

CHEMICAL  
THERMODYNAMICS

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**C3 Calculation of Enthalpy of Reaction :**

1. On the basis of enthalpy of formation value

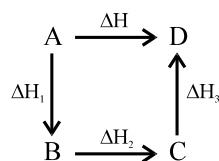
$$\Delta H = \sum \Delta H_f (\text{product}) - \sum \Delta H_f (\text{Reactant})$$

2. On the basis of bond energies of reactants

$$\Delta H = \{\text{sum of bond energies of reactants} - \text{sum of bond energies of products}\}$$

**C4 HESS'S LAW**

The total enthalpy change of a reaction is the same regardless of whether the reaction is completed in one step or in several steps.



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

**C5 Physical Meaning of Enthalpy**

From the above discussions, it is clear that Enthalpy is the total heat stored with the system and it is an extensive property i.e, it depends upon the nature as well as on the amount of the substance. Like internal energy, its absolute value can not be calculated. We can only determine the change in enthalpy through the heat of reaction. If  $H_r$  and  $H_p$  are enthalpies of reactants and products then

$$H_p - H_r = \Delta H = \text{heat of reaction}$$

Hence, enthalpy is a state function.

Exothermic and Endothermic reactions

Depending upon the nature of heat exchanged, the chemical reactions are of two types.

**C6 Bond Energy : Origin of Enthalpy change in a Reaction**

It is known that a chemical reaction involves the breaking of one or more bonds in the reactants and the formation of one or more bonds in the products. The bond breaking process is purely endothermic and the bond formation is an exothermic process. Therefore, the net heat change during any chemical reaction (enthalpy change) is given as :

$$\Delta H = \sum (\text{B.E.})_{\text{Reactants}} - \sum (\text{B.E.})_{\text{Products}}$$

**Calculation of Resonance Energy :**

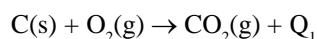
If a compound undergo resonance its experimental heat of formation and theoretical heat of formation will be different. Subtraction of  $\Delta H_{f(\text{exp})}$  and  $\Delta H_{f(\text{th})}$  is equal to resonance energy.

**C7 Different types of Heat of Reactions**

- (a) (i)
- Heat of Formation or Enthalpy of Formation**

It is the amount of heat evolved or absorbed when one g mole of a substance is formed from its constituent element e.g.

Formation of  $\text{CH}_4$



**(ii) Standard Heat of Formation (Q<sub>f</sub>)**

A substance is said to be in its standard state when it is present at 298 K (i.e. 25°C) under one atmospheric pressure.

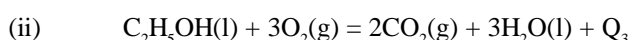
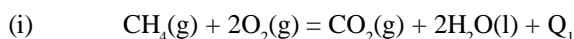
Standard heat of formation is the amount of heat evolved or absorbed when one mole of substance is formed from its elements in their standard states i.e., at 298 K and 1 atm.

“Conventionally, the heat of formation of element in its elemental state is zero”.

**(b) Heat of Combustion**

It is the amount of heat evolved when one mole of a compound (or any substance) is completely oxidised (or burnt) in the presence of oxygen.

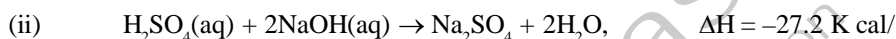
The heat of combustion is represented by an equation which refers the one mole of substance used in combustion e.g.

**Calorific Value of a fuel**

It is the amount of heat or energy released when one gram of a fuel is completely burnt in oxygen.

**(c) Heat of Neutralisation**

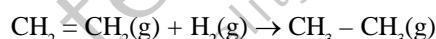
It is the amount of heat change (evolved) when 1 g equivalent of an acid in its aqueous and dilute solution is completely neutralised by a base through its dilute solution\* and vice versa. Various examples are :



But if in this process, either a weak acid or a weak base is involved, the heat of neutralisation is always less than 13.6 kcal/eq.

**(d) Heat of Hydrogenation**

It is the amount of heat change (evolved) when one mole of an unsaturated organic compound is completely hydrogenated.

**(e) Heat of Hydration**

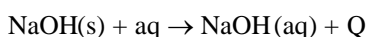
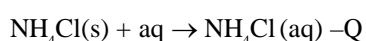
It is the amount of heat change when one mole of an anhydrous salt combines with the required number of moles of water to form its hydrate. e.g.



$$\Delta H_{\text{hydration (Anhydrous salt)}} = \Delta H_{\text{solu. (anhydrous salt)}} - \Delta H_{\text{solu. (Hydrated salt)}}$$

**(f) Heat of Solution**

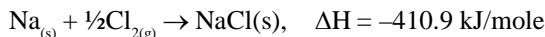
It is the amount of heat change when one mole of a substance is dissolved in such a large quantity of solvent so that further dilution does not give any further heat change e.g.,



(g) **Born Haber Cycle**

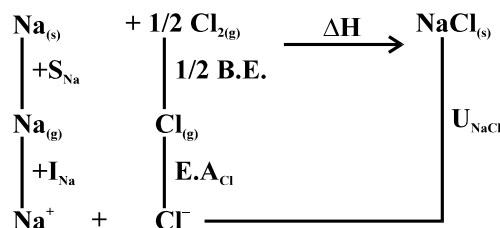
Lattice energies are calculated by employing energies involved in the various steps leading to the formation of an ionic compound. These steps can be shown graphically as a cycle hence the name Born - Haber cycle.

Let us take an example of formation of an ionic compound NaCl, by the reaction of solid Na and gaseous chlorine at 25°C and 1 atm. This process evolves 410.9 kJ/mole



This reaction consists of no. of steps. According to the principle of conservation of energy, the algebraic sum of the individual energy changes during various steps must be same as that of the overall change in energy.

The various steps can be represented by Born Haber Cycle as,

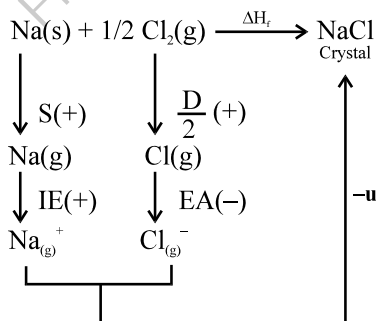


Hence the overall change in the reaction is

$$\Delta H = S + I + \frac{\text{B.E.}}{2} + \text{E.A.} + U \quad [\text{EA and U is -ve}]$$

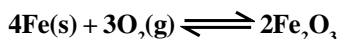
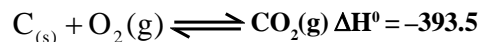
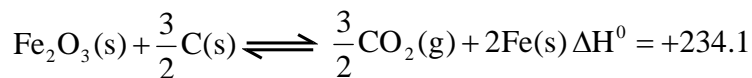
**Practice Problems :**

- $\Delta H_f^\circ$  for  $\text{CO}_2(\text{g})$ ,  $\text{CO}(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are respectively  $-339.5$ ,  $-110.5$  and  $-240.8 \text{ kJ, Mol}^{-1}$ . The standard enthalpy change in (kJ) for the reaction  $\text{CO}_2(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{CO}(\text{g}) + \text{H}_2\text{O}(\text{g})$  is  
 (a) 524.1                      (b) -11.8                      (c) -262.5                      (d) -41.2
- Given that  
 $\text{C} + \text{O}_2 \rightarrow \text{CO}_2; \quad \Delta H^\circ = -x \text{ kJ}$   
 $2\text{CO} + \text{O}_2 \rightarrow 2\text{CO}_2; \quad \Delta H^\circ = -y \text{ kJ}$   
 then enthalpy of formation of  $\text{CO}(\text{g})$  is  
 (a)  $y - 2x$                       (b)  $(2x - y)/2$                       (c)  $(y - 2x)/2$                       (d)  $(x - y)/2$
- Let us study the formation of NaCl then  $\Delta H_f$  of NaCl is



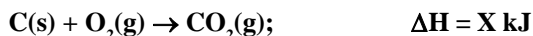
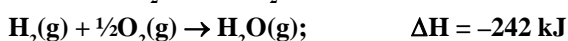
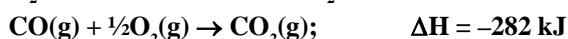
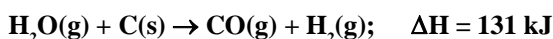
- |     |                                  |     |                                  |
|-----|----------------------------------|-----|----------------------------------|
| (a) | $S + \frac{1}{2}D + IE + EA + U$ | (b) | $S + \frac{1}{2}D + IE - EA + U$ |
| (c) | $S + \frac{1}{2}D - IE + EA + U$ | (d) | $S + \frac{1}{2}D + IE - EA - U$ |

4. Heat of hydrogenation of cyclohexene is  $x$  and that of benzene is  $y$ . Hence resonance energy of benzene is  
 (a)  $x - 3y$  (b)  $x + y$  (c)  $x - y$  (d)  $3x - y$
5. At  $25^\circ\text{C}$  the standard enthalpies in  $\text{kJ mol}^{-1}$  for following two reactions



is calculated as

- (a)  $3(-393.5) - 2(234.1)$  (b)  $-393.5 - 234.1$   
 (c)  $\frac{3}{2}(-393.5) + 234.1$  (d)  $\frac{3}{2}(-393.5) - 234.1$
6. Heat of neutralisation of NaOH and HCl is  $-57.46 \text{ kJ/equivalent}$ . The heat of ionisation of water will be  
 (a)  $-57.46 \text{ kJ/mol}$  (b)  $57.46 \text{ kJ/mol}$   
 (c)  $-114.92 \text{ kJ/mol}$  (d)  $114.92 \text{ kJ/mol}$
7. Heat released in neutralization of strong acid and strong base is  $13.4 \text{ kcal/mol}$ . The heat released on neutralization of NaOH with HCN is  $2.9 \text{ kcal/mol}$ , then  $\Delta H^\circ$  of ionization of HCN in water is  
 (a)  $10.5 \text{ kcal}$  (b)  $16.3 \text{ kcal}$  (c)  $9.5 \text{ kcal}$  (d)  $11.5 \text{ kcal}$
8. Based on the following thermochemical equations

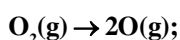
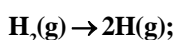
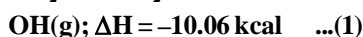
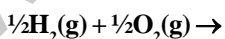


The value of  $X$  will be

- (a)  $-393 \text{ kJ}$  (b)  $-655 \text{ kJ}$  (c)  $+393 \text{ kJ}$  (d)  $+655 \text{ kJ}$
9. The  $\Delta H^\circ_f$  for chloride ion from the following data is  
 $\frac{1}{2}\text{H}_2(\text{g}) + \frac{1}{2}\text{Cl}_2(\text{g}) \rightarrow \text{HCl}(\text{g}) \quad \Delta H^\circ_f = -92.4 \text{ kJ}$   
 $\text{HCl}(\text{g}) + \text{aq} \rightarrow \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}); \quad \Delta H^\circ = -74.8 \text{ kJ}$   
 $\Delta H^\circ_f \text{H}^+(\text{aq}) = 0.0 \text{ kJ}$   
 (a)  $-17.2 \text{ kJ}$  (b)  $18.4 \text{ kJ}$  (c)  $19.2 \text{ kJ}$  (d)  $-167.2 \text{ kJ}$

10. The standard enthalpy of combustion at  $25^\circ\text{C}$  of  $\text{H}_2$ ,  $\text{C}_6\text{H}_{10}$  and cyclohexane ( $\text{C}_6\text{H}_{12}$ ) are  $-241$ ,  $-3800$ ,  $-3920 \text{ kJ mol}^{-1}$  respectively. The heat of hydrogenation of cyclohexene ( $\text{C}_6\text{H}_{10}$ ) is  
 (a)  $121 \text{ kJ}$  (b)  $150 \text{ kJ}$  (c)  $-121 \text{ kJ}$  (d) none
11. The dissociation energy of methane is  $360 \text{ kcal mol}^{-1}$  and that of ethane is  $620 \text{ kcal mol}^{-1}$ . The C – C bond energy is  
 (a)  $210$  (b)  $130$  (c)  $180$  (d)  $80$

12. The enthalpy change for the following reactions at  $25^\circ\text{C}$  are given below :



The O – H bond energy in hydroxyl radical is

- (a)  $121.31 \text{ kcal}$  (b)  $116.15 \text{ kcal}$  (c)  $110.11 \text{ kcal}$  (d)  $111.23 \text{ kcal}$

[Answers : (1) b (2) c (3) d (4) d (5) a (6) b (7) a (8) a (9) d (10) c (11) d (12) a]

**C8 First law of Thermodynamics**

Energy may be converted from one form to another, but it is impossible to create or destroy it. There are various ways of enhancing the first law of thermodynamics. Some of the selected statements are given below :

**C9 Mathematical Formulation of the First Law**

Suppose a system absorbs a quantity of heat  $q$  and its state change from A to B. This heat is used up.

- i) In increasing the internal energy of the system i.e.,  $\Delta E = E_B - E_A$
- ii) To do some external work 'w' by the system on its surroundings.

From the first law, we get.

Heat absorbed by the system = its internal energy + work done by the system.

$$\therefore q = \Delta E + w \quad \dots 1$$

The sign convention : According to latest S.I. convention,  $w$  is taken as negative if work is done by the system whereas it is taken as positive if work is done on the system. When heat is given by the system to surrounding it is given as negative sign. When heat is absorbed by the system from the surrounding then positive sign is given

- iii)  $q$  and  $w$  are not state function because changes in their magnitude is dependent on the path by which the change is accomplished. Mathematically  $q$  &  $w$  are not exact differential and we always write the inexact - differential by  $\delta q$ ,  $\delta w$  etc.
- iv) For a cyclic process, the change in the internal energy of the system is zero because the system is brought back to the original condition.

$$\oint \delta q = \oint \delta w \quad \text{i.e. the total work obtained is equal to the net heat supplied.}$$

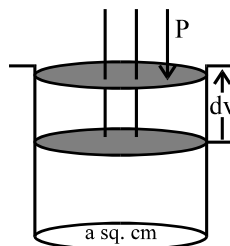
- v) In an isolated system, there is no heat exchange with the surrounding i.e.  $dQ = 0$

$$\therefore dE + dW = 0$$

$$\text{or } dw = -dE$$

**C10 Work in Reversible Process :**

- a) Expansion of a gas



Suppose  $n$  moles of a perfect gas is enclosed in a cylinder by a friction less piston. The whole cylinder is kept in large constant temperature bath at  $T_K$ . Any change that would occur to the system would be isothermal.

$$\therefore w = P \cdot dV$$





$$W = C_v \left( \frac{P_1 V_1}{R} - \frac{P_2 V_2}{R} \right) = \frac{C_v}{R} (P_1 V_1 - P_2 V_2)$$

or 
$$W = \frac{P_1 V_1 - P_2 V_2}{\gamma - 1}$$

(e) **Isochoric Process** :  $dW = 0$

**Limitations of first Law of Thermodynamics**

1. This law fails to tell us under what conditions and to what extent it is possible to bring about conversion of one form of energy into the other.
2. The first law fails to contradict the non-existence of a 100% efficient heat engine or a refrigerator.

**C11 Second law of thermodynamics**

It has been stated in several forms as follows.

- i) All the spontaneous process are irreversible in nature.
- ii) The entropy of universe is always increasing in the course of every spontaneous process.
- iii) Spontaneous or natural process are always accompanied with an increasing in entropy.