

Thermodynamics-1

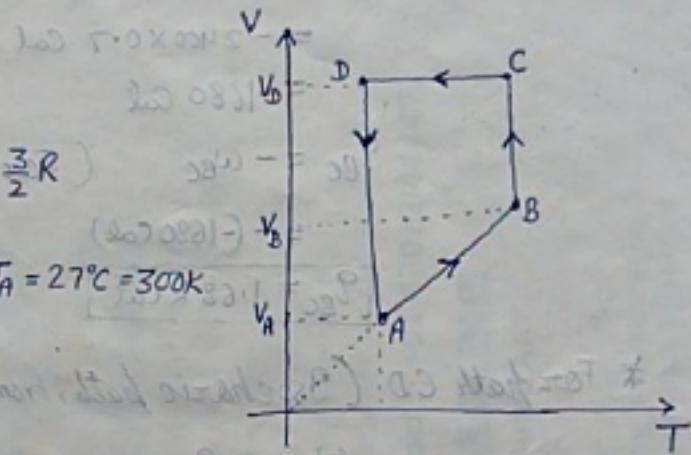
EXERCISE - S-II

Solution - 1 -

Given no. of moles $n = 2$

For monoatomic ideal gas $C_V = \frac{3}{2}R$

$$\frac{V_B}{V_A} = 2 ; \frac{V_D}{V_A} = 4 ; T_A = 27^\circ C = 300K$$



(a) For path AB

$V \propto T$ (From graph)

means $P = \text{Constant}$ (For ideal gas $PV = nRT$)

$$\Rightarrow \frac{V_B}{V_A} = \frac{T_B}{T_A}$$

(given $\frac{V_B}{V_A} = 2$)

$$\Rightarrow 2 = \frac{T_B}{300K} \Rightarrow T_B = 600K$$

(b) * For path AB (isobaric path; $P = \text{constant}$)

$$\Delta U_{AB} = nC_V \Delta T_{AB} = 2 \times \frac{3}{2}R \times (T_B - T_A)$$

$$\left(\frac{1}{2}\right) \times 2 \times \frac{3}{2}R \times (600 - 300) = 2 \times \frac{3}{2}R \times (600 - 300) = 900R = 900 \times 2 = 1800 \text{ Cal}$$

$$W_{AB} = -nR \Delta T_{AB} = -2 \times 2 \times (600 - 300) = -1200 \text{ Cal}$$

from 1st Law of Thermodynamics

$$\Delta U_{AB} = Q_{AB} + W_{AB}$$

$$1800 = Q_{AB} + (-1200) \Rightarrow Q_{AB} = 3000 \text{ Cal} = 3 \text{ KCal}$$

* For path BC (Isothermal path ; $T = T_B = T_C = 600\text{ K}$)

$$\Delta U_{BC} = n C_{Vm} \Delta T_{BC} = 0$$

$$W_{BC} = -nRT \ln\left(\frac{V_C}{V_B}\right)$$

$$= -2 \times 2 \text{ cal} \times 600 \ln(2)$$

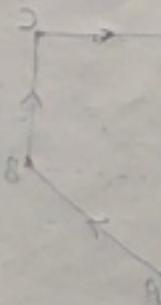
$$= -2400 \times 0.7 \text{ cal}$$

$$= -1680 \text{ cal}$$

$$q_{BC} = -W_{BC} \quad (\text{For Isothermal} ; \Delta U_{BC} = 0)$$

$$= -(-1680 \text{ cal})$$

$$q_{BC} = 1.68 \text{ kCal}$$



* For path CD (Isochoric path ; from graph $V_C = V_D = \text{Constant}$)

$$W_{CD} = 0$$

$$\Delta U_{CD} = n C_{Vm} \Delta T_{CD} = 2 \times \frac{3}{2} R (T_D - T_C)$$

$$= 2 \times \frac{3}{2} \times 2 \text{ cal} \times (300 - 600)$$

$$= -1800 \text{ cal}$$

$$\text{Now } q_{CD} = \Delta U_{CD} \quad (W_{CD} = 0 \text{ for Isochoric})$$

$$= -1800 \text{ cal}$$

$$q_{CD} = -1.8 \text{ kCal}$$

* For path DA (Isothermal path ; $T = T_D = T_A = 300\text{ K} = \text{Constant}$)

$$\Delta U_{DA} = n C_{Vm} (T_A - T_D) = 0$$

$$W_{DA} = -nRT \ln\left(\frac{V_A}{V_D}\right) = -2 \times 2 \text{ cal} \times 300 \cdot \ln\left(\frac{1}{4}\right)$$

$$= -1200 \times -2 \ln 2$$

$$= +2400 \times 0.7 \text{ cal} = 1680 \text{ cal}$$

$$q_{DA} = -W_{DA} \quad (\text{For Isothermal} ; \Delta U_{DA} = 0)$$

$$= -1680 \text{ cal}$$

$$q_{DA} = -1.68 \text{ kCal}$$

(c) Total work done on gas

$$W_{\text{total}} = W_{AB} + W_{BC} + W_{CD} + W_{DA}$$

$$= -1200 \text{ cal} + (-1680 \text{ cal}) + 0 + (1680 \text{ cal})$$

$$\boxed{W_{\text{total}} = -1.2 \text{ Kcal}}$$

So work done by gas = -1.2 Kcal ($\omega = 1.2 \text{ J} = -1.2 \text{ Kcal}$)

Solution-2-

no. of moles $n = 1$

Ideal gas : Lets first PV graph from given information

- (a) At constant volume ($V = \text{constant}$) Temperature rise from 298 K to 373 K
Isochoric path (Let AB path)

$P \propto T$

$$\underline{W_{AB} = 0} \quad (\text{isochoric path})$$

$$\text{Now } \Delta U_{AB} = Q_{AB} + W_{AB}^0 \quad (\text{from 1st law of thermodynamics})$$

$$\Rightarrow Q_{AB} = \Delta U_{AB} = nC_v \Delta T_{AB} \quad (\text{not useful, because } C_v \text{ not known})$$

- (b) At constant temperature (isothermally) volume doubled in vacuum freely

$$\underline{W_{BC} = 0} \quad (\text{free expansion; } P_{\text{ext}} = 0)$$

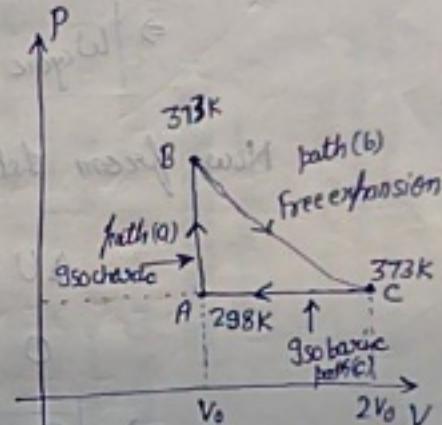
$$Q_{BC} = 0 \quad (\Delta T_{BC} = 0 ; \text{isothermal})$$

$$\Delta U_{BC} = 0 \quad (\Delta T_{BC} = 0 ; \text{isothermal})$$

- (c) Coiled reversibly at constant pressure (isobaric path) to 298 K

$$W_{CA} = -nR\Delta T_{CA} = -1 \times 8.314 \text{ J} \times (298 - 373) = -8.314 \times -75$$

$$\Rightarrow \underline{W_{CA} = 623.55 \text{ J}}$$



Since the whole process is cyclic

So

$$\boxed{\Delta U_{\text{cycle}} = 0}$$

(U, & H are state functions)

$$\boxed{\Delta H_{\text{cycle}} = 0}$$

$$W_{\text{cycle}} = W_{\text{total}} = W_{AB} + W_{BC} + W_{CA}$$

$$= 0 + 0 + 623.55 \text{ J}$$

$$\Rightarrow \boxed{W_{\text{cycle}} = 623.55 \text{ J}}$$

Now, from 1st law of thermodynamics

$$\Delta U = Q + W$$

$$0 = Q + 623.55 \text{ J}$$

$$\Rightarrow \boxed{Q_{\text{cycle}} = -623.55 \text{ J}}$$

Solution - 3

n-moles of gas following equation of state $P.V = nRT - \frac{n^2a}{V}$

$$\Rightarrow P = \frac{nRT}{V} - \frac{n^2a}{V^2}$$

work done by gas reversibly from v_i to v_f

$$W_{\text{gas}} = - \int_{v_i}^{v_f} P_{\text{ext.}} dv$$

$$= - \int_{v_i}^{v_f} P dv$$

$$= - \int_{v_i}^{v_f} \left(\frac{nRT}{V} - \frac{n^2a}{V^2} \right) dV \quad \left(P_{\text{ext.}} = P_{\text{gas}} = P \text{ for reversible path} \right)$$

$$= - \int_{V_i}^{V_f} \frac{nRT}{V} dV + \int_{V_i}^{V_f} \frac{an^2}{V^2} dV$$

$\omega = \text{Work done during expansion}$

$$= -nRT \int_{V_i}^{V_f} \frac{dV}{V} + an^2 \int_{V_i}^{V_f} \frac{dV}{V^2} \quad [T, n, a \rightarrow \text{constant}]$$

$$= -nRT \ln\left(\frac{V_f}{V_i}\right) + an^2 \left(-\frac{1}{V}\right) \Big|_{V_i}^{V_f}$$

$$\boxed{\omega_{\text{gas}} = -nRT \ln\left(\frac{V_f}{V_i}\right) - an^2 \left(\frac{1}{V_f} - \frac{1}{V_i}\right)}$$

Solution-4-

Initial value of monoatomic ideal gas

$$P_i = 32 \text{ bar}$$

$$V_i = 3 \text{ dm}^3 = 3 \text{ lit}$$

$$T_i = 600 \text{ K}$$

$$C_m = \frac{3}{2}R; C_p = \frac{5}{2}R \quad (\text{monoatomic ideal gas})$$

final Pressure of gas $P_f = 1 \text{ bar}$

(i) Isothermal and reversible expansion

$$T_f = 600 \text{ K} \quad (\text{Isothermal } T_i = T_f)$$

$$\text{Now } \Delta T = 0$$

$$\text{So } \boxed{\Delta U = 0} \times 52 \quad \left(\begin{array}{l} \Delta U = nC_m \Delta T \\ \Delta H = nC_p \Delta T \end{array} \right)$$

$$\boxed{\Delta H = 0} \quad \left(P_i V_i = nRT_f \right)$$

$$W = -nRT \ln\left(\frac{V_f}{V_i}\right) = -P_i V_i \ln\left(\frac{P_f}{P_i}\right)$$

$$\left[P_i V_i = nRT_f \right]$$

$$= -32 \text{ bar} \times 3 \text{ lit} \times \ln\left(\frac{32}{1}\right) = -96 \text{ lit bar} \times 5 \times 0.7 \quad [1 \text{ lit bar} = 100 \text{ J}]$$

$$= -336 \times 100 = -33600 \text{ cal}$$

$$(1 \text{ lit bar} = 100 \text{ J})$$

$$W = -8400 \text{ Cal}$$

$$q = -W \quad (\text{For isothermal as } \Delta U = 0)$$
$$= -(-8400 \text{ Cal})$$

$$\Rightarrow q = 8400 \text{ Cal}$$

(ii) Adiabatic reversible expansion

$$\therefore q = 0$$

For adiabatic reversible process

$$P_i^{1-\gamma} \cdot T_i^\gamma = P_f^{1-\gamma} \cdot T_f^\gamma$$

$$\Rightarrow T_f = T_i \left(\frac{P_i}{P_f} \right)^{\frac{1-\gamma}{\gamma}}$$

$$= 600 \left(\frac{32 \text{ bar}}{1 \text{ bar}} \right)^{\frac{1-\frac{5}{3}}{\frac{5}{3}}} \quad [\gamma = \frac{5}{3} \text{ for monoatomic gas}]$$

$$= 600 (32)^{-\frac{2}{5}}$$

$$= 600 (2^5)^{-2/5}$$

$$= 600 (2)^{-2} = \frac{600}{4}$$

$$= 150 \text{ K}$$

Now $W = \Delta U$ (For Adiabatic)

$$\Rightarrow W = \Delta U = n C_{Vm} \Delta T = \left(\frac{P_i V_i}{n R T_i} \right) \cdot \frac{3}{2} R \cdot (T_f - T_i)$$

$$= \frac{32 \times 3}{600} \times \frac{3}{2} \times (150 - 600) \text{ lit-bar}$$

$$= -108 \text{ lit-bar} = -10800 \text{ Joule}$$

$$= -\frac{10800}{4} \text{ Cal} = -2700 \text{ Cal}$$

(Here assume 1 Cal = 4 J)
But generally we take
1 Cal = 4.2 J

$$\Rightarrow \boxed{\omega = -2700 \text{ Cal}} = \frac{\Delta U}{\Delta V} = \frac{-2700}{\frac{1}{2} \times 100} = -54 \text{ J}^{-1}$$

$$\Rightarrow \Delta H = nC_{pm} \Delta T = \frac{P_1 \cdot V_1}{R \cdot T_1} \times \frac{5}{2} R (T_f - T_i)$$

$$= \frac{32 \times 3}{600 \times 2} \times \frac{5}{2} \times (150 - 600) \text{ lit bar}$$

$$= -\frac{96 \times 5}{600 \times 2} \times 450 \times 100 \text{ J} = -18000 \text{ J}$$

$$= -\frac{18000}{4} \text{ Cal} = 4500 \text{ Cal} \quad (\text{Assume } 1 \text{ Cal} = 4 \text{ J})$$

$$\boxed{\Delta H = -4500 \text{ Cal}}$$

(iii) Isothermal and Adiabatic expansion -

Isothermal $\Delta T = 0$; $\boxed{\Delta U = 0}$; $\boxed{\Delta H = 0}$

Adiabatic $\boxed{q = 0}$

$$\text{so } \Delta U = q + \bar{\omega} \quad (\text{FLOT: 1st Law of thermodynamics})$$

$$0 = 0 + \omega$$

$$(003-2-128), \frac{2}{2} \Rightarrow \boxed{\omega = 0}$$

(iv) Adiabatic expansion against 1 bar ($P_{ext} = 1 \text{ bar}$; irreversible)

$\boxed{q = 0}$; adiabatic

$$\text{so } \omega = \Delta U ; \text{ adiabatic irreversible}$$

$$\Rightarrow -P_{ext} \cdot \Delta V = -n C_{um} \Delta T$$

$$\Rightarrow -P_{ext} (V_2 - V_1) = n \cdot \frac{3}{2} R (T_f - T_i)$$

$$\Rightarrow -1 \text{ bar} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right) = n \cdot \frac{3}{2} R (T_f - T_i)$$

$$\left(\frac{1}{2} - \frac{1}{3} \right) T \Delta H \times 10^3 = \left(\frac{1}{3} - \frac{1}{2} \right) T \Delta H$$

$$\Rightarrow -1 \text{ bar} \cdot \left(\frac{T_f}{1 \text{ bar}} - \frac{600}{32 \text{ bar}} \right) = \frac{3}{2} (T_f - 600)$$

$$\Rightarrow -T_f + \frac{600}{32} = \frac{3}{2} T_f - \frac{3}{2} \times 600$$

$$\Rightarrow -T_f - \frac{3}{2} T_f = -\frac{600}{32} - \frac{3 \times 600}{2}$$

$$\Rightarrow \text{Ansatz } (600 - T_f) = \frac{1837.5}{5} = 367.5 \text{ K.}$$

$$\text{Now } \omega = \Delta U = n C_{Vm} \Delta T$$

$$= \left(\frac{P_i V_i}{R T_i} \right) \times \frac{3}{2} R (T_f - T_i)$$

$$= \frac{32 \text{ bar} \times 3 \text{ lit}}{600} \times \frac{3}{2} \times (367.5 - 600)$$

$$= 55.8 \text{ lit bar} = -55.8 \times 10^5 \text{ J}$$

$$= -5580 \text{ Cal} \quad (\text{again assume } 1 \text{ cal} = 4 \text{ J})$$

$$\Rightarrow \boxed{\omega = \Delta U = -1395 \text{ Cal}}$$

$$\text{Now } \Delta H = n C_{Vm} \Delta T = \left(\frac{P_i V_i}{R T_i} \right) \times \frac{5}{2} R (T_f - T_i)$$

$$= \frac{32 \text{ bar} \times 3 \text{ lit}}{600} \times \frac{5}{2} \times (367.5 - 600)$$

$$= 93 \text{ lit atm} = 9300 \text{ J} \quad (v)$$

$$= \frac{9300}{4} \text{ Cal} \quad (\text{use } 1 \text{ cal} = 4 \text{ J})$$

$$\boxed{\Delta H = 2325 \text{ Cal}}$$

(v) Isothermal expansion against 1 bar

$$\Delta T = 0 ; \text{ Isothermal} ; \boxed{\Delta U = 0} ; \boxed{\Delta H = 0}$$

$$\omega = -P_{ext} \cdot \Delta V = -P_{ext} (V_2 - V_1)$$

$$= -P_{ext} \left(\frac{n R T}{P_2} - \frac{n R T}{P_1} \right) = -P_{ext} \times n R T \left(\frac{1}{P_2} - \frac{1}{P_1} \right)$$

$$= -P_{\text{out}} \cdot P_i V_i \left(\frac{1}{P_f} - \frac{1}{P_i} \right) \quad [P_i V_i = n R T_i] \quad \text{calculated}$$

$$= -1.6 \text{ kJ} \times 32 \text{ bar} \times 31.7 \cdot \left(\frac{1}{1 \text{ bar}} - \frac{1}{32 \text{ bar}} \right)$$

$$= -3 \times 31 \text{ lit-bar}$$

$$= -9300 \text{ J}$$

$$\therefore Q = -\frac{9300}{4} \text{ Cal} \quad [\text{Note } 1 \text{ cal} = 4.18 \text{ Joule}]$$

$$W = -2325 \text{ Cal}$$

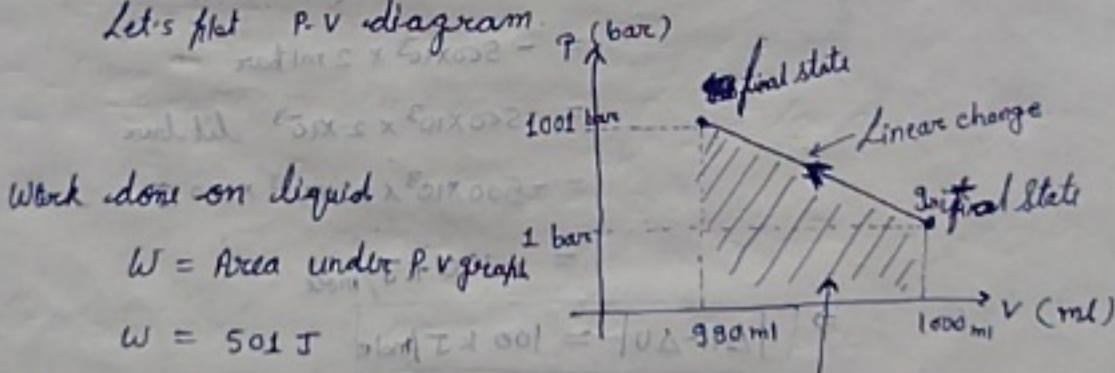
$$Q = -W = -(-2325 \text{ Cal}) \quad (\text{Isothermal } \Delta U = 0)$$

$$\Rightarrow Q = 2325 \text{ Cal}$$

Solution-5-

Pressure over 1000 ml liquid is 1 bar and gradually increased to 1002 bar so that volume becomes 990 ml, linear variation.

Let's plot P-V diagram.



Work done on liquid

$$W = \text{Area under P-V graph}$$

$$W = 501 \text{ J}$$

Since process done Adiabatically

$$\text{so } Q = 0$$

$$\text{Now } [\Delta U = W = 501 \text{ J}]$$

$$\text{Now } \Delta H = \Delta U + (P_f V_f - P_i V_i) = 501 \text{ J} + (1002 \text{ bar} \times 990 \text{ ml} - 1 \text{ bar} \times 1000 \text{ ml})$$

$$\Rightarrow \Delta H = 501 \text{ J} + 989.73 \text{ lit-bar} = 501 \text{ J} + 989.73 \text{ J} = 99500 \text{ J} \Rightarrow \boxed{\Delta H = 99.5 \text{ kJ}}$$

$$\text{Area} = \frac{1}{2} \times (1 \text{ bar} + 1002 \text{ bar}) \times 10 \text{ ml}$$

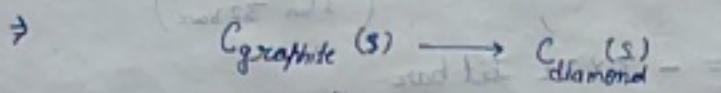
$$= \frac{1}{2} \times (1002) \times 10 \times 10^3 \text{ lit-bar}$$

$$= 501 \times 10 \times 10^3 \times 100 \text{ J}$$

$$= 501 \text{ J}$$

Solution - 6-

1 mole graphite to 1 mole diamond conversion



$$1 \text{ mole} = 12 \text{ gm} \quad 1 \text{ mole} = 12 \text{ gm}$$

$$\text{density} = 2 \text{ gm/cc} \quad \text{density} = 3 \text{ gm/cc}$$

$$= 2 \text{ gm/ml} \quad = 3 \text{ gm/ml}$$

$$\text{Volume } (V_G) = \frac{\text{mass}}{\text{density}} \quad \text{Volume } (V_D) = \frac{\text{mass}}{\text{density}}$$

$$\Rightarrow V_G = \frac{12 \text{ gm}}{2 \text{ gm/ml}} = 6 \text{ ml} \quad = \frac{12 \text{ gm}}{3 \text{ gm/ml}} = 4 \text{ ml}$$

$$\text{Now } \Delta H = \Delta U + P \cdot \Delta V$$

$$\Delta H - \Delta U \Rightarrow P(V_D - V_G)$$

$$= 500 \times 10^3 \text{ bar} \cdot (4 \text{ ml} - 6 \text{ ml})$$

$$= -500 \times 10^3 \times 2 \text{ ml/bar}$$

$$= -500 \times 10^3 \times 2 \times 10^{-3} \text{ lit/bar}$$

$$= -500 \times 10^3 \times 2 \times 10^{-3} \times 100 \text{ J/J bar} \text{ (Ans)}$$

$$= -100 \text{ KJ/mole}$$

$$\boxed{|\Delta H - \Delta U| = 100 \text{ KJ/mole}}$$

$$0.1 \times (\text{mod 1001} + \text{mod 2}) \times \frac{1}{2} = 0.05 \text{ KJ}$$

$$\text{and } 0.1 \times 1000 \times (5001) \times \frac{1}{2} =$$

$$5001 \times 0.1 \times 100 \times 10^3 =$$

$$500100 =$$

$$(0.05 + 500100) \times 10^3 = 500100.05 \times 10^3 = 500100.05 \text{ KJ}$$