CONTENT

1. Introduction

It has been observed that energy in the form of heat is, in general, either absorbed or released due to chemical change. This is mainly due to the breaking of bonds in the reactants and formation of new bonds in the products. ***The study of thermal changes accompanying chemical transformations is known as thermo chemistry.*** The practical application of the first law of thermodynamics is thermochemistry. Thermochemical data obtained through experimental measurements is helpful in obtaining enthalpies and internal energies of the substances and for calculating the bond energies of various inter- atomic bonds. There are two types of thermal changes occurs, firstly, those in which the surroundings gain heat from the system are called **exothermic**. Secondly, those in which the surroundings lose heat to the system are said to be **endothermic**.

2. Heat of Reaction

Heat of Reaction *of a chemical reaction is the difference between the heat contents of the products and the reactant when Stoichiometric gram molecular weights of the reactants in the chemical equation have reacted completely under standard condition*. It is signified by ΔH°.

$$\Delta H^\circ = Heat\ content\ of\ the\ products - Heat\ content\ of\ the\ reactants$$

Consider a reaction

$$A + B \rightarrow L + M \tag{1}$$

The heat of reaction is represented as,

$$\Delta H^o = H_l^{\ o} + H_M^{\ o} - H_A^{\ o} + H_B^{\ o} \tag{2}$$

$$\Delta H^o = (\Delta H_f^{\ o})_L + (\Delta H_f^{\ o})_M - (\Delta H_f^{\ o})_A + (\Delta H_f^{\ o})_B \tag{3}$$

Where, heats of formation of substances at standard state represented as $(\Delta H_f^{\ o})$

$$\Delta H^o = \sum(\Delta H_f^{\ o})_{products} - \sum(\Delta H_f^{\ o})_{reactants} \tag{4}$$

For example, the thermochemical equation

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \qquad \Delta H = -68.3\ Kcal \tag{5}$$

indicates that when 2 g mole of gaseous hydrogen combined with 1 g mole of gaseous oxygen to produce 2 g mole of liquid water and 68.3 Kcal decreases the heat content of the system. Hence, the heat of reaction is -68.3 Kcal and reaction is endothermic. Similarly, the thermochemical equation

$$C(s) + 2S(s) \rightarrow CS_2(g) \qquad\qquad \Delta H = +19.8\ Kcal \qquad\qquad\qquad (6)$$
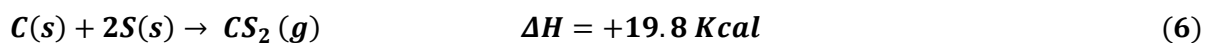
when 1 g of carbon react with 5.4 g of sulphur to give 6.4 g of liquid carbon disulphide, the heat content of the system increases by 19.8 Kcal. Therefore, the heat of reaction is +19.8 Kcal and reaction is exothermic.
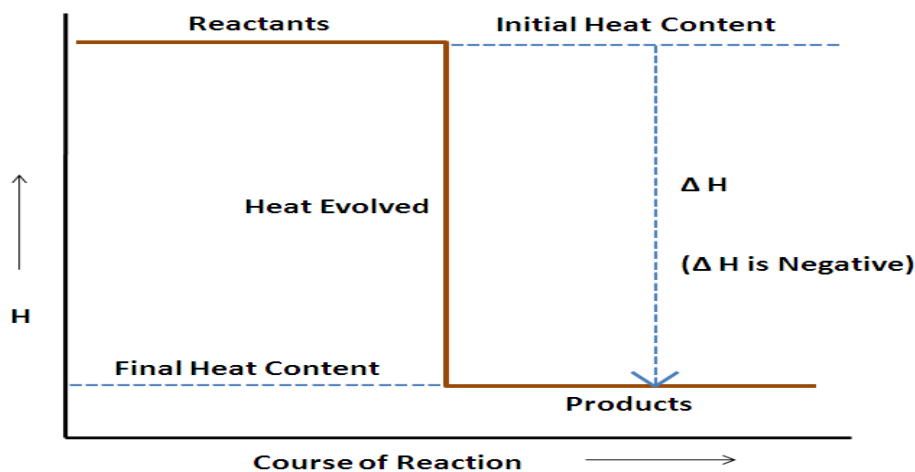
(a) Exothermic
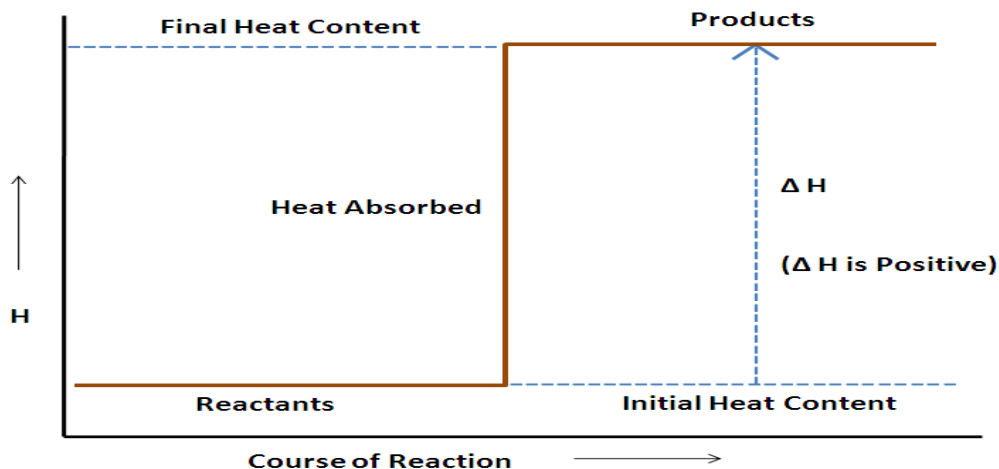
(a) Endothermic

Figure 1. Illustration of sign convention for heat of reaction (Δ H)

3. Hess's Law of Constant Heat Summation

Hess's law is defined as: the enthalpy change associated with a given chemical change is always constant and independent of the time taken and the intermediate steps involved.

Or

The value of enthalpy change for a reaction will be independent of the nature and number of intermediate reaction steps.

Let us suppose that a substance M can be changed into Z directly

$$M \rightarrow Z + Q_A \tag{7}$$

and the heat evolved in this reaction is Q_A Kcal. Now, suppose the same chemical reaction takes place in several step as follows:

$$M \rightarrow R + q_i \tag{8}$$

$$R \rightarrow S + q_j \tag{9}$$

$$S \rightarrow Z + q_k \tag{10}$$

The total evolution of heat $= q_i + q_j + q_k = Q_B$

According to Hess's law, $Q_A = Q_B$

4. Application of Hess's Law

Important applications of the Hess's law are following:

i. Determination of enthalpy of formation.

Determine the enthalpy of formation by directly or indirectly. By using the application of Hess's law, we can indirectly determine the heat or enthalpy of formation. Consider an example, when the combustion/oxidation of carbon to give carbon dioxide directly or the combustion/oxidation of carbon to give carbon monoxide first and further combustion/oxidation to yield carbon dioxide. It has been found that the total heat evolved is approximately equal or same in both cases.

Ist way:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H_1 = -94.05\ Kcal \qquad (11)$$

2nd way:

Step 1: $\qquad C + \frac{1}{2}O_2 \rightarrow CO \qquad \Delta H_2 = -26.42\ Kcal \qquad (12)$

Step 2: $\qquad CO + \frac{1}{2}O_2 \rightarrow CO_2 \qquad \Delta H_3 = -67.71\ Kcal \qquad (13)$

Overall reaction:

$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -94.13\ Kcal \qquad (14)$$
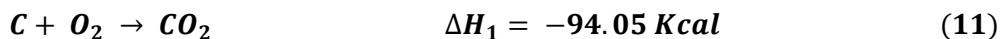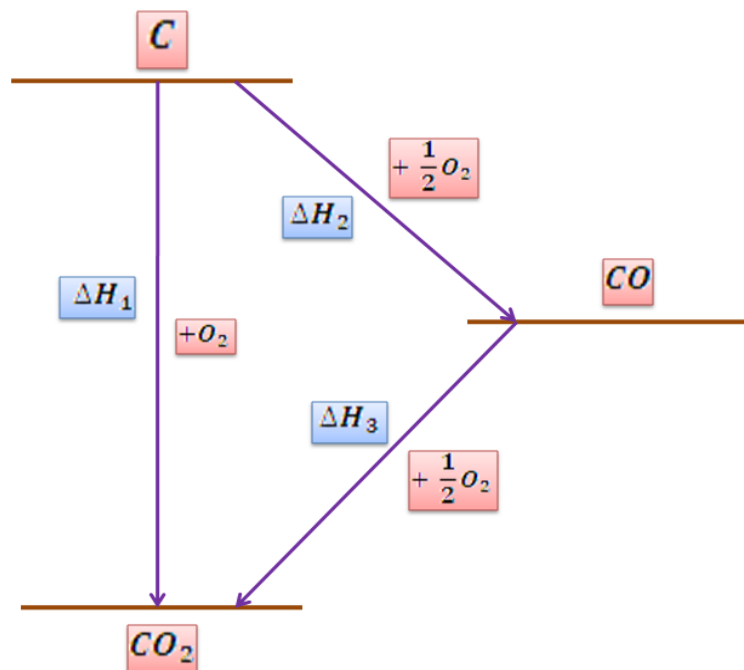
Figure2: Illustration of Hess's Law

According to Hess's Law, $\Delta H_1 = \Delta H_2 + \Delta H_3$

Enthalpy of Formation, $\Delta H = \Delta H_2 + \Delta H_3$

$\Delta H = -26.42 - 67.71 = -94.13$ Kcal

ii. Determination of enthalpy of transition

The following example will explain the heat of transition of C (graphite) to C (diamond).

$$C\ (graphite) + O_2\ (g) \rightarrow CO_2\ (g) \qquad\qquad \Delta H_{Comb.} = -93.69\ Kcal \qquad\qquad (15)$$

$$C\ (diamond) + O_2\ (g) \rightarrow CO_2\ (g) \qquad\qquad \Delta H_{Comb.} = -94.14 Kcal \qquad\qquad (16)$$

Substracting (16) from (15), we get

$$C\ (graphite) \rightarrow C\ (diamond) \qquad\qquad \Delta H = +0.45\ Kcal \qquad\qquad (17)$$

Hence, enthalpy of transition of graphite into diamond is +0.45 Kcal.

iii. Determination of enthalpy changes of slow reactions.

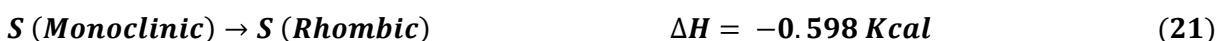This law is useful in determining enthalpies of many chemical reactions which take place very slowly. Consider an example of transformation of rhombic sulphur (S_R) into monoclinic sulphur (S_M) is extremely slow reaction, so, direct measurement of change in enthalpy is not possible. However, enthalpies of combustion are known for rhombic and monoclinic sulphur.

$$S\,(Rhombic) + \ O_2\,(g) \rightarrow SO_2\,(g) \qquad\qquad \Delta H = \ -70.83\,Kcal \qquad\qquad (18)$$

$$S\,(Monoclinic) + \ O_2\,(g) \rightarrow SO_2\,(g) \qquad\qquad \Delta H = \ -71.43\,Kcal \qquad\qquad (19)$$

$$S\,(Rhombic) \rightarrow S\,(Monoclinic) \qquad\qquad \Delta H = \ +0.598\,Kcal \qquad\qquad (20)$$

$$S\,(Monoclinic) \rightarrow S\,(Rhombic) \qquad\qquad \Delta H = \ -0.598\,Kcal \qquad\qquad (21)$$

The rhombic sulphur transformed into monoclinic sulphur with absorption of +0.598 Kcal of heat.

5. Enthalpy of Formation

Enthalpy of Formation is defined as the heat change (usually the heat evolved) when 1 mole of a substance is formed from the requisite quantities of its elements under standard condition. For example, the thermochemical equation

$$2C\,(s) + \ H_2(g) \rightarrow \ C_2H_2\,(g) \qquad\qquad \Delta H = \ +53.14\,Kcal \qquad\qquad (22)$$

$$C\,(s) + \ O_2(g) \rightarrow \ CO_2(g) \qquad\qquad \Delta H = \ -94.05\,Kcal \qquad\qquad (23)$$
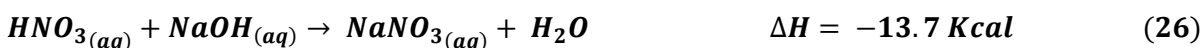
6. Enthalpy of Combustion

Enthalpy of Combustion of a compound or an element is the change in heat content when 1 g molecule of the substance is burnt completely in excess of oxygen. Since, *combustion reactions are always exothermic, so enthalpy of combustion is always negative.* Thus, enthalpy of combustion of methane is -19.0 Kcal.

$$CH_4\,(g) + \ 2\,O_2\,(g) \rightarrow \ CO_2\,(g) + \ 2H_2O\,(g) \qquad\qquad \Delta H = \ -19.0\,Kcal \qquad\qquad (24)$$
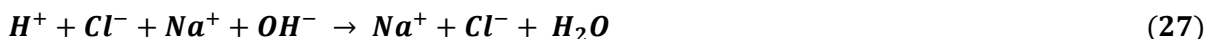
7. Enthalpy of Neutralization

*When aqueous solution of acids and bases react, heat is evolved. The value of enthalpy for the reaction in which 1 gram equivalent of an acid is neutralized by 1 gram equivalent of a base in dilute aqueous solution is known as the **Heat of neutralization** or an **enthalpy of neutralization** of acid.*

It found that the enthalpy of neutralization of any strong acid by a strong base is practically the same as shown in the following reactions

$$HCl_{(aq)} + NaOH_{(aq)} \rightarrow NaCl_{(aq)} + H_2O \qquad \Delta H = -13.7 \, Kcal \qquad (25)$$

$$HNO_{3(aq)} + NaOH_{(aq)} \rightarrow NaNO_{3(aq)} + H_2O \qquad \Delta H = -13.7 \, Kcal \qquad (26)$$

The constant value of -13.7 Kcal for the enthalpy of neutralization of a strong acid with a strong base indicates that the same chemical change is taking place in all these reactions. The neutralization of hydrochloric acid (HCl) by sodium hydroxide (NaOH) can be symbolized as:

$$H^+ + Cl^- + Na^+ + OH^- \rightarrow Na^+ + Cl^- + H_2O \qquad (27)$$

$$or \qquad H^+ + OH^- \rightarrow H_2O \qquad \Delta H = -13.7 \, Kcal \qquad (28)$$

Hence every neutralization reaction involves the combination of H$^+$ and OH$^-$ ions to form unionized water.

8. Enthalpy of Ionization

The enthalpy of neutralization of a strong acid with a strong base is always same which equivalent to -13.7 Kcal. The heat of neutralization of a weak acid or a weak base is not constant. This can be explained on the ground that in such cases, in addition to neutralization, the ionization or dissociation of the weak acid (or weak base) also take place.

*The amount of heat required (i.e. absorbed) for the ionization of 1 mole of the weak acid or the weak base (or in general any weak electrolyte) in dilute solution is called the **enthalpy of ionization** of that weak electrolyte at a particular temperature*

However, if either the acid or the base is weak or both are weak, **the heat of neutralization is less as some heat is used up to dissociate** the weak acid or the weak base. Consider an example, acetic acid (weak acid) is neutralized by sodium hydroxide solution

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O \qquad \Delta H = -13.25 \, Kcal \qquad (29)$$
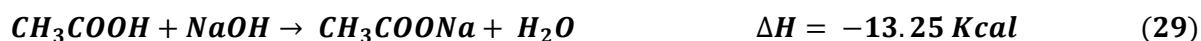
is in reality a two − stage process:

$$CH_3COOH \leftrightarrow CH_3COO^- + H^+ \qquad \Delta H = D \qquad (30)$$

Where D is the heat of dissociation and

$$H^+ + OH^- \rightarrow H_2O \qquad \Delta H = -13.7 \, Kcal \qquad (31)$$

The sum of equations (30) and (31) gives equation (29). Consequently

$$D + (-13.7) = -13.25$$

$$D = -13.25 + 13.7$$

$$\textit{Enthalpy of ionization}, \quad D = +0.45 \, Kcal$$

And, the neutralization of ammonium hydroxide solution (weak base) with hydrochloric acid

$$NH_4OH + HCl \rightarrow NH_4Cl + H_2O \qquad \Delta H = -12.3 \, Kcal \qquad (32)$$

$$NH_4OH \, (aq). \rightarrow NH_4{}^+ \, (aq) + OH^-(aq) \qquad \Delta H = D \qquad (33)$$

$$H^+ + OH^- \rightarrow H_2O \qquad \Delta H = -13.7 \, Kcal \qquad (34)$$

The sum of equations (33) and (34) gives equation (32).

$$D + (-13.7) = -12.3$$

$$D = -12.3 + 13.7$$

$$\textit{Enthalpy of ionization}, D = +1.4 \, Kcal$$

Hence, the enthalpy of ionization of NH_4OH is + 1.4 Kcal. Therefore, the enthalpy of ionization or enthalpy of dissociation of a weak acid or a weak base can be determined from the heat of neutralization data.

9. Enthalpy of Solution

Enthalpy of Solution *is defined as the change in heat content for a reaction when dissolved 1 g molecule of the substance in excess amount of water that any further dilution brings about no change in heat content*. Thus, the thermochemical equations

$$KCl\,(s) + aq\ \rightarrow KCl.\,aq \qquad\qquad \Delta H =\ +4.4\,Kcal \qquad\qquad (35)$$

$$MgSO_4(s) + aq\ \rightarrow MgSO_4.\,aq \qquad\qquad \Delta H =\ -20.28\,Kcal \qquad\qquad (36)$$

10. Integral Enthalpy of Solution

When a substance is dissolved, heat may be either liberated or absorbed depending on the relative amounts of energy which are used up in breaking down the crystal lattice on the one hand and the energy liberated during the hydration of the solute on the other hand. The quantity of heat evolved is not constant but varies with the concentration of the final solution. This may be due to a number of factors, e.g., the variation in the extent of hydration of the solute, and in some cases to the degree of dissociation.

The heat of solution of a substance also varies with the moles of water taken for dissolving one mole of the substance. *"The total heat evolved when dissolved 1 mole of a solute in a specified quantity of the solvent is known as its **Integral Enthalpy of Solution or Integral Heat of Solution** for the specified quantity of the solvent"*.

If the amount of solvent used is so large that a further addition of solvent no longer causes a change in the integral enthalpy of solution per mole of solute, is said to be **the heat of solution of substance at infinite dilution**. It is a limiting value of the integral heat of solution. It is sometime called **Total Heat of Solution**.

11. Differential Enthalpy of Solution

Differential enthalpy of solution is stated as the change in enthalpy required when dissolved 1 mole of a solute in large volume of solution of a specified concentration that further 1 mole of solute is added does not affect the concentration.

Consider a solution of one mole of potassium nitrate in 100 moles of water. If we take 20 litres of solution and dissolve one mole of potassium nitrate in this solution that produced the heat change is called differential enthalpy of solution of potassium nitrate when the solution is already at the specified concentration.

12. Enthalpy of Dilution

*When a solution of 1 mole of a solute is diluted from one concentration to another concentration that produced enthalpy change is called **enthalpy of dilution**.* For example,
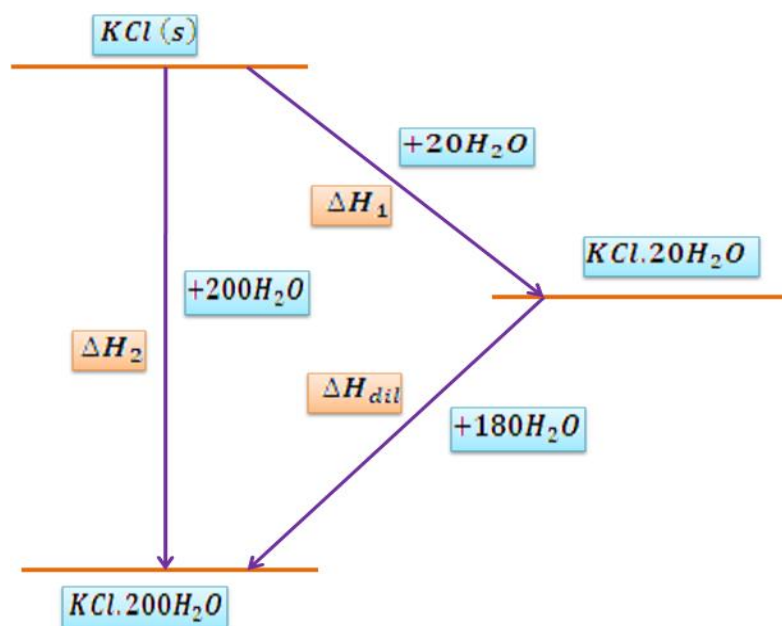
$$KCl\,(s) + 20H_2O \;\rightarrow\; KCl.20H_2O \qquad\qquad \Delta H_1 = +3.78\,Kcal \qquad\qquad (37)$$

$$KCl\,(s) + 200H_2O \;\rightarrow\; KCl.200H_2O \qquad\qquad \Delta H_2 = +4.4\,Kcal \qquad\qquad (38)$$

Figure 3: illustration of enthalpy of dilution by Hess's law

According to Hess's Law, $\Delta H_2 = \Delta H_1 + \Delta H_{dil}$

$Enthalpy\ of\ dilution,\ \Delta H_{dil} = \Delta H_2 - \Delta H_1$

13. Integral Enthalpy Dilution

Integral enthalpy of dilution is defined as enthalpy change occur when a solution containing 1 g mole of a solute is diluted from one concentration to another concentration.

14. Enthalpy of Hydration

Enthalpy of Hydration is the change in enthalpy when 1 mole of an anhydrous substance mixed with the requisite quantity of moles of water to give a specified hydrate. For example,
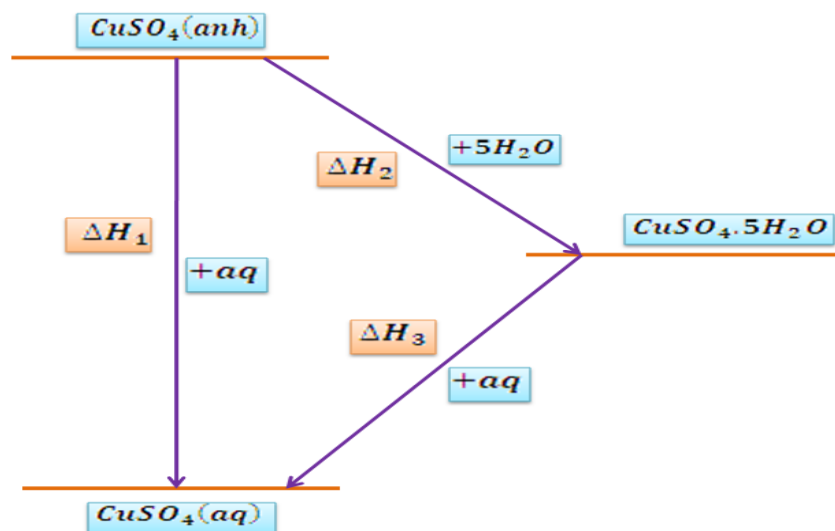
$$CuSO_4 + 5H_2O \rightarrow CuSO_4.5H_2O \qquad \Delta H = -18.5\ Kcal \qquad (39)$$

Figure 4: demonstration of enthalpy of Hydration by Hess's law

According to Hess's Law, $\Delta H_1 = \Delta H_2 + \Delta H_3$

ΔH₁ and **ΔH₃** are determined experimentally and enthalpy of hydration, i.e. **ΔH₂** can be calculated.

Enthalpy of hydration, $\Delta H_2 = \Delta H_1 - \Delta H_3$

15. Enthalpy of Transition

Enthalpy of transition is defined as the change in enthalpy during the transition of 1 mole of

the substance from one allotropic form to another. For example, thermochemical equation

$$S_R \rightarrow S_M \qquad\qquad \Delta H = +0.08\ Kcal \qquad\qquad (40)$$

Where, S_R represents Rhombic Sulphur and S_M represents monoclinic Sulphur.

16. Enthalpy of Precipitation

The heat evolved when precipitation of 1 mole of a sparingly soluble substance by mixing of

diluted solutions of appropriate electrolytes is called **Enthalpy of Precipitation** of that

substance.

For a reaction,

$$BaCl_2(aq) + Na_2SO_4(aq) \rightarrow BaSO_4(s) + 2NaCl(aq) \qquad \Delta H = -4.64\ Kcal \qquad (41)$$
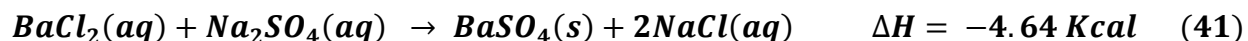
17. Enthalpy of Formation of the Bond or Bond Energy

The average amount of energy produced when 1 mole of bonds are formed from isolated gaseous atoms

*is known as **Enthalpy of Formation of the Bond or Bond Energy.***

The bond energies are very useful in calculating the heat of formation of any substance.

Consider an example, the C-H bond having bond energy is calculated as follows:

$$C\ (s) + 2H_2\ (g) \rightarrow CH_4\ (g) \qquad\qquad \Delta H_1 = -17.8\ Kcal \qquad\qquad (42)$$

$$C\ (s) \rightarrow C\ (g) \qquad\qquad \Delta H_2 = -171.3\ Kcal \qquad\qquad (43)$$

$$2H_2\ (g) \rightarrow 4H\ (g) \qquad\qquad \Delta H_3 = -207.1\ Kcal \qquad\qquad (44)$$

Where, ΔH_1, ΔH_2 and ΔH_3 represent enthalpy of formation of CH_4, enthalpy of sublimation of C and heat of dissociation of H_2, respectively.

ΔH_3 = 2 X -103.57 Kcal = -207.1 Kcal

These three equations give

$$C\ (g) + \ 4H\ (g)\ \rightarrow\ CH_4\ (g) \qquad\qquad \Delta H_4 = -360.6\ \textbf{Kcal} \qquad\qquad (45)$$

ΔH_4 = -171.3 - 207.1 - (- 17.8) = -360.6 Kcal

Thus, the heat of formation of four C-H bonds is -360.6 Kcal. Conversely, the heat of dissociation of four

C-H bonds would be +360.6 Kcal. Hence, the bond energy for each C-H bond is $\frac{-360.6}{4} =$

$$-90.15\ Kcal.$$

Consider an example of benzene, the (C=C), (C-C) and (C-H) bonds having bond enthalpies are 146.47

Kcal, 82.8 Kcal and 98.44 Kcal respectively. The experimentally calculated value for enthalpy of

formation of benzene is 1318.19 Kcal. Now, we calculate the enthalpy of formation of benzene on the

basis of Kekule structure.

From Kekule structure, it is seen that the formation of benzene require union of three (C=C),

three (C-C) and six(C-H) bonds.

$$\Delta H_{f\ (benzene)} = 3\ \times\ \Delta H_{C=C} + \ 3\ \times\ \Delta H_{C-C} + \ 6\times\ \Delta H_{C-H}$$

$$\Delta H_{f\ (benzene)} = 3\ \times 146.47 + \ 3\ \times 82.8 + \ 6\times\ 98.44$$

$$\Delta H_{f\ (benzene)} = 439.41 + 248.4 + 590.64 = 1278.45\ Kcal$$

The experimental value for $\Delta H_{f\ (benzene)}$ = 1318.19 Kcal. The difference 1318.19 -1278.45 = 39.74 Kcal is

the resonance energy of benzene.

18. Application of Bond Energy

I.   To calculate enthalpy of reaction

    II.   To calculate the resonance energy

    III.   To calculate enthalpy of formation of the substance.

19. Kirchhoff's Equation

Consider any process

$$A_{(reactants)} \rightarrow B_{(products)} \qquad (46)$$

The energy change at constant volume is given by

$$\Delta E = E_B - E_A \qquad (47)$$

The change in internal energy with temperature is

$$\left(\frac{\partial \Delta E}{\partial T}\right)_V = \left(\frac{\partial E_B}{\partial T}\right)_V - \left(\frac{\partial E_A}{\partial T}\right)_V \qquad (48)$$

By definition of C_V,

$$\left(\frac{\partial E}{\partial T}\right)_V = C_V \qquad (49)$$

$$\left(\frac{\partial \Delta E}{\partial T}\right)_V = (C_V)_B - (C_V)_A \qquad (50)$$

$$\left(\frac{\partial \Delta E}{\partial T}\right)_V = \Delta C_V \qquad (51)$$

The change in internal energy w. r. t. temperature is equivalent to the difference in the heat capacities of the products and the reactants at constant volume.

Similarly, the reaction carried out at constant pressure

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \left(\frac{\partial H_B}{\partial T}\right)_P - \left(\frac{\partial H_A}{\partial T}\right)_P \qquad (52)$$

Since, definition of C_P,

$$\left(\frac{\partial H}{\partial T}\right)_P = C_P \qquad (53)$$

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = (C_P)_B - (C_P)_A \tag{54}$$

$$\left(\frac{\partial \Delta H}{\partial T}\right)_P = \Delta C_P \tag{55}$$

Equations 51 & 55 are known as the **kirchhoff's equation**. Integrate above equation, we get,

$$\frac{\partial \Delta H}{\partial T} = \Delta C_P \tag{56}$$

$$d(\Delta H) = \Delta C_P dT \tag{57}$$

$$\int_{H_1}^{H_2} d(\Delta H) = \int_{T_1}^{T_2} \Delta C_P dT \tag{58}$$

$$\Delta H_2 - \Delta H_1 = \Delta C_P (T_2 - T_1) \tag{59}$$

Where, $$\Delta C_P = \sum C_{P\,(product)} - \sum C_{P(reactant)} \tag{60}$$

Where, ΔH_1 and ΔH_2 are the heats of reaction at constant pressure at temperature T_1 and T_2 respectively.