CHAPTER 5

ENERGETICS OF CHEMICAL REACTIONS

It is a matter of common observation that most of the things around us are in a continuous state of change or flux. These changes are important for all of us and we learn a great deal by looking at them and studying them carefully. One of the most observations is that all chemical changes are accompanied by important change in energy, that is energy is either absorbed or evolved. Heat energy is the most common form which is manifested in chemical reactions. Besides heat, other forms of energy are mechanical, electrical, chemical, radiant etc., which are stored in all substances.

A study based on the principle of conservation of energy is known as Thermodynamics. The laws of Thermodynamics are successfully used in Physics, Chemistry and Engineering.

Chemists are interested in the changes in materials and energy in the chemical reactions.

Chemical reactions which are accompanied by energy changes with the material changes, are generally known as Thermochemical reactions. In this chapter we are concerned with the energy changes taking place in chemical reactions in an elementary way. Thermochemical reactions are classified as (i) Exothermic reactions and (ii) Endothermic reactions.

(i) **Exothermic Reactions :** The chemical reactions which are accompanied by the liberation or emission of energy are called exothermic reactions. All combustion reactions are exothermic reactions.

e.g. $C + O_2 \longrightarrow CO_2 + \text{heat}$

$CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O + \text{heat}$

(ii) **Endothermic Reactions :** The chemical reactions are accompanied by the absorption of energy are called endothermic reactions.

e.g. $C + 2S + \text{heat} \longrightarrow CS_2$

$H_2 + I_2 + \text{heat} \longrightarrow 2H1$

The heat evolved or absorbed during chemical reactions depends upon (1) The amount of Chemical substances involved (2) The physical states of the substances involved (3) The temperature and (4) Whether the reaction occurs at constant pressure or constant volume.

5.1 THERMODYNAMIC TERMS (SYSTEM, SURROUNDINGS AND STATES)

The properties or changes of the matter are usually investigated by controlled experiments. Any real or imaginary portion of the universe or anything which is under examination or under consideration in the laboratory or elsewhere is called a system. The environments of a system or all the remaining portion of the universe which may act on the system are known as surroundings. The system and surroundings are separated from each other by real or imaginary boundries. For instance, when the hydrolysis of an ester is carried out in a reaction flask, placed in a thermostat then the contents of the flask is the system, the flask is the real boundry and the thermostat is the surrounding.

The properties of a system in bulk, rather than that of the part of the system, which are easily measurable are known as the macroscopic properties e.g. Pressure, temperature, volume, composition etc.

The properties of a system may be divided into two main groups (a) Intensive properties and (b) Extensive properties.

(a) **Intensive Properties :** It is a characteristic property of the system and is independent of the amount of material concerned. Density, pressure, temperature, viscosity, surface tension, refractive index, melting point, boiling point etc are the examples of Intensive properties.

(b) **Extensive Properties :** It is the property that depends upon the amount of the substance present in the system. The change in the extensive property is proportional to the change in the quantity of the material in the system. If the matter in a given system at a given condition is divided into two equal parts, the values of the extensive properties will become half of the original values. Mass, volume, Mole numbers, the Enthalpy, the entropy, the internal energy, the Gibb's free energy etc are the examples of extensive properties.

These Macroscopic properties give description of materials under a given set of experimental conditions. A system is said to be in a definite state when each of its properties has a definite value and thus the system is completely defined. The description of the system before it suffers any change is called as the initial state of the system while the description of the system after it undergoes a change is known as final state of the system. Changes in the system, therefore will be described by comparing the final and the initial states of the system. In other words, the change in state of a system is completely defined when its initial and final states are specified. For example if T_1 is the condition of temperature at the initial state and T_2 is the condition of temperature at the final state, then

$T_2 - T_1 = \Delta T$ which is the change in temperature of the system. Similarly, $V_2 - V_1 = \Delta V$ is the change in volume, $E_2 - E_1 = \Delta E$ is the change in the internal energy of the system and so on.

Thus,

Change in the property of a system = value of a property in the final state - value of the same property in the initial state.

5.2 FIRST LAW OF THERMODYNAMIC (ENERGY CONSERVATION)

First law of Thermodynamics was enunciated by Helmholtz in 1847. It states that energy can neither be created nor destroyed, although it may change from one form to another, in other words the total energy of a system and its surrounding must remain constant.

For the mathematical derivation of First law of Thermodynamics, imagine a system whose internal energy in the initial state is E_1, let a quantity of heat 'q' from the surroundings be absorbed by the system and does some work 'W' on the surroundings while the internal energy changes to E_2, due to heat and work operations, then the change in the internal energy $(E_2 - E_1)$, according to First law of thermodynamics is given by

$$E_2 - E_1 = \Delta E = q - W \quad \text{........................(i)}$$

This is the mathematical statement of first law of thermodynamics. ΔE depends only on the initial and final states of the system.

Pressure – Volume Work : Consider a cylinder of a gas having an area of cross-section 'A' fitted with a frictionless and weight less piston (Fig. 5.1). If the pressure on the piston is P, then the total force 'f' acting on the piston would be PA, since pressure is the force per unit area (P=f/A). If the piston goes up through a small distance 'dl', then the workdone δW is given by as,

$$\delta W = f \times dl = PAdl = Pdv$$

$$\text{where } Adl = dv$$

$$\text{Thus } W = P\Delta V$$

The value of workdone 'W' is substituted in eq (1), the equation of First law of Thermodynamics becomes as

$$\Delta E = q - P\Delta V$$

or

$$q = \Delta E + P\Delta V \quad \text{----------------} \quad (2)$$

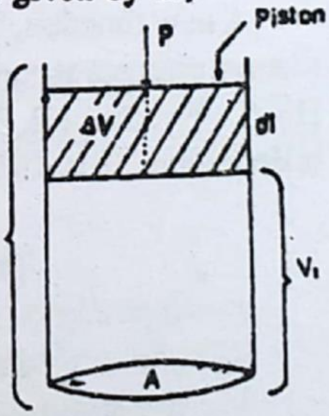

FIGURE 5.1

The absorption or evolution of heat during chemical reactions may take place (a) at constant volume and (b) at constant pressure. Let us consider these processes in some details.

(a) Process at Constant Volume : Let q_v be the heat absorbed at constant volume and at constant volume $\Delta V = 0$, So $P\Delta V$ also becomes zero, hence

$$q_v = \Delta E \quad \text{------------------------------} \ (3)$$

Thus in the process carried at constant volume, the heat absorbed or evolved is equal to the energy change i.e., ΔE.

(b) Process at Constant Pressure : Since most of the chemical reactions in the laboratory are carried out in open vessels, so chemists are more interested in the processes that take place at constant pressure.

Let q_p be the heat absorbed at constant pressure, then the eq. (2) remains same i.e.

$$q_p = \Delta E + P\Delta V$$

We know that $\Delta E = E_2 - E_1$ and $\Delta V = V_2 — V_1$, so

$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$
$$= E_2 + PV_2 — (E_1 + PV_1) \ \text{------------} \ (4)$$

A new function, 'H' called enthalpy (Heat content) is introduced to express thermal changes at constant pressure. This function is mathematically defined as $H = E + PV$. Since E, P and V are state functions, so 'H' is also state function and is dependent on the initial and final states.

Thus

$$E_2 + PV_2 = H_2$$
$$\text{and } E_1 + PV_1 = H_1$$

Substituting the values in eq. (4), we get

$$q_p = H_2 — H_1 = \Delta H \quad \text{---------} \ (5)$$
$$\therefore \Delta H = \Delta E + P\Delta V \quad \text{---------} \ (6)$$

5.3 Sign of ΔH

ΔH is the change in enthalpy. ΔH is the characteristic property of a system and depends on the initial and final states of a system and not on the means by which the changes are brought. For all exothermic processes, ΔH would be negative and for all endothermic process, ΔH is positive.

e.g. $C + O_2 \rightarrow CO_2 \qquad \Delta H = -394\ KJ\ mol^{-1}$

$C + 2S \rightarrow CS_2 \qquad \Delta H = +\ 117.6\ KJ\ mol^{-1}$

A summary of exothermic and endothermic reactions explained in terms of heat content is diagrammatized as follows:

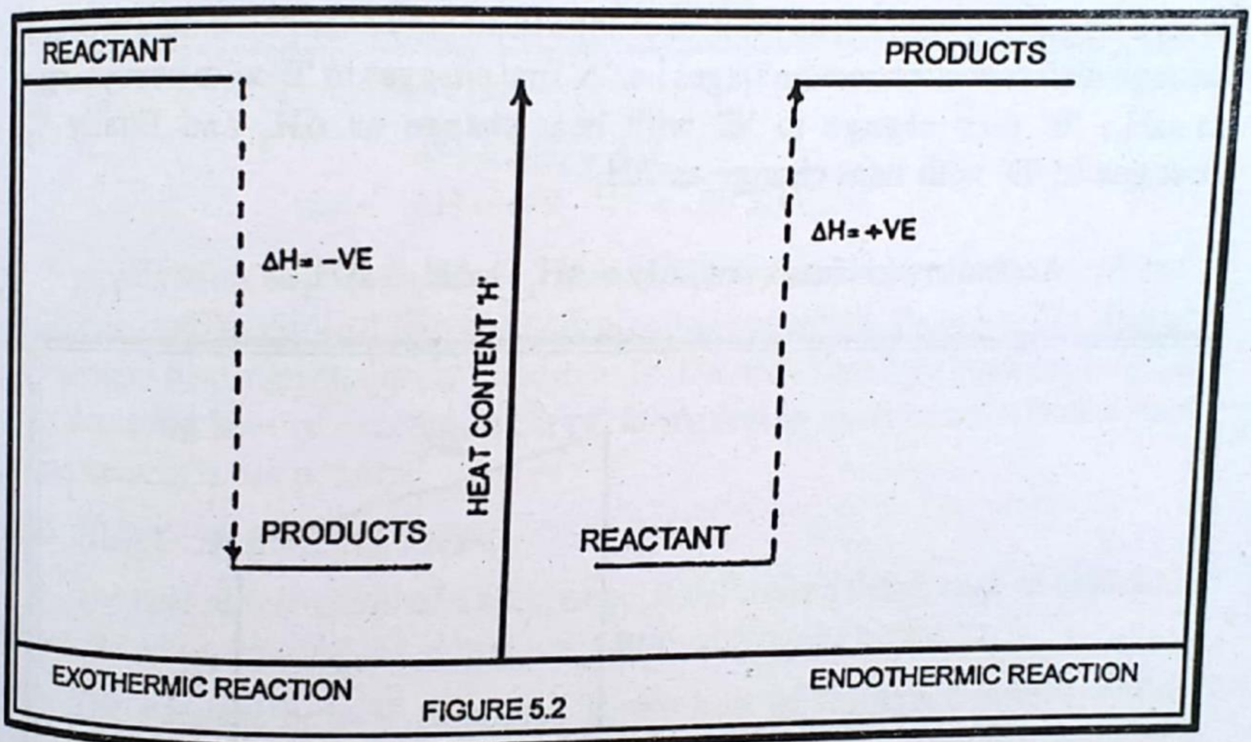

FIGURE 5.2

5.4 THERMOCHEMISTRY

The specific application of the first law of themodynamics is the study of chemical reactions is referred to as thermochemistry. Thermochemistry deals with the measurement or calculation of heat absorbed or given out in chemical reactions. The unit of energy is calorie and kilocalorie. The S.I units are however Joules and kilo joules.

(1 cal = 4.184J or 1Joule = 0.239 cal)

5.5 HESS'S LAW OF CONSTANT HEAT OF SUMMATION

G. H. HESS (1840) discovered a very important generalization which is known as Hess's law. It states that the heat evolved or absorbed in a given reaction must be independent of the particular manner in which the reaction takes place. It depends only on the initial and final states of the system. In other words, if a chemical reaction is made to take place in two or more different ways, whether in one or several steps, the amount of the total enthalpy change will be same, no matter by which method the change is brought about.

Consider a chemical reaction in which reactant 'A' changes to the product 'D' in a single step with ΔH as the heat change (Enthalpy change). It may proceed through different intermediate stages i.e. 'A' first changes to 'B' with heat change as ΔH_1, 'B' then change to 'C' with heat change as ΔH_2 and finally 'C' changes to 'D' with heat change as ΔH_3.

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

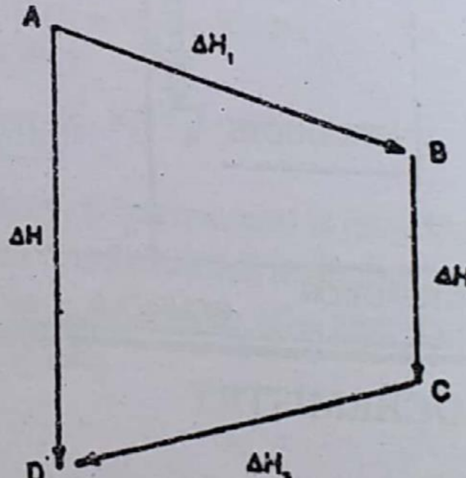

FIGURE 5.3

Illustration of the law is given by the following example :

Carbon dioxide gas reacts with excess of sodium hydroxide solution to give sodium carbonate with enthalpy or heat change about –90 KJ/mole. This reaction may easily be carried out via sodium bicarbonate formation in two steps. In the first step the enthalpy change is –49 KJ/mole and in the second step, the enthalpy change is –41 KJ/mole. It is given as follows:

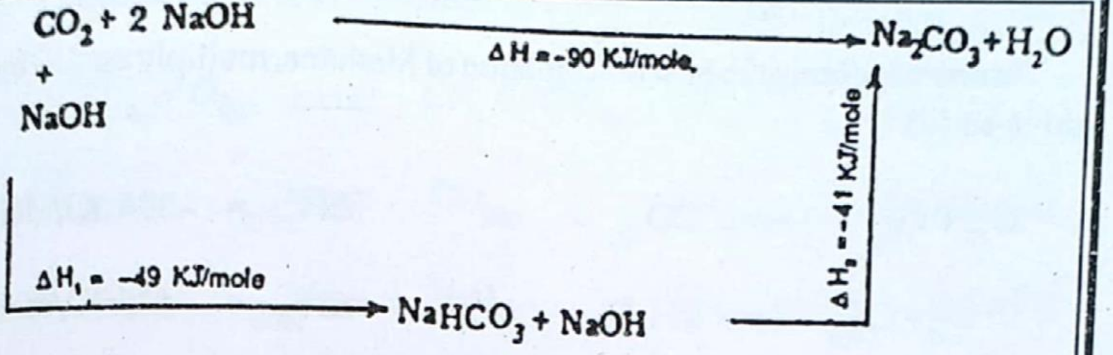

FIGURE 5.4

Hence according to Hess's law

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

$$\text{i.e.} \quad \Delta H = -49 - 41 = -90 \text{ KJ/mole}$$

Application of Hess's law:- Thermochemical equations may be added, subtracted and multiplied like ordinary algebraic equation, therefore Hess's law of constant heat summation is important in Thermochemistry because it helps in calculating heat of reaction, heat of formation in such cases where direct measurement is not possible.

5.6 HEAT OF FORMATION

The heat of formation of a compound is defined as the change of enthalpy when one gram mole of the substance is formed from its elements.

The standard heat of formation is the heat of formation when all the substances involved in the reaction are each at unit activity (i.e. at 25°C and one atmospheric pressure).

The heat of formation is generally represented by ΔH_F. For example, the heat of formation of CH_4 $(C + 2H_2)$ is –74.9 KJ/mole. It can be calculated from the following data:

(i) $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\qquad \Delta H_{25^\circ C} = ?$

(ii) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\qquad \Delta H_{25^\circ C} = -394$ KJ/mole

(iii) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\qquad \Delta H_{25^\circ C} = -286$-KJ/mole

(iv) $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\qquad \Delta H_{25^\circ C} = -890.34$ KJ/mole

Solution :

In order to obtain the heat of formation of Methane, multiply eg (iii) by 2 and add in eq (ii)

$$C_{(S)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_{25^\circ C} = -394 \text{ KJ/mole}$$

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(1)} \qquad \Delta H_{25^\circ C} = -572 \text{ KJ/mole}$$

$$C \;+ 2H_{2(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(1)} \qquad \Delta H_{25^\circ C} = -966 \text{ KJ/mole—(v)}$$

Finally subtracting eq (iv) from eq (v), we obtain

$$C + 2H_2 + \cancel{2O_2} \rightarrow C\cancel{O}_2 + 2H_2\cancel{O} \qquad \Delta H_{25^\circ C} = -966 \text{ KJ/mole}$$

$$\underset{-}{CH_4} + \underset{-}{\cancel{2O_2}} \rightarrow \underset{-}{\cancel{C}O_2} + \underset{-}{2\cancel{H_2}O} \qquad \Delta H_{25^\circ C} = -890.34 \text{ KJ/mole}$$

$$C + 2H_2 \rightarrow CH_4 \qquad \Delta H_{25^\circ C} = -75.66 \text{ KJ/mole}$$

This is the heat of formation of CH_4 which we can not measure directly.

PROGRESS TEST 5

1. What do you understand by the terms· system, surroundings and states? Illustrate with an example
2. (a) What are intensive and extensive properties of a system?
   (b) Catagorise the following properties of a system into extensive and intensive properties.
   Free energy, Vapour pressure. Temperature, Surface tension, Mass. Internal energy, Melting point
3. State the First law of Thermodynamics and also give its mathematical statement, $\Delta E = q - w$.
4. (a) State and explain Hess's law of constant heat summation. Give its applications.

(b) Calculate the heat of formation of acetic acid from the following data.

$2C_{(S)} + 2H_{2(g)} + O_{2(g)} = CH_3COOH_{(l)} \quad \Delta H_f = ? — (1)$

$C_{(S)} + O_{2(g)} = CO_{2(g)} \quad \Delta H_{25^\circ C} = -394$ KJ/mole (2)

$H_{2(g)} + {}^1/_2O_{2(g)} = H_2O_{(l)} \quad \Delta H_{25^\circ C} = -286$ KJ/mole (3)

$CH_3COOH_{(l)} + 2O_{2(g)} = 2CO_{2(g)} + 2H_2O_{(l)} \quad \Delta H_{25^\circ C} = -870.8$ KJ/mole(4)

(Ans: –489.2 KJ/mole)

5. (a) Define and explain the terms (i) Exothermic process (ii) Endothermic process (iii) Heat of formation.

(b) Calculate the heat of formation of Ethane at 25°C from the following data

(i) $2C_{(S)} + 3H_{2(g)} = C_2H_{6(g)} \quad \Delta H_F = ?$
(ii) $C_{(S)} + O_{2(g)} = CO_{2(g)} \quad \Delta H = -394.00$ KJ/mole
(iii) $H_{2(g)} + {}^1/_2O_{2(g)} = H_2O(l) \quad \Delta H = -286.0$ KJ/mole
(iv) $C_2H_{6(g)} + {}^7/_2O_{2(g)} = 2CO_{2(g)} + 3H_2O(l) \quad \Delta H = -1560.632$ KJ/mole

(Ans: –85.368 KJ/ mole)

6. (a) Show that the product of pressure and volume, PV has the dimension of energy.

(b) In a certain process 848J of heat is absorbed by a system, while 394J of work is done on the system. What is the change in the internal energy for the process ? (Ans: 1242J)

7. (a) If 1800 cals, of heat is added to a system while system does work equivalent to 2800 cals by expanding against the surrounding. What is the value of ΔE for the system? (Ans: –1000 cals).

(b) In a certain process, 500J of work is done on a system which gives off 200J of heat. What is the value of ΔE for the process ? (Ans: 300J)