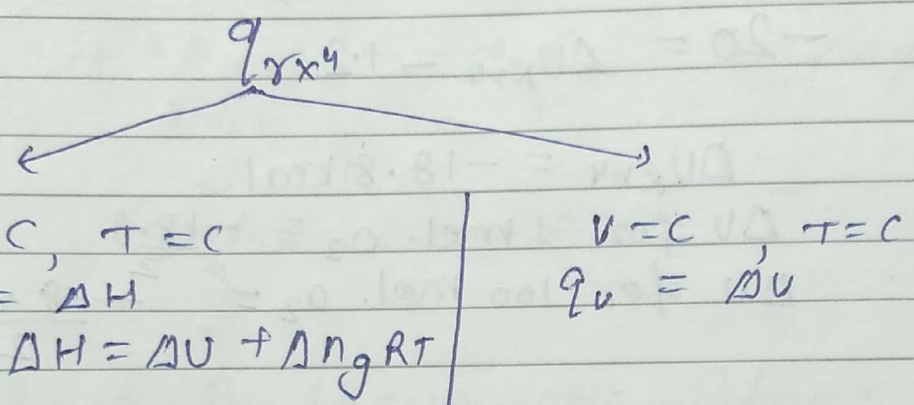


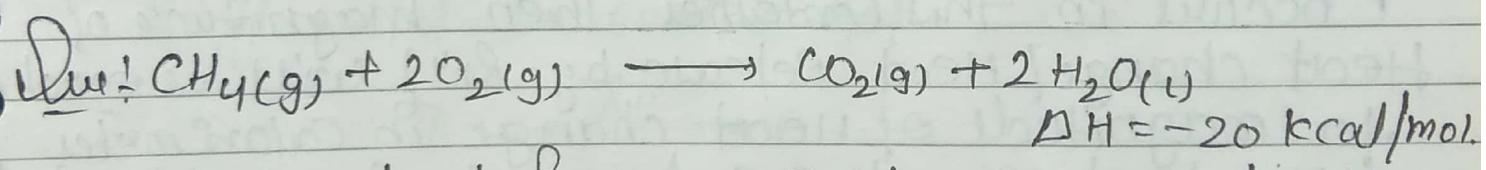
# SBG STUDY

19/07/17

## Thermochemistry



Ans:  $q_p = q_v + \Delta n_g RT$



At constant pressure 3.2 kg  $O_2$  react with excess amount of  $CH_4$  then calculate heat change in process

Ans:  $\Delta H = -20 \text{ kcal/mol}$

for 1 mol of  $O_2$   $\Delta H$  will be equal to  $= -10 \text{ kcal}$

$$\frac{3.2 \times 1000}{32} = 100 \text{ mol}$$

(ii) If above rxn occurs at 300k temp and at const volume then calculate rxn heat change rxn

if 3.2 kg  $O_2$  react with excess amount of  $CH_4$ .

$\Delta H = \Delta U + \Delta n_g RT$   
 $\Delta U = -\Delta H = \frac{3.2 \times -20}{100}$

$$\Delta H_{R_{xy}} = \Delta U_{R_{xy}} + \Delta n_g RT$$

$$-20 = \Delta U_{R_{xy}} - 2 \left( \frac{2}{1000} \right) (300)$$

$$-20 = \Delta U_{R_{xy}} - 1.2$$

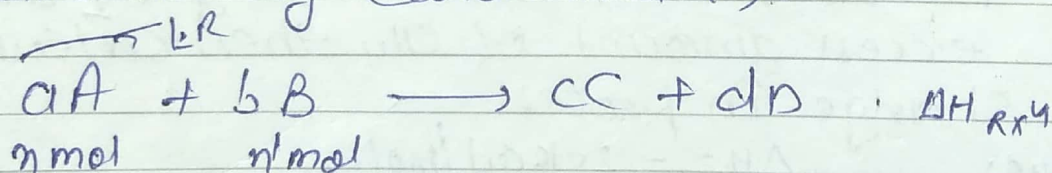
$$\Delta U_{R_{xy}} = -18.8 \text{ kcal}$$

$$\Delta U \text{ for 1 mol. } O_2 = -18.8$$

$$\Delta U \text{ for 100 mol. } O_2 = \frac{-18.8}{2} \times 100$$

### \* Concept of Calorimeter:

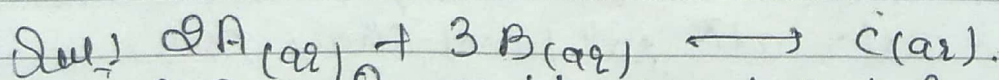
Calorimeter is adiabatic container. If  $R_{xy}$  occurs in this container then magnitude of Heat change (Heat Release by  $R_{xy}$ ) will be equal to magnitude of Heat change in calorimeter (Heat absorb by calorimeter).



$$q_{\text{process}} = -q_{\text{calorimeter}}$$

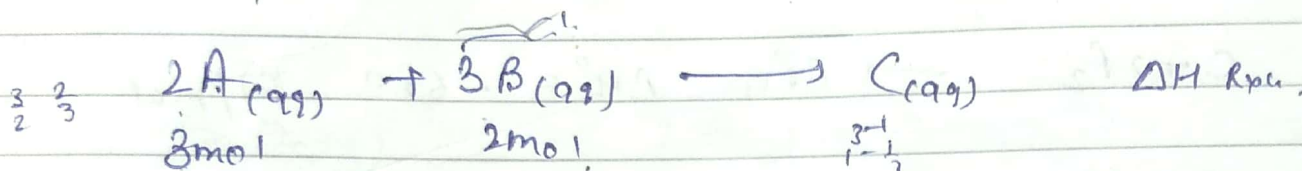
If  $R_{xy}$  occurs at constant pressure

$$\frac{\Delta H_{R_{xy}}}{\text{S.C of C.R}} \times \text{mol of L.R} = -C \Delta T$$



A sol<sup>n</sup> in which 3 mol A is present is mixed with a solution in which 2 mol of B is present in an adiabatic container at constant pressure

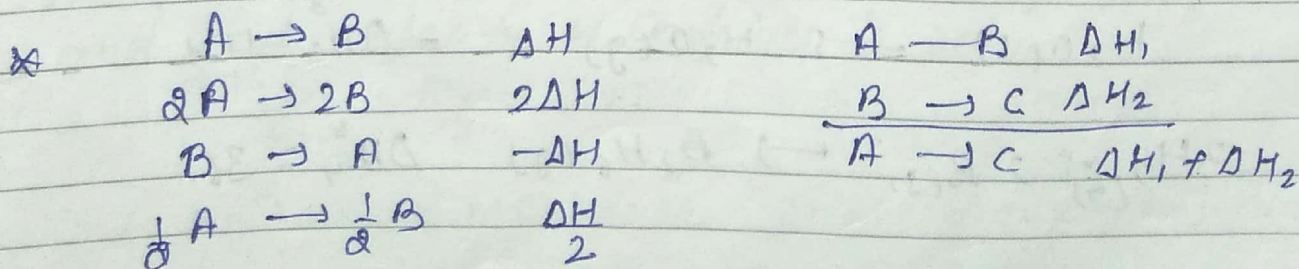
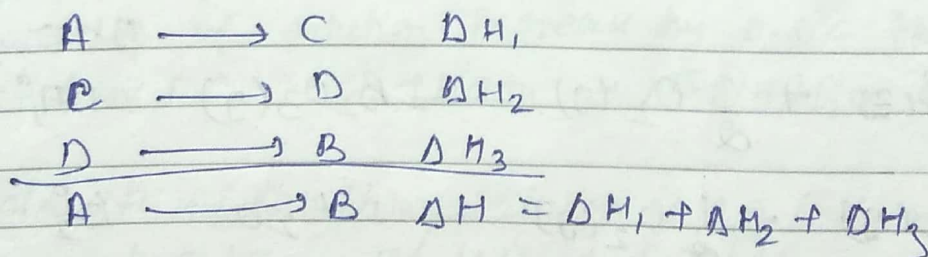
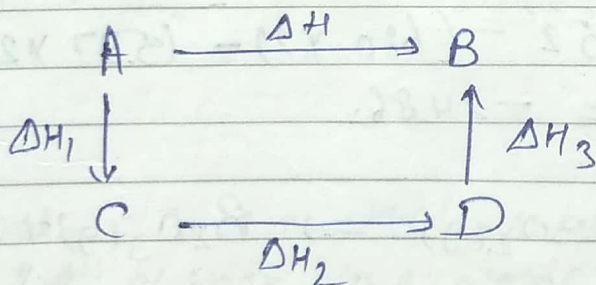
due to this temp. of Calorimeter Increase by  $1^{\circ}\text{C}$  if Heat Capacity of Calorimeter System is  $8\text{ cal/}^{\circ}\text{C}$  then calculate  $\Delta H_{\text{Rxn}}$ .

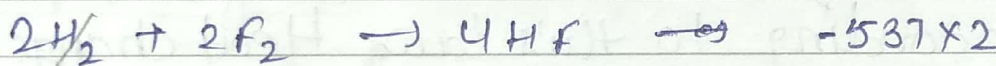
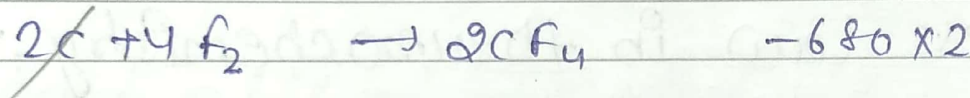
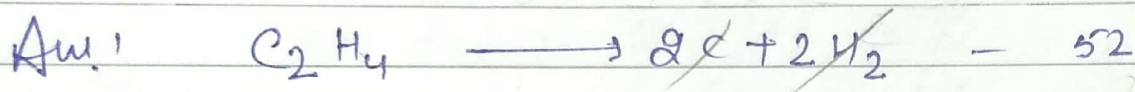
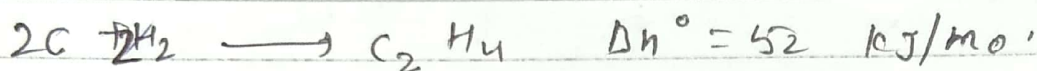
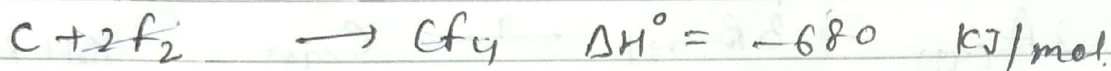
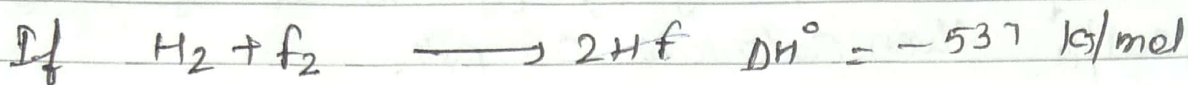
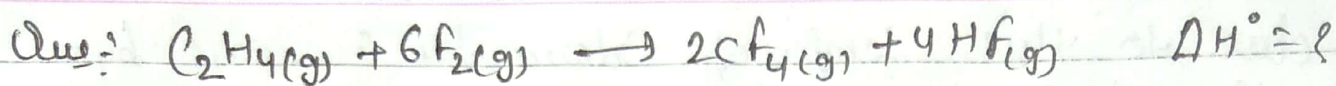


$$\frac{\Delta H_{\text{Rxn}} \times 2}{3} = -8 \times 1$$

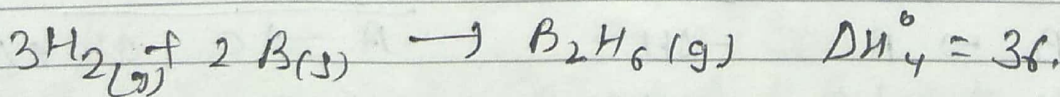
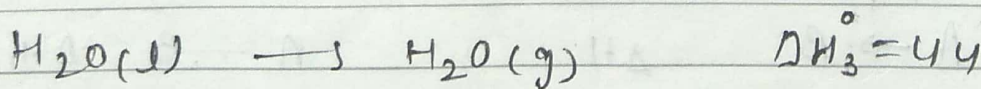
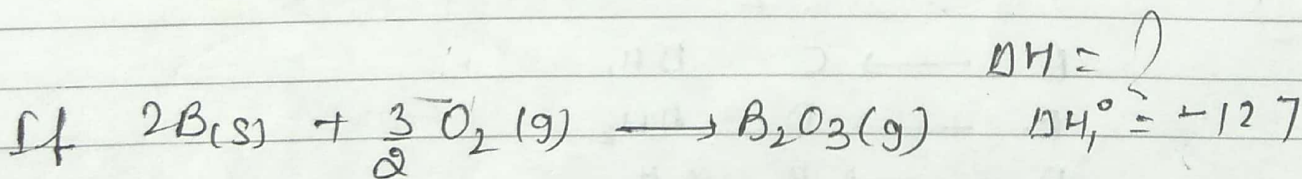
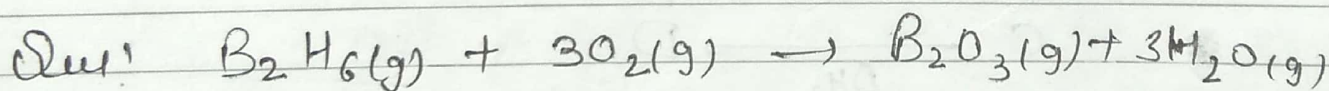
### \* Hess Law in thermochemistry:

According to this law Heat change in a Rxn will be equal whether a Rxn is caused out in single step or multiple step



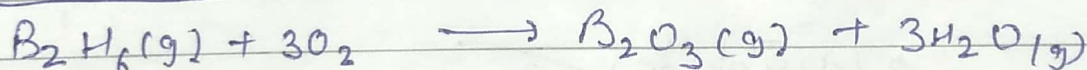
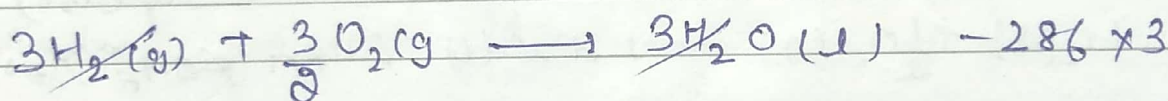
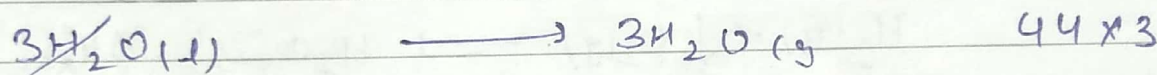
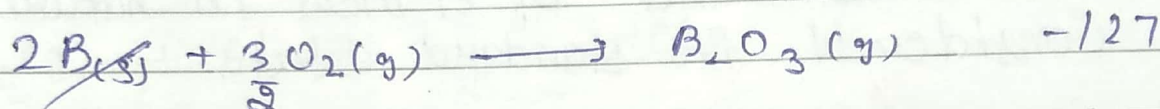
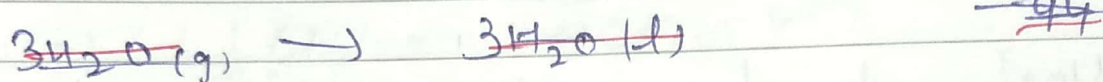
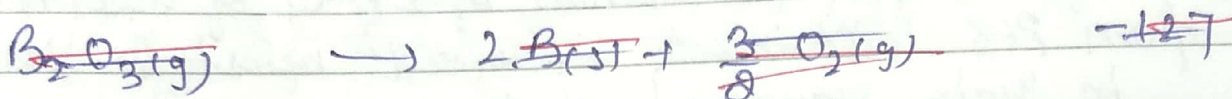
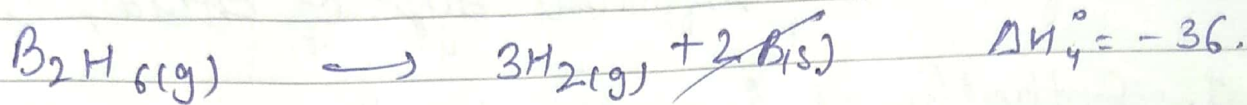


$\Delta H = -52 - (680 \times 2) - (537 \times 2)$   
 $= -2486$



Part - 2 H.W. :- 2-Main complet.  
 8-2 ⇒ 1, 2, 3, 4

Ans



$$\Delta H = -889.$$

Que: 500 ml 0.2 M HCl solution is mixed with 400 ml 0.1 M of sol<sup>n</sup> of NaOH in a calorimeter due to the reaction temp of solution increase by 0.6°C then calculate  $\Delta H$  for given rx<sup>n</sup>  $HCl + NaOH \rightarrow NaCl + H_2O$   $\Delta H_{rxn}$ .

Suppose density of resulting solution is 1 g/ml and specific heat capacity of sol<sup>n</sup> is 1 cal/gm/°C and heat capacity of container is zero.

$$\begin{array}{l} 500\text{ml} \quad 400\text{ml} \\ HCl + NaOH \rightarrow NaCl + H_2O \quad \Delta H_{rxn} \\ 100\text{ml} \quad 40\text{ml} \\ 60\text{ml} \quad 60\text{ml} \end{array}$$

$$= \frac{\Delta H}{1} \times 0.04 = -mcs\Delta T \Rightarrow \Delta H_{rxn} \times 0.04 = -(900)(1)(0.6)$$

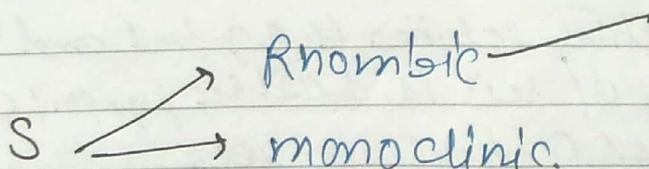
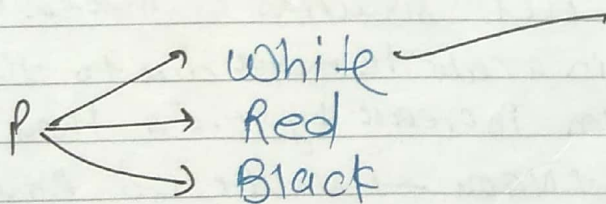
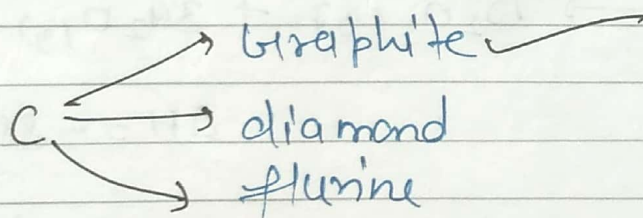
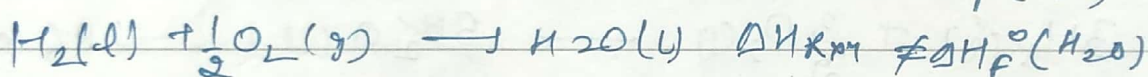
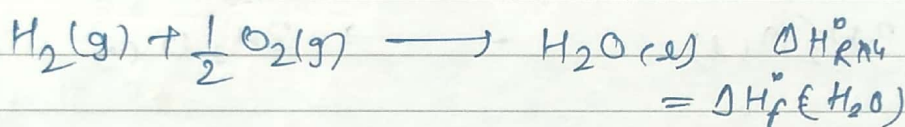
$$\Delta H_{rxn} = -13500 \text{ cal}$$

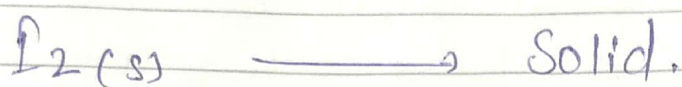
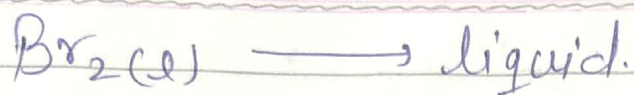
## \* Definition of Different type of Enthalpies

### 1. Enthalpy of formation ( $\Delta H_f^\circ$ ) :

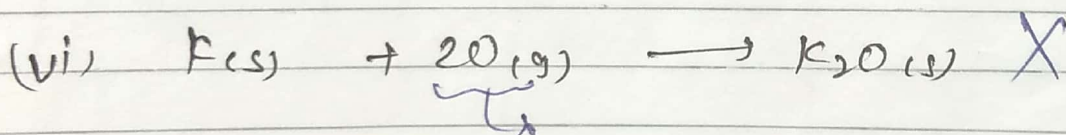
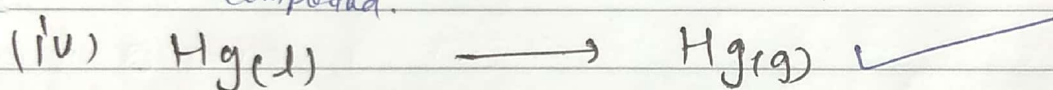
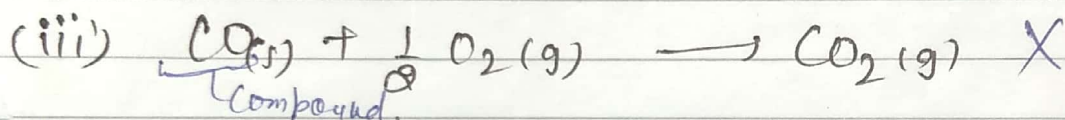
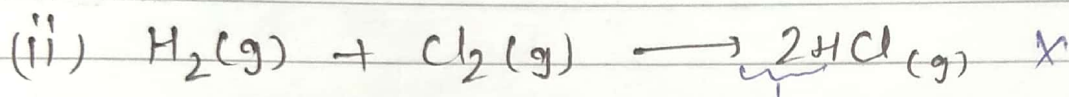
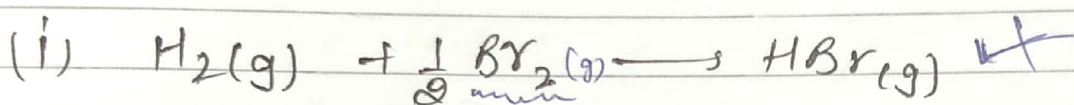
Define for formation of 1 mol of substance from its element. Elements must be present in their standard state

Most abundance of element in nature considered its standard state

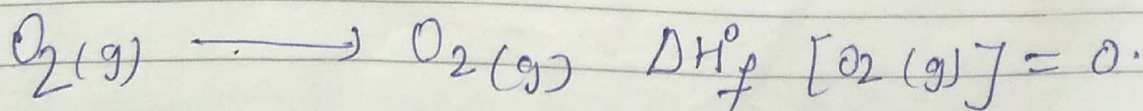
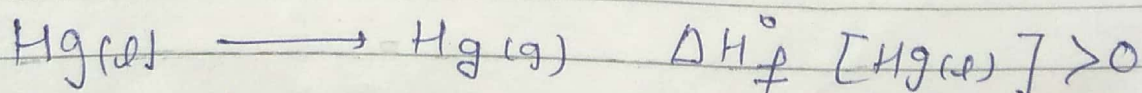
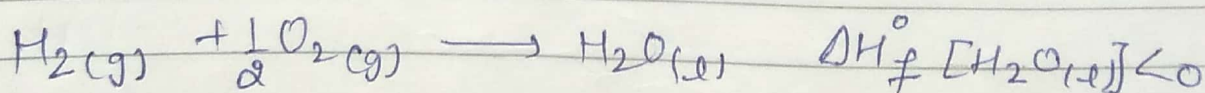




Que: Which of the following rxn & represent enthalpy of formation of product



~~Ans part~~  $\text{H}_2$   
(1) Value of formation enthalpy of formation can be negative, positive or zero.



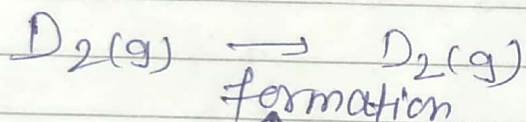
\*  $\Delta H^\circ_{\text{formation}}$ ,  $\Delta G^\circ_f$ ,  $\Delta S^\circ_f$  &  $\Delta U^\circ_f$  for elements in their standard state will be equal to zero.

$$\Delta H^\circ_f [\text{C (graphite)}] = 0$$

$$\Delta G^\circ_f [\text{Hg (l)}] \neq 0$$

$$\Delta G^\circ_f [\text{CO (g)}] \neq 0$$

$$\underline{\Delta H^\circ_f [\text{O}_2 (\text{g})]}$$



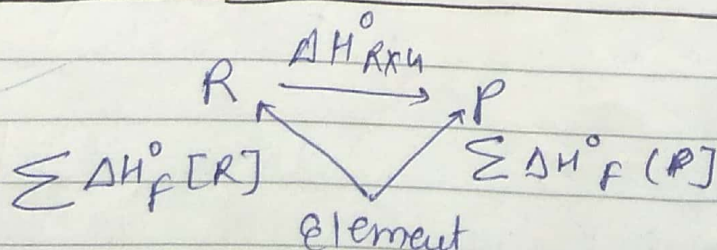
\* Enthalpy of all the ions in aqueous solution calculate with respect to  $\text{H}^+ (\text{aq})$  ion. So  $\Delta H^\circ_{\text{formation}}$  for  $\text{H}^+ (\text{aq})$  ion considered zero.

$$\Delta H^\circ_f [\text{H}^+ (\text{aq})] = 0$$

$$\Delta G^\circ_f [\text{H}^+ (\text{aq})] = 0$$



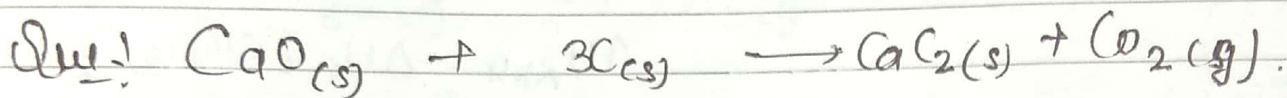
$$\Delta H^\circ_{\text{rxn}} = \sum \Delta H^\circ_f [\text{P}] - \sum \Delta H^\circ_f [\text{R}]$$





$$\Delta H^{\circ}_{\text{rxn}} + \sum \Delta H^{\circ}_f[\text{R}] = \sum \Delta H^{\circ}_f[\text{P}]$$

$$\Delta H^{\circ}_{\text{rxn}} = \sum \Delta H^{\circ}_f[\text{P}] - \sum \Delta H^{\circ}_f[\text{R}] =$$



$$\Delta H^{\circ}_f [\text{CaO}_{(s)}] = -152 \text{ kcal/mol}$$

$$\Delta H^{\circ}_f [\text{CaC}_2(s)] = -14 \text{ kcal/mol}$$

$$\Delta H^{\circ}_f [\text{CO}_2(g)] = -26 \text{ kcal/mol}$$

then calculate  $\Delta H^{\circ}_{\text{rxn}}$  also calculate heat change in rxn if 1.28 kg  $\text{CaC}_2(s)$  is produced by rxn at constant pressure.

$$= \cancel{+152} - 14 - \cancel{(-152)} - 14 + (-26) \times 2 =$$

$$\Delta H^{\circ}_f = ([\text{CaC}_2] + \Delta H^{\circ}_f[\text{CO}_2]) - (\Delta H^{\circ}_f[\text{CaO}] + 2\Delta H^{\circ}_f[\text{C}])$$

$$\Delta H^{\circ}_f = 152 - 40 = 112$$

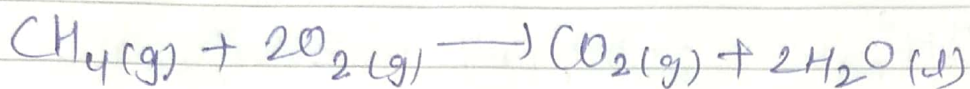
$$\text{mol of CaC}_2 = \frac{1280}{64} = 20$$

$$112 \times 20 = 2240$$

### \* Enthalpy of Combustion ( $\Delta H^{\circ}_c$ ):

Define for complete combustion of 1 mole substance in presence of excess amount of

Oxygen or air.



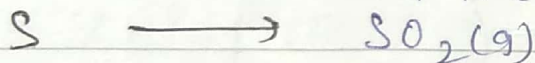
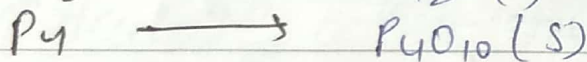
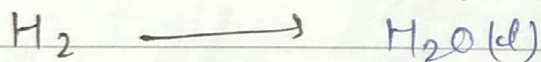
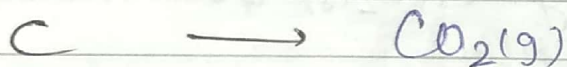
$$\Delta H_{\text{rxn}}^{\circ} = \Delta H_{\text{c}}^{\circ} [\text{CH}_4(\text{g})]$$



↑  
Incomplete Combustion

$$\Delta H_{\text{rxn}}^{\circ} \neq \Delta H_{\text{c}}^{\circ} [\text{CH}_4(\text{g})]$$

\* Substance                      Product after complete combustion



\* Combustion of  $\text{N}_2$  does not occur.

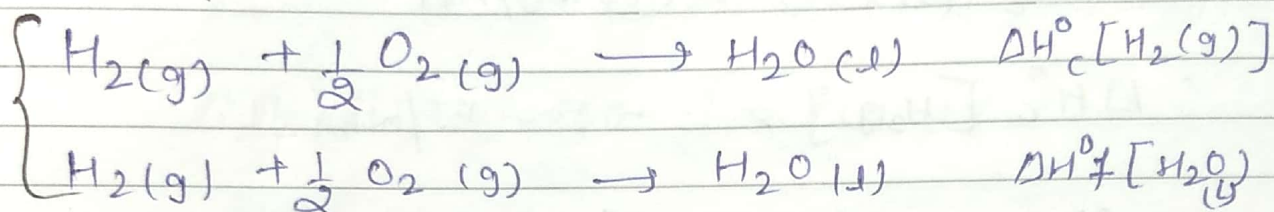
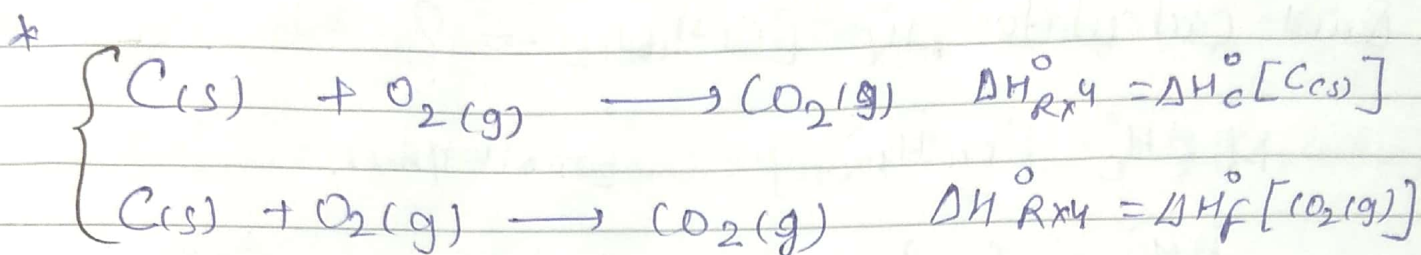
\* Important Point!

$$1. \left\{ \begin{array}{l} \Delta H_{\text{c}}^{\circ} [\text{CO}_2(\text{g})] = 0 \\ \Delta H_{\text{c}}^{\circ} [\text{H}_2\text{O}(\text{l})] = 0 \\ \Delta H_{\text{c}}^{\circ} [\text{O}_2(\text{g})] = 0 \end{array} \right.$$

v. imp

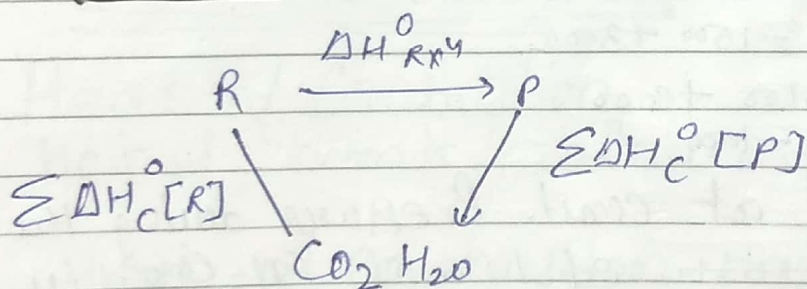
$$2 \rightarrow \left\{ \begin{array}{l} \Delta H_{\text{c}}^{\circ} [\text{C}(\text{s})] = \Delta H_{\text{f}}^{\circ} [\text{CO}_2(\text{g})] \\ \Delta H_{\text{c}}^{\circ} [\text{H}_2(\text{g})] = \Delta H_{\text{f}}^{\circ} [\text{H}_2\text{O}(\text{l})] \end{array} \right.$$

learn



\* Value of Enthalpy of combustion will be always Negative.

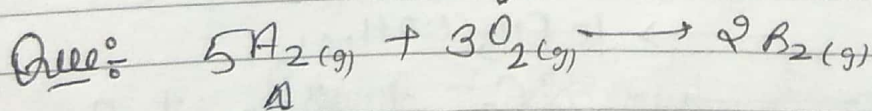
$$* \Delta H_{rxn}^\circ = \sum \Delta H_c^\circ [R] - \sum \Delta H_c^\circ [P]$$



$$\Delta H_{rxn}^\circ + \sum \Delta H_c^\circ [P] = \sum \Delta H_c^\circ [R]$$

$$\Delta H_{rxn}^\circ = \sum \Delta H_c^\circ [R] - \sum \Delta H_c^\circ [P]$$

↑  
oxidation



$$\Delta H_{rxn}^\circ = 5\Delta H_c^\circ [A_2(g)] - 2\Delta H_c^\circ [B_2(g)]$$

$$\Delta H_c^\circ [A_2(g)] = -100 \text{ kcal/mole}$$

$$\Delta H_c^\circ [B_2(g)] = -100 \text{ kcal/mole}$$

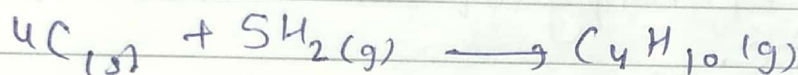
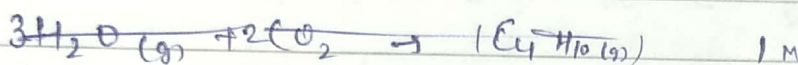
$$\Delta H_c^\circ = -200 - 3O_2(g) + 1700 = 0$$

Ques 1 Calculate  $\Delta H_f^\circ [C_4H_{10}(g)] = ?$

$$\Delta H_c^\circ [C_4H_{10}(g)] = -3000 \text{ kJ/mol}$$

$$\Delta H_c^\circ [C(s)] = -400 \text{ kJ/mol}$$

$$\Delta H_c^\circ [H_2(g)] = -300 \text{ kJ/mol}$$



$$4\Delta H_c^\circ [C(s)] + 5\Delta H_c^\circ [H_2(g)] - \Delta H_c^\circ [C_4H_{10}]$$

$$= 4 \times -400 + 5 \times (-300) - (-3000)$$

$$= -1600 - 1500 + 3000$$

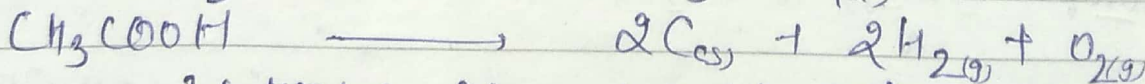
$$= -3100 + 3000$$

$$= -1000$$

Ques 2 Heat released at const. Pressure during the formation ~~CH<sub>3</sub>COOH~~ of 10 mol CH<sub>3</sub>COOH(l) is 5000 kJ. then calculate enthalpy of combustion CH<sub>3</sub>COOH(l) at 27°C.

$$\Delta H_c^\circ [C(s)] = \Delta H_f^\circ [CO_2(g)] = -400 \text{ kJ/mol}$$

$$\Delta H_c^\circ [H_2(g)] = \Delta H_f^\circ [H_2O(l)] = -300 \text{ kJ/mol}$$

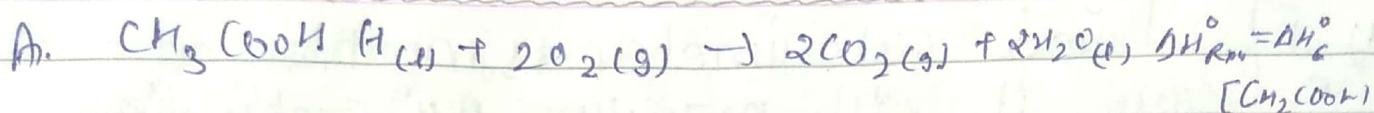


$$2(-400) + 2(-300) + 0 + 5000$$

$$= -800 - 600 + 5000$$

$$= -1400 + 5000$$

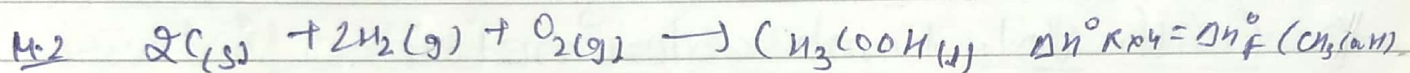
$$= 3600 \text{ kJ}$$



$$\Delta H_{\text{rxn}}^\circ = 2\Delta H_f^\circ[\text{CO}_2\text{(g)}] + 2\Delta H_f^\circ[\text{H}_2\text{O(l)}] - \Delta H_f^\circ[\text{CH}_3\text{COOH(l)}]$$

$$\Delta H_{\text{rxn}}^\circ = 2(-400) + 2(-300) - (-500)$$

$$\Delta H_{\text{rxn}}^\circ = -900$$



$$\Delta H_{\text{rxn}}^\circ = 2\Delta H_c^\circ[\text{C(s)}] + 2\Delta H_c^\circ[\text{H}_2\text{(g)}] - \Delta H_c^\circ[\text{CH}_3\text{COOH(l)}]$$

$$-500 = 2(-400) + 2(-300) - \Delta H_c^\circ[\text{CH}_3\text{COOH(l)}] = \Delta H_c^\circ[\text{CH}_3\text{COOH(l)}] = -900$$

### \* Bomb Calorimeter

- (1) Heat of Combustion is measured with the help of bomb calorimeter
- (2) Heat of Combustion define for complete Combustion of 1 mol of substance in presence of excess amount of oxygen or air

(3) At constant Pressure

$$q_{\text{comb}} = \Delta H_{\text{comb.}}^\circ \text{ and}$$

at constant Volume

$$q_{\text{comb}} = \Delta U_{\text{comb.}}^\circ$$

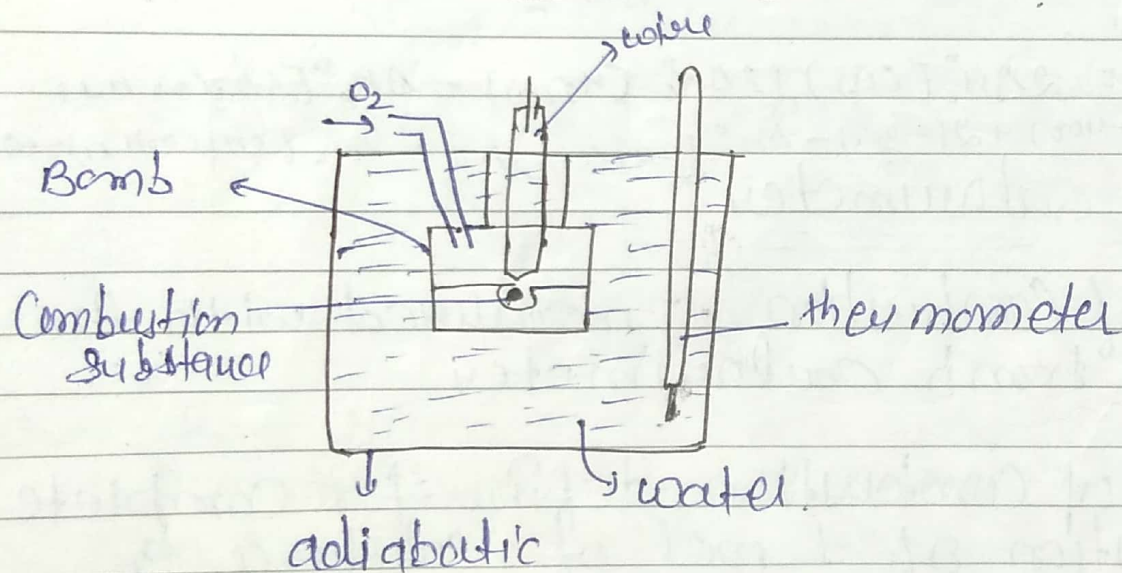
$$\Delta H = \Delta U + nRT \quad \Delta$$

(4) If bomb calorimeter is working at const. pressure it will measure  $\Delta H^\circ$  combustion

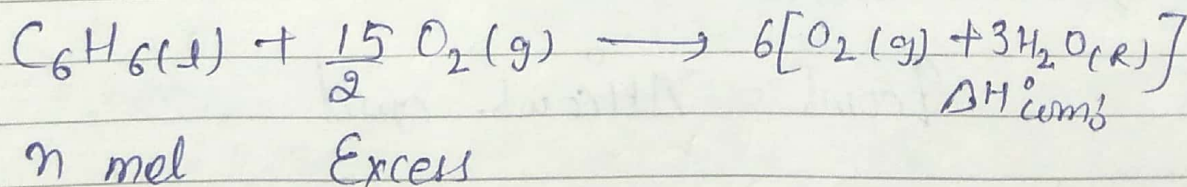
or if it is working ~~at~~ at const. volume it will measure  $\Delta U^\circ$  combustion.

(5) In general we use constant volume bomb calorimeter.

\* Const. Vol. bomb calorimeter!



\* Let combustion of  $n$  mol. benzene occur in calorimeter



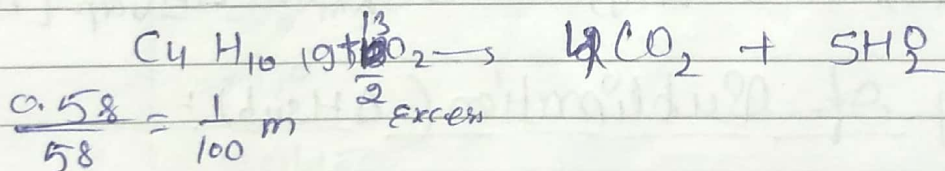
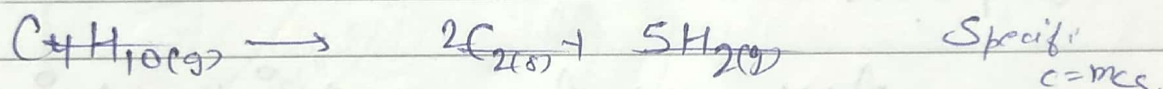
$$\Delta U^\circ_{comb} \cdot n = -C\Delta T$$

$C$  = Heat capacity of calorimeter system

Q. Combustion of 0.58g  $C_4H_{10}(g)$  occurs in a calorimeter system due to this Temp. of water in calorimeter system increase by  $0.75^\circ C$ . Heat Released during the rxn is absorb only by water present in calorimeter system. if specific heat capacity of water is  $4.18 J/gK$  and  $10kg$  water is used. Then answer of following Ques.

Heat of Comb. of butane at constant volume.  
Heat of combustion of butane at const pressure and  $27^\circ C$  temp.

(3) For complete process calculate  $q_{overall}$ ,  $w_{overall}$ .



$$\Delta U^{\circ}_{comb} \times \frac{1}{100} = - m c_s \Delta T$$

$$\Delta U^{\circ}_{comb} \times \frac{1}{100} = -10000 (4) (0.75)$$

$$\Delta U^{\circ}_{comb} = -3 \times 10^6 \text{ Joule/mol}$$

$$\Delta U^{\circ}_{comb} = -3 \times 10^3 \text{ KJ/mol}$$

$$\Rightarrow \Delta H^{\circ}_{comb} = \Delta U^{\circ}_{comb} + \Delta n_g RT$$

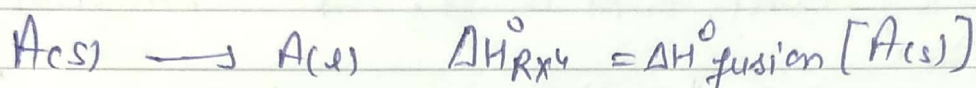
$$\Delta H^{\circ}_{comb} = -3000 - \frac{7}{2} \times \left( \frac{8.3}{1000} \right) (300)$$

$$q_{overall} = 0, w_{overall} = 0, \Delta U_{overall} = 0$$

## \* Defination of phase change enthalpies!

### (1) Enthalpy of fusion ( $\Delta H_{\text{fusion}}^{\circ}$ ):

Define for converting 1 mol solid substance into its liquid state



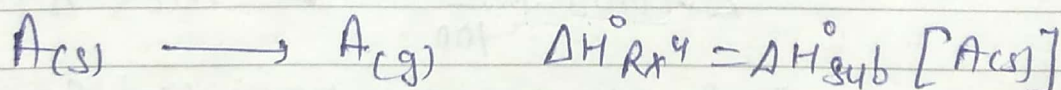
### (2) Enthalpy of vapourisation ( $\Delta H_{\text{vap}}^{\circ}$ ):

Define for converting 1 mol liquid into vapour.



### (3) Enthalpy of Sublimation ( $\Delta H_{\text{sub}}^{\circ}$ ):

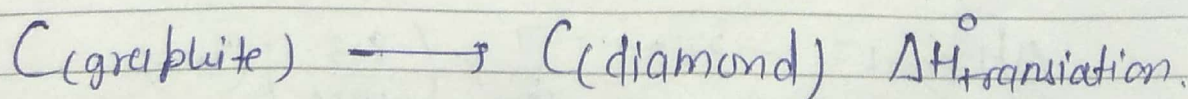
Define for converting 1 mole solid into gas



$$\Delta H_{\text{sub}}^{\circ} = \Delta H_{\text{fusion}}^{\circ} + \Delta H_{\text{vapourisation}}^{\circ}$$

### (4) Enthalpy of Transition:

Define for converting 1 Allotrope form of an element into another Allotrope form

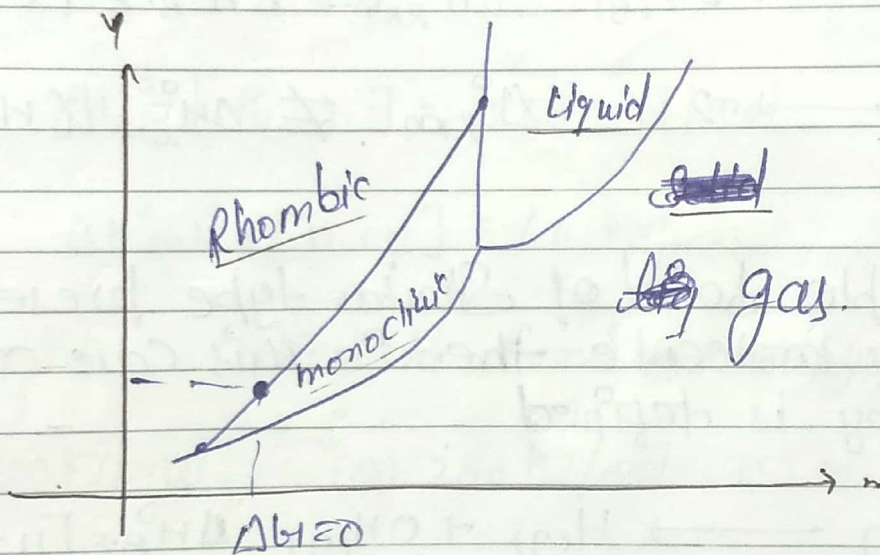




\* (1) Only an element can have different type of Allotrope. Allotrope of a compound not possible

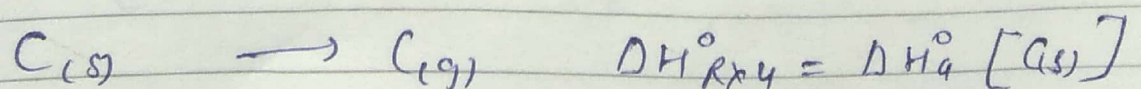
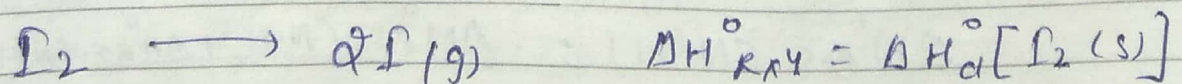
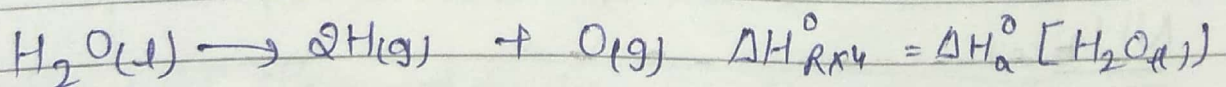
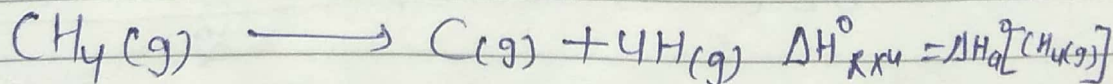
(2) different Allotrope are considered in diff. phase

\* Phase diagram of Sulphur:



\* Enthalpy of Atomisation ( $\Delta H_a^\circ$ )

Define for converting 1 mol substance into its gaseous isolated atoms completely



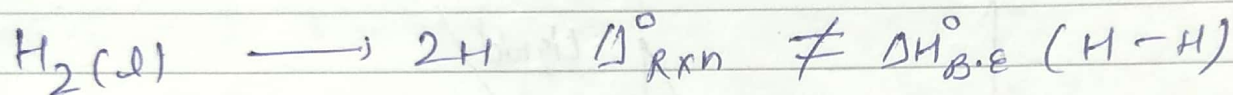
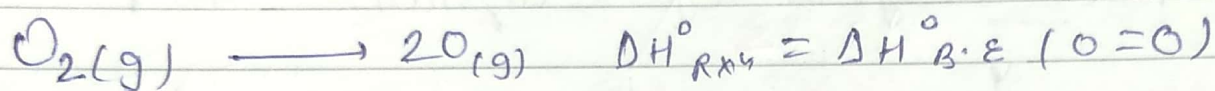
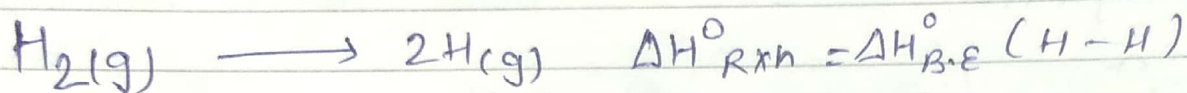
NOT Imp.

V. Dimp.

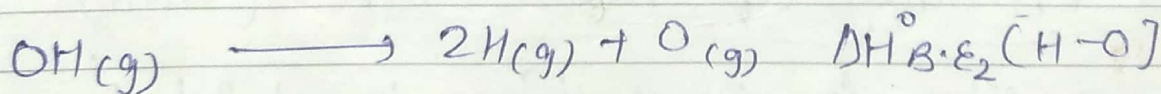
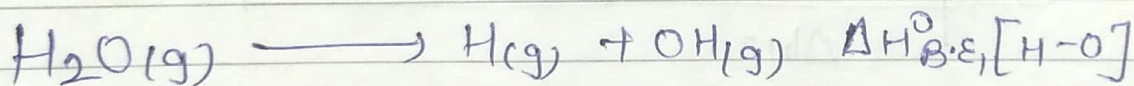
Chemical eq.  
Solid  
chemical

## \* Bond Enthalpy $^{\circ}$

Define for dissociation of 1 mol covalent bond into gaseous isolated atoms. Covalent bond must exist b/w gaseous atom during defining bond enthalpy.



\* If multiple bond of similar type present with in the molecule then in this case average bond enthalpy is defined

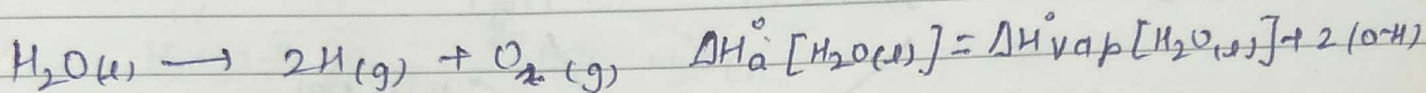
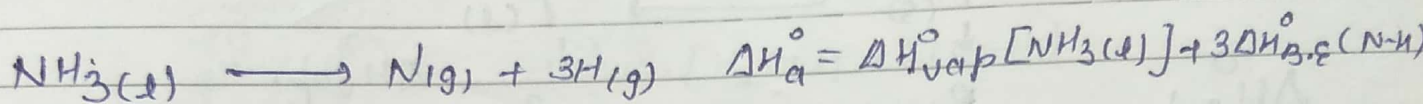
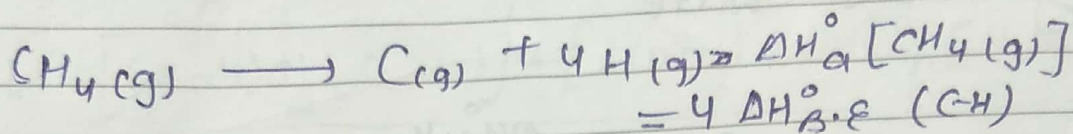


$$\Delta H^{\circ}_{\text{B.E}}(\text{O}-\text{H}) = \frac{\Delta H^{\circ}_{\text{B.E}_1}(\text{H}-\text{O}) + \Delta H^{\circ}_{\text{B.E}_2}(\text{H}-\text{O})}{2}$$

$\text{NH}_3(\text{g})$

$$\Delta H^{\circ}_{\text{B.E}}(\text{N}-\text{H}) = \frac{\Delta H^{\circ}_{\text{B.E}_1}(\text{N}-\text{H}) + \Delta H^{\circ}_{\text{B.E}_2}(\text{N}-\text{H}) + \Delta H^{\circ}_{\text{B.E}_3}(\text{N}-\text{H})}{3}$$

\* Relation b/w  $\Delta H_{\text{Atomisation}}$  and  $\Delta H_{\text{Bond enthalpy}}$



Ques!

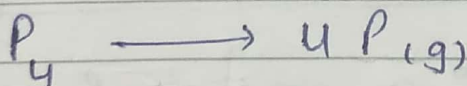
$$\Delta H_a^\circ[\text{P}_4(\text{s})] = 1260 \text{ kJ/mol}$$

$$\Delta H_{\text{sub}}^\circ[\text{P}_4(\text{s})] = 60 \text{ kJ/mol}$$

then calculate Bond enthalpy of (P-P)

- (A) 300 kJ/mol      (B) 200 kJ/mol      (C) 1200 kJ/mol      (D) None

Ans.



$$\Delta H_a^\circ[\text{P}_4(\text{s})] = \Delta H_{\text{sub}}^\circ[\text{P}_4(\text{s})] + 6(\text{P-P})$$

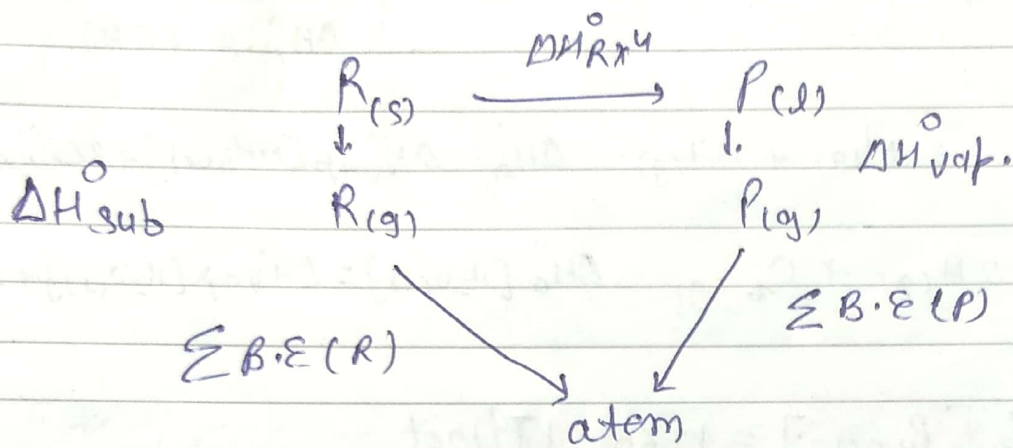
$$1260 = 60 + 6(\text{P-P})$$

\* For a Rxn  $\text{R}(\text{g}) \longrightarrow \text{P}(\text{g})$

$$\Delta H_{\text{Rxn}}^\circ = \sum \text{B.E}(\text{R}) - \sum \text{B.E}(\text{P})$$

This product formula is valid for gasses on reactant and product for in gaseous state

\* If Reactant and Product are not in gaseous state



$$\Delta H_{RXY}^{\circ} = \left( \Sigma \Delta H_{sub/vap}^{\circ}(R) + \Sigma B \cdot E(R) - \right. \\
 \left. - B \cdot E(P) + \Sigma \Delta H_{sub/vap}^{\circ}[P] \right)$$

Que: Calculate  $\Delta H_f^{\circ}(H_2O(l)) = ?$

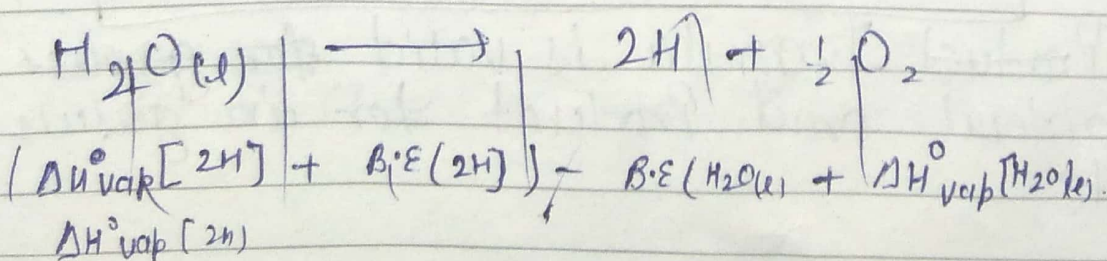
If

$$H-H \Rightarrow 100 \text{ kcal/mol}$$

$$O-H \Rightarrow 110 \text{ kcal/mol}$$

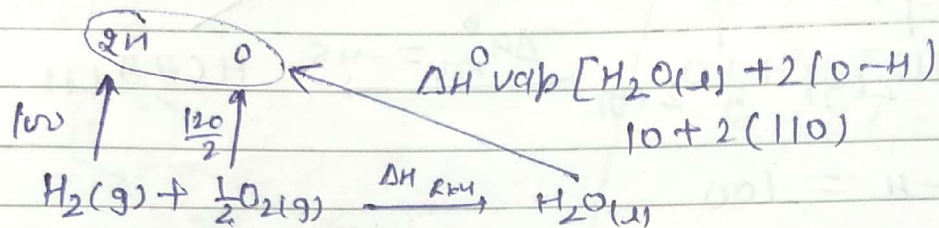
$$O=O \Rightarrow 120 \text{ kcal/mol}$$

$$\Delta H_{vap}^{\circ}[H_2O(l)] = 10 \text{ kcal/mol}$$



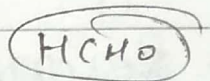


$$\Delta H_{rxn}^\circ = [2H + \frac{1}{2}(O=O)] - [2(O-H) + \Delta H_{var}^\circ[H_2O(l)]]$$



Ques: Calculate value of C-H bond

Sol



$$\Delta H_f^\circ [HCHO(l)] = -145 \text{ kcal/mol}$$

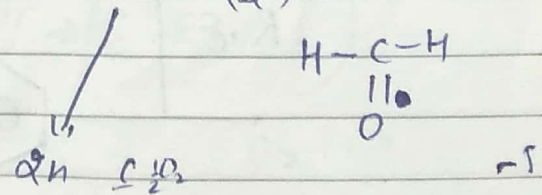
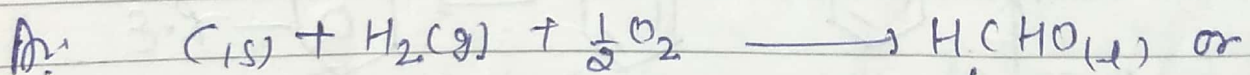
$$H-H \Rightarrow 100 \text{ kcal/mol}$$

$$C=O \Rightarrow 170 \text{ kcal/mol}$$

$$\Delta H_f^\circ [O(g)] = 60 \text{ kcal/mol}$$

$$\Delta H_f^\circ [C(g)] = 170 \text{ kcal/mol}$$

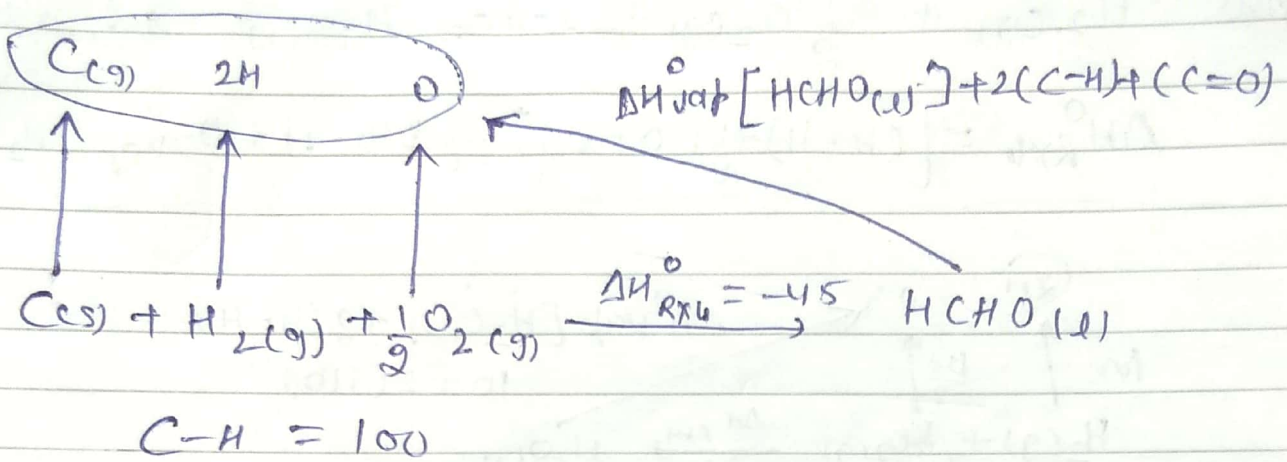
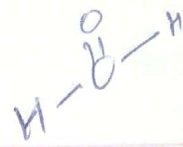
$$\Delta H_{var}^\circ [HCHO(l)] = 5 \text{ kcal/mol}$$



$$\Delta H_{rxn}^\circ = -45 = [\Delta H_{sub}^\circ [C(s)] + (H-H) + \frac{1}{2}(O=O)] - [2(C-H) + (C=O)]$$

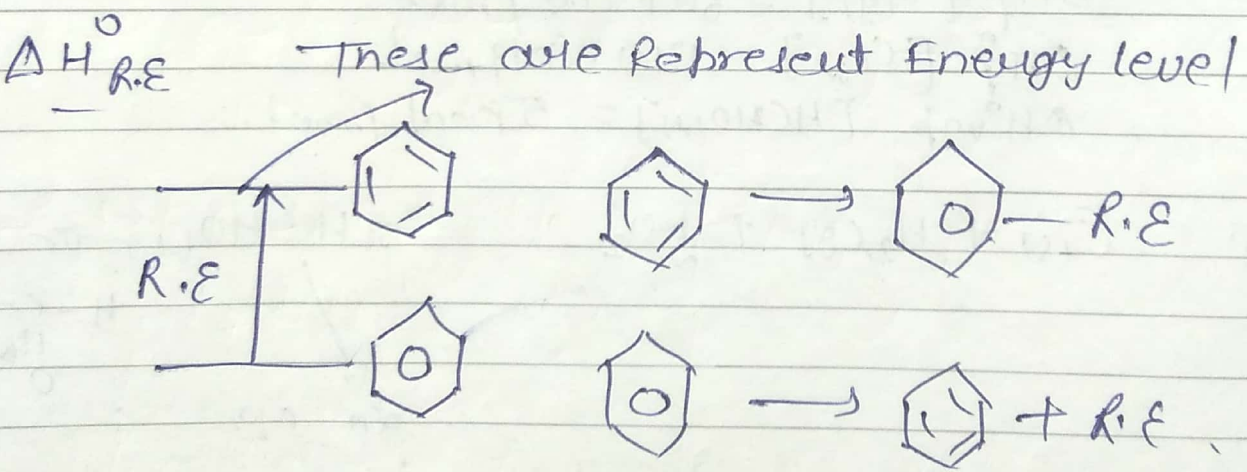
$$+ \Delta H_{var}^\circ [HCHO(l)]$$

$$-45 = [170 + 100 + \frac{1}{2}(120)] - [2(C-H) + 170 + 5]$$

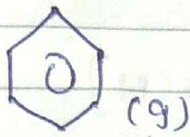
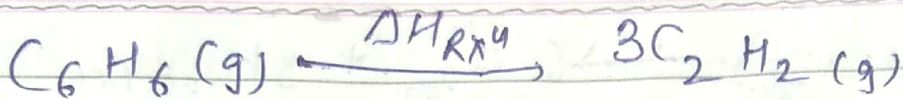


\* Resonance Enthalpy:

This is the energy difference b/w 1 mol hybrid structure to 1 mol most stable resonating structure



\* In Reality, hybrid structure exist in sample of its compound



|R.E.(C<sub>6</sub>H<sub>6</sub>)|



$$\begin{aligned} \Sigma B.E.(R) \\ = 3(C=C) + 3(C-C) \\ + 6(C-H) \end{aligned}$$

C, H

$$\begin{aligned} \Sigma B.E.(P) \\ = 3(C \equiv C) \\ + 6(C-H) \end{aligned}$$

R.E. is <sup>1</sup>/<sub>2</sub> always added on <sup>1</sup>/<sub>2</sub> of

$$\Delta H_{\text{Rxn}}^\circ = (|R.E.(C_6H_6(g)) + \Sigma B.E.(C)|) - (\Sigma B.E.(P))$$

$$\Delta H_{\text{Rxn}}^\circ = (|\Sigma R.E.(R) + \Sigma \Delta H_{\text{sub/vap}}(R) + \Sigma B.E.(R)|) - (\Sigma B.E.(P) + \Sigma \Delta H_{\text{sub/vap}}(P) + |\Sigma O.E.(P)|)$$

Ques: Calculate  $\Delta H_c^\circ(\text{C}_6\text{H}_6(l)) = ?$

Pf

C-C = 80

C=C ⇒ 150

C-H ⇒ 100

H-H ⇒ 100

O-H = 110

C=O ⇒ 170

O=O = 120

$\Delta H_{\text{R.E}}^\circ(\text{C}_6\text{H}_6(l)) = -40$

$\Delta H_{\text{R.E}}^\circ(\text{CO}_2(g)) = -30$

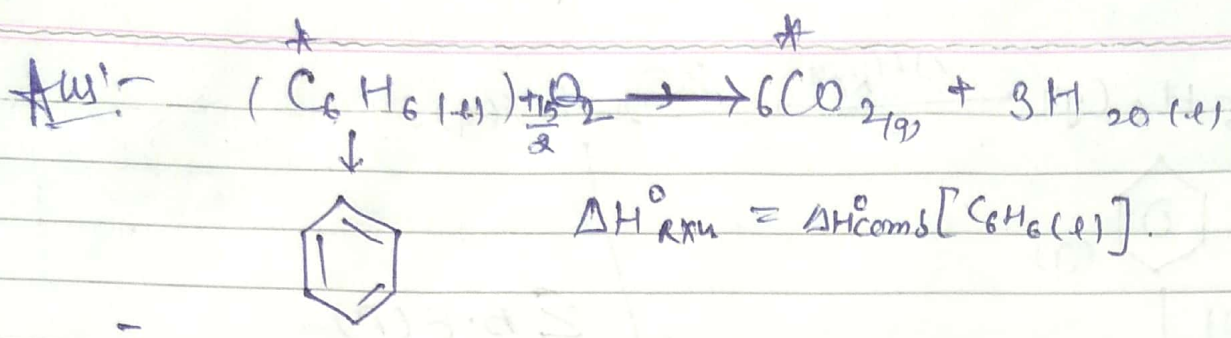
$\Delta H_{\text{vap}}^\circ[\text{C}_6\text{H}_6(l)] = +8$

$\Delta H_{\text{vap}}^\circ[\text{H}_2\text{O}(l)] = +10$

CO<sub>2</sub> + H<sub>2</sub>O

both resonance

all data are in kcal/mol



$\Delta H^\circ_{\text{rxn}} =$

$$\begin{aligned}
 &\Delta H^\circ_{\text{vap}}[\text{C}_6\text{H}_6\text{(l)}] + \Delta H^\circ_{\text{R.E}}[\text{C}_6\text{H}_6\text{(l)}] \\
 &+ 3(\text{C-C}) + 6(\text{C-H}) + \frac{15}{2}(\text{O=O}) - \left( 6(\text{C=O}) + 3(\text{H-O}) \right) \\
 &\hspace{15em} \begin{array}{l} \text{3(120)} \\ \text{6(+120)} \\ \hline \text{480} \end{array}
 \end{aligned}$$

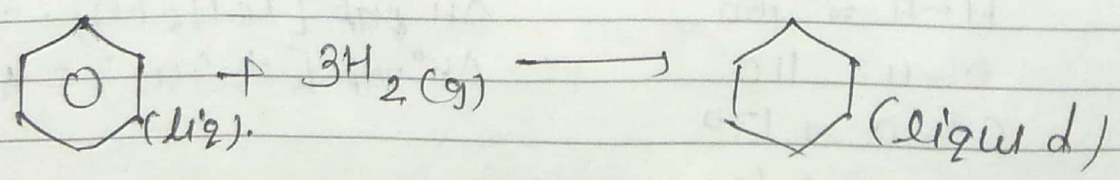
R.E (6CO<sub>2</sub>(g))

$$\Delta H^\circ_{\text{rxn}} = \left( \begin{array}{l} \text{R.E (C}_6\text{H}_6\text{(l))} \\ \text{+40} \end{array} \right) + \left( \begin{array}{l} \Delta H^\circ_{\text{vap}}(\text{C}_6\text{H}_6\text{(l)}) \\ \text{8} \end{array} \right) + \left( \begin{array}{l} 3(\text{C=C}) \\ \text{3(150)} \end{array} \right)$$

$$\left( \begin{array}{l} + 3(\text{C-C}) + 6(\text{C-H}) + \frac{15}{2}(\text{O=O}) \\ \text{3(80)} \quad \text{6(100)} \quad \frac{15}{2}(120) \end{array} \right) - \left( \begin{array}{l} 6(\text{R.E(CO}_2\text{(g))}) \\ \text{6} \times \text{30} \end{array} \right)$$

$$\left( \begin{array}{l} + 12(\text{C=O}) + 6(\text{H-O}) + 3\Delta H^\circ_{\text{vap}}[\text{H}_2\text{O(l)}] \\ \text{12} \times \text{(170)} \quad \text{6(110)} \quad \text{3(10)} \end{array} \right)$$

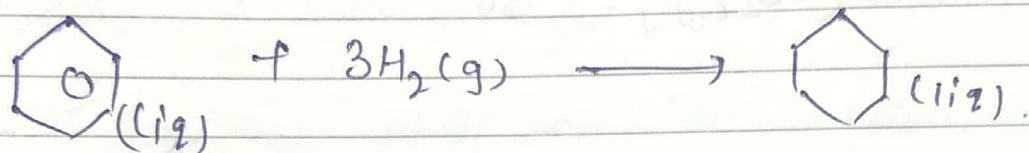
Ques! If enthalpy of formation of cyclohexane and Benzene is -150 kJ/mol and 50 kJ/mol respectively then calculate enthalpy of hydrogenation Benzene, if its is as





(ii) also calculate R.E. of Benzene if enthalpy of hydrogenation of cyclohexene is  $-120 \text{ kJ/mol}$

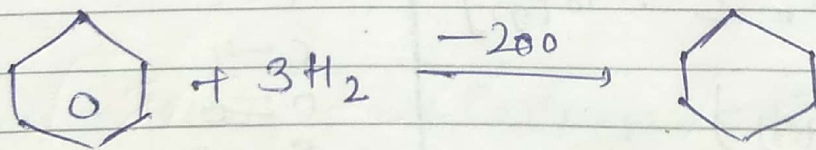
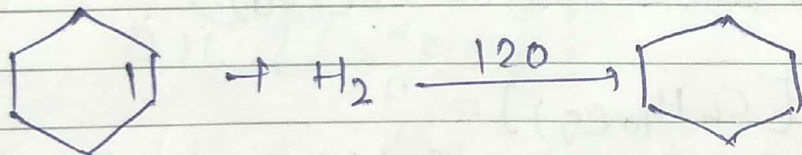
$$\Delta H_f^\circ = P - R.$$



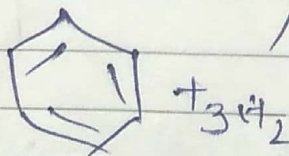
$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ [\text{Cyclohexane}] - \Delta H_f^\circ [\text{Cyclohexene}]$$

$$= -150 - 50 = -200 \text{ kJ}.$$

(ii)



R.E. (C<sub>6</sub>H<sub>6</sub>(H))



$$\uparrow -120 \times 3$$

6 B.E. R.F.

Ques. Calculate  $\Delta H_f^\circ [CO_2(g)] = ?$

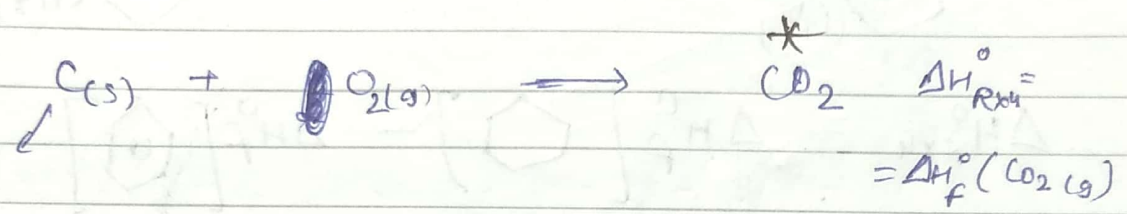
H

$$\Delta H_{sub}^\circ [C(s)] = 170$$

$$C=O \Rightarrow 170$$

$$O=O \Rightarrow 120$$

$$R.E. (CO_2(g)) = -30$$



$$\Delta H_{Rxn}^\circ = (\Delta H_{sub}^\circ [C(s)] + (O=O)) - (1 R.E. (CO_2(g)) + 2(C=O))$$

$$= (170 - 120) - (30 + 2(170))$$

Ques.  $\Delta H_c^\circ [C_4H_{10}(g)] = ?$

Part ①

$$\Delta H_f^\circ [C_4H_{10}(g)]$$

$$\Delta H_f^\circ (CO_2(g))$$

$$\Delta H_f^\circ (H_2O(l))$$

Part ②

C-C

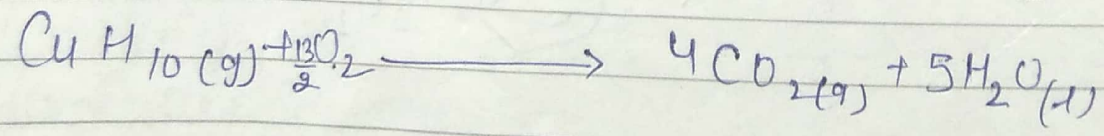
C-H

O=O

$$\Delta H_{sub}^\circ [C(s)]$$

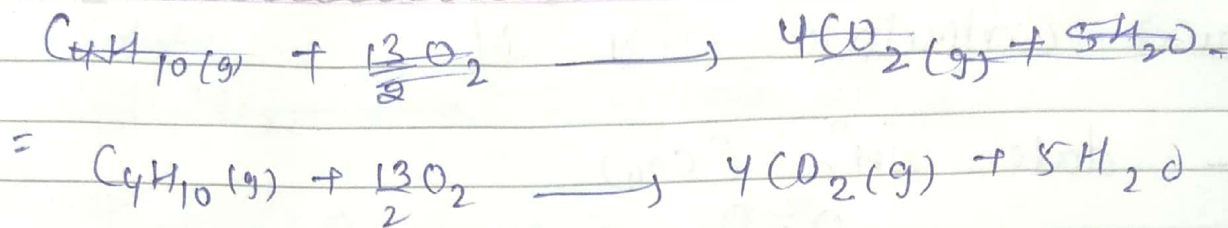
$$\Delta H_{vap}^\circ [H_2O(l)]$$

$$\Delta H_{R.E.}^\circ (CO_2(g))$$



$$\Delta H_{Rxn}^\circ = \Delta H_c^\circ [C_4H_{10}(g)]$$

$$4 \Delta H_f^\circ [CO_2(g)] + 5 \Delta H_f^\circ [H_2O(l)] - (\Delta H_f^\circ [C_4H_{10}(g)])$$



$$\Delta H_{\text{rxn}}^{\circ} = [3(\text{C}-\text{C}) + 10(\text{C}-\text{H}) + \frac{13}{2}(\text{O}=\text{O})] - [4/\text{R.E.}(\text{CO}_2(\text{g}))] + 8(\text{C}=\text{O}) + 5\Delta H_{\text{vap}}^{\circ}(\text{H}_2\text{O}(\text{l})) + 10(\text{O}-\text{H})$$

Ques:  $\Delta H_f^{\circ} [\text{C}_3\text{H}_8(\text{g})] = ?$

Part ①  $\Delta H_c^{\circ} [\text{C}(\text{s})]$

$\Delta H_c^{\circ} [\text{H}_2(\text{g})]$

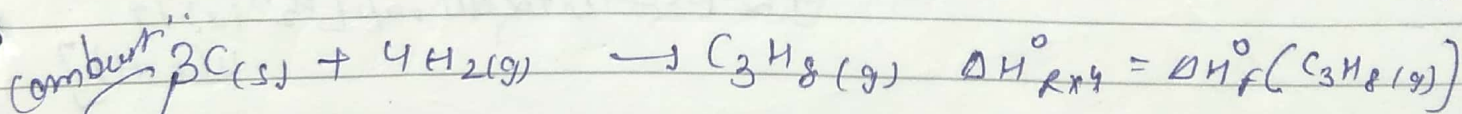
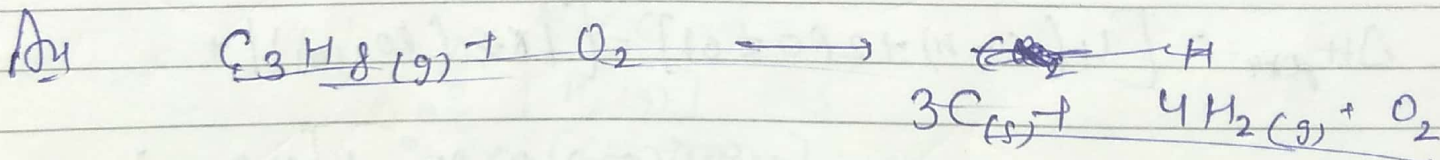
$\Delta H_c^{\circ} [\text{C}_3\text{H}_8(\text{g})]$

Part ②  $\Delta H_{\text{sub}}^{\circ} [\text{C}(\text{s})]$

C-C

H-H

C-H



$$\Delta H_{\text{rxn}}^{\circ} = [3\Delta H_c^{\circ}(\text{C}(\text{s})) + 4\Delta H_c^{\circ}(\text{H}_2)] - \Delta H_c^{\circ}(\text{C}_3\text{H}_8(\text{g}))$$

enthalpy  $\Delta H_{\text{rxn}}^{\circ} = 3\Delta H_c^{\circ}(\text{C}(\text{s})) + 4\Delta H_c^{\circ}(\text{H}_2) - (\Delta H_c^{\circ}[\text{C}_3\text{H}_8(\text{g})])$

$$\Delta H_{\text{rxn}}^{\circ} = [3\Delta H_{\text{sub}}^{\circ}(\text{C}(\text{s})) + 4(\text{H}-\text{H})] - [2(\text{C}-\text{C}) + 8(\text{C}-\text{H})]$$

Rx<sup>n</sup> write: enthalpy formula 781 (1/1/17) &

Ques: Calculate C-H if

data  $\Delta H_c^\circ$  (C<sub>4</sub>H<sub>4</sub>)

O=O

O-H

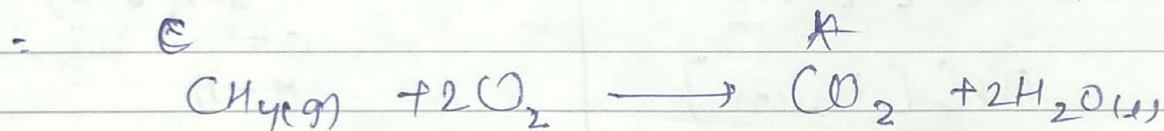
C=O

R.E (CO<sub>2</sub>)

$\Delta H_{\text{vap}}^\circ$  [H<sub>2</sub>O(l)]

A

$$\Delta H_{\text{rxn}}^\circ = [3 \Delta H_{\text{sub}}^\circ (\text{C}_{(s)}) + 4(\text{H}-\text{H})] - [2(\text{C}=\text{O}) + 8(\text{O}-\text{H})]$$



$\Delta H_c^\circ$  (C<sub>4</sub>H<sub>4</sub>(g))

$$\Delta H_{\text{rxn}} = [4(\text{C}-\text{H}) + 2(\text{O}=\text{O})] - [|\text{R.E}(\text{CO}_2(\text{g}))| +$$

$$+ 2(\text{C}=\text{O}) + 2\Delta H_{\text{vap}}^\circ [\text{H}_2\text{O}(\text{l})] + 4(\text{O}-\text{H})]$$

Ques!

if  $\text{C}-\text{O} = ?$   
 $\Delta H_f^\circ (\text{CH}_3\text{OH}(\text{l})) = -45$

$$\Delta H_f^\circ (\text{O}(\text{g})) = 60$$

$$\Delta H_f^\circ (\text{C}(\text{g})) = 170$$

$$\text{H}-\text{H} = 100$$

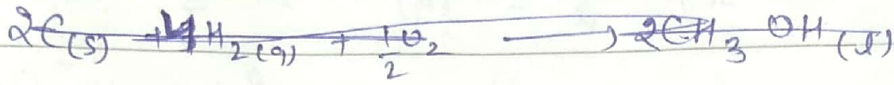
$$\text{C}-\text{H} = 80$$

$$\text{O}-\text{H} = 110$$

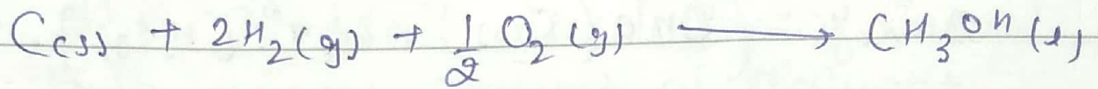
$$\Delta H_{\text{vap}}^\circ [\text{CH}_3\text{OH}(\text{l})] = 10$$

$$\Delta H_f^\circ [\text{CH}_3\text{OH}] = -45$$

Req ~~is~~  $\frac{1}{2}$  atoms formula  $\rightarrow$  1st condition is:



~~(1)~~



$$-45 = \left[ \Delta H_{\text{sub}}(\text{C}(s)) + 2(\text{H-H}) + \frac{1}{2}(\text{O=O}) \right] - \left[ \Delta H_{\text{vap}}[\text{CH}_3\text{OH}(l)] + \right.$$

$$\left. + 3(\text{C-H}) + (\text{C-O}) + (\text{O-H}) \right]$$

$$-45 = \left[ 170 + 2(106) + \frac{1}{2}(120) \right] - \left[ 10 + 3(80) + (\text{C-O}) + (\text{O-H}) + (110) \right]$$

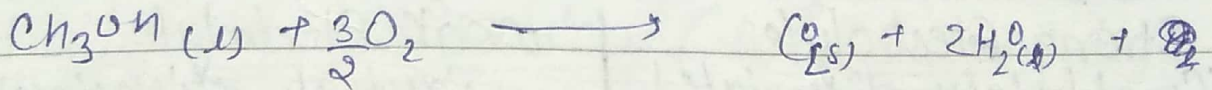
Que:  $\Delta H_f^\circ(\text{CH}_3\text{OH}(l)) = ?$

$\Delta H_f^\circ(\text{C}(s)) = a$

$\Delta H_f^\circ(\text{H}_2(g)) = b$

$\Delta H_f^\circ(\text{CH}_3\text{OH}(l)) = c$

=



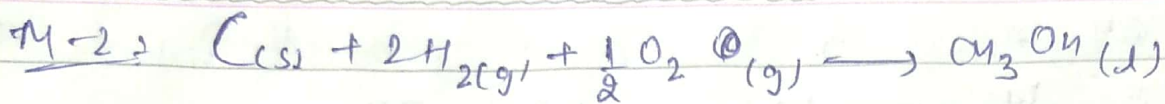
=  $\Delta H_{\text{rxn}}^\circ$  No-benefit

$$\Delta H_{\text{rxn}}^\circ = \Delta H_f^\circ[\text{CO}_2(g)] + 2\Delta H_f^\circ(\text{H}_2\text{O}(l))$$

$$- (\Delta H_f^\circ(\text{CH}_3\text{OH}(l)))$$

$$c = (a + 2b) - \Delta H_f^\circ(\text{CH}_3\text{OH}(l))$$

जिसका  $\Delta H$  असका  $R_{rxn}$  लिखनी है



$$\Delta H_{rxn}^\circ = \Delta H_f^\circ [CH_3OH(l)]$$

Combustion

$$\Delta H_{rxn}^\circ = (\Delta H_c^\circ(C(s)) + 2\Delta H_c^\circ(H_2(g)) - \Delta H_c^\circ(CH_3OH(l)))$$

$$\Delta H_{rxn}^\circ = a + 2b - c$$

\* ON the Basis of providing ions substance can be of two type.

Substance

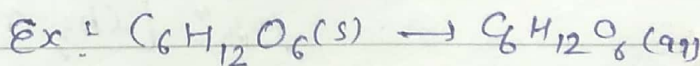
(i)

Electrolyte

(ii) Non-electrolyte

Provide ion in their solution

(Do not provide ion in their solution)



Strong Electrolyte  
(Completely dissociate)  
into ions

Weak Electrolyte  
(Partially dissociate)  
into ions

Strong acid:  $HCl, HI, HBr, HNO_3, H_2SO_4, HClO_4$

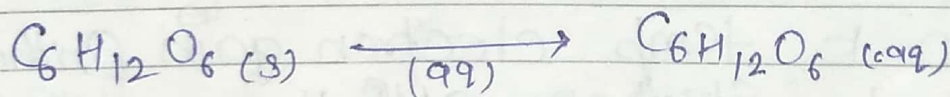
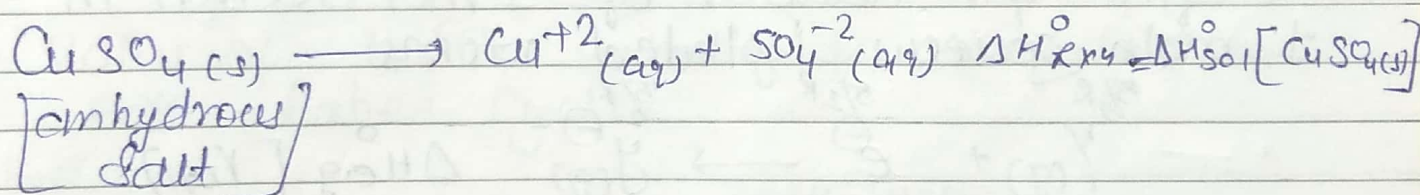
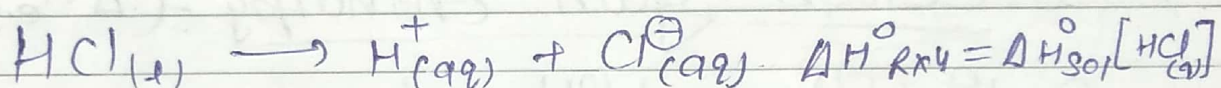
Strong base:  $NaOH, KOH, CsOH, Ca(OH)_2, Ba(OH)_2, Sr(OH)_2$

\* Salt: By default all salts are considered strong electrolytes.

★

\* Enthalpy of Solution:  $(\Delta H^{\circ}_{sol})^{\circ}$

Define for complete dissolution of 1 mol solute into excess amount of solvent generally water is used as a solvent in most of the solutions. So, water is also called universal solvent

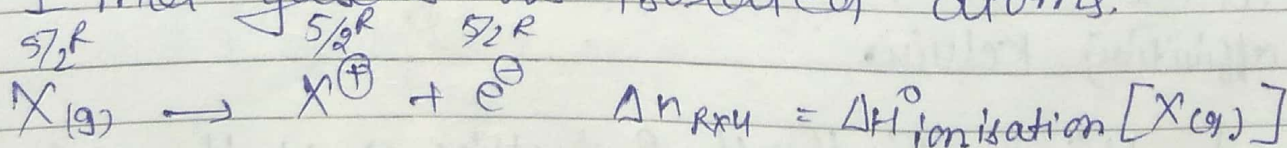


$$\Delta H^{\circ}_{rxn} = \Delta H^{\circ}_{sol}[\text{C}_6\text{H}_{12}\text{O}_6(s)]$$

[because this is not a electrolytes]

★ Enthalpy of Ionisation  $(\Delta H^{\circ}_{ionisation})^{\circ}$

Define for elimination of 1 mol.  $e^{-}$  from 1 mol gaseous ~~but~~ isolated atoms.



μ If ionisation enthalpy measured at 0°K temp. it is also called Ionisation Energy.

$$\epsilon g \epsilon \Rightarrow 0^\circ k$$

\* Value of Ionisation Energy can be calculated with the help of Kirchhoff equation

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta r C_p (T_2 - T_1)$$

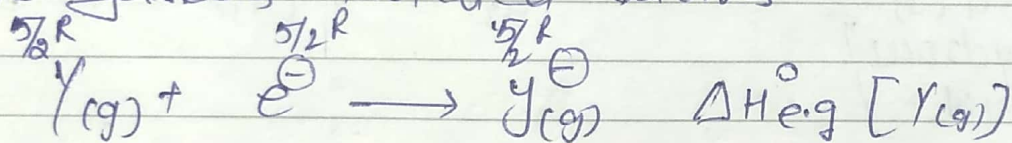
$\uparrow$                        $\uparrow$   
 0 kelvin              T kelvin      =  $\frac{5}{2} R (0 - T)$

$$f = 3N = 3$$

$$C_{vm} = \frac{f}{2} R$$

\* Electron gain Enthalpy  $(\Delta H_{e.g}^\circ)$ :

Define for addition of 1 mol electron in 1 mole gaseous isolated atoms



\* At zero K temp electron gain enthalpy is called electron affinity.

\* Value of  $e^-$  affinity can be calculated with the help of Kirchhoff equation.

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta r C_p (T_2 - T_1)$$

$\uparrow$                        $\uparrow$   
 at 0K              at T

( $e^-$  affinity) kelvins

\* Lattice Enthalpy: Lattice enthalpy of formation is defined for formation of one mole lattice from its gaseous ions

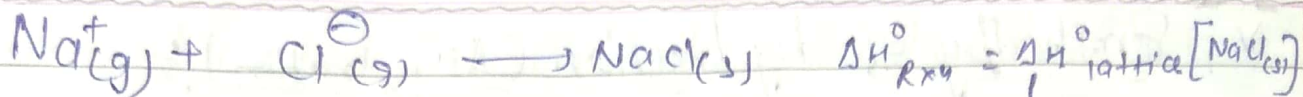


+ dis

Thermochemistry: 0-1 ⇒ 1 to 10

② 8-1 ⇒ 1 to 8.

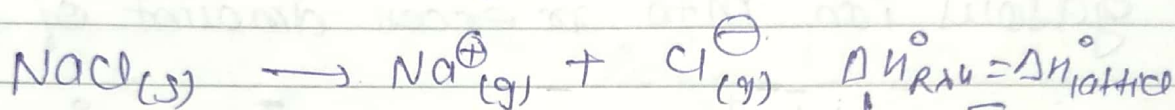
Race: 8



(-ve)

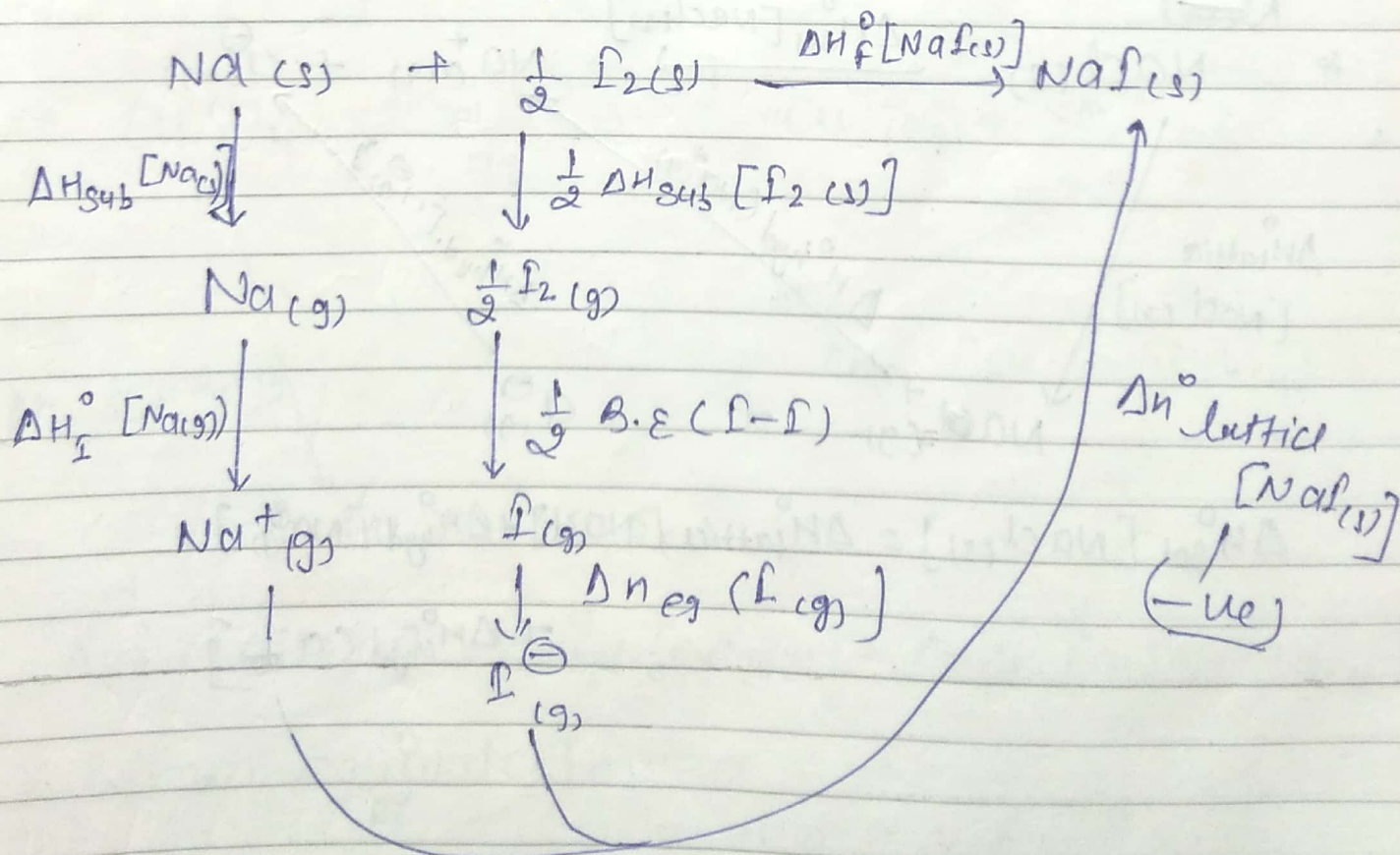
OK

Lattice Enthalpy of dissociation is defined for complete dissociation of 1 mol ionic lattice into its gaseous ions



[NaCl(s)]  
(+ve)

\* Value of lattice enthalpy is calculated by Born-Haber cycle



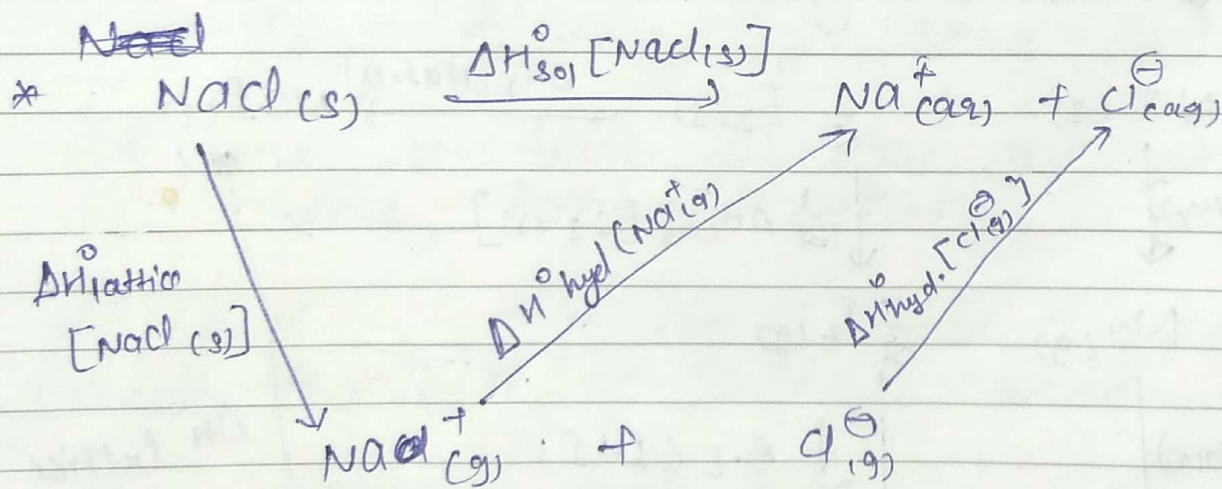
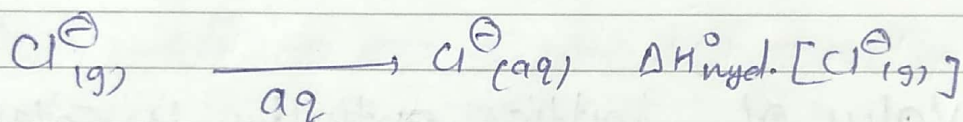
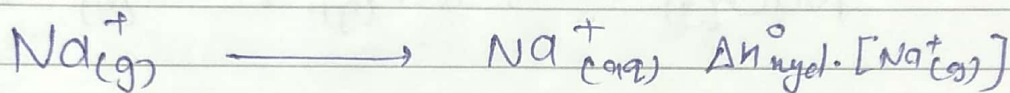
Break = +ve

## \* Enthalpy of hydration ( $\Delta H^\circ_{\text{hydration}}$ ):

(i)  $\Rightarrow$  Enthalpy of hydration define for gaseous ions and salts separately.

(i) Enthalpy of hydration for gaseous ion:

Define for complete dissolution of 1 mol gaseous ion into an excess amount of water



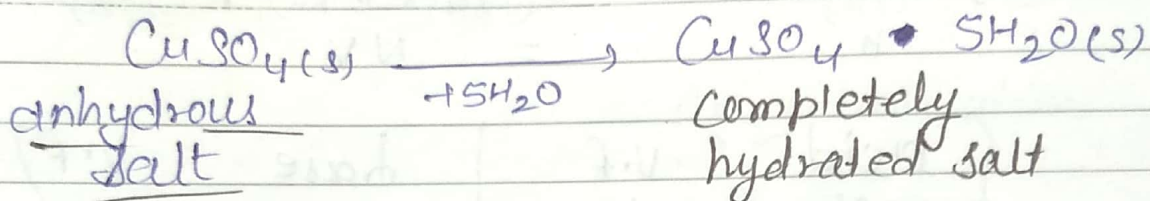
$$\Delta H^\circ_{\text{sol}}[\text{NaCl}_{(s)}] = \Delta H^\circ_{\text{ionisation}}[\text{NaCl}] + \Delta H^\circ_{\text{hyd}}[\text{Na}^+_{(aq)}] + \Delta H^\circ_{\text{hyd}}[\text{Cl}^-_{(aq)}]$$

Salt  $\rightarrow$  Strong electrolyte

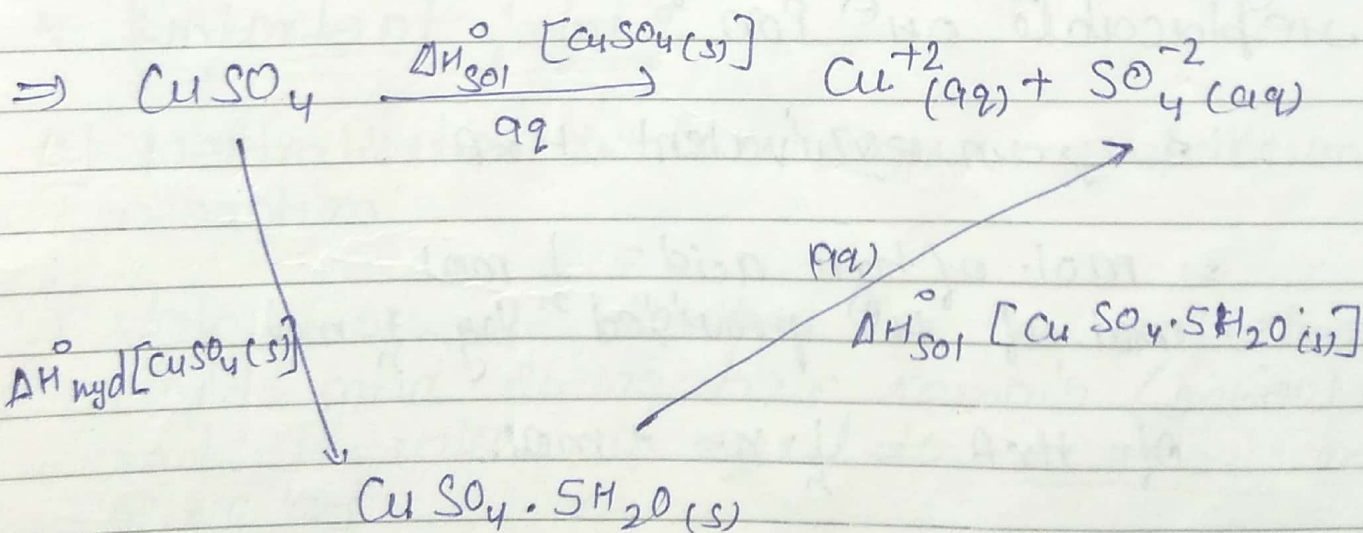
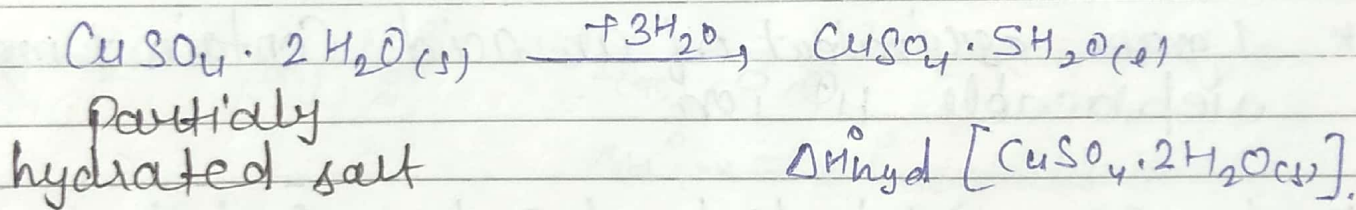
$\cdot nH_2O$  hydrated salt

### \* Enthalpy of hydration for salts.

Define  $\rightarrow$  Complete hydration of 1 mol of anhydrous or partially hydrated salt



$$\Delta H_{\text{hyd}}^\circ - [\text{CuSO}_4(s)]$$



$$\Delta H_{\text{sol}}^\circ [\text{CuSO}_4(s)] = \Delta H_{\text{hyd}}^\circ [\text{CuSO}_4(s)] + \Delta H_{\text{sol}}^\circ [\text{CuSO}_4 \cdot 5H_2O(s)]$$

\* Gram equivalent

or 
$$= \text{mol} \cdot \text{v.f}$$

\* gram equivalent :  $= \text{mol} \times \text{v.f}$

or  
Equivalents

"

$$= m \times \text{v.f}$$

Equivalents

"

$$= (m \times \text{v.f}) / n$$

$$= \frac{m}{N}$$

acid	v.f	base	v.f
HCl	1	NaOH	1
H <sub>2</sub> SO <sub>4</sub>	2	Ba(OH) <sub>2</sub>	2

} Example

\* 1 gram equivalent of an acid contain 1 mol replaceable H<sup>+</sup> ion

\* 1 gram equivalent of a base contain 1 mol replaceable OH<sup>-</sup> ion.

1 gram equivalent H<sub>x</sub>A

$$\Rightarrow \text{mol. of H}_x\text{A acid} = \frac{1}{n} \text{ mol}$$

$$\Rightarrow \text{mol of H}^+ \text{ provided }^n \text{ by } \frac{1}{n} \text{ mol}$$

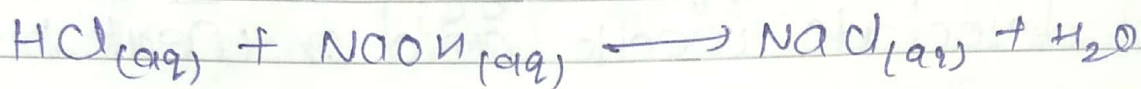
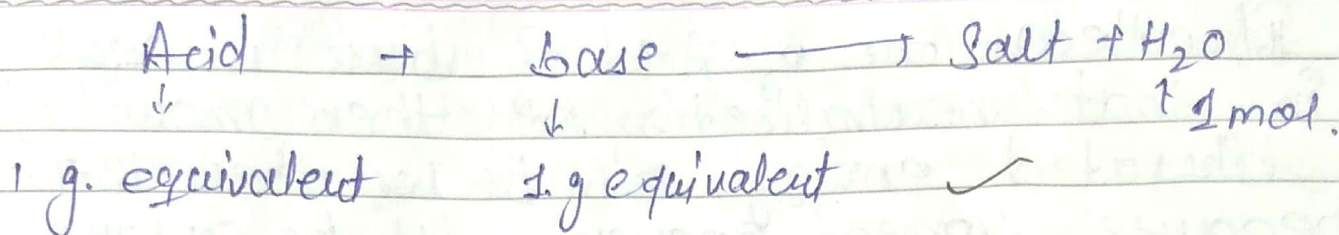
$$\text{of H}_x\text{A} = \frac{1}{n} \times n = 1 \text{ mol.}$$

\* Enthalpy of neutralisation : ( $\Delta H^{\circ}_{\text{neutralisation}}$ )

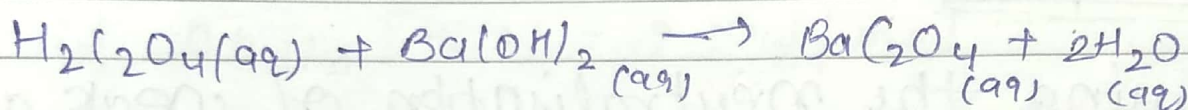
Define for complete neutralisation of 1 gram equivalent of an acid with one gram equivalent of a base in aqueous medium.

See 1 mol water

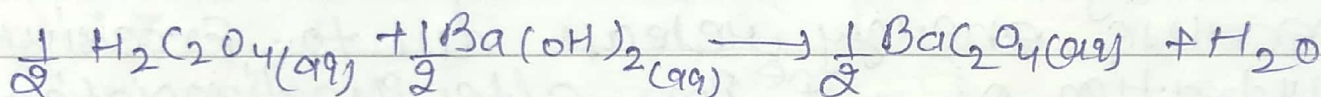
x 4.18



=  $\Delta H_{\text{neutralisation}}$



~~$\Delta H_{\text{rxn}} \neq \Delta H_{\text{neutralisation}}$~~

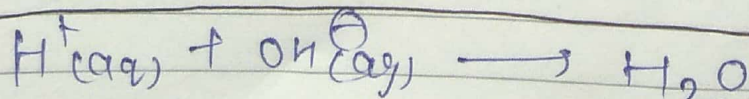
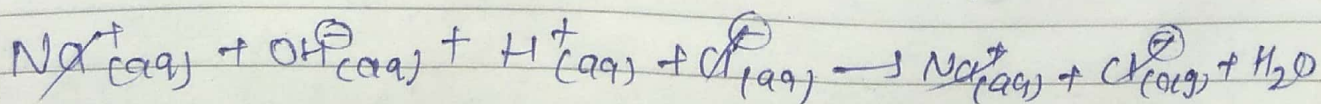
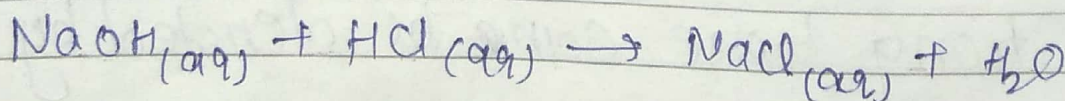


$\Delta H_{\text{rxn}} = \Delta H_{\text{neutralisation}}$

\* Important point:

1] Neutralisation rxn is always an exothermic reaction

2] Value of  $\Delta H_{\text{neutr}}$  for the rxn strong acid and strong base remain constant and it will be equal to -13.7 kcal or -57.6 kJ



$\Delta H = -13.7 \text{ kcal} / -57.6 \text{ kJ}$

\* If atleast one of Acid or base is weak in that neutralisation Rxn then amount of liberated energy will be less than 13.7 kcal because some of energy will be consumed to dissociate weak acid or weak base

### \* Exception!

During the neutralisation of weak acid HF (Hydrochloric acid) amount of liberated energy will be more than 13.7 kcal because energy release due to excessive hydration of  $F^-$  ion after its dissociation will be more as compared to energy given in dissociation.

### \* Enthalpy of dissociation of weak acid or weak base?

Define for complete dissociation of one mole weak acid or weak base completely into its ions.

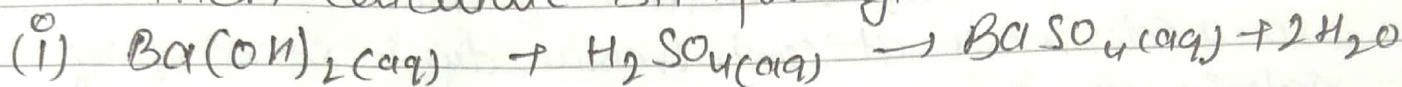
Strong acid can be denoted by  $H^+$

or Strong base can be denoted by  $OH^-$

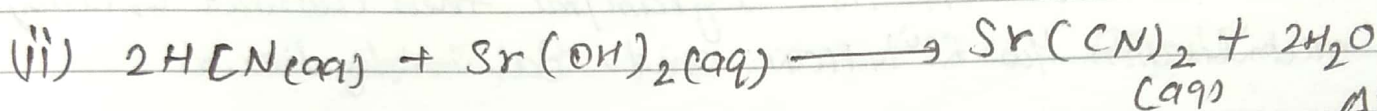
H.W:  $S \pm 1 = 9 + 16.$   
 $O - 1 \Rightarrow 11 + 18.$

Qw: if  $H^{\oplus} + OH^{\ominus} \rightarrow H_2O$   $\Delta H = -13 \text{ Kcal}$

then calculate  $\Delta H$  for given R<sub>N</sub>S



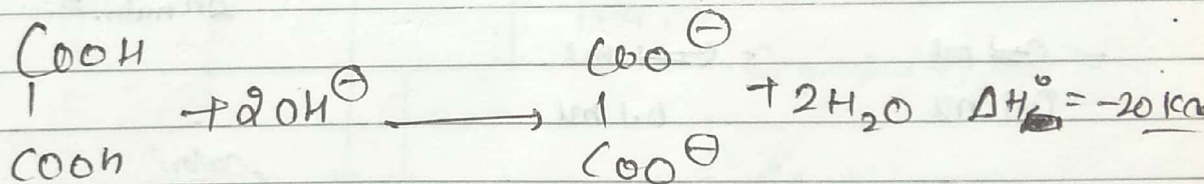
$\therefore$  Not neutralisation!  $\Delta H_{rxn} = -26 \text{ Kcal}$



if  $\Delta H_{diss} [HCN] = 2 \text{ Kcal/mol}$

$$\Delta H_{rxn} = -26 + 4 = -22 \text{ Kcal}$$

Qw: 2



$\Rightarrow$  if  $H^{\oplus} + OH^{\ominus} \rightarrow H_2O$   $\Delta H = -13 \text{ Kcal}$

then calculate  $\Delta H_{diss} [H_2C_2O_4]$  and

$\Delta H^{\circ}$  neutralisation of  $H_2C_2O_4$  with a strong base.

$$\Delta H_{rxn}^{\circ} = -26 + \Delta H_{diss} [H_2C_2O_4]$$

$$-20 = -26 + \Delta H_{diss} [H_2C_2O_4]$$

$$\Delta H_{diss} [H_2C_2O_4] = 6.$$

$$\Delta H^{\circ} \text{ neutralisation} = -10 \text{ Kcal}$$

Ques: 1 molar 100 ml aqueous solution of HCN is mixed with 1 molar 100 ml aqueous Barium hydroxide sol<sup>y</sup>.

In a calorimeter at const. Pressure due to Rx<sup>n</sup> temp. of calorimeter increase by 5.5°C if specific heat capacity of resultant solution is 10 cal/gm K and density of resultant solution is 1 gram/ml then calculate enthalpy of neutralisation the Rx<sup>n</sup> in HCN and Barium hydroxide.

Suppose only sol<sup>y</sup> absorb moderate heat in the calorimeter.



100 ml molar

100 ml molar

$\Delta H_{\text{neut.}}^\circ =$

= 100 ml

= 100 ml

0.1 m

0.1 m

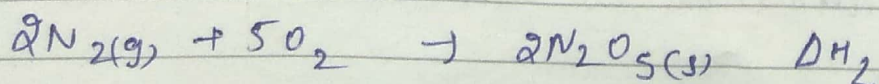
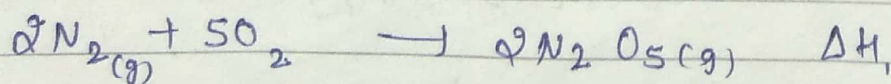
$$\frac{\Delta H_{\text{neut.}}^\circ \times 0.1}{1} = -m \overset{\text{calor}}{c} \Delta T$$

$$\frac{\Delta H_{\text{N}}^\circ \times 0.1}{1} = -200(10)(5.5)$$

$$\Delta H_{\text{N}}^\circ = -2000 \times 5.5$$

\* Factors affecting heat change of Rx<sup>n</sup>:

1. Physical State of Reactant or Product.



$$\Delta H_1 \neq \Delta H_2$$

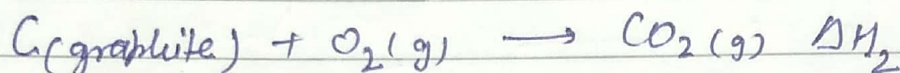
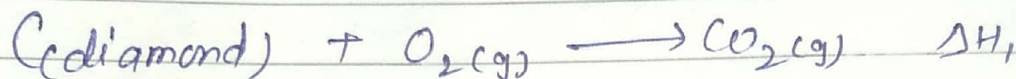


$\Delta H_{20}$

density  $>$  graphite  
stable graphite  $>$  stable carbon.

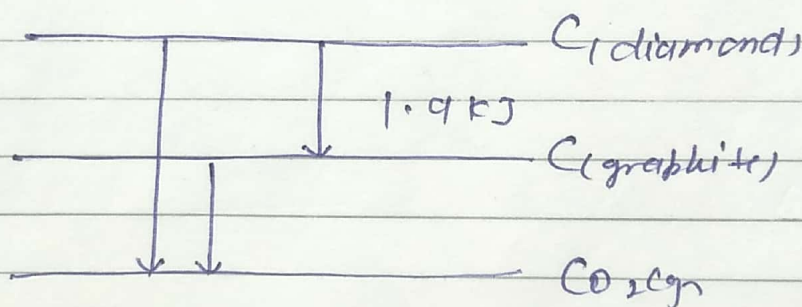
$$\Delta H_1 = \Delta H_2 + 2 \Delta H_{\text{sub}}^\circ [\text{N}_2\text{O}_5(\text{s})]$$

(ii) All the allotropic form of substance:



$$\Delta H_1 \neq \Delta H_2$$

Energy diagram



(3) on external condition of  $R, V$

Heat change of  $R, V$  on const pressure and const temp. will be different from heat change of  $R, V$  at const. vol. and temp.

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

$$q_p = q_v + \Delta n_g RT$$

(iv) on temperature:

Acc. to Kirchhoff equation, value of heat change will be different at diff. temp.

$$\Delta H_{T_2} - \Delta H_{T_1} = \Delta_r C_p (T_2 - T_1)$$

$$\Delta U_{T_2} - \Delta U_{T_1} = \Delta_r C_v (T_2 - T_1)$$

\* For a  $R_{14}$  if  $\Delta_r C_p = 0$   
then enthalpy change of  $R_{14}$  will not depend on  
temperature.