

## CHEMISTRY FOR JEE MAIN &amp; ADVANCED

## HINTS &amp; SOLUTIONS

## EXERCISE - 1

## Single Choice

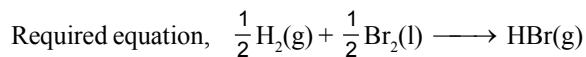
- 4.
- $C(s) \longrightarrow C(g)$
- can be obtained as,

$$\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 + \Delta H_4$$

- 5.
- $2C + O_2 \rightarrow 2CO$
- ;
- $\Delta H = -220 \text{ KJ}$

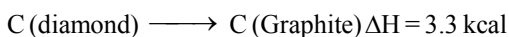
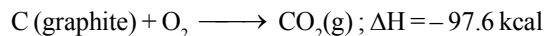
This reaction does not represent complete combustion of carbon, hence heat of combustion of carbon will not be equal to 110 kJ. The negative sign of  $\Delta H$  indicates that this reaction is exothermic. Also, despite being spontaneous reaction, it requires initiation.

- 6.
- $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$
- $\Delta H = \Delta H^\circ_1$
- ...
- (i)**

[eq<sub>1</sub> - eq<sub>2</sub>]

$$\Delta H = \left[ \frac{\Delta H^\circ_1 - \Delta H^\circ_2}{2} \right]$$

- 7.
- $C(\text{diamond}) + O_2 \longrightarrow CO_2(g)$
- ;
- $\Delta H = -94.3 \text{ kcal}$

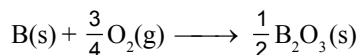


Heat required to convert 12 gram diamond to graphite = 3.3

 $\therefore$  Heat required to convert 1 gm diamond to graphite

$$= \frac{3.3}{12} = 0.275$$

10. Combustion reaction of solid boron



$$\Delta H^\circ_r = \Delta H^\circ_c = \frac{1}{2} \Delta H^\circ_f(B_2O_3, s) - \Delta H^\circ_f(B, s) - \frac{3}{4} \Delta H^\circ_f(O_2, g)$$

$\Delta H^\circ_f$  of element in stable state of aggregation is assumed to be zero.

$$\Delta H^\circ_c = \frac{1}{2} \Delta H^\circ_f(B_2O_3, s)$$

- 12.
- $CS_2(\ell) + 3O_2(g) \longrightarrow CO_2(g) + 2SO_2(g)$

$$\Delta H = -256 \text{ Kcal}$$

$$\text{Let } \Delta H_f(CO_2, g) = -4x \quad \text{and} \quad \Delta H_f(SO_2, g) = -3x$$

$$\Delta H_{\text{reaction}} = \Delta H_f(CO_2, g) + 2 \Delta H_f(SO_2, g) - \Delta H_f(CS_2, \ell)$$

$$-265 = -4x - 6x - 26$$

$$x = +23.9$$

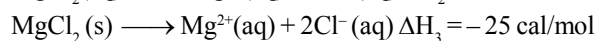
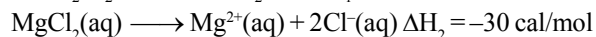
$$\therefore \Delta H_f(SO_2, g) = 3x = -71.7 \text{ Kcal/mol.}$$

- 13.
- $S + O_2 \longrightarrow SO_2$
- $\Delta H = -298.2 \text{ KJ/mole}$
- ...
- (1)**



Adding (1),(2),(3) and (4) we get desired equation.

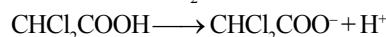
- 15.
- $MgCl_2 \cdot H_2O \longrightarrow MgCl_2(aq)$
- $\Delta H_1 = ?$



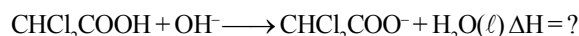
$$\Delta H_1 + \Delta H_2 = \Delta H_3$$

$$\Delta H_1 = \Delta H_3 - \Delta H_2 = -25 + 30 = +5 \text{ cal/mol.}$$

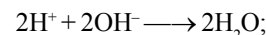
- 16.
- $H^+ + OH^- \longrightarrow H_2O(\ell)$
- $\Delta H = -13.7 \text{ kcal}$
- ...
- (i)**



$$\Delta H = 0.7 \text{ kcal} \dots\text{(ii)}$$

Adding equation **(i)** and **(ii)**  $\Delta H = -13 \text{ kcal.}$ 

- 17.
- $H_3PO_3 \longrightarrow 2H^+ + HPO_3^{2-}$
- ;
- $\Delta_f H = ?$



$$\Delta_f H = -55.84 \times 2 = -111.68$$

$$-106.68 = \Delta_{\text{ion}} H - 55.84 \times 2$$

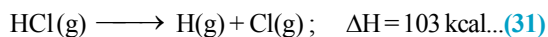
$$\Delta_{\text{ion}} H = 5 \text{ kJ/mol.}$$

- 20.
- $\frac{1}{2} A - A + \frac{1}{2} B - B \rightarrow AB$
- $\Delta H = -100 \text{ KJ/mole}$

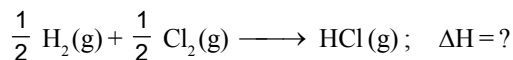
$$\frac{1}{2} x + \frac{1}{2} (0.5x) - x = -100 \Rightarrow \frac{x}{2} + 0.25x - x = -100$$

$$\Rightarrow -0.25x = -100 \quad \Rightarrow x = 400 \text{ KJ/mole}$$

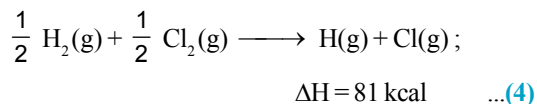
Bond enthalpy = **400 kJ/mol.**



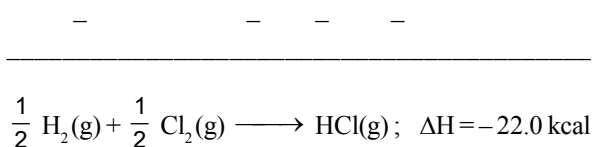
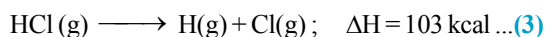
Heat of formation for HCl



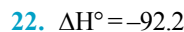
Divide equation (1) and (2) by 2, and then add



Subtracting equation (3) from equation (4)



$\therefore$  Enthalpy of formation of HCl gas = -22.0 kcal

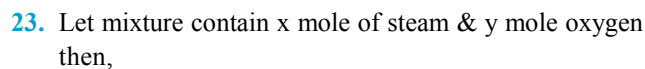


$\Delta C_p = 2C_p(\text{NH}_3, \text{g}) - C_p(\text{N}_2, \text{g}) - 3C_p(\text{H}_2)$   
 $= 2 \times 35.1 - 29.1 - 3 \times 28.8$   
 $= 70.2 - 29.1 - 86.4 = -45.3 \text{ J/K}$

$\Delta\text{H}^\circ_{100^\circ\text{C}} = \Delta\text{H}^\circ_{25^\circ\text{C}} + \Delta C_p(\Delta T) = -92.2 - \frac{45.3 \times 75}{1000}$

$\Delta\text{H}^\circ_{100^\circ\text{C}} = -92.2 - 1.3975 = -95.6 \text{ kJ/mole}$

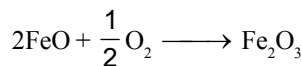
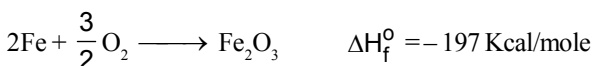
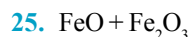
Then, reaction at 100°C as compared to that at 25°C will be more exothermic.



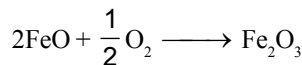
Here, temperature is constant. So, amount of heat released = amount of heat gain

$x \times 132 = y(220) \Rightarrow \frac{x}{y} = \frac{220}{132} = \frac{1.66}{1}$

$\Rightarrow y : x = 1 : 0.6$

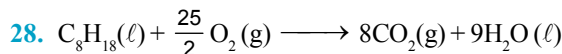


$\Delta\text{H} = -197 + 65 \times 2 \Rightarrow \Delta\text{H} = -67 \text{ Kcal/mole}$



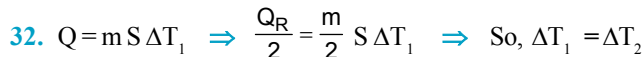
$\frac{\frac{2}{3} - 2x}{\frac{1}{3} + x} = \frac{1}{2} \Rightarrow x = \frac{1}{5}$

So, energy released =  $\frac{1}{5} \times 67 = 13.4 \text{ kcal/mole}$



$\Delta n_g = 8 - \frac{25}{2} = \frac{16 - 25}{2} = -\frac{9}{2} = -4.5$

$\Delta\text{H} - \Delta E = \Delta n_g RT = -\frac{4.5 \times 8.314 \times 298}{1000} = -11.15 \text{ kJ}$

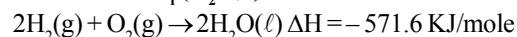
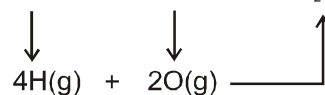
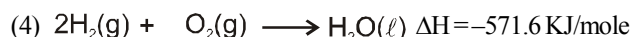
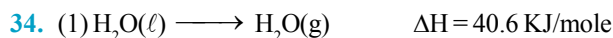


and specific heat is 4.2 J/gc

$q = ms\Delta T = 100 \times 4.2 \times 3$

millimoles of acid neutralized = 5

$\Delta\text{H} = -100 \times 4.2 \times 3 \times \frac{1000}{5} = -2.52 \times 10^2 \text{ kJ/mole.}$



$\Delta\text{H}_r^\circ = 2\Delta\text{H}_f^\circ(\text{H}_2\text{O}, \ell) - 2\Delta\text{H}_f^\circ\{\text{H}_2(\text{g})\} - \Delta\text{H}_f^\circ(\text{O}_2, \text{g})$

$\downarrow$

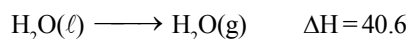
Zero

$\downarrow$

Zero

$-571.6 = 2\Delta\text{H}_f^\circ(\text{H}_2\text{O}, \ell)$  so  $\Delta\text{H}_f^\circ(\text{H}_2\text{O}, \ell) = -285.8$

(2) Calculation of  $\Delta H_f^\circ(\text{H}_2\text{O}, \text{g})$

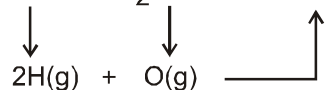


$$\Delta H_r = \Delta H_f^\circ(\text{H}_2\text{O}, \text{g}) - \Delta H_f^\circ(\text{H}_2\text{O}, \ell)$$

$$\Delta H_f^\circ(\text{H}_2\text{O}, \text{g}) = \Delta H_f^\circ(\text{H}_2\text{O}, \ell) + \Delta H_r$$

$$= -285.8 + 40 = -245.8$$

(3)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\text{g}) \quad \Delta H = -245.8$



$$\Delta H_r = \epsilon_{\text{H-H}} + \frac{1}{2} \epsilon_{\text{O-O}} - 2 \epsilon_{\text{O-H}}$$

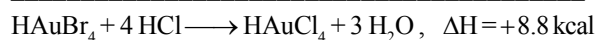
$$\Rightarrow -245.8 = +435 + \frac{1}{2}(489.6) - 2 \times \epsilon_{\text{O-H}}$$

$$2 \epsilon_{\text{O-H}} = 435 + 244.8 + 245.8$$

$$\Rightarrow 2 \epsilon_{\text{O-H}} = 925.6$$

$$\epsilon_{\text{O-H}} = 462.8$$

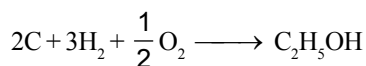
35.  $\text{Au}(\text{OH})_3 + 4 \text{HCl} \longrightarrow \text{HAuCl}_4 + 3 \text{H}_2\text{O}, \quad \Delta H = -28 \text{ kcal}$



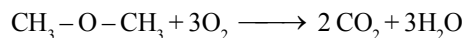
When 100% conversion, heat absorbed = 8.8 Kcal

$$\% \text{ conversion} = \frac{0.44}{8.8} \times 100 = 5\%$$

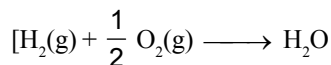
36.  $\Delta H_f^\circ \text{C}_2\text{H}_5\text{OH}(\ell) = -66 \text{ Kcal/mole}$



$$\Delta H = -66 \text{ kcal/mole} \quad \dots(1)$$



$$\Delta H = -348 \text{ kcal/mole} \quad \dots(2)$$



$$\Delta H_3 = -68 \text{ kcal/mole} \quad \dots(3)$$



Target equation = - eq 1 - eq 2 + 3eq 3 + 2 eq 4

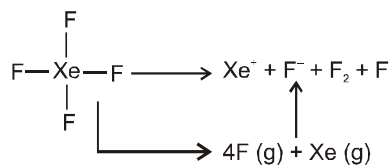
$$\Delta H = +66 + 348 - 3 \times 68 - 2 \times 94 = +66 + 348 - 204 - 188$$

$$\Rightarrow \Delta H = 22 \text{ K cal/mole}$$

$$\Delta H = \Delta E + \Delta n g R T \quad \Rightarrow 22 = \Delta E + 1 \times 2 \times 298 \times 10^{-3}$$

$$\Rightarrow \Delta E = 21.4 \text{ Kcal/mole}$$

37.



$$\Delta H = 4 \epsilon_{\text{Xe-F}} + \Delta H_{\text{ion}}[\text{Xe} \rightarrow \text{Xe}^+] - \Delta E_{\text{F-F}} - \Delta H_{\text{eg}}[\text{F} \rightarrow \text{F}^-]$$

$$= 4 \times 34 + 279 - 85 - 38 = 136 + 279 - 123 = 415 - 213$$

$$= 292 \text{ kcal/mole.}$$

39.  $-12250x - 13000(1-x) = -12500$

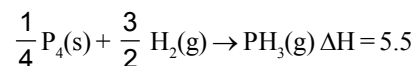
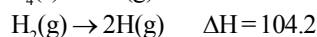
$$750x = 500 \quad \Rightarrow x = 2/3$$

$$\text{So, required ratio is} = \frac{2}{1}$$

40. 1 M  $\text{H}_2\text{SO}_4 = 2 \text{g eq. of } \text{H}_2\text{SO}_4$

$$\text{hence, } y = 2x \text{ or } x = \frac{1}{2} y.$$

42.  $\text{P}_4(\text{s}) \rightarrow 4\text{P}(\text{g}) \quad \Delta H = 53.2 \times 6$



$$\frac{1}{4} \times 6 \times 53.2 + \frac{3}{2} \times 104.2 - 3 \epsilon_{\text{P-H}} = 5.5$$

$$\Rightarrow \epsilon_{\text{P-H}} = 76.866 \text{ i.e. } 76.9 \text{ kcal mol}^{-1}$$

EXERCISE - 2

Part # I : Multiple Choice

3.  $\Delta H_r = [2(\Delta H_f)_{\text{N}_2\text{O}_5} + 4(\Delta H_f)_{\text{HPO}_3} - 4(\Delta H_f)_{\text{HNO}_3} - (\Delta H_f)_{\text{P}_4\text{O}_{10}}]$

$$\Delta H_r = [2(-43.1) + 4(-948.5) - 4(-174.1) - (-2984.0)]$$

$$= -199.8$$

5.  $\Delta H_r^\circ = [4\Delta H_{\text{C-H}} + 4\Delta H_{\text{Cl-Cl}} - 4\Delta H_{\text{C-Cl}} - 4\Delta H_{\text{C-Cl}}]$

$$= [4 \times 414 + 4 \times 243 - 4 \times 331 - 4 \times 4313]$$

$$\Delta H_r^\circ = 420$$

6. For  $\Delta H_g = 0, \Delta H = \Delta E$

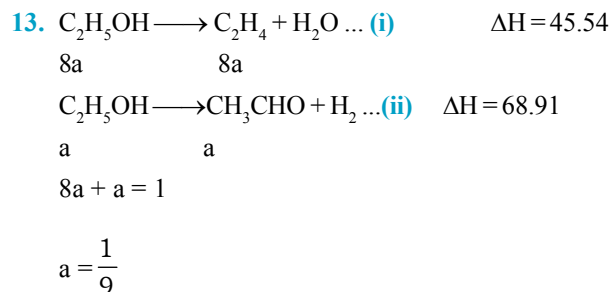
$$\Delta H_g \neq 0, \Delta H \neq \Delta E$$

9. Heat evolve =  $mC_v \Delta t = 100 \times 4.2 \times 10 = 4.2 \text{ kJ}$

for 0.1 mole the enthalpy change = 4.2 kJ

for 1 mole the enthalpy change = 42 kJ

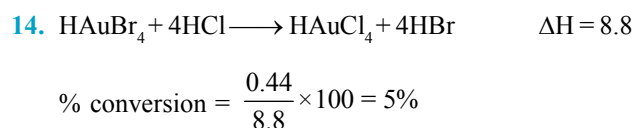
10.  $\text{HCl} + \text{NaOH} \longrightarrow \text{NaCl} + \text{H}_2\text{O}$   
 enthalpy change =  $mC_v dT = 100 \times 4.2 \times 3$   
 $= 1.26 \text{ kJ}$   
 enthalpy change for 5 millimole = 1.26 kJ  
 enthalpy change for 1 mole  $\Rightarrow \frac{1.26}{5 \times 10^{-3}}$   
 $\Rightarrow 2.52 \times 10^2 \text{ kJ}$



energy involve in (i) reaction =  $45.54 \times \frac{8}{9}$

energy involve in (ii) reaction =  $68.91 \times \frac{1}{9}$

total involve in (i) + (ii) are  $\Rightarrow 48.137 \text{ KJ}$



Part # II : Assertion & Reason

- Heat of neutralisation for strong acid and strong base combination is constant is equal to  $-13.7 \text{ Kcal}$  or  $-57.1 \text{ KJ}$ .
- For reaction  $\text{C(s)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$ ;  $\Delta H = \Delta U$

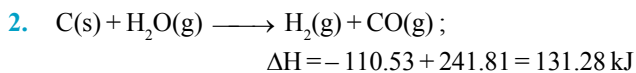
EXERCISE - 3

Part # I : Matrix Match Type

- (A) This is combustion reaction as well as formation reaction of  $\text{CO}_2$ .  
 (B) This is sublimation, atomization as well as formation reaction of  $\text{C}(\text{g})$ .  
 (C) This is combustion reaction of  $\text{CO}(\text{g})$ .  
 (D) This is atomization of  $\text{CH}_4(\text{g})$ .

Part # II : Comprehension

Comprehension # 1 :



For 100 moles of air heat liberated =  $21 \times 314 \text{ kJ}$ .

No. of moles of  $\text{H}_2\text{O}$  converted to product

$$= \frac{21 \times 314}{131.28} = 50.23$$

No. of moles of  $\text{H}_2\text{O}$  taken =  $\frac{50.23}{0.75} = 66.97$ .

Gas	$\text{H}_2$	$\text{CO}$	$\text{N}_2$	$\text{H}_2\text{O}$	$\text{CO}_2$
No. of moles	50.23	50.23	79	16.74	21
% (v/v)	23.1	23.1	36.4	7.7	9.7

Comprehension # 2 :

1.  $\Delta H_{\text{ionisation}} = \Delta H_{\text{neutralisation}} - \Delta H^\circ (\text{H} + \text{OH}^- \longrightarrow \text{H}_2\text{O})$   
 $= -49.86 - (-55.84) \text{ kJ/mole}$   
 $= 5.98 \text{ kJ/mole}$

- For max. rise in temp.; max. neutralization of  $\text{H}^+$  and  $\text{OH}^-$  required.  
 If we take equal volume, all  $\text{H}^+$  (5 m-mole) will react with all  $\text{OH}^-$  (5 m-mole).

Comprehension # 4 :

1.  $\Delta H_r = [(\Delta H_f)_{\text{C}_2\text{F}_4} + 2(\Delta H_f)_{\text{HCl}} - 2(\Delta H_f)_{\text{CHClF}_2}]$   
 $= [-658.3 + 2(-92.3) + 2(485.2)]$   
 $= 127.5 \text{ kJ/mole}$

2. Add eq. (i), (ii) and (iii)  
 $\text{CX}_4(\text{g}) \longrightarrow \text{C}(\text{g}) + 4\text{X}$   
 $\Delta H = -\Delta H_1 + 718 + 2D(\text{X}-\text{X})$   
 $\text{X} = \text{F}$   
 $\Delta H = +679.6 + 718 + 2 \times 154.7$   
 $\Delta H = 1707$

Average bond energy of  $\text{C}-\text{F}$  bond =  $\frac{1707}{4} = 426.75$

$\text{X} = \text{Cl}$   
 $\Delta H = 106.6 + 718 + 2(246.7) = 1318$   
 Average bond energy of  $\text{C}-\text{Cl}$  bond = 329.5 KJ

- $\text{C}-\text{Cl}$  bond energy = 329.5  
 $\text{C}-\text{H}$  bond energy = 416.1  
 $\text{C}-\text{F}$  bond energy = 426.75  
 Order of reactivity  $\text{C}-\text{Cl} > \text{C}-\text{H} > \text{C}-\text{F}$

Comprehension # 5 :

1. (i)  $\Delta H = (v + w + x + y + z)$

(ii)  $(\Delta H)_{\text{PK}^+} = \frac{w}{2}$

(iii)  $(\Delta H)_{\text{EA}}$  for H =  $\frac{y}{2}$

(iv)  $(\Delta H)_{\text{lattice}}$  for KH =  $\frac{z}{2}$

2. (i) electron affinity is exothermic

(ii) ionization is endothermic

3.  $(\Delta H)_r = 2 \times 90 + 2 \times 418 + 436 - 2 \times 78 - 2 \times 710$   
 $(\Delta H)_r = -124 \text{ kJ/mole}$

4.  $(\Delta H)_{\text{PKH}} = -\frac{124}{2} \Rightarrow -62 \text{ kJ/mole}$

6. Meq. of KH = Meq. of HCl

$$\frac{0.1}{E_{\text{KH}}} \times 1000 = 25 \times 0.1$$

Valency factor of K is 1 hence

$$\begin{aligned} E_{\text{K}} &= M_{\text{K}} & M_{\text{K}} &= 39 \\ E_{\text{KH}} &= 40 & E_{\text{KH}} &= E_{\text{K}} = E_{\text{H}} \\ 40 &= E_{\text{K}} + 1 & E_{\text{K}} &\Rightarrow 39 \end{aligned}$$

EXERCISE - 4

Subjective Type

3.  $\Delta H_2 - 24 = -0.024 \times (523 - 473) \text{ cal/g.}$

$\therefore \Delta H_2 = 22.8 \text{ cal/g.}$

4. When the heat capacities of all substances participating in a chemical reaction are assumed to be constant over the range of temperatures involved kirchoff's law integrates to

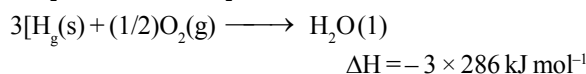
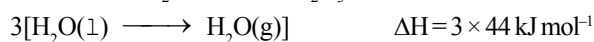
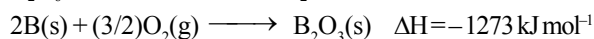
$$\Delta H^\circ(T_2) = \Delta H^\circ(T_1) + \Delta C_p(T_2 - T_1)$$

$$\Delta C_p = \sum_{\text{Products}} \nu C_{p,m}^0 - \sum_{\text{Reactants}} \nu C_{p,m}^0 -$$

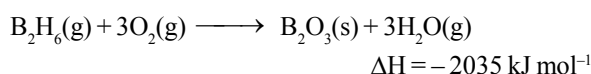
$$\begin{aligned} \Delta C_p &= C_p(\text{N}_2\text{O}_4\text{g}) - 2 C_p(\text{NO}_2\text{g}) \\ &= (77.28) - (2) \times (37.20 \text{ J K}^{-1} \text{ mol}^{-1}) \\ &= +2.88 \text{ JK}^{-1} \text{ mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta H^\circ(373 \text{ K}) &= \Delta H^\circ(298\text{K}) + \Delta C_p \Delta T \\ &= (-57.20 \text{ kJ mol}^{-1}) + (2.88 \text{ J K}^{-1}) \times (75 \text{ K}) \\ &= \{(-57.20) + (0.22)\} \text{ kJ mol}^{-1} \\ &= -56.98 \text{ kJ mol}^{-1} \end{aligned}$$

6. Given reaction can be obtained as follows :



Add \_\_\_\_\_

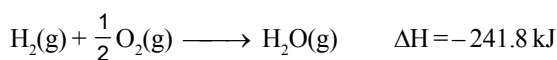


7. Equal volume of  $\text{H}_2(\text{g})$  &  $\text{CO}(\text{g})$

Total volume = 112 L

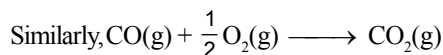
So, volume of  $\text{CO}$  = volume of  $\text{H}_2$  = 56 L

Mole of  $\text{CO}$  = Mole of  $\text{H}_2$  = 2.5 mole



For 1 mole  $\Delta H = -241.8 \text{ kJ}$

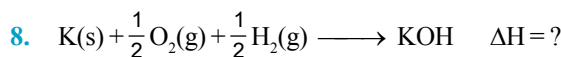
For 2.5 mole  $\Delta H = -241.8 \times 2.5$



$$\Delta H = -283 \text{ kJ}$$

$$\Delta H = -283 \times 2.5 \text{ kJ}$$

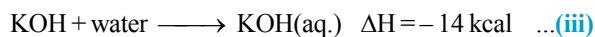
Total Heat evolved =  $[-241.8 + (-283)] 2.5 = -1312 \text{ kJ}$



... (i)



$$\Delta H = -48 \text{ kcal} \quad \dots \text{(ii)}$$



$$\Delta H_{\text{fKOH}} = \text{(i)} + \text{(ii)} - \text{(iii)}$$

$$\Delta H_{\text{fKOH}} = -48 - 68 - (-14) = -102 \text{ kcal.}$$

9. Heat generated =  $C_p \Delta T = 1260 \times 0.667 \text{ cal.}$

$$\therefore n_{\text{CH}_4} = \frac{1260 \times 0.667}{210.8 \times 10^3}$$

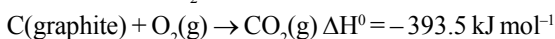
$$n_{\text{total}} = \frac{PV}{RT} = 3.98 \times 10^{-2}$$

$$\therefore \text{mol}\% = \frac{1260 \times 0.667}{210.8 \times 10^3 \times 3.98 \times 10^{-2}} \times 100\% = 10\% \text{ Ans.}$$

12. We have

$$\text{Amount of carbon} = \frac{12.0 \text{ g}}{12.0 \text{ g mol}^{-1}} = 1 \text{ mol}$$

The equations to be considered are



Let the amount  $x$  of carbon be converted into CO and the remaining (i.e.  $1.0 \text{ mol} - x$ ) into  $\text{CO}_2$ . we will have  $[x(-110.5) + (1.0 \text{ mol} - x)(-393.5)] \text{ kJ mol}^{-1} = -313.8 \text{ kJ}$

$$\text{Which gives } x = \frac{313.8 + 393.5}{393.5 - 110.5} \text{ mol} = 0.282 \text{ mol}$$

$$\text{Amount of oxygen needed} = \left[ \frac{0.282}{2} + (1.0 - 0.282) \right]$$

$$\text{mol} = 0.859 \text{ mol}$$

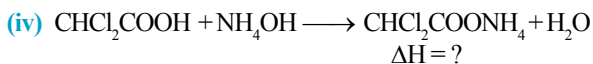
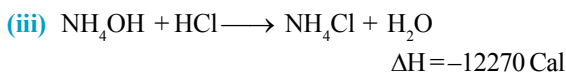
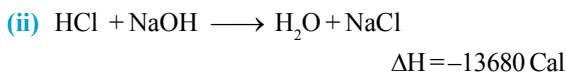
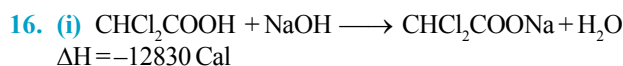
$$\text{Mass of oxygen needed} = (0.859 \text{ mol})(32 \text{ g mol}^{-1}) = 27.48 \text{ g}$$

15. Equation (vi) can be generated by the following manipulations.

$$\text{Eq. (i)} - \text{Eq. (ii)} - \text{Eq. (iii)} - \text{Eq. (iv)} - \frac{1}{2} \text{Eq. (v)}$$

Carrying out the corresponding manipulations on  $\Delta H^\circ_L$ , we get

$$\Delta H^\circ_L = (-563 - 419 - 88 + 322 - 79) \text{ kJ mol}^{-1} \\ = -829 \text{ kJ mol}^{-1}$$



$$\text{(iv)} = \text{(i)} + \text{(iii)} - \text{(ii)} = -12830 - 12270 + 13680 = -11420 \text{ Cal}$$

$$\text{Heats of ionization of } \text{CHCl}_2\text{COOH} = -13680 + 12830 \\ = -850 \text{ cal}$$

$$\text{Heats of ionization of } \text{NH}_4\text{OH} = -13680 + 12270 = -1410 \text{ cal}$$

17. Given total solution =  $200 + 400 = 600 \text{ mL}$ .

200 mL of 1 M HCl neutralize 400 mL of 0.5 M NaOH

$$\therefore \text{Meq.} = N \times V$$

$$\therefore \text{mM or Meq. of acid and base} = 200 \text{ (For mono valent}$$

nature)

i.e., 200 Meq. of HCl react with 200 Meq. of NaOH to produce heat =  $\Delta H$

1000 Meq. of HCl + 1000 Meq. of NaOH will give heat =  $5 \times \Delta H$ .

i.e, heat of neutralization. Now,

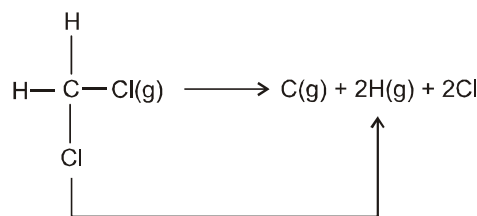
$\Delta H$ , i.e., Heat produced during neutralization of 200 Meq. of acid and base

$$= \text{Heat taken up by calorimeter + solution} = m_1 s_1 \Delta T + m_2 s_2 \Delta T$$

$$= 12 \times 4.4 + 600 \times 1 \times 4.4 = 2692.8 \text{ cal}$$

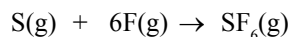
$$\therefore \text{Heat of neutralization} = -5 \times 2692.8 \text{ cal} = -13.464 \text{ kcal}$$

18.



$$\Delta H_r = 2\epsilon_{\text{C-H}} + 2\epsilon_{\text{C-Cl}} = 2 \times 414 + 2 \times 330 = 828 + 660 \\ = 1488 \text{ kJ/mol.}$$

20. To calculate the average S-F bond enthalpy, we determine the enthalpy change for the following reaction.

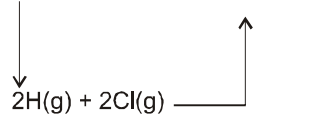
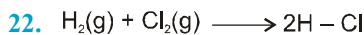


$$\Delta H_f^\circ 275 \text{ kJ mol}^{-1} \quad 80 \text{ kJ mol}^{-1} \quad 1100 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ = \Delta H_f^\circ(\text{SF}_6, \text{g}) - [\Delta H_f^\circ(\text{S}, \text{g}) + 6\Delta H_f^\circ(\text{F}, \text{g})] \\ = [-1100 - (275 + 6 \times 80)] \text{ kJ mol}^{-1}$$

$$\text{Hence } \epsilon(\text{S-F}) = \frac{-\Delta H_f^\circ(\text{SF}_6, \text{g})}{6} = \frac{1855 \text{ kJ mol}^{-1}}{6}$$

$$= 309.2 \text{ kJ mol}^{-1}$$



$$\Delta H_f^\circ = \epsilon_{\text{H-H}} + \epsilon_{\text{Cl-Cl}} - 2\epsilon_{\text{H-Cl}} = 435 + 240 - 2 \times 430$$

$$\Delta H_f^\circ = -185 \text{ kJ}$$

$$\Delta S = 2S_m^\circ \text{HCl} - S_m^\circ \text{H}_2(\text{g}) - S_m^\circ \text{Cl}_2(\text{g}) = 2 \times 187 - 131 - 223$$

$$\Delta S = 20 \text{ J/mole K}$$

$$\Delta G = \Delta H - T\Delta S = -185 - \frac{300 \times 20}{1000} = -186 - 6 = -191 \text{ KJ.}$$

23. Target equation :  $\text{N}_2\text{H}_4(\ell) + \text{O}_2(\text{g}) \rightarrow \text{N}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$   
which can be obtained by the given manipulation.

$$\frac{1}{4} \times \text{(i)} - \frac{3}{4} \times \text{(ii)} + \frac{9}{4} \times \text{(iv)} - \frac{1}{8} \times \text{(iii)}$$

Hence,  $\Delta H$  for targeted equation is

$$\frac{1}{4}(-1011) - \frac{3}{4}(-317) + \frac{9}{4}(-286) - \frac{1}{8}(-286)$$

$$= \frac{1}{4}[-1011 + 3 \times 317 - 9 \times 286 + 0.5 \times 286]$$

$$= -622.75 \text{ kJ/mole hydrazine}$$

Now,  $-622.75 = 2 \times (-286) - \Delta H_f(\text{N}_2\text{H}_4)$

$$\Rightarrow \Delta H_f(\text{N}_2\text{H}_4) = +50.75 \text{ kJ/mol}$$

Yes it is an endothermic compound.

25. (i)  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}); \Delta H_f^\circ = -393.33 \text{ KJ/mol};$

$$\Delta H_f^\circ = \frac{590}{18} \times 12$$

- (ii)  $\text{H}_2(\text{g}) + \frac{1}{2}\text{O}_2(\text{g}) \longrightarrow \text{H}_2\text{O}(\ell); \Delta H_f^\circ = -286 \text{ KJ/mol};$

$$\Delta H_f^\circ = \frac{15889}{55.5}$$

- (iii)  $\text{C}_6\text{H}_6(\ell) + \frac{15}{2}\text{O}_2(\text{g}) \longrightarrow 6\text{CO}_2(\text{g}) + 3\text{H}_2\text{O}(\ell)$

$$\therefore \Delta H^\circ = [6(-393.33) + 3(-286)] - 50 = -3268 \text{ KJ/mol}$$

$$\text{Mass of benzene is } = 0.87 \times 100 = 87 \text{ g}$$

$$\therefore \text{Heat evolved from 87 gm benzene} = 3645 \text{ KJ Ans.}$$

27.  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \longrightarrow 6\text{CO}_2 + 6\text{H}_2\text{O}(\ell)$

$$\text{No. of Mole of } \text{C}_6\text{H}_{12}\text{O}_6 = \frac{0.36}{180} = 2 \times 10^{-3} \text{ mole}$$

$$C = \frac{q}{\Delta T} \quad \therefore \quad q = C \times \Delta T = 640 \times 10 \text{ J} = 6.4 \text{ kJ}$$

$$\text{Heat released per mole} = \frac{6.4}{2 \times 10^{-3}} = 3.2 \times 10^3 \text{ kJ} = \mathbf{3.2 \text{ MJ}}$$

$$\Delta U = -3.2 \text{ MJ}$$

$$\Delta H = \Delta U + \Delta n_g RT \text{ here } \quad \Delta n_g = 0$$

$$\Delta H = \Delta U = -\mathbf{3.2 \text{ MJ mole}^{-1}}$$

28. By the equations  $C_p = f(T)$ , we find

$$\Delta C_p = (C_p)_{\text{CO}} - (C_p)_c - \frac{1}{2}(C_p)_{\text{O}_2}$$

$$= 2.37 - 4.973 \times 10^{-3} T + 1.585 \times 10^{-6} T^2$$

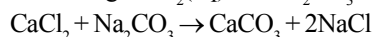
The condition where  $\Delta H^\circ$  does not depend on the temperature is the equation  $\Delta C_p = 0$ ,

$$\text{i.e. } 2.37 - 4.973 \times 10^{-3} T + 1.585 \times 10^{-6} T^2 = 0,$$

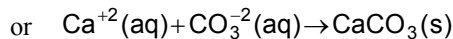
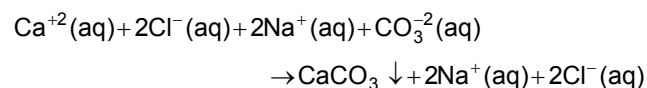
$$\text{where } T \approx 586.$$

Since the terms of the equation  $\Delta C_p = f(T)$  containing T are negative, then at  $T > 586$  we have  $\Delta C_p < 0$ . i.e. at this temperature  $\Delta H^\circ$  passes through a minimum.

30. On mixing  $\text{CaCl}_2(\text{aq})$  and  $\text{Na}_2\text{CO}_3$



Solutions are very dilute and thus, 100% dissociation occurs.



$$\therefore \Delta H = \sum H_{\text{Products}}^\circ - \sum H_{\text{reactants}}^\circ$$

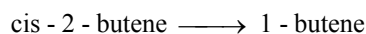
or  $\Delta H = \Delta H_{\text{fCaCO}_3}^\circ - [\Delta H_{\text{fCa}^{+2}}^\circ + \Delta H_{\text{fCO}_3^{-2}}^\circ]$

$$\therefore \Delta H^\circ \text{ of a compound} = \Delta H_{\text{formation}}^\circ$$

$$= -288.5 - (-129.80 - 161.65) = 2.95 \text{ kcal}$$

31. trans - 2 - butene  $\longrightarrow$  cis - 2 - butene

$$\Delta H = +0.95 \text{ kcal}$$

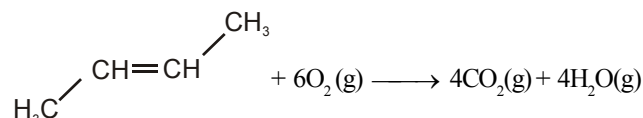
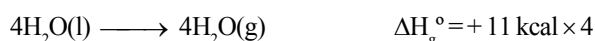
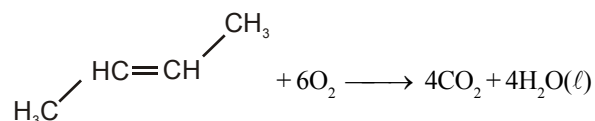
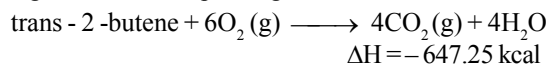


$$\Delta H = +1.8 \text{ kcal}$$



$$\Delta H = -650 \text{ kcal}$$

Adding above three equation gives :

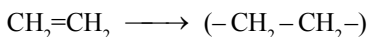


$$\Delta H = -603.25 \text{ kcal}$$

$$-603.25 = 8 \times 98 + 2 \times 80 + \text{B.E. (C=C)} + 6 \times 118 - 8 \times 196 - 8 \times 110$$

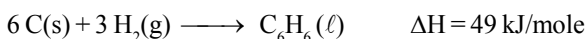
$$\text{B.E. (C=C)} = 192.75 \text{ kcal.}$$

32. In polymerisation of ethylene, double bond of ethylene is broken and two single bonds are formed.



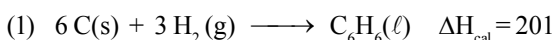
$$\Delta H_{\text{poly}} = E_{\text{C=C}} - 2 E_{\text{C-C}} = -72$$

$$\Rightarrow E_{\text{C=C}} - 2 E_{\text{C-C}} = -72 \quad \dots(1)$$

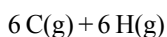
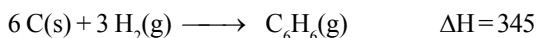


$$\Delta H_{\text{resonance}} = \Delta H_{\text{exp}} - \Delta H_{\text{cal}}$$

$$\Delta H_{\text{cal}} = 49 - (-\Delta H_{\text{resonance}}) = 49 - (-152) = 201$$



Adding 1 & 2



$$\Delta H = 6 \times 715 + 3 \times 436 - 6 E_{\text{C-H}} - 3 E_{\text{C=C}} - 3 E_{\text{C-C}}$$

$$345 = 4290 + 1308 - 6 \times 415 - 3 E_{\text{C=C}} - E_{\text{C-C}}$$

$$3 E_{\text{C=C}} + 3 E_{\text{C-C}} = 2763 \text{ So } E_{\text{C=C}} + E_{\text{C-C}} = 921$$

$$E_{\text{C=C}} + E_{\text{C-C}} = 921 \quad \dots\dots (i)$$

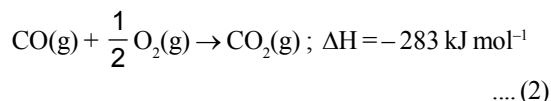
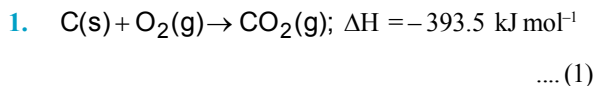
$$E_{\text{C=C}} - 2 E_{\text{C-C}} = -72 \quad \dots\dots (ii)$$

On solving (i) and (ii) equation,  $3 E_{\text{C-C}} = 993$

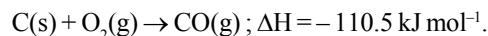
$$E_{\text{C-C}} = 331 \text{ kJ/mole, So, } E_{\text{C=C}} = 590 \text{ kJ/mole}$$

EXERCISE - 5

Part # I : AIEEE/JEE-MAIN



On subtraction equation (2) from equation (1), we get



The enthalpy of formation of carbon monoxide per mole =  $-110.5 \text{ kJ mol}^{-1}$ .

2. Let the bond dissociation energy of XY, X<sub>2</sub> and Y<sub>2</sub> be x, x and x,  $\frac{x}{2}$  KJ/mol respectively,

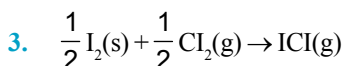


$\Delta H_{\text{reaction}} = [(\text{sum of bond dissociation energy of all reactants}) - (\text{sum of bond dissociation energy of all product})]$

$$= \left[ \frac{1}{2} \Delta H_{\text{X}_2} + \frac{1}{2} \Delta H_{\text{Y}_2} - \Delta H_{\text{XY}} \right]$$

$$= \frac{x}{2} + \frac{0.5x}{2} - x = -200$$

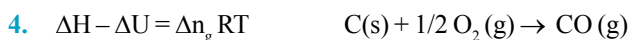
$$\therefore x = \frac{200}{0.25} = 800 \text{ KJ mol}^{-1}.$$



$$\Delta H_{f, \text{ICl}}(\text{g}) = \left[ \frac{1}{2} \Delta H_{\text{I}_2(\text{s}) \rightarrow \text{I}_2(\text{g})} + \frac{1}{2} \Delta H_{\text{I-I}} + \frac{1}{2} \Delta H_{\text{Cl-Cl}} \right] - [\Delta H_{\text{I-Cl}}]$$

$$= \left[ \frac{1}{2} \times 62.76 + \frac{1}{2} \times 151.0 + \frac{1}{2} \times 242.3 \right] - [211.3]$$

$$= 16.73 \text{ kJ/mol.}$$



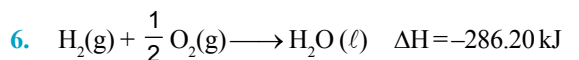
$$\Delta n_g = 1 - \frac{1}{2} = + \frac{1}{2}$$

$$\Delta H - \Delta U = \frac{1}{2} \times 8.314 \times 298$$

$$= 1238.78 \text{ J mol}^{-1}$$



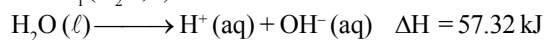
5.  $C + 2H_2 \rightarrow CH_4$ ;  $\Delta H^\circ = -74.8 \text{ kJ mol}^{-1}$   
 In order to calculate average energy for C – H bond formation we should know the following data.  
 $C(\text{graphite}) \rightarrow C(\text{g}); \Delta H_f^\circ =$  enthalpy of sublimation of carbon  
 $H_2(\text{g}) \rightarrow 2H(\text{g}); \Delta H^\circ$  bond dissociation energy of  $H_2$ .



$$\Delta H_r = \Delta H_f(H_2O, \ell) - \Delta H_f(H_2, \text{g}) - \frac{1}{2} \Delta H_f(O_2, \text{g})$$

$$-286.20 = \Delta H_f(H_2O(\ell))$$

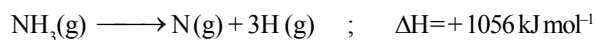
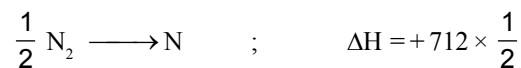
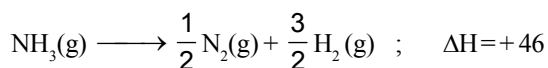
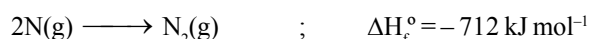
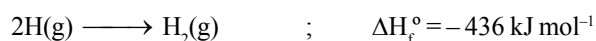
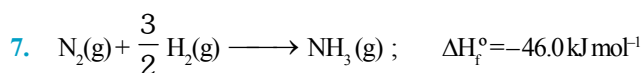
$$\text{So } \Delta H_f(H_2O, \ell) = -286.20 \text{ KJ/mole}$$



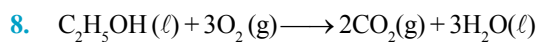
$$\Delta H_r = \Delta H_f(H^+, \text{aq}) + \Delta H_f(OH^-, \text{aq}) - \Delta H_f(H_2O, \ell)$$

$$57.32 = 0 + \Delta H_f(OH^-, \text{aq}) - (-286.20)$$

$$\Delta H_f(OH^-, \text{aq}) = 57.32 - 286.20 = -228.88 \text{ kJ.}$$



$$\text{Average bond enthalpy of N-H bond} = \frac{1056}{3} = +352 \text{ kJ mol}^{-1}$$

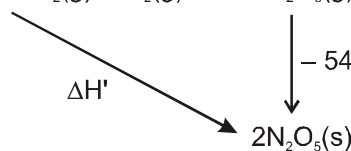
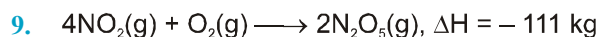


$$\Delta n_g = 2 - 3 = -1$$

$$\Delta U = \Delta H - \Delta n_g RT$$

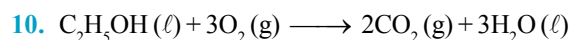
$$= -1366.5 - (-1) \times \frac{8.314}{10^3} \times 300$$

$$= -1366.5 + 0.8314 \times 3 = -1364 \text{ KJ}$$



$$-111 - 54 = \Delta H'$$

$$\Delta H' = -165 \text{ KJ}$$



$$\Delta E = -1364.47 \text{ kJ/mole}$$

$$\Delta H = ?$$

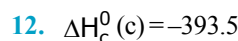
$$\Delta n_g = -1$$

$$\therefore \Delta H = -1366.95 \text{ kJ/mole}$$

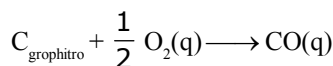
11.  $-\frac{R \times 298 \ln 1.6 \times 10^{12}}{2}$

$$= \Delta G_r^\circ = 2\Delta G_{NO_2}^\circ - 2\Delta G_{NO}^\circ$$

$$\Delta G_{NO_2}^\circ = 86.6 \times 10^3 - \frac{298K \ln 1.6 \times 10^{12}}{2}$$



$$\Delta H_c^\circ(\text{w,g}) = -283.5$$



$$\Delta H_f^\circ(\text{w,g}) = \Delta H_c^\circ(\text{c}) - \Delta H_c^\circ(\text{co, g})$$

$$= -393.5 + 283.5$$

$$= -110.0 \text{ KJ.}$$

Part # II : IIT-JEE ADVANCED

1.  $n = \frac{3.5}{28}$

$$\Delta T = T_2 - T_1 = 298.45 - 298 = 0.45$$

$$C_v = 2.5 \text{ kJ k}^{-1} = 2500 \text{ JK}^{-1}$$

$$C_p = C_v + R = 2500 + 8.314 = 2508.314 \text{ JK}^{-1}$$

$$Q_p = C_p \Delta T = 1128.74 \text{ J}$$

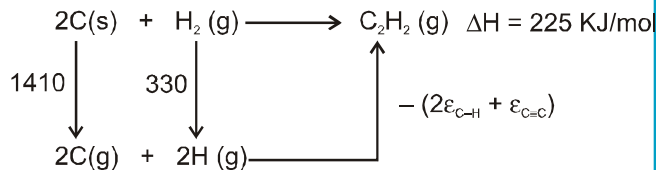
$$\Delta H = \frac{Q_p}{n} = \frac{1128.74}{3.5/28} = 9030 \text{ J mol}^{-1} = 9.030 \text{ KJ mol}^{-1} =$$

$$9 \text{ KJ mol}^{-1}.$$

2.  $\Delta H_f^\circ(\text{Cl}_2, \text{g}) = 0$ , As  $\Delta H_f^\circ$  of elements in their standard state is taken to be zero.

3.  $E_{\text{C-C}} \cong 100 \text{ KCal/mole}$ .

4.



$$\therefore \Delta H = +1410 + 330 - (350 \times 2) - \varepsilon_{\text{C-C}} = +225$$

$$\therefore \varepsilon_{\text{C-C}} = 1740 - 700 - 225 = +815 \text{ KJ/mol}$$

5.  $\text{C}_6\text{H}_{12}\text{O}_6(\text{s}) + 6\text{O}_2(\text{g}) \longrightarrow 6\text{CO}_2(\text{g}) + 6\text{H}_2\text{O}(\ell)$   
 $\Delta_c H = 6 \times \Delta_f H(\text{CO}_2) + 6 \Delta_f H(\text{H}_2\text{O}) - \Delta_f H(\text{C}_6\text{H}_{12}\text{O}_6) - 6\Delta_f H(\text{O}_2, \text{g})$

$$= 6 \times (-400 - 300) - (-1300) - 0$$

$$= -4200 + 1300$$

$$= -2900 \text{ KJ/mol}$$

For one gram of glucose, enthalpy of combustion

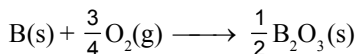
$$= -\frac{2900}{180} = -16.11 \text{ KJ/g}$$

**MOCK TEST**

3.  $\text{C}(\text{s}) \longrightarrow \text{C}(\text{g})$  can be obtained as,

$$\Delta H = \Delta H_1 - \Delta H_2 - \frac{1}{2} \Delta H_3 + \Delta H_4$$

4. Combustion reaction of solid boron

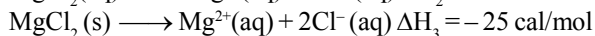
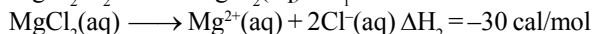


$$\Delta H_r^\circ = \Delta H_c^\circ = \frac{1}{2} \Delta H_f^\circ(\text{B}_2\text{O}_3, \text{s}) - \Delta H_f^\circ(\text{B}, \text{s}) - \frac{3}{4} \Delta H_f^\circ(\text{O}_2, \text{g})$$

$\Delta H_f^\circ$  of element in stable state of aggregation is assumed to be zero.

$$\Delta H^\circ \text{C} = \frac{1}{2} \Delta H^\circ \text{f}(\text{B}_2\text{O}_3, \text{s})$$

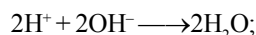
6.  $\text{MgCl}_2 \cdot \text{H}_2\text{O} \longrightarrow \text{MgCl}_2(\text{aq}) \Delta H_1 = ?$



$$\Delta H_1 + \Delta H_2 = \Delta H_3$$

$$\Delta H_1 = \Delta H_3 - \Delta H_2 = -25 + 30 = +5 \text{ cal/mol}$$

7.  $\text{H}_3\text{PO}_3 \longrightarrow 2\text{H}^+ + \text{HPO}_3^{2-}; \Delta_f H = ?$

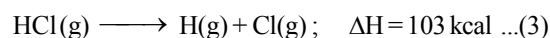


$$\Delta_f H = -55.84 \times 2 = -111.68$$

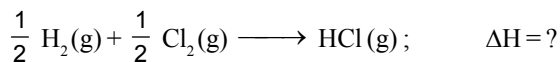
$$-106.68 = \Delta_{\text{ion}} H - 55.84 \times 2$$

$$\Delta_{\text{ion}} H = 5 \text{ kJ/mol}$$

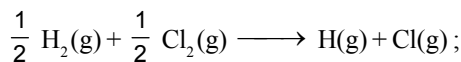
8. Given  $\text{H}_2(\text{g}) \longrightarrow 2\text{H}(\text{g}); \Delta H = 104 \text{ kcal} \dots(1)$



Heat of formation for HCl

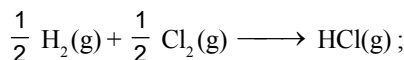
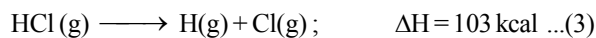


Divide equation (1) and (2) by 2, and then add



$$\Delta H = 81 \text{ kcal} \dots(4)$$

Subtracting equation (3) from equation (4)



$$\Delta H = -22.0 \text{ kcal}$$

$\therefore$  Enthalpy of formation of HCl gas = **-22.0 kcal**

10.  $\frac{1}{2} \text{A} - \text{A} + \frac{1}{2} \text{B} - \text{B} \rightarrow \text{AB} \Delta H = -100 \text{ KJ/mole}$

$$\frac{1}{2} x + \frac{1}{2} (0.5x) - x = -100 \Rightarrow \frac{x}{2} + 0.25x - x = -100$$

$$\Rightarrow -0.25x = -100 \Rightarrow x = 400 \text{ KJ/mole}$$

Bond enthalpy = **400 kJ/mol**.

13. Heat of neutralisation for strong acid and strong base combination is constant is equal to  $-13.7 \text{ Kcal}$  or  $-57.1 \text{ KJ}$ .

14. For reaction  $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}); \Delta H = \Delta U$

$$15. \Delta H_{\text{ionisation}} = \Delta H_{\text{neutralisation}} - \Delta H^\circ(\text{H} + \text{OH}^- \longrightarrow \text{H}_2\text{O})$$

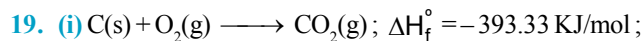
$$= -49.86 - (-55.84) \text{ kJ/mole}$$

$$= 5.98 \text{ kJ/mole}$$

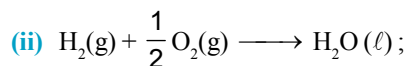
17. For max. rise in temp.; max. neutralization of  $\text{H}^+$  and  $\text{OH}^-$  required.

If we take equal volume, all  $\text{H}^+$  (5 m-mole) will react with all  $\text{OH}^-$  (5 m-mole).

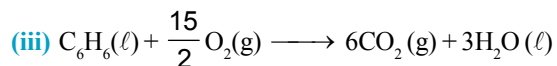
18. (A) This is combustion reaction as well as formation reaction of  $\text{CO}_2$ .  
 (B) This is sublimation, atomization as well as formation reaction of  $\text{C}$  (g).  
 (C) This is combustion reaction of  $\text{CO}$  (g).  
 (D) This is atomization of  $\text{CH}_4$  (g).



$$\Delta H_f^\circ = \frac{590}{18} \times 12$$



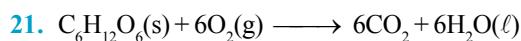
$$\Delta H_f^\circ = -286 \text{ KJ/mol}; \Delta H_f^\circ = \frac{15889}{55.5}$$



$$\therefore \Delta H^\circ = [6(-393.33) + 3(-286)] - 50 = -3268 \text{ KJ/mol}$$

$$\text{Mass of benzene is } = 0.87 \times 100 = 87 \text{ g}$$

$$\therefore \text{Heat evolved from 87 gm benzene} = 3645 \text{ KJ Ans.}$$



$$\text{No. of Mole of } \text{C}_6\text{H}_{12}\text{O}_6 = \frac{0.36}{180} = 2 \times 10^{-3} \text{ mole}$$

$$C = \frac{q}{\Delta T} \quad \therefore q = C \times \Delta T = 640 \times 10 \text{ J} = 6.4 \text{ kJ}$$

$$\text{Heat released per mole} = \frac{6.4}{2 \times 10^{-3}} = 3.2 \times 10^3 \text{ kJ} = \mathbf{3.2 \text{ MJ}}$$

$$\Delta U = -3.2 \text{ MJ}$$

$$\Delta H = \Delta U + \Delta n_g RT \text{ here } \Delta n_g = 0$$

$$\Delta H = \Delta U = \mathbf{-3.2 \text{ MJ mole}^{-1}}$$