

# 8

## SOME BASIC CONCEPTS OF THERMODYNAMICS AND THERMOCHEMISTRY

### 8.1 INTRODUCTION

When a chemical reaction occurs, it is accompanied by an energy change which may take any of several different forms. For example, the energy change involved in a reaction of fuels like kerosene, coal, wood, natural gas, etc., with air takes the form of heat and light. Electrical energy is obtained from chemical reaction in batteries. The formation of glucose,  $C_6H_{12}O_6$  by the process of photosynthesis requires the absorption of light energy from the sun. So we see that the energy change that accompanies a chemical reaction can take different forms. In this lesson, we shall study only those reaction in which heat is either evolved or absorbed. We shall be interested in reactions which give out heat as well as those which absorb heat.

### 8.2 OBJECTIVES

After reading this lesson, you will be able to.

- define the commonly used terms in themodynamics.
  - differentiate between exothermic and endothermic reactions.
-

- explain the first law of thermodynamics.
- explain internal energy.
- define enthalpy and enthalpy change.
- state the relationship between enthalpy change and internal energy change.
- define enthalpy of formation, enthalpy of neutralisation and enthalpy of combustion.
- state the relationship between enthalpy of reaction and enthalpies of formation of reaction and products.
- solve numerical problems based on the enthalpy changes.
- state Hess's law.
- calculate enthalpy of reaction using Hess's law.
- define bond enthalpy and bond dissociation enthalpy.
- calculate enthalpy of a reaction using bond enthalpies data.

### 8.3 SOME COMMONLY USED TERMS

In this lesson you would come across the terms which will be frequently used. Let us understand the meaning of these terms first.

#### 8.3.1 System and Surroundings

If we are studying the reaction of two substances A and B kept in a beaker, the reaction mixture of A and B is a system and the beaker and the room where it is kept are surroundings as shown in figure 8.1

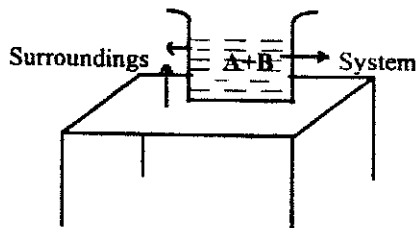


Fig 8.1 System and Surroundings

**System is the part of the physical universe which is under study, while the rest of the universe is surroundings.**

You know that hot tea/milk (let us call it a system) kept in a stoppered thermos flask remain hot for a couple of hours. If this flask is made of perfect insulating material, then there is no exchange of matter or energy between system and surroundings. We call such a system an isolated system.

**Isolated system is a system which can exchange neither matter nor energy with the surroundings.**

If we keep hot tea/milk in a stoppered stainless steel flask, it will not remain hot after a couple of minutes. Here energy is lost to the surroundings through the steel walls, but due to stopper, the matter will not be lost. We call this system as a closed system.

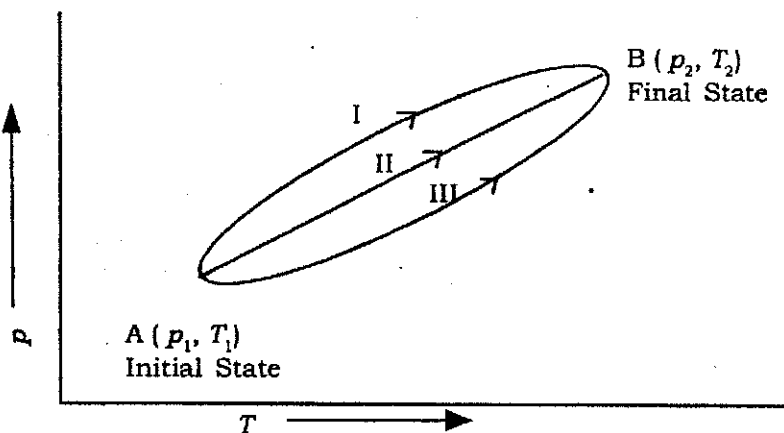
**Closed system is a system which can exchange energy but not the matter with the surroundings.**

If we keep stainless steel flask or thermos flask open, some matter will also be lost due to evaporation along with energy loss. We call such a system an open system. Plants, animals, human beings are all open systems, because they continuously exchange matter (food, etc) and energy with the surroundings.

**Open system is a system which can exchange both energy and matter with the surroundings.**

### 8.3.2 State of a System

We describe a state of a system by its measurable properties. For example, we can describe the state of a gas by specifying its pressure, volume, temperature, etc. These variable properties are called state variables or state functions, because their values depend only on the state of the system and not on the previous history or path taken by the system. i.e. when the state of a system is changed, the changes depend only on the initial and final states of the system. (Fig 8.2)



**Fig. 8.2** Change of state from initial state to final state through three paths I, II and III. The difference  $p_2 - p_1$  and  $T_2 - T_1$  are independent of the path since pressure and temperature are state functions.

**State functions are those functions which depend only on the initial state and the final state of the system.**

Change in state of a system is defined by giving the initial and the final state of the system. We can understand it by considering another example. We travel from one point to another. The distance travelled depends on the path or route we take. But the separation between these two points on the earth is fixed. Thus separation is a state function, but not the distance travelled.

State functions are very important in thermodynamics, because here we are concerned only with the equilibrium states and not with how a change in a particular state occurs.

### 8.3.3 Properties of a System

As we have said earlier, properties of a system are called state variables. They may be further divided into two main types.

- (i) **Extensive property** (variable) is one whose value depends upon size of the system. For example, mass, volume, weight, heat, capacity etc.
- (ii) **Intensive property** (variable) is one whose value is independent of the size of the system. For example, temperature, pressure, refractive index, viscosity, density, surface tension, etc.

You may note that the extensive property can become intensive property by specifying unit amount of the substance concerned. For example, mass and volume are extensive property, but density (mass per unit volume) and specific volume (volume per unit mass) are intensive properties.

### 8.3.4 Types of Process

Let us first understand what do we mean by a process. Let us consider the system in equilibrium with the surroundings. This means that the state variables do not change with respect to time and space.

**The transition from one equilibrium state (initial state) to another (final state) is called a process.**

Processes could be of different types. The different types of processes are explained below.

- a) **Isothermal process** : Ice melts at 273K and 1atm pressure. The temperature does not change as long as the process of melting goes on. Such processes are examples of isothermal process. We can define isothermal process as follows.

**When the temperature of the system is kept constant during various operations then the process is said to be isothermal. This is attained either by removing heat from the system or by supplying heat to the system.**

- b) **Adiabatic Process** : If an acid is mixed with a base in a closed thermos flask, the heat evolved is retained by the system. Such processes are known as adiabatic process because the thermos flask does not allow exchange of heat between the system and the surroundings. Adiabatic process can be defined as follows :

**In an adiabatic process there is no exchange of heat between the system and the surroundings. Thus in adiabatic processes there is always a change in temperature.**

- c) **Reversible Process** : In a reversible process, the initial and final states are connected through a succession of equilibrium states. All changes occurring in any

part of the process are exactly reversed when it is carried out in the opposite direction. Thus both the systems and its surroundings must be restored exactly to their original state, when the process has been performed and then reversed.

Let us understand it by an example. Imagine a liquid in equilibrium with its vapour in a cylinder closed by a frictionless piston, and placed in a constant temperature bath as shown in figure. 8.3. If the external pressure on the piston is increased by an infinitesimally small amount, the vapour will condense, but the

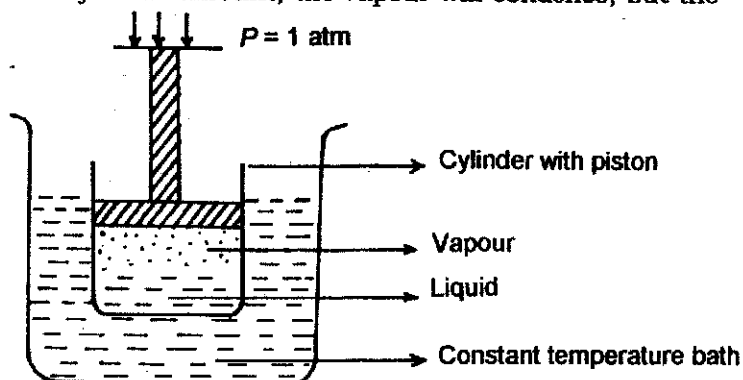


Fig. 8.3 A reversible process

condensation will occur so slowly that the heat evolved will be taken up by the temperature bath. The temperature of the system will not rise, and the pressure above this liquid will remain constant. Although condensation of the vapour is taking place, the system at every instant is in the state of equilibrium. If the external pressure is made just smaller than the vapour pressure, the liquid will vaporize extremely slowly, and again temperature and pressure will remain constant.

**Reversible processes are those processes in which the changes are carried out so slowly that the system and surroundings are always in equilibrium.**

d) **Irreversible Processes** In the above example rapid evaporation or condensation by the sudden decrease or increase of the external pressure, will lead to non-uniformity in temperature and pressure within the systems and the equilibrium will be disturbed. Process of this kind is not reversible. These are irreversible processes.

### 8.3.5 Standard States

You have seen that a system is described by the state variables. To permit a comparison of energies for different compounds, a standard set of conditions is chosen. This refers to the condition of 1 atmospheric pressure at any specified temperature with a substance in its stable form.

## 8.4 EXOTHERMIC AND ENDOTHERMIC REACTION

- (i) Add a few  $\text{cm}^3$  of dilute hydrochloric acid in a test tube containing a few pieces of granulated zinc and observe the evolution of a gas. Feel the test tube. It would be hot.
- (ii) You must have observed that when some water is added to quick lime to prepare white wash, a lot of heat is evolved.

- (iii) When fuel like cooking gas or coal is burnt in air, heat is evolved besides light.

In all the above cases, a chemical reaction leads to energy (heat) released to the surroundings. We call these type of reactions as exothermic reactions.

**Exothermic reactions are those reactions which proceed with the evolution of heat.**

Now we consider the following reactions :

- (i) Add a small amount of solid ammonium chloride in a test tube half-filled with water. Stir and feel the test tube. It will feel cold.
- (ii) Similarly repeat this experiment with potassium nitrate.
- (iii) Mix barium hydroxide with ammonium chloride in small quantities in water taken in a test tube. Feel the test tube. It will be cold.

In all these processes we see that heat is absorbed by the system from the surroundings. These are called endothermic reactions.

**Endothermic reactions are those reactions which proceed with absorption of heat from the surroundings.**

## 8.5 THERMOCHEMICAL EQUATIONS

You are familiar with equations for chemical reactions. Now we shall write the chemical equations which will specify heat energy changes and states of the reactants and products. These are called the thermochemical equations. For writing these equations, we follow the conventions listed below :

- (i) The heat evolved or absorbed in a reaction is affected by the physical state of the reacting substances. Gaseous, liquid and solid states are represented by putting symbols (g), (l), and (s) along side the chemical formulae respectively.

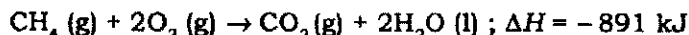
For example, to represent burning of methane in oxygen, we write



In writing thermochemical reactions, we denote the amount of heat evolved or absorbed by a symbol  $\Delta H$ . The amount of heat evolved or absorbed is written after the equation followed by semicolon.  $\Delta H$  is negative for exothermic reactions and it is positive for endothermic reactions.

For example :

Exothermic reaction is written as



Endothermic reaction is written as

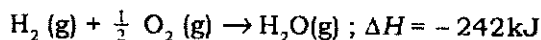


- (ii) In case of elements which exhibit allotropy, the name of allotropic modification is mentioned. For example,

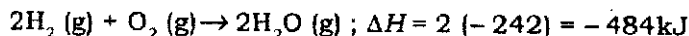
C (graphite), C (diamond), etc.

- (iii) The substances in aqueous solutions are specified using the symbol (aq). For example NaCl (aq) stands for an aqueous solution of sodium chloride.

- (iv) The coefficients of the substances of the chemical equations indicate the number of moles of each substance involved in the reaction and the  $\Delta H$  values given correspond to these quantities of substances.
- (v) In case the coefficients are multiplied or divided by a factor,  $\Delta H$  value must be also multiplied or divided by the same factor. Thermochemical equations may be balanced even by using fractional coefficients, if so desired. In such cases the  $\Delta H$  value will depend upon the coefficients. For example, in equation.



If coefficients are multiplied by 2, we would write the equation



## 8.6 FIRST LAW OF THERMODYNAMICS

You have learnt that chemical reactions are accompanied by energy change. How do we determine these energy changes? You know that we cannot create or destroy energy. Energy is only changed from one form to another. This is the observation by many scientists over many years. This observation has taken the form of first law of Thermodynamics. It has been found valid for various situations. We state this law as follows :

**Energy can neither be created nor destroyed. The total energy of the universe or an isolated system is constant.**

Mathematically first law of Thermodynamics is given as :

$$\Delta E = q + w$$

where  $\Delta E$  = change in internal energy,  $q$  = heat absorbed by the system

$w$  = work done on the system.

These terms are explained below .

### 8.6.1 Internal Energy

Every system has a definite amount of energy. It is the property of the system. This amount is different for different substances. First category includes translational energy of molecules, energy of vibration and rotation of molecules, energy of electrons and nuclei. This energy is characteristic property of the system itself and is the internal.

**The internal energy is the sum of the energies of all the atoms, molecules or ions contained in the system. It includes kinetic energy, potential energy, chemical energy, nuclear energy etc.**

It is a state variable. It is not possible to measure the absolute values of internal energy. However we can calculate the change in the internal energy. If internal energy in initial state is  $E_1$  and in final state is  $E_2$ , then change in internal energy  $\Delta E$  is independent of the path taken from state 1 to 2.

We can write this change as :

$$\Delta E = E_2 - E_1$$

The internal energy of the system can be changed in two ways

- (i) Either by allowing heat to flow into the system or out of the system
- (ii) By work done on the system or by the system.

### 8.6.2 Heat and Work

$q$  and  $w$  are not state functions. This is because the values of  $q$  and  $w$  depend upon the way in which the change is carried out.

Since the law deals with the transfer of quantities, we assign some signs to the quantities. *Any thing which increases the internal energy of a system is given a positive sign.*

Heat given to the system ( $q$ ) and work done on the system ( $w$ ) are given positive signs. Let us illustrate this with an example.

If a certain change is accompanied by absorption of 50 kJ of heat and expenditure of 30 kJ of work,

$$q = +50 \text{ kJ}$$

$$w = -30 \text{ kJ}$$

$$\text{change in internal energy } \Delta E = (+50 \text{ kJ}) + (-30 \text{ kJ}) = +20 \text{ kJ}$$

Thus the system has undergone a net increase in energy of +20 kJ.

Change in the internal energy of the surroundings will be -20 kJ.

### 8.6.3 Work of expansion

Let us assume that pressure  $p$  is constant and the volume changes from  $V_1$  to  $V_2$ , the work done by a system is given as

$$W = -p(V_2 - V_1) = -p\Delta V \quad 8.2$$

(Here we have taken minus sign, because the work is done by the system)

Let us substitute the expression given for  $W$  in equation 8.1,

We get

$$\Delta E = q - p\Delta V \quad 8.3$$

If the process is carried out at constant volume

i.e  $\Delta V = 0$ , then

$$\Delta E = q_v \quad 8.4$$

The subscript  $v$  in  $q_v$  denotes that volume is constant.

The equation 8.4 shows that we can determine internal energy change if we measure the heat change at constant volume. However, in chemistry, the chemical reactions are generally carried out at constant pressure (atmospheric pressure). What do we do then? Let us define another state function enthalpy.

### 8.6.4 Enthalpy

For measuring heat changes at constant pressure, we define a new state function called Enthalpy. It is denoted by a symbol  $H$ .

$$H = E + pV$$

Enthalpy change will be  $\Delta H$

$$\Delta H = \Delta E + \Delta(pV)$$

$$\text{or } \Delta H = \Delta E + p \Delta V + V \Delta p \quad 8.6$$

If the change is carried out at constant pressure,

then  $\Delta p = 0$ , so equation 8.6 will become

$$\Delta H = \Delta E + p \Delta V \text{ (at constant pressure)} \quad 8.7$$

Substituting the value of  $\Delta E$  from equation 8.3 in equation 8.7, we get

$$\begin{aligned} \Delta H &= q - p \Delta V + p \Delta V \\ &= q \text{ (at constant pressure)} \end{aligned}$$

We denote  $q$  at constant pressure by  $q_p$ , hence

$$\Delta H = q_p \quad 8.8$$

Equation 8.8 shows that by measuring heat changes at constant pressure, we can measure enthalpy change.

### 8.6.5 Relation Between $\Delta H$ and $\Delta E$

For liquids and solids, the differences between  $H$  and  $E$  are not significant. But for gasses, the difference is significant as we will see here.

If  $V_A$  is the total volume of the gaseous reactants.

$V_B$  is the total volume of the gaseous products.

$n_A$  is the number of moles of gaseous reactants.

$n_B$  is the number of moles of gaseous products at constant pressure and temperature.

Then, using ideal gas law, we can write

$$p V_A = n_A RT$$

$$p V_B = n_B RT$$

Change in volume is given by

$$p V_B - p V_A = n_B RT - n_A RT = (n_B - n_A) RT$$

$$p (V_B - V_A) = p \Delta V = \Delta n RT$$

At constant pressure

$$\Delta H = \Delta E + p \Delta V$$

$$\text{Therefore } \Delta H = \Delta E + \Delta n RT \quad 8.9$$

Here  $\Delta n = (\text{no. of moles of gaseous products}) - (\text{no. of moles of gaseous reactants})$

Thus we can find the value of  $\Delta H$  from  $\Delta E$  or vice versa.

For solids and liquids  $\Delta V$  is very small. We can neglect terms  $p \Delta V$ , hence  $\Delta H$  is nearly the same as  $\Delta E$ .

## INTEXT QUESTION 8.1

- Which of the following is false ?
  - The reaction  $\text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightarrow 2\text{HCl}(\text{g}) + 185 \text{ kJ}$  is endothermic.
  - Enthalpy change is a state function.
  - Standard state condition for a gaseous system is 1 atm pressure at a specified temperature.
- For the reaction at 298 K
 
$$\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightarrow \text{NH}_3(\text{g}); \Delta H = -46 \text{ kJ}$$
  - What is the value of  $\Delta n$  ?  
.....
  - What is the value of  $\Delta E$  ?  
.....
- Which of the following will increase the internal energy of a system.
  - Heat given to the system .
  - Work done by the system .  
.....

## 8.7 STANDARD ENTHALPY OF REACTIONS

We take total enthalpy of reactants as  $H_{\text{reactants}}$  and total enthalpy of products as  $H_{\text{products}}$ . The difference between these enthalpies,  $\Delta H$ , is the enthalpy of the reaction

$$\Delta H = H_{\text{prod.}} - H_{\text{react.}}$$

When  $H_{\text{prod.}}$  is greater than  $H_{\text{react.}}$ , then  $\Delta H$  is positive and heat is absorbed in the reaction, and the reaction will be endothermic. For example,  $\text{H}_2(\text{g}) + \text{I}_2(\text{g}) \rightarrow 2\text{HI}(\text{g}); \Delta H = 52.5 \text{ kJ}$

When  $H_{\text{prod.}}$  is less than  $H_{\text{react.}}$ , then  $\Delta H$  is negative and heat is evolved in the reaction, and the reaction will be exothermic.

For example,  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{l}); \Delta H = -890.4 \text{ kJ}$

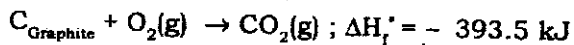
Enthalpy of a reaction changes with pressure and temperature. It is convenient to report enthalpies of the reactions in terms of standard state of substances as we defined earlier. When substances are in the standard states, we call the enthalpy of reaction as *standard enthalpy of reaction*. It is defined as the enthalpy change for a reaction, when the reactants and the products are in their standard states at constant temperature and constant pressure. It is denoted by  $\Delta H^\circ$ .

### 8.7.1 Enthalpy of Formation

The enthalpy change when one mole of a pure compound is formed from its elements is called the enthalpy of formation and is denoted by  $\Delta H_f^\circ$ .

When the reacting elements and the products formed are all in their standard state, the enthalpy change accompanying the chemical reaction is called the standard enthalpy of formation and is denoted by  $\Delta H_f^\circ$ . By convention, we take the standard enthalpy of formation of an element in its standard state as zero.

For example :

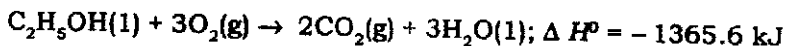


This means that carbon dioxide is formed from its elements in their standard states. Carbon is in the form of graphite at 1 atm and at room temperature and gases being at 1 atmosphere.

### 8.7.2 Enthalpy of Combustion

**Enthalpy of combustion is the enthalpy change (heat evolved) accompanying the complete combustion of 1 mole of a compound in oxygen at a given temperature and 1 atm pressure.**

For example :

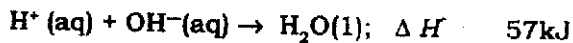


Enthalpy of combustion of  $C_2H_5OH(l)$  is  $-1365.6 \text{ kJ mol}^{-1}$

### 8.7.3 Enthalpy of Neutralization

Enthalpy of neutralization is the enthalpy change (heat evolved) when one mole of hydrogen ions ( $H^+$ ) is neutralized by one mole of hydroxyl ions ( $OH^-$ ) in dilute aqueous medium to form water.

For example :

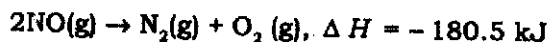


Enthalpy of neutralization of a strong acid with a strong base is always constant having a value of  $-57 \text{ kJ}$ . However, enthalpy of neutralization of strong acid with a weak base or weak acid with a strong base will be different, because of varying degree of ionization of weak acids and weak bases.

## 8.8 LAWS OF THERMOCHEMISTRY

In this section you shall learn about the laws of thermochemistry.

**Lavoisier Laplace Law** : When a chemical equation is reversed, the sign of  $\Delta H$  is changed. For example,



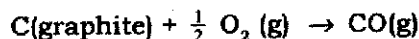
**Hess's Law of Constant Heat Summation** : Hess's law states that the enthalpy of reaction is independent of the number and nature of the intermediate steps.

You have learnt that standard enthalpy change of the reaction



is equal to  $-393.5 \text{ kJ}$ .

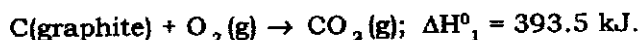
However, there are some reactions for which the direct measurement of enthalpy in the laboratory is not possible. The value can be determined in a calorimeter. In following case the standard enthalpy change for the reaction,



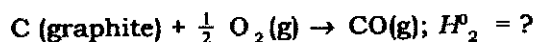
is difficult to determine in the calorimeter. The combustion of carbon is in complete unless an excess of oxygen is used. If excess of oxygen is used, some of the CO is oxidized to  $\text{CO}_2$ . How can then we determine the enthalpy change for the reaction or for this type of reactions when direct measurement is not possible.

Since  $\Delta H$  is a state function, it is not dependent on the way the reactions are carried out. Let us carry out the reactions as follows :

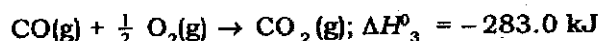
- (1) First carry out the following reaction and let  $\Delta H_1^0$  be the enthalpy of reaction.



- (2) Now let us write the reaction for which we have to determine enthalpy of reaction and let it be  $\Delta H_2^0$



- (3) Let us carry out the following reactions and let  $\Delta H_3^0$  be the enthalpy of reaction



We have obtained the products  $\text{CO}_2(\text{g})$  from carbon and oxygen through two routes, namely first as in step (1) and second as in step (2) + (3).

According to Hess's Law

$$\Delta H_1^0 = \Delta H_2^0 + \Delta H_3^0$$

or

$$\Delta H_2^0 = \Delta H_1^0 - \Delta H_3^0$$

Fig 8.4 shows alternate paths for the conversion of carbon and oxygen to carbon dioxide.

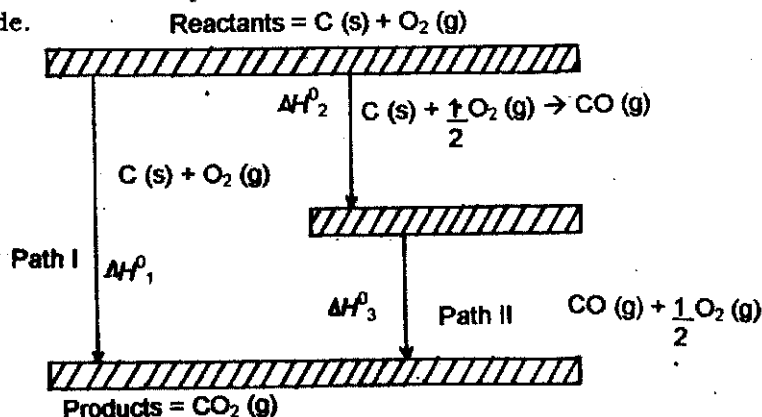
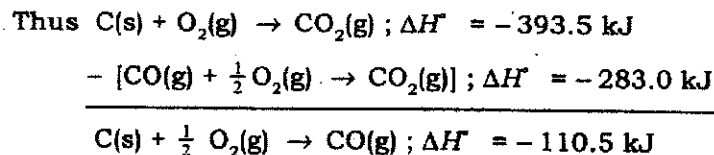


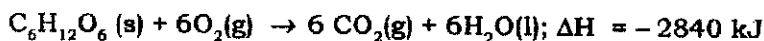
Fig. 8.4 Alternate paths for the conversion of carbon and oxygen to carbon dioxide

One result of Hess's law is that thermochemical equations can be added and subtracted just like algebraic equations to get the desired reaction. A useful practical application of this law is that we can calculate enthalpy changes for the reactions which cannot be studied directly as we just saw.

To obtain the enthalpy of the reaction, we algebraically combine the known values of  $\Delta H^\circ$  in the same way as the reactions themselves,

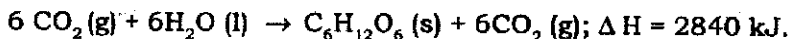


**Example 8.1** The heat involved in the combustion of glucose is shown in the following equation :



How much energy will be required for production of 1.08 g of glucose ?

**Solution :** Glucose will be prepared by the reverse reaction.

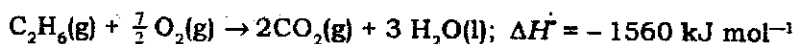
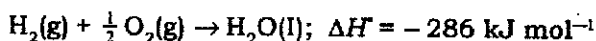
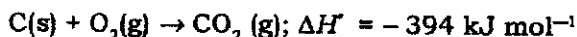


This equation refers to 1 mol of glucose (180 g of glucose).

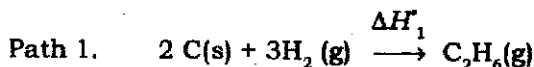
Production of 180 g of glucose requires 2840 kJ of energy. Therefore, production of 1.08 g will require :

$$\begin{aligned} & \frac{2840 \text{ kJ}}{180 \text{ g}} \times 1.08 \text{ g energy} \\ & = 17.04 \text{ kJ} \end{aligned}$$

**Example 8.2** Calculate the standard enthalpy of formation of ethane, given

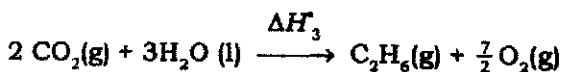
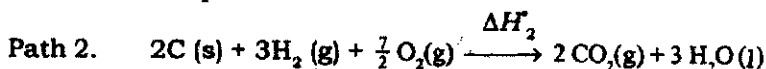


**Solution :** (1) Starting with reaction for which you want to calculate  $\Delta H^\circ$ , begin to construct an energy cycle ; similar to that shown in figure 8.5



2) Find another path where you can obtain  $\text{C}_2\text{H}_6(\text{g})$ . Write the following equations

Add first two equations



Note that  $\frac{7}{2} \text{O}_2(\text{g})$  makes no difference to  $\Delta H_1^\circ$

(3) Use Hess' Law

$$\Delta H_1^\circ = \Delta H_2^\circ + \Delta H_3^\circ$$

(4) Substitute the values of  $\Delta H_2^\circ$  and  $\Delta H_3^\circ$

$$x\Delta H_2^\circ = 2(-394) + 3(-286)$$

$$= -1646 \text{ kJ mol}^{-1}$$

$$\Delta H_3^\circ = - (\text{Enthalpy of combustion of } \text{C}_2\text{H}_6(\text{g}))$$

$$= - (-1560) = +1560 \text{ kJ mol}^{-1}$$

5.  $\Delta H_1^\circ = \Delta H_2^\circ + \Delta H_3^\circ$

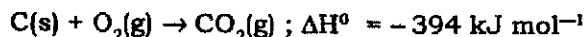
$$= -1646 \text{ kJ mol}^{-1} + 1560 \text{ kJ mol}^{-1} = -86 \text{ kJ mol}^{-1}$$

Standard enthalpy of formation of Ethane =  $-86 \text{ kJ mol}^{-1}$

## INTEXT QUESTIONS 8.2

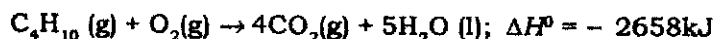
1. Which of the following is true ?

- (a) Enthalpy of formation is the heat evolved or absorbed when one gram of a substance is formed from its elements.
- (b) When one mole of  $\text{H}^+$  (aq) and 1 mole of  $\text{OH}^-$  (aq) react, 57.1 kJ of energy is absorbed .
- (c) In the thermochemical equation,



$\Delta H^\circ$  is known as enthalpy of formation of  $\text{CO}_2(\text{g})$

2. Calculate the enthalpy change in complete combustion of 29.0g of butane, if



3. Calculate the standard enthalpy of the reaction



given

$$\Delta H_f^\circ(\text{H}_2\text{S}) = -20.6 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ(\text{SO}_2) = -296.9 \text{ kJ mol}^{-1}$$

$$\Delta H_f^\circ[\text{H}_2\text{O}(\text{l})] = -289.9 \text{ kJ mol}^{-1}$$

## 8.9 BOND ENTHALPIES

In a chemical reaction, you have seen that either the energy is absorbed or evolved. Do you know the origin of this change of energy? You know that bonds are broken and reformed in the chemical reactions. Energy changes take place in breaking bonds of the reactants and in forming new bonds of the products. So the energy changes in a chemical reaction are a result of energy changes in breaking and forming of bonds. Let us consider the gaseous reactions, because in these, we encounter the energy changes due to breaking and forming of bonds only.

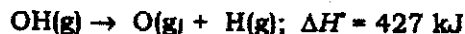
At high temperature, hydrogen molecules dissociate into atoms as



The heat absorbed in this reaction goes to break the chemical bonds holding hydrogen atoms together in the  $\text{H}_2$  molecules.

For a diatomic molecule like  $\text{H}_2(\text{g})$ , we define bond dissociation energy as the enthalpy change of the reaction in which the gaseous molecule is separated into gaseous atoms.

Now let us consider a polyatomic molecule like  $\text{H}_2\text{O}(\text{g})$ . The dissociation may involve fragmenting the molecules into an atom and a group of atoms, called a radical, as in



In the first reaction, one of the two OH bonds in  $\text{H}_2\text{O}(\text{l})$  dissociates with enthalpy change of 502 kJ and in the second reaction second OH bond dissociates with enthalpy change of 427 kJ. It is clear that the dissociation energy of the O-H bond is sensitive to its environment. However the difference is not very large. We take the average value (464.5 kJ in this case) in case of polyatomic molecules and call it bond enthalpy.

**Bond enthalpy is defined as the average amount of bond dissociation enthalpies for a given type of bond present in different gaseous compound when one mole of bonds is broken in the gaseous state.**

Now you know the distinction between bond dissociation enthalpy and bond enthalpy. Bond dissociation enthalpy refers to break a particular bond in a particular molecule whereas bond enthalpy is the average value of bond dissociation energies for a given type of bond. Table 8.1 is a short list of bond enthalpies.

By using bond enthalpies (B.E.) it is possible to estimate the energy released when a gaseous molecule is formed from its gaseous atoms. For example, the energy released at constant pressure for the reaction ( $\Delta H$ ),



is the sum of the energies of three C-H bonds, and one C-Cl bond, all taken with a negative sign because energy is released. Using the values of bond enthalpies (B.E)

from table 8.1, we have for this case,

$$\begin{aligned} \Delta H &= -3 \times \text{B.E. (C-H)} - \text{B.E. (C-Cl)} \\ &= -1239 \text{ kJ mol}^{-1} - 335 \text{ kJ mol}^{-1} \\ &= -1574 \text{ kJ mol}^{-1} \end{aligned}$$

We now show you how to use bond enthalpy data to estimate the enthalpy of a reaction, when direct calorimetric data are not available. Note that in section 8.7 we used enthalpy of formation in data to estimate enthalpy of a reaction. In principle, bond enthalpy data can be used to calculate  $\Delta H$  for a chemical reaction occurring in gaseous state making use of difference in the energy absorbed in breaking the reactant bonds and energy released in making the products bonds as

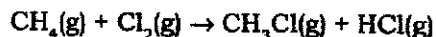
$$\Delta H = \Sigma \text{B.E. (reactants)} - \Sigma \text{B.E. (products)} \quad 8.10$$

or, Enthalpy of the reaction = Total energy absorbed + Total energy released

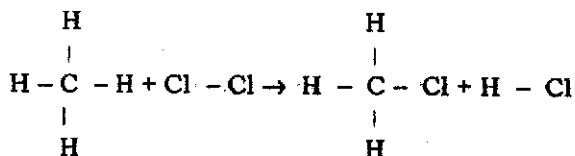
**TABLE 8.1 BOND ENTHALPIES**

BOND	BOND ENTHALPY (kJ mol <sup>-1</sup> )
H-H	435
C-H	415
C-Br	284
C-C	356
C	598
Br-Br	193
Cl-Cl	242
C-Cl	339
F-F	155
H-Cl	431
H-O	462
H-N	390
H-F	563
H-Br	366
HI	296
C-O	355
C=O	723
C-N	291
C=N	619
C≡N	878
C≡C	832

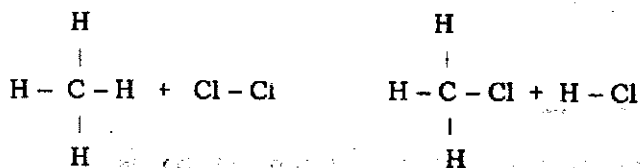
**Example 8.3 :** Use bond enthalpy data given in table 8.1 to calculate the enthalpy of the reaction.



**Solution :** 1. Write the equation using structural formulae



2. List the bonds broken and bonds made under the equation as shown



number of bonds broken      number of bonds made

$$\text{C} - \text{H} = 4$$

$$\text{C} - \text{Cl} = 1$$

$$\text{Cl} - \text{Cl} = 1$$

$$\text{H} - \text{Cl} = 1$$

3. Look up the values of bond enthalpies for the bonds in the reactants and products and list them as shown

Reactants

Products

$$\text{B.E. (C - H)} = 435 \text{ kJ mol}^{-1}$$

$$\text{B.E. (Cl - C)} = 339 \text{ kJ mol}^{-1}$$

$$\text{B.E. (Cl - Cl)} = 242 \text{ kJ mol}^{-1}$$

$$\text{B.E. (H - Cl)} = 431 \text{ kJ mol}^{-1}$$

4. Use equation 8.10,

$$\text{Enthalpy of the reaction } \Delta H = \sum \text{B.E. (reactants)} - \sum \text{B.E. (products)}$$

$$= 677 - 770$$

$$= -93 \text{ kJ}$$

**Note :** Alternatively this can be solved as follows after step 3.

$$\text{Total energy absorbed (reactants)} = 677 \text{ kJ}$$

$$\text{Total energy released (products)} = -770 \text{ kJ}$$

$$\text{Energy change} = 667 - 770$$

$$= -93 \text{ kJ}$$

Now let us take one example in which we calculate the enthalpy of a reaction using (i) Enthalpy of formation data and (ii) Bond enthalpy data.

**Example 8.4 :** Calculate  $\Delta H$  for the reaction



(a) Using enthalpy of formation data

$$\Delta H_f^\circ(\text{HCl}) = -92.5 \text{ kJ}$$

$$\Delta H_f^\circ(\text{HF}) = -269 \text{ kJ}$$

- (b) using bond enthalpy data  
 B.E.(H - Cl) = 431 kJ mol<sup>-1</sup>  
 B.E.(F - F) = 155 kJ mol<sup>-1</sup>  
 B.E.(H - F) = 563 kJ mol<sup>-1</sup>  
 B.E.(Cl - Cl) = 242 kJ mol<sup>-1</sup>

**Solution :** (a) Using enthalpy of formation of compounds,

$$\begin{aligned}\Delta H &= 2\Delta H_f^\circ(\text{HCl}) - 2\Delta H_f^\circ(\text{HF}) \\ &= 2(-92.5 \text{ kJ}) - 2(-269 \text{ kJ}) \\ &= -185 \text{ kJ} + 538 \text{ kJ} \\ &= +353 \text{ kJ}\end{aligned}$$

- (b) Using bond enthalpies

$$\begin{aligned}\Delta H &= \sum \text{B.E. (reactants bonds)} - \sum \text{B.E. (products bonds)} \\ &= [\text{B.E. (Cl - Cl)} + 2 \text{B.E. (H - F)}] - [\text{B.E. (F - F)} + 2\text{B.E. (H - Cl)}] \\ &= [242 + 2(563)] \text{ kJ} - [155 + 2 \times 431] \text{ kJ} \\ &= 1368 \text{ kJ} - 1017 \text{ kJ} \\ \Delta H &= 351 \text{ kJ}\end{aligned}$$

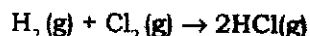
$\Delta H$  calculated by these two different methods are nearly identical.

### INTEXT QUESTIONS 8.3

- Write True or false
  - Enthalpy of a reaction is equal to the sum of the enthalpy of formation of products minus the sum of the enthalpy of formation of the reactants.
  - Enthalpy of formation of any elementary substance is equal to zero.
  - If a reaction can be carried out in several steps, the enthalpy change for the over all reaction is equal to enthalpy change in the last step.
  - Bond enthalpy and bond dissociation energy are same for polyatomic molecules.
- Calculate the bond enthalpy of N- H in NH<sub>3</sub> (g) given



3. Calculate the enthalpy of the reaction



given;

Bond enthalpy (H - H) = 435 kJ mol<sup>-1</sup>

Bond enthalpy (Cl - Cl) = 242 kJ mol<sup>-1</sup>

Bond enthalpy (H - Cl) = 431 kJ mol<sup>-1</sup>

---

## 8.10 WHAT YOU HAVE LEARNT

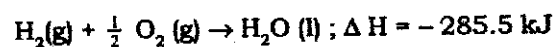
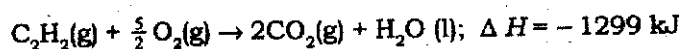
- System is the part of the physical universe which is under study, while the rest of the universe is surroundings.
  - Isolated system is a system which can exchange neither matter nor energy with the surroundings.
  - Closed system is a system which can exchange energy but not the matter with the surroundings.
  - Open system is a system which can exchange both energy and matter with the surroundings.
  - State functions are those functions which depend only on the initial state and the final state of the system.
  - Extensive properties depend upon size of the system where as intensive properties do not depend upon size of the system.
  - When the temperature of the system is kept constant during various operations then the process is said to be isothermal.
  - In an adiabatic process there is no exchange of heat between the system and the surroundings.
  - Reversible processes are those processes in which the changes are carried out so slowly that the system and surroundings are always in equilibrium.
  - Exothermic reactions are those reactions which proceed with the evolution of heat.
  - Endothermic reactions are those which proceed with absorption of heat from the surroundings.
  - First law of Thermodynamics states that energy can neither be created nor destroyed.
  - Internal energy is the sum of the energies of all the atoms, molecules or ions contained in the system.
  - The state function enthalpy (H) is given by the relation  $H = E + PV$ .
-

- When a chemical equation is reversed, the sign of  $\Delta H$  is changed.
- The enthalpy of reaction is independent of the number and nature of the intermediate steps.
- Bond enthalpy is the average amount of bond dissociation enthalpies for a given type of bond present in different gaseous compounds, when one mole of bonds is broken in the gaseous state.

### 8.11 TERMINAL EXERCISE

1. Enthalpy of combustion of ethyl alcohol,  $C_2H_5OH$ , is  $-950 \text{ kJ mol}^{-1}$ . How much heat is evolved when one gram of ethyl alcohol burns ?
- .....

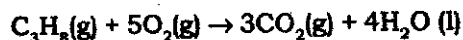
2. Given



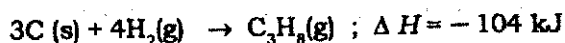
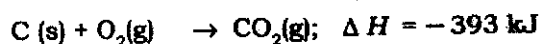
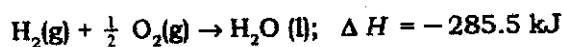
Calculate enthalpy of formation of  $C_2H_2(g)$ .

.....

3. Calculate the enthalpy of combustion of propane

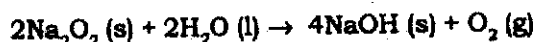


Given the following :



4. When two moles of  $H_2$  and one mole of  $O_2$  react to produce two moles of gaseous water at  $100^\circ C$  and 1 atm, a total of 484 kJ are evolved. What are (a)  $\Delta H$  and (b)  $\Delta E$  for the production of a single mole of  $H_2O(g)$ .
- .....

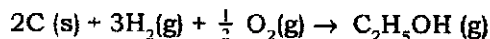
5. Calculate enthalpy of the reaction :



Enthalpy of formation of  $NaOH(s)$ ,  $Na_2O_2(s)$  and  $H_2O(l)$  are  $-426.4 \text{ kJ mol}^{-1}$ ,  $504 \text{ kJ mol}^{-1}$  and  $-285 \text{ kJ mol}^{-1}$  respectively.

.....

6. Calculate the heat of formation of gaseous ethyl alcohol,



given that bond enthalpies of C - C (s), H - H, O - O are  $714 \text{ kJ mol}^{-1}$ ,  $435 \text{ kJ mol}^{-1}$  and  $498 \text{ kJ mol}^{-1}$  respectively in the reactants, and bond enthalpies of C - C, C - H, C - O, O - H, are  $347 \text{ kJ mol}^{-1}$ ,  $415 \text{ kJ mol}^{-1}$ ,  $355 \text{ kJ mol}^{-1}$  and  $462 \text{ kJ mol}^{-1}$  respectively in the product.

## CHECK YOUR ANSWERS

### INTEXT QUESTIONS 8.1

- (a)
- (a)  $\Delta n = 1 - \frac{1}{2} - \frac{1}{2} = -1$   
 (b)  $\Delta E = \Delta H - \Delta n RT$   
 $= 46000 \text{ (J mol}^{-1}\text{)} - (-1) (8.314 \text{ Jk}^{-1} \text{ mol}^{-1}) \times (298 \text{ K})$   
 $= -46000 \text{ (J mol}^{-1}\text{)} + 2247.6 \text{ (J mol}^{-1}\text{)}$   
 $= -43.5 \text{ kJ mol}^{-1}$
- (i)

### INTEXT QUESTIONS 8.2

- (c)
- 1329 kJ
- $\Delta H^\circ = 2\Delta H_f^\circ(\text{H}_2\text{O}) - 2\Delta H_f^\circ(\text{H}_2\text{S}) - \Delta H_f^\circ(\text{SO}_2)$   
 $= -241.7 \text{ kJ}$

### INTEXT QUESTIONS 8.3

- (a) T  
 (b) T  
 (c) F  
 (d) F
- $\Delta H^\circ = \sum \text{B.E (reactant bonds)} - \sum \text{B.E (products bonds)}$   
 or  $-46 \text{ (kJ mol}^{-1}\text{)} = 3 \times 218 \text{ (kJ mol}^{-1}\text{)} + 973 \text{ (kJ mol}^{-1}\text{)} - \text{B.E (NH}_3\text{(g) Bonds)}$   
 $\text{B.E. (NH}_3\text{(g) Bonds)} = 1673 \text{ kJ mol}^{-1}$   
 $\text{B.E. (N-H)} = 557.7 \text{ kJ mol}^{-1}$
- $\Delta H^\circ = -185 \text{ kJ mol}^{-1}$

### TERMINAL EXERCISE

- 20.65 kJ
- 227.5 kJ
- 2217 kJ

$$4. \quad (a) \quad \Delta H = \frac{-484 \text{ (mJ)}}{2} = -242 \text{ kJ mol}^{-1}$$

$$(b) \quad \Delta E = \Delta H - p \Delta V = \Delta H - \Delta n RT$$

$$= -242 \text{ (kJ mol}^{-1}\text{)} + \frac{1}{2} \times 8.314 \text{ (J mol}^{-1}\text{K}^{-1}\text{)} (373 \text{ K)}$$

$$= -242 \text{ kJ mol}^{-1} + 1.55 \text{ kJ mol}^{-1}$$

$$= -240 \text{ kJ mol}^{-1}$$

$$(5) \quad -127.6 \text{ kJ}$$

$$(6) \quad \Delta H^{\circ} = \sum \text{B.E (reactant bonds)} - \sum \text{B.E (products bonds)}$$

$$= 2 (714 \text{ kJ mol}^{-1}) + 3 \times 435 \text{ (kJ mol}^{-1}\text{)} + \frac{1}{2} \times 498 \text{ (kJ mol}^{-1}\text{)}$$

$$- 5 \times 415 \text{ (kJ mol}^{-1}\text{)} - 347 \text{ (kJ mol}^{-1}\text{)} - 355 \text{ (kJ mol}^{-1}\text{)} - 462 \text{ (kJ mol}^{-1}\text{)}$$

$$= 2982 \text{ (kJ mol}^{-1}\text{)} - 3239 \text{ (kJ mol}^{-1}\text{)}$$

$$= -257 \text{ kJ mol}^{-1}$$

---