

Ans 1 Assuming ideal gas behavior, volume at 1 atm (V_1) = 22.4 L

$$\text{Volume at } 400 \text{ atm } (V_2) = \frac{22.4}{400} = 0.056 \text{ L}$$

$$W = - \int_{V_1}^{V_2} P dV = - \int_{V_1}^{V_2} \left(\frac{nRT}{V-nb} - \frac{n^2 a}{V^2} \right) dV$$

$$= -nRT \ln \frac{V_2 - nb}{V_1 - nb} - n^2 a \left[\frac{1}{V_2} - \frac{1}{V_1} \right]$$

$$= -1 \text{ mol} \times 8.314 \text{ K}^{-1} \text{ J mol}^{-1} \cdot 273 \text{ K} \ln \frac{0.056 - 0.0428}{22.4 - 0.0428} - (1)^2 \text{ mol}^2 (2.264 \text{ atm L}^2 \text{ mol}^{-2}) \left[\frac{1}{0.056} - \frac{1}{22.4} \right] \text{ L}^{-1}$$

$$= -2269.7 \text{ J} \ln(0.00059) - 2.264 \text{ L atm} (17.81)$$

$$= -2269.7 \times (-7.436) \text{ J} - 2.264 \times 101.325 \text{ J} \times 17.81$$

$$= (16877.48 - 4085.61) \text{ J} = 12791.86 \text{ Joules}$$

$$(ii) \left(\frac{\partial U}{\partial V} \right)_T = \frac{n^2 a}{V^2}$$

$$\therefore \Delta U = \int_{V_1}^{V_2} \frac{n^2 a}{V^2} dV = -n^2 a \left[\frac{1}{V_2} - \frac{1}{V_1} \right]$$

$$\Delta U = -2.264 \text{ atm L}^2 \text{ mol}^{-2} \times 1^2 \text{ mol}^2 \left[\frac{1}{0.056} - \frac{1}{22.4} \right] \text{ L}^{-1}$$

$$= -2.264 \text{ L atm} \times 17.81$$

$$= -40.32 \times 101.325 \text{ Joules} = -4085.6 \text{ Joules}$$

$$\therefore Q = \Delta U - W = -4085.6 \text{ J} - 12791.86 \text{ J} = -16,877.46 \text{ J}$$

Ans2: (1) The expansion occurs suddenly as P_{opp} is sufficiently less than the pressure of the system. So, the process can be regarded irreversible.

$$W = -P_{\text{opp}} (V_{\text{final}} - V_{\text{initial}})$$

or

$$= -P_{\text{ex}} (V_2 - V_1) = -nRT \cdot P_{\text{ex}} \left(\frac{1}{P_2} - \frac{1}{P_1} \right)$$

$$= -(10 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) (1 \text{ atm}) \left[\frac{1}{1} - \frac{1}{10} \right] \text{ atm}^{-1}$$

$$= -24,942 \text{ J} \times 0.9 = -22,447.8 \text{ Joules}$$

(2) As the process is occurring slowly, \therefore process can be considered as a reversible process.

$$\therefore W = - \int_{V_i}^{V_f} P_{\text{ext}} \cdot dV$$

$$= - \int_{V_1}^{V_2} \frac{nRT}{V} dV = -nRT \ln \frac{V_2}{V_1} = -nRT \ln \frac{P_1}{P_2}$$

$$= -(10 \text{ mol}) (8.314 \text{ J K}^{-1} \text{ mol}^{-1}) (300 \text{ K}) \cdot 2.303 \log \frac{10}{1}$$

$$= -5744.43 \text{ Joules}$$

Ans3: Relationship between temperature T and volume V from the adiabatic gas equation is,

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

$T_i, V_i \rightarrow$ initial Temp & Volume

$T_f, V_f \rightarrow$ final Temp & Volume

$$\text{So, } T_i V_i^{\gamma-1} = T_f V_f^{\gamma-1} \Rightarrow T_f = T_i \left(\frac{V_i}{V_f} \right)^{\gamma-1}$$

$$T_f = 292 \left(\frac{1}{1.28} \right)^{1.40-1}$$

$$= 292 \left(\frac{1}{1.28} \right)^{0.4} = 264.5 \text{ K} \approx 265 \text{ K}$$

Ans 4. $\mu_{J,T} = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$

$$\therefore dH_T = -C_p \cdot \mu_{J,T} dP$$

$$= -C_p [0.0142 - 2.60 \times 10^{-4} P] dP$$

$$\therefore \Delta H_T = \int_{45 \text{ atm}}^{30 \text{ atm}} -C_p [0.0142 - 2.60 \times 10^{-4} P] dP$$

$$= -C_p \times 0.0142 [30 - 45] + \frac{C_p}{2} [2.60 \times 10^{-4}] [30^2 - 45^2]$$

$$= -C_p [0.0142 \times 15] + \frac{C_p \times 2.60 \times 10^{-4} \times 1125}{2}$$

$$= \frac{7}{2} \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} [0.213 - 0.14625]$$

$$= 1.942 \text{ J mol}^{-1}$$

Ans 5. w.k.t $\mu_{J,T} = -\frac{1}{C_p} \left(\frac{\partial H}{\partial P} \right)_T$ — (1)

$$H = f(P, T)$$

$$dH = \left(\frac{\partial H}{\partial P} \right)_T dP + \left(\frac{\partial H}{\partial T} \right)_P dT$$

we know, $H = U + PV$

$$dH = dU + PdV + VdP = Tds + VdP$$

dividing by dP at constant T

$$\left(\frac{\partial H}{\partial P} \right)_T = T \left(\frac{\partial S}{\partial P} \right)_T + V \quad \text{— (2)}$$

From Maxwell's Relation we get

$$\left(\frac{\partial S}{\partial P} \right)_T = - \left(\frac{\partial V}{\partial T} \right)_P \quad \text{— (3)}$$

Putting the Maxwell's relation (3) in (2)

$$\left(\frac{\partial H}{\partial P}\right)_T = -T\left(\frac{\partial V}{\partial T}\right)_P + V \quad - (4)$$

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(4) in (1)

$$\mu_{J,T} = \frac{-1}{C_p} \left[V - T\left(\frac{\partial V}{\partial T}\right)_P \right]$$

$$\mu_{J,T} = \frac{1}{C_p} \left[T\left(\frac{\partial V}{\partial T}\right)_P - V \right] \quad - (5)$$

for one mole of an ideal gas

$$PV = RT$$

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

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$\mu_{J,T} = \frac{1}{C_p} \left[\frac{T \cdot R}{P} - V \right] = \frac{1}{C_p} [V - V] = 0$$