

VIVEKANANDA COLLEGE  
THAKURPUKUR  
KOLKATA-700063

NAAC ACCREDITED 'A' GRADE



Topic:	Thermochemistry
Course Title:	General Physical Chemistry
Paper:	BCMA CC3
Unit:	Biophysical Properties
Semester:	2
Name of the Teacher:	<b>Dr. Subharthi Banerjee</b>
Name of the Department:	Biochemistry

## Thermochemistry:



→ Deals with the transfer of heat between a chemical system and its surroundings when a change of phase or chemical reaction occurs.

→ Since most chemical reactions are carried out under constant pressure ( $p$ ) conditions, the heat exchanged is equal to the change in enthalpy ( $H$ ) of the system.

→ Molar enthalpy ( $H_m$ ) is the enthalpy for 1 mole of a substance.

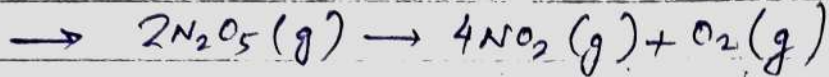
$$H_m = f(T, P)$$

$H_m^\circ$  = Standard molar enthalpy

Here the pressure dependence is removed by defining standard state of a substance at 1 bar pressure.

e.g.  $H_m^\circ(\text{H}_2\text{O}, l, 273\text{K})$  means the molar enthalpy of liquid water at 273 K and 1 bar pressure.

→ If the reactants and products are at the same  $T$  and  $p$ , the  $\Delta H$  value ~~so~~ gives the enthalpy change for the chemical reaction only.



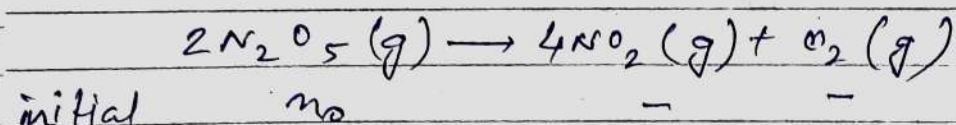
Progress of a reaction is defined as

$$\xi = \frac{\text{Total amount of reactants consumed}}{\text{Stoichiometric no. of reactant}}$$

$$\xi = \frac{\text{Total amount of product formed}}{\text{Stoichiometric no. of product}}$$

$\rightarrow$  Let  $n_0$  be the initial amount of  $\text{N}_2\text{O}_5$ .

$$\therefore H_{\text{initial}} = n_0 H_m(\text{N}_2\text{O}_5) \text{ at } \xi = 0$$



$$\text{Unit of } \xi = \text{mol}$$

$$\therefore H_{\text{final}} = (n_0 - 2\xi) H_m(\text{N}_2\text{O}_5) + 4\xi H_m(\text{NO}_2) + \xi H_m(\text{O}_2)$$

$$\therefore \Delta H = H_{\text{final}} - H_{\text{initial}}$$

$$= -2\xi H_m(\text{N}_2\text{O}_5) + 4\xi H_m(\text{NO}_2) + \xi H_m(\text{O}_2)$$

$$\begin{aligned} \therefore \text{unit of } \Delta H &= (\text{unit of } \Sigma) (\text{unit of } H_m) \\ &= \text{mol} \times \text{kJ mol}^{-1} \\ &= \text{kJ} \end{aligned}$$

→ Enthalpy of a reaction  $\rightarrow \Delta H$

$$\Delta_r H = \frac{\Delta H}{\Sigma}$$

∴ for the above reaction,

$$\Delta_r H = -2H_m(\text{N}_2\text{O}_5) + 4H_m(\text{NO}_2) + H_m(\text{O}_2)$$

$$\therefore \text{unit of } \Delta_r H = \text{kJ mol}^{-1}$$

→  $\Delta_r H$  considers the entire chemical equation for its evaluation.

→  $\Delta_r H$  is the difference of enthalpy between the reactants and products for the entire chemical reaction.

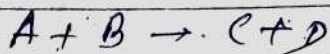
$$\Delta_r H = \sum_{\text{products}} \nu_B H_m(B) - \sum_{\text{reactants}} \nu_B H_m(B)$$

$\nu_B$  → Stoichiometric number in the equation

$H_m(B)$  → molar enthalpy of species B

- Endothermic reactions have  $\Delta_r H = \text{positive}$   
 → Exothermic " " "  $\Delta_r H = \text{negative}$

→ Let us consider a chemical reaction



This can be written as

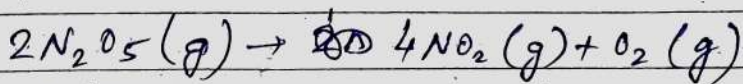
$$0 = C + D - A - B$$

ie. 
$$0 = \sum_B \nu_B B$$

$\nu_B \rightarrow$  Stoichiometric no. of species B.

$\nu_B =$  negative for reactants  
 = positive for products

→ For the same previous reaction:



We can write,

$$0 = 4NO_2(g) + O_2(g) - 2N_2O_5(g)$$

If  $(n_B)_0$  be the initial amount of any species B in the reaction, and  $n_B$  be the amount after the reaction has progressed by  $\xi$ ,

We can write

$$n_B = (n_B)_0 + \nu_B \xi$$

$$\Rightarrow n_B - (n_B)_0 = \nu_B \xi$$

[Note that for reactants  $(n_B)_0 > n_B$   
for products  $n_B > (n_B)_0$ ]

$$\therefore \boxed{dn_B = \nu_B d\xi}$$

$$\therefore dH = \sum_B H_m(B) dn_B$$

$$= \sum_B H_m(B) (\nu_B d\xi)$$

$$\therefore \Delta_r H = \left( \frac{\partial H}{\partial \xi} \right)_{T, P} = \sum_B \nu_B H_m(B)$$

i. e. enthalpy of a reaction ( $\Delta_r H$ ) is the rate of change of enthalpy of a system with the extent of a reaction ( $\xi$ ) at constant  $T$  and  $p$ .

→ Enthalpy of a reaction:  $\Delta_r H$

→ Standard enthalpy of a reaction:  $\Delta_r H^\circ$

$$\Delta_r H^\circ = \left( \frac{\partial H^\circ}{\partial \xi} \right)_{T, p} = \sum_B \nu_B^\circ H_m^\circ(B)$$

→ Standard enthalpy of formation:  ~~$\Delta_f H$~~

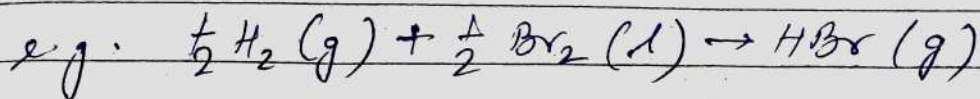
$$\Delta_f H^\circ$$

→ The standard enthalpy of formation of every element in its stable state of aggregation at 1 bar pressure and at a specified temperature is assigned a value of zero.

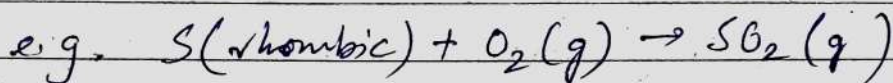
e.g.  $\Delta_f H^\circ(\text{O}_2, \text{g}) = 0$

$$\Delta_f H^\circ(\text{C, graphite}) = 0.$$

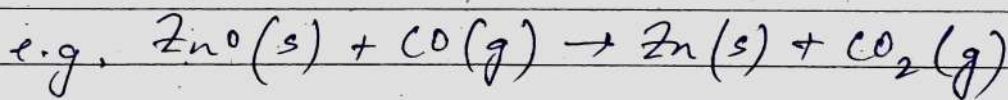
→ The standard enthalpy of formation of a compound is the change in the standard enthalpy when 1 mole of the compound is formed from the requisite amount of its reactants in their stable states of aggregation.



$$\begin{aligned} \Delta_f H^\circ(\text{HBr}, \text{g}) &= \sum_B \nu_B H_m^\circ(\text{B}) \\ &= H_m^\circ(\text{HBr}, \text{g}) - \frac{1}{2} H_m^\circ(\text{H}_2, \text{g}) \\ &\quad - \frac{1}{2} H_m^\circ(\text{Br}_2, \text{g}) \end{aligned}$$



$$\begin{aligned} \Delta_f H^\circ(\text{SO}_2, \text{g}) &= H_m^\circ(\text{SO}_2, \text{g}) - H_m^\circ(\text{S, rhombic}) \\ &\quad - H_m^\circ(\text{O}_2, \text{g}) \end{aligned}$$



If  $\Delta_f H^\circ(\text{ZnO}, \text{s}) = -350 \text{ kJ mol}^{-1}$

$$\Delta_f H^\circ(\text{CO}, \text{g}) = -110 \text{ kJ mol}^{-1}$$

$$\Delta_f H^\circ(\text{CO}_2, \text{g}) = -390 \text{ kJ mol}^{-1}$$

Then,  $\Delta_r H^\circ = \sum_B \nu_B \Delta_f H^\circ(\text{B})$

$$\begin{aligned} &= \Delta_f H^\circ(\text{Zn}, \text{s}) + \Delta_f H^\circ(\text{CO}_2) \\ &\quad - \Delta_f H^\circ(\text{ZnO}, \text{s}) - \Delta_f H^\circ(\text{CO}, \text{g}) \end{aligned}$$

[Note that  $\Delta_f H^\circ(\text{Zn}, \text{s}) = 0$  as defined earlier]

→ Hess' Law of constant heat summation: →

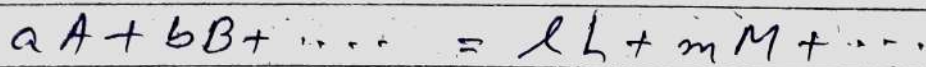
The heat involved in a given chemical equation is the same whether the process occurs in a single step or multiple steps.

→ Thus if a given chemical equation is reversed, the numerical value of  $\Delta_r H$  remains the same but its sign changes. (Lavoisier & Laplace law)

→ Kirchoff's relation: →

It gives the variation of enthalpy of a reaction with temperature ( $T$ ).

For a general reaction:



we can write

$$\Delta_r H = \sum_B \sum_B H_m(B)$$

$$= (lH_{m,L} + mH_{m,M} + \dots)$$

$$- (aH_{m,A} + bH_{m,B} + \dots)$$

$$\therefore \left. \frac{\partial \Delta_r H}{\partial T} \right|_P = \left\{ l \left( \frac{\partial H_{m,L}}{\partial T} \right)_P + m \left( \frac{\partial H_{m,M}}{\partial T} \right)_P + \dots \right\}$$

$$- \left\{ a \left( \frac{\partial H_{m,A}}{\partial T} \right)_P + b \left( \frac{\partial H_{m,B}}{\partial T} \right)_P + \dots \right\}$$

Again,  $\left( \frac{\partial H}{\partial T} \right)_P = C_p$ .

$$\therefore \left( \frac{\partial \Delta_r H}{\partial T} \right)_P = \left[ l C_{p,m}(L) + m C_{p,m}(M) + \dots \right] - \left[ a C_{p,m}(A) + b C_{p,m}(B) + \dots \right]$$

Equation (1)

Since,  $\Delta_r H = \sum_B \nu_B H_m(B)$

$$\Rightarrow \left( \frac{\partial \Delta_r H}{\partial T} \right)_P = \sum_B \nu_B \left( \frac{\partial H_m(B)}{\partial T} \right)_P$$

$$= \sum_B \nu_B C_{p,m}(B)$$

$$= \Delta_r C_p$$

Equation (1) reduces to

$$\left( \frac{\partial \Delta_r H}{\partial T} \right)_P = \Delta_r C_p$$

$$\therefore d(\Delta_r H) = \Delta_r C_p dT \text{ at const. } p.$$

$$\therefore \int d(\Delta_r H) = \int \Delta_r C_p dT$$

$$\Rightarrow \boxed{\Delta_r H = \int \Delta_r C_p dT + I,}$$

Where  $I = \text{const. of integration.}$

$\Rightarrow$  This is Kirchoff's relation. It has 2 possibilities.

(1)  $C_p$  does not depend on  $T$ .

$$\Rightarrow \Delta_r H = \Delta_r C_p (\Delta T) + I$$

$$\text{i.e. } \Delta_r H_{T_2} - \Delta_r H_{T_1} = \Delta_r C_p (T_2 - T_1)$$

(2)  $C_p$  depends on  $T$ .

$$C_{p, m} = a' + b'T + c'T^2 + \dots$$

where  $a/b/c$  are constants.

$$\therefore \Delta_r C_p = (\Delta_r a') + (\Delta_r b')T + (\Delta_r c')T^2 + \dots$$

$$\text{Now, } \Delta_r H = I + \int \Delta_r C_p dT$$

$$\therefore \Delta_r H = I + \int \left\{ (\Delta_r a') + (\Delta_r b')T + (\Delta_r c')T^2 + \dots \right\} dT$$

$$\Rightarrow \Delta_r H = I + \Delta_r a' T + \Delta_r b' \frac{T^2}{2} + \Delta_r c' \frac{T^3}{3} + \dots$$

$$\Rightarrow \text{Unit of } \Delta_r H = \text{K} \cdot \text{J mol}^{-1}$$

$$\text{Unit of } \Delta_r C_p = \text{J mol}^{-1} \text{K}^{-1}$$

[Note that the constant  $I$  can be easily evaluated if we know the value of  $\Delta_r H$  at a particular temperature say  $298 \text{ K}$ ].