14. Chemical thermodynamics

Q1.

Sol: In isothermal process,

$$W = -2.303\ nRT \log \frac{V_f}{V_i}$$

$$= -\ 2.303 \times 1 \times 0.0821 \times 298 \log \frac{50}{15}$$

$$= -56.34 \log 3.33 = -29.458 \text{ atm lit}$$

$$= -29.458 \times 10^5 \text{ N/m}^2 - 10^{-3} \text{ m}^2 = -2945.8 \text{ J} = \frac{-2945.8}{4.18} = -7.8 \text{cal}$$

Ans

Q2.

Sol: At constant temperature

$$\Delta U = O$$

∴ From first law of thermodynamics

$$\Delta Q + W = \Delta U = O$$

$$\Delta Q = -W = -\left(-2.303\, nRT \log \frac{P_i}{P_f}\right)$$

$$= 2.303 \times \frac{100}{240} \times 128 \times 373 \ \log \frac{10}{0.1} = \frac{2.303 \times 10 \times 372 \log 100}{2.02}$$

$$= \frac{2.303 \times 10 \times 3.73 \times 2}{2.02} = 8576.0 \text{ cal}$$ **Ans**

Q3.

Sol: $\Delta H = \Delta E + nRT$

$$1440 \text{ cal} = \Delta E + P\Delta V = \Delta E + 1\text{atm}(0.013 - 0.0196)$$

$$= \Delta E + \left(\frac{-1.6 \times 10^{-3} \times 10^2}{4.2} \text{cal}\right)$$

$$\Delta E = 1440 \text{cal} + \frac{1.6 \times 10^{-1}}{4.2} = 1440 \text{cal} + 0.04 \text{cal}$$

$$= 1440.04 \text{ cal}$$

Q4.

Sol: $G_{graphite} + \frac{1}{2} O_2(g) \longrightarrow Co(g)$ at 298 K and 1 atm

$$\Delta H = -26416 \text{cal}$$

$$V_{molar} = 0.0053 \ \text{lit}$$

$$\Delta H = \Delta E + P(V_f - V_i)$$

$$= \Delta E + 1\left(\left(1-\frac{1}{2}\right)\times 24.466 - 0.0053\right)\text{atm lit}$$

$\because$ at T = 298 K & P = 1 atm ($V_{molar} = 24.46$ lit)

$-26416 = \Delta E + (296.94 \text{ cal})$

$\Delta E = -26416 - 296.54 = -26712.52$ cal **Ans**

Q5.

Sol: $\Delta Q + W = \Delta u = O$

$$\Delta Q = -W = -\left(-2.303\,nRT\log\frac{V_f}{V_i}\right)$$

$$= 2.303 \times 1 \times 8.314 \times 300 \log\frac{20}{5}$$

$$= 2.303 \times 8314 \times 300 \log 4 = 3458.32 \text{ J}$$

& $W = -\Delta Q = -3458.2$ J **Ans**

Q6.

Sol: $2C(S) + 2H_2 \longrightarrow C_2H_4(g)$, ΔH = Heat of formation of ethylene

given

(1) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H_1 = -65\,\text{Kcal}$

(2) $C(s) + O_2(g) \longrightarrow CO_2(g);\ \Delta H_2 = -97$ Kcal

(3) $C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l),\ \Delta H_3 = -340$ Kcal

$2\times(2) + 2\times(1) - (3) = 2C(s) = 2H_2(g) \longrightarrow C_2H_4(g)$

$\Delta H = 2\Delta H_2 + 2\Delta H_1 - \Delta H_3 = 16$ Kcal **Ans**

Q7.

Sol: (1) $C(S) + O_2(g) \longrightarrow CO_2(g);\ \Delta H_1 = -84$ Kcal

(2) $2CO(g) + O_2(g) \longrightarrow 2CO_2(g);\ \Delta H_2 = -136$ Kcal

$(1) - \frac{1}{2}\times(2) : C(S) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$

$\Delta H = \Delta H_1 - \frac{1}{2}\Delta H_2 = -94 - \left(\frac{1}{2}\times -136\right) = -26$ KCal **Ans**

Q8.

Sol: $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)\ \Delta H = -330$ kcal

$\therefore \Delta H_{comb}$ is always – w

Given $\Delta H_f(CO_2(g)) = -94.3\,\text{Kcal}$

$\Delta H_f(H_2O(l)) = -68.5\,\text{Kcal}$

Heat of formation of most compounds are –Ve

$\therefore \Delta H_{comb} = 2\times\Delta H_{f(CO_2)} + 3\Delta H_{f(H_2O(l))} - 1\times\Delta H_{f(C_2H_5OH)}$

(ΔH_f of $O_2 = 0$; because it is in natural state)

$-330 = +2\times(-94.3) + 3(68.5) - \Delta H_f(C_2H_5OH)$

$-330 = -394.1 - \Delta H_f(C_2H_5OH)$

$\Delta H_f(C_2H_5OH) = -394.1 + 330 = -64.1$ Kcal **Ans**

Q9.

Sol: $CH_3OH(l) + \frac{3}{2}O_2 \longrightarrow CO_2(g) + 2H_2O(l)$

$$\Delta H\,comb = -173.651$$

$\therefore H_{comb} = 1.\ \Delta H_f CO_{2(g)} + 2\Delta H_{f H_2O(l)} - \Delta H_{f\,CH_3OH}$

$-173.65\text{ Kcal} = -94.05\text{ kcal} - 2\times 68.32\text{ kcal} - \Delta H_{f\,CH_3OH}$

$\Delta H_{f\,CH_3OH} -230.69 + 173.65 = -57.04$ kcal **Ans**

Q10.

Sol: (1) $2C_6H_6(g) + 15O_2(g) \longrightarrow 12CO_2(g) + 6H_2O(l);\ \Delta E_1 = -162$ kcal

(2) $2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(l);\ \Delta E_2 = -620$ Kcal

$3\times(2) - (1) \Rightarrow 6C_2H_2(g) \longrightarrow 2C_6H_6(g)$

$$\Delta E = 3\Delta E_2 - E_1$$

$$= -1860 + 1600 = -260 \text{ Kcal}$$

$\therefore 3C_2H_2(g) \longrightarrow C_6H_6(g),\ \Delta E = \frac{-260}{2} = -130$ Kcal

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

$= -180\text{ Kcal} + (1-3)\times 1.98\times 10^{-3}\times 300$

$= -180 - 2\times 0.198\times 3 = -130 - 1.188 = -131.188$ Kcal **Ans**

Q11.

Sol: (1) $CH_3COOH(l) + 2CO_2(g) \longrightarrow 2CO_2(g) + 2H_2O(l),\ \Delta H_1 = -208.31$ kcal

(2) $C(S) + O_2(g) \longrightarrow CO_2(g),\ \Delta H_2 = -94.05$ Kcal

(3) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H_3 = -68.32$ kcal

(1) $\Delta H_1 = 2\Delta H_{f\,CO_2} + 2\Delta H_{f\,H_2O} - \Delta H_{f\,CH_3COOH} - 2\Delta H_{f\,O_2}$

$= 2\times(94.05) + 2(-68.32) - (-208.34) - 2\times 0$

$= -324.74 + 208.34$

$\Delta H_1 = -116.4$ Kcal **Ans**

Q12.

Sol: $NH_3(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g); \Delta H^0 = 11.04$ Kcal

$\Delta H^0 = \Delta E^0 + \Delta nRT$

$11.04\text{ Kcal} = \Delta E^0 + \left(\frac{1}{2} + \frac{3}{2} - 1\right)\times 1.98\times 10^{-3}\times 298$

$= \Delta E^0 + 1\times 1.98\times 0.298$

$$11.04 = \Delta E^0 + 0.59$$

$$\Delta E^0 = 11.04 - 0.69 = 10.44\,\text{Kcal}$$ **Ans**

Q13.

Sol: In question it is given that

$H_f^0 Ag_2O(s) = -73.1\,\text{Kcal}$

$H_f^0\,HCl(g) = -22.06\,\text{kcal}$

$H_f^0\,H_2O(l) = -63.82\,\text{kcal}$

$$Ag_2O\,(s) + 2HCl\,(g) \longrightarrow 2AgCl\,(s) + H_2O\,(l);\ \Delta H^0 = -77.61\,\text{Kcal}$$

$$\Delta H^0 = 2.\Delta H^0 f_{Agcl(s)} + 1.\,\Delta^0{}_{f\,H_2O(l)} - \Delta Hf_{Ag_2O(s)} - 2\Delta H^0 f\,HCl(g)$$

$$-77.61\ \text{Kcal} = 2\,\Delta H^0{}_{fAgCl(s)} - 63.82 - (-73.1) - 2(-22.0)$$

$$-77.61\ \text{Kcal} = 2\,\Delta H^0{}_{f\,Agcl\,(s)} + 53.04$$

$$2\Delta H^0{}_{f\,AgCl(s)} = -131.01$$

$$\therefore \Delta H^0{}_{f\,AgCl} = -65.5\,\text{Kcal}$$ **Ans**

Q14.

Sol: Enthalpy of formation of HBr

$$\frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \longrightarrow HBr(g),\ \Delta H = ?$$

Given

1. $SO_2(aq) + \frac{1}{2}O_2(g) \longrightarrow SO_3(aq), \Delta H_1 = -63.7$

2. $Br_2(g) + SO_2(aq) + H_2O\,(l);\ \longrightarrow 2HBr(aq) + SO_3\,(aq);\ \Delta H_2 = -54\,\text{kcal}$

3. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H_3 = -68.4\,\text{Kcal}$

4. $HBr\,(g) + aq \longrightarrow HBr\,(aq),\ \Delta H_4 = -20\,\text{Kcal}$

(2) + (3) – (1) – (2) × (4)

$$Br_2\,(g) + H_2O\,(g) \longrightarrow 2HBr(g)$$

$$\Delta H = \Delta H_2 + \Delta H_3 - \Delta H_1 - 2\Delta H_4$$

$$= -54 - 68.4 - (-63.7) - 2(-20)$$

$$= 103.7 - 122.4 = -18.7\ \text{Kcal}$$

$$\therefore \frac{1}{2}H_2(g) + \frac{1}{2}Br_2(g) \longrightarrow HBr(g)$$

$$\Delta H = -9.35\,\text{Kcal}$$ **Ans**

Q15.

Sol: **1.** $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l); \Delta H_1 = -68.3\,\text{Kcal}$

2. $CaO\,(s) + H_2O\,(l) \longrightarrow Ca(OH)_2(s)\,;\ \Delta H_2 = -15.3\,\text{Kcal}$

3. $Ca(s) + \frac{1}{2}O_2(g) \longrightarrow CaO(S); \Delta H_3 = -151.8\,Kcal$

(1) + (3) + (2)

$Ca(s) + H_2(g) + O_2(g) \longrightarrow Ca(OH)_2(S),$

$$\Delta H = \Delta H_1 + \Delta H_3 = \Delta H_2$$
$$= -68.3 - 151.8 + (-15.3)$$
$$= -235.4\ Kcal$$ **Ans**

Q16.

Sol: $K + \frac{1}{2}H_2(g) + \frac{1}{2}O_2(g) \longrightarrow KOH, \Delta H =$ heat of formation of KOH

Given:

(1) $K + H_2O + aqs \longrightarrow KOH\ (aq) + \frac{1}{2}H_2;\ \Delta H_1 = -48.4\ Kcal$

(2) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O; \Delta H_2 = -68.44\,Kcal$

(3) $KOH + aqs \longrightarrow KOH\ (aqs)\ ;\ \Delta H_3 = -14.01\ Kcal$

(1) + (2) − (3)

$K + \frac{1}{2}O_2 + \frac{1}{2}H_2 \longrightarrow KOH$

$$\Delta H = \Delta H_1 + \Delta H_2 - \Delta H_3$$
$$= -48.4 - 68.44 + 14.01$$
$$= -102.46\ Kcal$$ **Ans**

Q17.

Sol: $6C + 3H_2 \longrightarrow C_6H_6,\ \Delta H = ?$

Given

(1) $C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O, \Delta H_1 = -754\ Kcal$

(2) $C + O_2 \longrightarrow CO_2,\ \Delta H_2 = -34\ Kcal$

(3) $H_2 + \frac{1}{2}O_2 \longrightarrow H_2O(l), \Delta H_3 = -68\,Kcal$

In reaction (2) & (3) CO_2 & H_2O are forming from their constitutent elements from their natural state & hence ΔH comb (CO) = $\Delta H_{formation}(CO_2)$

$$\Delta\ comb\ (H_2) = \Delta H_{formation}(H_2O)$$

From (1)

$\Delta H_1 = 6.\ \Delta H_{f(CO_2)} + \ +3.\ \Delta H_{for(H_2O)} - \Delta H_{f(C_6H_6)}$

$-754 = 6 \times (-94) + 3(-63) - \Delta H_{f\ C_6H_6}$

$\Delta H_{f\ C_6H_6} = -768 + 754 = -14\ Kcal$ **Ans**

Q18.

Sol: $Fe_2O_3 + 3\,CO \longrightarrow 2Fe + 3CO_2;\ \Delta H = ?$

(1) $2Fe + \frac{3}{2}O_2 \longrightarrow Fe_2O_3;\Delta H = -177.1\,Kcal$

(2) $C + \frac{1}{2}O_2 \longrightarrow CO;\Delta H = -32.8\,Kcal$

(3) $C + O_2 \longrightarrow CO_2;\ \Delta H = -94.3\ Kcal$

$\Delta H = 2.\Delta H_{f\,Fe} + 3\,\Delta H_{f\,CO_2} - 1.\ \Delta H_{f\,Fe_2O_3} - 3\,\Delta H_{f\,CO}$

$= 2\times 0 + 3\times(-94.3) - (-177.1) - 3(-32.8)$

$= -282.9 + 275.5 = -7.4\ Kcal$ **Ans**

Q19.

Sol: $\Delta H_{f\,Na_2B_4O_7(s)} = -742\ kcal$ $\qquad \Delta H_{f\,Na_2B_4O_7}.10\ H_2O(s) = -1460\ kcal$

$Na_2B_4O_7(s) + 10\,H_2O \longrightarrow Na_2B_4O_7.10\,H_2O(s)$

$\Delta H_{hyd} = \Delta H_{f\,Na_2B_4O_7.10H_2O} - \Delta H_{f\,Na_2B_4O_7}$

$= -1460 + 742 = -718\ Kcal$

Note:- ΔH_f of water is not considered because was molecule is not dissociating & then reacting w $Na_2B_4O_7$ solid. It just attachs itself to the solid compound.

Q20.

Sol: At 298 K

(1) $C(graphite) + O_2 \longrightarrow CO_2(g),\ \Delta H_1 = -393\ KJ/mole$

(2) $C(diamond) + O_2 \longrightarrow CO_2(g),\ \Delta H_2 = -395\ KJ/mole$

Specific heat capacity of C(graphite) = 720 J / Kg.K

" " " " " C (diamond) = 505 J / kg K

$C(graphite) \longrightarrow C(diamond)$

$\Delta H = \Delta H_1 - \Delta H_2 = -393 + 395 = 2\ KJ/mole$

T = 298 K.

$$\begin{tikzcd}
C\,(graphite) \arrow[r, "T_2=298K"] & C(diamond) \\
C(graphite) \arrow[u] \arrow[r, "T_2=273K"] & C(diamond)
\end{tikzcd}$$

By Krichoff's law

$\Delta H_{T_2} + 1.C_{V_{graphite}}(T_2 - T_1) + 1.C_{V_{diam}}(T_1 - T_2) = \Delta H_{T_1}$

$\Rightarrow\ 2 + (C_{V_{graph}} - C_{C_{diagram}})(T_2 - T_1) = \Delta H_{T1}$

$\Rightarrow\ 2 + \left(0.720\times\frac{12}{1000} - 0.505\times\frac{12}{1000}\right)(298 - 273)$

$\Rightarrow\ 2 + 0.0645 = \Delta H_{T_1}\qquad \Rightarrow\ \Delta H_{T_1} = 2.0645\ KJ/mole$ **Ans**

Q21.

Sol: $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

$\Delta H_{heat} = -50.6\,KJ/eq$

$\Delta H_{ion} = \Delta H_{ionisation} - 57.7\,KJ/eq$

$-50.6 = \Delta H_{ion}(CH_3COOH) - 57.2\,KJ/eq$

$\Delta H_{ion}(CH_3COOH) = -50.6 + 57.2 = 6\ 66\ KJ/eq$

$NH_4OH + HCl \longrightarrow NH_4Cl + H_2O$

$\Delta H_{heat} = 51.4\,KJ\,eq^{-1}$

$\Delta H_{heat} = \Delta H_{ion} - 57.2$

$-51.4 = \Delta H_{ion}(NH_4OH) - 57.2$

$\Delta H_{ions(NH_4OH)} = -51.4 + 57.2 = 5.8\ KJ\ eq^{-1}$

For $CH_3COOH + NH_4OH \longrightarrow CH_3COONH_4 + H_2O$

$\Delta H_{hent} = \Delta H_{ions} = -57.2$

$= (6.66 + 5.8) - 57.2$

$\Delta H_{hent} = -44.74\,KJ/eq$ **Ans**

Q22.

Sol: **For** combustion of C_2H_4

$C_2H_4(g) + 3O_2(g) \longrightarrow 2CO_2(g) + 2H_2O\,(l)$

$\Delta H_{comb} = 2\Delta H_{fCO_2} + 2\Delta H_{fH_2O} - \Delta H_{fC_2H_4(g)} - 3\Delta H_{fO_2}$

$= 2(-393.5) + 2(-285.8) = 52.3 - 3 \times 0$

$= -1400.9\ KJ/mol$

$\therefore \Delta H_{comb/gm} = \dfrac{1410.9\,KJ}{28} = 50.39\,KJ/g$

$C_4H_{10}\,(g) + \dfrac{13}{2}O_2(g) \longrightarrow 4CO_2(g) + 5H_2O(l)$

$\Delta H_{Comb} = 4\Delta H_{fCO_2(g)} + 5\Delta H_{fH_2O(l)} - 1.\Delta H_{fC_4H_{10}(g)} - \dfrac{13}{2}\Delta H_{fO_2}$

$\Delta H_{Comb} = 4(-393.5) + 5(-285.8) - (-126.1)$

$= 2876.9\ KJ/mole\ ((\Delta H_{fO_2} = O)$

$\therefore \Delta H_{comb}$ per gm $= \dfrac{2876.9\,KJ}{58} = 49.6\,KJ.gm$

Q23.

Sol: $Fe_2O_3 + 2Al \longrightarrow 2Fe + Al_2O_3$

$\Delta H = 2\,2\Delta H_{fFe} + \Delta H_{fAl_2O_3} - \Delta H_{fFe_2O_3} - 2.\Delta H_{fAl}$

$= 0 + 1675.60 - (-821.32) \qquad = -1675.60 + 821.32 = -854.28\ KJ$ **Ans**

Note:- in question ΔH_f of Al_2O_3 is given +Ve, which should be – ve actually

Q24.

Sol: From first law of Thermodynamics

$\Delta Q + W = \Delta U$

A/q, $\Delta Q = -1.50$ J

$w = +Pdv = +Fds = +2.20 \times 9.8 \times 0.25$

$\downarrow \qquad = +5.39$ J

work done on system

$\therefore \Delta U = -1.50 + 5.39 = 3.89$ J **Ans**

Q25.

Sol: $CaF_2(s) \longleftrightarrow Ca^{2+}(aqa) + 2F^-(aqs)$

$\Delta G^0_f(CaF_2(s)) = -1162\,KJ/mole$

$\Delta G^0_f(Ca^{2+}(aqs)) = -553.0 \;\&\; \Delta G^0_f(F^-(aqs)) = -276.5\,KJ/mole$

$\Delta G^0 = 2\Delta G^0 F^- + \Delta G^0_{Ca^{2+}} - \Delta G^0_{CaF_2}$

$= 2\times(-276.5) + (-553) - (-1162) = 56$ KJ/mole **Ans**

Now

$\Delta G^0 = -2.303 RT \log ksp$

$56 = -2.303 \times 8.314 \times 10^{-3} \times 298 \log Ksp$

$\log Ksp = -9.7145$

$Ksp = 1.99 \times 10^{-10} = 2 \times 10^{10}$ **Ans**

Q26.

Sol: $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$

$\Delta H = \Delta H_{FMgO} + \Delta_{fCO_2} - \Delta H_{fMgCO_3}$

$= -601.2 - 393.5 + 1112 \;= +117.3$ KJ

$\Delta S = S^0_{MgO} + S^0_{CO_2} - S^0_{MgCO_3}$

$= 26.9 + 213.7 - 65.9 = 174.7$ J/K.

For decomposition at Temp T,

$\Delta G \le O$

$\Delta H - T\Delta S < O \qquad T > \dfrac{\Delta H}{\Delta S} = \dfrac{117.3\times10^3}{174.7}$

$T > 6 + 1.44$ K

Temperature will be min-^{m} = 671.44 K **Ans**

Q27.

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

As ΔH & ΔS remain constant with temperature, (as given in question)

So if T is increased, ΔG decreases

$\Delta G_{T=500^0C} = -92.38\,KJ - 773 \times (-198.2) \times 10^{-3}\,KJ$

$= 60.830$ KJ **Ans**

Also $\Delta H = -92.38$ KJ = exothermic reaction

So if temp. is increased, according to the chat her principle reac-^{n} will move in that direction in which it consimes the added heat. i.e in endothermic dir-^{n} So reaction will move in backward direction as T increase.

Q28.

Sol: For heat pump

W = work done $= 10 \times 9.8 \times 12 = 98 \times 12 = 1176$ J

$$\text{Now } n = \frac{W}{q_2} = \frac{T_2 - T_1}{T_2} = \frac{313 - 288}{313}$$

$$\frac{1.176\text{KJ}}{q_2} = \frac{25}{313}$$

$$q_2 = \frac{1.176 \times 313}{25}\text{KJ} = 14.72\text{KJ}$$

Ans

Q29.

Sol: (1) $N_2(g) + 2O_2(g) \longrightarrow 2NO_2(g)$; $\Delta H_1 = 16.18$ Kcal

(2) $N2(g) + 2O_2(g) \longrightarrow N_2O_4(g)$; $\Delta H = -\Delta H_1 + \Delta H_2$

$= -16.18 + 2.31 = -13.87$ Kcal **Ans**

N_2O_4 is not stable at this temperature because energy needed to decompose N_2O_4 (13.87 Kcal) is available to any molecule at this temperature

Q30.

Sol: ΔH will remain same, as it is a state function quantity where as q is a path function quantity i.e, if the process is done with different path, it will have different value

Q31.

Sol: n = 2 moles; $P_i = 10$ atm; T = 273 K; $P_f = 0.4$ atm

For isothermal process

$$W = -2.303\, nRT \log \frac{P_i}{P_f}$$

$$= -2.303 \times 0.0821 \times 273 \log \frac{10}{0.4}$$

$= -144.317$ l atm $= -144.317 \times 10^3\, m^3 \times 10^5\, N/m^2 = -14431.7$ J **Ans**

$\Delta Q + W = \Delta E = 0$ (In isothermal process $\Delta E = nC\Delta T = 0$)

$\therefore \Delta G = -W = 14431.7$ J

$\Delta E = nC_V \Delta T = 0$ Since T = constant $\Delta T = 0$

$\Delta H = nCp\Delta T = 0$

Q32.

Sol: $P(V - b) = RT$; $P = \dfrac{RT}{V - b}$

For dp to be exact differential,

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

L.H.S: $\frac{\partial P}{\partial V}=\frac{-RT}{(V-b)^2}$

$$\frac{\partial}{\partial T}\left(\frac{\partial P}{\partial T}\right)=\frac{-R}{(V-b)^2}$$

For R.H.S: $\frac{\partial P}{\partial T}=\frac{R}{(v-b)}$

$$\frac{\partial}{\partial v}\left(\frac{\partial P}{\partial T}\right)=\frac{-R}{(v-b)^2}$$

Since both L.H.S & R.H.S equal, so

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

& hence dp is an exact differential

Q33.

Sol: $\bar{V}=\frac{RT}{P}$

For $d\bar{v}$ to be exact differential,

$$\frac{\partial}{\partial T}\left(\frac{\partial \bar{V}}{\partial T}\right)=\frac{\partial}{\partial T}\left(\frac{\partial \bar{V}}{\partial T}\right)$$

$$\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)=\frac{\partial}{\partial T}\left(\frac{--RT}{P^2}\right)=\frac{-R}{P^2}$$

$$\frac{\partial}{\partial T}\left(\frac{\partial V}{\partial T}\right)=\frac{+\partial}{\partial P}\left(\frac{R}{P}\right)=\frac{-R}{P^2}$$

$$\therefore \frac{\partial}{\partial T}\left(\frac{\partial V}{\partial P}\right)=\frac{\partial}{\partial P}\left(\frac{\partial V}{\partial T}\right)=\frac{-R}{P^2}$$

So $d\bar{v}$ is an exact differential

Q34.

Sol: $Zn(s) + 2HCl\,(aq) \longrightarrow ZnCl_2(aq) + H_2(g)$

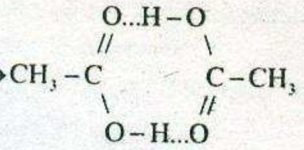
2 moles of zn produces 2 moles of H_2 gas

$W = -P\Delta V = -P(V_f - V_i) = -PV_f\ (\because V_i = O)$

$= -nRT_f = -2\times 8.314\times 308 \quad = -5.12\times 10^3\ J$ **Ans**

Q35.

Sol: $2CH_3COOH \longrightarrow$



Additional bond forms in product = (2 hydrogen bonds)

$\therefore \Delta = -$ (B.E. of each H – bond)

$= -(66.5\text{ KJ}) = -66.5\text{ KJ}$

Also $\Delta G^0 = -2.303\ RT \log Kp$ (must be in atm will be discussed in class)

$= 2.303 \times 8.314 \times 10^{-3} \times 298 \log 1.3 \times 10^3$

$= -5.7 \log 1.3 \times 10^3 = -17.77\text{ KJ}$

We have

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

$$\Delta G^0 - \Delta H^0 = -T\Delta S^0$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{+17.77 - 66.5}{298}$$

$$= -0.16\text{ KJ / mol K.}$$

Q36.

Sol: For cannot cycle / engine

$\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100 = 40$ $\quad$ T_1 = temp of sink

$1 - \frac{T_2}{T_1} = \frac{40}{100}$ $\quad$ T_2 = temp of same

$$\frac{T_2}{T_1} = 1 - \frac{4}{10} = \frac{6}{10}$$

If $T_2 = 280$ K.

$$T_1 = \frac{T_2 \times 10}{6} = \frac{2800}{6} = 466.6\text{K}$$

Ans

Q37.

Sol: T_1 = temp of same = 400 K

$Q_1 = 200$ cal ; $Q_2 = 150$ cal

$$\frac{Q_1 - Q_2}{Q_1} = \frac{T_1 - T_2}{T_1}$$

$$\frac{50}{200} = 1 - \frac{T_2}{T_1}$$

$$\frac{T_2}{T_1} = 1 - \frac{50}{200} = \frac{15\cancel{0}}{20\cancel{0}}$$

$$T_2 = \frac{15}{20} \times 400 = 300\text{K}$$

Efficiency of engine : $\eta = \left(1 - \frac{T_2}{T_1}\right) \times 100 = \left(1 - \frac{300}{400}\right) \times 100 = \frac{1}{4} \times 100 = 25\%$ Ans

Q38.

Sol: n = 1 mole

$V_i = 22.4$ lit

$V_f = 224$ ml

T = 300 K

$$W = -2.303\ nRT \log \frac{V_f}{V_i}$$

$$= -2.303 \times 1 \times 8.314 \times 10^{-3} \times 300 \log \frac{224}{22.4}$$

$$= -2.303 \times 8.314 \times 0.3 \times 1$$

$$= -5.74\ KJ$$

$\Delta Q + W = O$ (in isothermal process $\Delta E = O$)

$\Delta Q = -W = 5.74$ KJ

$\Delta H = nC_p \Delta T = \theta$ (since $\Delta T = O$)

ΔG = Work done in reversible process which is maximum work done = -5.74 KJ Ans

Now

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

$-5.74 = 0 - 300 \times \Delta S$

$$\Delta S = \frac{5.74 \times 10^3}{300} = \frac{57.4}{3} = 19.1 \quad J/K$$

Ans

Q39.

Sol: $$\log\left(\frac{ksp_1}{ksp_2}\right) = \frac{-\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\left(\frac{1.782 \times 10^{-10}}{4.159 \times 10^{-10}}\right) = \frac{-\Delta H}{2.303 \times 8.314}\left(\frac{308 - 298}{298 \times 308}\right)$$

$$\Delta H^0 = \frac{-2.303 \times 8.314 \times 298 \times 308}{10} \log\left(\frac{1.782}{4.159}\right) = 64.655\ KJ$$ **Ans**

Now At 25°C (Standard condition for ΔG)

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$\Delta G^0 = 64.655 - 298 \times \Delta S^0 - (1)$

$\Delta G^0 = -2.303 RT \log ksp$

$$= -2.303 \times 8.314 \times 10^{-3} \times 300 \log (1.782 \times 10^{-10})$$

$$= -5.744 \log (1.782 \times 10^{-10})$$

$$= -56\ KJ$$

$(1) \Rightarrow +56 = 64.655 - 298 \times \Delta S^0$

$$\Delta S^0 = \frac{64.655 - 56}{298} = 297 / mol K$$

Ans

Q40.

Sol: $C(S) + O_2(g) \longrightarrow CO_2(g)$

$\Delta H^0 = -393.51 KJ/mole$

$\Delta S^0 = 2.86 J/mole-K$ at $T = 25^0C$

$\Delta G^0 = \Delta H^0 - T\Delta S^0$

$= -393.51 - 0.8523$

$= -394.36$ KJ. $< O$ favourable at 25^0C

As temp increases,

ΔG becomes more –ve, so it becomes more favomable at higher temperature

Q41.

Sol: $2H_2O_2(l) \longrightarrow 2H_2O\ (l) + O_2(g($

$\Delta G^0 = -ve$ at 25^0C, so H_2O_2 will spontaneously de comes into H_2O & O_2. So at this temperature H_2O_2 is not stable

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

H_2O_2 will be stable when $\Delta G > O$

$\Delta H - T\Delta S > O$

$\Delta H > T\Delta S$

$$\Rightarrow T < \frac{\Delta H}{\Delta S} = \frac{-233.6\times10^3 J}{125.6 J/K}$$

$T < -1586$ K

So temperature should be less than –1586 K **Ans**

Q42.

Sol: (a) $\Delta S = +Ve$

entropy increases as molecule in liquid water is more random than molecules in ice.

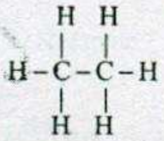
(b) $\Delta S = -Ve$ } Same as b

(d) $\Delta S = -Ve$

Q43.

Sol: $2C\ (graphite) + 3H_2\ (g) \longrightarrow C_2H_6\ (g)$

$\Delta H = -20.3 Kcal$



$$H-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-H$$

$\Delta H = 2\Delta H_{atm}(C) + 6.\ \Delta H_{atm}(H) - (B.E_{C-C} + 6.B.E_{C-H})$

-20.3 Kcal $= 2\times170.9 + 6\times52.1 - B.E_{C-C} - 6\times99$

$-20.3 = 60.4 - B.E_{CC}$

$\Rightarrow B.E_{CC} = 60.4 + 20.3 = 80.7$ Kcal **Ans**

Q44.

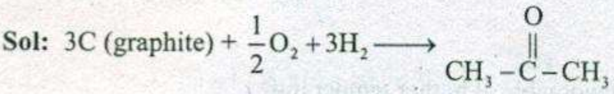
Sol: $N_2 + 3H_2 \longrightarrow 2NH_3,\quad \Delta H = -20 Kcal$

$\Delta H = B.E_{N\equiv N} + 3.B.E_{H-H} - 6.B.E_{N-H}$

$-20 = B.E_{N\equiv N} + 3\times104 - 6\times93$

$B.E_{N\equiv N} = 246 - 20 = 226$ Kcal **Ans**

Q45.



Sol: $3C\ (graphite) + \frac{1}{2}O_2 + 3H_2 \longrightarrow CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$

ΔH = heat of formation of acetate

$\Delta H = 3.\Delta H_{C(g)>C(g)}\Delta H_{atom\,O}\,6.\Delta H_{atom\,H} - (\ 2B.E_{C-C} + B.E + 6.B.E_{C-H})$

$\Delta H = 3\times171.7 + 59.16 + 6\times52.1 - (2\times80 + 81 + 6\times99)$

$= 886.86 - (835) \quad = 51.86$ Kcal **Ans**

Q46.

Sol: $C(graphite) + \frac{1}{2}O_2(g) + 2H_2(g) \longrightarrow CH_3-OH\ (g)$ ΔH = heat of formation of methyl alcohol

$\Delta H = \Delta H_{atom\,C} + \Delta H_{atom\,O} + 4.\Delta H_{atom\,H} - \left(3B.E_{C-H} + B.E_{C-O} + B.E_{O-I}\right)$

$= (170.9 + 59.6 + 4\times52.1) - (3\times99 + 84 + 110.55)$

$= 438.9 - 491.55 \quad = -52.65$ Kcal

Now $\Delta CH_3OH(g) \longrightarrow CH_3OH(l)$

$CH_3OH(g) \longrightarrow CH_3OH(l)$

$\Delta H_{liquation} = -8.4$

$\Delta H_{lignation} = \Delta H_{f\,CH_3OH(l)} - \Delta H_{f\,CH_3OH}(g)$

$-8.4 = \Delta H_{f\,CH_3OH(l)} - (-52.65)$

$\Delta H_{f\,CH_3OH}(l) = -8.4 - 52.65 \quad = -61.05$ Kcal **Ans**

Q47.

Sol: $CH_4 + 4F_2 \longrightarrow CF_4 + 4HF : \Delta H =$ heat of there

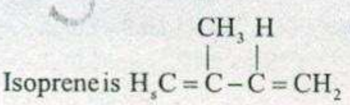
$\Delta H = 4.B.E_{C-H} + 4B.E_{F-F} - \left(B.E_{C-F} + 4.B.E_{H-F}\right)$

$= 4\times99.3 + 4\times38 - (4\times116 + 4\times135)$

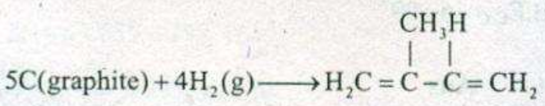
$= 549.2 - (1004) \quad = -454.8$ Kcal **Ans**

Q48.

Sol:



Isoprene is $H_sC = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle H}{|}}{C} = CH_2$



$5C(graphite) + 4H_2(g) \longrightarrow H_2C = \overset{\overset{\displaystyle CH_3}{|}}{C} - \overset{\overset{\displaystyle H}{|}}{C} = CH_2$

$\Delta H = 5\Delta H_{Sub\,C} + 4B.E_{H-H} - \left(8B.E_{C-H} + 2B.E_{C=C} + 2B.E_{C-C}\right)$

$= 5\times171.7 + 4\times10.4.0 - (8\times98.8 + 2\times147.0 + 2\times83.1)$

$= 1273.5 - (1250.6) \quad = +23.9$ Kcal **Ans**

Q49.

Sol: $C_2H_4 \xrightarrow{+H_2} C_2H_6$, ΔH = heat of hydrogenation

$$\Delta H = (4.B.E_{C\text{-}H} + B.E_{C=C} + B.E_{H\text{-}H}) - (B.E_{C\text{-}C} + 6.B.E_{C\text{-}C})$$

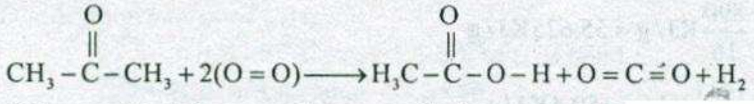
$$= (4 \times 98.8 + 147 + 104) - (83.1 + 6 \times 98.8)$$

$$= 251 - 83.1 - 2 \times 98.8$$

$\Delta H = -29.7$ Kcal **Ans**

Q50.

Sol: $CH_3COCH_3 + 2O_2 \longrightarrow CH_3COOH + CO_2 + H_2O$



$$CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + 2(O=O) \longrightarrow H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-H + O=C=O + H_2$$

$\Delta H_{W.O.R}$ = Heat change without considering resonance

$$= (6.B.E_{C\text{-}H} + 2B.E_{C\text{-}C} + B.E_{C=C} + 2B.E_{O=O})$$

$$- (3.B.E_{C\text{-}H} + B.E_{C\text{-}C} + B.E_{C\text{-}O} + 3B.E_{C=O} + 3B.E_{O\text{-}H})$$

$$\Delta H_{W.O.R} = (6 \times 414.99 + 2 \times 347.92 + 724.32 + 2 \times 494.04)$$

$$- (3 \times 414.49 + 347.92 + 967.13 + 3 \times 724.32 + 3 \times 462.64)$$

$$= 4895.18 - 6119.4 = -1224.22 \text{ Kcal}$$

Now

$\Delta H_{W.R}$ = Heat change assuming resonance is happening

$$= \Delta H_{W.O.R} + R.E_{prod} - R.E_{react} = \Delta H_{W.O.R} + R.E_{Prod} - O$$

$$= 1224.22 + (-117.23 + (-136.18) = -1477.63 \text{ KJ}$$ **Ans**

Q51.

Sol: $N_2 + \frac{1}{2}O_2 \longrightarrow N_2O \quad (N=N=O)$

$$\Delta H_{W.O.R} = \left(B.E_{N\equiv N} + \frac{1}{2}B.E_{O=O}\right) - (B.E_{N=N} + B.E_{N=O})$$

$$= \left(946 + \frac{1}{2} \times 498\right) - (418 + 607) = 1195 - 1025 = 170 \text{ KJ/mole}$$

$$\Delta H_{W.R} = \Delta H^f_{exp} = 82 \text{ KJ/mole}$$

Also

$$\Delta H_{W.R} = \Delta H_{W.O.R} + R.E_{Product} - R.E_{Product}$$

$$82 = 170 - 0 + R.E_{Product}$$

$R.E_{Product} = 82 - 170 = -88$ KJ **Ans**

$R.E_{N_2O} = -88$ KJ **Ans**

Objective Question

Q1. Ans - (d) Heat of formation will be defined ΔH in the reaction

$$\frac{1}{2}H_2(g)+\frac{1}{2}Cl_2(g)\longrightarrow HCl(g);\Delta H=\frac{-44}{2}\text{Kcal}=-22\text{Kcal}$$

Q2. Ans - (a) Explained same as 1.

Q3. Ans - (a) heat of atomisation is the energy needed to get one atom from the natural state of the element.

$$H_2\longrightarrow 2H\ ;\ \Delta H=104\,\text{Kcal}$$

$$\Rightarrow\quad \frac{1}{2}H_2\longrightarrow H\ ;\ \Delta H=\frac{104}{2}=52\,\text{Kcal}$$

Q4. Ans - (b) Fuel value $CH_4=\frac{890}{16}\text{KJ/g}=55.625\,\text{KJ/g}$

Fuel value $C_2H_4=\frac{1411}{28}\text{KJ/g}=50.4\,\text{KJ/g}$

Fuel value $C_2H_6=\frac{1560}{30}\left(\text{KJ}/\text{g}\right)=52\,\text{KJ/mole}$

∴ Hence lowest fuel value for C_2H_4.

Q5. Ans - (c) $Fe\ +\ S\ \longrightarrow FeS$

If 2.1 g $\quad\Delta H=-3.77\,\text{KJ}$

∴ 1g $\quad\Delta H=\frac{-3.77}{2.1}$

∴ 56g $\quad\Delta H=\frac{-3.77}{2.1}\times 56=-100.51\,\text{KJ}$

Q6. Ans - (b) mole of C_2H_4 combusted $=\dfrac{6226\,\text{KJ}}{1411\,\text{KJ}/\text{mole}}=4.412\,\text{mole}$

$$V_{O_2}\ (\text{at NTP})=4.412\left(2+\frac{4}{4}\right)\times 22.4\text{ lit}=296.5\text{ lit}$$

For 1 mole C_XH_Y mole of O_2 required = $(x+y/4)$

Q7. Ans - (a) moles of water gas at NTP $=\frac{112}{22.4}=5$ So it will contain 2.5 moles of H_2& 2.5 moles of CO; so heat evolved

$$=2.5\,\Delta H_1+2.5\Delta H_2=2.5(-241.8-283)\text{ KJ}=1312\text{ KJ}$$

Q8. Ans - (a) Ratio of heat evolved when C_2H_2 and H_2 are evolved $=\dfrac{-1300}{-241.8\text{KJ}}=5.376:1$

Heat of volume contain equal moles at same condition

Q9. Ans - (a) Heat of neutralisation for strong acid & base is equal to -13.7 Kcal & it is defined per eq. So it doesn't make any difference in ΔH neutralisation.

Q10. Ans - (a) When 10 ml is added, heat evolved will be twice but at the same time mass increases twice the hence ΔT will remain same.

$\therefore \Delta Q=ms\Delta T$

Q11. Ans - (a) Neutralisation reaction is actually $H^+ + OH^- \rightleftharpoons H_2O$

Q12. Ans - (c) When maximum amount of strong & strong base react, maximum heat will evolve. In 25 ml acid & 25 ml base complete reaction occur which is not the case for any other option.

Q13. Ans - (b) Heat of dissociation = (55.9 – 12.1) = 43.8 KJ

Q14. Ans - (d) Dissociation of energy of CH_4 base

$$= \frac{\text{Dissociation energy of } CH_4}{4} = \frac{360}{4} = 90\text{Kcal/mole}$$

Dissociation energy of C_2H_6

$620 = 1(\text{B.E of C-C bond} + 6 \text{ B.E of C-H bond}$

$620 = \text{B.E. of C-C bond} + 6 \times 90$

$\text{B.E. of C.C bond} = 620 - 540 = 80 \text{ Kcal/mole}$

Q15. Ans - (d) In polymerisation, more no of molecules form a less no. of giant molecule & hence entropy decrease.

Q16. Ans - (c) Gas has more entropy than liquid, so $\Delta S + ve$

Q17. Ans - (b) $\Delta G = \underset{\text{+ve in melting of ice}}{\underset{|}{\Delta H}} - T\Delta S(+ve)$

However we have to give heat to melt Heat 15^0C because normal melting point is 0^0C.

At $T = 0^0C,\ \Delta G = 0$

$T > 0^0C,\ \Delta G < O\ \ \&\ \ T < 0^0C,\ \Delta G > O$

Q18. Ans -(b) A reaction will be spontaneous if

$\Delta G < O$

$\Delta H - T\Delta S < O \quad \Rightarrow \Delta H < T\Delta S$

Q19. Ans - (a) $\Delta G = -Ve$ if $\Delta H = -ve$ & $\Delta S = +ve$. At any temp, because $T(K) > 0$ always.

Q20. Ans - (b) $\Delta G = +ve$ if $\Delta H = +ve$ & $\Delta S = -ve$ which is non spontaneous condition at any temp.

Q21. Ans - (a) $\Delta H - \Delta E = \Delta nRT$

$= (12 - 15) \times 8.314 \times 10^{-3} \times 298 = -3 \times 8.314 \times 0.298 = -7.433$ KJ

Q22. Ans - (b) ∵ At eq-^{b}, temp doesn't increase only ice will convert into water. i.e, $\Delta T = O$

$\therefore \Delta Q = ms\Delta T$

$$S = \frac{\Delta Q}{m\Delta T} \rightarrow \infty \text{ as } \Delta T = O$$

Q23. Ans - (d)

$C(\text{graphite}) + O_2 \longrightarrow CO_2(g)$

$\Delta H = \text{heat of combustion of C(graphite)} = \Delta H \text{ formation of } CO_2(g)$

Q24. Ans - (d)

$\because \Delta S_{mix} = \underset{-Ve}{\underset{\downarrow}{\Delta S_{sys}}} + \underset{\text{must be +ve by larger amount}}{\underset{\downarrow}{\Delta S_{Surr}}} > O$ for spontaoeous process

Q25. Ans : $\Delta G = \Delta H - T\Delta S < O$ [for spontaneous process].

$$34KJ - 358 \times \Delta S < O$$

$$\Delta S >= \frac{34 \times 000}{358} = 94.972 J/K$$

min-^{m} value of $\Delta S = 94.972$ J/K. No option corr

Q26. Ans - (c) $\frac{1}{2}A_2 + \frac{1}{2}B_2 \longrightarrow AB; \Delta H = -50cal$

$$\Delta H = \frac{1}{2}(B.E_{A_2} + B.E_{B_2}) - B.E_{A-B}$$

$$\% \; 50 = \frac{1}{2}\left(x + x/2\right) - x = \frac{3x}{4} - x = +x/4$$

$$X = 200$$

Q27. Ans -(c) $\Delta H = \Delta E + (P_2V_2 - P_1V_1)$

$\Delta H = 30.01.atm + (4 \times 5 - 2 \times 3) \quad = (30 + 14) = 44.0$ l-a

Q28. Ans - (d) mass depend an amount of sub taken & so if is an extensive properties.

Q29. Ans - (d) $mass/vol$ = density is independent from the amount of substance taken & so it is an intensive properties.

Q30. Ans - (a) will read in electrochemistry

$$\Delta G^0 = -nf\,E^0_{Cell}$$

$$E^0_{Cell} = \frac{-\Delta G^0}{nf} = \text{Independent from n}$$

Q31. Ans - (a) work depend as path, so it is a path function

Q32. Ans - (a) Exact differential are those function if

$$\frac{\partial}{\partial T}\left(\frac{\partial f}{\partial P}\right) = \frac{\partial}{\partial P}\left(\frac{\partial f}{\partial T}\right)$$

Where f is the function of P & T. Increase of q, it will not be equal, so it will be not exact function.

Q33. Ans - (a) $\Delta E = nC_V \Delta T$. (depend on n).

Q34. Ans - (b) ΔW is path so will not be equal to O in a cyclic process.