

## Thermochemistry

\* Thermochemical equation.

Enthalpy ( $H$ ) = Heat of rxn.



If  $\Delta H > 0 \Rightarrow$  Endothermic rxn.

If  $\Delta H < 0 \Rightarrow$  Exothermic rxn.

$\Delta_H$  = Heat of rxn or enthalpy change  
of a rxn.



## # Rules for thermochemical equation:-

1. On reversing the chemical rxn,  
the magnitude of enthalpy remains  
same but sign of enthalpy changes.





2) Enthalpy is an extensive property therefore if a rxn is multiplied by any number then enthalpy will be also multiplied by the same number.



3) Enthalpy is an extensive property hence it is also additive in nature. P.e.

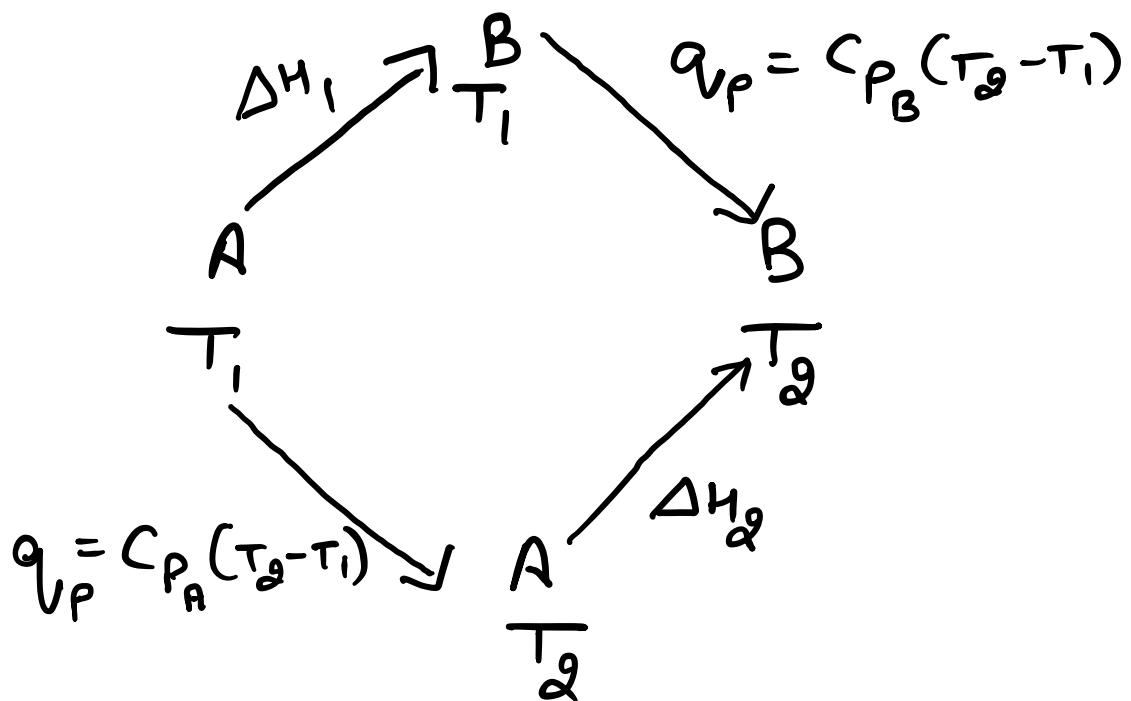


4) Enthalpy of the rxn is a function of temperature. Enthalpy of the rxn is given at a particular

temperature, of temp. changes then  
enthalpy changes i.e. the enthalpy  
of a rxn is defined at a fixed  
temperature.

# variation of enthalpy with  
temperature :-

$\Rightarrow$  Kirchhoff's equation :-



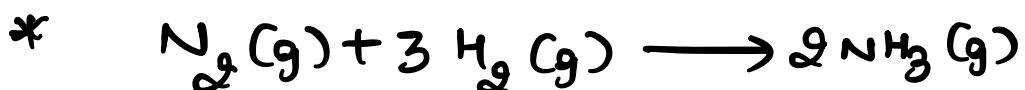
$$\Rightarrow \Delta H_1 + C_{P_B}(T_2 - T_1) = \Delta H_2 + C_{P_A}(T_2 - T_1)$$

$$\Delta H_2 - \Delta H_1 = (C_{P_B} - C_{P_A})(T_2 - T_1)$$

$$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$$

$$\Delta C_p = \frac{\Delta H_2 - \Delta H_1}{T_2 - T_1}$$

$$\Delta C_p = C_p(\text{Product}) - C_p(\text{Reactant})$$



$$\Delta C_p = 2 \times C_p(NH_3) - C_p(N_2) - 3 C_p(H_2)$$

\* If  $\Delta C_p$  is a function

of temp.

$$\Delta H_2 - \Delta H_1 = \int_{T_1}^{T_2} \Delta C_p dT$$

\* If process is carried

out at constant vol.

$$\frac{\Delta E_2 - \Delta E_1}{T_2 - T_1} = \Delta C_v$$

Ques.



The enthalpy of fusion of water at  $0^\circ C$  is  $40 \text{ kJ/mol}$ . Find the enthalpy of fusion at  $-10^\circ C$ .

Given  $C_p H_2O(l) = 75 \text{ kJ/mol}$ .

$C_p H_2O(s) = 67 \text{ kJ/mol}$ .

Sol. Acc. to Kirchhoff's eqn.

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = [C_p H_2O(l) - C_p H_2O(s)]$$

$$\frac{\Delta H_f - \Delta H_i}{-10 - 0} = 8$$

$$\Delta H_f - \Delta H_i = -80$$

$$\Delta H_f = -80 + 40$$

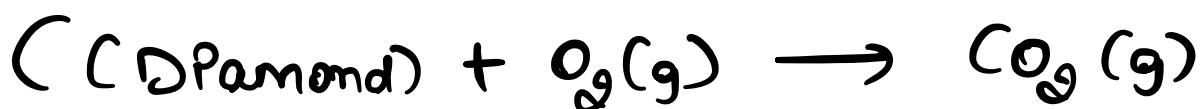
$$\boxed{\Delta H_f = -40 \text{ kJ/mol}}$$

1) Enthalpy of formation :-  
 (Heat of formation)

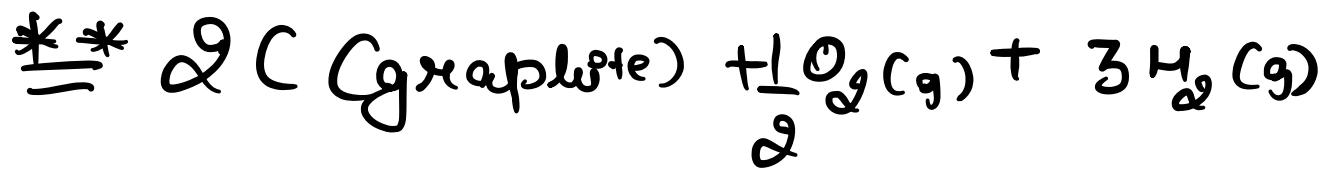
\* Enthalpy change during the formation of 1 mole of Compound from pts most Stable common occurring form of elements.



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



$$\Delta H^\circ \neq \Delta H_f^\circ \text{CO}_2(g)$$



$$\Delta H^\circ = \Delta H_f^\circ \text{C}_2\text{H}_5\text{OH}$$

Element

Most stable common  
occurring form.

H

$\text{H}_2(g)$

O

$\text{O}_2(g)$

N

$\text{N}_2(g)$

$\text{U}$	$\text{Cl}_2(g)$
$\text{Br}$	$\text{Br}_2(l)$
$\text{I}$	$\text{I}_2(s)$
$\text{P}$	$\text{P}(\text{white})$
$\text{S}$	$\text{S}_8(\text{Rhombic})$
$\text{Hg}$	$\text{Hg}(l)$
$\text{Al}$	$\text{Al}(s)$

- Ques :- In which of the following reactions  $\Delta H^\circ = \Delta H_f^\circ$
- $\text{N}_2(g) + 3\text{H}_2(g) \rightarrow 2\text{NH}_3(g)$
  - $\frac{1}{2}\text{H}_2(g) + \frac{1}{2}\text{I}_2(g) \rightarrow \text{HI}(g)$
  - $\frac{1}{9}\text{F}_2(g) + \frac{1}{9}\text{H}_2(g) \rightarrow \text{HF}(g)$



$\Rightarrow$  Rules for writing enthalpy of a rxn :-

Rule-I :- Enthalpy of the rxn from heat of formation.



$$\Delta_{rx}H^\circ = \Delta H_f^\circ (\text{Product}) - \Delta H_f^\circ (\text{Reactant})$$

$$\Delta_{rx}H^\circ = 3 \Delta H_f^\circ C - 2 \Delta H_f^\circ A - \Delta H_f^\circ B$$

\* Heat of formation of most stable common occurring form of element at standard state is assumed to be zero



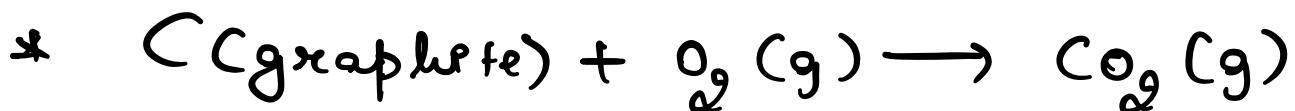
$$\Delta_{rx}H^\circ = \Delta H_f^\circ \text{CO}_2$$

$$\Delta_H^\circ = \Delta H_f^\circ \text{CO}_2 - \cancel{\Delta H_f^\circ \text{C (s)}} - \cancel{\Delta H_f^\circ \text{O}_2}$$

$$\Delta_H^\circ = \Delta H_f^\circ \text{CO}_2$$

$\Rightarrow$  Heat of Combustion or enthalpy of Combustion :-

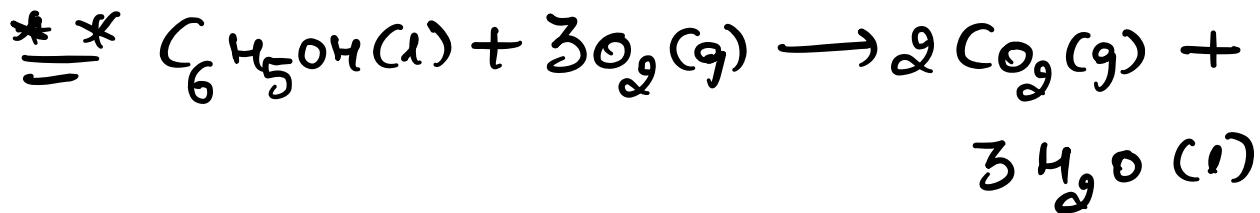
\* Enthalpy change during the Complete Combustion of 1 mole of substance or compound with  $\text{O}_2$ . e.g.



$$\Delta H^\circ = \Delta H_C^\circ \text{C (graphite)} = \Delta H_f^\circ \text{CO}_2 (\text{g})$$



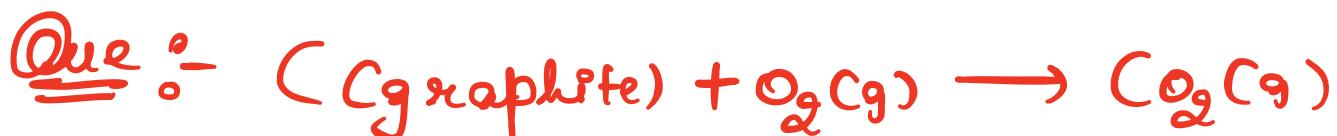
$$\Delta H^\circ = \Delta H_C^\circ \text{H}_2 (\text{g}) = \Delta H_f^\circ \text{H}_2\text{O (l)}$$



$$\Delta H^\circ = \Delta H_c^\circ C_6H_5OH(l)$$

$$\Delta H^\circ = 2\Delta H_f^\circ CO_2 + 3\Delta H_f^\circ H_2O -$$

$$\Delta H_f^\circ C_6H_5OH$$



$$\Delta H = -x$$



$$\Delta H = -y.$$

Select the correct statement.

- (A)  $y > x$  (B)  $y = x$  (C)  $x > y$

(D) None.

Sol<sup>n</sup>o - Reverse any one of these two chemical rxns.



$$\Delta H^\circ = -x + y.$$

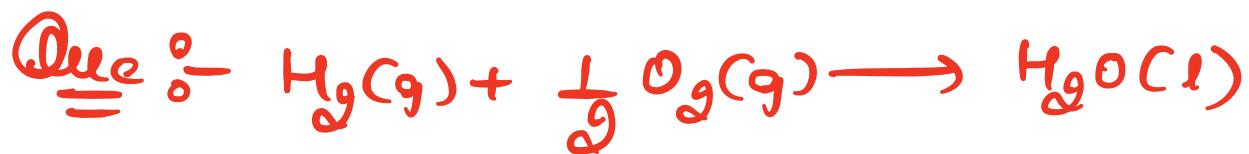


↓  
Stability Order.

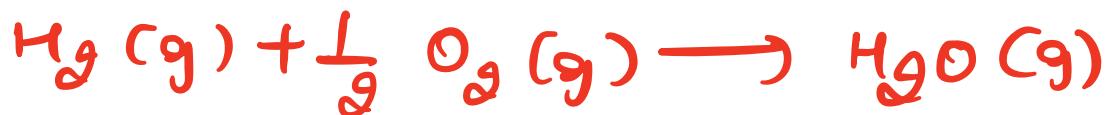
\* for conversion of an stable allotrop into an unstable allotrop heat must be given.

$$\Delta H^\circ = -x + y > 0$$

$$y > x$$



$$\Delta H^\circ = -x \text{ kJ/mol.}$$



$$\Delta H^\circ = -y \text{ kJ/mol.}$$

(A)  $x > y$  (B)  $y > x$  (C)  $x = y$

(D) None.

On reversing 1st rxn.



$$\Delta H^\circ = x - y.$$

\* On conversion of a liquid into a gas, heat must be given.

$$\Delta H^\circ = x - y > 0$$

$$x > y$$

Ans 6-  $P(\text{Black}) > P(\text{Red}) > P(\text{white})$

$$P(\text{white}) + \vartheta O_g(g) + \frac{3}{g} H_2(g) \longrightarrow$$

$$H_3 \text{ Po}_4(1) \quad \Delta H^\circ = -x$$

$$P(\text{Black}) + \vartheta O_g(g) + \frac{3}{g} H_2(g) \longrightarrow H_3 \text{ Po}_4(1)$$

$$\Delta H^\circ = -y.$$

$$P(\text{Red}) + \vartheta O_g(g) + \frac{3}{g} H_2(g) \longrightarrow H_3 \text{ Po}_4(1)$$

$$\Delta H^\circ = -z$$

(A)  $x > y > z$  (B)  $x > z > y$

(C)  $y > x > z$  (D) None.

Soln: from eqn ① & ②

on reversing eqn ①

$P(\text{Black}) \longrightarrow P(\text{white})$

$$\Delta H^\circ = x - y.$$

\* As  $P(\text{black}) > P(\text{white})$

Stability.

$$\Rightarrow \Delta H^\circ = x - y > 0$$

$$x > y$$

from eqn ② & ③

On reversing eqn ③

$P(\text{black}) \longrightarrow P(\text{Red})$

$$\Delta H^\circ = z - y.$$

\* As  $P(\text{black}) > P(\text{Red})$

$$z - y > 0$$

$$z > y$$

$$\Rightarrow x > z > y$$

Rule - II

$\Rightarrow$  Enthalpy of rxn from heat of combustion :-

$$\Delta_H^\circ = \Delta H_C^\circ(\text{Reactants}) - \Delta H_C^\circ(\text{Produ.})$$

Ques :- If  $\Delta H_C^\circ C_2H_6 = -x$

$$\Delta H_C^\circ H_2 = -y, \quad \Delta H_C^\circ C_2H_4 = -z$$

Find  $\Delta H^\circ$  for



Soln :-

$$\Delta_H^\circ = -z - y + x$$

Heat of Combustion is always exothermic

\*



⇒ Bond energy :-

\* Bond energy term is defined only for gaseous molecules.

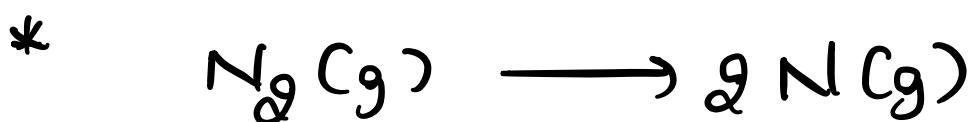
\* Enthalpy change during the breaking of 1 mole bonds of gaseous molecules into gaseous atoms is known as bond energy.



$$\Delta H^\circ = \sum H - H = 2 \Delta H_f^\circ H(g)$$



$$\Delta H^\circ = \sum O = O = 2 \Delta H_f^\circ O(g)$$

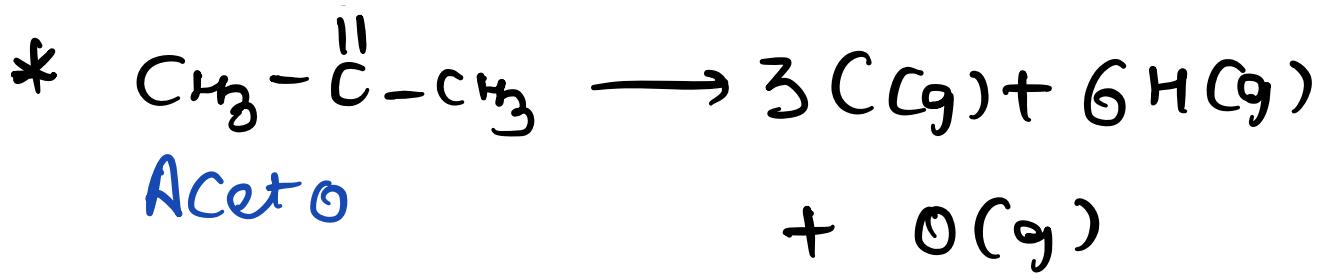


$$\Delta H^\circ = \sum N \equiv N = 2 \Delta H_f^\circ N$$

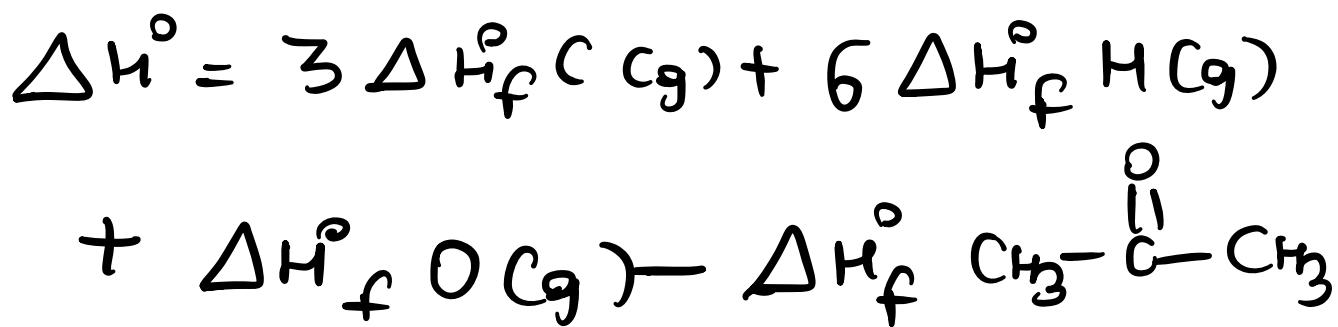


$$\begin{aligned} \Delta H^\circ &= 4 \sum C - H = \Delta H_f^\circ C(g) + \\ &4 \Delta H_f^\circ H(g) - \Delta H_f^\circ CH_4(g) \end{aligned}$$

O

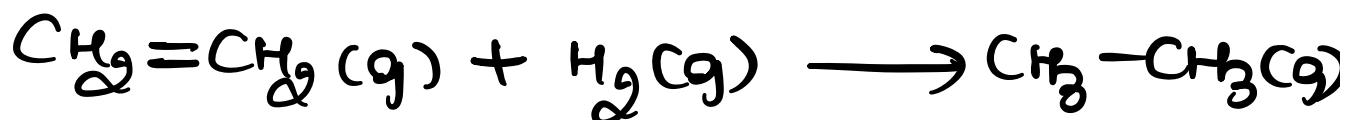


$$\Delta H^\circ = 6 \sum C-H + \sum C - 2 \sum C-C$$



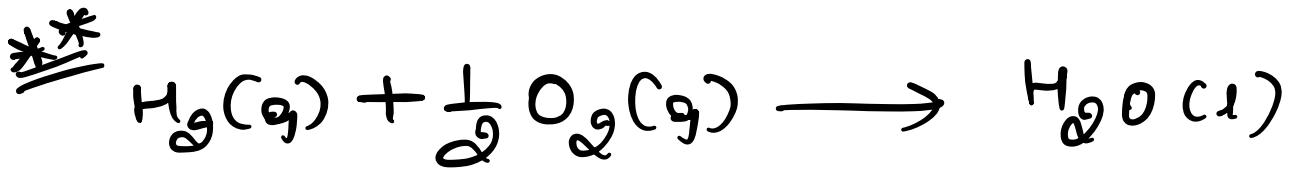
### Rule - III :-

\*\* Enthalpy of the rxn from bond energy :-



$$\Delta H^\circ = \sum \text{Reactants} - \sum \text{Products.}$$

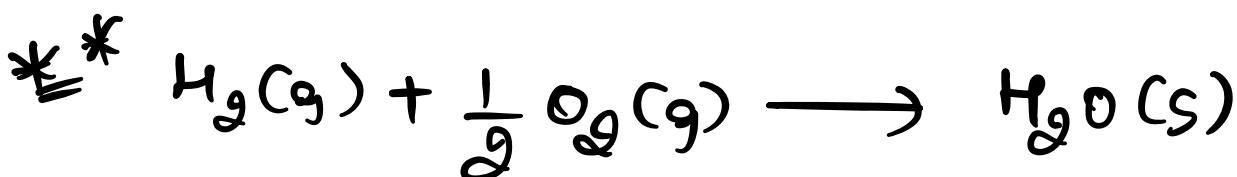
$$= \left[ 4 \sum C-H + \sum C=C + \sum H-H \right] - \\ \left[ 6 \sum C-H + \sum C-C \right]$$



$$\Delta H^\circ = \left[ \sum H-H + \frac{1}{2} \sum O=O \right] - \\ \left[ \Delta H_{\text{vap.}}^\circ H_2O(l) + 2 \sum O-H \right]$$



$$\Delta H^\circ = \Delta H_{\text{vapourisation.}}^\circ$$



$$\Delta H^\circ = \left[ \sum H-H + \frac{1}{2} \sum O=O \right] - \left[ \Delta H_{\text{sub.}}^{H_2O(s)} + 2 \sum O-H \right]$$

## # Resonance energy :-

\* The energy difference b/w most stable canonical structure and resonance hybrid is known as resonance energy.

"Due to resonance compound gains extra stability hence energy will be lowered"

→ Resonance energy is always exothermic.





$$\Delta H^\circ = 6 \sum C-H + 3 \sum C=C + 3 \sum C-C$$

\* Extra amount of energy must be given to the benzene to overcome its extra stability so that extra energy is equals to the resonance energ.

$$\Delta H^\circ = 6 \sum C-H + 3 \sum C=C + 3 \sum C-C + \text{I.R.E.I}$$

## # Heat of atomisation :-

\* Enthalpy change during the conversion of molecule or element into gaseous atom is K/A heat of atomisation.



$\Delta H^\circ =$  [Heat of atomisation of  $H_2$ ]  
Or

$$= \sum H-H \quad \text{Or} \quad 2\Delta H_f^\circ H_2(g)$$



$\Delta H^\circ =$  Heat of atomisation of  $CH_4$   
Or

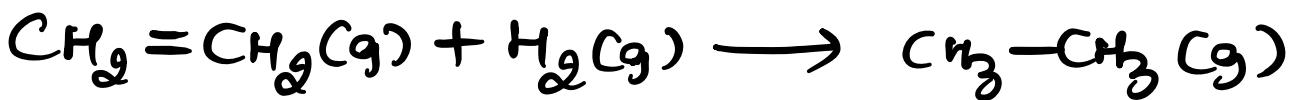
$$= 4 \sum C-H$$

$$= \Delta H_f^\circ (C) + 4 \Delta H_f^\circ H(g) - \Delta H_f^\circ CH_4(g)$$

# Heat of hydrogenation :-

\* Enthalpy change during the addition of hydrogen in an unsaturated compound.

"H-O-H is always exothermic"



$\Delta H^\circ = \text{H.O.H. of } \text{C}_2\text{H}_4$

### # Heat of solution :-

Enthalpy change when 1 mole of solute is dissolved in excess of solvent is K/A heat of soln.



$\Delta H^\circ = \text{Heat of soln of KCl(s)}$

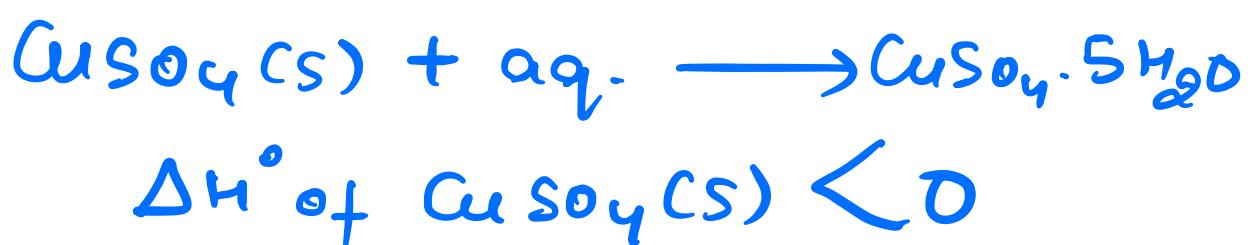


$\Delta H^\circ = \text{Heat of soln of CuSO}_4(\text{s})$



$\Delta H^\circ = \text{Heat of soln of CuSO}_4 \cdot 5\text{H}_2\text{O}$

① Heat of soln will be exothermic for those type of anhydrous form of the salt which can form pts hydrates e.g.



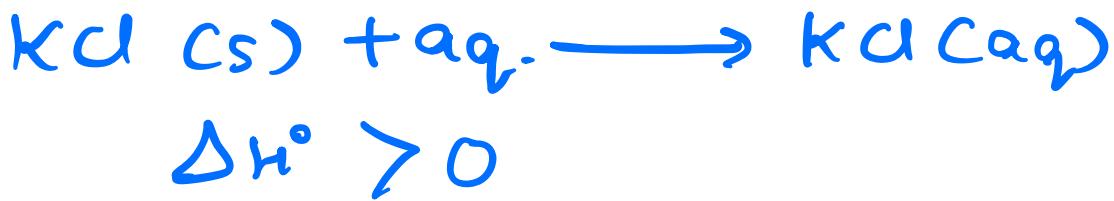
$\text{Na}_2\text{SO}_4(s)$ ,  $\text{KCl}(s)$ ,  $\text{CaCl}_2(s)$  etc.

② Heat of soln will be endothermic for the hydrated form of the salt.

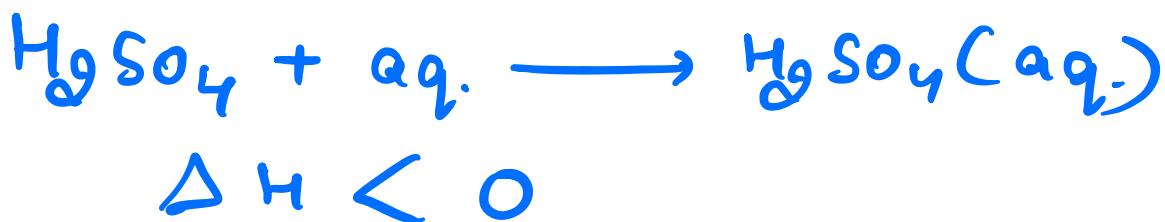


③ Heat of soln will be endothermic for those type

of salts which cannot form  
pts hydrates.



④ Heat of soln of strong acid and strong base  
is always exothermic.



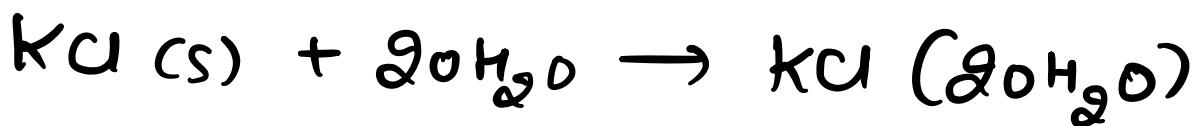
⑤ Heat of soln of any Cation or anion will be exothermic.

# Integral heat of soln :-

Enthalpy change when 1 mole of Solute is dissolved in

a given amount of solvent  
per kg of a solution.

\* A solute can have infinite  
no. of integral heats of  
solution.



$\Delta H = \alpha$  = Integral heat of  
KCl(s)

# Heat of dilution :-

Enthalpy change during the  
dilution of any soln per  
kg of dilution.



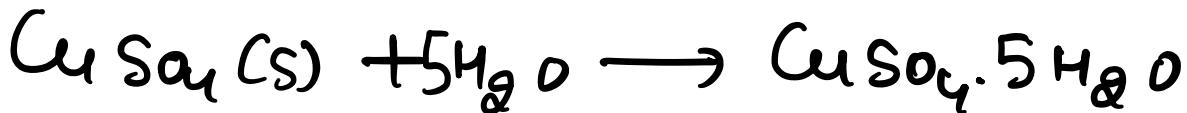


$$\Delta H^\circ = y - x.$$

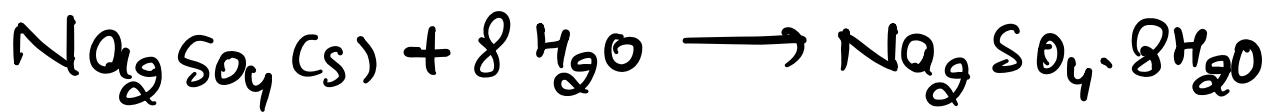
$y - x$  = Heat of dilution of  $\text{KCl}(\text{anhyd})$

# Heat of hydration :-

Enthalpy change during the formation of hydrated form of the salt from its anhydrous form.



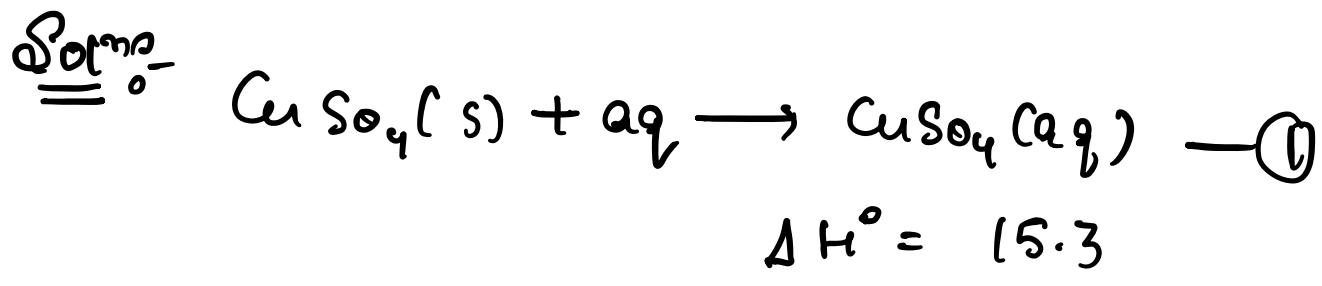
$\Delta H^\circ$  = Heat of hydration of  $\text{CuSO}_4(\text{s})$



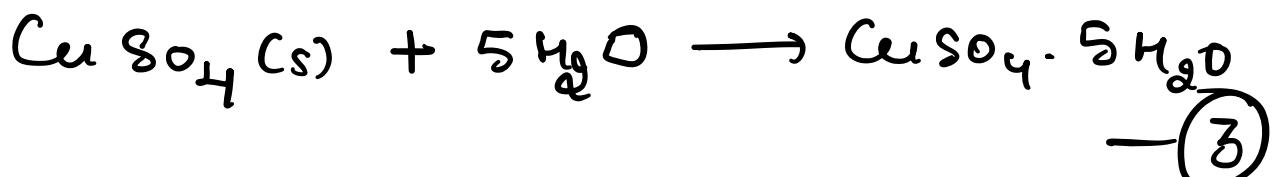
$\Delta H^\circ$  = Heat of hydration of  
 $\text{Na}_2\text{SO}_4(s)$

"Heat of hydration is always exothermic".

Ques:- If the heat of soln of  $\text{CuSO}_4(s)$  and  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}(s)$  are 15.3 & 17.7 kJ/mole respectively then find the heat of hydration of  $\text{CuSO}_4(s)$



$$\Delta H^\circ = 17.7$$



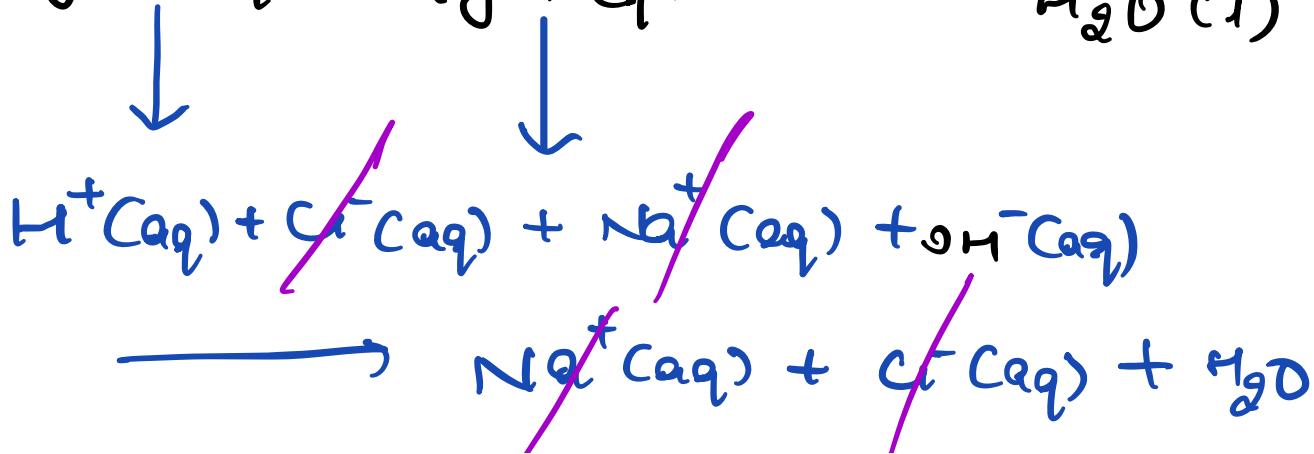
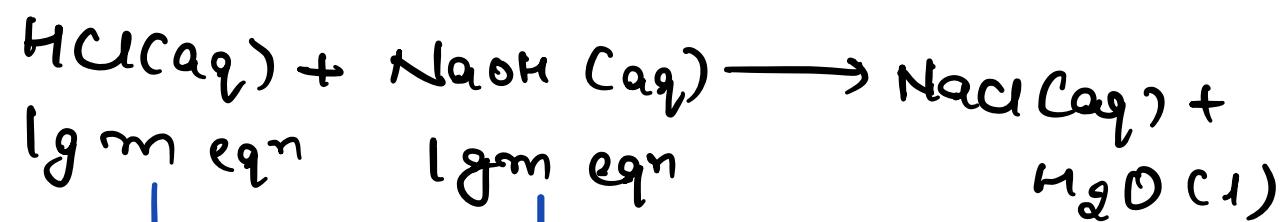
$$\Delta H^\circ = ?$$

On reversing ② & add to ①

$$\Delta H^\circ = -15.3 - 17.7 = -33.0$$

## # Heat of neutralisation :-

Enthalpy change during the neutralisation of 1 gm eqn of strong acid with 1 gm eqn of a g. B in dilute soln  
is k/a heat of neutralisation.





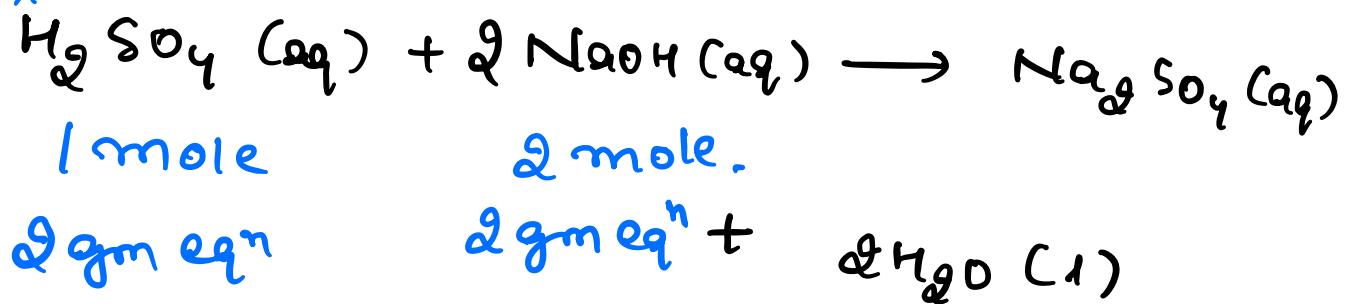
$$\Delta H^\circ = -13.7 \text{ K Cal/eqn}$$



Experimental value.

"Heat of neutralisation of S.A.  
is s.b. ps independent of the  
nature of S.A & S.B."

\*\*



$$N = M \times n_f$$

$$N = 1 \times 2$$

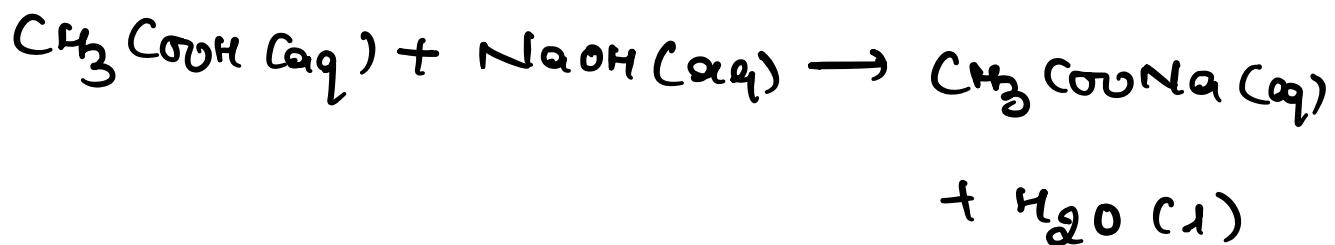
$$N = 2 \text{ gm eqn}$$

$$\Delta H^\circ \text{ for } 1 \text{ gm eqn} = -13.7$$

$$\Delta H^\circ \text{ " } 2 \text{ gm eqn} = -13.7 \times 2$$

$$= -27.4 \text{ K cal/eqn}$$

# Heat of neutralisation of weak acid/Base with strong Base/ acid :-

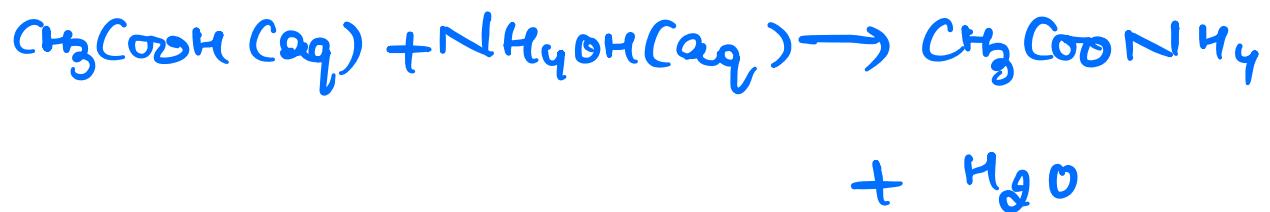


$$\Delta H^\circ = -[13.7 - x] \text{ K cal. / eqn.}$$

$x$  = Dissociation energy or ionisation energy of  $\text{CH}_3\text{COOH}$

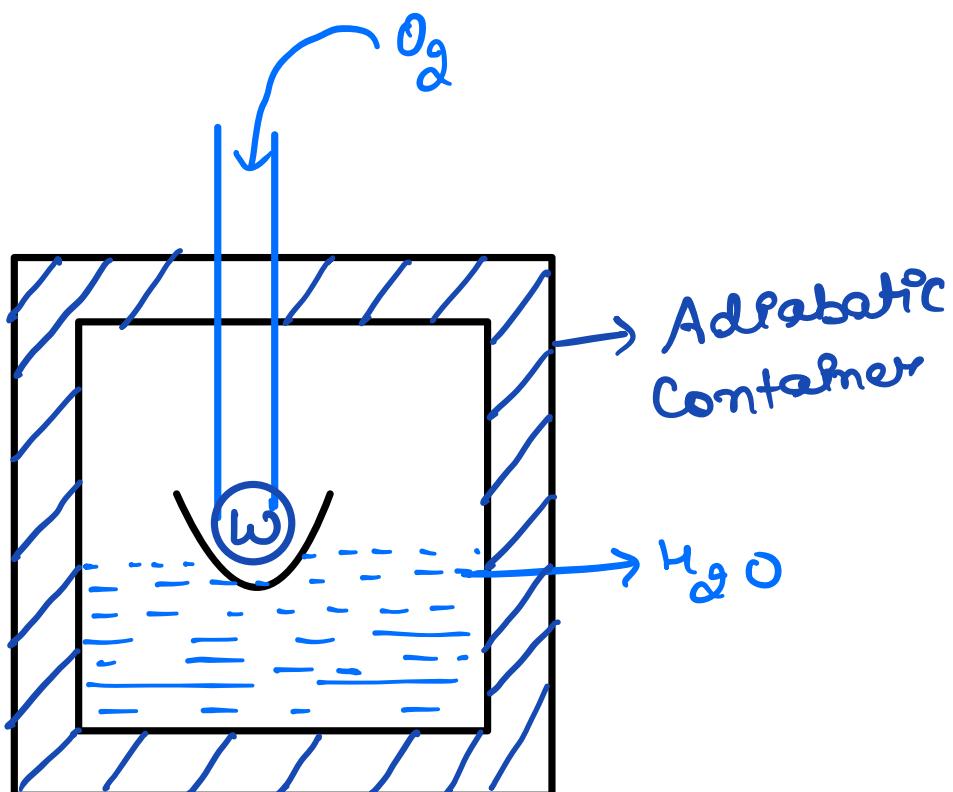
Heat of neutralisation  $\propto$  Acidic st. of acid.

\* If both acid and base will be weak :-



$$\Delta H^\circ = - [13.7 - x - y] \text{ Kcal/eqn}$$

## # Bomb Calorimeter:-



Heat evolved = Heat absorbed by the water  
+ Heat absorbed by the inner walls of

the container.

$$= m s \Delta T + C_1 \Delta T$$

$\hookrightarrow$  Heat capacity  
of inner  
walls.

We know that

Heat capacity  $q_r = C \Delta T$

$\Rightarrow$  Total heat capacity  
of the system  $= C_1 + C_2$ .  
including water ( $q$ )

Heat of Combustion  $= -\frac{q_r}{w/M}$



H.O.C is always -ve.

$$H.O.C = -\frac{M}{w} C \Delta T$$

$$= -\frac{M}{\omega} (C_i + C_g) \Delta T$$

$$C = C_i + C_g$$

# Lattice energy :-

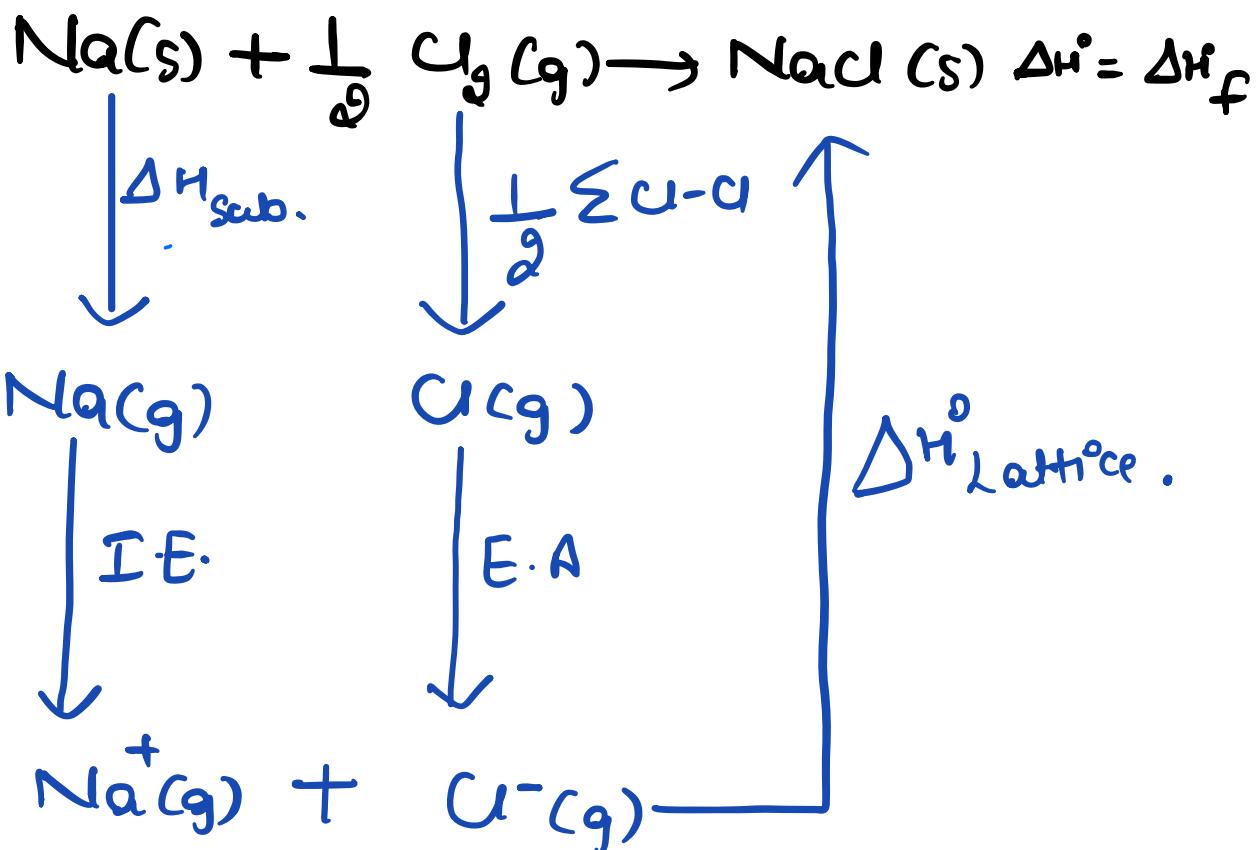
Enthalpy change during the formation of 1 mole of ionic solid from gaseous cation & anion is K/A lattice energy.



$$\Delta H^\circ = \Delta H_{\text{lattice}}^\circ \text{ of NaCl}$$

$$\Delta H_{\text{lattice}}^\circ < 0$$

# lattice energy from Born Haber's cycle :-



\* Acc. to Hess's law :-

$$\begin{aligned} \Delta H_f^\circ \text{ NaCl} &= \Delta H_{\text{sub.}} \text{ Na(s)} + \text{I.E.} + \frac{1}{2} \sum \text{Cl-Cl} \\ &\quad + \text{E.A.} + \Delta H_{\text{lattice}}^\circ. \end{aligned}$$