

Chemical Energetics



C11CH5



Learning Objectives

Upon completion of this topic, learners will:

- Identify the systems and the surroundings in the chemical process
- Identify the ways in which energy is transferred in the chemical process
- Investigate the relationship between internal energy and enthalpy
- Calculate change in enthalpy of a reaction using Hess' Law of heat
- Calculate change in standard enthalpy of a reaction using tables of change in enthalpy of formation
- Appreciate the origin of heat release in net bond breakage and
- Discuss the concept of ionic systems.

5.1. THERMODYNAMICS

Thermodynamics, literally, means conversion of heat into work and *vice versa* because **therm** refers to *heat* and **dynamics** refers to *movement*. Now-a-days the term thermodynamics is used in much wider sense as it deals with almost all forms of energies. **Thermodynamics** may, therefore, be defined as *the branch of science which deals with the quantitative relationship between heat and other forms of energies*. When we confine our study to thermodynamics of chemical processes, it is referred to as **chemical thermodynamics**.

Thermodynamics is primarily based upon three fundamental generalisations which have been arrived at, purely on the basis of human experience. These generalisations are called first, second and third laws of thermodynamics. In addition to these laws another generalisation was put forth at a later stage which came to be known as zeroth law of

thermodynamics. These laws of thermodynamics apply only when the system is in equilibrium or move from one equilibrium state to another equilibrium state. The predictions based upon these laws have been verified in most of the cases and so far no case has been reported where these laws break down. In general,

- **Zeroth Law** provides the basis for the measurement of temperature.
- **First Law** deals with the equivalence of different forms of energies.
- **Second Law** deals with the direction of chemical change.
- **Third Law** helps to evaluate the thermodynamic parameters like entropy.

Scope and Limitations of Thermodynamics

The **importance** of thermodynamics lies in its ability to

- (i) provides explanation of the macroscopic (*i.e.*, bulk) properties of matter in terms of the concepts which are supported by the microscopic views of our material world.
- (ii) predict the feasibility of the chemical reaction under the given set of conditions.
- (iii) predict the extent to which the chemical reaction can occur before the equilibrium is attained.

The significant **limitations** of thermodynamics include the following:

- (a) its failure to tell about the speed or rate of the reaction,
- (b) its inability to tell the mechanism or path of the reaction because it deals with initial and final states of the system and
- (c) its non-applicability to microscopic systems such as individual atoms and molecules.

Thermodynamic Terms

In this section, we shall study some basic terms and concepts of thermodynamics which are needed in the study of laws of thermodynamics and other parameters.

System and Surroundings

For the study of thermodynamics, the Universe is divided into two parts, system and surroundings.

A system is defined as that part of the Universe which is under investigation. **For example**, if we are interested in investigating the

neutralization of NaOH with HCl, the solutions of sodium hydroxide and hydrochloric acid constitute the system. Similarly, if we are studying the effect of temperature on the properties of water, then water will be taken as the system.

The part of the Universe other than the system is known as surroundings.

Thus, $Universe = System + Surroundings$

The entire universe, other than the system is not affected by the changes taking place in the system. Therefore for all practical purposes, the surroundings represent that portion of the remaining universe which can interact with the system. Generally, the region of space in the neighbourhood of the system constitutes its surroundings.

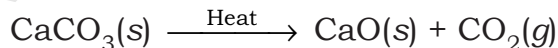
In order to keep track of exchange of matter and energy between system and surroundings, it is necessary to think of the system as separated from the surroundings by some sort of wall which may be real or imaginary. The wall which separates the system from the surroundings is called **boundary**. For example, if a reaction mixture is taken in a beaker, the reaction mixture constitutes the system, the walls of the beaker constitute the boundary and everything else is the surroundings.

Types of System

Systems may be classified into three types on the basis of movement of matter and energy in and out of the system:

- (a) *Open system*
- (b) *Closed system*
- (c) *Isolated system.*

(a) **Open System.** *A system which can exchange mass as well as energy with the surroundings, is called an **open system**.* For example, heating of calcium carbonate in an open vessel. In this case heat is supplied to the system by the burner, while CO_2 escapes into the surroundings.



(b) **Closed System.** *A system which can exchange energy with the surroundings but not mass is called a **closed system**.* For example, calcination of CaCO_3 taken in sealed bulb. On heating, CaCO_3 decomposes into CaO and CO_2 , however, CO_2 cannot escape and remains trapped in the bulb.

(c) **Isolated System.** *A system which can neither exchange mass nor energy with the surroundings is called an isolated system.* For example, a reaction carried out in a closed, well insulated container (such as

thermos flask). The open, closed and isolated systems have been shown in Fig. 5.1.

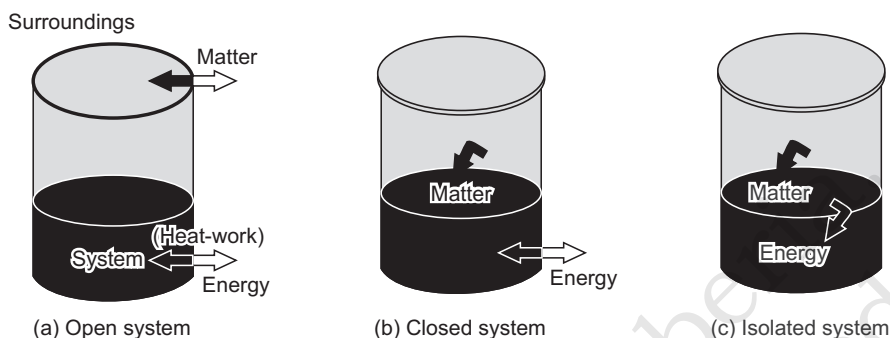


Fig. 5.1. Open, closed and isolated systems.

Homogeneous System: A system is said to be homogeneous when all its constituents are in the same phase and are uniform throughout the system.

Example: column of atmospheric gas

Heterogeneous System: A system is said to be heterogeneous which its constituents are in two or more phase and are not uniform throughout the system.

Example: Ice, water and steam. This system has three homogeneous bodies *e.g.*, steam, water and ice. The chemical composition of three phases is same but their physical properties differ significantly.

Change of State of the System

We know that thermodynamics is a process of transformation of thermodynamic system from an initial thermodynamic state to a second thermodynamical state. The change of state can be studied from the change of thermodynamic state variables like temperature, pressure, volume, internal energy, enthalpy, heat capacity, and entropy.

In order to make useful calculations, it is necessary to describe the system completely before and after it undergoes any change. The state of the system can be described by specifying certain minimum number of macroscopic properties such as *pressure (p)*, *volume (V)*, *temperature (T)* and *amount (n)* or *composition*. Once these minimum number of properties are fixed, the other macroscopic properties automatically acquire definite values. Some notable features about the thermodynamic state are as follows:

- Variation in one or more macroscopic properties brings a **change in the state** of the system, when other macroscopic properties attain new values. The macroscopic properties are thus, called **state variables** or **state functions**.
- **Initial state** refers to the starting state of system in equilibrium. After interaction with surroundings (involving exchange of matter or energy or both) the system attains another equilibrium state which is referred to as a **final state** of the system.
- Thermodynamic state of the system must not be confused with *physical state* or *phase*.
- A system is said to be in thermodynamic equilibrium state if its macroscopic properties do not change with time.

State Functions

The thermodynamic properties whose values depend only on the initial and final states of the system are called **state functions**. These are independent of the manner as to how the change is brought about. The concept of state function can be easily understood from the following analogy. If we consider 'h' as the height between the top and bottom of the mountain, then 'h' is independent of the path followed in reaching the top of the mountain. Here, the parameter *h* is analogous to state function. In thermodynamics, some common state functions are *internal energy (U)*, *enthalpy (H)*, *entropy (S)*, *Gibb's free energy (G)*, *pressure (p)*, *temperature (T)*, *volume (V)*, etc. It may be noted that two very important thermodynamic parameters namely; *heat (q)* and *work (w)* are not the state functions because they are *path dependent*.

The Thermodynamic Process

The operation which brings about the changes in the state of the system is termed as **thermodynamic process**. A thermodynamic process may be further classified into different types depending upon the conditions under which the changes are brought about. These are:

- Isothermal Process.** It is a process which is carried out at *constant temperature* ($\Delta T = 0$).
- Adiabatic Process.** It is a process in which *no heat exchange* occurs between the system and the surroundings ($\delta q = 0$).
- Isobaric Process.** It is a process which is carried out at *constant pressure* ($\Delta p = 0$).

(iv) **Isochoric Process.** It is a process which is carried out at constant volume ($\Delta V = 0$).

The graphical representation of various chemical processes w.r.t. pressure volume behaviour of given amount of ideal gas has been shown in Fig. 5.2.

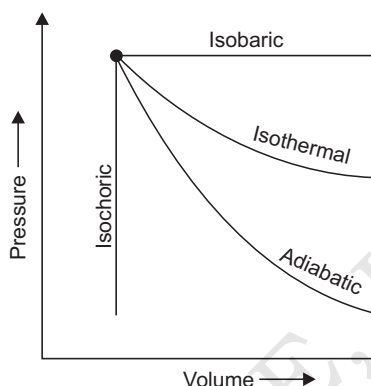


Fig. 5.2. Graphic representation of various thermodynamic processes.

(v) **Cyclic Process.** It is a process in which the system returns to the original state after undergoing series of changes. **For example,** in a process shown below the system returns to the original state **A** after successive changes.

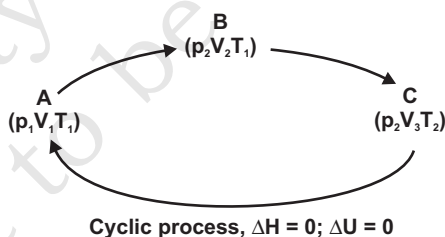


Fig. 5.3

Table 5.1. Difference between Reversible and Irreversible Process

Reversible Process	Irreversible Process
1. It is process which follows reversible path.	1. It is process which follows irreversible path.
2. It is an ideal process and takes infinite time.	2. It is a spontaneous process and takes finite time.

3. It occurs through infinite number of steps under equilibrium conditions at each step.	3. Equilibrium exists only in the beginning and at the completion stage.
4. In this process, the opposing force and driving force differ only by infinitesimally small magnitude.	4. In this process, there is large difference between driving and opposing force.
5. Work obtained is maximum.	5. Work obtained is not maximum.
6. It is only an imaginary process and cannot be realised in actual practice.	6. It is a natural process and occurs in a particular direction under given set of conditions.

Chemical Energy

Chemical energy is the energy stored in bonds of a chemical compound. This chemical energy may be released during a chemical reaction as in **exothermic** reactions. Some times energy input is required in chemical energy as in **endothermic** reactions.

Examples of stored chemical energies are, batteries, biomass, natural gas, petroleum and coal.

Heat and Work

The exchange of energy between the system and surroundings can occur in several ways. *Heat and Work* are two important modes of transference of energy between system and surroundings.

1. Heat (q)

The transference of energy takes place as **heat** if the system (reaction mixture) and surroundings are at different temperatures. The exchange of heat occurs through the thermally conducting walls which constitute boundary between system and surrounding. If the system is at higher temperature, the energy is lost to the surrounding as heat, causing a fall in the temperature of the system. The energy transfer continues till the system and the surroundings attain the same temperature. If the system is at lower temperature than the surroundings, the energy is gained by the system from the surroundings causing a rise in the temperature of the system. The amount of heat gained or lost by the system is represented by **q** . According to the international conventions,

Heat absorbed by the system is positive, i.e., $q > 0$.

Heat given out by the system is negative, i.e., $q < 0$.

2. Work (w)

Exchange of energy between system and surrounding can occur in the form of work. Which may be *mechanical work*, *pressure volume work* or *electrical work*. For example let us take a system containing some quantity of water in a thermos flask which does not allow any exchange of heat between system and surrounding. Let temperature of water be T_A . We now insert a set of small paddles in water and rotate them causing churning of water for sometimes. This will result in the increase in the temperature of water. This indicates increase in the internal energy of water by adding **mechanical work** to the system. The same increase in the temperature of water can be produced by adding equal amount of **electrical work** with the help of an immersion rod. Let us now become familiar with **pressure volume work**. The exchange of energy as pressure-volume work can occur if system consists of gaseous substance and there is a difference of pressure between system and surrounding. The amount of work done by the system or on the system is denoted by w . According to international conventions,

Work done on the system is positive, i.e., $w > 0$

Work done by the system is negative, i.e., $w < 0$

The sign conventions of heat and work have been diagrammatically represented in Fig. 5.4.

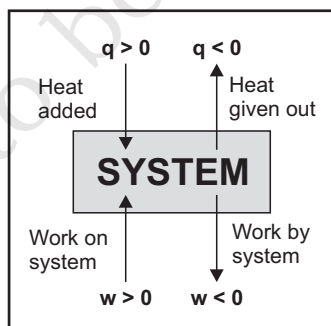


Fig. 5.4. Sign conventions of heat (q) and work (w).

Units of work. In CGS units, the work is expressed in *ergs* but in SI units, work is expressed in *joules*. The equivalence between joules and other units of work is

$$1 \text{ J} = 10^7 \text{ ergs} = 1 \text{ Nm} = 1 \text{ kg m}^2 \text{ s}^{-2}.$$

The common forms of work that we come across in the study of the thermodynamics are:

- (a) *Pressure volume work* and
 (b) *Electrical work*.

(a) **Pressure volume work.** This type of work is also called **expansion work** and it is significant in systems which consist of gases and involve changes in volume against the external pressure.

Expression for pV-work. In order to derive the expression for the pressure-volume (pV) work let us consider a 1 mol of ideal gas enclosed in a cylinder fitted with a frictionless piston having area of cross-section equal to 'a'. The total volume of the gas is V_i and the pressure inside the cylinder is p_{in} . Let the pressure on the piston is p_{ex} which is less than the internal pressure of the gas. This pressure difference causes the gas to expand against the external pressure p_{ex} forcing the piston to move out through a small distance l . Now, work of expansion is given by

$$\begin{aligned} w &= \text{Force} \times \text{displacement} \\ &= F \times l \end{aligned}$$

F, the force responsible for moving the piston is given by the product of *pressure* and *area* i.e.,

$$\begin{aligned} \therefore F &= p_{ex} \times a \\ w &= p_{ex} \times al \end{aligned}$$

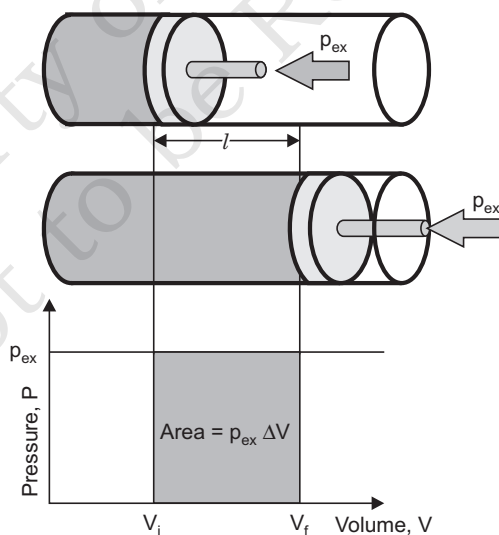


Fig. 5.5. Irreversible expansion against the constant pressure p_{ex} .

Since al refers to the change in volume (ΔV), i.e., $(V_f - V_i)$, therefore, work done is given by

$$w = p_{ex} \Delta V$$

During expansion, the work is done by the system and ΔV , i.e., $(V_f - V_i)$, is *positive*. Therefore, in order to satisfy the sign conventions, a negative sign is put in the expression for work

$$w = - p_{\text{ex}} \Delta V$$

It may be noted that above expression of work also holds good even for compression process in which the work is done on the system. ΔV , for compression is *negative*. Therefore, work as obtained from the above expression comes out to be *positive* and satisfies the conventions.

Following the above discussion, *the general expression for all type of pV-work can be written as:*

$$w = - p_{\text{ex}} \Delta V \quad \dots(5.1)$$

The above expression of work represents the work done during **irreversible expansion**. The work done during expansion of ideal gas in a reversible manner and in isothermal conditions can be calculated as follow.

Difference between Heat and Work

In order to understand the difference between heat and work, let us compare the effect of adding heat and work to a gaseous system.

- (i) When heat is added to a gas, its molecules start moving faster in different directions causing increase in disorder or randomness. Thus heat can be regarded as a mode which stimulates the random motion.
- (ii) When work is done on a system by forcing the piston down, the initial effect is to force the molecules to move in the direction of movement of piston. Thus, work can be regarded as a mode that stimulates the organised motion.

To conclude, *HEAT refers to random form of energy whereas WORK refers to organised form of energy.*

Internal Energy (U) and Internal Energy Change (ΔU) of the System

Since chemical changes are always accompanied by energy changes, it indicates that reactants and products must be having certain amounts of energy. A fixed quantity of any substance is associated with a definite amount of energy which depends upon chemical nature of the substance and its state of existence. This energy is called **internal energy or intrinsic energy** of the substance and is represented by **U**. Internal energy of the system, is the energy possessed by all its constituent molecules. The various forms of energies which contribute towards the

energy of the molecule are *translational energy* (E_t), *rotational energy* (E_r), *vibrational energy* (E_v), *electronic energy* (E_e), *nuclear energies of constituent atoms* (E_n) and *potential energy due to interaction with neighbouring molecules* (E_{PE}). Internal energy is an *extensive property* and is also a *state function*. Its value depends upon state of the substance but does not depend upon how that state is achieved. For example, CO_2 can be obtained by various methods such as by heating calcium carbonate or by burning coal. However, one mole of CO_2 at S.T.P. is associated with a definite amount of internal energy which does not depend upon the source from which it is obtained.

It may be noted that the absolute value of internal energy cannot be determined because it is not possible to determine the exact values for the constituent energies such as translational, vibrational, rotational energies, etc. However, we can determine the change in internal energy (ΔU) of the system when it undergoes a change from initial state (U_i) to final state (U_f). For example, the change in internal energy (ΔU) of a reaction is the difference between the internal energies of the products (ΣU_p) and the reactants (ΣU_r).

$$\Delta U = \Sigma U_p - \Sigma U_r$$

Significant Features of U

- Internal energy depends upon the quantity of substance in the system and hence, it is an *extensive property*.
- Change in internal energy (ΔU) represents the **heat evolved or absorbed in a reaction at constant temperature and constant volume**.
- For processes involving evolution of energy, $U_p < U_r$. Thus, $\Delta U < 0$ or *sign of ΔU is negative*.
- For processes involving absorption of energy, $U_p > U_r$. Thus, $\Delta U > 0$ or *sign of ΔU is positive*.
- For isothermal processes involving ideal gas, T is constant. Hence, $\Delta U = 0$.

Thermodynamic Scale of Temperature

In our daily routine we come across different objects having different degree of hotness according to our physical senses. In order to differentiate different degree of hotness or coldness, we need to develop some parameter or scale with reference to which measurement of hotness can be made. **Temperature** is one such parameter and one of the familiar

scale of temperature is *celcius scale*. In celcius scale, the reference points are ice point (0°C) and steam point (100°C) for water and the interval between them has been divided into 100 equal parts called **degrees**. The zero point of this scale is arbitrary creation of its inventor. In 1954, **international committee on weights and measures** adopted **Kelvin Scale** of temperature which is based on *absolute zero* of temperature (-273.16°C) and **triple point** of water. The triple point of water is a fixed temperature and pressure (0.01°C and 4.58 torr) at which all the three physical states of water, *ice*, *water* and *water vapour* exist in equilibrium. **Kelvin (K)** has been adopted as the basic SI unit of temperature which is

$\frac{1}{273.16}$ of the triple point temperature (273.16 K) of water. This kelvin

scale of temperature is called **thermodynamic temperature scale** and its zero point refers to the lowest possible temperature.

Law of conservation of energy (First Law of Thermodynamics)

It is a common experience that energy cannot be generated without consuming energy of some other kind. If a certain amount of one kind of energy is produced, an equal amount of some other kind of energy disappears so that the total energy of the Universe remains constant. This observation forms the basis of **first law of thermodynamics** which is also known as **law of conservation of energy**. The law states that:

Energy can neither be created nor destroyed although it may be changed from one form to another.

From this statement it follows that *total energy of the universe, i.e., system and surroundings taken together is always constant during any physical or chemical process.*

Mathematical Expression of First Law

In order to derive mathematical expression for first law of thermodynamics let us assume that a system having internal energy U_1 absorbs a certain amount of heat energy (q).

\therefore Its internal energy becomes $= q + U_1$.

Let a w amount of work be done on it, so that its internal energy changes to U_2 .

Now, final internal energy U_2 is given by

$$U_2 = U_1 + q + w$$

or $U_2 - U_1 = q + w$ or $\Delta U = q + w$... (5.2)

i.e., (Change in internal energy) = (Heat absorbed)
+ (Work done on the system)

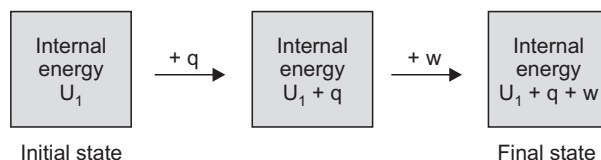


Fig. 5.6

Let the change in volume during the process be ΔV at constant pressure p , then the work is referred to as pressure-volume work and its expression is given as $-p \Delta V$.

Thus, $w = -p \Delta V$... (5.3)

Now if there is only pressure-volume work, expression (5.2) can be written as

$$\Delta U = q - p \Delta V \quad \dots(5.4)$$

Some Important Results From the First Law Equation, $\Delta U = q + w$

1. For *isothermal reversible* as well *irreversible expansion* of ideal gas $\Delta U = 0$

$$\therefore 0 = q + w \quad \text{or} \quad q = -w$$

- (a) For *irreversible expansion*, $w = -p_{\text{ext}} \Delta V$

$$q = -w = p_{\text{ext}} \Delta V \quad \dots(5.5)$$

- (b) For *reversible expansion*,

$$w = -2.303 nRT \log \frac{V_2}{V_1}$$

$$\therefore q = -w = 2.303 nRT \log \frac{V_2}{V_1} \quad \dots(5.6)$$

2. For *expansion of ideal gas into vacuum*

$$\Delta U = 0; w = 0 \quad \therefore q = 0$$

3. For *adiabatic process*, $q = 0$

$$\therefore \Delta U = -w_{\text{ad}} \quad \dots(5.7)$$

4. For *isochoric process*, $\Delta V = 0$

$$\therefore \Delta U = q_{(v)} \quad \dots(5.8)$$

Equation (5.8) implies that ΔU represents heat change taking place during the process occurring at constant temperature and constant volume.

Example 5.1. A gas expands isothermally against constant external pressure of 1 atm from a volume of 10 dm³ to a volume of 20 dm³. In the process, it absorbs 800 J of thermal energy from surroundings. Calculate the value of internal energy change.

Solution. Here, $p_{\text{ex}} = 1 \text{ atm}$

$$\Delta V = (V_2 - V_1) = (20 - 10) = 10 \text{ dm}^3$$

$$w = -p_{\text{ex}} \Delta V = -1 \times 10 = -10 \text{ dm}^3\text{-atm}$$

$$= -10 \times 101.3 \text{ J} = -1013 \text{ J}$$

$$q = +800 \text{ J}$$

$$\therefore \Delta U = q + w = 800 + (-1013) = -213 \text{ J.}$$

Enthalpy (H)-Another Useful State Function

We have studied that energy change occurring during the reaction at *constant temperature* and *constant volume* is given by internal energy change. However, most of the reactions in the laboratory are carried out in open beakers or test tubes, etc. In such cases, the reacting system is open to atmosphere. Since atmospheric pressure is almost constant, therefore, such reactions may involve the changes in volume. The energy change occurring during such reactions may not be equal to the internal energy change. In order to understand this, let us assume a chemical reaction involving gaseous substances which proceeds with the evolution of heat. When the reaction is carried out at constant pressure, two possibilities arise.

- If the reaction proceeds with the increase in volume the system has to expand against the atmospheric pressure and energy is required for this purpose. The heat **evolved** in this case would be little less than the heat **evolved** at constant volume because a part of the energy has to be utilised for expansion.
- If the reaction proceeds with decrease in volume at constant pressure, the work is done on the system and heat **evolved** will be greater than the heat **evolved** at constant volume.

Thus, it can be concluded from the above discussion that heat changes occurring at constant pressure and constant temperature are not simply due to the changes in internal energy alone but also include energy changes due to expansion or contraction against the atmospheric pressure. In order to study the heat changes of chemical reactions at constant temperature and pressure a new function, *enthalpy* is introduced. **Enthalpy** is the total energy associated with any system which includes its internal energy and also energy due to environmental

factors such as pressure-volume conditions. This can be understood as follows:

A substance has to occupy some space in its surroundings depending upon its volume (V). It does so against the compressing influence of the atmospheric pressure (p). Due to this, the substance possesses an additional energy called pV energy which is given by the product of pressure (p) and volume (V) of the system.

The sum of internal energy and pV energy of any system, under given set of conditions, is called **enthalpy**. It is denoted by H and is also called **heat content** of the system.

Mathematically, it may be put as

$$H = U + pV \quad \dots(5.9)$$

Some important features of enthalpy are:

- It is a state function and is an extensive property,
- It is also called **heat content** of the system,
- Its value depends upon amount of the substance, chemical nature of the substance and conditions of temperature and pressure.

Enthalpy Change (ΔH)

It is not possible to determine the absolute value of enthalpy of a system because absolute value of internal energy (U) is not known. However, change in enthalpy (ΔH) taking place during the process can be experimentally determined. Change in enthalpy is equal to difference between the enthalpies of products (ΣH_p) and reactants (ΣH_R).

The change in enthalpy may be expressed as

$$\Delta H = \Sigma H_p - \Sigma H_R$$

Significance of ΔH

Significance of ΔH also follows from the first law of thermodynamics

$$\Delta U = q - p\Delta V$$

or

$$\begin{aligned} q &= \Delta U + p\Delta V = (U_2 - U_1) + p(V_2 - V_1) \\ &= (U_2 + pV_2) - (U_1 + pV_1) \\ &= H_2 - H_1 = \Delta H \end{aligned}$$

or

$$\Delta H = q_p \quad \dots(5.10)$$

In short:

ΔU : Heat Changes at Constant T and V .

ΔH : Heat Changes at Constant T and P .

Exothermic and Endothermic Reactions

We know that the chemical reactions are always accompanied by the energy changes. There are many reactions in which energy is evolved while in others energy is absorbed. Depending upon the evolution or absorption of energy, the chemical reactions can be classified into two types: *exothermic* and *endothermic*.

Exothermic Reactions

The chemical reactions which proceed with the evolution of heat energy are called **exothermic reactions**. The heat energy produced during the reaction is indicated by writing + q or more precisely by giving the actual numerical value along with products. In general, exothermic reactions may be represented as :

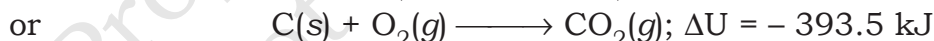
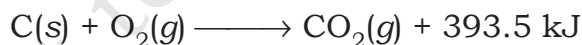


The heat evolved is expressed in the units of *joules (J)* or *kilo joules (kJ)*.

Now, if the reaction is carried out *at constant temperature and constant volume*, heat evolved is equal to internal energy change (ΔU). For exothermic reactions there is an evolution of heat energy and consequently, the energy of the products (ΣU_P) becomes less than internal energy of the reactants (ΣU_R). Thus, ΔU will be **negative**.

$$\begin{aligned} \Delta U &= \Sigma U_P - \Sigma U_R \\ \text{As } \Sigma U_P &< \Sigma U_R \\ \therefore \Delta U &= -ve \end{aligned}$$

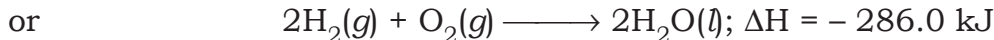
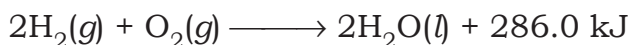
For example, when one mole of carbon (coal) is burnt in oxygen, there is an evolution of 393.5 kJ of energy. It can be expressed as:



For a reaction carried out *at constant temperature and constant pressure*, the heat evolved is equal to enthalpy change (ΔH). In exothermic reactions the enthalpy of products (ΣH_P) becomes less than the enthalpy of reactants (ΣH_R). Therefore, the enthalpy change for exothermic reaction is **negative**.

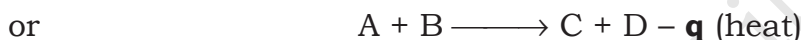
$$\begin{aligned} \Delta H &= \Sigma H_P - \Sigma H_R \\ \text{As } \Sigma H_P &< \Sigma H_R \\ \therefore \Delta H &= -ve. \end{aligned}$$

For example, formation of one mole of water from hydrogen and oxygen gases is accompanied by the evolution of 286.0 kJ of heat. It can be expressed as:



Endothermic Reactions

The chemical reactions which proceed with the absorption of heat energy are called endothermic reactions. The heat energy absorbed during the reaction can be indicated by writing $+q$ (or the actual numerical value) with the reactants. It can be indicated by writing $-q$ (or the actual numerical value) with the products. In general, an endothermic reaction can be represented as:



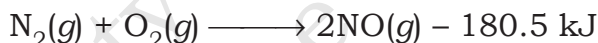
where q is the heat absorbed.

When the reaction is carried out at *constant temperature* and *constant volume* the internal energy of the products (ΣU_p) will become more than the internal energy of the reactants (ΣU_R) due to absorption of heat. Consequently, the value of ΔU will be **positive**.

$$\Delta U = \Sigma U_p - \Sigma U_R, \text{ As } \Sigma U_p > \Sigma U_R$$

$$\Delta U = +ve$$

For example, formation of nitric oxide from nitrogen and oxygen proceeds with the absorption of 180.5 kJ of heat. It can be represented as:



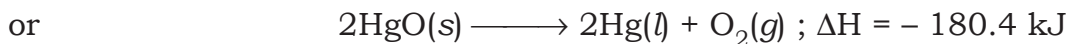
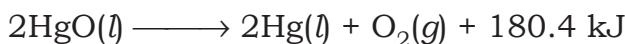
When, endothermic reaction is carried out at *constant temperature* and *constant pressure*, the heat absorbed increases the enthalpy of the products. In such a case the **enthalpy change** of the reaction is **positive**.

$$\Delta H = \Sigma H_p - \Sigma H_R, \text{ As } \Sigma H_p > \Sigma H_R$$

\therefore

$$\Delta H = +ve$$

For example, decomposition of 2 moles of mercuric oxide at a constant temperature and pressure proceeds with the absorption of 180.4 kJ of heat. It can be represented as:



The enthalpy changes for exothermic and endothermic reactions have been shown in Figs. 5.7 (a) and (b) respectively.

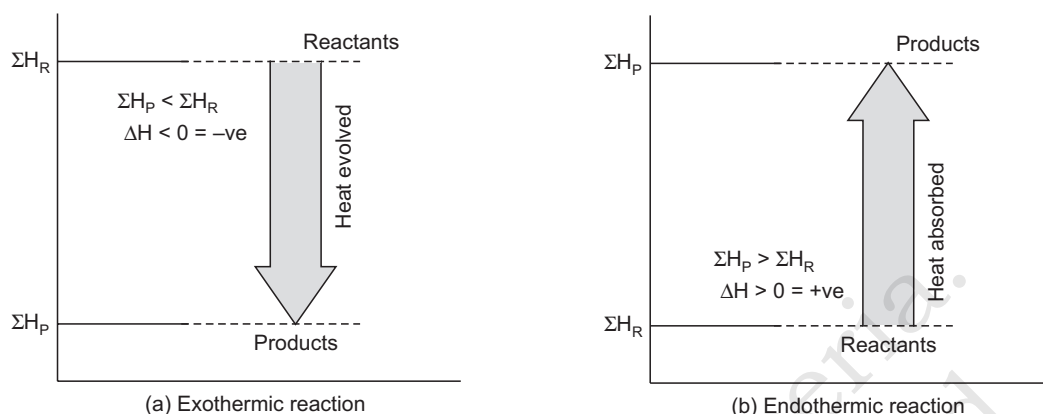


Fig. 5.7

EXPERIMENT 1

Aim: Demonstrate experiment to explain exothermic and endothermic reactions.

Theory: Exothermic reactions are those reactions during which energy or heat is liberated while endothermic reactions are those reactions in which energy or heat is required or absorbed.

Chemicals and Apparatus: Beaker, water, white vinegar, steelwool, detergent, sodium bicarbonate, thermometer etc.

Procedure:

1. Take 4 beakers.

S. No.	Solvent	Solid	Initial temp.	Final temp.	Type of reaction
1.	Water	Detergent			Exothermic
2.	H ₂ SO ₄	Sugar			Exothermic
3.	Vinegar	Sodium bicarbonate			Endothermic
4.	Water	NaCl			Endothermic

2. Half fill four beakers with solvent as given in the table.
3. Note down temperature of solvent in all four beakers and record in the table.
4. Now add solid solute as mentioned in the table.

5. Note down temperature of solution after 2 minutes of adding the solid solute.
6. If final temperature is more than reaction is exothermic and if final temperature that is less reaction is endothermic.

Thermochemical Equations

Chemical equation is a brief representation of a chemical change in terms of symbols or formulae of reactants and products. When the heat change accompanying the chemical reaction is also included in the chemical equation it is known as *thermochemical equation*. Thus, a **thermochemical equation** may be defined as *a chemical equation which indicates the amount of heat evolved or absorbed during the chemical reaction in addition to the quantities of reactants or products*. It may be noted that in thermochemical equations the fractional coefficients are also commonly used contrary to our usual practice for balancing the chemical equations. A thermochemical equation can be written in two ways:

(a) Heat effect can be written as one of the term along with the products.

For example,



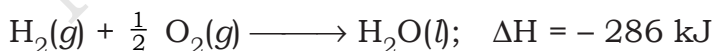
(b) Heat evolved or absorbed can be expressed in terms of ΔH .

For example,

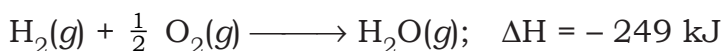


It is very important to mention the **physical states** of various reactants and products while writing thermochemical equations because change of physical state is also accompanied by the enthalpy changes. For example:

When 1 mol of hydrogen gas reacts with $\frac{1}{2}$ mol of oxygen gas to produce 1 mol of liquid water, 286 kJ of heat is produced.



On the other hand, if 1 mol of water vapours is produced instead of 1 mol of liquid water, the value of ΔH will be different.



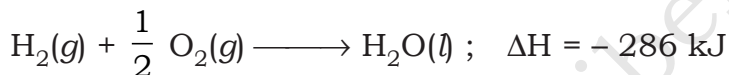
Some Important Conventions about Thermochemical Equations

1. The coefficients of various substances of chemical equation represent the number of their respective moles. In thermodynamic interpretation of

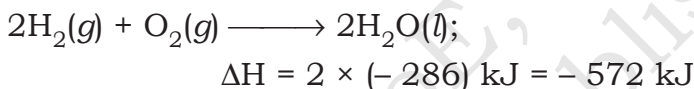
an equation, we never interpret the coefficients as number of molecules. Hence, it is acceptable to write coefficients in fractions wherever necessary.

2. The value of ΔH in a thermochemical equation corresponds to the enthalpy change taking place when a specified number of moles of various reactants and products (as indicated by the coefficients of the various substances in the chemical equation), are involved in the reaction.

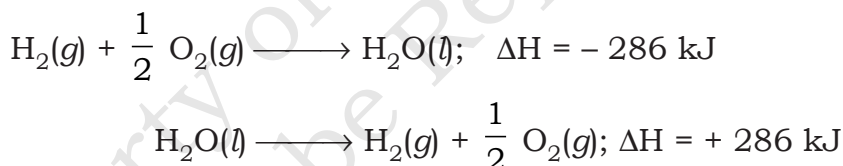
3. In case, the coefficients in the chemical equation are multiplied or divided by some integer, the ΔH value must also be multiplied or divided by the same integer. **For example:**



If the whole equation is multiplied by 2, the ΔH for the new thermochemical equation is given as:

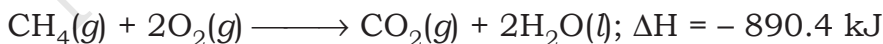
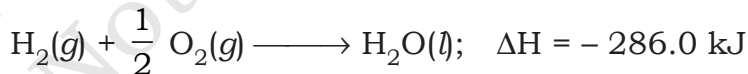


4. When a chemical equation is reversed, the magnitude of the ΔH remains same, however, its sign is reversed. For example, if ΔH is +ve for the forward reaction, it would be negative for the reverse reaction.

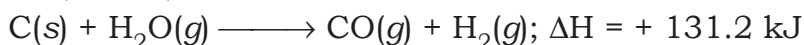
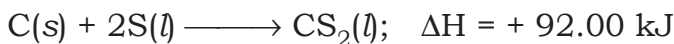


The thermochemical equations for some exothermic and endothermic reactions are given as follows:

Exothermic reactions ($\Delta H = -ve$):



Endothermic reactions ($\Delta H = +ve$):



Heat Capacity

In the previous sections, we have been studying about the heat changes. In this section, we shall focus on the measurement of heat change. The heat transferred to the system appears as a rise of its temperature. The increase in temperature (ΔT) is directly proportional to the quantity of heat (q) absorbed by the system. It can be put as

$$q \propto \Delta T \quad \text{or} \quad q = C\Delta T \quad \dots(5.11)$$

where C is called **heat capacity** of the system the value of which depends upon the size, composition and nature of the system.

Now, if the temperature difference (ΔT) is unity, *i.e.*, 1° celsius or 1 kelvin then, $q = C$. Thus, **heat capacity of the system is defined as the quantity of heat required to raise its temperature through 1° .**

Equation 5.15 reveals that a given amount of heat will raise the temperature of the system to a smaller extent if its heat capacity is large and *vice versa*.

The units of heat capacity are JK^{-1} or $\text{J}(\text{C}^{-1})$

Specific Heat Capacity (c)

This term is used more frequently for *solids* and *liquids*. Heat capacity of the system is extensive property and therefore, depends upon the quantity of matter in the system. For example, large block of aluminium has a higher heat capacity than does a small piece of the same metal. **Specific heat capacity** or **specific heat** (c) is a heat capacity of 1 g of the sample of the substance. It is *the quantity of heat required to raise the temperature of 1 gram of substance through 1 K (or 1°C).*

$$\text{Specific heat capacity } (c) = \frac{\text{Heat capacity}}{\text{Mass}} = \frac{C}{m}$$

$$\text{Now,} \quad C = \frac{q}{\Delta T}$$

$$\therefore \text{ Specific heat capacity } (c) = \frac{q}{m \Delta T} \quad \dots(5.12)$$

Units of specific heat capacity are:

$$\text{Jg}^{-1} \text{K}^{-1} \quad \text{or} \quad \text{Jg}^{-1} (\text{C}^{-1})$$

Combining equation 5.15 and 5.16 we get

$$q = c \times m \times \Delta T = C\Delta T$$

Molar Heat Capacity

This term is generally used for gaseous systems.

The molar heat capacity (C_m) of the substance is the **heat required to raise the temperature of 1 mol of the gaseous system through 1°**. If C is the heat capacity of n mol of the system then its molar heat capacity, C_m is given by $C_m = \frac{C}{n}$ or $C_m = \frac{q}{n \Delta T}$.

The units of molar heat capacity (C_m) are:

$$\mathbf{J \ mol^{-1}K^{-1} \ or \ J \ mol^{-1} \ (^{\circ}C^{-1})}$$

The specific heat capacity (c) and molar heat capacity (C_m) of the substance are related as

$$\mathbf{C_m = c \times \ molar \ mass} \quad \dots(5.13)$$

Molar Heat Capacities at Constant Volume and Constant Pressure

We know that heat is not a state function but depends on the path. Likewise *heat capacity is also a path function*. Thus, conditions such as *constant volume* or *constant pressure* have to be specified to define the path for calculating the heat capacity of a system particularly if it is a gas. The heat capacities of 1 mole of a gas at constant volume and that at constant pressure are represented by C_v and C_p respectively.

Relationship between C_p and C_v

Consider 1 mol of ideal gas whose temperature is to be raised through one degree (1 K). When the gas is heated at constant volume, no external work is done by the gas. Heat supplied increases the internal energy of gas. However, when the gas is heated at constant pressure, there will be increase in its volume. The gas will expand and do some external work. Some extra heat must be supplied to the gas to enable it to perform this external work. Thus, heat capacity at constant pressure (C_p) is larger than that at constant volume (C_v). The difference between the two *i.e.*, ($C_p - C_v$), evidently gives the work done by 1 mol of the gas in expansion when it is heated through one degree. In other words, it represents *work done per mol per degree rise in temperature* which is nothing but universal gas constant (R). Thus,

$$\mathbf{C_p - C_v = R}$$

Experimental Data Analysis

The heat changes associated with chemical reactions can be measured by experimental technique called **calorimetry**. In calorimetry, the

process is carried out in a vessel called calorimeter, which is immersed in a known volume of a liquid. Knowing the heat capacity of the liquid in which calorimeter is immersed and the heat capacity of calorimeter, it is possible to determine the heat evolved or absorbed in the process by measuring temperature changes. Measurements are made under two different conditions:

- (a) at constant volume, q_v or ΔU
- (b) at constant pressure, q_p or ΔH

(a) **ΔU measurements:**

There are different types of calorimeters depending upon the requirements of a particular experiment. In general, reactions taking place at constant volume and involving gases are carried out in a closed container with rigid walls which could withstand high pressures developed. One such vessel is a **bomb calorimeter**. It is made of heavy steel. The steel vessel is coated inside with gold or platinum to avoid oxidation of steel during the chemical reactions. The vessel is fitted with a tight screw cap. There are two electrodes R_1 and R_2 which are connected to each other through a platinum wire S as shown in Fig. 5.8. The wire S remains dipping in a platinum cup just below it.

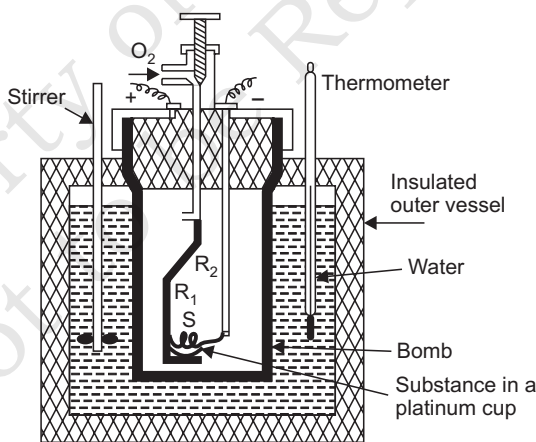


Fig. 5.8. Bomb calorimeter.

A small amount of the substance under investigation is taken in platinum cup. The vessel is then filled with excess of oxygen at a pressure of about 20 to 25 atmospheres and is subsequently sealed. It is now dipped in a insulated water bath which is also provided with a mechanical stirrer and a thermometer, sensitive enough to read upto 0.01°C (Beckmann's thermometer).

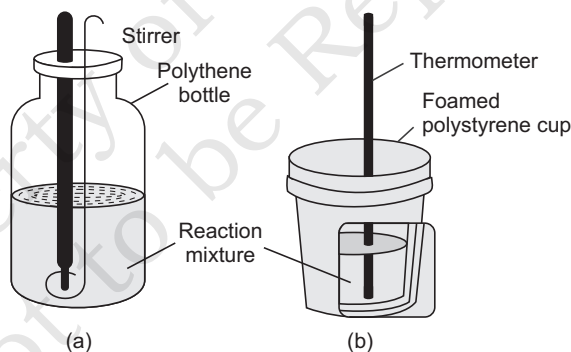
The initial temperature of water is noted and combustion is initiated by passing electric current through the platinum wire. The heat evolved during the chemical reactions raises the temperature of water which is recorded from the thermometer. By knowing the heat capacity of calorimeter and also the rise in temperature, the heat of combustion at constant volume can be calculated by using the following expression.

$$\Delta U = C \times \Delta T \times \frac{M}{w}$$

where, C = Heat capacity of calorimeter system
 ΔT = Rise in temperature
 M = Molar mass of the substance
 w = Mass of substance taken in grams.

(b) Measurement of ΔH

The change in enthalpy of a reaction can also be measured by calorimetry. The reaction is carried out in a calorimeter which is polythene bottle or foamed polystyrene cup fitted with thermometer and stirrer as shown in Fig. 5.9. The calorimeter is, however kept open to atmosphere so as to carry out the process at constant pressure.



**Fig. 5.9. (a) Polythene bottle as calorimeter.
 (b) Foamed polystyrene cup with cover**

In case the calorimeter is made of conducting walls, it may be immersed in an insulated water bath fitted with stirrer and thermometer. The temperature of the bath is noted in the beginning and after the reaction and the rise (or fall) in temperature ΔT is recorded. Knowing the heat capacity (C) of water bath and calorimeter system, the heat evolved or absorbed in the reaction can be calculated. From the data so obtained enthalpy change (ΔH) of the reaction can be determined.

EXPERIMENT 2

Aim: Use calorimeter to determine the heat of reaction. (Heat of combustion of graphite)

Theory: Graphite burns in excess of oxygen to form carbon dioxide with release of heat.



Chemicals and Apparatus: A calorimeter, thermometer, graphite

Procedure:

1. Take a calorimeter, fit it with a thermometer.
2. Take 18 g of graphite in solid form in the calorimeter cup.
3. The vessel surrounding the calorimeter cup is filled with water.
4. Now burn the graphite is burnt in the calorimeter in excess of oxygen.
5. Note down temperature before burning graphite and temperature when burning is over.
6. Do necessary calculations as per the formula.

Observations

$$t_1 = \dots\dots$$

$$t_2 = \dots\dots$$

$$\Delta T = \dots\dots$$

If heat capacity of the calorimeter is 20.7 kJ K^{-1}

Heat absorbed by the calorimeter = $C\Delta T$.

$$q = C\Delta t$$

$$\text{Heat of reaction} = C \times \Delta T \times \frac{M}{w}$$

where C is heat capacity of calorimeter

ΔT = Rise in temperature

M = Molar mass of graphite

m_w = Mass of graphite taken

5.2. ENTHALPY CHANGE OF A REACTION, $\Delta_r H$ REACTION ENTHALPY

The **enthalpy of a reaction** is defined as the *enthalpy change accompanying the chemical reaction when the molar quantities of reactants and products are the same as indicated in the chemical equation*. It is also known as *heat of reaction or reaction enthalpy*. It is represented by $\Delta_r H$.

It can be mathematically expressed as follows

$$\begin{aligned}\Delta_r H &= [\text{Sum of enthalpies of products}] \\ &\quad - [\text{Sum of enthalpies of reactants}] \\ &= \sum a_i H_{\text{Products}} - \sum b_i H_{\text{Reactants}}\end{aligned}$$

here, the symbol sigma Σ represents summation, whereas a_i and b_i represent stoichiometric coefficients of products and reactants respectively.

Standard Enthalpy of Reaction ($\Delta_r H$)

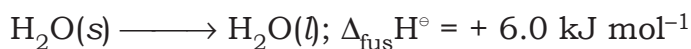
The reaction enthalpy $\Delta_r H$ depends on the conditions at which the reaction is carried out. Therefore, for the sake of comparison. It is more appropriate to express the values of $\Delta_r H$ for different reactions at their standard state conditions. *The standard state of a substance at a specified temperature is its pure form at one bar pressure.* For example, standard state of ethanol at 298 K is pure liquid ethanol at 1 bar, standard state of iron at 500 K is solid pure iron at 1 bar. The thermodynamic data is generally taken at 298 K. According to IUPAC recommendations, *the enthalpy change of a reaction when all the participating substances (reactants and products) are in their standard state is called **standard enthalpy of the reaction** and is denoted by $\Delta_r H^\ominus$.* The superscript ($^\ominus$) represents standard state. It is worthwhile to mention here, *that unless otherwise mentioned, the ΔH values are the standard enthalpy changes of the reactions.*

Enthalpy Changes During Phase Transformations

It is a matter of common observation that energy is required to convert a *solid* into *liquid* or a *liquid* into *gas*. The conversion of solid into liquid is called *melting* or *fusion* and the process of conversion of liquid into gas is termed as **vaporisation**. These processes are collectively known as **phase transformations** or **phase changes**. The magnitude of enthalpy change accompanying the phase transition depends largely on the strength of intermolecular forces in the substance undergoing phase transformation. Let us study the enthalpy changes accompanying the phase changes.

Standard or Molar Enthalpy of Fusion ($\Delta_{\text{fus}} H^\ominus$)

It is the enthalpy change accompanying the melting of 1 mole of a solid substance in standard state at its melting point. For example, when one mole of ice changes into water at its melting point 273 K, 6.0 kJ of heat is absorbed. It is represented as:



The values of enthalpy of fusion give an idea about the magnitude of interparticle forces in solids. For example, ionic solids have very strong interparticle forces. Consequently, they have high values of enthalpy of fusion. On the other hand, molecular solids have weak interparticle forces which reflect that their values of enthalpy of fusion are low. The enthalpies of fusion of some substances are given in Table 5.2.

Standard or Molar Enthalpy of Vaporisation ($\Delta_{\text{vap}}H^\ominus$) or Evaporation

It is the enthalpy change accompanying the conversion of one mole of a liquid in standard state into its vapours at the boiling point and standard pressure (1 bar). For example, when one mole of water is converted into steam at 273 K, the enthalpy change accompanying the process is 40.6 kJ. It can be expressed as:



The values of enthalpy of vaporisation give some idea about the magnitude of interparticle forces in liquids. The values of enthalpy of vaporisation of some substances are given in Table 5.2.

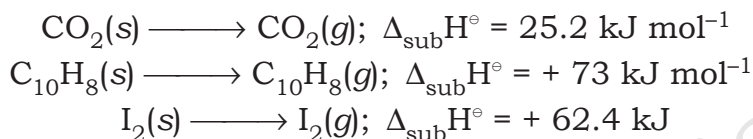
Table 5.2. Standard Enthalpy Changes of Fusion and Vaporisation

Substance	$T_f(K)$	$\Delta_{\text{fus}}H^\ominus$ (kJ mol ⁻¹)	$T_b(K)$	$\Delta_{\text{vap}}H^\ominus$ (kJ mol ⁻¹)
O ₂	55	0.45	90	0.67
He	03	0.021	04	0.092
N ₂	63.15	0.72	77.35	5.59
NH ₃	195.40	5.65	239.73	23.35
HCl	159.0	1.992	188.0	16.15
CO	68.0	6.836	82.0	6.04
CH ₃ COCH ₃	177.8	5.72	329.4	29.1
CCl ₄	250.16	2.5	349.69	30.0
H ₂ O	273.15	6.01	373.15	40.79
NaCl	1081.0	28.8	1665.0	170.0
C ₆ H ₆	278.65	9.83	353.25	30.8

Enthalpy of Sublimation ($\Delta_{\text{sub}}H^\ominus$)

It is the enthalpy change accompanying the sublimation of one mole of a solid substance into its gaseous state at a constant temperature below its melting point at the standard pressure.

Sublimation is direct conversion of a solid into vapour. **For example** solid CO_2 (*dry ice*) sublimates at 195 K with $\Delta_{\text{sub}}H^\ominus = 25.2 \text{ kJ mol}^{-1}$. Similarly $\Delta_{\text{sub}}H^\ominus$ of naphthalene and iodine are 73.0 kJ mol^{-1} and 62.4 kJ mol^{-1} respectively. The thermochemical equations are as under



The enthalpy of sublimation can be calculated with the help of Hess's law. The process of sublimation consists of change of solid state into vapour state in one step. The same change may be brought about in two steps:

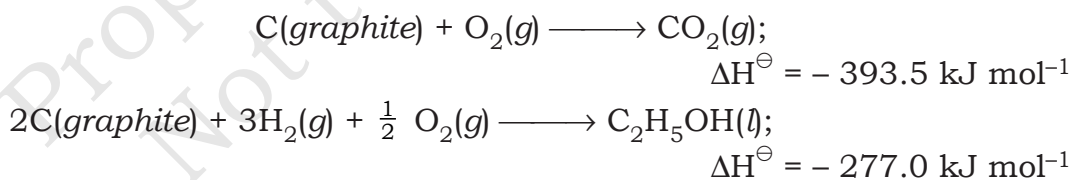
- (i) the melting of solid into its liquid and the enthalpy change is $\Delta_{\text{fus}}H^\ominus$.
- (ii) the vapourisation of the liquid into its gaseous state and the enthalpy change is $\Delta_{\text{vap}}H^\ominus$

$$\Delta_{\text{sub}}H^\ominus = \Delta_{\text{fus}}H^\ominus + \Delta_{\text{vap}}H^\ominus.$$

Standard Enthalpy of Formation ($\Delta_f H^\ominus$)

The **standard molar enthalpy of formation** of a compound is defined as the *enthalpy change accompanying the formation of one mole of a compound from its constituent elements in their most stable state of aggregation (also called reference state)*. It is generally denoted by $\Delta_f H^\ominus$ where, the subscript 'f' represents the word *formation*.

For example, standard enthalpy of formation of carbon dioxide (CO_2) and that of ethyl alcohol ($\text{C}_2\text{H}_5\text{OH}$) are -393.5 and $-277.0 \text{ kJ mol}^{-1}$ respectively. These are expressed as follows:



It may be noted that:

- (i) *The reference state of elements is the pure element in its most stable state of aggregation at 298 K and one bar pressure.* For example, the reference state of carbon, oxygen, sulphur, mercury, bromine, and iodine are: **C (graphite), O₂(g), S₈ (rhombic), Br₂(l) and I₂(s)** respectively.
- (ii) *By conventions, the standard molar enthalpies of formation of free elements in their reference state are taken to be zero.*

(iii) *Standard molar enthalpy of formation of the substance is also called its standard enthalpy and can also be denoted as H^\ominus .*

The values of standard molar enthalpies of formation of some substances at 298 K are given in Table 5.2.

Importance of standard molar enthalpies of formation. The knowledge of standard molar enthalpies of formation of various substances can help us to calculate standard enthalpy change of any reaction. Standard enthalpy change of a reaction is equal to the difference of the standard molar enthalpies of formation of all the products and standard molar enthalpies of formation of all the reactants.

$$\left[\begin{array}{c} \text{Standard} \\ \text{enthalpy} \\ \text{of} \\ \text{reaction} \end{array} \right] = \left[\begin{array}{c} \text{Sum of standard} \\ \text{molar enthalpies} \\ \text{of formation} \\ \text{of products} \end{array} \right] - \left[\begin{array}{c} \text{Sum of standard} \\ \text{molar enthalpies} \\ \text{of formation} \\ \text{of reactants} \end{array} \right]$$

or
$$\Delta_r H^\ominus = \sum \Delta_f H^\ominus (\text{Products}) - \sum \Delta_f H^\ominus (\text{Reactants})$$

For example, consider a hypothetical reaction



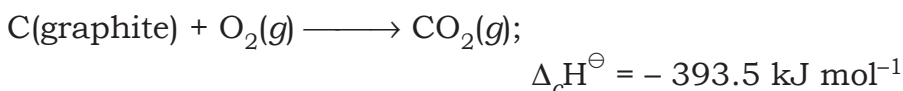
$$\begin{aligned} \Delta_r H^\ominus &= \sum \Delta_f H^\ominus (\text{Products}) - \sum \Delta_f H^\ominus (\text{Reactants}) \\ &= [l\Delta_f H^\ominus (L) + m\Delta_f H^\ominus (M)] - \\ &\quad [a\Delta_f H^\ominus (A) + b\Delta_f H^\ominus (B)]. \end{aligned}$$

Standard Enthalpy of Combustion ($\Delta_c H^\ominus$)

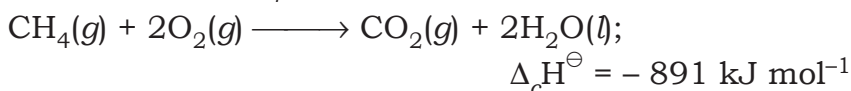
*It is the enthalpy change accompanying the complete combustion of one mole of a substance in excess of oxygen or air all the reactants and products being in their standard state at the specified temperature. It is denoted by $\Delta_c H^\ominus$ where subscript **c** represents the word combustion.*

It may be noted that combustion reactions are always exothermic, thus, the values of $\Delta_c H^\ominus$ is always negative. The combustion reactions find tremendous applications in industry, rocketry and other walks of life. Some examples of combustion reactions are as follows.

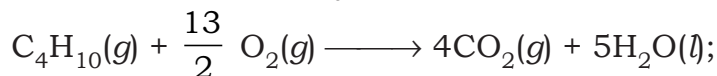
(i) Combustion of *carbon*



(ii) Combustion of *methane* (CH_4)



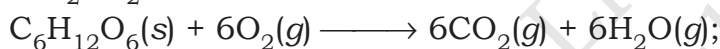
(iii) Combustion of *butane* (C_4H_{10})



$$\Delta_c H^\ominus = -2658 \text{ kJ mol}^{-1}$$

Combustion of Food in our Bodies

Our body requires energy for performing various functions. This energy mainly comes from carbohydrates and fats that we take as food. Carbohydrates are decomposed into glucose or its derivatives in the stomach. Glucose is soluble in blood. It is transported by blood cells to various parts of the body where it reacts with oxygen in a series of steps producing CO_2 , H_2O and energy.



$$\Delta H = -2900 \text{ kJ}$$

This combustion of glucose, in the human body, takes place at the body temperature because of the catalytic action of enzymes.

Efficiency of Foods and Fuels

Just as the major source of energy in our bodies is the combustion of foods in the similar way, the major source of energy for industries is the combustion of fuels. The efficiency of foods and fuels is compared in terms of their *calorific values*. The **Calorific Value** of food or fuel is defined as the *amount of heat produced when one gram of the substance (food and fuel) is completely burnt*. The calorific values of some common foods and fuels are given below:

Food	Calorific Value (kJ g^{-1})	Fuel	Calorific Value (kJ g^{-1})
Curd	2.5	Wood	17
Milk	3.2	Charcoal	33
Egg	7.3	Kerosene	48
Meat	12.0	Fuel oil	45
Honey	13.3	Butane (LPG)	55
Ghee	37.6	Hydrogen	150

The normal human needs 3000 kcal ($\approx 14450 \text{ kJ}$) of energy per day. The food consisting of carbohydrates, fats, oils, vitamins proteins, mineral salts which provide required calories is termed as **balanced diet**.

5.3. HESS'S LAW OF CONSTANT HEAT SUMMATION

On the basis of numerous thermochemical observations, the Russian Chemist, *Germain Henry Hess* gave one of the most important generalisation of thermochemistry in 1840 which is known after his name as **Hess's Law**. This generalisation is primarily based on the fact that enthalpy is a path independent thermodynamic function. In other words, the enthalpy change in a chemical reaction is same whether it occurs in one step or in more than one steps. This may be stated in the form of Hess's law as follows. *The standard enthalpy of reaction is the algebraic sum of the standard enthalpies of intermediate reactions into which the overall reaction may be splitted or divided at the same temperature.*

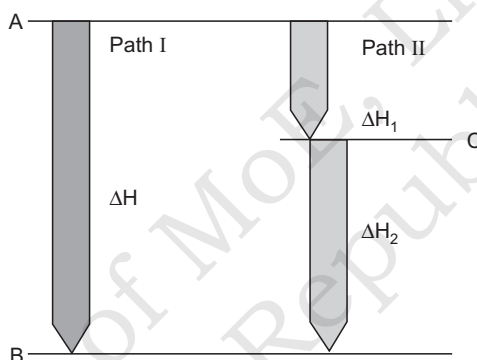


Fig. 5.10. Illustration of Hess's law.

Consider a process involving the conversion of reactant A into B in one step (path I). The enthalpy change of a process is represented by ΔH . Now suppose the process is split up into two steps involving a change from A to C and C to B according to path II, (Fig. 5.10). Let ΔH_1 and ΔH_2 be enthalpy changes from A to C and C to B respectively. Then, according to Hess's law:

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

Hess's law is simply a corollary of the law of conservation of energy. It implies that the enthalpy change of reaction depends only on the states of reactants and products and not on the manner by which the change is brought about. If ΔH were not independent of the manner in which the corresponding change was brought about, it would have been possible to create or destroy energy, by taking a system from A to B by one path and then returning it to state A by second path.

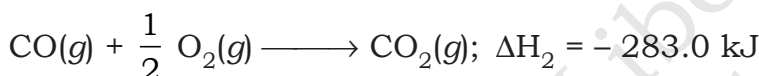
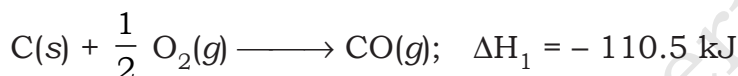
Illustration of Hess's Law

Let us consider the formation of carbon dioxide from carbon and oxygen. There are two ways by which the change can be brought about.

(a) Conversion of carbon to carbon dioxide



(b) Conversion of carbon to carbon monoxide and subsequent oxidation of carbon monoxide to carbon dioxide.



The two paths by which carbon can be converted into carbon dioxide have been shown in Fig. 5.11.

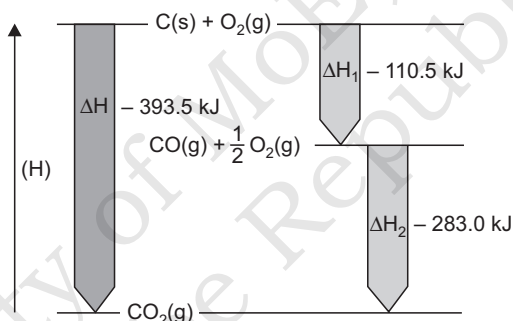


Fig. 5.11. Hess's law cycle for CO_2 .

As is clear,

$$\begin{aligned} \Delta\text{H} &= \Delta\text{H}_1 + \Delta\text{H}_2 \\ -393.5 \text{ kJ} &= -110.5 + (-283.0) \text{ kJ} \\ &= -393.5 \text{ kJ}. \end{aligned}$$

Applications of Hess's Law

The practical utility of Hess's law lies in the fact that it allows us to carry out thermochemical calculations to predict the enthalpies of different reactions whose direct measurement is not possible. The thermochemical equations, like the algebraic equations can be added or subtracted, multiplied or divided by any numerical factor. Some of the important applications of Hess's law are discussed below:

1. **Determination of Standard Enthalpy of Formation:** There are large number of compounds such as methane, benzene, carbon monoxide,

ethane, etc., which cannot be directly synthesised from their elements. Hence, their standard enthalpies of formation cannot be determined by the calorimetric method. In case of such substances the standard enthalpies of formation can be determined by an indirect method based upon Hess's law. The unknown reaction is made one segment of the closed cycle of reactions. The enthalpy changes of the reactions which represent other segments of the cycle can be determined experimentally. Then by applying Hess's law the desired value of ΔH can be calculated.

For example, let us study the calculation of enthalpy of formation of SO_3 .

The enthalpy of formation of SO_2 (ΔH_1) and enthalpy of combustion of SO_2 (ΔH_2) have been found to be $-297.4 \text{ kJ mol}^{-1}$ and $-97.9 \text{ kJ mol}^{-1}$ respectively. These changes have been shown in Fig. 5.12.

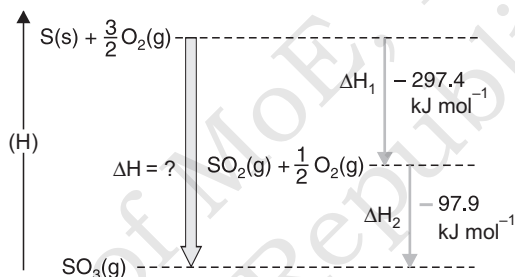


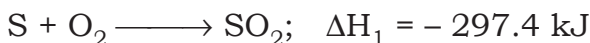
Fig. 5.12. Hess's law cycle for SO_3 .

Now according to Hess's law,

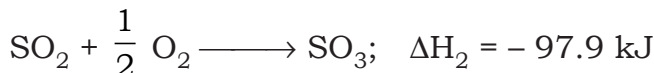
$$\Delta H = \Delta H_1 + \Delta H_2 = -297.4 + (-97.9) = -\mathbf{395.3 \text{ kJ}}$$

The same result can be arrived at by means of thermochemical calculations

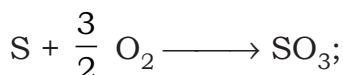
(i) Conversion of sulphur to sulphur dioxide



(ii) Combustion of sulphur dioxide to SO_3



Add equations (i) and (ii),



$$\Delta H = \Delta H_1 + \Delta H_2 = -297.4 - 97.9 = -\mathbf{395.3 \text{ kJ}}$$

2. Determination of Enthalpy of Transition: Transition implies the conversion of one allotropic form of a substance to another. For example, change of graphite to diamond, red phosphorus to yellow phosphorus and rhombic sulphur to monoclinic sulphur, etc. Such reactions are very slow and enthalpy change accompanying them cannot be measured directly. However, Hess's law is quite helpful in determining the enthalpy of transition.

For example, let us calculate the enthalpy of the process $S_{(R)} \longrightarrow S_{(M)}$ from the enthalpies of combustion of monoclinic sulphur ($S_{(M)}$) and rhombic sulphur ($S_{(R)}$) which have been found to be -296.4 and -295.1 kJ mol^{-1} respectively. Now Hess's law cycle is constituted as $S_{(R)} \longrightarrow \text{SO}_2$ (path I) and $S_{(R)} \longrightarrow S_{(M)} \longrightarrow \text{SO}_2$ (path II). These changes have been shown in Fig. 5.13.

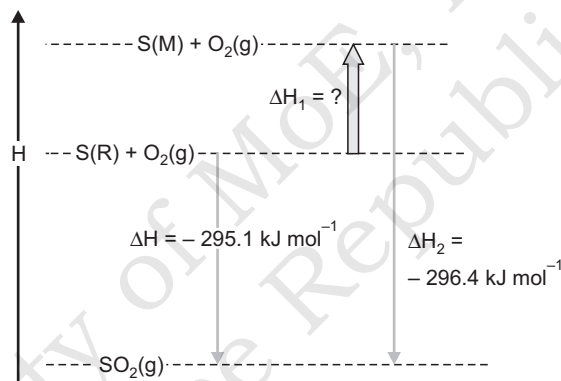


Fig. 5.13. Hess's law cycle for $S_{(R)}$ to SO_2 .

Now according to Hess's law:

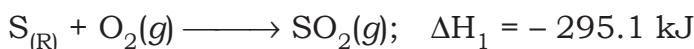
$$\Delta H = \Delta H_1 + \Delta H_2$$

or
$$\Delta H_1 = \Delta H - \Delta H_2 = -295.1 - (-296.4)$$

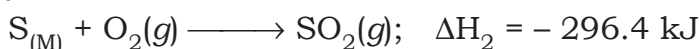
$$= \mathbf{1.3 \text{ kJ mol}^{-1}}.$$

The enthalpy of allotropic transformation of rhombic sulphur to monoclinic sulphur can also be calculated as follows by thermochemical calculations:

1. *Combustion of rhombic sulphur*



2. *Combustion of monoclinic sulphur*



Subtracting equation (2) from equation (1)

$$\begin{aligned} S_{(R)} &\longrightarrow S_{(M)}; \quad \Delta H = \Delta H_1 - \Delta H_2 \\ &= -295.1 - (-296.4) = + \mathbf{1.3 \text{ kJ mol}^{-1}}. \end{aligned}$$

3. Determination of Standard Enthalpy of Reaction: Hess's law cycle can also be used for the determination of standard enthalpy of the reaction from the knowledge of standard enthalpies of formation of various reactants and the products. The Hess's law cycle for elements in their standard states, reactants and products can be written as shown in Fig. 5.14.

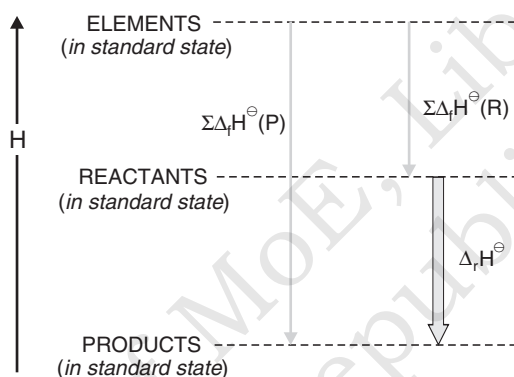


Fig. 5.14. Hess's law cycle for enthalpy of reaction.

$\Sigma\Delta_f H^\ominus(R)$ = Sum of the standard enthalpy of formation of reactants

$\Sigma\Delta_f H^\ominus(P)$ = Sum of the standard enthalpy of formation of the products

$\Delta_r H^\ominus$ = Standard enthalpy change of the reaction

Now according to Hess's law,

$$\Sigma\Delta_f H^\ominus(P) = \Sigma\Delta_f H^\ominus(R) + \Delta_r H^\ominus$$

or

$$\Delta_r H^\ominus = \Sigma\Delta_f H^\ominus(P) - \Sigma\Delta_f H^\ominus(R)$$

Let us now proceed to solve some numerical problems based upon *thermochemical calculations*.

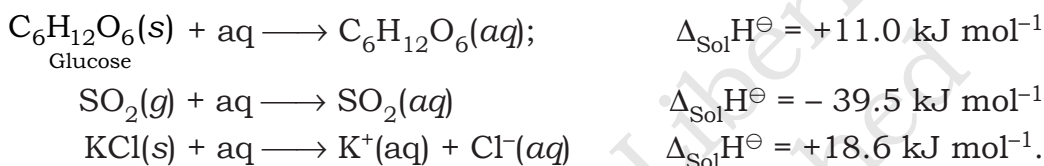
5.4. ENTHALPY CHANGE FOR DIFFERENT TYPES OF REACTIONS

In this section, we shall focus on the enthalpy change associated with different chemical processes.

Standard Enthalpy of Solution ($\Delta_{\text{sol}}H^\ominus$)

It is the enthalpy change accompanying the dissolution of one mole of a substance in specified amount of a solvent under standard conditions. The enthalpy change observed by dissolving one mole of substance in infinite amount of solvent so that interaction between solute molecules are negligible, is called **enthalpy of solution at infinite dilution**.

If water is the solvent, then the notation (aq) is used to represent aqueous solution at infinite dilution. Some examples are as follows.



Dissolution of Ionic Salts

Dissolution of ionic compounds can be viewed in terms of following steps.

(i) *Breaking of solute-solute interactions*: This step involves dismentalling of ionic crystal by breaking off the interionic attractions to form ions in gaseous state. This is endothermic process. The energy required for this purpose is expressed in the form of *lattice enthalpy*.

Lattice Enthalpy ($\Delta_{\text{L}}H^\ominus$). It is the enthalpy change taking place when 1 mole of ionic compound dissociates into gaseous ions of opposite charge at the standard conditions. For example, lattice enthalpy of NaCl(s) is +788 kJ mol⁻¹.



(ii) *Setting up of solute-solvent interactions*. Once the ions leave their ordered position in the crystal lattice, they get surrounded by the solvent molecules and start moving freely in the solution.

The interactions between the solvent molecules and the particles of solute is termed as **solvation**, in general, or **hydration** if the solvent is water. The hydration of ions releases energy which is expressed in terms of **enthalpy of hydration of ions** and is represented by $\Delta_{\text{Hyd}}H^\ominus$. It is defined as *the energy released by hydration of the ions furnished by one mole of the ionic compound*. These energy changes are related to standard enthalpy of solution. $\Delta_{\text{sol}}H$ according to Hess's law cycle as shown in Fig. 5.15.

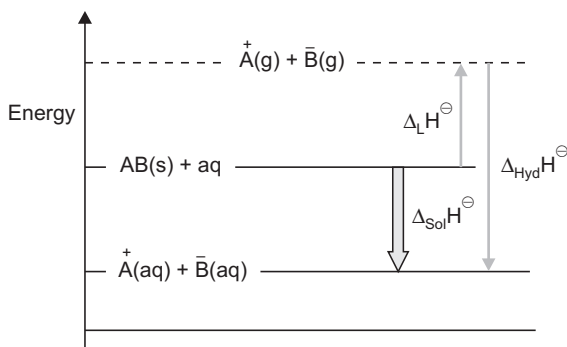


Fig. 5.15. Hess's law cycle for dissolution of ionic salt in water.

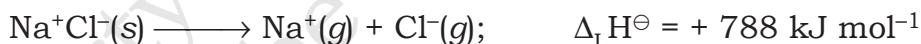
It is quite clear that

$$\Delta_{\text{Sol}}H^{\ominus} = \Delta_{\text{L}}H^{\ominus} + \Delta_{\text{Hyd}}H^{\ominus}$$

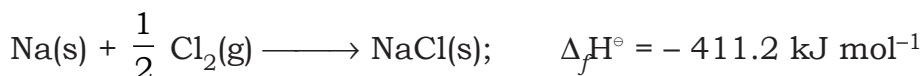
The value of $\Delta_{\text{Sol}}H^{\ominus}$ can be +ve or -ve depending upon the relative magnitudes of $\Delta_{\text{L}}H^{\ominus}$ and $\Delta_{\text{Hyd}}H^{\ominus}$. Dissolution of salt may not occur if the value of $\Delta_{\text{L}}H^{\ominus}$ is very high and that $\Delta_{\text{Hyd}}H^{\ominus}$ is very low.

Lattice Enthalpy and Born Haber Cycle

The **Lattice enthalpy** of ionic compound is the enthalpy change which occurs when one mole of ionic compound in solid state dissociates into its gaseous ions and vice versa at the standard conditions. It is represented by $\Delta_{\text{L}}H^{\ominus}$.



The magnitude of lattice enthalpy gives the idea of the stability of the ionic crystal. It is not possible to determine lattice enthalpies of ionic compounds directly by experimental techniques. However, we can use indirect method by constructing an enthalpy diagram called **Born Haber Cycle**. Born Haber cycle is a simplified method which was developed in 1919 by *Max Born* and *Fritz Haber* to correlate lattice energies of ionic crystals to other thermodynamic data. The development of Born Haber cycle was primarily based on Hess's law. Let us consider the energy changes during the formation of sodium chloride crystal from the *metallic sodium* and *chlorine gas* to calculate lattice enthalpy of $\text{NaCl}(\text{s})$. The net enthalpy of formation of sodium chloride is given as $\Delta_{\text{f}}H^{\ominus}(\text{NaCl}) = - 411.2 \text{ kJ mol}^{-1}$.

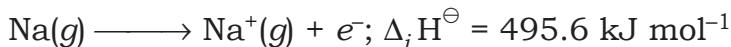


The overall process can be imagined to occur in following steps.

(i) *Sublimation of metallic sodium*

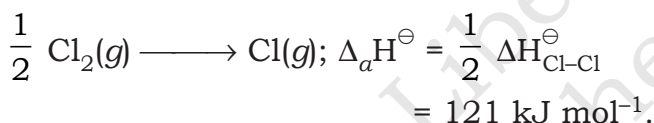


(ii) *Ionization of sodium atoms*



$\Delta_i\text{H}^{\ominus}$ is ionization enthalpy of sodium.

(iii) *Atomisation of Cl_2* . This step involves dissociation of $\text{Cl}_2(\text{g})$ into $\text{Cl}(\text{g})$ atoms. The reaction enthalpy is half of the *bond dissociation enthalpy* of chlorine.



(iv) *Conversion of $\text{Cl}(\text{g})$ to $\text{Cl}^-(\text{g})$* .



$\Delta_e\text{H}^{\ominus}$ is electron gain enthalpy of chlorine.

(v) *Combination of $\text{Na}^+(\text{g})$ and $\text{Cl}^-(\text{g})$ ions to form 1 mole of $\text{NaCl}(\text{s})$* . The energy released here is called lattice enthalpy ($\Delta_L\text{H}^{\ominus}$). The sequence of steps I-V is shown in Fig. 5.16 and is known as Born Haber cycle. The sum of the enthalpy changes round a cycle is zero.

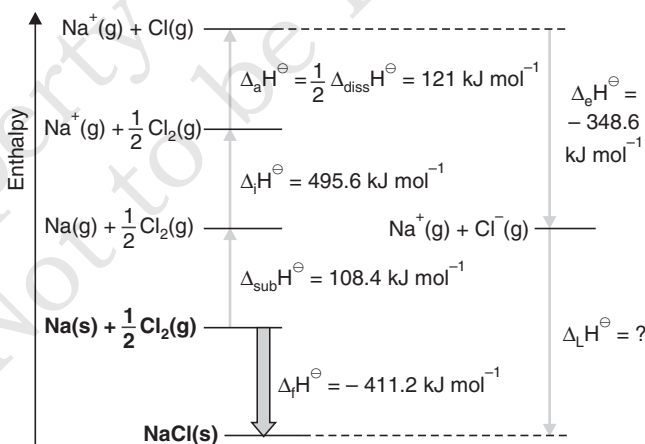


Fig. 5.16. Born Haber cycle for lattice enthalpy of NaCl.

Applying Hess's law we get

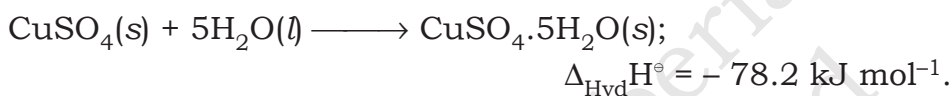
$$\Delta_f\text{H}^{\ominus} = \Delta_{\text{sub}}\text{H}^{\ominus} + \Delta_i\text{H}^{\ominus} + \frac{1}{2} \Delta_{\text{diss}}\text{H}^{\ominus} + \Delta_e\text{H}^{\ominus} + \Delta_L\text{H}^{\ominus}$$

or
$$\Delta_{\text{L}}H^{\ominus} = -411.2 - 108.4 - 121 - 495.6 + 348.6$$

$$= -787.6 \text{ kJ.}$$

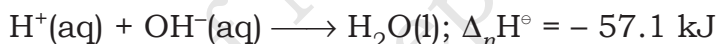
Enthalpy of Hydration Anhydrous Salt ($\Delta_{\text{HYD}}H^{\ominus}$)

It is the enthalpy change accompanying the hydration of one mole of an anhydrous salt by combining with specific number of moles of water. For example, enthalpy of hydration of anhydrous copper sulphate can be represented as:



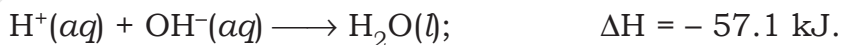
Standard Enthalpy of Neutralisation ($\Delta_{\text{n}}H^{\ominus}$)

Neutralisation process refers to the combination of H^+ ions furnished by acid and OH^- ions furnished by the base in aqueous solutions to form H_2O molecules. The formation of 1 mol of water by combination of 1 mol of H^+ ions and 1 mol of OH^- ions in aqueous solution proceeds with liberation of 57.1 kJ of heat. Thus, enthalpy of neutralisation can be represented as

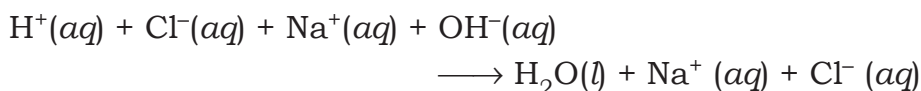


The enthalpy of neutralisation may, therefore, be defined as the *enthalpy change accompanying the formation of one mole of H_2O by combination of one mol H^+ ions furnished by acid and one mole of OH^- ions furnished by base in dilute solutions at the standard conditions.*

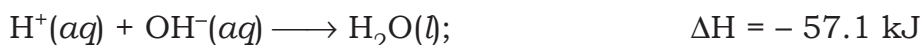
- $\Delta_{\text{n}}H^{\ominus}$ of strong acid-strong base is constant. i.e., $-57.1 \text{ kJ mol}^{-1}$. According to arrhenius theory of ionisation the strong acids and strong bases are almost completely ionised in dilute aqueous solutions. The neutralisation of strong acid and strong bases simply involve the combination of H^+ ions (from acid) and OH^- ions (from base) to form water molecules.



For example, the net process in the neutralisation of $\text{HCl}(\text{aq})$ and $\text{NaOH}(\text{aq})$ can be represented as:



or cancelling out the common ions on both sides of arrow, we get



During neutralisation of all strong acids and strong bases same reaction takes place. Hence *the value of enthalpy of neutralisation of strong acid or strong base is constant.*

- $\Delta_n H^\ominus$ of weak acid-strong base or vice-versa is less negative than -57.1 kJ.

If either acid or base is weak, then its ionization is not complete in aqueous solutions. Therefore, a part of the energy liberated during combination of H^+ ions and OH^- ions is utilised for the ionisation of weak acid (or base). Consequently, *the value of enthalpy of neutralisation of weak acid/strong base or strong acid/weak base is numerically less than 57.1 kJ.*

For example, enthalpy of neutralisation of weak acid, CH_3COOH and $NaOH$ is -56.1 kJ. The difference between the values $-56.1 - (-57.1)$, i.e., 1.0 kJ mol^{-1} represents the **enthalpy of ionisation** of CH_3COOH . Similarly, enthalpy of neutralisation of ammonium hydroxide (weak base) and hydrochloric acid (strong acid) is -51.5 kJ. Therefore, enthalpy of ionisation of NH_4OH is $-51.5 - (-57.1)$, i.e., 5.6 kJ mol^{-1} .

Enthalpy of Atomisation ($\Delta_a H^\ominus$)

The **enthalpy of atomisation** ($\Delta_a H^\ominus$) may be defined as *the enthalpy change accompanying the dissociation of one mole of the substance completely into its atoms in the gaseous state.*

In case of elements, however, the enthalpy of atomisation is enthalpy change accompanying the formation of **one mole of gaseous atoms.**

Let us study few examples

- (i) Enthalpy of atomisation of hydrogen is represented as



- (ii) Enthalpy of atomisation of sodium is represented as



In this case enthalpy of atomisation also represents *enthalpy of sublimation* of sodium.

- (iii) Enthalpy of atomisation of methane is represented as



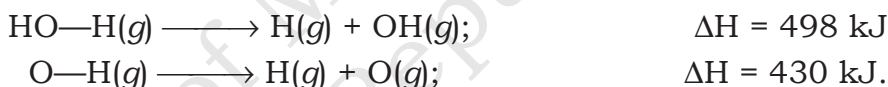
5.5. BOND ENTHALPY ($\Delta_{\text{BOND}}H^\ominus$)

We have learnt in unit 4 that the process of formation of a chemical bond is accompanied by the release of energy. Conversely, the energy has to be supplied for the breaking of a bond. *The energy required to break a particular bond in a gaseous molecule* is referred to as **bond dissociation enthalpy**. It is a definite quantity and is expressed in kJ mol^{-1} .

In a **diatomic molecule**, the *bond dissociation enthalpy* is same as *bond enthalpy*. For example, the energy required to break one mol of H—H bonds in gaseous state is 435.4 kJ. Therefore, bond enthalpy of H—H bond is $435.4 \text{ kJ mol}^{-1}$. This may be expressed as:

$$\Delta_{\text{H-H}}H^\ominus = 435.4 \text{ kJ mol}^{-1}$$

However, in a **polyatomic molecule** having more than one similar bonds the bond dissociation enthalpy is not the same for successive bonds. Therefore, in such a case the bond enthalpy is not equal to the bond dissociation enthalpy. For example, in H_2O molecule, the bond dissociation enthalpies of the two O—H bonds differ from one another as described below:



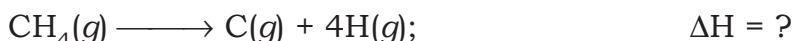
In such a case, therefore, the *bond enthalpy* is expressed as the average of the *bond dissociation enthalpies* of various similar bonds. For example, the **average bond enthalpy** of O—H bond is expressed as

$$\Delta_{\text{O-H}}H^\ominus = \frac{498 + 430}{2} = 464 \text{ kJ mol}^{-1}.$$

Thus, **mean bond enthalpy**, in general, may be defined as the *average amount of energy required to break one mole bonds of that type in gaseous molecules*.

Calculation of Bond Enthalpies

The thermochemical data makes it possible to calculate the bond enthalpies of different bonds. As an illustration the bond enthalpy of C—H bond in methane can be obtained if enthalpy of atomisation of methane is known.



The bond enthalpy of C—H bond is one fourth of the ΔH value for the above reaction. The value of ΔH can be calculated from the type of data available to us.

(a) Direct use of Hess's law if $\Delta_f H^\ominus$ values of $H(g)$, $C(g)$ and $CH_4(g)$ are given.

$\Delta_f H^\ominus$ values of $H(g)$; $C(g)$ and $CH_4(g)$ are 218.0, 717.0 and 750 kJ mol⁻¹ respectively.

$$\begin{aligned}\text{Now,} \quad \Delta_r H^\ominus &= \Sigma \Delta_f H^\ominus (\text{Products}) - \Sigma \Delta_f H^\ominus (\text{Reactants}) \\ &= 4\Delta_f H^\ominus H(g) + \Delta_f H^\ominus C(g) - \Delta_f H^\ominus CH_4(g) \\ &= 4(218) + 717 - (-75.0) = 1664 \text{ kJ}\end{aligned}$$

$$\therefore \Delta_{C-H} H^\ominus = \frac{1664}{4} = 416 \text{ kJ mol}^{-1}.$$

(b) Use of thermochemical calculations if the data has values other than $\Delta_f H^\ominus$.

Let the given data be:

$$\Delta_d H^\ominus \text{ of } H_2(g) = + 436 \text{ kJ mol}^{-1}$$

$$\Delta_{\text{Sub}} H^\ominus \text{ of carbon} = + 717 \text{ kJ mol}^{-1}$$

$$\Delta_c H^\ominus \text{ of Carbon, Hydrogen and Methane}$$

are - 394 kJ, - 286 kJ and - 891 kJ respectively.

Let us write thermochemical equation of each of the above.

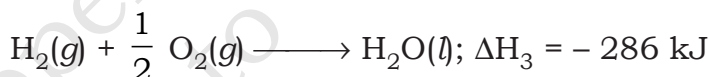
(i) Enthalpy of combustion of methane



(ii) Enthalpy of combustion of carbon



(iii) Enthalpy of combustion of hydrogen



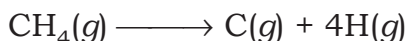
(iv) Enthalpy of sublimation of carbon



(v) Enthalpy of dissociation of hydrogen molecule



From the above equations enthalpy change for the atomisation of methane



can be calculated as follows:

Multiply equation (v) and also equation (iii) by 2. Now add equation (i), equation (iv) and twice of equation (v). From the resulting expression subtract equation (ii) and twice of equation (iii). The resulting value of enthalpy change comes out to be

$$\begin{aligned}\Delta H &= \Delta H_1 - \Delta H_2 - (2 \times \Delta H_3) + \Delta H_4 + (2 \times \Delta H_5) \\ &= -891 - (-394) - (-2 \times 286) + (717) + (2 \times 436) \\ &= +1664 \text{ kJ}\end{aligned}$$

This represents the energy required for the cleavage of **four** C—H bonds.

$$\text{Therefore, } \Delta_{\text{C-H}}H^\ominus = \frac{1664}{4} = \mathbf{416 \text{ kJ mol}^{-1}}.$$

The bond enthalpies of various bonds are given Table 5.3.

Table 5.3. Bond Enthalpies of Some Bonds

<i>Bond</i>	<i>Bond Enthalpy*</i> (kJ mol ⁻¹)	<i>Bond</i>	<i>Average Bond Enthalpy**</i> (kJ mol ⁻¹)
H—H	435.4	C = C	619
H—F	565	C ≡ C	812
H—Cl	431	O—H	463
H—Br	364	N—H	389
H—I	297	C—H	413
F—F	155	C—Cl	328
Cl—Cl	242	C—O	335
Br—Br	190	C = O	707
I—I	149	C—N	293
O = O	494	C = N	616
N ≡ N	941	C ≡ N	879
		C—Br	275.6
		O—O	138
		N—N	159
		N = N	418
		C—C	347

*These bond enthalpies are the dissociation energies of diatomic molecules that have only one bond, they are, therefore, exact values.

**These bond enthalpies are obtained from molecules that contain more than one bond, therefore, they are average values.

Use of Bond Enthalpy Data

The bond enthalpy data given in Table 6.4 is quite useful in determining the standard enthalpies of the reactions. The chemical reaction involves

the cleavage of old bonds in reacting species and formation of new bonds to give product molecules. In general,

$$\left[\begin{array}{c} \text{Standard enthalpy} \\ \text{of reaction} \end{array} \right] = \left[\begin{array}{c} \text{Sum of bond enthalpies} \\ \text{of reactants} \end{array} \right] - \left[\begin{array}{c} \text{Sum of bond enthalpies} \\ \text{of products} \end{array} \right]$$

or $\Delta_r H^\circ = \sum \text{Bond Enthalpies}_{(\text{Reactants})} - \sum \text{Bond Enthalpies}_{(\text{Products})}$

Thus, the values given in bond enthalpy data can help us in:

- (i) *Calculating standard enthalpy of reactions.*
 - (ii) *Calculation of bond enthalpies of some specific bond in the molecule.*
- Some examples are being discussed as follows.

Limitations of Bond Enthalpy

Values of bond enthalpy calculated using the enthalpy terms are approximate and are far from the actual values of enthalpy found experimentally. These values are average values and do not consider the situations in which bond strength is different from the average.

Bond enthalpy is measured over a range of different gaseous molecules and do not take into account any inter or intra molecular forces which may influence the actual bond energy value of the molecule under consideration.

Reasons of these variations in the value of bond enthalpy are

(i) **The inductive effect:** Other electronegative atoms in the vicinity of a bond may weaken the bond by pulling the electrons toward themselves.

(ii) **Steric factors:** Sometimes weakening of bonds is caused by strain in the molecule caused by orientation of bonds in un-natural configuration, hence changing the bond enthalpy. example: propane bond enthalpy 348 kJ while cyclopropane bond enthalpy 210 kJ.

(iii) **Delocalization:** In cyclo compounds bonding is delocalised, causing reducing of bond length hence affecting the bond enthalpy

e.g., the C – C single bond length is = 0.159 nm

C = C bond length is = 0.134 nm, while

C – C bond length in benzeze is 0.139 nm.

Hence calculation of bond enthalpies using average bond energy can not be applied accurately to molecules containing benzene rings.

Limitations of Ionic Models

Dot and cross model of ions and ionic compound show the way ionic bonds are formed and the ratio atoms react but it does not show what way ions are arranged in space. A dot and cross model of NaCl shows that it is made up of a pair of sodium and chloride ions but it is not true.

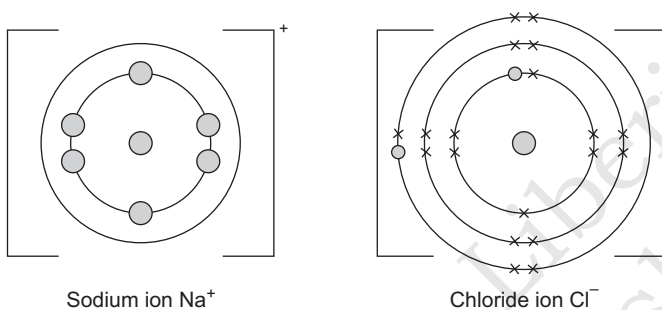


Fig. 5.17

In sodium chloride, Na^+ and Cl^- ions are arranged in a giant ionic lattice structure with equal number of sodium and chloride ions. Ionic lattice structure of NaCl needs a 3D model or 2D representation of 3D model.

3D Models of Ionic Compounds

3D model shows arrangement of ions in a lattice structure. Different coloured balls are used to represent the ions and sticks to show the ionic bonds.

Limitations of 3D models:

- (i) This model is not to scale hence does not give accuracy.
- (ii) It gives no information about the forces of attraction between the ions, or the movement of electrons to form the ions. (Fig. 5.18)

2D representation of ionic compounds.

This 2D model shows the arrangement of one layer of ions but it does not show where the ions are located on the other layers. There may be different **possible arrangements** of the ions. (Fig. 5.19)

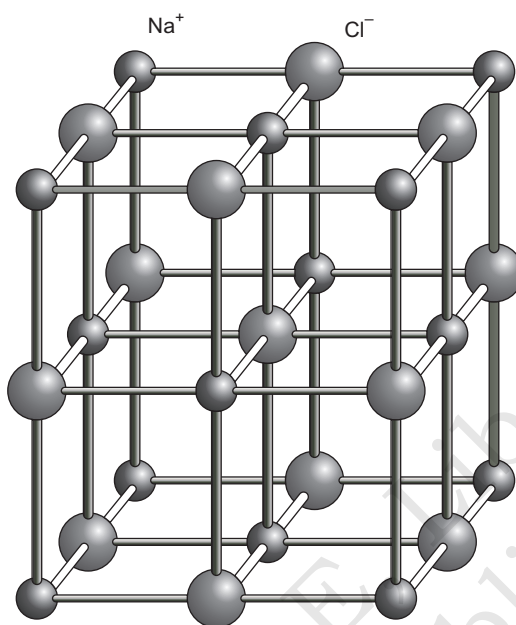


Fig. 5.18. 3D model of ionic lattice in sodium chloride.

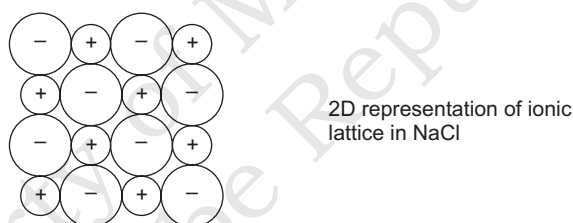


Fig. 5.19. 2D representation of ionic lattice in NaCl

5.6. FUELS

Fuels are dense repositories of energy that are consumed to provide energy services such as heating transportation and electrical generation. Sun is the ultimate source of energy. All fuels ultimately get energy from sun but even then they are considered as **Primary Energy Source**. **Primary fuels** provide about 95% of **human primary energy**. 85 of primary energy to generate electricity comes from primary fuels most of the fuels are non renewable, but as they are found extensively enough as to be considered sustainable.

Primary fuels: Primary fuels include

- (i) Nuclear fuels
- (ii) Bio fuels
- (iii) Fossil fuels

Primary fuels are obtained from natural resources.

Secondary fuels: The fuels which are not directly obtained from natural resources but are derived from primary fuels are called secondary fuels. *e.g.*, gasoline, kerosene, diesel such fuels are also called **energy currencies**.

Fuels vary considerably energy density, cost and environmental impact *e.g.*, uranium has a significantly higher energy density than fossil fuels but is very expensive.

Classification of Fuels: Fuels can also be classified on the basis of their state or on the basis of their occurrence.

Classification on the basis of state

1. Solid Fuels
2. Liquid Fuels
3. Gaseous Fuels

Classification on the basis of their occurrence

1. Natural Fuels
2. Artificial Fuels

1. **Solid Fuels:** Solid fuels are various forms of solid material that can be burnt to release energy providing heat and light through the process of combustion. Commonly used solid fuels are wood, charcoal, peat, coal, hexamine fuel tablets, dry dung, wood pallets. Solid fuels are commonly used since ages to produce fire.

- (a) **Wood:** Wood fuel can refer to fuels such as fire wood, charcoal, wood chips sheets, pallets and saw dust. Wood fuel can be used for cooking, heating and occasionally for fueling steam engines, and steam turbines that generate electricity, wood may be used indoors in furnace or fire place.
- (b) **Biomass:** Of course wood is a biomass but actually biomass refers to other natural plant material that can be burnt for fuel. Common biomass fuel includes waste wheat, straw, nut shells and other fibrous material.
- (c) **Peat:** Accumulation of decayed vegetation or organic matter that can be burnt when sufficiently dried. It has low calorific value.

- (d) **Coal:** Coal is extracted from coal mines (opencast and underground mines). It is a combustible black or brownish black sedimentary rock. It is used as energy resource primarily burnt for the production of heat and electricity. It is also used for industrial purposes such as refining metals. It is the largest source of energy for generation of electricity world wide. By products of coal burning have environmental and health effects. Smokeless coal can be formed naturally in the form of **anthracite**.
- (e) **Coke:** Coke is made from coal and has few impurities. It is derived from destructive distillation of low ash, low sulphur, bituminous coal. Petroleum coke or pet coke is derived from oil refinery cokes units.
- (f) **Smokeless fuel:** Smokeless fuel is a solid fuel which produces little smoke and volatile and is made from powdered anthracite coal and supplied in the form of briquettes for domestic use. It burns at highest temperature.
- (g) **Rocket propellant:** Solid rocket propellant consists of a solid oxidizer (NH_4NO_3) bond with flakes or powder of energy compounds (such as RDX) plus binders, plasticisers stabilizers and other additives. It has higher energy density and is much easier to store.

Advantage and disadvantage of solid fuels: Solid fuels are easy to store and easy to transport. Their production cost is less and ignition temperature is moderate.

Disadvantages: Wastage of energy is more. Ash content is high. Cost of handling is high in comparison to other type of fuels.

2. Liquid Fuels: Most of the fuels are obtained from dead remains of dead plants and animals by the exposure to heat and pressure in earth's crust. Fumes of liquid fuels are flammable. Liquid fuels are combustible or energy generating. Most of liquid fuels are fossil fuels, hydrogen fuel, ethanol and biodiesel are some examples of liquid fuels.

- (a) **Petroleum fuels:** Most of the liquid fuels are derived from petroleum. **Gasoline** or **petrol** is derived by distillation of crude oil. **Diesel** is a mixture of alliphatic hydrocarbons extracted from petroleum **kerosene** is used in stoves, kerosene lamps and small engines. Highgrades kerosene is used as jet fuels. Kerosene is used as an additive in diesel fuel to prevent waxing in cold temperatures. **Liquefied Petroleum Gas (LPG)** is a mixture of propane and Butane. It is denser than air and is compressed easily. It is used for cooking and space heating.

- (b) **Non-petroleum fossil fuels:** Liquid fuels can be derived from coal or natural gas by using Fischer-Tropsch process.
- (c) **Natural gas:** Natural gas composed mainly of methane can be compressed to a liquid and can be used as a fuel in automobiles as GNG. Its boiling point is less hence need to be stored a high pressure to keep it in the liquid state. It ignites at high temperature and has low density.
- (d) **Biodiesel:** Biodiesel is derived from plant. It has higher octane rate 45–60 compared to 45–50 for crude oil derived diesel. It gives 10% less energy than ordinary diesel.
- (e) **Alcohols:** All alcohols are flammable but **ethanol** and **methanol** are used as fuels being sufficiently inexpensive. Methanol and ethanol are mixed with petrol to increase octane number.
- (d) **Liquefied Hydrogen:** Liquefied hydrogen is used as rocket fuel, and fuel in internal combustion engines or fuel cells.
- (e) **Ammonia:** Liquid ammonia was once used in place of petrol when petrol was unavailable.

3. Gaseous Fuels: Fuel gases are produced by chemical transformations of solids, liquids, or gases. Some of the fuel gases are

- **Coal gas:** Produced by pyrolysis of coal
- **Water gas:** Produced from coke
- **Producer gas:** Produced from coke
- **Syn gas:** Produced from natural gas
- **Wood gas:** Produced from wood
- **Bio gas:** Obtained from landfills
- Oil gas and blast furnace gas.

Characteristics of Ideal Fuel

1. An ideal fuel should be easily available.
2. An ideal fuel should be cheap.
3. An ideal fuel should be readily flammable.
4. It should release high amount of energy (High calorific value)
5. It should not leave any harmful byproduct.
6. It should not be harmful to the environment
7. It should be easy to store, transport and handle
8. It should have low content of non-volatile substance.

SUMMARY

- **Chemical Thermodynamics.** Branch of science which deals with the energy changes associated with chemical reactions.
- **System.** Part of the universe selected for investigations.
- **Surroundings.** Part of the universe other than the system.
- **State of System.** The conditions of existence of a system when its macroscopic properties have definite values.
- **State Function.** The thermodynamic quantity which depends only on initial and final state of the system.
- **Heat (q).** It is a random form of energy. It is one of the mode of transference of energy between system and surroundings across the boundary.
- **Work (w).** It is organised form of energy. It is another mode of transference of energy between system and surroundings across the boundary.
- **Enthalpy (H).** It is sum total of internal energy and pV-energy of the system at particular conditions of temperature and pressure. It is also called heat content of the system

$$(H = U + pV).$$

- **Law of Conservation of Energy.** It is also called **first law of thermodynamics** and states that energy of universe always remain constant during chemical or physical changes. Mathematically,
$$\Delta U = q + w.$$
- **Relation between C_p and C_v :** $C_p - C_v = R$ for 1 mole of ideal gas
 $C_p - C_v = nR$ for n mole of ideal gas.
- **Enthalpy of Reaction.** The enthalpy change accompanying the chemical reaction in which number of moles of reactants consumed and those of products formed are the same as the stoichiometric coefficients.
- **Standard Enthalpy of Formation ($\Delta_f H^\ominus$).** It is the enthalpy change accompanying the formation of 1 mole of the substance from its constituent elements in their standard state. $\Delta_f H^\ominus$ can be > 0 or < 0 .
- **Standard Enthalpy of Combustion ($\Delta_c H^\ominus$).** It is the enthalpy change occurring during the combustion of one mole of the substance in excess of oxygen. $\Delta_c H^\ominus$ is always less than zero.

- **Standard Enthalpy of Vaporisation ($\Delta_{\text{vap.}}\mathbf{H}^\ominus$).** It is the enthalpy change taking place during the vaporisation of one mole of liquid at its boiling point.
- **Enthalpy of Neutralisation ($\Delta_{\text{n}}\mathbf{H}$).** It is the enthalpy change taking place during formation of 1 mole of water by combination of 1 mole of H^+ ions and 1 mol of OH^- ions in dilute solutions.
- **Hess's Law.** The enthalpy change in a chemical or physical process is same whether the process is carried out in one step or in several steps.
- **Bond Enthalpy ($\Delta_{\text{bond}}\mathbf{H}^\ominus$).** The average amount of energy required to break one mole of the bonds of a particular type in gaseous molecules.



EVALUATION

I. Multiple Choice Questions

1. Which of the following statements is correct?
 - (a) The presence of reacting species in a covered beaker is an example of open system.
 - (b) There is an exchange of energy as well as matter between the system and the surroundings in a closed system.
 - (c) The presence of reactants in a closed vessel made up of copper is an example of a closed system.
 - (d) The presence of reactants in a thermos flask or any other closed insulated vessel is an example of a closed system.
2. The volume of gas is decreased to half. The specific heat of the gas will
 - (a) remain same
 - (b) be reduce to half
 - (c) increase four times
 - (d) be doubled.
3. The enthalpies of elements in their standard states are arbitrarily taken as zero. The enthalpy of formation of compound
 - (a) is never negative
 - (b) can be positive or negative
 - (c) is always negative
 - (d) is never positive.
4. Which of the following is not a state function?
 - (a) T
 - (b) H
 - (c) q
 - (d) S.

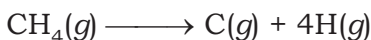
5. The bond energy (in kCal mol⁻¹) of C—C bond is approximately
 (a) 1 (b) 10
 (c) 100 (d) 1000.
6. The species which by definition has ZERO standard molar enthalpy of formation is
 (a) Br₂(g) (b) Cl₂(g)
 (c) H₂O(g) (d) CH₄(g).
7. For a reversible reaction,
 $A(s) + B(g) \rightleftharpoons C(g) + D(g); \Delta G = -350 \text{ kJ}$
 Which one of the following statement is true?
 (a) The entropy change is negative
 (b) The equilibrium constant is greater than zero
 (c) The reaction should be instantaneous
 (d) The reaction is thermodynamically not feasible.
8. Based on First law of thermodynamics which one of the following is correct?
 (a) For an isochoric process, $\Delta U = -q$
 (b) For an adiabatic process, $\Delta U = -w$
 (c) For an isothermal process, $q = +w$
 (d) For a cyclic process, $q = -w$.
9. $\Delta_f U^\ominus$ of formation of CH₄(g) at certain temperature is -393 kJ mol^{-1} . The value of $\Delta_f H^\ominus$ is:
 (a) $> \Delta_f U^\ominus$ (b) equal to $\Delta_f U^\ominus$
 (c) zero (d) $< \Delta_f U^\ominus$.
10. The standard enthalpy of formation of H₂ from its atoms is -436 kJ mol^{-1} and that of N₂ from its atoms is -712 kJ mol^{-1} . The average bond enthalpy of N—H bond in NH₃ is
 (a) -964 kJ mol^{-1} (b) 1056 kJ mol^{-1}
 (c) $+352 \text{ kJ mol}^{-1}$ (d) $-1102 \text{ kJ mol}^{-1}$.

II. Fill in the Blanks

- The standard enthalpy of formation of elementary substances is taken to be _____.
- The amount of heat produced in the combustion of a 1 gram of a fuel is called _____.
- A fuel having larger value of enthalpy of combustion _____ have larger calorific value.
- $\Delta G = \Delta H -$ _____.
- The sign of ΔH and ΔU for combustion process is _____.

III. Descriptive Questions

1. What type of system is constituted by coffee placed in thermos flask?
2. Heat capacity (C) is an extensive property but specific heat (c) is an intensive property. What is the relationship between them for 1 mole of water?
3. Which thermodynamic parameters are taken to be zero at reference state of elements?
4. The enthalpy of atomisation for the reaction



is 1665 kJ mol^{-1} . What is the bond enthalpy of C—H bond?

5. What is the basic difference between enthalpy of formation and enthalpy of reaction? Illustrate with example.
6. Write the thermochemical equations from each of the following data:
 - (i) $\Delta_f H^\circ$ for freon (CHClF_3) is $-480.0 \text{ kJ mol}^{-1}$
 - (ii) $\Delta_f H^\circ$ of Rb is 403 kJ mol^{-1}
 - (iii) $\Delta_e H_2^\circ$ of sulphur is 590 kJ mol^{-1}
 - (iv) $\Delta_f H^\circ$ of $\text{CaCl}_2(s)$ is $2870.8 \text{ kJ mol}^{-1}$
 - (v) $\Delta_f H^\circ$ of CaCl_2 is -795 kJ mol^{-1} .
7. First law of thermodynamics refers to conservation of energy. Yet the world is facing severe energy crisis. Does it goes against the first law? Comment.
8. Calculate the values of ΔU and ΔH when 1 mol of a diatomic ideal gas is heated at constant pressure of 1.0 atm. from 27°C to 57°C .

IV. Numerical Questions

1. (i) 2.5 mol of ideal gas at 2 atm and 27°C expands isothermally to 2.5 times of its original volume against the external pressure of 1 atm. Calculate the work done.
(ii) If same gas expands isothermally in a reversible manner, then what will be the volume of work done?
2. A system gives out 20 J of heat and also does 40 Joules of work. What is the internal energy change? **(Ans. -60 J)**
3. Heat produced by combustion of 1.0 g of benzene (C_2H_6) at constant volume is 41.80 kJ at 298 K. Calculate the value of enthalpy of combustion of benzene at 29 K. **(Ans. $-3264.1 \text{ kJ mol}^{-1}$)**
4. The standard enthalpies of formation of four substances O_3 , CaO , NH_3 , HI are $+142.2$, -634.9 , -46 and $+25.95 \text{ kJ mol}^{-1}$ respectively. Arrange them in order of increasing stability with respect to decomposition into their elements. **(Ans. $\text{O}_3 < \text{HI} < \text{NH}_3 < \text{CuO}$)**