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

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

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

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

$$= -1 mol \times 8.314 \, K^{-1} J mol^{-1} \cdot 273 K \ln \dfrac{0.056 - 0.0428}{22.4 - 0.0428} - (1)^2 mol^2 (2.264 atm \, L^2 mol^{-2})\left[\dfrac{1}{.056} - \dfrac{1}{22.4}\right] L^{-1}$$

$$= -2269.7 \, J \ln(0.00059) - 2.264 L atm (17.81)$$

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

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

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

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

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

$$= -2.264 \, L atm \times 17.81$$

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

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

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.

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

or

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

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

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

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

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

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

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

$$= -5744.43 \, Joules$$

Ans 3: Relationship between temperature T and volume V from the adiabatic gas equation is,

$$TV^{Y-1} = constant$$

$T_i, V_i \rightarrow$ initial Temp & Volume
$T_f, V_f \rightarrow$ final Temp & Volume

So, $T_i V_i^{Y-1} = T_f V_f^{Y-1}$ ⟹ $T_f = T_i\left(\frac{V_i}{V_f}\right)^{Y-1}$

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

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

Ans4. $\mu_{J,T} = -\dfrac{1}{c_p}\left(\dfrac{\partial H}{\partial P}\right)_T$

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

$= -c_p\left[0.0142 - 2.60\times10^{-4}\,P\right] dP$

$\therefore \Delta H_T = \displaystyle\int_{45atm}^{30atm} -c_p\left[0.0142 - 2.60\times10^{-4}\,P\right] dP$

$= -c_p \times 0.0142\,[30-45]k + \dfrac{c_p}{2}\left[2.60\times10^{-4}\right]\left[30^2-45^2\right]$

$= -c_p\left[0.0142\times-15\right]k - c_p\dfrac{2.60\times10^{-4}\times1125}{2}$

$= \dfrac{7}{2}\times8.314\,J\,k/mol\,k\left[0.213 - 0.14625\right]$

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

Ans5. w.k.t $\quad \mu_{J,T} = -\dfrac{1}{c_p}\left(\dfrac{\partial H}{\partial P}\right)_T \quad$ — (1)

$H = f(P,T)$

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

we know, $H = U + PV$

$dH = dU + PdV + VdP = TdS + VdP$

dividing by dP at constant T

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

From Maxwell's Relation we get

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

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

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

(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

$$PV = RT$$

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

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

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