

# Thermochemistry

## Thermochemistry:

The study of energy transferred as heat during the course of a chemical reaction is called thermochemistry

OR

The branch of chemistry which deals with energy changes involved in a chemical rxn.

→ Thermochemistry is a branch of thermodynamics becoz a rxn vessel and its contents form a system, and chemical rxns results in the exchange of energy b/w the system and the surroundings.

Calorimetry can be used to measure the energy supplied or discarded as heat by a reaction. Can be identify with

$$q_v = \Delta U ; q_p = \Delta H$$

# Change in internal energy in a chemical reaction:

$$\Delta U = q_v \quad (\text{at const. temp and const volume})$$

$$\Delta U = U_p - U_R = q_v = \text{heat of rxn at const. volume.}$$

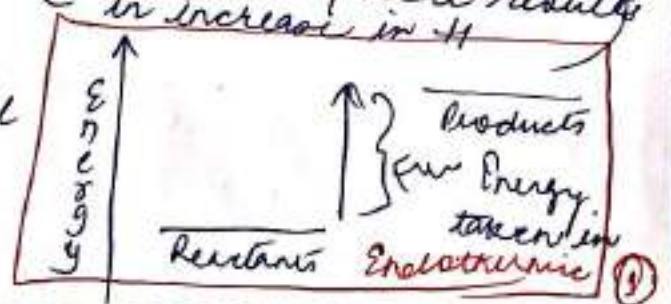
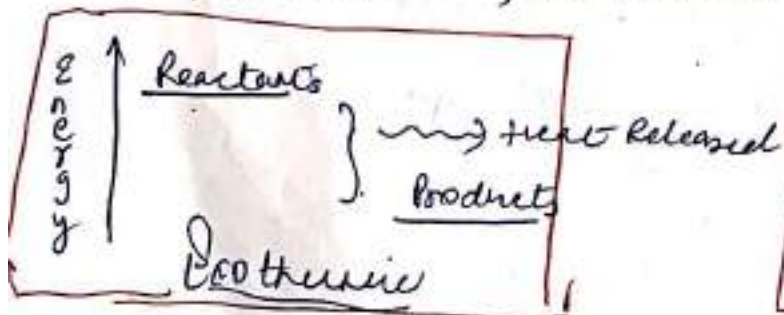
# Change in Enthalpy in a chemical reaction:

$$\Delta H = q_p = H_p - H_R = \text{heat of rxn at const. Pressure.}$$

⇒ Exothermic & Endothermic rxns :- Heat released or abs. may be classified as

$H_p < H_R \Leftrightarrow \Delta H < 0$  ; exothermic (release of heat signifies) ↓ in enthalpy

$H_p > H_R \Leftrightarrow \Delta H > 0$  ; endothermic (Absorption of heat results in increase in H)





# # Standard Enthalpy changes

→ Changes of enthalpy for a process taking place under a set of standard conditions. The standard enthalpy change  $\Delta H^\circ$ ; the change of enthalpy at initial and final substances are in standard states

Standard state conds.

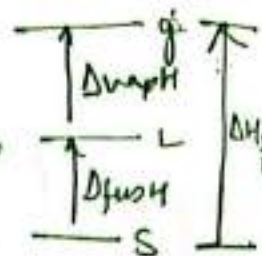
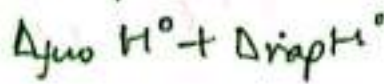
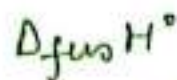
The standard state of a substance at a specified temp i.e. at 25°C or 298K and at 1 bar pressure

→ The standard enthalpy change that accompanies a change of physical state is called standard enthalpy of transition

$\Delta_{\text{trans}} H^\circ$

<u>Transition</u>	<u>Process</u>	<u>Symbol</u>
Transition	Phase $\alpha \rightarrow \beta$	$\Delta_{\text{trans}} H^\circ$
Fusion	S $\rightarrow$ L	$\Delta_{\text{fus}} H^\circ$
Vapourisation	L $\rightarrow$ G	$\Delta_{\text{vap}} H^\circ$
Sublimation	S $\rightarrow$ G	$\Delta_{\text{sub}} H^\circ$
Mixing	Pure $\rightarrow$ mixture	$\Delta_{\text{mix}} H^\circ$
Solution	Solute $\rightarrow$ solution	$\Delta_{\text{sol}} H^\circ$
Hydration	$X^{\pm}(g) \rightarrow X^{\pm}(aq)$	$\Delta_{\text{hyd}} H^\circ$
Atomization	Species (s, l, g) $\rightarrow$ atoms (g)	$\Delta_{\text{at}} H^\circ$
Ionization	$X(g) \rightarrow X^+(g) + e^-(g)$	$\Delta_{\text{ion}} H^\circ$
Electron gain	$X(g) + e^-(g) \rightarrow X^-(g)$	$\Delta_{\text{eg}} H^\circ$
Reaction	Reactants $\rightarrow$ products	$\Delta_r H^\circ$
Combustion	Compounds (s, l, g) + $O_2(g) \rightarrow CO_2(g), H_2O(l, g)$	$\Delta_c H^\circ$
Formation	Elements $\rightarrow$ compound	$\Delta_f H^\circ$
Activation	Reactants $\rightarrow$ Activated complex	$\Delta^\ddagger H^\circ$

(2)



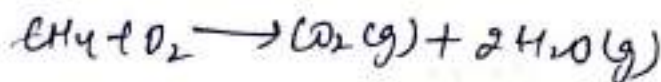
## # Enthalpy of chemical change

enthalpy changes that accompany chemical rxns

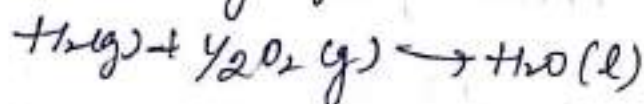
### 1) Enthalpy of combustion:

→ enthalpy changes accompanying complete combustion of 1 mole of a substance at 25°C at 1 bar pressure;

→ Methane combustion

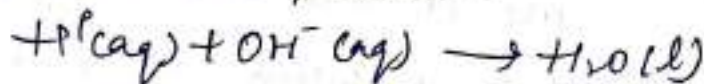


Combustion of hydrogen

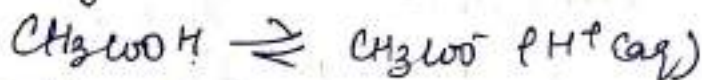


### 2) Enthalpy of neutralization:

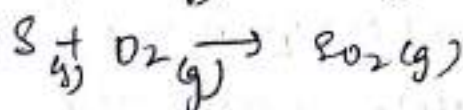
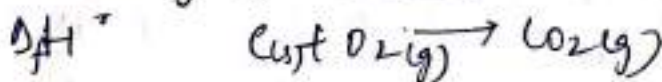
enthalpy change accompanying the neutralization of 1 mole of acid at 25°C at 1 bar pressure.



### 3) Enthalpy of dissociation:



### 4) Enthalpy of formation:



## # Determination of Enthalpy of Rxns:-

$$\Delta H^\circ = \sum \Delta H_f^\circ(\text{Products}) - \sum \Delta H_f^\circ(\text{Reactants})$$

$\Delta H_f^\circ$  values of elements in std state are taken as zero

### Std Enthalpy of Rxn

$$\Delta_r H^\circ = \sum_{\text{products}} \nu H_m^\circ - \sum_{\text{reactants}} \nu H_m^\circ$$

$\nu$  = stoichiometric coeff.,  $H_m^\circ \Rightarrow$  Std. molar enthalpy

## # Temperature dependence of Reaction Enthalpies

governed by Kirchoff's Law (variation of enthalpy of rxn with temp)

The standard rxn enthalpies at diff. temp. may be calculated from heat capacities and rxn enthalpies at diff temp.

$$\Delta H = H(T_2) - H(T_1) = \int_{T_1}^{T_2} C_p dT \quad \text{OR} \quad \left( \int d(\Delta H) = \Delta C_p + \int_{T_1}^{T_2} dT \right)$$

$$\Delta_r H^\circ(T_2) - \Delta_r H^\circ(T_1) = \int_{T_1}^{T_2} \Delta_r C_p^\circ dT$$

Kirchoff's Law

Standard rxn enthalpy changes  $\Delta_r H^\circ \Rightarrow \Delta_r H = \Delta C_p (T_2 - T_1)$

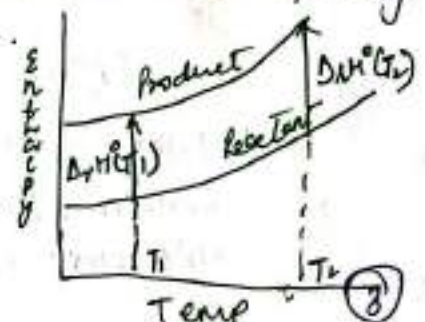
$\Delta_r C_p^\circ \rightarrow$  diff. of molar heat capacities of prod. and reactants

$$\Delta_r C_p^\circ = \sum_{\text{prod}} \nu C_{p,m}^\circ - \sum_{\text{reactant}} \nu C_{p,m}^\circ$$

$\Delta_r C_p^\circ$  is independent of temp. whereas individual heat capacity may vary, their diff. varies less significantly.

\* Law states that the variation of  $\Delta H$  of a rxn with Temp. at const. pressure is equal to  $\Delta C_p$  of the sys.

$$\left( \frac{\partial \Delta H}{\partial T} \right)_p = \Delta C_p \quad \text{OR} \quad d\Delta H = \Delta C_p dT$$





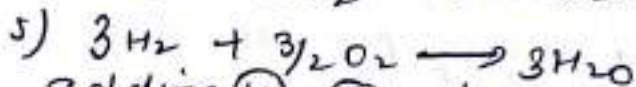
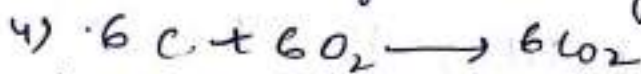
### 8) Calculation of enthalpies of formation

enthalpy of formation which is not possible from expts. can be determined by Hess's Law.

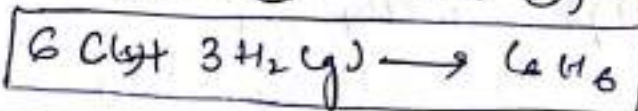
Ex: -

- 1)  $C_6H_6(l) + 15/2 O_2(g) \rightarrow 6CO_2(g) + 3H_2O(l) \quad \Delta H = -3267.7 \text{ kJ}$
- 2)  $C(s) + O_2(g) \rightarrow CO_2(g) \quad \Delta H = -393.5 \text{ kJ}$
- 3)  $H_2(g) + 1/2 O_2 \rightarrow H_2O(l) \quad \Delta H = 285.9 \text{ kJ}$

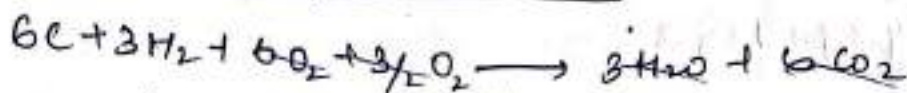
multiply eqn ii by 6 and 3 by 3  $\rightarrow$



adding (4) & (5) and sub (1), we get

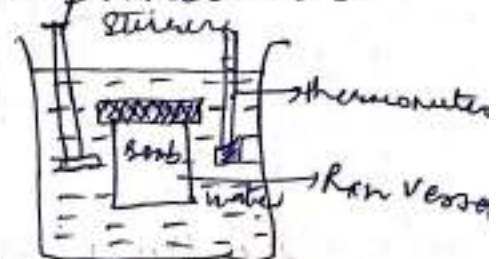


i.e.



### 4) measuring enthalpy of combustion (by bomb calorimeter)

Calorimeter is used to determine enthalpies of combustion known as bomb calorimeter.

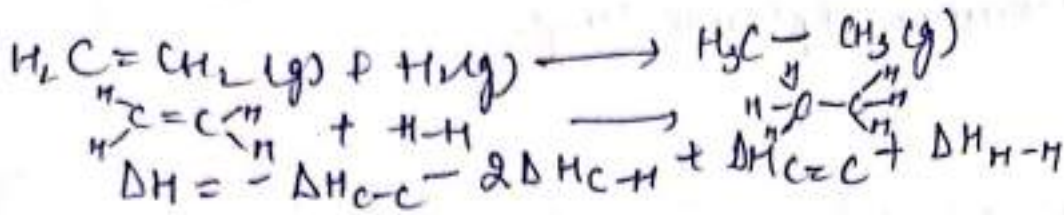




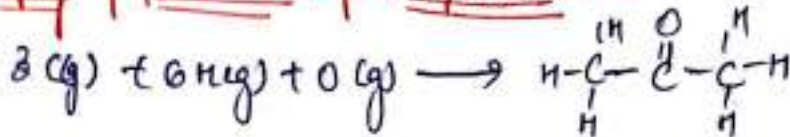


## \* Applications of Bond energies :-

### 1) Determination of enthalpies of rxns :-

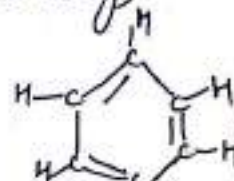
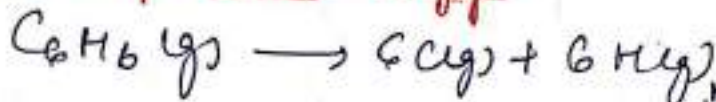


### 2) Enthalpy of formation of compounds :-



$$\Delta H_{\text{form}}^{\text{Acetone}} = \left[ 3(\Delta H_{\text{H}-\text{H}} + \frac{1}{2}\Delta H_{\text{O}=\text{O}} + 2\Delta H_{\text{C}=\text{C}}) \rightarrow \text{C}_{\text{eq}} \right] - \left[ 2\Delta H_{\text{C}=\text{C}} + 6\Delta H_{\text{C}-\text{H}} + \Delta H_{\text{C}=\text{O}} \right]$$

### 3) Determination of resonance energy



$$\Delta H_d = 3(\Delta H_{\text{C}=\text{C}}) + 3(\Delta H_{\text{C}=\text{C}}) + 6(\Delta H_{\text{C}-\text{H}})$$

## \* Flame and Explosion Temperatures :-

Combustion of a gaseous fuel in air takes place so suddenly that the heat produced during combustion does not get any opportunity to be dissipated to the surroundings. Therefore, the combustion process is therefore practically equiv. to an adiab. process.

→ The entire amount of heat produced goes to heat the gases (resultant gases) liberated by during combustion.

\* The max. temp. obtained by the flame-zone (containing the resultant gases) due to the heat liberated by the combustion of fuel under adiabatic condn at constt. pressure is known as max. flame temperature.

# The combustion is carried out under adiabatic condn.  
at const. volume, the max temp. obtained is called.  
Maximum explosion temp.