in the process assuming isothermal operation. ↪ at 27°C

(A) -1200 cal      (B) -1800 cal      (C) +1800 cal      (D) +1200 cal

Sol<sup>n</sup> → molar mass of Zn = 65 gm/mol  
no. of moles of Zn = 2

$$w = -\Delta n_g \cdot RT$$



$$\Delta n_g = 2$$

$$w = -(2RT) = -2 \times 2 \times 300 \\ = -1200 \text{ cal.}$$



21. One mole of solid Zn is placed in excess of dilute  $\text{H}_2\text{SO}_4$  at  $27^\circ\text{C}$  in a cylinder fitted with a piston. Find the work done for the process if the area of piston is  $500\text{ cm}^2$  and it moves out by  $50\text{ cm}$  against a pressure of  $1\text{ atm}$  during the reaction.



- (A)  $-1.53\text{ KJ}$  (B)  $-2.53\text{ KJ}$  (C) zero (D)  $2.53\text{ KJ}$

Sol<sup>n</sup> →

$$W = -P_{\text{ext}} \cdot \Delta V$$

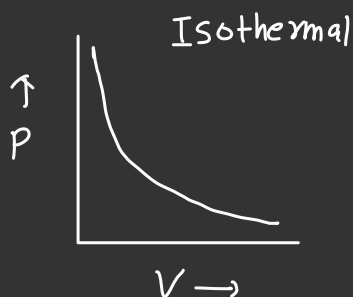
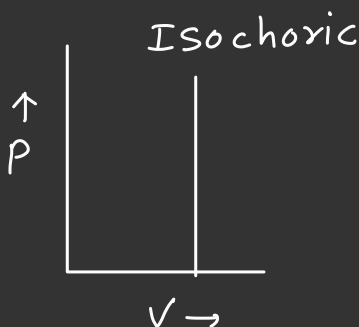
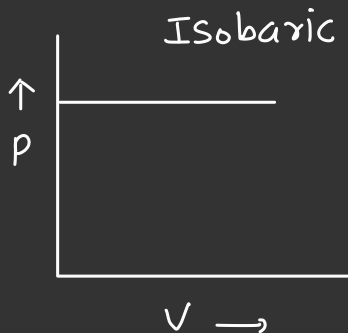
$$= -1 \times 500 \times 50 \quad (\Delta V = A \cdot \Delta x)$$

$$= -25000\text{ atm-cm}^3$$

$$= -25000 \times 1.01325 \times 10^5 \frac{\text{N}}{\text{m}^2} \times 10^{-6} \text{ m}^3$$

$$= -2.53\text{ KJ}$$

P-V curves →



Slope of P-V curve  $\Rightarrow \frac{dP}{dV}$   
for isothermal process

$$(PV = K)$$

$$\text{slope} = \frac{dP}{dV} = -\frac{K}{V^2}$$

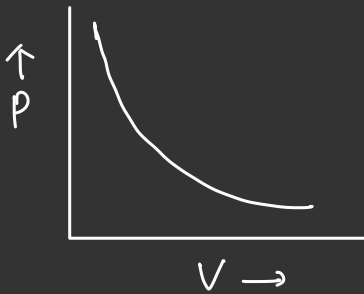
$$= -\frac{PV}{V^2} = -\frac{P}{V}$$

For adiabatic Process

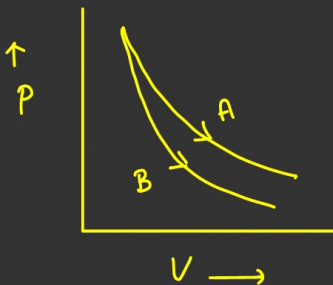
$$PV^\gamma = K \Rightarrow P = K V^{-\gamma}$$

$$\text{slope} = \frac{dP}{dV} = -K\gamma V^{-\gamma-1}$$

$$= -PV^\gamma \cdot \gamma \cdot V^{-\gamma-1} = -\gamma \frac{P}{V}$$

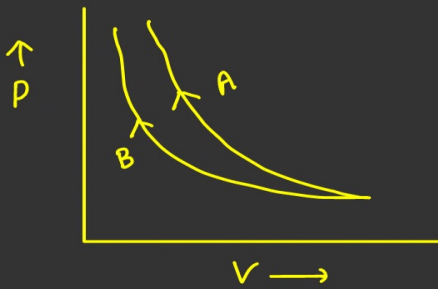


Q. Identify Isothermal and adiabatic Process in the following curves —



A = Isothermal

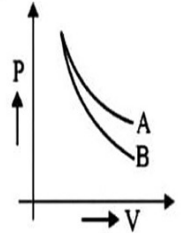
B = adiabatic



A = Adiabatic  
B = Isothermal

41. P - V plot for two gases (assuming ideal) during adiabatic processes are given in the figure. Plot A and plot B should correspond respectively to :

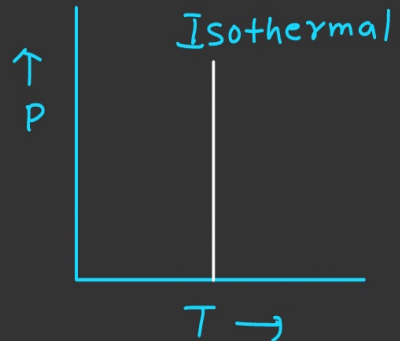
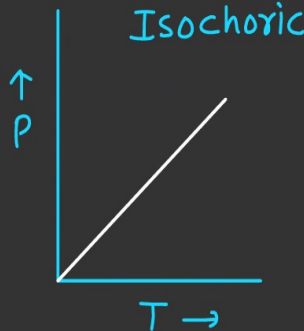
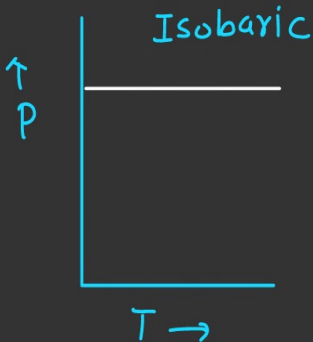
- (A) He and H<sub>2</sub>                      (B) H<sub>2</sub> and He  
(C) He and Ne                      (D) H<sub>2</sub> and Cl<sub>2</sub>



Sol<sup>n</sup>       $\gamma_B > \gamma_A$

$$\gamma_{He} = \frac{5}{3} \quad , \quad \gamma_{H_2} = \frac{7}{5}$$

p-T curve for different processes →



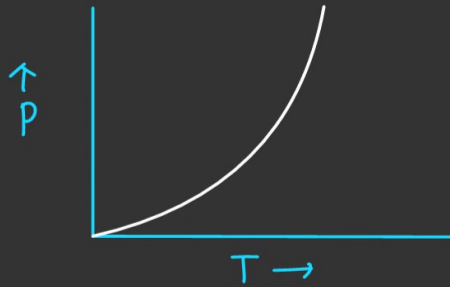
For adiabatic Process  $\rightarrow$

$$P^{1-\gamma} \cdot T^{\gamma} = K_3 \text{ (const.)}$$

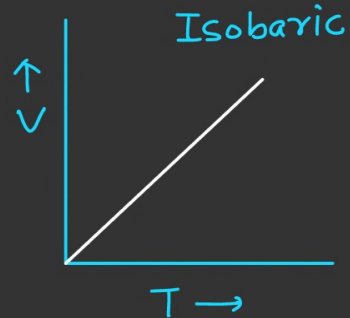
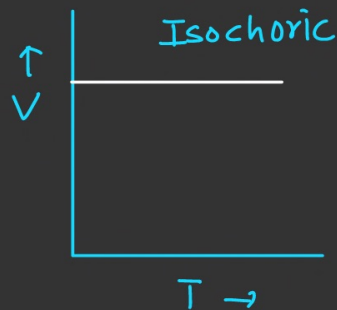
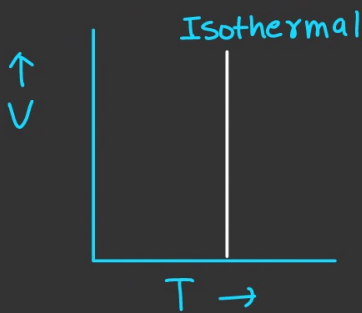
$$P \cdot T^{\frac{\gamma}{1-\gamma}} = K_3'$$

$$P = K_3' \cdot T^{\frac{\gamma}{\gamma-1}}$$

$$\therefore \frac{\gamma}{\gamma-1} > 1$$



V-T curve for different processes  $\rightarrow$

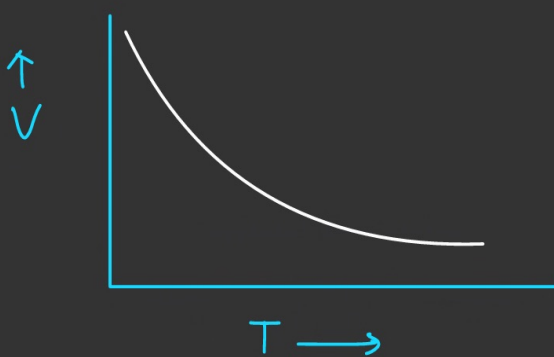


For adiabatic Process  $\rightarrow$

$$T V^{\gamma-1} = K_4 \text{ (const.)}$$

$$V \cdot T^{\frac{1}{\gamma-1}} = K_4'$$

$$V = K_4' \cdot T^{\frac{1}{1-\gamma}}$$



- \* During adiabatic expansion, cooling of gas takes place.
- \* During adiabatic compression, heating of gas takes place.

### Limitations of first law of thermodynamics (FLOT) →

- (1) F.L.O.T. is unable to predict the direction of change or feasibility (spontaneity) of a process in a particular direction.
- (2) F.L.O.T. doesn't give any information about the extent to which the change takes place.

Ex. Practically it is found that all of heat can be converted into work but F.L.O.T. fails to tell the extent to which interchange of heat into work takes place.

