UNIT # 06

THERMODYNAMICS EXERCISE # 1

1. $m_{Zn}.S_{Zn}.(T_f - T_i) + m_{H_2O}.S_{H_2O}.(T_f - T_i) = 0$

$(65.38\ gm)\ (0.4\ J/g\ C)\ (T_f - 20\ C) + 180\ gm$

$(4.20\ J/g\ C) \quad (T_f - 100\ C) = 0$

$\Rightarrow [(65.38)\ (0.4) + 180(4.20)]$

$T_f = (65.38)\ (0.4)\ (20) + (180)\ (4.20)\ (100)$

$$T_f = \left[\frac{(65.38)(0.4)(20)+(180)(4.20)(100)}{(65.38)(0.4)+(180)(4.20)}\right] = 97.3°C$$

2. $\Delta U = q + w$

heat absorb (q) = 45 joule

w = –70 joule since

Work done by the system.

(तंत्र द्वारा किया गया कार्य)

$\Delta U = q + w = 45 - 70 = -25$ joule

3. Decrease in internal energy = $-\Delta U$

(आन्तरिक ऊर्जा में कमी)

work done by the system = –w

$-\Delta U = -w \Rightarrow \Delta U = w \Rightarrow q = 0$

The process is adiabatic. (प्रक्रम रूद्धोष्म है)

4. At constant volume $w_{PV} = 0$

$\Rightarrow \quad \boxed{\Delta U = q}$ first law

5. The energy due to external field is not included in internal energy like gravitational field, earth's magnetic field etc.

(बाह्य क्षेत्र के कारण ऊर्जा को आन्तरिक ऊर्जा में सम्मिलित नहीं किया जाता, जैसे गुरूत्वीय क्षेत्र, पृथ्वी का चुम्बकीय क्षेत्र आदि)

6. Heat and work are path dependent, or indefinite quantity.

(उष्मा तथा कार्य पथ पर निर्भर करते है या अपरिमित मात्राऐं है)

7. For monoatomic ideal gas total degree of freedom = 3 (एक परमाण्विक आदर्श गैस के लिए स्वतंत्रता की कुल कोटि = 3)

Three translational mode of motion (गति के तीन स्थानान्तरण रूप)

$C_V = 3 \quad \frac{1}{2}R = \frac{3}{2}R \qquad C_P = C_V + R = \frac{5}{2}R$

$r = \frac{C_P}{C_V} = \frac{5}{3}$

8. Ar = monoatomic ideal gas $\quad C_V = \frac{3}{2}R$

At constant pressure $q = \Delta H = nC_P\Delta T$

$q = (0.25\ \text{mole})\frac{5}{2}.(8.314\ J/K\ mole)\ (16)$

9. Reversible process-involve infinitesimally small driving force. Hence system and surrounding remains in equilibrium.

(उत्क्रमणीय प्रक्रम में प्रेरित बल अत्यन्त सुक्ष्म होता है। अतः तंत्र तथा परिवेश साम्य में होते है)

10. temperature at 'a' = $T_0 = \frac{PV}{R}$

at (a) $T_0 = \frac{P_0V_0}{R}$ ....(i)

at (c) $T_C = \frac{(2P_0)(4V_0)}{R} = 8\,T_0$

$\Delta U = nC_V(T_f - T_i) = \frac{3}{2}R(8T_0 - T_0)$

$$\boxed{\Delta U = \frac{21RT_0}{2} = 10.5\,RT_0}$$

12. Work done in adiabataic process (रूद्धोष्म प्रक्रम में किया गया कार्य)

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

$w = (2)(12.5)(200 - 300)$

13. The case of irreversible adiabatic process.

$w = -P(V_f - V_i)$

$\Rightarrow \quad nC_V(T_2 - T_1) = -P(V_f - V_i) \qquad n = 1$

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

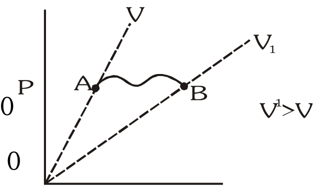
$T_2 = \frac{-P(V_f - V_i)}{nC_V} + T = T - \frac{(1atm)(2L - 1L)}{\frac{3}{2}(R)}$

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

15. $V_B > V_A$ and $T_B > T_A$

$\Delta H = nC_P(T_B - T_A) > 0$

$w = -P_{ext}(V_B - V_A) < 0$



16. Heat of reaction at const. pressure = Δ_rH

Heat of reaction at const. pressure = Δ_rU

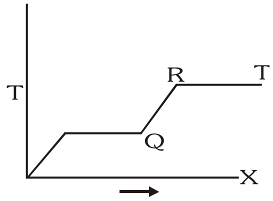
$\Delta_rH = \Delta_rU + \Delta n_gRT$

$\Delta n_g = -3$

$\Delta_rH - \Delta_rU = (-3\ RT)$

18. Fusion and vaporisation are example of isothermal processes -

(गलन तथा वाष्पीकरण समतापीय प्रक्रम के उदाहरण हैं)



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

19. $\underset{0\ C}{H_2O(s)} \xrightarrow{q_1} \underset{0\ C}{H_2O(l)} \xrightarrow{q_2} \underset{25\ C}{H_2O(l)}$

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

$q_1 = 6.01 \quad 2 = 12.02$ kJ

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

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

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

(जब बर्फ $\rightleftharpoons$ द्रव : प्रक्रम उत्क्रमणीय गलन है। गलन समतापीय प्रक्रम है)

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

21. $\Delta U = q + w$

P = constant since $\Delta H = q_p$

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

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

$\Delta U = 0$

22. For reversible adiabatic process (उत्क्रमणीय रूद्धोष्म प्रक्रम के लिए)

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

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 $\Delta S_{transition} = \frac{\Delta H_{transition}}{T_{transition}}$

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

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

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

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

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

$P = 300\ R = (300 \quad 0.0821)$ atm

final pressure = 1 atm

final volume ; $P_fV_f = P_iV_i$

$\Rightarrow \quad V_f = \frac{P_iV_i}{P_f} = \left(\frac{(300)R}{1}\right) = 24.6\,L$

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

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

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

(स्वत: अभिक्रिया के लिए)

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

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

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

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

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

(अत: ΔS_{syst} ऋणात्मक हो सकता है, लेकिन आंकिक रूप से $\frac{X}{298}$ से छोटा होता है)

27. For dissociation reactions (वियोजन अभिक्रिया के लिए)

$\Delta H > 0$ 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

$3Fe(s) + 2O_2(g) \longrightarrow Fe_3O_4(s)$; $\Delta G = ?$

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

$= -242.3$ kcal/mole

30. $T = \frac{\Delta H^\circ}{\Delta S^\circ}$

$\Delta H = -110 - (-266.3)$

$\Delta S = 197.6 + 27.28 - 5.74 - 54.49$

Above this temperature the process becomes spontaneous. (इस ताप के ऊपर प्रक्रम स्वत: होगा)

1. Intensive property (गहन गुण)

$$= \frac{\text{extensive property (विस्तीर्ण गुण)}}{\text{extensive property}}$$

pH $\propto$ concentration = mole/volume

though pH is a dimensionless number and intensive property (यद्यपि pH विमारहित संख्या तथा गहन गुण है)

EMF $= \frac{\text{energy}}{\text{charge}}$ = 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.
(नियत T पर, अधिकतम संख्या वाले अणु के आन्तरिक ऊर्जा अधिकतम होती है)

3. $q = 0$ $\quad\quad \Delta U = W$

$\Rightarrow$ $3000 = C_V(T_2 - T_1)$

$T_2 - T_1 = \frac{3000}{20} = 150 \quad\quad T_2 = T_1 + 150 = 450$ K

4. Irreverssible adiabatic process (अनुत्क्रमणीय रूद्धोष्म प्रक्रम)

$W = -P_{ext}\left(\frac{nRT_2}{P_2} - \frac{nRT_1}{P_1}\right) \quad\quad P_2 = P_{ext} = 2$ atm

$P_1 = 1$ atm $\quad\quad T_1 = 300$ K

$W = -(2\text{ atm})\left[\frac{2(R).T_2}{2\text{ atm}} - \frac{2R(350)}{1\text{ atm}}\right]$

and $W = 2C_V(T_2 - 350) = 2 \quad \frac{5}{2}R(T_2 - 350)$

$5R(T_2 - 350) = (750\ R - 2\ RT_2)$

$5T_2 - 1750 = 1400 - 2T_2$

$7T_2 = 3150 \quad\quad T_2 = 450$ K

$W = 2 \quad C_V (450 - 350)$

$= 2 \quad \frac{5}{2}R \times (100) = 500$ R

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

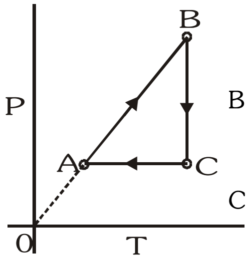
$= -P_0(V_B - V_A) - nRT_B \ln\left(\frac{V_C}{V_B}\right) - \frac{P_0}{2}(V_D - V_C)$

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

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

$q = 2\ P_0V_0\ \ln 2$

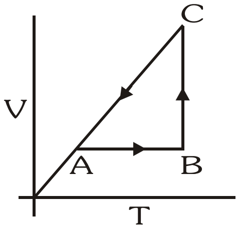
5.



AB = isochoric heating (समआयतनिय तापन)

BC = isothermal expansion (समतापीय प्रसार)

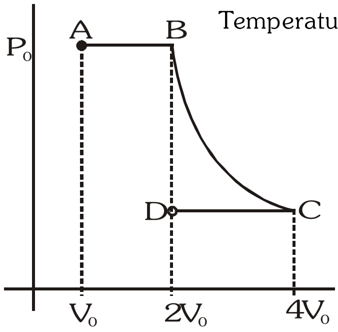
CA = isobaric cooling (समदाबीय शीतलन)



AB = isochoric heating

BC =

6.



Temperature at A (T_A) $= \frac{P_0V_0}{nR}$

$T_B = \frac{2P_0V_0}{nR}$

$T_C = \frac{2P_0V_0}{nR}$

$T_D = \frac{(P_0/2).2V_0}{nR} = \frac{P_0V_0}{nR} = T_A$

now $\because$ $T_D - T_A$: $\Delta U = \Delta H = 0$

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

7.

$$\begin{tikzcd}[column sep=huge, row sep=huge] A\ (P_1,V_1,T_1) \arrow[r, "\begin{matrix}\text{Isochoric}\\ \text{heating}\end{matrix}", "\Delta H_1"'] & B(P_2,V_1,T_2) \arrow[d, "\begin{matrix}\text{irr. adiabatic}\\ \text{process}\\ (q=0)\end{matrix}", "\Delta H_2"'] \\ & C(P_3,V_2,T_2) \end{tikzcd}$$

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

$\Delta H_1 = \Delta U_1 + (P_2V_1 - P_1V_1)$

$\Delta H_1 = C_V(T_2 - T_1) + (P_2V_1 - P_1V_1)$

$\Delta H_2 = \Delta U_2 + (P_3V_2 - P_2V_1)$

$\Delta H_2 = -P_3 (V_2 - V_1) + (P_3V_2 - P_2V_1)$

$\Delta H_2 = P_3V_1 - P_2V_1$

$\Delta H_{overall} = C_V(T_2 - T_1) + (P_2V_1 - P_1V_1) + P_3V_1 - P_2V_1$

$= C_V(T_2 - T_1) + P_3V_1 - P_1V_1$

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

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

$\eta \quad 100 =$

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

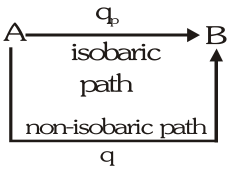
$$\eta = \frac{500 - 300}{500} = \frac{2}{5}$$

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

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

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.

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

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

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.

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

$$\Rightarrow \quad T_f = \frac{T_H - T_H}{2}$$

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

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

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

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

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

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

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

$y = C + mX$

$\Rightarrow \quad \Delta H = C$

$m = -\Delta S$

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

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

$\Rightarrow \quad \Delta S > 0$

15. Melting of $H_2O(s)$ at 0 C and 1 atm is a reversibly procers $\Rightarrow \Delta S_{Total} = 0$

Vaporisation of $H_2O(l)$ at 373 K is a reversible process $\Delta S_{Total} = 0$

Below 0 C – $H_2O(s) \longrightarrow H_2O(l)$ is non spontaneous not feasible.

$H_2O(l) \longrightarrow H_2O(s)$ (freezing) is feasible above 0 C

$H_2O(s) \longrightarrow H_2O(l)$

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

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

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

$= -\ 6000$ cal

20. $H_2O(l) \longrightarrow H_2O(g)$

373 K 373 K

1atm 1atm

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

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

THERMODYNAMICS EXERCISE # 3

COMPREHENSION # 1

1. $U = \alpha\sqrt{V}$ Here U = Kinetic energy of ideal gas (आदर्श गैस की गतिज ऊर्जा)

$U = nC_VT$

$\Rightarrow nC_VT = \alpha\sqrt{V}$ ...(i) $T = \frac{PV}{nR}$ ...(ii)

sub. (2) in (1)

$$\left(\frac{C_V}{R}\right).PV = \alpha\sqrt{V}$$

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

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

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

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

work done by the gas = $-w = 2(\alpha)$ $(\gamma - 1)\left(\sqrt{V_2} - \sqrt{V_1}\right)$

2. For diatomic gas with no vibrational degree of freedom

$$C_V = \frac{3}{2}R + 2\quad\frac{1}{2}R$$

$C_V = 5/2\ R$

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

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

∵ $\gamma = \frac{C_P}{C_V} = \frac{7}{5}$

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

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

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

$q = 180\ J$

COMPREHENSION # 2

1. $\Delta_rS = S\,(CH_3OH,\ g)$

$-\ [S\,(CO,\ g) + 2\quad S\,(H_2,\ g)]$

$= 240 - 198 - 29\quad 2 = -\ 16$ J/K-mole

2. $\Delta_rH = \Delta_fH\,(CH_3OH,\ g)$

$-\ \Delta_fH\,(CO,\ g) = -\ 201 - (114) = -87$ kJ/mol

3. $$\Delta_rS^\circ_{T_2} - \Delta_rS^\circ_{T_1} = \Delta C^\circ_P \ln\frac{T_2}{T_1}$$

$$\Delta C_P = C^\circ_{P,m}(CH_3OH) - \left[C^\circ_{P,m}(CO) + 2C^\circ_{P,m}(H_2)\right]$$

$= 44 - (29.4 + 2\quad 28.8) = -\ 43$ J/K-mol

$$\Delta_rS^\circ_{T_2} - (-16) = (-43)\ \ln\frac{320}{300}$$

$\Delta_rS_{T_2} = -\ 13.225$ J/K-mol

4. $$\Delta_rH^\circ_{T_2} - \Delta_rH^\circ_{T_1} = \Delta_rC^\circ_P(T_2 - T_1)$$

$\Delta_rH^\circ_{T_2} - (-87) = -43(320 - 300)$

$\Delta_rH^\circ_{T_2} = -87.86$ kJ/mol

5. $\Delta_rG = \Delta_rH^\circ_{T_2} - T\Delta\ T\Delta S^\circ_{T_2}$

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

$= -81.91$ kJ/mol

THERMODYNAMICS EXERCISE # 4[A]

1.(i) $H_2O\ (g) \longrightarrow H_2O(\ell)$

$V_{(g)} > V_{(\ell)}$

$W = -P_{ext}(V_{(\ell)} - V_{(g)})$

$W = +ve$

(ii) $H_2O\ (s) \longrightarrow H_2O(g)$

$V_{(g)} > V_{(s)}$

$W = -\ ve$

(iii) $H_2O\ (\ell) \longrightarrow H_2O(s)$

$V_{(s)} > V_{(\ell)}$

$W = -P_{ext}(V_{(s)} - V_{(\ell)})$

$= -ve$

(iv) $3H_2\ (g) + N_2(g) \longrightarrow 2NH_3(g)$

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

$= -P_{ext}(n_2RT - n_1RT)$

$= -\Delta n_gRT$

$W = +Ve$

(v) $CaCO_3\ (s) \longrightarrow CaO\ (s) + CO_2(g)$

$W = -P_{ext}\,\Delta V$

$\Delta V > 0$

$= -ve$

2. $\Delta E = -65$ J $\qquad w = 20$ J

$\Delta q = \Delta V - w \qquad -65 = \Delta V - 20$

$\Delta V = -45$ J

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

(a) Energy need to climb 3m = Mgh= $62.5 \quad 10 \quad 3$

$\Delta q = 1875$ Joule

Now useful energy from 1 mole of glucose

$= 2808 \quad \frac{1}{4} = 702$ kJ

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

$= 2.67 \quad 10^{-3}$ mole

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

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

⇒ wt. should be 10^3 time = 0.4807 kg

4. $q_p = q_v + \Delta n_gRT$

$40.66 \quad 2 = q_v + 2 \quad 8.314 \quad 373$

⇒ $q_v = (81.32 - 6.202)$ kJ

$q_v = 75.118$ kJ

5. $\Delta H = 1$ kcal

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

$1 \quad 10^3 \quad 4.18 = \Delta E + 1.013 \quad 10^5 \quad 3 \quad 10^{-3}$

$\Delta E = (4180 - 30.39)$ Joule $= \left(\frac{4149.61}{4.18}\right)$cal

$\Delta E = 0.993$ kcal

6. $NH_4CN(s) + \frac{3}{2}O_2(g) \longrightarrow N_2(g) + CO_2(g) + H_2O(\ell)$

$\Delta H_{298} = \Delta E + \Delta n_gRT = -742.7 + \frac{1}{2} \quad 8.314 \quad 298$

$= -742.7 + 1.239$

$\Delta H_{298} = -741.46$

7. $\Delta H = 1440$ cal

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

$1440 = \Delta E + 1.013 \quad 10^5(0.0180 - 0.0196) \quad 10^{-3}$

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

$\Delta E = 1440.168$

8. $W = \int P_{ext}dV$

$= -\int P(V_2 - V_1) = -\ 1.01 \quad 10^5\ (0.1) \quad 10^{-3}$

$W = -10.1$ J

9. $Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$

$\Delta H = -36.5$ kJ

$\Delta Q = \Delta E - W\ -36.5$ kJ

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

$\Delta E = -39.03$ kJ

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

$W = -2.53$

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

$W_{irr} = -9.353$ kJ

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

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

$W_{rev} = -17.29$ kJ

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

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

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

11. $n_1 = 1$

$T_1 = 300 \quad V_2 = 27\ V_1 \qquad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

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

$T_2 = 100$ K

Adiabatic condition $\Delta Q = 20 \Rightarrow \Delta E = W = nC_V(T_2 - T_1)$

$W = 1 \quad 25 \quad -200 \qquad W = -5.000$ kJ/mole

12. Process reversibly adiabatic

$T_1 = 298.15$ K $\qquad V_2 = 2V_1$

$T_2 = 248.44$ K $\qquad Pv^{\gamma} = K \qquad PV = nRT$

$\frac{T}{V}.V^{\gamma} = K \quad T_1V_1^{\gamma-1} = T_2V_2^{\gamma-1}$

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

$1.2 = 2^{\gamma-1} \qquad \log 1.2 = \log 2\ .\ (\gamma-1)$

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

Now $nC_V\ (T_2 - T_1) = \frac{P_2V_2 - P_1V_1}{\gamma - 1}$

$C_{V_1m} = \left(\frac{R}{\gamma-1}\right) = \frac{nR(T_2 - T_1)}{(\gamma - 1)}$

$C_{V_1m} = \frac{8.314}{0.263} \qquad C_{V_1m} = 31.61$

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

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

$W = -3.988$ kJ

14.

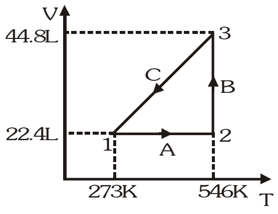


Table-1			
State	**P**	**V**	**T**
1	1	22.4L	273
2	2atm	22.4	546K
3	1atm	44.8	546K

State - 1

$PV = nRT \Rightarrow P = 1$ atm

State - 2

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

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

State - 3

$P_1V_1 = P_2V_2$

$2 \quad 22.4 = 44.8 \quad P_2$

$P_2 = 1$ 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 ln2	–546R ln2	0	0
C	Isotherm	$\frac{-5}{2}R(273)$	R(273)	$\frac{3}{2}R(273)$	$\frac{-5}{2}R(273)$
overall					

State - A $\rightarrow$ (Isochoric)

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

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

$\Delta H = nC_pdT \qquad \Delta H = 1 \quad \frac{5}{2}R(273)$

State - B $\rightarrow$ (Isothermal)

$\Delta E = 0 \qquad \Delta H = 0$

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

is $Q = -\ w = +2.303 \quad 1 \quad 8.314\ \log(2) \quad 546$

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

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

State - C $\rightarrow$ (Isobaric)

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

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

15. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(\ell)$

$\Delta Cp_{\text{reaction}} = Cp_{H_2O(\ell)} - Cp_{H_2(g)} - \frac{1}{2}Cp_{O_2(g)}$

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

$\Delta Cp_{\text{reaction}} = 21.90$ kJ

$\Delta H_{373} = \Delta H_{298} + nCp\ \Delta T$

$= (-285.76 + 1 \quad 21.9 \quad 75 \quad 10^{-3})$ kJ

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

16. $C_p = 22.34 + 48.1 \quad 10^{-3}\ T\ JK^{-1}\ mol^{-1}$

$\Delta H = \int^{n=1} nC_pdT = \int_{T_1}^{T_2}(22.34 + 48.1 \times 10^{-3}T)dT =$

$22.34 \quad 298 + \frac{48.1 \times 10^{-3} \times 298 \times 3}{2} \quad 298$

$\Delta H = 13.064$ kJ/mole

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

$W = -\ 20477$

$\Delta E = 13.064 - 2.477$

$\Delta E = 10.587$ kJ

17. $\Delta S = 28.8\ J/K \quad \Delta H = 30.5\ kJ$

$\Delta H = T\Delta S \quad \dfrac{30.5\times10^3}{28.8} = T = 1059\ K$

18. $\Delta S = \dfrac{nC_p dT}{T}$

$=1 \quad \int(\dfrac{25.5}{T} + 13.6 \quad 10^{-3} - 42.5 \quad 10^{-7}\ T)\ dT$

$= 2.303 \quad 25.5\ \log 2 + 13.6 \quad 10^{-3} \quad 300 - 42.5$

$10^{-7}\dfrac{(600^2 - 300^2)}{2}$

$\Delta S = 20.618\ kJ$

19. $Br_2(\ell) + Cl_2(g) \longrightarrow 2BrCl(g)$, $\Delta H = 29.3\ kJ$

$\Delta S_{Br} = 152.3 \qquad \Delta S_{Cl_2(g)} = 223.0$

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

$\Delta S_R = 2 \quad 239.7 - 223 - 152.3 = 104.4$

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

$= 29300 - 298 \quad 104.4 = -1721.8\ J$

20. $CCl_4(\ell) \longrightarrow CCl_4(g)$

$P = 1atm$

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

$\Delta_r H = \Delta H_p - \Delta H_r = (-106.7 \quad + 139.3)\ kJ$

$= 32.6\ kJ/mol$

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

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

$\Delta_r G = 4.296\ kJ/mol$

21. $H_2O\ (g) + CO(s) \rightleftharpoons H_2(g) + CO_2(g)$

(i) $\Delta_r H_{\ 298}$

$= \Delta_r H_2\ (g) + \Delta_r H\ CO_2\ (g) - \Delta_r H_{CO\ -}(s)\ \Delta_r\ H_2O(g) =$

$-94.05 + 26.42 + 57.8 = -9.83\ k\ cal/mol$

(ii) $\Delta_r G = -94.24 + 0 + 32.79 + 54.64$

$\Delta_r G = -6.81$

(iii) $\Delta_r G = \Delta_r H - T\Delta_r S \ -6.81 = -9.83 - 298\ \Delta_r S$

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

$\Delta_r S = -10.13\ cal/\ mole$

(iv) but at constant P

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

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

(v) $S_{\ 298}\ [H_2O(g)]$

$\Delta_r S = \Delta_s H_2O(g) + \Delta S_{CO} - \Delta_r S_{H_2} - \Delta_r S_{CO}$

$-10.13 = -\Delta_r S\ H_2O(g) + 47.3 + 31.2 + 51.1$

$\Delta_r S_{H_2O}(g) = 45.13\ cal/\ K\ mole$

THERMODYNAMICS EXERCISE # 4[B]

1. Step-1 (पद-1)

Ice (200 K) $\longrightarrow$ Ice (273 K)

बर्फ (200 K) $\longrightarrow$ बर्फ (273 K)

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

$\Delta S_1 = 650.312\ J/\ C$

Step-2 (पद-2)

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

$\Delta S_2 = \dfrac{\Delta H_f}{273} = \dfrac{3.34\times10^5}{273} = 1223.44\ J/\ C$

Step-3 (पद-3)

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

$\Delta S_3 = 1 \quad 4.18 \quad 10^3 \ln\dfrac{373}{273} = 1304.6\ J/\ C$

Step-4 (पद-4)

Water (373 K) $\rightleftharpoons$ Steam (373 K)

जल (373 K) $\rightleftharpoons$ भाप (373 K)

$\Delta S_4 = \dfrac{\Delta H_v}{373} = \dfrac{22.6\times10^5}{373} = 6058.98\ J/\ C$

Step-5 (पद-5)

Steam (373 K) $\longrightarrow$ Steam (400 K)

(भाप (373 K) $\longrightarrow$ भाप (400 K)

$\Delta S_5 = 1 \quad 2.09 \quad 10^3 \ln\dfrac{400}{373} = 146.06\ J/\ C$

$\Delta S_T = 9383.4\ J/\ C$

2. $\gamma = \dfrac{5}{3}$, $P_1 = 1\ atm$, $T_1 = 300\ K$, $P_2 = 2\ atm$

(a) PV^{γ} = constant (नियतांक)

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

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

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

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

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

$w = 1195.37\ J$

$V_2 = \dfrac{nRT_2}{P_2} = 16.25L$

(b) $\Delta U = w$

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

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

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

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

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

$w = 1496.52\ J$

3. $V_1 = 20\ L,\ \gamma = 7/5,\ T_1 = 673\ K,$

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

$n = \frac{P_1V_1}{RT_1} = 2.5$

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

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

$q = 17.52\ kJ \qquad w = -17.52\ kJ$

(ii) $P_1V_1^{\gamma} = P_2V_2^{\gamma}$

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

$T_2 = \frac{P_2V_2}{nR} = 470.46\,K$

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

$w = \Delta U = -\ 10.524\ kJ$

$\Delta H = 2.5 \quad 3.5 \quad 8.314\ (470.46 - 673) = -\ 14.73kJ$

(iii) $q = w = \Delta U = \Delta H = 0$

(iv) $q = 0,\ \Delta U = w$

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

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

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

$T_2 = 536.91\ K$

$w = \Delta U = 2.5 \quad 2.5 \quad 8.314\ (-136) = -\ 7.1\ kJ$

$\Delta H = 2.5 \quad 3.5 \quad 8.314\ (-136) = -\ 9.9\ kJ$

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

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

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

$w = -98.13 \quad 101.3 = -9940.9\ J$

$w = -\ 9.94\ kJ \qquad q = -w = 9.94\ kJ$

4.(i) The entropy change of the system $\Delta S_{sys.}$ will be same in all the three process as it is state function. (तंत्र की एण्ट्रॉपी में परिवर्तन $\Delta S_{\text{तंत्र}}$ जैसा कि एक अवस्था फलन है सभी तीनों प्रक्रमों में समान रहेगा।)

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

For reversible process (उत्क्रमणीय प्रक्रम के लिए)

$\Delta S_T = 0$

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

(ii) $\Delta S_{sys.} = 9.134\ J/K$

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

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

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

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

(मुक्त प्रसार में तंत्र कोई उष्मा अवशोषित नहीं करता है अतः $q = 0$)

$\Delta S_{sys.} = 0$

$\Delta S_T = \Delta S_{sys.} = 2.807\ J/K$

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

(ii) $\Delta U = w,\ \Rightarrow n\ C_v\,(T_2 - T_1) = -\ P_2((V_2 - V_1)$

$0.5 \quad 1.5 \quad 8.314\ (T_2 - 473)$

$= -101.3 \quad 2 \quad 0.5 \quad 0.0821\left(\frac{T_2}{2} - \frac{473}{5}\right)$

$T_2 - 473 = -\ 1.333\left(\frac{T_2}{2} - 94.6\right)$

$T_2 = 359.49\ K$

$\Delta S_{sys.} = n\left[C_p\ \ln\frac{T_2}{T_1} + R\ln\frac{P_1}{P_2}\right]$

$= 0.5\ \left[2.5 \times 8.314 \ln\frac{359.49}{473} + 8.314 \ln\frac{5}{2}\right]$

$\Delta S_{sys.} = 0.957\ J/K$

since no heat is transfered (चूंकि ऊर्जा स्थानान्तरित नहीं होती है) $q = 0$

$\Delta S_{surr.} = 0$

$\Delta S_T = \Delta S_{sys.} = 0.957\ J/K$

(iii) In free expansion (मुक्त प्रसार में) $q = w = \Delta U = 0$

T is constant. (T स्थिर है।)

$\Delta S_{sys.} = nR\ \ln\frac{P_1}{P_2} = 0.5 \quad 8.314 \quad \ln\frac{5}{2} = 3.81\ JK$

$\Delta S_{surr.} = 0$

$\Delta S_T = \Delta S_{sys} = 3.81\ J/K$

6. $P_1 = 1\ atm,\ V_1 = 1\ L$

$P_2 = 1001\ atm,\ V_2 = 0.99L$ Let $P = a + bV$

On finding (प्राप्त करने पर) $a = 100001,\ b = -10^5$

so

$P = (100001 - 10^5V)$

$w = -\int PdV = \int_{V_1}^{V_2}(100001 - 10^5\,V)dV$

$w = -\ 100001\ (V_2 - V_1) + \frac{10^5}{2}(V_2^2 - V_1^2)$

$w = -\ 100001\ (-0.01) + \frac{10^5}{2}(-0.0199) = 5.01$ L-atm

$w = 501J \qquad \Delta U = w = 501J$

$\Delta H = \Delta U + (P_2V_2 - P_1V_1)$

$= 501 + (1001 \quad 0.99 - 1 \quad 1) \quad 100 = 99500J$

$\Delta H = 99.5\ kJ$

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

$\Delta S_T = 0$ (Reversible process (उत्क्रमणीय प्रक्रम))

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

(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. $G = H - TS = U + PV - TS$

$dG = dU + PdV + VdP - TdS - SdT$

$w = 0,\ dV = 0,\ dV = dq = T\ dS$ so

$dG = TdS + VdP - TdS - SdT$

$dG = VdP - SdT \Rightarrow \Delta G = V\Delta P\ -\int S\,dT$

$VdP = V\ (P_2 - P_1)$

$\frac{P_2}{T_2} = \frac{P_1}{T_1} \Rightarrow \frac{P_2}{400} = \frac{1}{300} \Rightarrow P_2 = \frac{4}{3}$

$VdP = 24.6\ (4/3 - 1) = 8.2$ L-atm = 820 J

$\int SdT = \int_{T_1}^{T_2}(10 + 0.01T)dT = 10(T_2 - T_1) + 0.005(T_2^2 - T_1^2)$

$SdT = 10(100) + 0.005\ (400^2 - 300^2) = 1350$

$\Delta G = 820 - 1350 = -530$ J

9. $n = 2$

$V_1 = \frac{2\times 0.0821\times 300}{1} = 49.26$ L

$\frac{V_1}{T_1} = \frac{T_2}{V_2} \Rightarrow \frac{49.26}{300} = \frac{V_2}{550} \Rightarrow V_2 = 90.31$ L

(i) $w = -P\Delta V = 1(90.31 - 49.26) = -41.05$ L-atm

$w = -41.05 \quad 101.3 = -4158.36$ J $= -4.15$ k

$q = \Delta H = \int n C_p\,dT$

$= 2\left[12.552(T_2 - T_1) + \frac{8.368\times 10^{-3}}{2}\left(T_2^2 - T_1^2\right)\right]$

$q = \Delta H = 2\left[12.552(250) + \frac{8.368\times 10^{-2}}{2}(212500)\right]$

$q = \Delta H = 24.04$ kJ

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

$\Delta U = \int nC_v dT = 19.9$ kJ

(iii) $w = 0$

$q = \Delta U = 19.9$ kJ

$\Delta H = \int nC_p dT = 24.04$ kJ

10. At 298 K,

$\Delta G = -6333$ kJ/mole

$\Delta H = -5737$ kJ/mole

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

so $\Delta S = 2$ kJ/mole

At 310 K

$\Delta G = -5737 - 2 \quad 310 = -6357$ kJ/mole

Additional non-PV work (अतिरिक्त अन-PV कार्य) = $|\Delta G - \Delta G| = 24$ kJ/mole

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

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

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

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

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

$= 115$ J/K mole

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

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

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

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

$= 5594.35$ J $= 5.59$ kJ/mole