

MAINS+ADVANCED

TOPIC
THERMODYNAMICS

SOLUTIONS

THERMODYNAMICS

Exercise-01

- $m_{Zn} \cdot S_{Zn} \cdot (T_f - T_i) + m_{H_2O} \cdot S_{H_2O} \cdot (T_f - T_i) = 0$
 $(65.38 \text{ gm}) (0.4 \text{ J/g}^\circ\text{C}) (T_f - 20^\circ\text{C}) + 180 \text{ gm}$
 $(4.20 \text{ J/g}^\circ\text{C}) \times (T_f - 100^\circ\text{C}) = 0$
 $\Rightarrow [(65.38) (0.4) + 180(4.20)]$
 $T_f = (65.38) (0.4) (20) + (180) (4.20) (100)$
 $T_f = \left[\frac{(65.38)(0.4)(20) + (180)(4.20)(100)}{(65.38)(0.4) + (180)(4.20)} \right] = 97.3^\circ\text{C}$
- $\Delta U = q + w$
 heat absorb (q) = 45 joule
 $w = -70$ joule since
 Work done by the system.
 $\Delta U = q + w = 45 - 70 = -25$ joule
- Decrease in internal energy = $-\Delta U$
 work done by the system = $-w$
 $-\Delta U = -w \Rightarrow \Delta U = w \Rightarrow q = 0$
 The process is adiabatic.
- At constant volume $w_{PV} = 0$
 $\Rightarrow \Delta U = q$ first law
- The energy due to external field is not included in internal energy like gravitational field, earth's magnetic field etc.
- Heat and work are path dependent, or indefinite quantity.
- For monoatomic ideal gas total degree of freedom = 3
 Three translational mode of motion

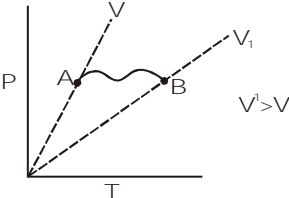
- $C_V = 3 \times \frac{1}{2} R = \frac{3}{2} R$ $C_P = C_V + R = \frac{5}{2} R$
 $r = \frac{C_P}{C_V} = \frac{5}{3}$
- Ar = monoatomic ideal gas $C_V = \frac{3}{2} R$
 At constant pressure $q = \Delta H = nC_P \Delta T$
 $q = (0.25 \text{ mole}) \frac{5}{2} (8.314 \text{ J / K mole}) (16)$
- Reversible process involve infinitesimally small driving force. Hence system and surrounding remains in equilibrium.
- temperature at 'a' = $T_0 = \frac{PV}{R}$
 at (a) $T_0 = \frac{P_0 V_0}{R}$ (i)
 at (c) $T_c = \frac{(2P_0)(4V_0)}{R} = 8 T_0$
 $\Delta U = nC_V (T_f - T_i) = \frac{3}{2} R (8T_0 - T_0)$
 $\Delta U = \frac{21RT_0}{2} = 10.5 RT_0$
- Work done in adiabatic process
 $\Delta U = w = nC_V \Delta T$
 $w = (2)(12.5)(200 - 300)$
- The case of irreversible adiabatic process.
 $w = -P(V_f - V_i)$
 $\Rightarrow nC_V (T_2 - T_1) = -P(V_f - V_i)$ $n = 1$

$$C_V = \frac{3}{2}R \quad T_1 = T$$

$$T_2 = \frac{-P(V_f - V_i)}{nC_V} + T = T - \frac{(1\text{atm})(2\text{L} - 1\text{L})}{\frac{3}{2}(R)}$$

$$T_2 = T - \frac{2(\text{L atm})}{3 \times 0.0821 (\text{L atm K}^{-1} \text{mole}^{-1})}$$

15. $V_B > V_A$ and $T_B > T_A$
 $\Delta H = nC_p(T_B - T_A) > 0$
 $w = -P_{\text{ext}}(V_B - V_A) < 0$



16. Heat of reaction at const. pressure = $\Delta_r H$

Heat of reaction at const. pressure = $\Delta_r U$

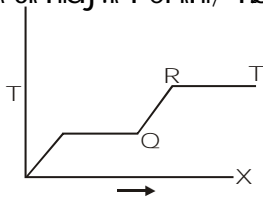
$$\Delta_r H = \Delta_r U + \Delta n_g RT$$

$$\Delta n_g = -3$$

$$\Delta_r H - \Delta_r U = (-3 RT)$$

18. Fusion and vaporisation are example of isothermal processes -

(xyu rFlk ok' i hdj.k l erkih; i Øe dsmnkj.k gš)



$$T_f < T_b \quad PQ - T_f \quad RT - T_b$$

19. $\text{H}_2\text{O}(s) \xrightarrow{q_1} \text{H}_2\text{O}(l) \xrightarrow{q_2} \text{H}_2\text{O}(l)$
 $0^\circ\text{C} \quad 0^\circ\text{C} \quad 25^\circ\text{C}$

$$q_1 = \Delta H_{\text{fusion}} (\text{kJ/mole}) \left(\frac{36}{18} \text{mole} \right)$$

$$q_1 = 6.01 \times 2 = 12.02 \text{ kJ}$$

$$q_2 = mS \Delta T = (36 \text{ gm}) (4.18 \text{ J/K gm}) 25$$

$$q_{\text{NET}} = q_1 + q_2 = \left[12.02 + \frac{(36)(25)(4.18)}{1000} \right] \text{kJ}$$

20. When ice \rightleftharpoons liquid : the process is reversible fusion. The fusion is isothermal process.

(1 1 (\rightleftharpoons æo % i Øe mRØe.kh; xyu gš xyu l erkih; i Øe gš

$$C = \frac{dq}{dT} = \frac{dq}{0} \rightarrow \infty$$

21. $\Delta U = q + w$

$P = \text{constant}$ since $\Delta H = q_p$

$$202.6 = \Delta U + 1 \text{ atm} (2 \text{ litres})$$

$$\Rightarrow \Delta U = 202.6 - 2(\text{L atm}) (101.325 \text{ J/L atm})$$

$$\Delta U = 0$$

22. For reversible adiabatic process (mRØe.kh; : } Øe i Øe ds fy,)

$$q_{\text{rev}} = 0 \Rightarrow \Delta S_{\text{system}} = 0$$

23. $\Delta S = nC_V \ln \frac{T_2}{T_1} + nR \ln \left(\frac{V_2}{V_1} \right)$

$$\Delta S = 5 \ln \frac{373}{298} + R \ln \left(\frac{10}{1} \right)$$

24. Using $\Delta S_{\text{transition}} = \frac{\Delta H_{\text{transition}}}{T_{\text{transition}}}$

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

$$\Delta S_{\text{trans}} = \frac{-401.7}{368}$$

$$\Delta S_{\text{surr}} = \frac{+401.7}{273}, \because \text{temperature of ice bath} = 273\text{K}$$

$$\Delta S_{\text{total}} = \frac{-401.7}{368} + \frac{401.7}{273}$$

25. Initial pressure $P = \frac{RT}{V}$

$$P = 300 \text{ R} = (300 \times 0.0821) \text{ atm}$$

final pressure = 1 atm

$$\text{final volume ; } P_f V_f = P_i V_i$$

$$\Rightarrow V_f = \frac{P_i V_i}{P_f} = \left(\frac{(300)R}{1} \right) = 24.6 \text{ L}$$

$$\Delta S = nRT \ln \frac{V_2}{V_1}$$

$$\Delta S = R \ln \left(\frac{24.6}{1} \right)$$

26. for spontaneous reactions $\Delta S_{\text{total}} > 0$

(Lor% vflkØ; k ds fy,)

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

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} - \left(\frac{-X}{298} \right)$$

$$\Delta S_{\text{total}} > 0 \Rightarrow \Delta S_{\text{syst}} + \frac{X}{298} > 0$$

$$\Delta S_{\text{syst}} > \left(\frac{-X}{298} \right)$$

Hence ΔS_{syst} can be negative but numerically smaller than $\frac{X}{298}$.

vr% $\Delta S_{\text{syst}} \frac{1}{2}$. kRred gš l drk gš yfdu vfkdd

: i l s $\frac{X}{298}$ l s Nk/k gš k gš

27. For dissociation reactions (fo; kst u vflkfØ; k dsfy,) $\Delta H > 0$ and $\Delta n_g > 0 \Rightarrow \Delta_r S > 0$
28. $\Delta G = \Delta H - T\Delta S$
 $\Delta G = -33000 - [\pi(-58)]$
 $\Delta G = -33000 + 58 T$
 spontaneous but less than certain temperature.
29. Formation of Fe_3O_4
 $3Fe(s) + 2O_2(g) \longrightarrow Fe_3O_4(s)$; $\Delta G = ?$

$$\Delta G = \frac{1}{3} \times (-19 \text{ kcal}) + \frac{2}{3} (-177 \text{ kcal})$$

$$= -242.3 \text{ kcal/mole}$$

30. $T = \frac{\Delta H^\circ}{\Delta S^\circ}$
 $\Delta H^\circ = -110 - (-266.3)$
 $\Delta S^\circ = 197.6 + 27.28 - 5.74 - 54.49$
 Above this temperature the process becomes spontaneous. (bl rki ds Åij i Øe Lor% glsk)

Exercise-02

1. Intensive property (xgu xqk)

$$= \frac{\text{extensive property (foLrtk xqk)}}{\text{extensive property}}$$

 $pH \propto \text{concentration} = \text{mole/volume}$
 though pH is a dimensionless number and intensive property (fi pH foekjfg r l Å; k rFlk xgu xqk gS)

EMF = $\frac{\text{energy}}{\text{ch arge}}$ = Intensive property
 Boiling point(T_b) = temperature = intensive property
 entropy (s) = $\frac{q}{T} = \frac{\text{extensive}}{\text{intensive}}$ = extensive property

2. At constant T, the molecule with maximum atoms have greatest internal energy.

fu; r T ij. vf/kdre l Å; k okys v. kq ds vkrfjd Åtkl vf/kdre glrh gS

3. $q = 0$ $\Delta U = W$
 $\Rightarrow 3000 = C_V(T_2 - T_1)$
 $T_2 - T_1 = \frac{3000}{20} = 150$ $T_2 = T_1 + 150 = 450 \text{ K}$

4. Irreversible adiabatic process (vullØe.kh; : }kØe i Øe)

$$W = -P_{\text{ext}} \left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1} \right)$$

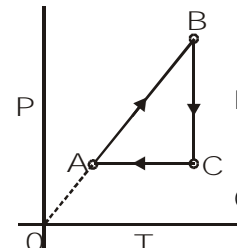
$P_2 = P_{\text{ext}} = 2 \text{ atm}$ $T_1 = 300 \text{ K}$
 $P_1 = 1 \text{ atm}$
 $W = -(2 \text{ atm}) \left[\frac{2(R) \cdot T_2}{2 \text{ atm}} - \frac{2R(350)}{1 \text{ atm}} \right]$
 and $W = 2C_V(T_2 - 350) = 2 \times \frac{5}{2} R(T_2 - 350)$
 $5R(T_2 - 350) = (750 R - 2 RT_2)$
 $5T_2 - 1750 = 1400 - 2T_2$
 $7T_2 = 3150$ $T_2 = 450 \text{ K}$
 $W = 2 \times C_V(450 - 350)$
 $= 2 \times \frac{5}{2} R \times (100) = 500 R$

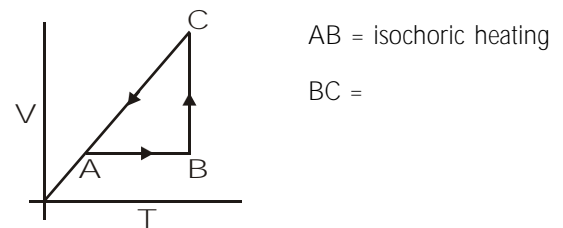
$$W = W_{AB} + W_{BC} + W_{CD}$$

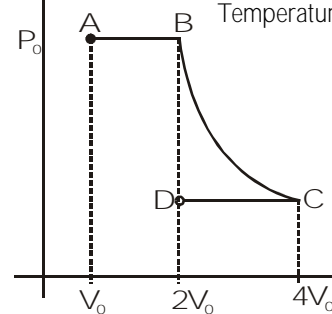
$$= -P_0(V_B - V_A) - nRT_B \ln \left(\frac{V_C}{V_B} \right) - \frac{P_0}{2}(V_D - V_C)$$

$$W = -P_0(2V_0 - V_0) - 2P_0V_0 \ln \left(\frac{4V_0}{2V_0} \right) - \frac{P_0}{2}(2V_0 - 4V_0)$$

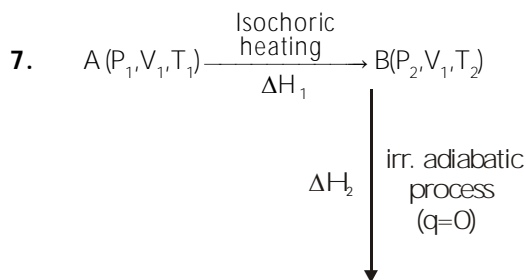
$$W = -2P_0V_0 \ln 2$$
 and $q = -W$ ($\because \Delta U = 0$)
 $q = 2 P_0V_0 \ln 2$

5.  AB = isochoric heating (l evk; rfu; rki u)
 BC = isothermal expansion (l erkih; i l kj)
 CA = isobaric cooling (l enkch; 'khyu)



6.  Temperature at A (T_A) = $\frac{P_0 V_0}{nR}$
 $T_B = \frac{2P_0 V_0}{nR}$
 $T_C = \frac{2P_0 V_0}{nR}$
 $T_D = \frac{(P_0/2) \cdot 2V_0}{nR} = \frac{P_0 V_0}{nR} = T_A$
 now $\because T_D = T_A$; $\Delta U = \Delta H = 0$

$$\left\{ \begin{array}{l} \text{remember for ideal gas } \Delta U = nC_V \Delta T \\ \Delta H = nC_P \Delta T \end{array} \right\}$$



$$\Delta H_{\text{overall}} = \Delta H_1 + \Delta H_2$$

$$\Delta H_1 = \Delta U_1 + (P_2 V_1 - P_1 V_1)$$

$$\Delta H_1 = C_V(T_2 - T_1) + (P_2 V_1 - P_1 V_1)$$

$$\Delta H_2 = \Delta U_2 + (P_3 V_2 - P_2 V_1)$$

$$\Delta H_2 = -P_3(V_2 - V_1) + (P_3 V_2 - P_2 V_1)$$

$$\Delta H_2 = P_3 V_1 - P_2 V_1$$

$$\Delta H_{\text{overall}} = C_V(T_2 - T_1) + (P_2 V_1 - P_1 V_1) + P_3 V_1 - P_2 V_1$$

$$= C_V(T_2 - T_1) + P_3 V_1 - P_1 V_1$$

8. $\eta = \frac{T_2 - T_1}{T_2}$

$$\eta = \frac{373 - 298}{373} = \left(\frac{75}{373}\right)$$

$$\eta \times 100 =$$

9. $\eta = \frac{T_2 - T_1}{T_2}$

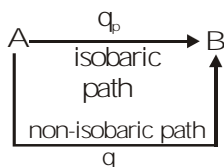
$$\eta = \frac{500 - 300}{500} = \frac{2}{5}$$

$$\eta = \frac{W_{\text{by}}}{q_{\text{source}}} \Rightarrow W_{\text{by}} = (\eta C) (q_{\text{source}})$$

$$= \left(\frac{2}{5}\right) (2 \text{ kcal}) = 0.8 \text{ kcal}$$

10. $\Delta H = q_p$

since H is state function ΔH will remain same from both path-isobaric and non-isobaric



But $q = q_p$ only when path was isobaric.

$\Delta H = q_p$ only for isobaric path.

11. Greater the Δn_g greater the value of ΔS .

12. $\Delta S = nC_V \ln\left(\frac{T_2}{T_1}\right)$ for isochoric change.

$$\Delta S = 2 \times \left(\frac{3}{2} R\right) \ln\left(\frac{573}{473}\right)$$

$$\Delta S = 3R \ln\left(\frac{573}{473}\right)$$

13. The net heat absorbed by hot and cold body is equal to zero.

$$q_H + q_C = 0$$

Let C_V is the total heat capacity of hot and cold body.

$$C_V(T_f - T_C) + C_V(T_f - T_H) = 0$$

$$\Rightarrow T_f = \frac{T_H + T_C}{2}$$

Entropy change $\Delta S_{\text{Total}} = \Delta S_{\text{hot body}} + \Delta S_{\text{cold body}}$

$$\Delta S_{\text{hot body}} = C_V \cdot \ln\left(\frac{T_f}{T_H}\right)$$

$$\Delta S_{\text{cold body}} = C_V \cdot \ln\left(\frac{T_f}{T_C}\right)$$

$$\Delta S_{\text{Total}} = C_V \left(\ln \frac{T_f}{T_H} + \ln \frac{T_f}{T_C} \right)$$

$$= C_V \left(\ln \frac{T_f^2}{T_H \cdot T_C} \right)$$

$$\Delta S_{\text{Total}} = C_V \ln \left[\frac{(T_f + T_C)^2}{4 T_H \cdot T_C} \right]$$

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

$$y = C + mX$$

$$\Rightarrow \Delta H = C$$

$$m = -\Delta S$$

from intercept $C > 0 \Rightarrow \Delta H > 0$

$$m < 0 \Rightarrow -\Delta S < 0$$

$$\Rightarrow \Delta S > 0$$

15. Melting of $H_2O(s)$ at $0^\circ C$ and 1 atm is a reversibly process

$$\Rightarrow \Delta S_{\text{Total}} = 0$$

Vaporisation of $H_2O(l)$ at 373 K is a reversible process

$$\Delta S_{\text{Total}} = 0$$

Below 0°C - $\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l})$ is non spontaneous not feasible.

$\text{H}_2\text{O}(\text{l}) \longrightarrow \text{H}_2\text{O}(\text{s})$ (freezing) is feasible above 0°C

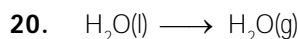
$\text{H}_2\text{O}(\text{s}) \longrightarrow \text{H}_2\text{O}(\text{l})$

feasibly $\Rightarrow \Delta G = -$ ive for melting process $\Rightarrow \Delta S_{\text{Total}}$ increases

19. $\Delta G = \Delta H + \Delta E$

$$\Delta G = -3000 - 1 \times 2 \times 300 + 3000$$

$$= -6000 \text{ cal}$$



$$373 \text{ K} \quad 373 \text{ K}$$

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

$$\Delta S = \frac{\Delta H_{\text{vap}}}{T}$$

$$\Delta G = \Delta H_f - \Delta H_i = 0$$

Exercise-03

COMPREHENSION # 1

1. $U = \alpha \sqrt{V}$ Here $U =$ Kinetic energy of ideal gas

(वक्र की x अक्ष की दर से आती है)

$$U = nC_v T$$

$$\Rightarrow nC_v T = \alpha \sqrt{V} \quad \dots(i) \quad T = \frac{PV}{nR} \quad \dots(ii)$$

sub. (2) in (1)

$$\left(\frac{C_v}{R}\right) \cdot PV = \alpha \sqrt{V}$$

$$\Rightarrow P = \left(\frac{\alpha R}{C_v}\right) \frac{1}{\sqrt{V}}$$

$$w = -\int PdV = -\left(\frac{\alpha R}{C_v}\right) \int \frac{dV}{\sqrt{V}}$$

$$= -(\alpha) (\gamma - 1) \cdot \frac{1}{(1/2)} (\sqrt{V}) \Big|_{V_1}^{V_2}$$

$$w = -2(\alpha) (\gamma - 1) (\sqrt{V_2} - \sqrt{V_1})$$

work done by the gas = $-w = 2(\alpha)$

$$(\gamma - 1) (\sqrt{V_2} - \sqrt{V_1})$$

2. For diatomic gas with no vibrational degree of freedom

$$C_v = \frac{3}{2} R + 2 \times \frac{1}{2} R$$

$$C_v = 5/2 R$$

$$\Delta U = \alpha (\sqrt{V_2} - \sqrt{V_1}) = 100 \text{ J}$$

$$w = 2(\alpha) (\gamma - 1) (\sqrt{V_2} - \sqrt{V_1}) = (2) (\gamma - 1) \times 100$$

$$\therefore \gamma = \frac{C_p}{C_v} = \frac{7}{5}$$

$$(\gamma - 1) = \left(\frac{7}{5} - 1\right) = \left(\frac{2}{5}\right)$$

$$w = (2) \left(\frac{2}{5}\right) (100 \text{ J}) = 80 \text{ J}$$

3. $\Delta U = q + w \Rightarrow 100 \text{ J} = q - 80 \text{ J}$

$$q = 180 \text{ J}$$

COMPREHENSION # 2

1. $\Delta_r S^\circ = S^\circ(\text{CH}_3\text{OH}, \text{g})$

$$- [S^\circ(\text{CO}, \text{g}) + 2 \times S^\circ(\text{H}_2, \text{g})]$$

$$= 240 - 198 - 29 \times 2 = -16 \text{ J/K-mole}$$

2. $\Delta_r H^\circ = \Delta_r H^\circ(\text{CH}_3\text{OH}, \text{g})$

$$- \Delta_r H^\circ(\text{CO}, \text{g}) = -201 - (114) = -87 \text{ kJ/mol}$$

3. $\Delta_r S_{T_2}^\circ - \Delta_r S_{T_1}^\circ = \Delta C_p^\circ \ln \frac{T_2}{T_1}$

$$\Delta C_p^\circ = C_{p,m}^\circ(\text{CH}_3\text{OH}) - [C_{p,m}^\circ(\text{CO}) + 2C_{p,m}^\circ(\text{H}_2)]$$

$$= 44 - (29.4 + 2 \times 28.8) = -43 \text{ J/K}\cdot\text{mol}$$

$$\Delta_r S_{T_2}^\circ - (-16) = (-43) \ln \frac{320}{300}$$

$$\Delta_r S_{T_2} = -13.225 \text{ J/K}\cdot\text{mol}$$

4. $\Delta_r H_{T_2}^\circ - \Delta_r H_{T_1}^\circ = \Delta_r C_p^\circ (T_2 - T_1)$

$$\Delta_r H_{T_2}^\circ - (-87) = -43(320 - 300)$$

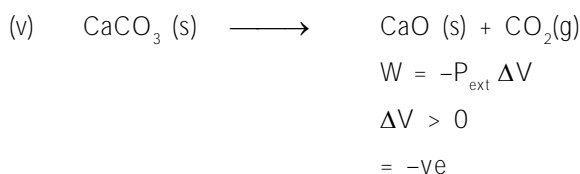
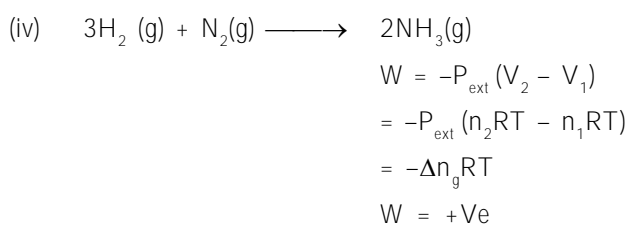
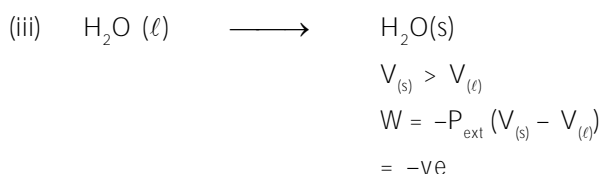
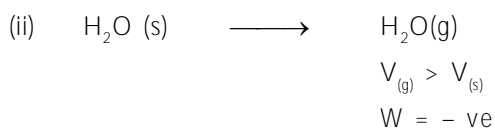
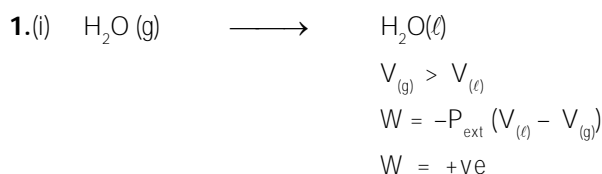
$$\Delta_r H_{T_2}^\circ = -87.86 \text{ kJ/mol}$$

5. $\Delta_r G^\circ = \Delta_r H_{T_2}^\circ - T \Delta_r S_{T_2}^\circ$

$$= -87860 - 320(-13.225)$$

$$= -81.91 \text{ kJ/mol}$$

Exercise-4(A)



2. $\Delta E = -65 \text{ J}$
 $\Delta q = \Delta V - w$
 $\Delta V = -45 \text{ J}$

3. $\Delta H_{\text{glucose}} = -2808 \text{ kJ mol}$

(a) Energy need to climb 3m = $Mgh = 62.5 \times 10 \times 3$
 $\Delta q = 1875 \text{ Joule}$
 Now useful energy from 1 mole of glucose

$$= 2808 \times \frac{1}{4} = 702 \text{ kJ}$$

$$\Rightarrow \text{No. of mole of glucose required} = \frac{1875}{702 \times 10^3}$$

$$= 2.67 \times 10^{-3} \text{ mole}$$

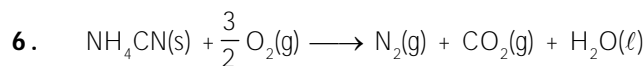
$$\text{grams of glucose} = 180 \times 2.67 \times 10^{-3} = 0.4807 \text{ gm}$$

(b) Energy need to climb 3000 m will be 10^3 time.

$$\Rightarrow \text{wt. should be } 10^3 \text{ time} = 0.4807 \text{ kg}$$

4. $q_p = q_v + \Delta n_g RT$
 $40.66 \times 2 = q_v + 2 \times 8.314 \times 373$
 $\Rightarrow q_v = (81.32 - 6.202) \text{ kJ}$
 $q_v = 75.118 \text{ kJ}$

5. $\Delta H = 1 \text{ kcal}$
 $\Delta H = \Delta E + P \Delta V$
 $1 \times 10^3 \times 4.18 = \Delta E + 1.013 \times 10^5 \times 3 \times 10^{-3}$
 $\Delta E = (4180 - 30.39) \text{ Joule} = \left(\frac{4149.61}{4.18} \right) \text{ cal}$
 $\Delta E = 0.993 \text{ kcal}$



$$\Delta H_{298} = \Delta E + \Delta n_g RT = -742.7 + \frac{1}{2} \times 8.314 \times 298$$

$$= -742.7 + 1.239$$

$$\Delta H_{298} = -741.46$$

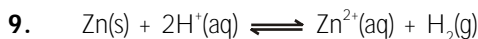
7. $\Delta H = 1440 \text{ cal}$
 $\Delta H = \Delta E + P(V_2 - V_1)$
 $1440 = \Delta E + 1.013 \times 10^5 (0.0180 - 0.0196) \times 10^{-3}$

$$\Delta E = 1440 - 1.013 \times 0.0016 \times 10^{-3}$$

$$\Delta E = 1440.168$$

8. $W = \int P_{\text{ext}} dV$
 $= -\int P(V_2 - V_1) = -1.01 \times 10^5 (0.1) \times 10^{-3}$

$$W = -10.1 \text{ J}$$



$$\Delta H = -36.5 \text{ kJ}$$

$$\Delta Q = \Delta E - W - 36.5 \text{ kJ}$$

$$= \Delta E + 1.01 \times 10^5 (500 \times 50 \times 10^{-6})$$

$$\Delta E = -39.03 \text{ kJ}$$

$$W = -P_{\text{ext}}(V_2 - V_1) = -1.013 \times 10^5 \times 500 \times 50 \times 10^{-6}$$

$$W = -2.53$$

10. $W_{\text{irr}} = -nRT \left(1 - \frac{P_2}{P_1} \right) = -5 \times 8.314 \times 300 \left(1 - \frac{1}{4} \right)$

$$W_{\text{irr}} = -9.353 \text{ kJ}$$

$$W_{\text{rev}} = -2.303 nRT \log \left(\frac{V_2}{V_1} \right)$$

$$W_{\text{rev}} = -2.303 \times 5 \times 8.314 \times 300 \log 4$$

$$W_{\text{rev}} = -17.29 \text{ kJ}$$

and $\Delta q = \Delta E - W$

at $\Delta T \rightarrow 0 \quad \Delta E \rightarrow 0 \quad \Delta H \rightarrow 0$

$$W_{\text{rev}} = -q = 17.29 \text{ kJ}$$

11. $n_1 = 1$

$$T_1 = 300 \quad V_2 = 27 V_1 \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\left(\frac{T_1}{T_2} \right) = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \quad T_2 = 300 \left(\frac{1}{27} \right)^{\frac{1}{3}}$$

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

Adiabatic condition $\Delta Q = 0 \Rightarrow \Delta E = W = nC_v(T_2 - T_1)$

$$W = 1 \times 25 \times -200 \quad W = -5.000 \text{ kJ/mole}$$

12. Process reversibly adiabatic

$$T_1 = 298.15 \text{ K} \quad V_2 = 2V_1$$

$$T_2 = 248.44 \text{ K} \quad P_1 V_1^\gamma = P_2 V_2^\gamma \quad PV = nRT$$

$$\frac{T}{V} \cdot V^\gamma = K \quad T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$$

$$\left(\frac{T_1}{T_2} \right) = \left(\frac{V_2}{V_1} \right)^{\gamma-1} \quad \left(\frac{298.15}{248.44} \right) = 2^{\gamma-1}$$

$$1.2 = 2^{\gamma-1} \quad \log 1.2 = \log 2 \cdot (\gamma-1)$$

$$\gamma - 1 = \frac{\log 1.2}{\log 2} \quad \gamma - 1 = 0.263$$

$$\text{Now } nC_v(T_2 - T_1) = \frac{P_2 V_2 - P_1 V_1}{\gamma - 1}$$

$$C_{v,m} = \left(\frac{R}{\gamma - 1} \right) = \frac{nR(T_2 - T_1)}{(\gamma - 1)}$$

$$C_{v,m} = \frac{8.314}{0.263} \quad C_{v,m} = 31.61$$

13. $W = -2.303 nRT \log \left(\frac{P_1}{P_2} \right)$

$$= -2.303 \times 1 \times 8.314 \times 298 \log \left(\frac{1}{5} \right)$$

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

14.

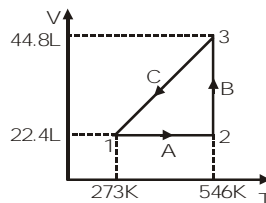


Table-1			
State	P	V	T
1	1	22.4L	273
2	2atm	22.4	546K
3	1atm	44.8	546K

State - 1

$$PV = nRT \Rightarrow P = 1 \text{ atm}$$

State - 2

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \Rightarrow P_2 = 2 \text{ atm}$$

$$P_2 = \frac{546}{273} \times 1 \text{ atm}$$

State - 3

$$P_1 V_1 = P_2 V_2$$

$$2 \times 22.4 = 44.8 \times P_2$$

$$P_2 = 1 \text{ atm}$$

Step	Name of process	q	w	ΔE	ΔH
A	Isochoric	$\frac{3}{2}R(273)$	0	$\frac{3}{2}R(273)$	$\frac{5}{2}R(273)$
B	Isotherm	$546R \ln 2$	$-546R \ln 2$	0	0
C	Isotherm	$\frac{5}{2}R(273)$	$R(273)$	$\frac{3}{2}R(273)$	$\frac{5}{2}R(273)$
overall					

State - A → (Isochoric)

$$W = 0 \quad \Delta q = \Delta E$$

$$\Rightarrow 1 \times \frac{3}{2}R(273)$$

$$\Delta H = nC_p dT \quad \Delta H = 1 \times \frac{5}{2}R(273)$$

State - B → (Isothermal)

$$\Delta E = 0 \quad \Delta H = 0$$

$$\therefore \Delta H = \Delta E + \Delta PV$$

$$\text{is } Q = -w = +2.303 \times 1 \times 8.314 \log(2) \times 546$$

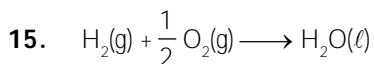
$$Q = 546 R \ln 2 \quad W = -546 R \ln 2$$

$$\Delta E = nC_V \Delta T \quad W = nR(T_2 - T_1)$$

$$\text{State - C} \rightarrow \text{(Isobaric)}$$

$$\Delta q = \Delta E - w = \Delta E + P(V_2 - V_1)$$

$$\text{or } \Delta H = \Delta E + P\Delta V = \frac{5}{2}R(-273)$$

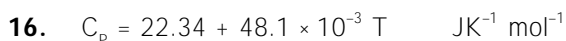


$$\begin{aligned} \Delta C_{p_{\text{reaction}}} &= C_{p_{\text{H}_2\text{O}(\ell)}} - C_{p_{\text{H}_2(\text{g})}} - \frac{1}{2} C_{p_{\text{O}_2(\text{g})}} \\ &= 75.312 - 38.83 - \frac{1}{2} \times 29.16 \end{aligned}$$

$$\Delta C_{p_{\text{reaction}}} = 21.90 \text{ kJ}$$

$$\begin{aligned} \Delta H_{373} &= \Delta H_{298} + nC_p \Delta T \\ &= (-285.76 + 1 \times 21.9 \times 75 \times 10^{-3}) \text{ kJ} \end{aligned}$$

$$\Delta H_{373} = -284.12 \text{ kJ}$$



$$\begin{aligned} \Delta H &= \int_{T_1}^{T_2} nC_p dT = \int_{T_1}^{T_2} (22.34 + 48.1 \times 10^{-3} T) dT = \\ &22.34 \times 298 + \frac{48.1 \times 10^{-3} \times 298 \times 3}{2} \times 298 \end{aligned}$$

$$\Delta H = 13.064 \text{ kJ/mole}$$

$$W = -P(V_2 - V_1) = -nR(T_2 - T_1)$$

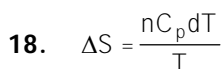
$$W = -20477$$

$$\Delta E = 13.064 - 2.477$$

$$\Delta E = 10.587 \text{ kJ}$$

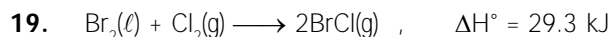


$$\Delta H = T\Delta S \quad \frac{30.5 \times 10^3}{28.8} = T = 1059 \text{ K}$$



$$\begin{aligned} &= 1 \times \int \left(\frac{25.5}{T} + 13.6 \times 10^{-3} - 42.5 \times 10^{-7} T \right) dT \\ &= 2.303 \times 25.5 \log 2 + 13.6 \times 10^{-3} \times 300 - 42.5 \times 10^{-7} \\ &\quad \times \frac{(600^2 - 300^2)}{2} \end{aligned}$$

$$\Delta S = 20.618 \text{ kJ}$$



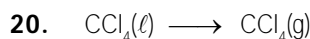
$$\Delta S_{\text{Br}} = 152.3 \quad \Delta S_{\text{Cl}_2(\text{g})} = 223.0$$

$$\Delta S_{\text{BrCl}(\text{g})} = 239.7 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Delta S_{\text{R}} = 2 \times 239.7 - 223 - 152.3 = 104.4$$

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

$$= 29300 - 298 \times 104.4 = -1721.8 \text{ J}$$



$$P = 1 \text{ atm}$$

$$T = 298 \text{ K} \quad \Delta S = 94.98 \text{ JK}^{-1}$$

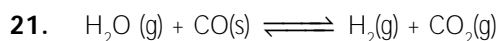
$$\Delta_r H = \Delta H_p - \Delta H_r = (-106.7 + 139.3) \text{ kJ}$$

$$= 32.6 \text{ kJ/mol}$$

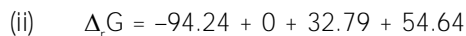
$$\Delta_r G = \Delta H_r - T\Delta S$$

$$\Delta_r G = 32.6 \times 10^3 - 298 \times 94.98$$

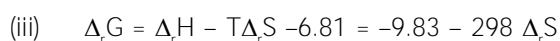
$$\Delta_r G = 4.296 \text{ kJ/mol}$$



$$\begin{aligned} &= \Delta_r H_2(\text{g}) + \Delta_r H_{\text{CO}_2(\text{g})} - \Delta_r H_{\text{CO}(\text{s})} - \Delta_r H_{\text{H}_2\text{O}(\text{g})} = \\ &-94.05 + 26.42 + 57.8 = -9.83 \text{ k cal/mol} \end{aligned}$$



$$\Delta_r G = -6.81$$



$$\frac{9.83 - 6.81}{298} = -\Delta_r S$$

$$\Delta_r S = -10.13 \text{ cal/ mole}$$



$$\Delta H = \Delta E + \Delta PV \quad \therefore \Delta n_g = 0$$

$$\Delta_r H = \Delta_r E_{298} = -9.83 \text{ k cal/mol}$$



$$\Delta_r S = \Delta_r S_{\text{H}_2\text{O}(\text{g})} + \Delta_r S_{\text{CO}} - \Delta_r S_{\text{H}_2} - \Delta_r S_{\text{CO}}$$

$$-10.13 = -\Delta_r S_{\text{H}_2\text{O}(\text{g})} + 47.3 + 31.2 + 51.1$$

$$\Delta_r S_{\text{H}_2\text{O}(\text{g})} = 45.13 \text{ cal/ K mole}$$

Exercise-04(B)

1. Step-1 (in-1)

Ice (200 K) \longrightarrow Ice (273 K)**cQl**(200 K) \longrightarrow **cQl**(273 K)

$$\Delta S_1 = m C_p \ln \frac{T_2}{T_1} = 1 \times 2.09 \times 10^3 \ln \frac{273}{200}$$

$$\Delta S_1 = 650.312 \text{ J/}^\circ\text{C}$$

Step-2 (in-2)

Ice (273 K) \rightleftharpoons Water (273 K)

$$\Delta S_2 = \frac{\Delta H_f}{273} = \frac{3.34 \times 10^5}{273} = 1223.44 \text{ J/}^\circ\text{C}$$

Step-3 (in-3)

Water (273 K) \longrightarrow Water (373 K)

$$\Delta S_3 = 1 \times 4.18 \times 10^3 \ln \frac{373}{273} = 1304.6 \text{ J/}^\circ\text{C}$$

Step-4 (in-4)

Water (373 K) \rightleftharpoons Steam (373 K)**ty** (373 K) \rightleftharpoons **Hki** (373 K)

$$\Delta S_4 = \frac{\Delta H_v}{373} = \frac{22.6 \times 10^5}{373} = 6058.98 \text{ J/}^\circ\text{C}$$

Step-5 (in-5)

Steam (373 K) \longrightarrow Steam (400 K)**Hki** (373 K) \longrightarrow **Hki** (400 K)

$$\Delta S_5 = 1 \times 2.09 \times 10^3 \ln \frac{400}{373} = 146.06 \text{ J/}^\circ\text{C}$$

$$\Delta S_T = 9383.4 \text{ J/}^\circ\text{C}$$

2. $\gamma = \frac{5}{3}$, $P_1 = 1 \text{ atm}$, $T_1 = 300 \text{ K}$, $P_2 = 2 \text{ atm}$ (a) $PV^\gamma = \text{constant}$ (**fu; rkd**)

$$P^{1-\gamma} T^\gamma = \text{constant}$$

$$TP^{(1-\gamma)/\gamma} = \text{constant}$$

$$T_1 P_1^{(1-\gamma)/\gamma} = T_2 P_2^{(1-\gamma)/\gamma}$$

$$T_2 = 300 \left(\frac{1}{2} \right)^{-2/5} = 395.85$$

$$w = \Delta U = n C_v dT = 1 \times \frac{3}{2} \times 8.314 \times 95.85$$

$$w = 1195.37 \text{ J}$$

$$V_2 = \frac{nRT_2}{P_2} = 16.25 \text{ L}$$

(b) $\Delta U = w$

$$1 \times 1.5 \times 8.314 (T_2 - 300)$$

$$= -2 \times 101.3 \left(\frac{RT_2}{P_2} - \frac{RT_1}{P_1} \right)$$

$$(T_2 - 300) = 1.333 \left(300 - \frac{T_2}{2} \right)$$

$$T_2 = 420 \text{ K} \quad V_2 = \frac{nRT_2}{P_2} = 17.24 \text{ L}$$

$$w = \Delta U = 1.5 \times 8.314 (420 - 300)$$

$$w = 1496.52 \text{ J}$$

3.

$$V_1 = 20 \text{ L}, \gamma = 7/5, T_1 = 673 \text{ K},$$

$$P_1 = 0.2 \text{ MPa} = 2 \text{ atm}, P_2 = 0.7 \text{ MPa} = 7 \text{ atm}$$

$$n = \frac{P_1 V_1}{RT_1} = 2.5$$

(i) $\Delta U = \Delta H = 0$

$$q = -w = nRT \ln \frac{P_1}{P_2} = 2.5 \times 8.314 \times 673 \ln \frac{7}{2}$$

$$q = 17.52 \text{ kJ} \quad w = -17.52 \text{ kJ}$$

(ii)

$$P_1 V_1^\gamma = P_2 V_2^\gamma$$

$$7(20)^\gamma = 2(V_2)^\gamma \Rightarrow V_2 = (3.5)^{5/7} = 48.92 \text{ L}$$

$$T_2 = \frac{P_2 V_2}{nR} = 470.46 \text{ K}$$

$$q = 0, w = \Delta U = 2.5 \times 2.5 \times 8.314 (470.46 - 673)$$

$$w = \Delta U = -10.524 \text{ kJ}$$

$$\Delta H = 2.5 \times 3.5 \times 8.314 (470.46 - 673) = -14.73 \text{ kJ}$$

(iii)

$$q = w = \Delta U = \Delta H = 0$$

(iv)

$$q = 0, \Delta U = w$$

$$2.5 \times 2.5 \times 8.314 (T_2 - 673)$$

$$= -101.3 \times 2 \times 2.5 \times 0.0821 \left(\frac{T_2}{2} - \frac{T_1}{7} \right)$$

$$T_2 - 673 = -0.79 \left(\frac{T_2}{2} - 96.142 \right)$$

$$T_2 = 536.91 \text{ K}$$

$$w = \Delta U = 2.5 \times 2.5 \times 8.314 (-136) = -7.1 \text{ kJ}$$

$$\Delta H = 2.5 \times 3.5 \times 8.314 (-136) = -9.9 \text{ kJ}$$

(v)

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

$$V_2 = \frac{nRT}{P_2} = \frac{2.5 \times 0.821 \times 673}{2} = 69 \text{ L}$$

$$w = -P_2 (V_2 - V_1) = -2 \times 49 = -98.13 \text{ L-atm}$$

$$w = -98.13 \times 101.3 = -9940.9 \text{ J}$$

$$w = -9.94 \text{ kJ}$$

$$q = -w = 9.94 \text{ kJ}$$

4.(i)

The entropy change of the system ΔS_{sys} will be same in all the three process as it is state function.(re dh, .VNH eafjorU $\Delta S_{\text{re}} = \text{ts k fd}$, d volFkk Qyu gS I Hkh rhuka i Øeka ea I eku jgskA)

$$\Delta S_{\text{sys}} = nR \ln \frac{V_2}{V_1} = 1 \times 8.314 \ln 3 = 9.134 \text{ J/K}$$

For reversible process (mRØe.kh; i Øe ds fy,)

$$\Delta S_T = 0$$

$$\Delta S_{\text{surr}} = -\Delta S_{\text{sys}} = -9.134 \text{ J/K}$$

(ii)

$$\Delta S_{\text{sys}} = 9.134 \text{ J/K}$$

$$\Delta S_{\text{surr}} = \frac{-q_{\text{irrev}}}{T} = - \left[\frac{q_{\text{rev}} - 836.6}{298} \right]$$

$$= -\Delta S_{\text{sys}} + 2.807$$

$\Delta S_T = \Delta S_{sys} + (-\Delta S_{sys} + 2.807) = 2.807 \text{ J/K}$

(iii) For free expansion system doesn't absorb any heat so $q = 0$

$\Delta S_{sys} = 0$

5.(i) $\Delta S_{sys} = 0, \Delta S_{surr.} = 0, \Delta S_T = 0$

(ii) $\Delta U = w, \Rightarrow n C_v (T_2 - T_1) = -P_2(V_2 - V_1)$
 $0.5 \times 1.5 \times 8.314 (T_2 - 473)$
 $= -101.3 \times 2 \times 0.5 \times 0.0821 \left(\frac{T_2}{2} - \frac{473}{5} \right)$
 $T_2 - 473 = -1.333 \left(\frac{T_2}{2} - 94.6 \right)$
 $T_2 = 359.49 \text{ K}$
 $\Delta S_{sys} = n \left[C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2} \right]$
 $= 0.5 \left[2.5 \times 8.314 \ln \frac{359.49}{473} + 8.314 \ln \frac{5}{2} \right]$
 $\Delta S_{sys} = 0.957 \text{ J/K}$
 since no heat is transferred $q = 0$
 $\Delta S_{surr.} = 0$
 $\Delta S_T = \Delta S_{sys} = 0.957 \text{ J/K}$

(iii) In free expansion $q = w = \Delta U = 0$
 T is constant. (T is constant.)
 $\Delta S_{sys} = nR \ln \frac{P_1}{P_2} = 0.5 \times 8.314 \times \ln \frac{5}{2} = 3.81 \text{ JK}$
 $\Delta S_{surr.} = 0$
 $\Delta S_T = \Delta S_{sys} = 3.81 \text{ J/K}$

6. $P_1 = 1 \text{ atm}, V_1 = 1 \text{ L}$
 $P_2 = 1001 \text{ atm}, V_2 = 0.99 \text{ L}$ Let $P = a + bV$
 On finding $a = 100001, b = -10^5$ so
 $P = (100001 - 10^5 V)$
 $w = -\int P dV = -\int_{V_1}^{V_2} (100001 - 10^5 V) dV$
 $w = -100001 (V_2 - V_1) + \frac{10^5}{2} (V_2^2 - V_1^2)$
 $w = -100001 (-0.01) + \frac{10^5}{2} (-0.0199) = 5.01 \text{ L-atm}$
 $w = 501 \text{ J} \quad \Delta U = w = 501 \text{ J}$
 $\Delta H = \Delta U + (P_2 V_2 - P_1 V_1)$
 $= 501 + (1001 \times 0.99 - 1 \times 1) \times 100 = 99500 \text{ J}$
 $\Delta H = 99.5 \text{ kJ}$

7.(i) $\Delta S_{sys} = n C_v \ln \frac{T_2}{T_1} = 1 \times \frac{3}{2} R \ln \frac{1000}{100} = \frac{3}{2} R \ln 10$
 $\Delta S_T = 0$ (Reversible process)

$\Delta S_{surr.} = -\Delta S_{sys} = -\frac{3}{2} R \ln 10$

(ii) $\Delta S_{sys} = \frac{3}{2} R \ln 10$
 $w = 0$
 $q = \Delta U = -\frac{3}{2} R (900)$
 $\Delta S_{surr.} = -\frac{q}{T} = \frac{-3R(900)}{2 \times 1000} = -\frac{3}{2} R (0.9)$
 $\Delta S_T = \frac{3}{2} R \ln 10 - \frac{3}{2} R (0.9) = \frac{3}{2} R (1.402)$

8. $G = H - TS = U + PV - TS$
 $dG = dU + PdV + VdP - TdS - SdT$
 $w = 0, dV = 0, dU = dq = T dS$ so
 $dG = TdS + VdP - TdS - SdT$
 $dG = VdP - SdT \Rightarrow \Delta G = \int VdP - \int SdT$
 $VdP = V(P_2 - P_1)$
 $\frac{P_2}{T_2} = \frac{P_1}{T_1} \Rightarrow \frac{P_2}{400} = \frac{1}{300} \Rightarrow P_2 = \frac{4}{3}$
 $VdP = 24.6 (4/3 - 1) = 8.2 \text{ L-atm} = 820 \text{ J}$
 $\int SdT = \int_{T_1}^{T_2} (10 + 0.01T) dT = 10(T_2 - T_1) + 0.005(T_2^2 - T_1^2)$
 $SdT = 10(100) + 0.005(400^2 - 300^2) = 1350$
 $\Delta G = 820 - 1350 = -530 \text{ J}$

9. $n = 2$
 $V_1 = \frac{2 \times 0.0821 \times 300}{1} = 49.26 \text{ L}$
 $\frac{V_1}{T_1} = \frac{V_2}{T_2} \Rightarrow \frac{49.26}{300} = \frac{V_2}{550} \Rightarrow V_2 = 90.31 \text{ L}$

(i) $w = -P\Delta V = 1(90.31 - 49.26) = -41.05 \text{ L-atm}$
 $w = -41.05 \times 101.3 = -4158.36 \text{ J} = -4.15 \text{ kJ}$
 $q = \Delta H = \int n C_p dT$
 $= 2 \left[12.552(T_2 - T_1) + \frac{8.368 \times 10^{-3}}{2} (T_2^2 - T_1^2) \right]$
 $q = \Delta H = 2 \left[12.552(250) + \frac{8.368 \times 10^{-2}}{2} (212500) \right]$
 $q = \Delta H = 24.04 \text{ kJ}$

$$C_v = C_p - R = 4.238 + 8.368 \times 10^{-2} \text{ T}$$

$$\Delta U = \int nC_v dT = 19.9 \text{ kJ}$$

(iii) $w = 0$

$$q = \Delta U = 19.9 \text{ kJ}$$

$$\Delta H = \int nC_p dT = 24.04 \text{ kJ}$$

10. At 298 K,

$$\Delta G^\circ = -6333 \text{ kJ/mole}$$

$$\Delta H^\circ = -5737 \text{ kJ/mole}$$

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

$$\text{so} \quad \Delta S^\circ = 2 \text{ kJ/mole}$$

At 310 K

$$\Delta G = -5737 - 2 \times 310 = -6357 \text{ kJ/mole}$$

$$\text{Additional non-PV work (vfrfjDr vu-PV dk; } \int = |\Delta G - \Delta G^\circ| = 24 \text{ kJ/mole}$$

11. $\Delta_r C_p = 33.305 - 75.312 = -42.007 \text{ J/K mole}$

$$\Delta_r S_{323} = \frac{\Delta H}{T} = \frac{40639}{323} = 108.95 \text{ J/K mole}$$

$$d(\Delta_r S) = \frac{\Delta_r C_p dT}{T}$$

$$\Delta_r S_{373} - \Delta_r S_{323} = \Delta_r C_p \ln \frac{T_2}{T_1}$$

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

$$= 115 \text{ J/K mole}$$

$$d(\Delta_r H) = \Delta_r C_p dT$$

$$\Delta_r H_{373} - \Delta_r H_{323} = -42.007 (50)$$

$$\Delta_r H_{373} = 42739.35 \text{ J/mole}$$

$$\Delta_r G_{323} = 42739.35 - 323 (115)$$

$$= 5594.35 \text{ J} = 5.59 \text{ kJ/mole}$$