

Unit -11

Thermochemistry

After reading this unit, the students will be able to:

- Define thermodynamics. (Remembering)
- Classify reactions as exothermic or endothermic. (Understanding)
- Define the terms system, surrounding, boundary, state function, heat, heat capacity, internal energy, work done and enthalpy of a substance. (Remembering)
- Name and define the units of thermal energy. (Remembering)
- Relate a change in enthalpy to the heat of reaction or heat of combustion of a reaction. (Applying)
- Relate change in internal energy of a system with thermal energy at constant temperature and constant pressure. (Applying)
- Define bond dissociation energy. (Remembering)
- Use the experimental data to calculate the heat of reaction using a calorimeter. (Applying)
- Specify conditions for the standard heat of reaction. (Applying)
- Apply Hess's Law to construct simple energy cycles. (Understanding)
- Describe how heat of combustion can be used to estimate the energy available from foods. (Analysing)
- Explain reaction pathway diagram in terms of enthalpy changes of the reaction. (Born Haber's Cycle) (Applying)

Teaching

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Assessment

01

Weightage %

08



Chemistry Grade XI

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Introduction

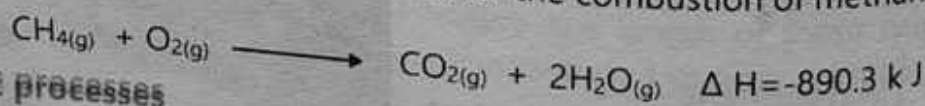
Thermochemistry, is the part of thermodynamics which, deals with the study, measurement, and calculations of thermal energy changes occurring during chemical reactions. The SI unit of thermal energy is Joule (J). Since, the thermal energy changes associated with chemical reactions are usually large, it is appreciable to express it in kilojoules (kJ). Thermodynamics is branch of science which deals with the study of transformation of thermal energy that takes place in physical and chemical processes.

11.1 Energy in Chemical Reactions

Thermodynamics has importance in chemistry because energy changes take place during chemical and physical processes. For example, burning of natural gas (CH_4), dissolution of sodium hydroxide in water and neutralization of acid and base produce heat while, heat is absorbed during evaporation of liquids, melting of ice, dissolving of ammonium chloride in water and cracking of alkanes etc. The first type of processes are called exothermic and second type are endothermic processes.

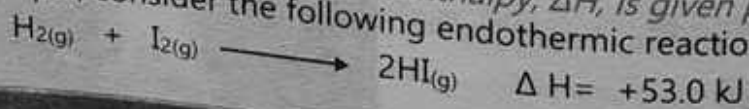
Exothermic processes

Exothermic processes are those in which energy is released in some form. In these reactions energy is released because the bonds of reactant molecules are broken and new bonds between the atoms are formed to make product molecules. For example, in burning of methane gas, CH_4 , in the presence of oxygen produces water, carbon dioxide, and energy. In this reaction, bonds in CH_4 and O_2 molecules, are broken which needs energy (endothermic reaction) and new bonds are formed between hydrogen and oxygen to make H_2O and between carbon and oxygen to make carbon dioxide (CO_2). This is exothermic reaction. In exothermic reactions the total energy of the products is less than the total energy of the reactants. *An exothermic reaction gives out energy or heat to the surrounding and the system loses energy.* In this case change in enthalpy (ΔH) has negative value. For example, consider the combustion of methane gas as follows.



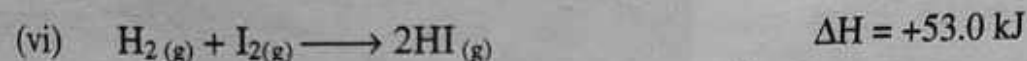
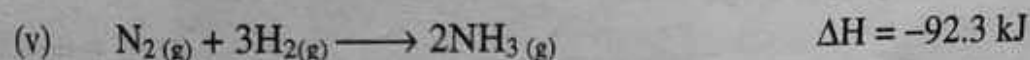
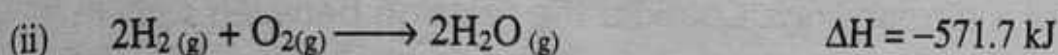
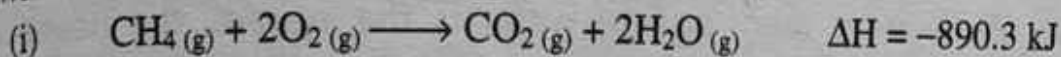
Endothermic processes

An endothermic process takes in energy from surrounding and the system gains energy, here the change in enthalpy, ΔH , is given positive sign. For example, consider the following endothermic reaction,



In this reaction, one mole of H_2 gas reacts with one mole of gaseous I_2 to form two moles of HI and 53.0 kJ of energy is ~~evolved~~ *absorbed*.

A few examples of exothermic and endothermic processes measured at 25°C and one atmospheric pressure are given as follows:



Science, Technology and Society

The most common forms of energy are: heat, electromagnetic radiations, electric, kinetic, potential, and mechanical energies. Albert Einstein in 1905 proposed his classic theory that matter and energy are equivalent. A simple relationship that expresses this equivalence is $E=mc^2$. According to this expression, the conversion of one gram of matter to energy yields 2.2×10^{13} calories of heat. This amount of heat could raise the temperature of 250,000 tons of water from 0°C to 100°C .

It should be recognized that the amount of this energy available in a given sample of matter is dependent only on the mass of the matter and not on the characteristics of the matter itself.

The amount of energy evolved during an ordinary chemical reaction is extremely small in contrast to the total mass of matter involved in the chemical change. For instance, during the combustion of 3000 tons of coal the amount of energy evolved is equal to the energy evolved by 1 gram of matter in a nuclear reaction. Since this minute difference in mass cannot be detected by routine procedures, the loss in mass during the burning process is usually ignored.

11.2 Thermodynamics

Thermodynamics deals with the flow of heat or any other form of energy into or out of a system. In the study of thermodynamics, it is essential to understand the meanings of some terms employed in it.

a) System and Surrounding

To analyse energy changes involved in chemical reactions it is important to define first the system and surrounding. *A system is the specific part of the*

universe that is of interest to us for the purpose of scientific observations, while the surrounding is rest of the universe outside the system where we make our measurements. Both system and surroundings are separated by a real or imaginary surface called boundary. For instance, if boiling water in a beaker is under observation then, boiling water is the system, the beaker and the heat source is surroundings. Consider the reaction between sodium chloride and silver nitrate solutions, which can be called a system under observation. The flask and the air are the surroundings.

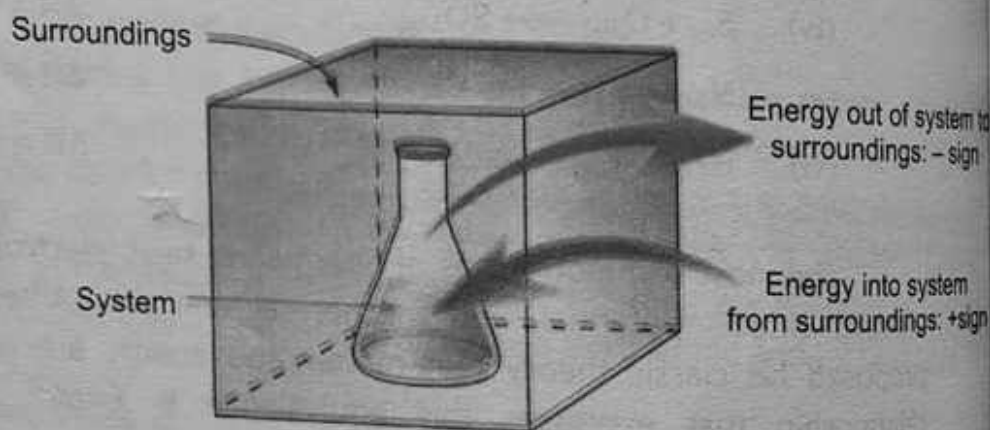


Fig. 11.1 The system and surrounding

b) State and State Function

In thermodynamics, we study changes in the state of the system. The state of the system is defined by the values of macroscopic properties, such as, temperature, pressure, volume, energy, and composition. In other words, the state of a system is the condition of the system in terms of temperature, pressure, volume and composition. State functions or state variables are the properties that are determined by the state of the system and dependent only on the current state of the system and independent of the path by which that state is reached. It means that when the state of a system changes, the magnitude of change in any state function depends only on the initial and final state of the system and not on how the change was carried out. If one mole of a gas in a state of V_1 at temperature T_1 is heated to the temperature T_2 , the volume of the gas becomes V_2 . Hence V_1, T_1 specifies the initial state while V_2, T_2 is the final state of the gas. The change in temperature changes the volume of the system. Hence such properties, like volume, temperature and pressure, in which the change of one property changes the state of the system, are called state variables or state functions. There are two characteristics of state function.

1. A state function is that property of the system which depends on the initial and final states and is independent of the path adopted to bring about the change. For example, if we heat a sample of water from 0°C to 25°C , the change in temperature is equal to the difference of the final and initial temperatures. The way the temperature change is brought about has no effect on the result.

$$\Delta T = T_{\text{final}} - T_{\text{initial}}$$

$$25^{\circ}\text{C} - 0^{\circ}\text{C} = 25^{\circ}\text{C}$$

2. When a state of the system is specified by giving values to some of the state functions, the values of all other state functions are fixed. For example, if one mole of a gas occupies a volume of 5 dm^3 at 25°C , the pressure must have some fixed value (governed by $P = RT/V$).

There are some properties which are path dependent and are not state functions, e.g. heat and work. They are not the property of a system but simply represent mode of transfer of energy from the system to the surrounding and vice versa.

Reading check

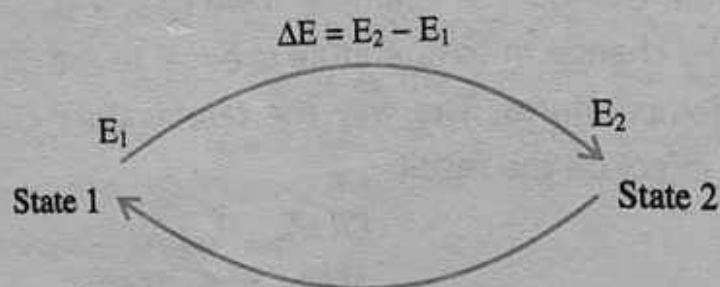
- Define exothermic and endothermic processes.
- Explain the terms:
 - (i) system and surrounding
 - (ii) state and state function.

11.3 Internal Energy 'E'

The internal energy is the sum of the kinetic and potential energies of all the atoms, ions, and molecules in the system. Internal energy is a definite energy possessed by a system. It is the sum of all possible types of energies that are possessed by all the atoms, molecules or ions within a system. Internal energy is a state function. It is the property of the state of the system. This implies that the change in the internal energy between two states of a system is independent of the path followed to achieve it.

The energy of the system changes because energy is transferred into or out of the system. The two ways of transferring energy from the system to surroundings and vice versa are heat and work. Moreover, as you will know later that, internal energy change of a reaction, ΔE , is the heat change when the reaction is carried out at constant volume, i.e. $\Delta E = q_v$ where q_v is heat supplied at constant volume.

Internal energy of a system cannot be determined, however, change in internal energy, denoted by ΔE , can be measured and calculated.



An increase in internal energy of a chemical system has three possible consequences.

- Increase in internal energy of a system can increase the temperature of the system by increasing the kinetic energy of the molecules.
- Increase in internal energy of a system can result in phase change of system, e. g., melting or evaporation may occur.
- Increase in internal energy can result in a chemical reaction if energy supplied is sufficient to break the bonds.

11.4 First Law of Thermodynamics

It was Josiah Willard Gibbs who in 1873, on the basis of experimental work, stated the First Law of Thermodynamics. The first law of thermodynamics is, in fact, the law of conservation of energy. According to Gibbs the *first law states that energy can neither be created nor destroyed although it may be transferred or changed from one form to another. It can also be stated that "the total energy of the system and its surroundings is conserved"*. For example, an electric bulb converts electric energy into light energy. The potential energy of a falling ball is converted into kinetic energy.

Energy is exchanged between the system and surroundings in the form of heat and work. A system may lose energy to the surroundings in the form of heat, but, at the same time, the same amount of energy is absorbed by the surroundings. Hence, the amount of energy lost by the system is equal to the amount of energy gained by the surroundings.

A way of expressing the first law of thermodynamics is that, any change in internal energy (ΔE) of a system is given by the sum of the heat (q) that flows across its boundaries and the work (w) done on the system by the surroundings.

$$\Delta E = q + w \quad (11.1)$$

Eq. 11.1 says that the change in the internal energy of a system is the sum of the heat exchanged 'q' between the system and the surrounding and the work done 'w' on (or by) the system. The sign convention for 'q' and 'w' are as follows.

Table 11.1: Sign Convention for Work and Heat

Process	Sign
Work done by the system on the surrounding	w (negative)
Work done on the system by the surrounding	w (positive)
Heat absorbed by the system from the surroundings	q (positive)
Heat absorbed by the surroundings from the system	q (negative)

Energy Inputs and Outputs

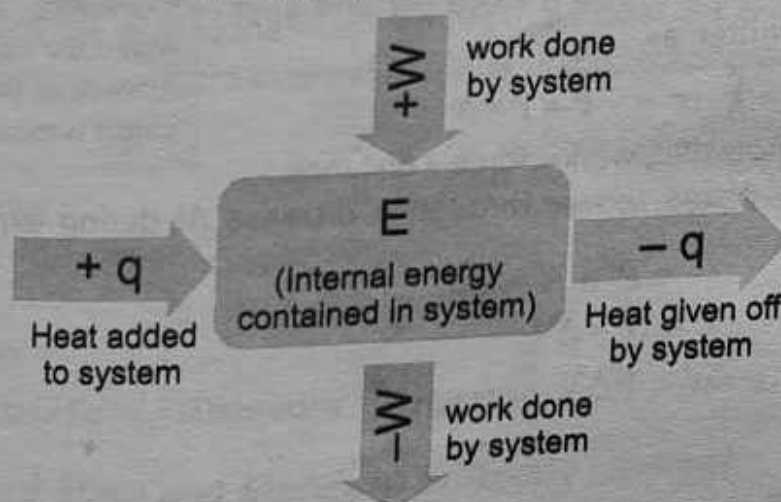


Fig. 11.2 Sign convention for work and heat

The first law of thermodynamics states that the change in internal energy for the system (ΔE) is equal to the amount of heat provided to the system (q) minus the amount of work done by the system (w).

$$\Delta E = q - w \quad (i)$$

In some books you can find this equation as

$$\Delta E = q + w \quad (ii)$$

Tidbit

Work has opposite signs in physics and chemistry. Work done by system is represented as negative ($-w$) in chemistry and as positive ($+w$) in physics.

The difference between the two equations is that in the first one 'w' is work done by the system, whereas, in the second one, it is the work done on the system.

Pressure-Volume Work

The only type of work in thermodynamics is the work of expansion or pressure-volume (PV) work. This is the work done when a system expands against an opposing pressure.

Consider a gas contained in a cylinder of cross sectional area, A, fitted with a weightless and frictionless piston. The pressure on the piston is P. Since, pressure is force per unit area so P can be written as.

$$P = \frac{F}{A} \text{ or } F = P \times A$$

We know that, work = force $\times$ distance

If the piston moves through a distance Δl during expansion, the work done will be,

$$\begin{aligned} \text{Since, } w &= P \times A \times \Delta l, \\ A \times \Delta l &= \Delta V \\ \text{Thus, } w &= P \Delta V \quad (11.2) \end{aligned}$$

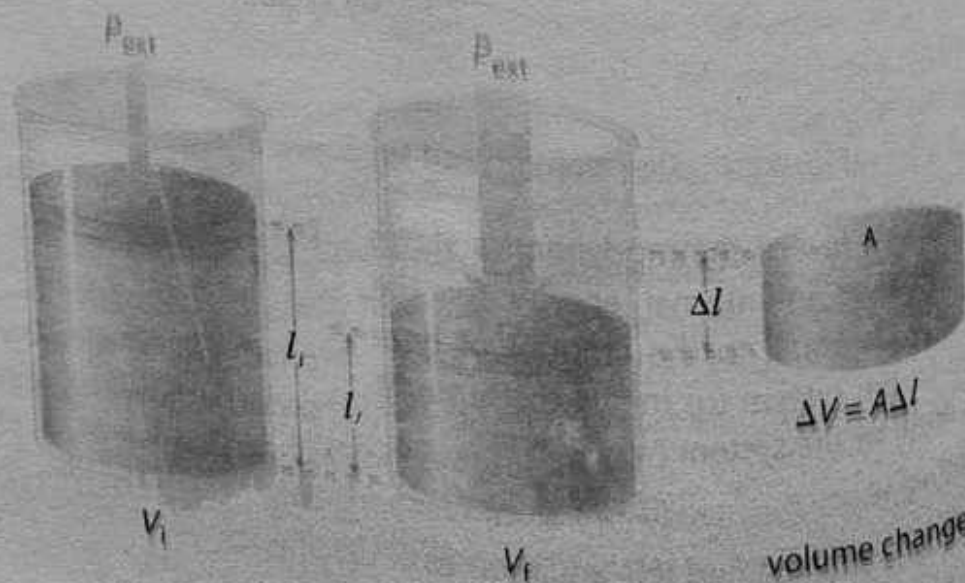


Fig. 11 : 3 Pressure-volume work

Tidbit

Units of Work

In physics work is product of force and displacement. SI unit of work is Joule (J), which is defined as the work done by a force of one Newton through a displacement of one meter i.e. Newton meter (Nm). One Nm is equal to one Joule which is SI recommended unit of work.

Thermal energy is the energy possessed within an object or system due to movement of the particles within the object or the system. Amount of thermal energy in an object is measured in Joules (J).

This is called pressure-volume work and is positive when it is done on the system. Here, ΔV is change in volume in the case of expansion or contraction. In the light of Equation 11.2 Equation 11.1 becomes

$$\Delta E = q + P\Delta V \quad (11.3)$$

Whereas, work is negative ($-P\Delta V$), when it is done by the system.

$$q = \Delta E - P \Delta V \quad (11.4)$$

If the volume of the system is kept constant then $\Delta V = 0$ and hence, $P\Delta V = 0$, so Eq. 11.3, at constant volume becomes

$$\Delta E = q_v \quad (11.5)$$

Hence, heat absorbed at constant volume is utilized to increase the internal energy only and no work is done.

Units of work and heat in SI system are,

$$\text{Nm}^{-2} \times \text{m}^3 = \text{Nm or Joules (J)}.$$

Example 11.1

Calculate the work done when 1 mole of an ideal gas expands from 15 dm^3 to 20 dm^3 against a constant external pressure of 2 atmospheres.

Solution:

$$P = 2 \text{ atm}$$

$$\Delta V = V_2 - V_1 = 20 \text{ dm}^3 - 15 \text{ dm}^3 = 5 \text{ dm}^3$$

Since

$$w = P\Delta V$$

$$w = 2 \text{ atm} \times 5 \text{ dm}^3 = 10 \text{ atm dm}^3$$

Self-Assessment

- What are the consequences of an increase in internal energy of a chemical system.
- Define first law of thermodynamics.

11.5 Standard State and Standard Enthalpy changes

First law of thermodynamics can be applied to processes carried out under different conditions. There are two main conditions under which the processes can occur, i.e., at constant volume and at constant pressure which is the most common way of carrying out chemical reactions. Eq. (11.3) shows the first law of thermodynamics. It has also been shown that processes at constant volume follow the equation $\Delta E = q_v$.

Now let us establish equation for most commonly occurring processes which take place at constant pressure. Starting from first law equation (11.3)

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

When we supply heat ' q ' to a gas it expands to keep its pressure constant which results in performing work on the surrounding against external

pressure, thus, the equation takes the form, considering the sign convention, as $\Delta E = q - P\Delta V$. On rearranging this equation we get

$$q_p = \Delta E + P\Delta V \quad (11.4a)$$

Here q_p stands for heat supplied at constant pressure condition. Now we introduce a new thermodynamic function of a system called *enthalpy (H)*, or heat content of the system which is defined by the equation

$$H = E + PV \quad (11.6)$$

Thus, the total heat content of a system, 'H', at constant pressure is equal to the internal energy plus PV work

Change in enthalpy, ' ΔH ' at constant pressure is given by

$$\Delta H = \Delta E + P\Delta V \quad (11.7)$$

Comparing Eq.(11.4a) and (11.7) we can easily demonstrate that

$$q_p = \Delta H \quad (11.8)$$

Thus, from Eq.(11.8), heat supplied at constant pressure is equal to change in enthalpy.

Thus, we have proved that heat supplied at constant volume, $q_v = \Delta E$ and heat supplied at constant pressure, $q_p = \Delta H$

Hence, heat evolved or absorbed at constant pressure during a process or a reaction is equal to change in the enthalpy of the system. Since, ΔH is the heat of the reaction, it can be calculated theoretically and measured experimentally. Its units are expressed in energy units, i.e. kJ or Joules.

From the above discussion it is concluded that.

1. Since E, P, and V are state functions so according to Eq. (11.6), enthalpy is also a state function.
2. ΔH is positive when the heat is absorbed and it is negative when the heat is released by the system.
3. Processes involving solids and liquids have their $\Delta H = \Delta E$, since the change in volume (ΔV) is very small and closed to zero hence the term $P\Delta V$ in Eq. (11.7) can be neglected.

Example 11.2:

When 1 mole of ice melts at 0°C and constant pressure of 1 atmosphere, 6025 J of heat is absorbed by the system. The molar volumes of ice and water are 0.020 and 0.018 dm^3 , respectively. Calculate ΔH and ΔE .

Solution:

$$a. \Delta H = q_p = 6025 \text{ J}$$

$$P = 1 \text{ atm}$$

$$P\Delta V = P \times (V_2 - V_1)$$

$$= 1 \text{ atm} \times (0.018 \text{ dm}^3 - 0.020 \text{ dm}^3)$$

$$P\Delta V = -0.002 \text{ dm}^3 \text{ atm}$$

$$\text{Since } 1 \text{ dm}^3 = 101.25 \text{ J}$$

$$\text{So } P\Delta V = -0.002 \text{ dm}^3 \text{ atm} \times 101.25 \text{ J dm}^3 \text{ atm}^{-1} = -0.2025 \text{ J}$$

$$b. \Delta H = \Delta E + P\Delta V$$

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

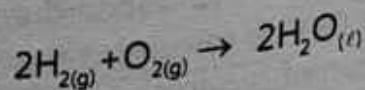
$$= 6025 \text{ J} - (-0.2025 \text{ J})$$

$$\Delta E = 6025.20 \text{ J}$$

(i) Standard Enthalpy Change, ΔH°

The change in enthalpy measured at room temperature (298K) and one atmospheric pressure when the reactant and products are in their standard (natural) states is called the standard enthalpy change.

It should be mentioned that there is no way to measure absolute value of enthalpy of a substance; only values relative to an arbitrary reference can be determined. Furthermore, it is important to state the conditions under which a reaction is performed. Thus, arbitrary reference point is the set of conditions of temperature and pressure. These conditions of temperature and pressure, for thermochemical measurements, are 298 K (25°C) and one atmosphere respectively. Any enthalpy change measured under these conditions is described as a standard enthalpy change and given the symbol ΔH° or ΔH_{298}° . This implies that all the substances involved in the reaction are in their normal and natural state at 298K and 1 atmosphere. This state is called the standard state. Thus, ΔH_{298}° for reaction corresponds to gaseous hydrogen, oxygen and liquid water (not steam) which are their most stable and normal state or standard states.



(ii) The standard enthalpy of formation (ΔH_f°)

It is defined as the heat change that results when 1 mole of a compound is formed from its elements where all the reactants and products are at their standard state i.e. 298K and 1 atm. pressure. The standard enthalpy of formation of all the elements in their most stable form is arbitrarily taken as zero. For example molecular oxygen (O_2) is more stable than its allotropic form ozone (O_3) at 1 atm and 25°C. A list of standard enthalpies of formation for some elements and compounds is given in Table 11.2. These values are helpful to calculate standard enthalpies of reactions ($\Delta H_{\text{reaction}}^\circ$).

The standard heat of formation of CO_2 is $-393.51 \text{ kJ mol}^{-1}$ and that of SO_2 is $-296.83 \text{ kJ mol}^{-1}$ as shown below.

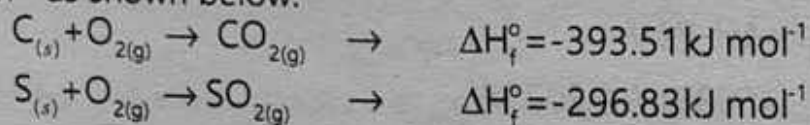


Table 11.2: Standard Enthalpies of Formation at 298K

Substance	ΔH_f°	Substance	ΔH_f°
All elements in their standard states	0.00	$CaC_{2(s)}$	-62.5
$C_{(s)}$ (graphite)	0.00	$CS_{2(l)}$	+89.7
$C_{(s)}$ (diamond)	+1.90	$HCl_{(g)}$	-92.31
$P_{(s)}$ (white)	0.00	$NaCl_{(s)}$	-411.00
$P_{(s)}$ (red)	-17.60	$HBr_{(g)}$	-36.40
$H_2O_{(l)}$	-285.84	$HI_{(g)}$	+26.48
$SO_{2(g)}$	-296.83	$NH_{3(g)}$	-46.11
$CO_{(g)}$	-110.53	$H_2S_{(g)}$	-20.63
$CO_{2(g)}$	-393.51	$CH_{4(g)}$	-74.81
$Fe_2O_{3(s)}$	-824.2	$C_2H_{2(g)}$	+226.73
$Fe_3O_{4(s)}$	-1118.4	$H_2SO_{4(l)}$	-813.99
$CaO_{(s)}$	-635.5	$HNO_{3(l)}$	-174.10

(iii) Standard Enthalpy of Reaction ($\Delta H_{\text{Reaction}}^\circ$)

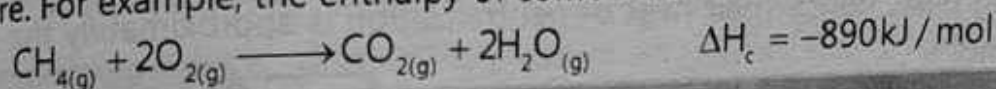
The standard enthalpy of reaction, (ΔH_r°), is the change in enthalpy for a given reaction calculated from the standard enthalpies of formation for all reactants and products. It can be calculated from the difference between the total enthalpies of formation of products and reactants as follows

$$\Delta H^\circ_r = \sum \Delta H^\circ_{\text{(products)}} - \sum \Delta H^\circ_{\text{(Reactants)}}$$

For example, $2\text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{H}_2\text{O}(\text{l})$ $\Delta H^\circ_{\text{(Reaction)}} = -572 \text{ kJ mol}^{-1}$

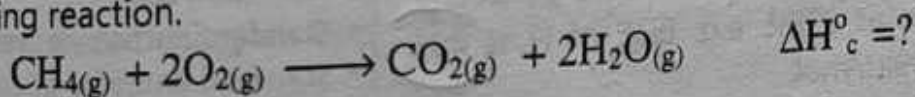
(iv) Standard Enthalpy of Combustion (ΔH°_c)

It is the amount of heat produced when one mole of a compound in its standard state, is completely burnt in excess of air or oxygen at 298K and 1atm. pressure. All the substances involved are in their standard states and the reaction is carried out under standard conditions, i.e. 298 K (25°C) and one atmospheric pressure. For example, the enthalpy of combustion of CH_4 is -890 kJ mol^{-1} .



Example 11.3

The heats of formation of $\text{CH}_{4(\text{g})}$, $\text{CO}_{2(\text{g})}$, and $\text{H}_2\text{O}_{(\text{g})}$ are: $-74.85 \text{ kJ mol}^{-1}$, $-393.50 \text{ kJ mol}^{-1}$ and $-285.81 \text{ kJ mol}^{-1}$, respectively. Calculate the heat of combustion of the following reaction.



Solution:

$$\text{Heat of the reaction} = \Delta H^\circ_r = \sum [\Delta H^\circ_{f \text{ products}}] - \sum [\Delta H^\circ_{f \text{ reactants}}]$$

$$\Delta H^\circ_c = [\Delta H^\circ_{f \text{CO}_2} + 2\Delta H^\circ_{f \text{H}_2\text{O}}] - [\Delta H^\circ_{f \text{CH}_4} + 2\Delta H^\circ_{f \text{O}_2}]$$

$$\Delta H^\circ_c = [-393.50 + 2(-285.81)] - [-74.85 + 2 \times 0] \text{ kJ mol}^{-1}$$

$$\Delta H_c = [-965.12 + 74.85] \text{ kJ mol}^{-1} = -890.27 \text{ kJ mol}^{-1}$$

Tidbit

The potential energy stored in food stuff is experimentally determined by combustion analysis. Calculate your daily intake of food calories, the method of calculation is given in an example given below.

To calculate energy available from food, multiply the number of grams of carbohydrate, protein, and fat by 4, 4, and 9, respectively. Then add the result together.

Example: One slice of bread with a tablespoon of peanut butter on it contains 16 g carbohydrate, 7 g protein, and 9 g fat. Calculate total energy consumed in this intake.

Solution: 16 g carbohydrate x 4 kcal/g	= 64 kcal
7 g protein x 4 kcal/g	= 28 kcal
9 g fat x 9 kcal/g	= 81 kcal
Total	= 173 kcal

(v) **Standard Enthalpy of Neutralization (ΔH°_n)**

It is the amount of heat evolved when one mole of hydrogen ions, (H^+) from an acid, react with one mole of hydroxide ions, (OH^-) from a base, to form one mole of water. A strong acid and a strong base are completely ionized in solution. The reaction between such acid and a base is given below. The following net reaction takes place in neutralization reaction.



Since, the same reaction occurs for neutralization of any strong acid with any strong base, hence their heat of neutralization is approximately the same i.e. $-57.4 \text{ kJ mol}^{-1}$.

(vi) **Bond Dissociation Energy**

Bond dissociation energy (BDE) is a measure of the bond strength. It is defined as the enthalpy change taking place when a particular bond is broken at 298K, e.g. BDE of H_2 is 436 kJ/mol, O_2 is 499 kJ/mol.

Reading Check

Define the following:

- Standard enthalpy change ΔH°
- Standard enthalpy of formation ΔH°_f
- Standard enthalpy of reaction ΔH°_r
- Standard enthalpy of combustion ΔH°_c

11.6 Heat Capacity

There are three different heat capacity terms namely, heat capacity, specific heat capacity, and molar heat capacity. These are defined as follows.

(i) **Heat Capacity**

The heat capacity (C) of a substance is the amount of heat required to raise the temperature of a given amount of the substance by 1 degree Celsius ($^\circ\text{C}$) or Kelvin (K). It is an extensive property and depends on the amount of the substance. The SI units of heat capacity is J K^{-1} .

(ii) **Specific Heat Capacity**

The specific heat (s) of a substance is the amount of heat required to raise the temperature of one gram of the substance by one degree Celsius or Kelvin. It is also called as specific heat capacity. It is an intensive property which does not depend on the quantity of substance. The SI units of specific heat capacity is $\text{J g}^{-1} \text{K}^{-1}$.

The relationship between specific heat capacity and heat capacity is

$$C = m s \quad (11.9)$$

Where, m is the mass of the substance in gram. The specific heat of water, for example, is $4.184 \text{ J g}^{-1} \text{K}^{-1}$ and heat capacity of 50 g of water can be calculated using Eq.(11.9), as

$$209.2 \text{ J K}^{-1} = (50\text{g}) (4.184 \text{ J g}^{-1} \text{K}^{-1})$$

If we know the specific heat and amount of substance, then the change in the temperature of the sample (Δt) will tell us the amount of heat (q) that has been absorbed or released in a particular process. The equation for calculating the heat change is given by

$$q = m s \Delta t \quad (11.10)$$

or in the light of Eq.(11.9) and 11.10 may be written as,

$$q = C \Delta t \quad (11.11)$$

(iii) Molar Heat Capacity

In chemistry we come across another unit of heat capacity that is the *Molar Heat Capacity*. It is defined as the amount of heat required to raise the temperature of one mole of a substance through 1°C or 1K . The units of molar heat capacity is $\text{J mol}^{-1} \text{K}^{-1}$.

11.7 Calorimetry

The enthalpy changes, brought about by chemical or physical processes, are measured using an apparatus called the calorimeter. *The process or method of measurement of enthalpy changes during chemical reactions or physical changes is called calorimetry.* Here we will discuss the use of simple constant pressure calorimeter for the measurement of enthalpy changes.

Measurement of Enthalpy Change

The enthalpy changes occurring in chemical processes may be measured by two main methods. One is direct calorimetry and other is indirect calorimetry.

1. Direct Calorimetry

In a calorimeter, heat changes (ΔH) of those reactions are measured which go to completion without side reactions. For example, the heat of neutralization, of an aqueous solutions of a strong acid by a strong base, can be measured by a calorimeter.

A schematic diagram of a simple calorimeter is shown in Figure 11.3. It consists of an insulated container in which a reaction vessel is placed, wherein the reaction under investigation is carried out. In case of an exothermic reaction, the heat generated cause an increase in temperature of water, which is measured with a thermometer.

The heat given out by the reactants = heat gained by the water

From the specific heat of the system, and the temperature change, the amount of heat (Q) evolved or absorbed in the reaction can be calculated by using equation.

$Q = n C \Delta T$ where, n may be taken as number of moles and C is the molar heat capacity and ΔT is the change in temperature.

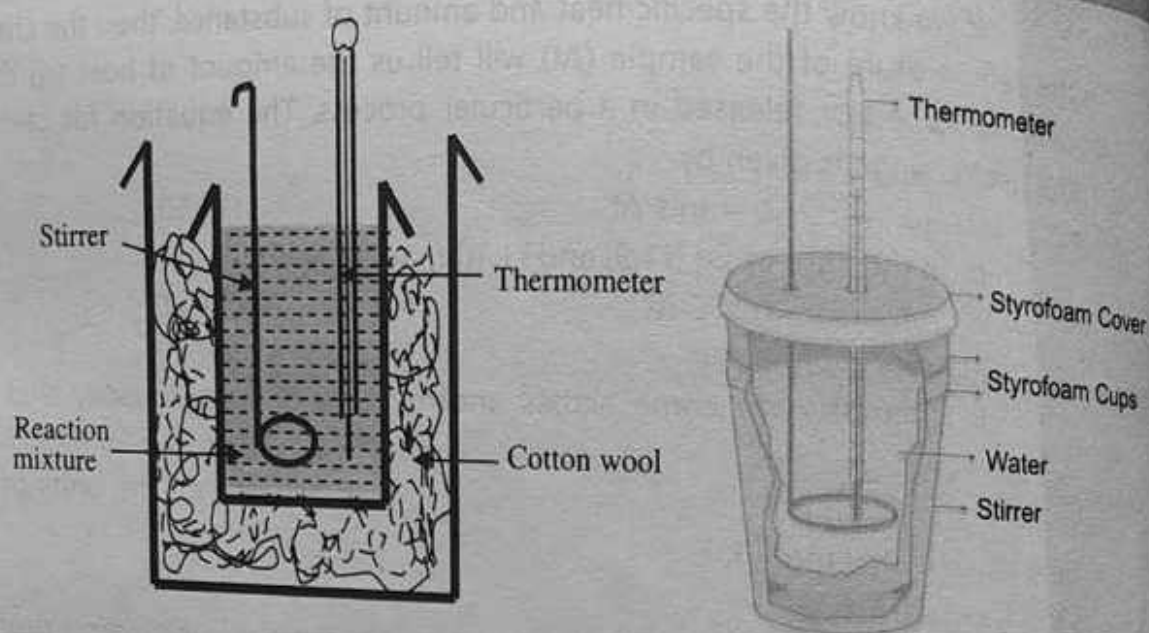
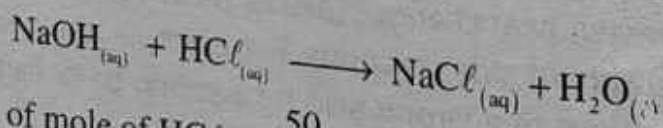


Fig. 11.4: A simple calorimeter

Example 11.4

When 50 cm^3 of 2 mol dm^{-3} HCl is added to 50 cm^3 of 2 mol dm^{-3} NaOH solution. The temperature rise is 13.6°C . Calculate the heat of neutralization per mole where the specific heat of water is $4.2 \text{ J g}^{-1}\text{K}^{-1}$.

Solution:



$$\text{No. of mole of HCl} = \frac{50}{1000} \times 2 = 0.1 \text{ mol}$$

$$\text{No. of mole of NaOH} = \frac{50}{1000} \times 2 = 0.1 \text{ mol}$$

$$\text{Total volume of solution} = 50 + 50 = 100 \text{ cm}^3$$

Since the solutions are dilute so we can use the density of water instead the density of solution. Where density of water = 1 gm/cm^3

$$\text{Mass of solution} = dv = 1 \times 100 = 100 \text{ g.}$$

$$\text{Heat of neutralization} = m \times t_c^\circ \times c_w$$

$$\begin{aligned} \text{Heat neutralization} &= 100 \times 13.6 \times 4.2 \\ &= -5712 \text{ J/0.1 mol} \end{aligned}$$

0.1 mole of acid and 0.1 mole of NaOH give heat of neutralization = -5712 J

$$\begin{aligned} 1 \text{ mole of acid and 1 mole of NaOH give heat of neutralization} &= \frac{-5712}{0.1} \\ &= -57120 \text{ J} \end{aligned}$$

Or heat of neutralization = $-57.12 \text{ kJ mol}^{-1}$.

2. Indirect Calorimetry

In this method, enthalpy change is calculated indirectly using Hess's law.

11.8 Hess's Law (Enthalpy change calculations)

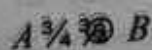
In certain chemical reactions enthalpy of formation (ΔH°_f) cannot be determined directly due to the following reasons:

- (i) Some compounds cannot be directly synthesized from their elements.
- (ii) The rate of some reactions are very slow to be subjected for enthalpy measurement.
- (iii) In some cases side reactions take place and produce products other than the desired one.

In such cases ΔH°_f can be determined by an indirect method, which is based on the Hess's law of constant heat summation, or simply *Hess's law which states that the amount of heat evolved or absorbed in a chemical reaction is the same whether the reaction takes place in a single or several steps*. This means that the net heat of reaction depends only on the initial and final states and not on intermediate steps.

Let a substance 'A' changes to 'B' in two ways:

- i) 'A' changes directly to 'B' and 'Q' is the amount of heat absorbed in this process.



$$\Delta H^\circ = +Q$$

- ii) 'A' changes to 'B' indirectly in three steps, as represented diagrammatically, in Fig. 11.5. According to Hess's law, the total absorption of heat is the sum of heats involved in different steps.

Hence

$$Q = q_1 + q_2 + q_3$$

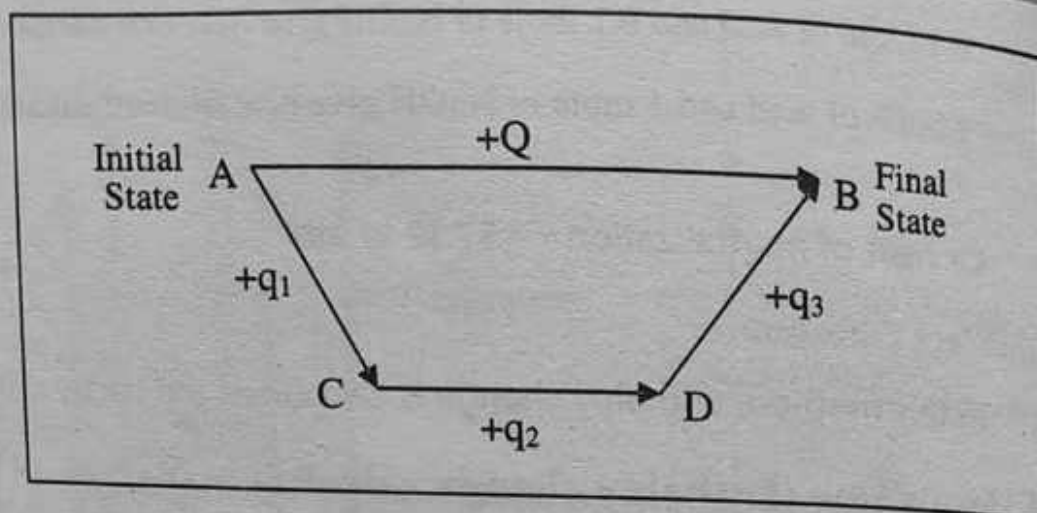
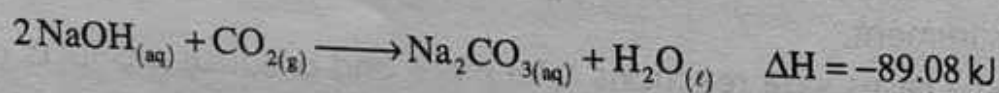


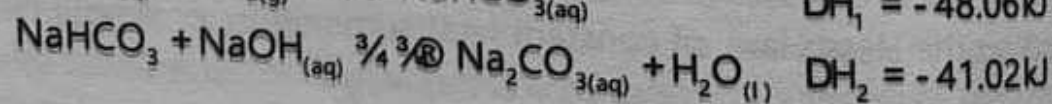
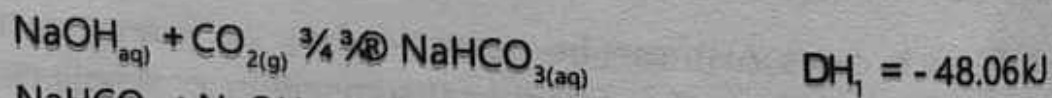
Fig. 11.5 Two ways of changing A to B.

Following example of formation of Na_2CO_3 with the reaction of NaOH and CO_2 illustrates the Hess's law

Single step process



Two step process



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

Putting the values

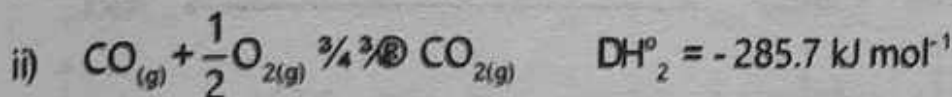
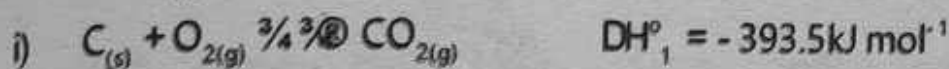
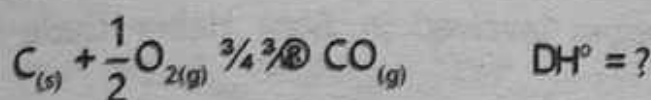
$$\Delta H = -48.06 - 41.02$$

$$\Delta H = -89.08 \text{ kJ}$$

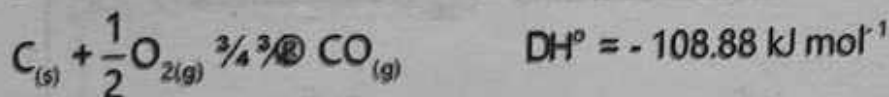
By applying the Hess's law the heat of all those reactions can be calculated, which cannot be measured directly. Some of its applications are as follows.

Heat of Formation

Carbon monoxide, for example, is prepared by reacting carbon with oxygen, but along with carbon monoxide, carbon dioxide is also formed. So to determine the heat of reaction for CO formation, an indirect method is used as follows.



Subtracting equation (ii) from (i) and similarly subtracting ΔH_2 from ΔH_1 We get



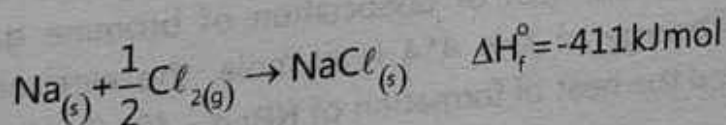
The **lattice energy** can be calculated from the available thermodynamic data by a cyclic process known as Born-Haber Cycle, which is based on Hess's law.

11.9 Born Haber Cycle

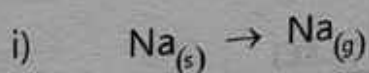
The Born-Haber Cycle is based on the principle, that the sum of energy changes which occur in a closed cycle, from the same initial and final states, is zero. This principle involves the law of conservation of energy in accordance with the first law of thermodynamics.

The Born Haber cycle may be considered for NaCl as an example. *The standard heat of formation ΔH°_f of NaCl is the amount of heat given out when one mole of NaCl is formed from its elements, solid Na and gaseous chlorine. Lattice energy cannot be measured directly, but it can be determined indirectly. We measure ΔH°_f for NaCl as follows:*

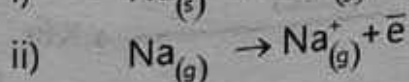
Direct



Stepwise

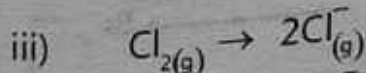


$$\Delta H^\circ_{\text{Sub}} = 109 \text{ kJ mol}^{-1}$$

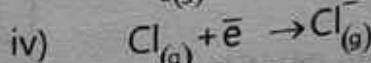


$$\Delta H^\circ_{\text{LE}} = 496 \text{ kJ mol}^{-1}$$

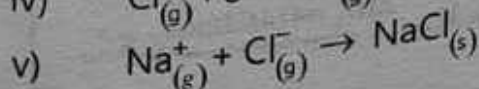
Similarly Cl is formed in the following two steps:



$$\Delta H^\circ_{\text{Diss}} = 242 \text{ kJ mol}^{-1}$$

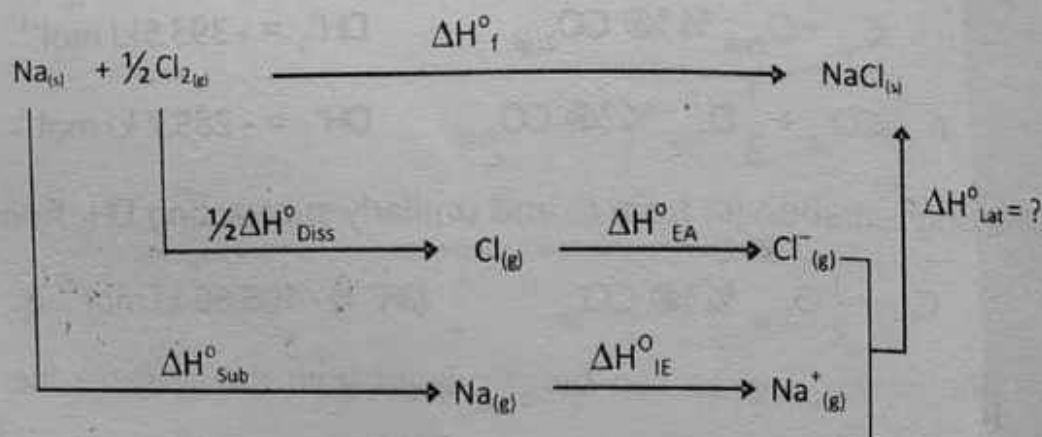


$$\Delta H^\circ_{\text{EA}} = -348 \text{ kJ mol}^{-1}$$



$$\Delta H^\circ_{\text{Lat}} = U = ?$$

The various energies involved in Born Haber Cycle for NaCl can be summarized as follows



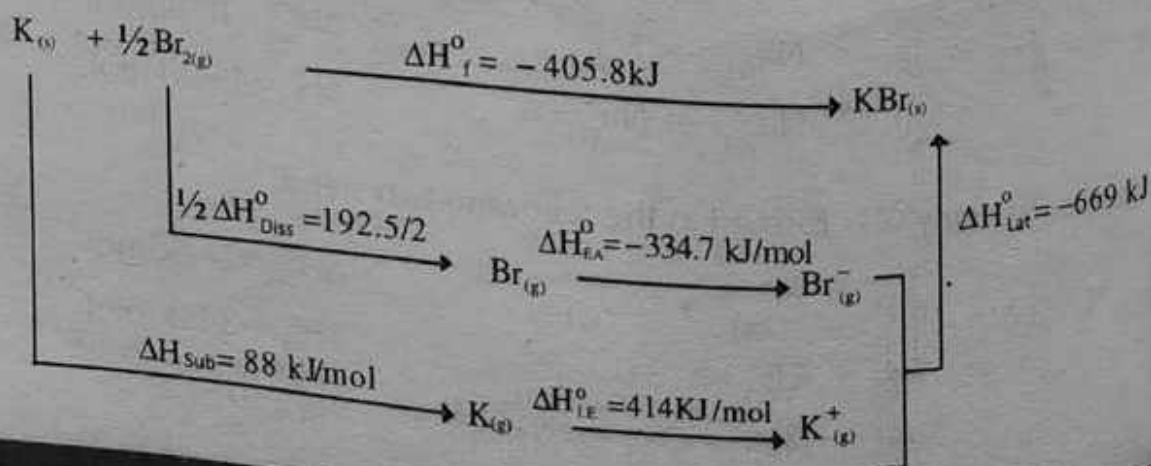
According to Hess's law the sum of all the five steps lead to the heat of formation of NaCl(s).

$$\Delta H^\circ_f = \Delta H^\circ_{\text{Sub}} + \Delta H^\circ_{\text{IE}} + \frac{1}{2} \Delta H^\circ_{\text{Diss}} + \Delta H^\circ_{\text{EA}} + \Delta H^\circ_{\text{Lat}}$$

$$\begin{aligned} \Delta H^\circ_{\text{Lat}} &= \Delta H^\circ_f - \Delta H^\circ_{\text{Sub}} - \Delta H^\circ_{\text{IE}} - \frac{1}{2} \Delta H^\circ_{\text{Diss}} - \Delta H^\circ_{\text{EA}} \\ &= -411 \text{ kJ/mol} - 109 \text{ kJ/mol} - 496 \text{ kJ/mol} - 121 \text{ kJ/mol} - (-348 \text{ kJ/mol}) \\ \Delta H^\circ_{\text{Lat}} \text{ of NaCl(s)} &= -789 \text{ kJ/mol} \end{aligned}$$

Example 11.5

Calculate the lattice energy of KBr. The heat of sublimation of potassium is 88 kJ/mole, the heat of dissociation of bromine gas is 192.5 kJ/mole. The ionization energy of K is 414 kJ/mole, the electron affinity of Br is -334.7 kJ/mole and the heat of formation of KBr is -405.8 kJ/mole.



$$\Delta H_f^\circ = \Delta H_{\text{Sub}}^\circ + \Delta H_{\text{IE}}^\circ + \frac{1}{2} \Delta H_{\text{Diss}}^\circ + \Delta H_{\text{EA}}^\circ + \Delta H_{\text{Lat}}^\circ$$

$$\Delta H_{\text{Lat}}^\circ = \Delta H_f^\circ - \Delta H_{\text{Sub}}^\circ - \Delta H_{\text{IE}}^\circ - \frac{1}{2} \Delta H_{\text{Diss}}^\circ - \Delta H_{\text{EA}}^\circ$$

$$= -405.8 - 88 - 414 - \frac{1}{2} 192.5 - (-334.7)$$

$$\Delta H_{\text{Lat}}^\circ = -669.3 \text{ kJ/mol}$$

Self-Assessment

1. Define calorimetry and how to measure enthalpy change with the help of calorimeter.
2. State the Hess's law.
3. On which principle Born Harber cycle is based?

KEY POINTS

- Thermochemistry is the branch of chemistry which deals with the heat changes involved in chemical reactions and physical processes.
- The reactions are exothermic if internal energy of the reactants is greater than that of the products.
- The difference of internal energy is released as heat energy.
- The reactions in which the internal energy of the products is greater than that of the reactants, heat is absorbed from the surroundings such reactions are called endothermic reactions.
- According to first law of thermodynamics, the energy of the system and surrounding is conserved, mathematically, it can be written as $q = \Delta E + w$. In SI system, the unit of work and heat is Nm or Joules (J).
- Enthalpy is a state function. It is the heat content of a system.
- The change in enthalpy (ΔH) is the amount of heat absorbed or released at constant pressure.
- Standard enthalpy change, ΔH° is enthalpy change at 298K and 1 atmospheric pressure when all the reactants and products are in their standard states.
- Standard enthalpy change can be expressed in different ways depending on the nature of a reaction. Heat of formation (ΔH_f°) is the change of enthalpy when one mole of a substance is formed from its elements. Similarly heat of combustion (ΔH_c°) is the enthalpy change when one mole of a substance is completely burnt in excess of air.
- The heat capacity of a system is the heat absorbed by a system, in raising the temperature by one degree (K or $^\circ\text{C}$). SI units of heat capacity is Joules per Kelvin i.e., JK^{-1} .
- The lattice energy can be calculated from the available thermodynamic data by a cyclic process known as Born-Haber Cycle, which is based on Hess's law. The Born-Haber Cycle is based on the principle, "that the total enthalpy change of the reaction is the net sum of enthalpy changes of all the individual steps of the reaction."

EXERCISE

Choose the correct option.

- ΔH per mole is expressed in the units of
a) k J b) $^{\circ}\text{F}$ c) $^{\circ}\text{C}$ d) K
- Which one of the following is NOT a state function?
a) enthalpy b) heat c) temperature d) pressure
- For solids and liquids
a) $\Delta H = \Delta E$ b) $\Delta H > \Delta E$ c) $\Delta H < \Delta E$ d) $\Delta E = 0$
- 1 k cal is equal to
a) $41.8 \times 10^3 \text{ J}$ b) $418 \times 10^3 \text{ J}$ c) $4.18 \times 10^3 \text{ J}$ d) $0.418 \times 10^3 \text{ J}$
- Standard enthalpy (ΔH°) for 1 mole of a substance, which exists in its natural state, at 1 atm. pressure is measured at
a) 0 K b) 298 K c) 273 K d) 0°C
- ΔH can be measured indirectly by applying
a) Avogadro's law b) Gas laws
c) Hess's law d) Faraday's law
- Enthalpy means
a) Disorder b) Transition state
c) Rate constant d) Heat content
- No work is done at constant
a) Pressure b) Volume c) Temperature d) Mass
- Heat capacity depends on
a) Pressure b) Volume c) Composition d) Mass
- Which one of the following reactions is spontaneous?
a) Endothermic b) Exothermic c) Reversible d) Irreversible
- The energy possessed by water in a dam is
a) Potential Energy b) Kinetic Energy
c) Electric Energy d) Heat Energy
- When heat is absorbed from the surrounding, the process is
a) Reversible b) Mechanical
c) Exothermic d) Endothermic
- The sum of all the energies of all the molecules or atoms of a substance is called its:
a) Specific heat b) Heat capacity
c) Latent heat d) Internal energy

14. Which one of the following processes has ΔH positive
- Ionization energy
 - Electron affinity
 - Combustion
 - Exothermic reaction

Short Questions

- Explain the following short questions with reasons.
 - Total energy of the system and its surroundings remains constant.
 - Ionic reactions are very fast.
 - The work done has positive and negative values.
 - Heat of combustion is always negative.
 - Enthalpy change is a state function but heat is not.
 - ΔH for solids and liquids becomes equal to ΔE .
 - Enthalpy of neutralization of strong acids and strong bases has always the same value.
- What do you mean by state of a system? What are state functions?

Long Questions

- State and explain Hess's law of constant heat summation. Show that it is a direct consequence of the first law of thermodynamics.
- How does Born Haber cycle help in calculating lattice energy?
- What is meant by heat of a reaction? Explain how the heat of a reaction at constant volume differs from the heat of a reaction at constant pressure?
- What is meant by pressure volume work? How it is related to the first law of thermodynamics?

Numerical

- Apply Hess's law to calculate ΔH° for the sublimation of one mole of iodine from the following equations.
 - $\text{H}_{2(g)} + \text{I}_{2(s)} \rightarrow 2\text{HI}_{(g)} \quad \Delta H^\circ = 51.8 \text{ kJ mol}^{-1}$
 - $\text{H}_{2(g)} + \text{I}_{2(g)} \rightarrow 2\text{HI}_{(g)} \quad \Delta H^\circ = -10.5 \text{ kJ mol}^{-1}$ (Ans. 62.3 kJ mol^{-1})
- Calculate heat of formation of an aqueous solution of NH_4Cl from the following data.

(i)	$\text{NH}_{3(g)} + \text{aq} \rightarrow \text{NH}_{3(aq)}$	$\Delta H^\circ = -35.16 \text{ kJ mol}^{-1}$
(ii)	$\text{HCl}_{(g)} + \text{aq} \rightarrow \text{HCl}_{(aq)}$	$\Delta H^\circ = -72.41 \text{ kJ mol}^{-1}$
(iii)	$\text{NH}_{3(aq)} + \text{HCl}_{(aq)} \rightarrow \text{NH}_4\text{Cl}_{(aq)}$	$\Delta H^\circ = -51.48 \text{ kJ mol}^{-1}$

(Ans. $-159.08 \text{ kJ mol}^{-1}$)

3. Liquid ethanol when burnt in oxygen at 25°C liberates heat i.e. $\Delta H^{\circ} = 1402.14 \text{ kJ mol}^{-1}$. The heats of formation of CO_2 and H_2O are -393.50 and $285.81 \text{ kJ mol}^{-1}$, respectively, at the same temperature. Calculate the heat of formation of ethanol at 25°C . (Ans. $-242.37 \text{ kJ mol}^{-1}$)
4. A chemical reaction takes place in a container of cross sectional area of 0.01 m^2 , fitted with a weightless and frictionless piston. The piston is moved up through 0.01m against an external pressure of 101325 Pa as a result of the reaction. Calculate the work done by the system. (Ans. 101.3 J)
5. Determine ΔH° for the following reaction with the help of given data.
- $$2\text{C}_{(\text{s})} + 2\text{H}_{2(\text{g})} \rightarrow \text{C}_2\text{H}_{4(\text{g})} \quad \Delta H^{\circ} = ?$$
- i) $\text{C}_{(\text{s})} + \text{O}_{2(\text{g})} \rightarrow \text{CO}_{2(\text{g})} \quad \Delta H^{\circ}_1 = -393.5 \text{ kJ mol}^{-1}$
- ii) $\text{H}_{2(\text{g})} + \frac{1}{2} \text{O}_{2(\text{g})} \rightarrow \text{H}_2\text{O}_{(\text{g})} \quad \Delta H^{\circ}_2 = -285.7 \text{ kJ mol}^{-1}$
- iii) $\text{C}_2\text{H}_{4(\text{g})} + 3\text{O}_{2(\text{g})} \rightarrow 2\text{CO}_{2(\text{g})} + 2\text{H}_2\text{O}_{(\text{g})} \quad \Delta H^{\circ}_3 = -1430.9 \text{ kJ mol}^{-1}$
- (Ans 72.8 kJ mol^{-1})

Project

Determination of specific heat capacity of iron.

Take two beakers and an iron bolt. Determine the weight of the bolt and record it. Place the bolt in a beaker containing water in it and leave for a while so as the temperature of the water and the bolt comes to an equilibrium and record the temperature of the water by a thermometer, this corresponds to the temperature of the bolt. Now, take another dry beaker and record its weight. Add 100 mL water in this beaker and weigh again. Find the weight of the water by difference. Heat the water up to 70 to 80°C and transfer the water into a calorimeter. Record the temperature of the water T_1 in calorimeter and transfer the bolt from cold water to the calorimeter and record the temperature of water in calorimeter carefully. The temperature will fall to a minimum value. Record it as T_2 . Calculate $\Delta T = T_1 - T_2$ heat delivered to the bolt by water $q_w = m_w \times s_w \times \Delta T$ where m_w and s_w are the mass and specific heat of the water, respectively. Note that the same amount of heat, ($q_b = q_w$), has been absorbed by the bolt. Thus, specific heat of the bolt, s_b , can be calculated as $s_b = q_b / m_b$.