

## THERMODYNAMICS

## EXERCISE – I

## SINGLE CORRECT (OBJECTIVE QUESTIONS)

Sol.1 [C]

Sol.2 [D]

For 3 moles of  $\text{Cl}_2$  &  $\text{HCl}$   
 $\Delta U = -3 \times 185 = -555 \text{ kJ}$

Sol.3 [D]

2 mole  $\text{HCl}$  is consumed completely  
 for 1 mole consumption of  $\text{HCl}$   
 $\Delta U = \Delta H - \Delta n_g RT$

$$= -72.3 + \frac{8.314 \times 300}{1000} \text{ (as, } \Delta n_g = -1)$$

$$= -69.8 \text{ kJ}$$

For 2 mole  $\text{HCl}$

$$\Delta U = 2x - 69.8 = -139.6 \text{ kJ}$$

Sol.4 [B]

$$\Delta U = q + w$$

$$= \frac{100 \times 10^3 - 1.5 \times 10^5}{10^3} = -50 \text{ kJ}$$

Sol.5 [C]

$$w = nC_v \Delta T$$

$$\Rightarrow -3 \times 1000 = 1 \times 20 \times (T - 300)$$

$$T = 150 \text{ K}$$

Sol.6  $\Delta U = Q + w$ 

$$Q = -124 \text{ J}$$

$$W = -P_{\text{ext}}(v_2 - v_1)$$

$$= -\frac{1520}{760} (177 - 377) = 400 \text{ Atm ml} = 40 \text{ J}$$

$$\Delta U = -124 + 40 = -84 \text{ J}$$

Sol.7 [C]

Heat released by 500 gm of liquid

$$= \frac{500}{18} \times 75.6 \times 20$$

Heat absorbed by 'n' no of ice each 9 gm

$$= \frac{9}{12} n \times 6000 \text{ J}$$

Heat absorbed = Heat released

Which gives  $n = 14$

Sol.8 [A]

$$\text{Area of } \triangle ABC = -\text{Area of } \triangle ACD$$

Sol.9 [B]

$$C_p = \frac{1}{n} \left( \frac{dq}{dT} \right)_p$$

$$dT = 0$$

Sol.10 [C]

Sol.11 [D]

$$nC_v \Delta T = 100 \times 4.2 - 209$$

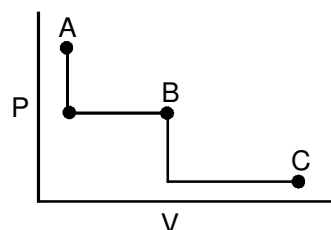
$$= 420 - 209 = 211 \text{ J}$$

$$n \times \frac{5R}{2} \times \Delta T = 211$$

$$n\Delta T = \frac{211 \times 2}{5R}$$

$$C_m = \frac{q}{n\Delta T} = \frac{420}{211 \times 2} \times 5R \approx 5R$$

Sol.12 [C]



$$\begin{aligned} \text{Total work done} &= -2(16 - 4) - 1(32 - 16) \\ &= -24 - 16 = -40 \text{ bar litre} \\ &= -4000 \text{ J} \\ q &= -w = 4000 \text{ J} \end{aligned}$$

Sol.13 [A]

Sol.14 [C]

$$y = \frac{7}{5}$$

$$y - 1 = \frac{2}{5}$$

$$T_2 = T_1 \left( \frac{v_1}{v_2} \right)^{\frac{2}{5}}$$

$$= 600 \times \left( \frac{1}{32} \right)^{2/5} = 150 \text{ K}$$

$$\therefore \Delta H = nC_p (T_2 - T_1) = -\frac{7}{2} R \times 450 = -1575 R$$

Sol.15 [C]

$$w_{1-2} = R \times 300 \ln 2$$

$$w_{2-3} = P_{\text{ext}}(v_3 - v_2) \quad (\text{Here } p_{\text{ext}} = \frac{R \times 300}{20})$$

$$= 15R)$$

$$= -15R \times 20 = -300R$$

$$w_{3-4} = -R \times 600 \ln \frac{10}{40}$$

$$w_{4-1} = 0$$

$$w_T = \sum w_i$$

Sol.16 [D]

$$\omega = nC_V(T_2 - T_1) = -p_{\text{ext}} \times nR \left[ \frac{T_2}{P_2} - \frac{T_1}{P_1} \right]$$

$$\Rightarrow \frac{5}{2}R(T_2 - 350) = -2R \left[ \frac{T_2}{2} - \frac{350}{T} \right]$$

$$\therefore T_2 = 450 \text{ K}$$

$$\therefore \omega = nC_V(T_2 - T_1) = 2 \times \frac{5}{2}R \times 100 = 500R$$

Sol.17 [A]

$$\Delta U = \Delta U_1 + \Delta U_2 = q + \omega = 0$$

$$\Rightarrow n_1 C_V(T_f - T_1) + n_2 C_V(T_f - T_2) = 0$$

$$\text{Where, } n_1 = \frac{p_1 v_1}{RT_1} \text{ \& } n_2 = \frac{p_2 v_2}{RT_2}$$

$$\therefore T_f = \frac{T_1 T_2 (p_1 v_1 + p_2 v_2)}{p_1 v_1 T_2 + p_2 v_2 T_1}$$

Sol.18 [A]

$$\eta = \frac{T_2 - T_1}{T_2} = \frac{323 - 298}{373} = 20.11 \%$$

Sol.19 [B]

$$\frac{T_2 - T_1}{T_2} = \frac{\text{work}}{Q_2}$$

$$\Rightarrow \omega = 0.8 \text{ kCal}$$

Sol.20 [C]

$$\frac{1000 - T_2}{1000} = \frac{T_2 - 360}{T_2}$$

$$T_2 = 600 \text{ K}$$

Sol.21 [A]

$$\Delta G = \Delta H - T\Delta S$$

$$\text{Also, } \Delta H = \Delta U + \Delta n_g RT$$

$$= -3000 - 1 \times 2 \times 300$$

$$= -3600 \text{ Cal}$$

$$\therefore \Delta G = -3600 + 10 \times 300 = -600 \text{ Cal}$$

Sol.22 [C]

$$\Delta S = nC_V \ln \frac{T_2}{T_1}$$

Sol.23 [D]

The process is at equilibrium

Sol.24 [C]

Sol.25 [A]

$$\Delta G = \Delta H - T\Delta S$$

$$-\Delta S = \text{negative (slope)}$$

$$\therefore \Delta S = \text{positive}$$

$$\text{From graph } \Delta H > 0$$

Sol.26 [C]

$$\Delta_s = \frac{-300 \times 30}{300} \quad \left( \because \Delta s = \frac{\Delta H_v}{T} \right)$$

$$= -30 \text{ J/mol K}$$

Sol.27 [C]

$$(\Delta S)_{\text{sys}} = nR \ln \frac{p_1}{p_2} = 10 \times 8 \times \ln 2 = 10 \times 8 \times 0.7 = 56 \text{ J/K}$$

$$(\Delta S)_{\text{surr}} = \frac{-q_{\text{sys}}}{T} = \frac{w_{\text{irr}}}{T} = \frac{-p_{\text{ext}}}{T} \left[ \frac{nRT}{p_2} - \frac{nRT}{p_1} \right]$$

$$= -1 \times 10 \times R \left[ \frac{1}{1} - \frac{1}{2} \right]$$

$$= -5R = -5 \times 8 = -40 \text{ J/K}$$

$$(\Delta S)_T = 56 - 40 = 16 \text{ J/K}$$

Sol.28 [C]

$$4 \times (\ell) \rightarrow 4 \times (\text{g}) \quad \Delta H = 30 \times 4 = 120 \text{ kJ}$$

$$\dots(i)$$

$$x_4(\text{g}) \rightarrow x_4(\ell) \quad \Delta H = -72 \text{ kJ} \quad \dots(ii)$$

$$4 \times (\text{g}) \rightarrow x_4(\text{g}) \quad \Delta H = -100 \text{ kJ} \quad \dots(iii)$$

$$\text{Adding (i), (ii) \& (iii) we have, } 4 \times (\ell) \rightarrow x_4(\ell)$$

$$\Delta G = -52 \text{ kJ}$$

$$\text{Now, } \Delta h = \Delta H - T\Delta S$$

$$= -52 + \frac{300 \times 125}{1000}$$

$$= -14.5 \text{ kJ/mol}$$

Sol.29 [D]

$$\Delta S = nR \ln \frac{v_2}{v_1}$$

Sol.30 [C]

$$\Delta S_{\text{rxn}} = S_{\text{product}} - S_{\text{reactants}}$$

$$= 50 - \frac{3}{2} \times 40 - \frac{1}{2} \times 60$$

$$= -40 \text{ J K}^{-1} \text{ mole}^{-1}$$

$$\text{At equation } \Delta G = 0$$

$$T\Delta S = \Delta H$$

$$\Rightarrow T = 750 \text{ K}$$

Sol.31 [D]

$$C(T_h - T_f) = C(T_f - T_c)$$

$$T_f = \frac{(T_h + T_c)}{2}$$

$$(\Delta S)_T = C \ln \frac{T_f}{T_h} + C \ln \frac{T_f}{T_c}$$

$$= C \ln \frac{(T_f)^2}{T_h T_c} = \frac{C \ln(T_c + T_h)^2}{4 T_h T_c}$$

Sol.32 [D]

Sol.33 [D]

Sol.34 [D]

Sol.35 [D]

For container B

$$\frac{P_2}{P_1} = \left( \frac{v_1}{v_2} \right)^\gamma = (8)^{5/3} = 32$$

$$P_2 = 32 \times P_1 = 32 \text{ atm}$$

Sol.36 [A]

$$T_A = \frac{P_A V_A}{nR}$$

$$V_A = 44.8 - \frac{22.4}{8} = 42 \text{ litre}$$

$$\therefore T_A = \frac{32 \times 42}{10 \times 0.083} = 1638 \text{ K}$$

Sol.37 [B]

$$\Delta H = n C_p \Delta T = 10 \times \frac{5}{2} R \times (1638 - 27.3)$$

Cal

$$= 10 \times \frac{5}{2} \times 2 (16.38 - 27.3) \times 10^{-1}$$

kCal

$$= 80.53 \text{ kCal}$$

Sol.38 [C]

Sol.39 [C]

Sol.40 [B]

$$w = -p \Delta v$$

$$= -1 (-0.45)$$

$$= 0.45 \text{ L-atm}$$

$$= 45 \text{ J}$$

Sol.41 [B]

Sol.42 [C]

$$w = -nR \Delta T = -2 \times 2 \times 200 = -400 \text{ R}$$

$$\therefore \text{Work done by the gas} = 400 \text{ R}$$

Sol.43 [B]

$$w_{DA} = -2R \times 300 \ln \frac{1}{2} = 600 R \ln 2$$

$$= 414 \text{ R}$$

Sol.44 [B]

$$w_T = w_{AB} + w_{CD} + w_{DA} + w_{BC} + w_{BC}$$

$$(w_{BC} = -2R \times 500 \ln 2)$$

$$= -400 \text{ R} \ln 2 \quad \text{Also, } w_{AB} + w_{CD} = 0$$

$$= -276 \text{ R}$$

Sol.45 [A] → P,R,S

[B] → Q,R,S

[C] → Q,R,S

[D] → R,S

Sol.46 [A] → S

[B] → P,R

[C] → P,S

[D] → P,R

Sol.47 [A] → P,S

[B] → P,R,S

[C] → Q

[D] → R,S

Sol.48 [A] → Q

[B] → P,S

[C] → P,S

[D] → S

Sol.49 [A] → P,S,R

[B] → R, P

[C] → P

[D] → Q,R,S

**EXERCISE – II****MULTIPLE CORRECT (OBJECTIVE QUESTIONS)****Sol.1 [A,B,D]**

From graph

$$P = a + bv$$

$$\frac{nRT}{v} = a + bv$$

$$nRT = av + bv^2$$

$$T = \frac{av}{nR} + \frac{b}{nR} v^2 \rightarrow \text{Equation of parabola}$$

**Sol.2 [A,C]****Sol.3 [B,C]**

For reversible process

$$(\Delta S)_{\text{sys}} = 0 \quad (\text{at const } T \text{ \& } P)$$

 $(\Delta S)_T$  is maximised at equation

$$\Delta G^\circ = f(T) \quad (\text{For an ideal gas})$$

**Sol.4 [A,C]****Sol.5 [A,C,D]**

At high temperature vibrational degree of freedom is active.

**Sol.6 [A,B,C]**

$$\frac{p_B}{T_B} = \frac{p_C}{T_C}$$

$$\Rightarrow P_B = \frac{1 \times 500}{250} = 2 \text{ bar}$$

Also, for process CD

$$nC_V (T_D - T_C) = -p_{\text{ext}} \left[ \frac{nRT_D}{p_D} - \frac{nRT_C}{p_C} \right]$$

$$\Rightarrow d \frac{3}{2} (T_B - T_C) = -3 \left[ \frac{T_D}{3} - \frac{T_C}{1} \right]$$

$$\Rightarrow T_D = 450 \text{ K}$$

$$\begin{aligned} \text{Also, } \Delta H_{CD} &= nC_p \Delta T = 2 \times \frac{5}{2} R \times 200 \\ &= 1000 R \end{aligned}$$

**Sol.7 [A,B,D]**

$$\Delta G = -T \Delta S \quad (\Delta S, \Delta H = 0)$$

$$\text{As } \Delta S < 0$$

$$\Delta G > 0$$

**Sol.8 [B]**we know that internal energy is an extensive property so we can't comment on  $\Delta U$ **Sol.9 [A,B,D]**

$$\Delta H_{AB} = nC_p \Delta T = \frac{5}{2} R \times 300 = 750 R$$

$$\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \frac{v_2}{v_1} > 0$$

$$\text{As } v = f(T) \quad (\text{Linear equation})$$

$$p = f(v)$$

$$w = - \int p dv = -1496.52 \text{ J}$$

$$\text{Also, } q + w = \Delta U = nC_V \Delta T$$

$$= \frac{3}{2} \times R \times 300 = 450 R$$

$$q = 450 R - w = 5237.82 \text{ J}$$

**Sol.10 [A,B]**

$$\left( p + \frac{a}{v^2} \right) (v - b) = RT$$

Calculate  $p = f(v)$ 

$$w = - \int_{v_1}^{v_2} p dv$$

## EXERCISE – III

## SUBJECTIVE QUESTIONS

- Sol.1** (i)  $\rightarrow \oplus \longrightarrow$  on system  
 (ii)  $\rightarrow \ominus \longrightarrow$  On surrounding  
 (iii)  $\rightarrow \ominus \longrightarrow$  On surrounding  
 (iv)  $\rightarrow \oplus \longrightarrow$  On system  
 (v)  $\rightarrow \ominus \longrightarrow$  On surrounding

**Sol.2**  $\Delta U = q + w$   
 $q = -65 \text{ J}, w = 20 \text{ J}$   
 $\Delta U = -65 + 20 = -45 \text{ J}$

**Sol.3**  $\text{C}_2\text{H}_2 + 2\text{H}_2 \longrightarrow \text{C}_2\text{H}_6$   
 Initially 50 50 0  
 Vol in  $\text{m}^3$   
 After  $R \times n$  50 – 25 50 – 50 25  
 $\Delta V = 50 - 100 = -50 \text{ m}^3 = -50 \times 10^{-3} \text{ m}^3$   
 $\Delta H = \Delta U + P\Delta V$   
 $-0.31 = \Delta U + (-1.5 \times 50 \times 10^{-3} \times 1.013 \times 10^2) \times 10^{-3}$   
 $\Delta U = -0.3024 \text{ kJ}$

**Sol.4** (a) Actual energy needed =  $mgh = 62.5 \times 9.8 \times 3$   
 $= 2808 \times 10^3 \times n \times 0.25$   
 Where  $n$  is no of moles of glucose  
 $\therefore$  wt of glucose =  $2.6 \times 10^{-3} \times 180 = 0.47 \text{ gm}$   
 (b)  $0.47 \times 1000 = 0.47 \text{ kg}$

**Sol.5**  $\Delta U = \Delta H - \Delta n_g \times RT$   
 $= 2 \times 40.66 - 2 \times 8.314 \times 373 \times 10^{-3}$   
 $= 75.11 \text{ kJ}$

**Sol.6**  $\Delta E = \Delta H - P\Delta V$   
 $= q_p - p\Delta V$   
 $\Delta H = q_p = 1 \text{ kCal}$   
 $\Delta E = 1 - \frac{1(1.5 - 1.2) \times 101.3}{4.2} \times 10^{-3}$   
 $= 0.993 \text{ kCal}$

**Sol.7**  $\Delta n_g = 2 - \frac{3}{2} = \frac{1}{2}$   
 $\Delta H = \Delta U + \Delta n_g RT$   
 $= -742.7 + \frac{1}{2} \times 8.314 \times 298 \times 10^{-3}$   
 $= -741.5 \text{ kJ}$

**Sol.8**  $\Delta U = q + w = q - \int p dv = q - p\Delta v$   
 $= 1440 - \frac{(0.0180 - 0.0196) \times 101.3}{4.2}$   
 $\approx 1440 \text{ Cal}$

$$\Delta H \approx \Delta U = 1440 \text{ Cal}$$

**Sol.9**  $w = -1 (1.1 - 1.0)$   
 $= -0.1 \text{ L. atm}$   
 $= -10 \text{ J}$

**Sol.10**  $\Delta U = q + w$   
 $= 177.9 - 2.5 = 175.4 \text{ kJ}$   
 Where,  $w = -p(V_2 - V_1)$   
 $= -1.013 \times 10^5 (V_2 - V_1) = -2.5 \text{ kJ}$   
 Also,  $V_2 = (24.4 + 16.9 \times 10^{-3}) \times 10^{-3} \text{ m}^3$   
 $V_1 = 34.2 \times 10^{-3} \times 10^{-3} \text{ m}^3$

**Sol.11** We have,  $\Delta U = q + w$   
 Where,  $q = -36.5 \text{ kJ}$   
 and  $w = -p\Delta v$   
 $= -1.013 \times 10^5 (500 \times 10^{-4} \times 50 \times 10^{-2})$   
 $= -2.53 \times 10^3 \text{ J} = -2.53 \text{ kJ}$   
 $\therefore \Delta U = -39.03 \text{ kJ}$

**Sol.12** For Adiabatic irreversible process

$$nC_v(T_2 - T_1) = -p_{\text{ext}} nR \left[ \frac{T_2}{p_2} - \frac{T_1}{p_1} \right] \dots (1)$$

Where,  $C_v = \frac{5}{2} R$

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

$$P_{\text{ext}} = 1 \text{ Atm } P_2 = 2 \text{ Atm}$$

$$P_1 = 5 \text{ Atm}$$

Solving equation (1)  $T_2 = 270 \text{ K}$

Now,  $\Delta U = q + w = w$  As  $q = 0$

$$\therefore w = nC_v \Delta T = 2 \times \frac{5}{2} \times 8.314 (270 - 300)$$

$$= -1246.1 \text{ J}$$

$$\Delta H = \Delta U = nR\Delta T$$

$$= -1745.9 \text{ J}$$

**Sol.13** (a) Yest process is isochoric

$$(b) w = - \int p dv = 0$$

$$\Delta U = nC_V \Delta T = 4 \times 15 \times (400 - 300) = 6000 \text{ J}$$

$$\Delta U = q + w = q$$

$$\therefore q = 6000 \text{ J}$$

$$\Delta H = nC_p \Delta T = 4 \times (15 + 8314) \times 100 = 9325.6 \text{ J}$$

$$\text{Also, } \left( \frac{p_2}{p_1} \right)^{(y-1)} = \left( \frac{T_2}{T_1} \right)^\tau$$

$$p_2 = p_1 \times \left( \frac{T_2}{T_1} \right)^{\frac{y}{(y-1)}} = 5.21 \text{ Atm}$$

$$v_2 = \frac{nRT_2}{P_2} = 11.8 \text{ litre}$$

$$\text{Sol.14 } nC_V(T_2 - T_1) = -p_{\text{ext}} nR \left[ \frac{T_2}{p_2} - \frac{T_1}{p_1} \right] \dots (1)$$

$$\Rightarrow -p_{\text{ext}} = 1 \text{ Atm} = p_2$$

$$p_1 = 10 \text{ Atm}$$

$$C_V = \frac{R}{\gamma - 1} = \frac{R}{1.33 - 1} = \frac{R}{0.33}$$

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

From equation (i)

$$T_2 = \frac{930}{4} \text{ K}$$

$$w = nC_V(T_2 - T_1) \approx -1700 \text{ J} \approx -1.7 \text{ kJ}$$

$$\text{Sol.17 } \frac{T_2}{T_1} = \left( \frac{v_1}{v_2} \right)^{(y-1)}$$

$$\Rightarrow \frac{248.44}{298.15} = \left( \frac{1}{2} \right)^{(y-1)}$$

$$C_V = \frac{R}{(y-1)} = 31.6 \text{ JK}^{-1} \text{ mol}^{-1}$$

$$\text{Sol.18 } w = -nRT \ln \frac{p_1}{p_2}$$

$$= (-1 \times 8.314 \times 298 \ln 5) \text{ Joule}$$

$$= -3.988 \text{ kJ}$$

**Sol.19** (a)  $w_T = \text{Area under the curve}$

$$= -\frac{1}{2} \times v^0 \times 2p^0 = -p^0 v^0 \text{ (- sign for clockwise)}$$

(b) For process CA

$$q_{CA} = nC_p \Delta T = \frac{5}{2} nR$$

$$\left( \frac{p^0 v^0}{nR} - \frac{p^0 \times 2v^0}{nR} \right) = \frac{-5}{2} p^0 v^0$$

**Sol.15** (a)  $TV^{y-1} = \text{Const}$

$$\Rightarrow \frac{T_2}{300} = \left( \frac{1}{27} \right)^{\frac{1}{3}} = \frac{1}{3}$$

$$T_2 = 100 \text{ K}$$

$$(b) w = nC_V \Delta T = -1 \times 25.08 \times 200 = -5016 \text{ J} = -5.016 \text{ kJ}$$

**Sol.16**  $q = 0$

$$\Delta U = nC_V \Delta T = w = 3 \times 27.5 \times 50 = 4125 \text{ J}$$

$$\Delta H = nC_p \Delta T = 3 \times (27.5 + 8.314) 50 = 5372.1 \text{ J}$$

$$q_{AB} = \Delta U = nC_V \Delta T = n \times \frac{3}{2} R$$

$$\left( \frac{3p^0 v^0}{nR} - \frac{p^0 v^0}{nR} \right) = 3p^0 v^0$$

(c)  $\Delta U$  for cyclic process =  $w$

$$\Delta U = 0 = q_T + w_T$$

$$= q_{AB} + q_{BC} + q_{CA} - p^0 v^0$$

$$\Rightarrow 3p^0 v^0 + q_{BC} + \left( \frac{-5p^0 v^0}{2} \right) - p^0 v^0 =$$

0

$$\Rightarrow q_{BC} = \frac{p^0 v^0}{2}$$

(d) Linear equation between p and v

$$(p - 3p^0) = \frac{-2p^0}{v^0} (v - v^0)$$

$$p = 3p^0 - \frac{2p^0}{v^0} (v - v^0)$$

$$T = \frac{pv}{nR} = \frac{3p^0 v - \frac{2p^0}{v^0} v^2 + 2p^0 v}{nR} \dots(i)$$

Now

$$\frac{dT}{dV} = 0$$

$$\Rightarrow v = \frac{5v^0}{4}$$

$$\therefore T_{\max} = \frac{25p^0 v^0}{8nR} \text{ from equation (i)}$$

$$= \frac{25p^0 v^0}{8R}$$

**Sol.20** Process A (Isochoric)

$$\Delta U = q = nC_V \Delta T = \frac{3}{2} R \times 273$$

$$w = 0$$

$$\Delta H = nC_p \Delta T = \frac{5}{2} R \times 273$$

Process B (Isothermal)

$$\Delta U = nC_V \Delta T = 0$$

$$w = -nRT \ln \frac{v_2}{v_1} = -R \times 546 \ln 2$$

$$q = -w, \Delta H = nC_p \Delta T = 0$$

Process C (Isobaric)

$$\Delta U = nC_V \Delta T = \frac{3}{2} R (273 - 546)$$

$$= -\frac{3}{2} R \times 273$$

$$\Delta U = q + w$$

$$w = -p (v_2 - v_1)$$

$$= \frac{-R \times 546}{44.8} (22.4 - 44.8)$$

$$= 273 R$$

$$q_p = \Delta H = nC_p \Delta T = -\frac{5}{2} R \times 273$$

$$\text{Sol.21 } T_1 = \frac{P_1 V_1}{nR} = \frac{1 \times 22.4}{1 \times 0.082} = 273 \text{ K}$$

Process A (Isobaric)

$$\Delta U = nC_V \Delta T = 1 \times \frac{3}{2} R (546 - 273) = \frac{3}{2} R$$

$$\times 273$$

$$\Delta U = q + w$$

$$w = p_1 \Delta v = -1 \times 22.4 \text{ l Atm}$$

$$w = -\frac{nRT_1}{v_1} \times 22.4$$

$$= \frac{-R \times 237}{22.4} \times 22.4 = 273 R$$

$$q = C_p \Delta T = \frac{5}{2} R \times 273$$

$$\Delta H = q_p = \frac{5}{2} R \times 273$$

Process B Isochoric

$$w = 0$$

$$\Delta U = nC_V \Delta T = \frac{3}{2} R (-273) = -\frac{3}{2} R \times 273$$

$$\Delta U = q + w = q$$

$$\Rightarrow q = -\frac{3}{2}R \times 273$$

$$\Delta H = \Delta U + nR\Delta T = C_p\Delta T$$

$$= \frac{5}{2}R(-273) = -\frac{5}{2}R \times 273$$

Process C (Isothermal)

$$\Delta U = nC_v\Delta T = 0$$

$$w = -nRT \ln \frac{V_2}{V_1} = 273R \ln 2$$

$$q = -w = -273R \ln 2$$

$$\Delta H = C_p\Delta T = 0$$

For Cyclic Process

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

$$w = w_A + w_B + w_C$$

$$= -273R + 0 + 273R \ln 2$$

$$q = q_A + q_B + q_C$$

$$= -w = 273R - 273R \ln 2$$

**Sol.22** Path CA – Isothermal compression

Path AB – Isobaric expansion

Path BC – Isochoric change

For temperature  $T_1$  (For C) :  $pV = nRT_1$

$$2 \times 10 = 1 \times 0.082 \times T_1$$

$$T_1 = 243.6 \text{ K}$$

$$\text{For } T_2 \text{ (For C \& B)} : \frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\frac{2 \times 10}{T_1} = \frac{20 \times 10}{T_2}$$

$$T_2 = 243.6 \times 10 = 2436 \text{ K}$$

Path CA

$$\Delta U = 0$$

$$w = -nRT_1 \ln \frac{V_f}{V_i}$$

$$= -1 \times 2 \times 243.6 \ln \frac{1}{10}$$

$$= 1122.02 \text{ Cal}$$

Path AB

$$w = -p(V_f - V_i)$$

$$= -20(10 - 1) = -180 \text{ l-atm}$$

$$= \frac{-180 \times 2}{0.082} = -4384.9 \text{ Cal}$$

$$\Delta U \text{ for Path AB} = 6577.2 \text{ Cal}$$

$$\text{Now } q \text{ for path AB} = \Delta U - w_{AB}$$

$$= 6577.2 + 4384.9 = 10962.1 \text{ Cal}$$

Path BC

$$w = -p(V_f - V_i) = 0$$

$$\text{Also, } q = nC_v\Delta T = \Delta U$$

$$= \frac{3}{2}R(243.6 - 2436)$$

$$= -6577.2 \text{ Cal}$$

$$\text{Cycle } \Delta U = 0, q = -w_T = -[1122.02 - 4384.9 + 0]$$

$$= 3262.88 \text{ Cal}$$

**Sol.23** (a) For the path ABC,

$$w = w_{AB} + w_{BC} = \text{Area under } p\text{-}v \text{ curve} = -60 \text{ J}$$

$$w_{AC} = -\left[\frac{1}{2}(5+15) + (b-2)\right]$$

$$= -40 \text{ J}$$

$\therefore$  The work done along AC is least

(b) According to 1<sup>st</sup> law of thermodynamics for the path AC

$$q = \Delta U - w$$

$$\text{or } \Delta U = q + w = 200 - 40 = 160 \text{ J}$$

$$\text{or } U_C - U_A = 160 \text{ J}$$

$$\therefore U_C = 160 + 10 = 170 \text{ J}$$

(c) For path AB

$$q = \Delta U = U_B - U_A = 20 - 10 = 10 \text{ J}$$

**Sol.24** For the given cyclic process



$$\frac{V_B}{V_A} = 2, \quad \frac{V_D}{V_A} = 4 \quad T_A = 300 \text{ K}$$

(a) For Isobaric process AB

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

$$T_B = T_A \times \frac{V_B}{V_A} = 300 \times 2 = 600 \text{ K}$$

$$\begin{aligned} \text{(b) } q_{AB} &= nC_p \Delta T = 2 \times \frac{5}{2} R \times 300 \\ &= 3000 \text{ Cal} \end{aligned}$$

$$q_{BC} = \Delta U - w = -w \quad (\text{Isothermal process})$$

$$q_{BC} = \int p dv$$

$$= nRT_B \ln \frac{V_D}{V_B} = 1.663 \times 10^3 \text{ Cal}$$

$$\begin{aligned} q_{CD} &= nC_v \Delta T = 2 \times \frac{3}{2} \times 2 (300 - 600) \\ &= -1800 \text{ Cal} \end{aligned}$$

$$\begin{aligned} q_{DA} &= nRT \ln \frac{V_A}{V_D} = 2 \times 2 \times 300 \ln \frac{1}{4} \\ &= -1.663 \times 10^3 \text{ Cal} \end{aligned}$$

$$\therefore q_T = 3000 + 1663 - 1800 - 1663 = 1200 \text{ Cal}$$

(c) For cyclic process

$$\Delta U = 0$$

$$q = -w$$

$$\therefore w = -1200 \text{ Cal}$$

$$\text{Sol.25 } (\Delta H_r)_{T_2} - (\Delta H_r)_{T_1} = (\Delta C_p)_r (T_2 - T_1)$$

$$\text{Now, } (\Delta C_p)_r = C_p(\text{H}_2\text{O}, \ell) - \frac{1}{2} C_p(\text{O}_2) - C_p$$

(H<sub>2</sub>)

$$= 75.312 - \frac{1}{2} \times 29.16 - 38.83$$

$$= 21.9 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\begin{aligned} \therefore (\Delta H_r)_{373} &= (\Delta H_r)_{298} + (\Delta C_p)_r (373 - 298) \\ &= (-285.76 + 21.9 \times 10^{-3} \times 75) \text{ kJ} \\ &= -284.11 \text{ kJ} \end{aligned}$$

$$\text{Sol.26 (a) } \Delta H = \int_{T_1}^{T_2} C_p dt$$

$$\begin{aligned} &= \int_{298}^{596} (22.34 + 48.1 \times 10^{-3} T) dT \\ &= 13.064 \text{ kJ mol}^{-1} \end{aligned}$$

$$\text{(b) } \Delta U = \Delta H - R \Delta T$$

$$= \left( 13.064 - \frac{2.314 \times 298}{1000} \right) \text{ kJ mol}^{-1}$$

1

$$= 10.587 \text{ kJ mol}^{-1}$$

$$\begin{aligned} \text{Sol.27 } \Delta S &= \frac{\Delta H_f}{T_m} = \frac{30.5 \times 10^3}{T} = 28.8 \\ \Rightarrow T &= 1059 \text{ K} \end{aligned}$$

$$\text{Sol.28 } \Delta S = \int_{T_1}^{T_2} C_p \frac{dT}{T}$$

$$\begin{aligned} &= \int_{300}^{600} (25.5 + 13.6 \times 10^{-3} T - 42.5 \times 10^{-7} T^2) \frac{dT}{T} \\ &= 21.18 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\text{Sol.29 (i) } \eta_1 = \frac{760 - 650}{760} = 0.1447$$

$$\eta_{\text{rev}} = \frac{380 - 280}{380} = 0.2631$$

$\therefore$  Cyclic is irreversible as  $\eta_1 \neq \eta_{\text{rev}}$

$$\text{(ii) } \eta_2 = \frac{760 - 560}{760} = 0.2631$$

as  $\eta_2 = \eta_{\text{rev}}$  the cycle is reversible

$$(iii) \eta_3 = \frac{760 - 504}{760} = 0.33$$

as  $\eta_3 > \eta_{rev}$

This is an impossible cycle

**Sol.30**  $\Delta$

S

$$\begin{aligned} &= \int_0^{200} C_p(s) \frac{dT}{T} + \int \frac{\Delta H_f}{T_m} + \int_{200}^{300} C_p(l) \frac{dT}{T} + \frac{\Delta H_v}{T_b} \\ &\quad + \int_{300}^{600} C_p(g) \frac{dT}{T} \\ &= \\ &\int_0^{200} 0.035T \frac{dT}{T} + \frac{7500}{200} + \int_{200}^{300} (60 + 0.016T) \frac{dT}{T} \\ &\quad + \frac{30,000}{300} + \int_{300}^{600} 50 \frac{dT}{T} \\ &= 205.08 \text{ J K}^{-1} \text{ mol}^{-1} \end{aligned}$$

**Sol.31**  $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

$$\begin{aligned} \Delta S^\circ &= 2 \times S^\circ(\text{BrCl}) - S^\circ(\text{Br}_2) - S^\circ(\text{Cl}_2) \\ &= 2 \times 239.7 - 223 - 152.3 \\ &= 104.1 \text{ J mol}^{-1} \text{ K}^{-1} \\ \therefore \Delta G^\circ &= 29.3 - 298 \times 0.1041 = -1.72 \text{ kJ} \end{aligned}$$

**Sol.32**  $(\Delta H^\circ)_r = -106.6 + 139.3$

$$\Delta G^\circ = \Delta H_r - T(\Delta S^\circ)_r$$

$$\begin{aligned} &= -106.7 + 139.3 - \frac{298 \times 94.98}{1000} \\ &= 4.29 \text{ kJ} > 0 \end{aligned}$$

As  $\Delta G^\circ > 0$  the process is not spontaneous

**Sol.33**  $\Delta G = \Delta H - T\Delta S$

$$\begin{aligned} &= -2808 - \frac{310 \times 182.4}{1000} \\ &= -2864.54 \text{ kJ} \end{aligned}$$

$$\text{Sol.34 } \Delta h_r = \Delta H_r + \frac{T}{T_0} (\Delta G_r^0 - \Delta H_r)$$

$$= -5737 + \frac{310}{298} (-6333 + 5737)$$

$$= -6357 \text{ kJ}$$

$$\begin{aligned} \text{Additional Non p.v. work} &= -\Delta G_r + \Delta G_r^0 \\ &= +6357.6333 \\ &= +24 \text{ kJ} \end{aligned}$$

**Sol.35**

$$\begin{aligned} (i) \Delta_r H^\circ &= [\Delta_f H(\text{H}_2) + \Delta_f H(\text{CO}_2)] \\ &\quad - [\Delta_f H(\text{H}_2\text{O}) + \Delta_f H(\text{CO})] \\ &= (0 - 94.05) - (-57.8 - 26.42) \\ &= -94.05 + 84.22 \\ &= -9.83 \text{ k cal/ mole} \end{aligned}$$

$$\begin{aligned} (ii) \Delta_r G^\circ &= (0 - 94.24) - (-54.64 - 32.79) \\ &= -6.81 \text{ k cal/mole} \end{aligned}$$

$$\begin{aligned} (iii) \Delta_r G^\circ &= \Delta_r H^\circ - T\Delta_r S^\circ \\ -6.81 &= -9.83 - 298 \Delta_r S^\circ \\ \Delta_r S^\circ &= \frac{-6.81 + 9.83}{-298} = -0.01013 \\ &= -10.13 \text{ cal/mole K} \end{aligned}$$

$$\begin{aligned} (iv) \Delta H &= \Delta U + \Delta n_g RT \\ \Delta_r U^\circ &= \Delta_r H^\circ - \Delta n_g RT \quad (\Delta n_g = 0) \end{aligned}$$

$$\begin{aligned} (v) -10.13 &= S^\circ_m(\text{H}_2) + S^\circ_m(\text{CO}_2) - S^\circ_m(\text{H}_2\text{O}) - S^\circ_m(\text{CO}) \\ -10.13 &= 31.2 + 51.1 - S^\circ_m(\text{H}_2\text{O}) - 47.3 \\ S^\circ_m(\text{H}_2\text{O}) &= 45.13 \text{ cal/K mole} \end{aligned}$$

**EXERCISE – IV****ADVANCED SUBJECTIVE QUESTIONS****Sol.1**

$$(a) \Delta U = nC_V \Delta T = w$$

For reversible adiabatic process

$$TV^{\lambda-1} \text{ constant}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{\frac{\lambda-1}{\lambda}} = \left(\frac{2}{1}\right)^{2/5}$$

$$T_2 = 300 \times 1.32 = 395.85 \text{ K}$$

$$w = nC_V(T_2 - T_1) = \frac{3}{2}R(T_2 - T_1)$$

$$= \frac{3}{2} \times 8.314(395.85 - 300)$$

$$= 1195.3 \text{ J}$$

Also,

$$V_2 = \frac{nRT_2}{P_2} = \frac{0.082 \times 395.85}{2} = 16.23 \text{ } \ell$$

(b) For irreversible Adiabatic process

$$w = nC_V(T_2 - T_1) = P_{\text{ext}} \left[ \frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right]$$

$$\frac{3}{2}R(T_2 - T_1) = -2R \left[ \frac{T_2}{2} - T_1 \right]$$

$$T_1 = 300$$

$$\therefore T_2 = 420 \text{ K}$$

$$\therefore w = \frac{3}{2} \times 8.31 \times (420 - 300) = 1.89652 \text{ J}$$

$$V_2 = \frac{nRT_2}{P_2} = \frac{0.082 \times 420}{2} = 17.22 \text{ } \ell$$

**Sol.2**

$$C_{V, \text{mix}} = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2} = \frac{0.5 \times \frac{3}{2}R + 0.5 \times \frac{5}{2}R}{0.5 + 0.5}$$

$$= 2R$$

$$C_{p, \text{mix}} = \frac{n_1 C_{V_1} + n_2 C_{V_2}}{n_1 + n_2} = 3R$$

$$\gamma_{\text{mix}} = \frac{C_{p, \text{mix}}}{C_{V, \text{mix}}} = \frac{3}{2}$$

For reversible adiabatic process

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} = \left(\frac{1}{\Delta}\right)^{1/2} = \frac{1}{2}$$

$$T_2 = 150 \text{ K}$$

$$\Delta H = nC_p \Delta T$$

$$= 3R(-150)$$

$$= -450 \times 2 = -900 \text{ Cal}$$

**Sol.3**

(i) For reversible isothermal process

$$\Delta U = 0$$

$$\Delta H = 0$$

$$w = -9$$

$$w = -nRT + \ln \frac{V_f}{V_i} = -nRT \ln \frac{P_i}{P_f}$$

$$= -P_i V_i \ln \frac{P_i}{P_f}$$

$$= 0.7 \times 10^6 \times 20 \times 10^{-3} \ln$$

$$\frac{0.7}{0.2}$$

$$= 17.54 \text{ kJ}$$

$$\partial = -w = 17.54 \text{ KJ}$$

(ii)

For adiabatic reversible process

$$\Delta U = nC_V \Delta T = w$$

$$\text{No. of moles} = \frac{P_i V_i}{RT_i} = \frac{0.7 \times 10^6 \times 20 \times 10^{-3}}{8.314 \times 673} =$$

$$2.5$$

Also,

$$\frac{T_2}{T_1} = \left( \frac{P_2}{P_1} \right)^{\frac{\gamma-1}{\gamma}} = \left( \frac{2}{7} \right)^{2/7}$$

$$\therefore \Delta U = 2.5 \times \frac{5R}{2} (470.5 - 673)$$

$$= -10.52 \text{ KJ}$$

$$\Delta H = nC_p \Delta T = 2.5 \times \frac{7R}{2} (470.5 - 673)$$

$$= -14.73 \text{ KJ}$$

$$\partial = 0$$

(iii) For Adiabatic & Isothermal process

$$\Delta U = 0$$

$$\partial = 0$$

$$w = 0$$

$$\Delta H = 0$$

(iv) For adiabatic irreversible process

$$\partial = 0$$

$$nC_v(T_2 - T_1) = -p_{e_{xt}} nR \left[ \frac{T_2}{P_2} - \frac{T_1}{P_1} \right]$$

$$\frac{5R}{2} (T_2 - 673) = -0.2 \times 10^6$$

$$R \left[ \frac{T_2}{0.2 \times 10^6} - \frac{673}{0.7 \times 10^6} \right]$$

Putting the value of  $T_2$  from this expression in

$$\Delta U = nC_v(T_2 - T_1) = -7.14 \text{ KJ}$$

$$w = \Delta U = -7.14 \text{ KJ}$$

$$\Delta H = nC_p \Delta T = -9.996 \text{ KJ}$$

(V) For irreversible isothermal process

$$\Delta U = 0$$

$$\partial = -w$$

$$\Delta H = 0$$

$$w = -p_{e_{xt}} nRT \left[ \frac{1}{P_2} - \frac{1}{P_1} \right]$$

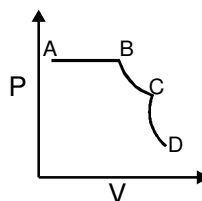
$$= -0.2 \times 10^6 \times 2.5 \times 8.314$$

$$\left[ \frac{1}{0.2 \times 10^6} - \frac{1}{0.7 \times 10^6} \right]$$

$$\approx -10 \text{ KJ}$$

$$\partial = -w = 10 \text{ KJ}$$

**Sol.4**



For process AB (Isobaric)

$$\Delta U = nC_v \Delta T = 1 \times 1.5 R (373 - 298) = 0.93533 \text{ KJ}$$

$$w = - \int p dv$$

$$= -nR \Delta T = -1 \times 8.314 (373 - 298)$$

$$= -623.55 \text{ J}$$

$$\partial = \Delta U - w$$

$$= 935.33 + 623.55$$

$$= 1558.88 \text{ J} = 1.558 \text{ KJ}$$

$$\Delta H = \partial_p = 1.558 \text{ KJ}$$

For process BC (Reversible isothermal)

$$\Delta U = nC_v \Delta T = 0$$

$$\partial = -w$$

$$w = -nRT \ln \frac{V_2}{V_1} = (-1 \times 8.314 \times 373 \ln 2) \text{ Joule}$$

$$= -2149.7 \text{ J}$$

$$\approx 2.15 \text{ KJ}$$

$$\Delta H = 0$$

For process CD (Adiabatic reversible)

$$\partial = 0$$

$$\Delta U = w = nC_v \Delta T = 1 \times \frac{3}{2} R (308 - 373)$$

$$= -810.62 \text{ J}$$

$$\Delta H = nC_p \Delta T = 1 \times \frac{5}{2} R (308 - 373)$$

$$= -1351.03 \text{ J}$$

$$\text{For overall process } \Delta = \sum \Delta_i = 3708.59 \text{ J}$$

$$w = \sum w_i = -3583.88 \text{ J}$$

$$\Delta U = \sum \Delta U_i = 124.71 \text{ J}$$

$$\Delta H = \sum \Delta H_i = 207.85 \text{ J}$$

**Sol.5**

$$(i) w = -nRT \ln \frac{P_1}{P_2}$$

$$= -P_1 V_1 \ln \frac{P_1}{P_2}$$

$$= -2 \times 4 \ln \frac{2}{20} = 18.42 \text{ bar L}$$

$$(ii) w = -P_{\text{ext}} (V_2 - V_1)$$

$$= -20 \left( \frac{2}{5} - 4 \right)$$

$$= 72 \text{ bar L}$$

$$\text{Where } V_2 = \frac{P_1 V_1}{P_2} = \frac{2 \times 4}{20} = \frac{2}{5} \text{ Litre}$$

$$(iii) w_1 = -P_{\text{ext}} [V' - V_i]$$

$$= -10 \left[ \frac{4}{5} - 4 \right] = 32 \text{ bar L}$$

$$w_2 = -P_{\text{ext}} [V_f - V'] = -20 \left[ \frac{2}{5} - \frac{4}{5} \right]$$

$$= 8 \text{ bar L}$$

$$\text{Where } P'V' = P_i V_i = P_f V_f$$

$$\Rightarrow V' = \frac{P_i V_i}{P'} = \frac{4}{5} \text{ L}$$

$$\text{Total work, } w_T = 32 + 8 = 40 \text{ bar L}$$

**Sol.6**

$$(a) w = -P_{\text{ext}} (V_2 - V_1)$$

$$\Rightarrow \left| \frac{-mg}{A} (V_2 - V_1) \right| = mgh$$

$$\therefore A = \frac{V_2 - V_1}{h}$$

Where, A is cross sectional area

$$\therefore P_2 = \frac{mgh}{(V_2 - V_1)}$$

$$\therefore m = \frac{P_2 (V_2 - V_1)}{gh} = \frac{p_2}{gh} \left[ \frac{nRT}{P_2} - \frac{nRT}{P_1} \right]$$

$$= \frac{nRT}{gh} \left[ 1 - \frac{P_2}{P_1} \right]$$

$$(b) P_{\text{ext}} = \frac{mg}{A} = P_1$$

$$|w| = |-P_1 (V_1 - V_2)|$$

$$= P_1 (V_2 - V_1) = m'gh$$

$$\Rightarrow \frac{m'g}{A} = \frac{V_2 - V_1}{h}$$

$$A = \frac{V_2 - V_1}{h}$$

From eq. (1) & (2)

$$\frac{m'gh}{V_2 - V_1} = P_1$$

$$m' = \frac{P_1 (V_2 - V_1)}{gh} = \frac{P_1}{gh} nRT \left[ \frac{1}{P_2} - \frac{1}{P_1} \right]$$

$$= \frac{nRT}{gh} \left[ \frac{P_1}{P_2} - 1 \right]$$

(C) Net mass lowered =  $m' - m$ 

$$= \frac{nRT}{gh} \left[ \frac{P_1}{P_2} - 1 - 1 + \frac{P_2}{P_1} \right]$$

$$= \frac{nRT}{gh} \frac{(P_1 - P_2)^2}{P_1 P_2}$$

**Sol.7**suppose  $p = a + bv$ adiabatic  $dw = du = -pdv$  $q = 0$ 

$$w = - \int_{v_1}^{v_2} (a + bv) dv \text{ after integration}$$

$$w = (v_1 - v_2) \left[ a + \frac{b}{2}(v_1 + v_2) \right]$$

$$P_1 = a + bv_1; P_2 = a + bv_2$$

$$p_1 + p_2 = 2a + b(v_1 + v_2)$$

$$\Rightarrow \frac{p_1 + p_2}{2} = a + \frac{b}{2}(v_1 + v_2)$$

$$\Rightarrow w = (v_1 - v_2) \left( \frac{p_1 + p_2}{2} \right)$$

$$\Rightarrow w = \left( \frac{1000 - 990}{1000} L \right) \left( \frac{1 + 1001}{2} \right) \text{ bar}$$

$$\Delta u = w = \frac{10}{1000} \times 501 = 5.01 \text{ L-bar} = 501 \text{ J}$$

$$\Delta H = \Delta U + (p_2 v_2 - p_1 v_1)$$

$$= 5.01 + \left( \frac{990 \times 1001 - 1 \times 1000}{1000} \right) \text{ L-bar}$$

$$= 5.01 + (989.99) = 995 \text{ L-bar} = 99500 \text{ J}$$

**Sol.8**(a)  $(P_1, V_1, T) \rightarrow (P_2, V_2, T)$ 

$$V_2 > V_1$$

isothermal

single stage - irreversible

$$w = -p_{\text{ext}}(V_2 - V_1)$$

$$p_{\text{ext}} = P_2 \text{ (If not given)}$$

$$w = -P_2 \left( \frac{nRT}{p_2} - \frac{nRT}{p_1} \right)$$

$$= -nRT \left( 1 - \frac{p_2}{p_1} \right) = -nRT \left( 1 - \frac{V_1}{V_2} \right)$$

|work| = potential energy

$$\Rightarrow nRT \left( 1 - \frac{V_1}{V_2} \right) = mgh$$

$$\Rightarrow m = \frac{nRT}{gh} \left( 1 - \frac{V_1}{V_2} \right) \left( \frac{V_1}{V_2} = \frac{p_2}{p_1} \right)$$

$$m = \frac{nRT}{gh} \left( 1 - \frac{p_2}{p_1} \right)$$

(b)  $P_2, V_2, T \rightarrow P_1, V_1, T$ 

$$\text{work} = -P_1 \left( \frac{nRT}{p_1} - \frac{nRT}{p_2} \right)$$

$$w = -nRT \left( 1 - P_1/P_2 \right)$$

$$w = nRT (P_1/P_2 - 1)$$

$$nRT \left( \frac{p_1}{p_2} - 1 \right) = m'gh$$

$$\Rightarrow m' = \frac{nRT}{gh} \left( \frac{p_1}{p_2} - 1 \right)$$

$$(c) \text{ net work} = -nRT \left( 1 - \frac{p_2}{p_1} \right) + nRT \left( \frac{p_1}{p_2} - 1 \right)$$

$$= nRT \left[ \frac{p_2^2 + p_1^2}{p_1 p_2} - 2 \right]$$

$$\frac{nRT}{p_1 p_2} [(p_2 - p_1)^2] > 0$$

work done on the system by surrounding

$$\text{net mass lowered} = m'' = m' - m = \text{net work}$$

$$\Rightarrow m'' = \frac{nRT}{gh} \left[ \frac{(p_1 - p_2)^2}{p_1 p_2} \right]$$

**Sol.9**

(a)  $\Delta U = 0$  (no temp change)

$$\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$= 0 + (1 \times 0.9 - \frac{532}{760} \times 0.9)$$

$$= 0.27 \text{ L-atm} = 27 \text{ J}$$

$$(b) \Delta U = \Delta U_1 + \Delta U_2$$

(for state 1 to 2) (for state 2 to 3)

$$\Delta U = \Delta U_2 = \Delta H_2 - \Delta n_g RT$$

$$\Delta H_2 = \Delta H_{\text{temp. rise}} + \Delta H_{\text{vap.}}$$

$$= mc \Delta T + \frac{40 \times 0.45 \times 1000}{18}$$

$$= 0.9 \times 10^3 \times \frac{4.2 \times 20}{1000} + 1000 = 1075.6 \text{ KJ}$$

$$\Delta U_2 = 1075.6 - \Delta n_g RT = 1075.6 -$$

$$\left( \frac{25 \times 8 \times 373}{1000} \right)$$

$$= 1001 \text{ KJ}$$

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$= 0.027 + 1075.6 = 1075.627 \text{ KJ}$$

**Sol.10**

$$w = - \int_{v_1}^{v_2} P dv = \int_{v_1}^{v_2} \left( \frac{nRT}{v} - \frac{n^2 a}{v^2} \right) dv$$

$$= -nRT \ln \frac{v_f}{v_i} - n^2 a \left[ \frac{1}{v_f} - \frac{1}{v_i} \right]$$

**Sol.11**

$$\Delta S_f^0 = \sum S_f^0 = \sum S_{\text{products}}^0 - \sum S_{\text{reactants}}^0$$

$$(i) - 90.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$(ii) - 374.5 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$(iii) - 3.26 \text{ J mol}^{-1} \text{ K}^{-1}$$

**Sol.12** (i) isothermal, reversible  $n = 1, v_2 = 3v_1$

$$\Delta S_{\text{gas}} = nR \ln \left( \frac{v_2}{v_1} \right) = 1 \times 8.314 \times \ln(3)$$

$$= 9.134 \text{ J/K}$$

$$q_i = T \Delta S = 298 \times 9.134 = 2721.97$$

$$\text{reversible} \Rightarrow \Delta S_{\text{total}} = 0$$

(ii) irreversible, isothermal

$$\Rightarrow \Delta S_{\text{total}} = \Delta S_{\text{gas}} + \Delta S_{\text{surr}} > 0$$

$$\Delta S_{\text{gas}} = nR \ln \left( \frac{v_2}{v_1} \right) = 1 \times 8.314 \times \ln(3) = 9.13$$

$$\Delta S_{\text{surr}} = -\frac{q_{\text{irr}}}{T} \Rightarrow q_{\text{irr}} = q_i - 836.8 = 2721.9 -$$

$$836.8$$

$$= 1885.1 \text{ J}$$

$$\Delta S_{\text{surr}} = \frac{-1885.1}{298} = -6.326 \text{ J/K}$$

$$\Delta S_{\text{total}} = \Delta S_{\text{gas}} + \Delta S_{\text{surr}} = 9.134 - 6.326 = 2.988 \text{ J/K}$$

(ii) free expansion, irreversible, isothermal

$$\Delta S_{\text{gas}} = 9.314 \text{ J/K}$$

$$\Delta S_{\text{gas}} + \Delta S_{\text{surr}} = \Delta S_{\text{total}}$$

$$\Delta S_{\text{surr}} = 0 \text{ (free expansion)}$$

$$\Delta S_{\text{gas}} = \Delta S_{\text{total}} = 9.314 \text{ J/K}$$

13. A (l) [ 200k, 1-atm]  $\rightarrow$  A(g) [200k, 1-atm]

$$\Delta H = 22 \text{ KJ/mole at } 200\text{k}$$

$$\Delta C_{pm} = C_{pm} (A, g) - C_{pm} (A, l)$$

$$= 30 - 40 = -10 \text{ J/mole.k}$$

$$\Delta H_{300} - \Delta H_{200} = \Delta C_{pm} (T_2 - T_1) = -10 \times (300 - 200) = -1000$$

$$\Delta H_{300} = \Delta H_{200} - 1000 = 22 \times 10^3 - 1000 = 21000 \text{ J/mole} = 21 \text{ KJ/mole}$$

$$\Delta G = \Delta H - T\Delta S$$

at 300K,  $\Delta G = 0$  normal boiling point equilibrium

$$\text{at } T = 300 \text{ k}$$

$$\Delta S_{300} = \frac{\Delta H}{T} = \frac{21000}{300} = 70 \text{ J/mole.k}$$

$$\Delta S_{300} - \Delta S_{200} = \Delta C_p \ln \left( \frac{T_2}{T_1} \right)$$

$$70 - \Delta S_{200} = -10 \ln \left( \frac{300}{200} \right)$$

$$\Delta S_{200} = 70 + 10 \ln \left( \frac{300}{200} \right)$$

$$= 70 + 10 \times 0.405 = 70 + 4.05$$

$$= 74.05 \text{ J/k}$$

14.  $\Delta S_{\text{total}} = \Delta S_{\text{sys}} + \Delta S_{\text{surr}}$

$$\Delta S_{\text{sys}} = nR \ln \left( \frac{P_1}{P_2} \right) = 10 \times 8 \times \ln 2$$

$$= 56$$

$$\Delta S_{\text{surr}} = \frac{q_{\text{irr}}}{T}$$

$$w = -q \Rightarrow (\text{because at isothermal } \Delta U = 0)$$

$$w = -1 (v_2 - v_1) = -1 \times nRT \left( \frac{1}{P_2} - \frac{1}{P_1} \right)$$

$$= -10 \times 8 \times T \left( \frac{1}{1} - \frac{1}{2} \right) = -40T$$

$$\Rightarrow q = 40T$$

$$\Delta S_{\text{surr}} = \frac{-40T}{T} = -40$$

$$\Delta S_{\text{Total}} = 56 - 40 = 16 \text{ J/k}$$

15.  $\text{H}_2\text{O} (l) \rightarrow \text{H}_2\text{O} (g)$

$$1\text{-atm} \quad 1\text{-atm}$$

$$323\text{k} \quad 323\text{k}$$

$$\Delta C_p = 33.305 - 75.312 = -42.007$$

$$\Delta_r G_{323\text{k}} = \Delta_r H_{323\text{k}} - 323 \times \Delta_r S_{323\text{k}}$$

$$\Delta_r H_{373\text{K}} = \Delta_r H_{\text{vap}} = 40.639 \times 10^3$$

$$\Delta_r H_{373} - \Delta_r H_{323} = \Delta C_p (373 - 323)$$

$$40.639 \times 10^3 - \Delta_r H_{323} = -42.007 \times 50$$

$$\Delta_r H_{323} = 40.639 \times 10^3 + 42.007 \times 50$$

$$= 42739.35 \text{ J}$$

$$\text{At } 373 (\text{ normal b.p.}) \Delta_r G = 0 \Rightarrow \frac{\Delta_r H_{373}}{7} = \Delta_r S_{373}$$

$$\Delta_r S_{373} = \frac{40.639 \times 10^3}{373} = 108.95 \text{ J/k}$$

$$\Delta_r S_{373} - \Delta_r S_{323} = \Delta C_p \ln \left( \frac{373}{323} \right)$$

$$108.95 - \Delta_r S_{323} = -42.007 \ln \left( \frac{373}{323} \right)$$

$$\Rightarrow \Delta_r S_{323} = 114.99 \text{ J/k}$$

$$\Rightarrow \Delta_r G_{323} = 42739.35 - 323 \times 114.99$$

$$= 5597.58 \text{ J} = 5.597 \text{ KJ/mole}$$



**EXERCISE – IV****ADVANCED SUBJECTIVE QUESTIONS****Sol.1 [A,D]**

$$\text{or, } T_B = \frac{30 \times 10^3}{75} = \frac{30 \times 40}{3} = 10 \times 40$$

**Sol.2 [A]** (Use second law of thermodynamics)

$$= 400 \text{ K}$$

**Sol.3 [A]****Sol.9 [C]** $n = 1$  mole, nonideal gas**Sol.4 [D]**

$$\Delta U = 30 \text{ L atm}$$

$$\Delta S_{AB} = 50 + 30 - 20 = 60 \text{ e.u.}$$

$$\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

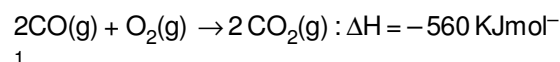
$$\text{or } 30 + (4 \times 5 - 2 \times 3) = 44 \text{ L atm}$$

**Sol.5 [A]****Sol.10 [A]**

Work is a path function

$$C_m = C_{v,m} + \frac{R}{1-n}$$

$$\frac{p}{v} = 1 \Rightarrow pv^{-1} = \text{const} \Rightarrow \boxed{n = -1}$$

**Sol.11**

$$\therefore cm = \frac{R}{\left(\frac{5}{3}-1\right)} + \frac{R}{1+1} = \frac{3R}{2} + \frac{R}{2} = \frac{4R}{2}$$

$$= 2R$$

$$V_1 = 1 \text{ L}, T_1 = 500 \text{ K}, P_1 = 70 \text{ atm}$$

$$P_2 = 40 \text{ atm}$$

$$\Delta U = ?$$

$$\Delta H = \Delta U + P\Delta V + V\Delta P$$

$$-560 = \Delta U + 1(40 - 70) \times 0.1$$

$$\Delta U = -560 + 3 = -557 \text{ K J mol}^{-1}$$

**Sol.6 [C]****Sol.7 [C]**

$$n = 2, T = \text{constant } V_1 = 1\text{L}, V_2 = 10\text{L}, T = 300\text{K}$$

$$\Delta H = ?$$

reversible isothermal

$$\Delta H = 0 \text{ at } T \text{ is constnat}$$

**Sol.12**

$$n = 1 \text{ mole } P_1 = 1 \text{ bar}, 100 \text{ ml}$$

$$Q = 0, P_2 = 100 \text{ bar} \quad \Delta V = 1 \text{ ml}$$

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

$$= -100 \text{ bar} \left( \frac{99}{1000} - \frac{100}{1000} \right) \text{ litre}$$

$$= 0.1 \text{ L bar.}$$

$$\therefore \Delta U = w = 0.1 \text{ L bar}$$

$$\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$$

$$= 0.1 + \left( \frac{100 \times 99}{1000} - \frac{1 \times 100}{1000} \right)$$

$$= 0.1 + 9.9 - 0.1$$

$$= 9.9 \text{ L bar}$$

**Sol.8 [B]**

$$\Delta H_{\text{vap}} = 30 \text{ KJmol}^{-1}$$

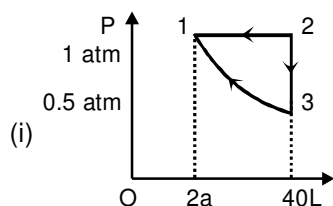
$$\Delta S_{\text{vap}} = 75 \text{ KJmol}^{-1}$$

$$T_B = ? \text{ at } 1 \text{ atm}$$

$$\frac{\Delta H_{\text{vap}}}{T_B} = \Delta S_{\text{vap}}$$

## Sol.13

$$n = 2$$



(iii)  $\Delta U = \Delta H = \Delta S = 0$  (for cyclic process).

$$(ii) W_{\text{total}} = W = W_{12} + W_{23} + W_{31}$$

$$-1(40 - 20) + 0 - nRT \ln \frac{V_1}{V_3}$$

$$\text{or } w = -20 - P_1 V_1 \ln \frac{V_1}{V_3}$$

$$= -20 - 1 \times 20 \ln \frac{20}{40} = -20 + 20 \ln 2$$

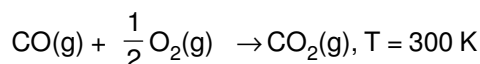
$$= -20 + 20 \times 0.693$$

or

$$w = -20 + 13.86 \text{ Latm} = -6.14 \text{ L atm}$$

$$= -6.14 \times 101.3 \text{ J} = -Q_{\text{total}}$$

## Sol.14



$$\Delta S^\circ = -0.094 \text{ KJ mol}^{-1} \text{ K}^{-1}.$$

$$\Delta G^\circ = \sum (\Delta G_f^\circ)_P - \sum (\Delta G_f^\circ)_R$$

or

$$\Delta G^\circ = -394.4 - (-137.2)$$

$$= -257.2 \text{ KJ mol}^{-1}$$

Since  $\Delta G^\circ = (-)$  ve  $\Rightarrow$  reversible is spontaneous at solid state.

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

$$-257.2 = \Delta H^\circ + 300 \times 0.094$$

$$\text{or } \Delta H^\circ = -257.2 - 28.2$$

$$= -285.4 \text{ KJ mol}^{-1}$$

$\Rightarrow$  reversible is exothermic

## Sol.15

$$P_1 = 1 \text{ atm}, T_1 = 300 \text{ K}$$

$$\text{rev. adiabatic } V_1 = 1.25 \text{ dm}^3, V_2 = 2.5 \text{ dm}^3$$

$$C_{v,\text{rev}} = 12.48 \text{ JK}^{-1} \text{ mol}^{-1} \quad \gamma = 5/3 \quad (\therefore \text{monoatomic C})$$

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

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

$$\text{or } T_2 = 300 \left( \frac{1.25}{2.5} \right)^{(5/3-1)} = 300(0.5)^{2/3} = 300$$

$$\times 0.63$$

$$= 189 \text{ K}$$

$$n = \frac{P_1 V_1}{RT_1} = \frac{1 \times 1.25}{0.0821 \times 300} = 0.05 \text{ mole}$$

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

$$= 0.05(12.48 + 8.314)(189 - 300)$$

$$= 0.05 \times 20.794 \times (-111)$$

$$= -115 \text{ J}$$

## 16. solid line reversible (isothermal)

$$w_s = -nRT \ln \left( \frac{V_2}{V_1} \right)$$

$$= -pv \ln \left( \frac{V_2}{V_1} \right)$$

$$= -2 \ln \left( \frac{5.5}{0.5} \right) = -2 \ln 11$$

$$W_s = -4.7$$

$$|w_{\text{dot}}| = [4 \times (2 - 0.5)] + [1(3 - 2)] + [2/3(5.5 - 3)]$$

$$|w_{\text{dot}}| = 6 + 1 + 5/3 = 8.67$$

$$|w_{\text{dot}}| = -8.67 \Rightarrow w_d/w_s = \frac{-8.67}{-4.7} = 1.8$$

$$= 2$$

## 17.

(A) P, R, S

(B) R, S

(C) T ( $\Delta n_g < 0$ )

(D) P, Q, T ( $\Delta H < 0$ )