Chapter 07

Thermochemistry

Internal Energy and First Law of Thermodynamics

Energy of the system

A system containing some quantity of matter has definite amount of energy present in it. This energy is the sum of kinetic as well as the potential energies of the particles contained in the system.

Kinetic energy

The kinetic energy is due to the translational, rotational and vibrational movements of particles.

Potential energy

The potential energy accounts for all the types of attractive forces present in the system. These attractive forces include all the types of bonds and the van der Waal's forces present among the particles.

Internal energy

The total of all the possible kinds of energies of the system is called its internal energy, E.

Internal energy as state function

The change in internal energy of the system ΔE is a state function.

Measurement of Internal energy

It is not possible to measure the absolute value of internal energy of a system but it is often possible to measure the value of ΔE for a change in the state of the system.

Ways to transfer energy

There are two fundamental ways of transferring energy to or from a system.

1. Heat
2. Work.

Heat

It is defined as the quantity of energy that flows across the boundary of a system during a change in its state due to the difference in temperature between the system and the surroundings.

Heat is not a property of a system. It is not a state function. Heat evolved or absorbed by the system is represented by a symbol q.

Work

Work is also a form in which energy is transferred from one system to another. It is defined as the product of force and distance.

$$W = F \times S$$

Units

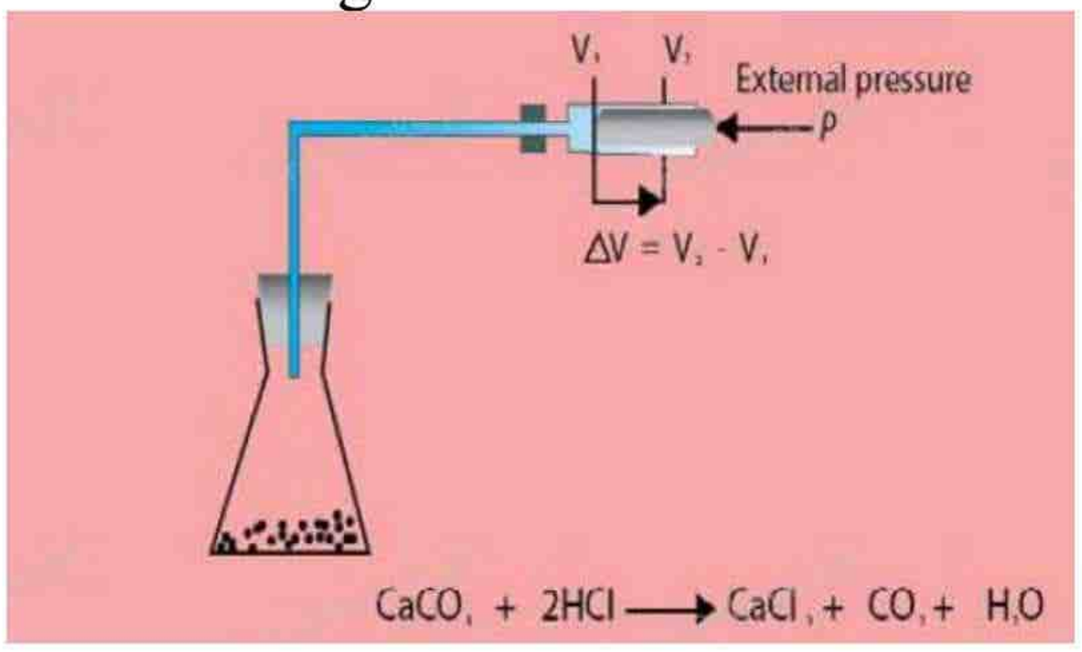
Work is measured in Joules in SI units.

Type of work in thermochemistry

Pressure-volume work.

Example

Expansion can occur when a gas is evolved during a chemical reaction.



The work W done by the system is given by

$$W = -P \Delta V$$

Force = pressure
Distance =volume change
P =external pressure
ΔV =change in volume.
Work is not a state function.
The sign of W is positive when work is done on the system and it is negative when work is done by the system.
The sign of q is positive when heat is absorbed by the system from surroundings, and it is negative when heat is absorbed by the surroundings from the system.

First Law of Thermodynamics

Statement

The first law of thermodynamics, also called the law of conservation of energy, states that

Energy can neither be created nor destroyed, but can be changed from one form to another.

OR

A system cannot destroy or create energy. However, it can exchange energy with its surroundings in the form of heat and work.
The energy change is the sum of both heat and work so that the total energy of the system and its surroundings remains constant.

Experimental

Consider, a gas enclosed in a cylinder having a frictionless piston. When a quantity of heat 'q' is supplied to the system, its internal energy E_1 changes to E_2 and piston moves upwards. The change in internal energy ΔE is given by the following equation.

$$\Delta E = E_2 - E_1 = q + w$$

$$\Delta E = q + w \qquad \text{..eq 1}$$

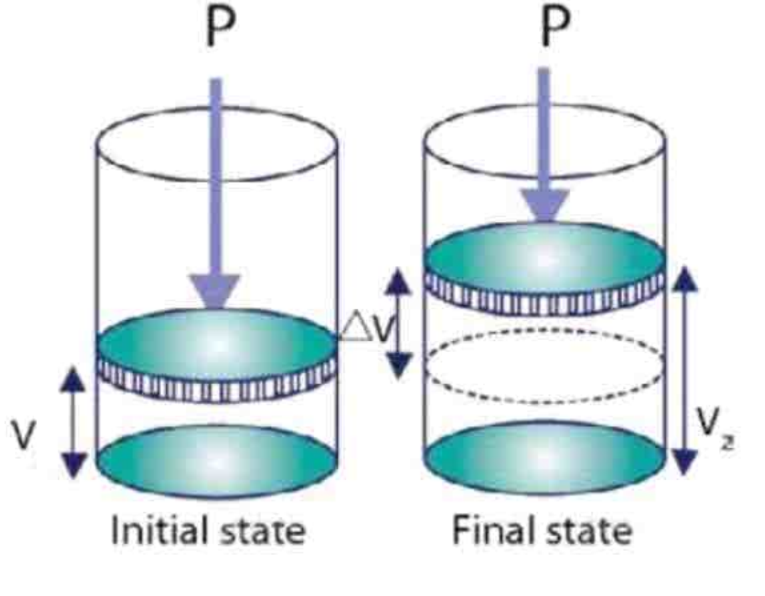
q =amount of heat absorbed by the system
W =work done by the system in moving the piston up
For pressure-volume work the above expression assumes the following form:

$$\Delta E = q - P\Delta V \qquad \text{... eq 2}$$

When the volume of the gas is not allowed to change then $\Delta V = 0$ and equation (2) will take the following form.

$$\Delta E = q_v \qquad \text{..eq (3)}$$

A change in internal energy of a system at constant volume is equal to heat absorbed by the system.



Enthalpy

Definition

To take account of increase in internal energy and accompanying work done by the gas, there is another property of the system called enthalpy or heat content. It is represented by H. Enthalpy is equal to the internal energy, E plus the product of pressure and volume (PV).

$$H= E + PV$$

Units

Joules

Enthalpy is a state function.

Experimental Proof

A quantity of heat q is given to the system (gas) which is now kept at constant atmospheric pressure. A part of this heat is used to increase the internal energy of the gas and the rest is used to do work on the surroundings. This work is done by the gas when it expands against a constant pressure.

Measurement

It is not possible to measure the enthalpy of a system in a given state. Change in enthalpy (ΔH) can be measured for a change in the state of system.

Mathematical Equation

A change in enthalpy of a system can be written as:

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

$$\Delta H = \Delta E + V\Delta P + P\Delta V \quad ..eq\ (1)$$

At constant pressure, $\Delta P=0$. Hence,

$$\Delta H = \Delta E + P\Delta V \quad ..eq\ (2)$$

For Solids and Liquids

In case of liquids and solids, the changes in state do not cause significant volume change i.e. $\Delta V = 0$. For such process, ΔH and ΔE are approximately the same i.e. $\Delta H \approx \Delta E$

First Law of Thermodynamics

$$\Delta E = q + w \quad ..eq\ (3)$$

If W is pressure-volume work done by the system, then:

$$w = - P\Delta V \quad ..eq\ (4)$$

$$\Delta E = q - P\Delta V \quad ..eq\ (5)$$

Putting the value of ΔE in equation (5)

$$\Delta H = q - P\Delta V + P\Delta V$$

$$\Delta H = q$$

Since the pressure is constant.

$$\Delta H = q_p$$

Change in enthalpy is equal to heat of reaction at constant pressure.

Work with ΔH value

The reactions are carried out at constant pressure more frequently than at constant volume. So, working with ΔH is more convenient rather than ΔE.

Glass Calorimeter

Purpose

It is used to determine the enthalpy of neutralization. It determines the value of ΔH.

Enthalpy of Neutralization

The standard enthalpy of neutralization is the amount of heat evolved when one mole of hydrogen ions [H^+] from an acid, react with one mole of hydroxide ions from a base to form one mole of water. For example, the enthalpy of neutralization of sodium hydroxide by hydrochloric (OH^-) acid is -57.4 kJ mol^{-1}.

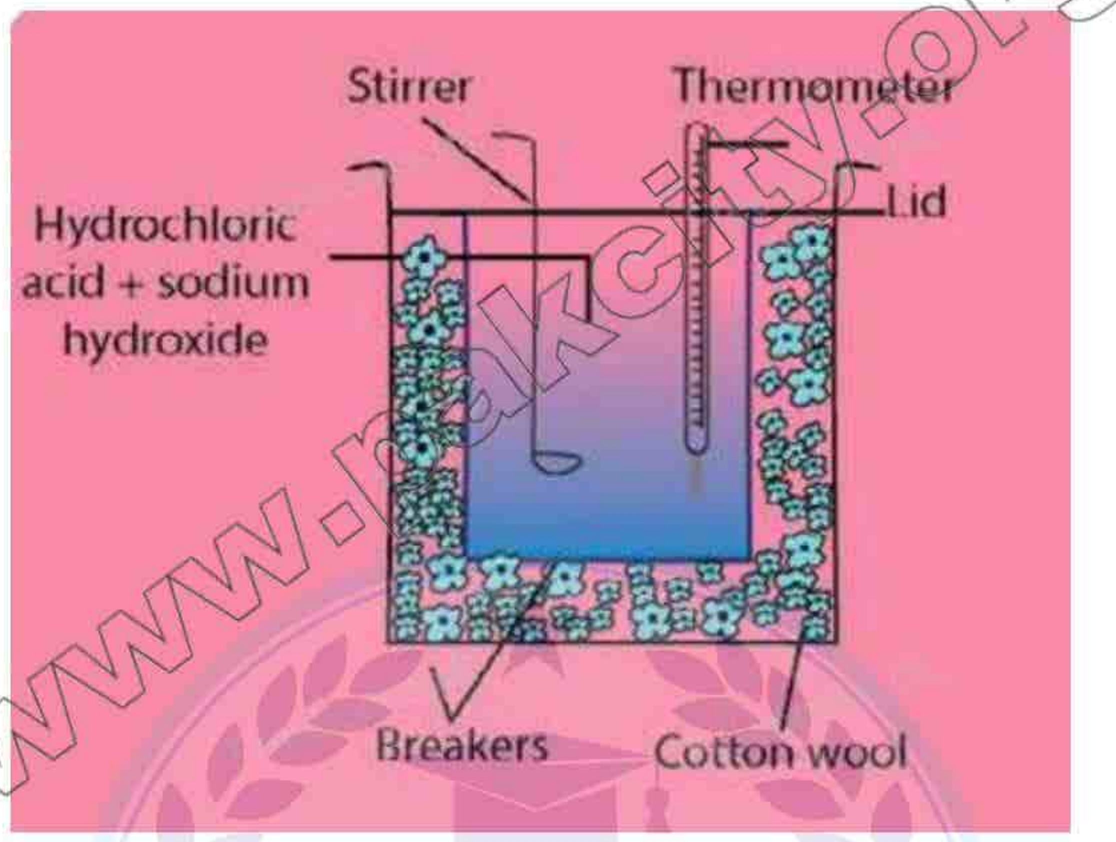
Assembly

Following are the key features of the assembly of glass calorimeter:

1. This usual type of calorimeter is basically an insulated container. To serve the purpose of insulation broken pieces of glass or cotton wool is used.

2. It has a thermometer.

3. It has a stirrer.



Working

Following are the steps involved in working of glass calorimeter:

1. Reactants in stoichiometric amounts are placed in the calorimeter.
2. When the reaction proceeds, the heat energy evolved or absorbed will either warm or cool the system.
3. The temperature of the system is recorded before and after the chemical reaction.
4. Knowing the temperature change the mass of reactants present and the specific heat of water, we can calculate the quantity of heat q evolved or absorbed during the reaction. Thus:

$$q = m \times s \times \Delta T$$

Where m = mass of reactants

s = specific heat of the reaction mixture

ΔT = change in temperature

Heat Capacity

The product of mass and specific heat of water is called heat capacity of the whole system.

Bomb Calorimeter

Purpose

A bomb calorimeter is usually used for the accurate determination of the enthalpy of combustion for food, fuel and other compounds.

Enthalpy of combustion

The standard enthalpy of combustion of the substance is the amount of heat evolved when one mole of the substance is completely burnt in excess of oxygen under standard conditions. It is denoted by ΔH ºC.

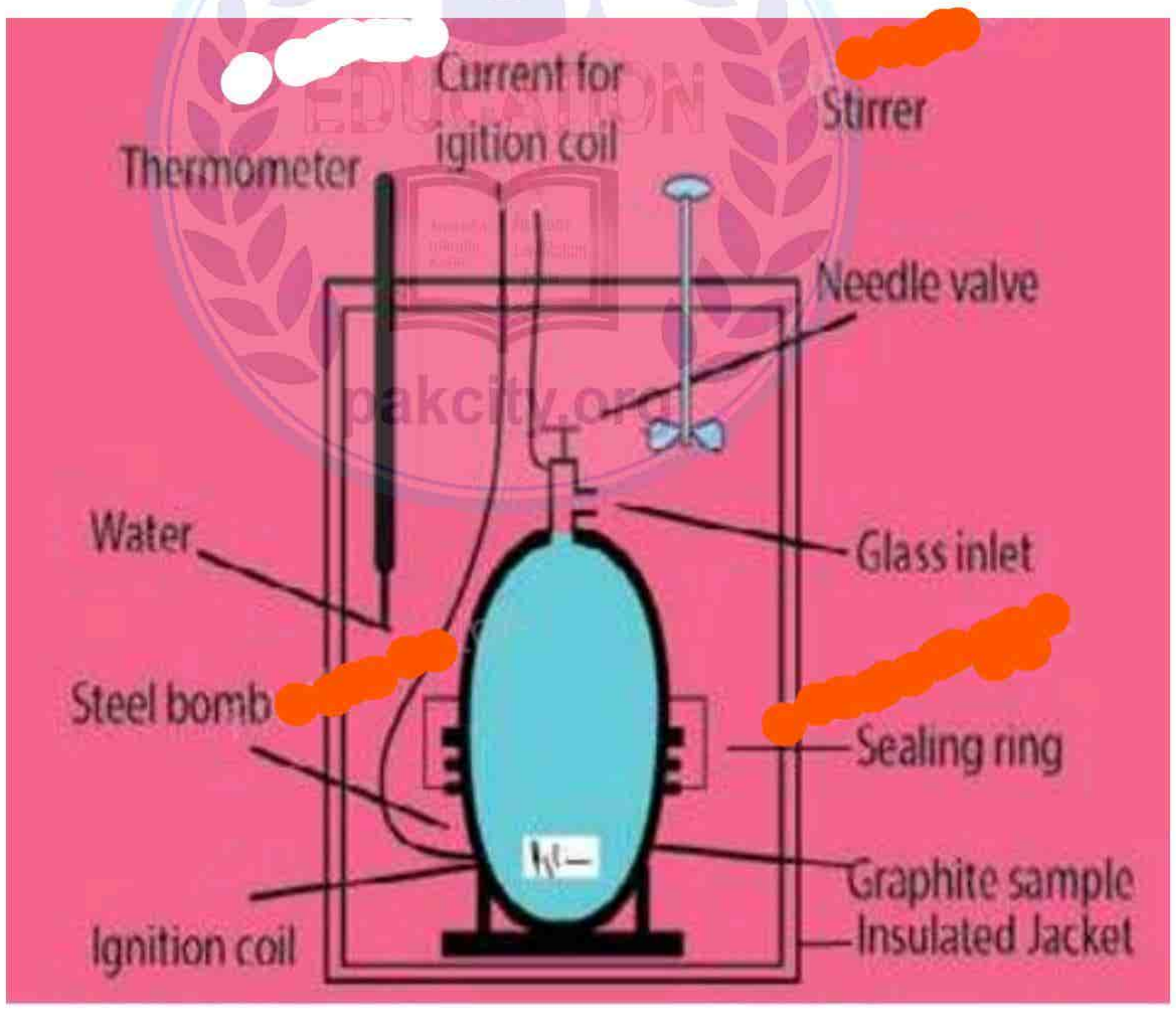
Example

Standard enthalpy of combustion of ethanol ΔH^{o}_{C} is -1368 kJ mol^{-1}.

Assembly

Following are the key features of assembly of bomb calorimeter:

1. It consists of a strong cylindrical steel vessel
2. It is lined with enamel to prevent corrosion.
3. It is provided with a thermometer and a stirrer.
4. Platinum crucible is inside the steel bomb to hold the sample.
5. Ignition coil is also provided.



Working

Following are the key points of working of bomb calorimeter:

1. A known mass (about one gram) of the test substance is placed in a platinum crucible inside the bomb.
2. The lid is screwed on tightly and oxygen is provided in through a valve until the pressure inside is about 20 atm.
3. After closing the screw valve, the bomb calorimeter is then immersed in a known mass of water in a well insulated calorimeter.
4. It is allowed to attain a steady temperature.
5. The initial temperature is measured, by using the thermometer present in the calorimeter.
6. The test substance is then ignited electrically by passing the current through the ignition coil.
7. The temperature of water, which is stirred continuously, is recorded at 30 sec intervals.
8. From the increase of temperature ΔT, heat capacity (c) in kJK^{-1} of bomb calorimeter including bomb, water etc., we can calculate the enthalpy of combustion.

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

Where c=heat capacity
ΔT=change in temperature

Heat capacity

The heat capacity 'c' of a body or a system is defined as the quantity of heat required to change its temperature by 1 Kelvin.

Hess's Law of Constant Heat Summation

Statement

If a chemical change takes place by several different routes, the overall energy change is the same, regardless of the route by which the chemical change occurs, provided the initial and final conditions are the same.

Explanation

For many reactions, ΔH cannot be measured directly by calorimetric method.

Examples

1. Preparation of tetrachloromethane (CCl_4) from carbon and chlorine.
2. Decomposition of tetrachloromethane into its constituent elements.
3. Boron oxide (B_2O_3) and aluminium oxide (Al_2O_3) provide problems for the measurement of standard enthalpies of their formation as it is difficult to burn these elements completely in oxygen because a protective layer of oxides covers the surface of the unreacted element.
4. Heat of formation of CO cannot be measured directly due to the formation of CO_2 with it.

Mathematical Expression

$$\begin{tikzcd}
A \arrow[r, "\Delta H"] \arrow[d, "\Delta H_1"] & D \\
B \arrow[r, "\Delta H_2"'] & C \arrow[u, "\Delta H_3"']
\end{tikzcd}$$

$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3$ …eq (1)

Oxidation of carbon

The reaction occurs in two steps.

$$C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_{(graphite)} = -393.7 kJ\ mol^{-1}$$

$$CO_{(gas)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H_2(CO) = -283 kJ\ mol^{-1}$$

$$C_{(graphite)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H_1(CO) = ?$$

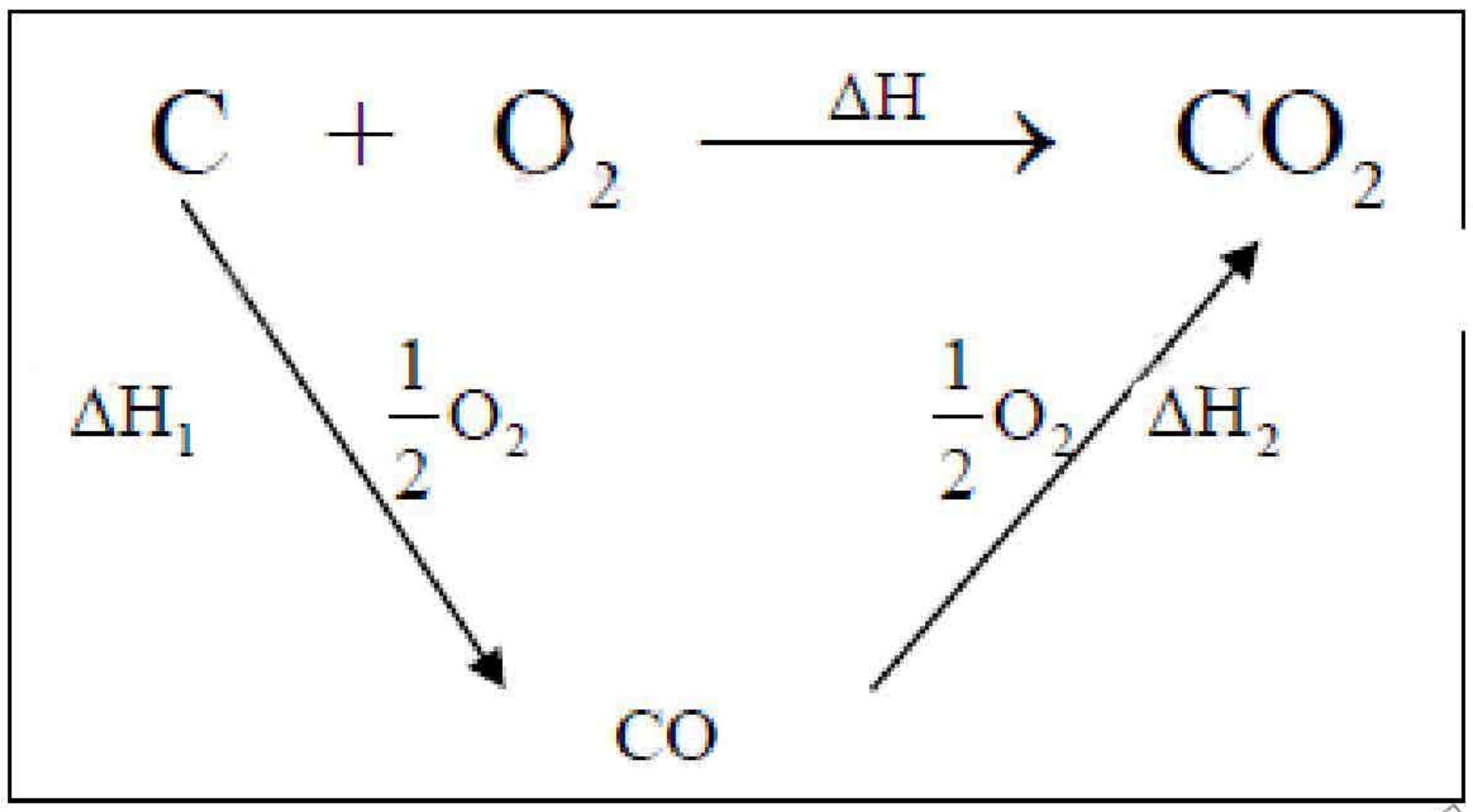
Calculations

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

$\Delta H_1 = \Delta H - \Delta H_2$

$= -393 - (-283)$

$= -110 kJ\ mol^{-1}$



Formation of Sodium Carbonate from Sodium Hydrogen Carbonate
Single Step Process

$$2NaOH_{(aq)} + CO_{2(g)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(\ell)} \qquad \Delta H = -89.08 kJ$$

Two Step Process

$$NaOH_{(aq)} + CO_{2(g)} \rightarrow NaHCO_{3(aq)} \qquad \Delta H_1 = -48.06 kJ$$

$$NaHCO_{3(aq)} + NaOH_{(aq)} \rightarrow Na_2CO_{3(aq)} + H_2O_{(\ell)} \qquad \Delta H_2 = -41.02 kJ$$

According to Hess's law

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

$$-89.08 = -48.06 - 41.02$$

$$-89.08 = -89.08$$

This proves Hess's law.

The Born-Haber Cycle

Statement

Energy change in a cyclic process is always zero.

Application

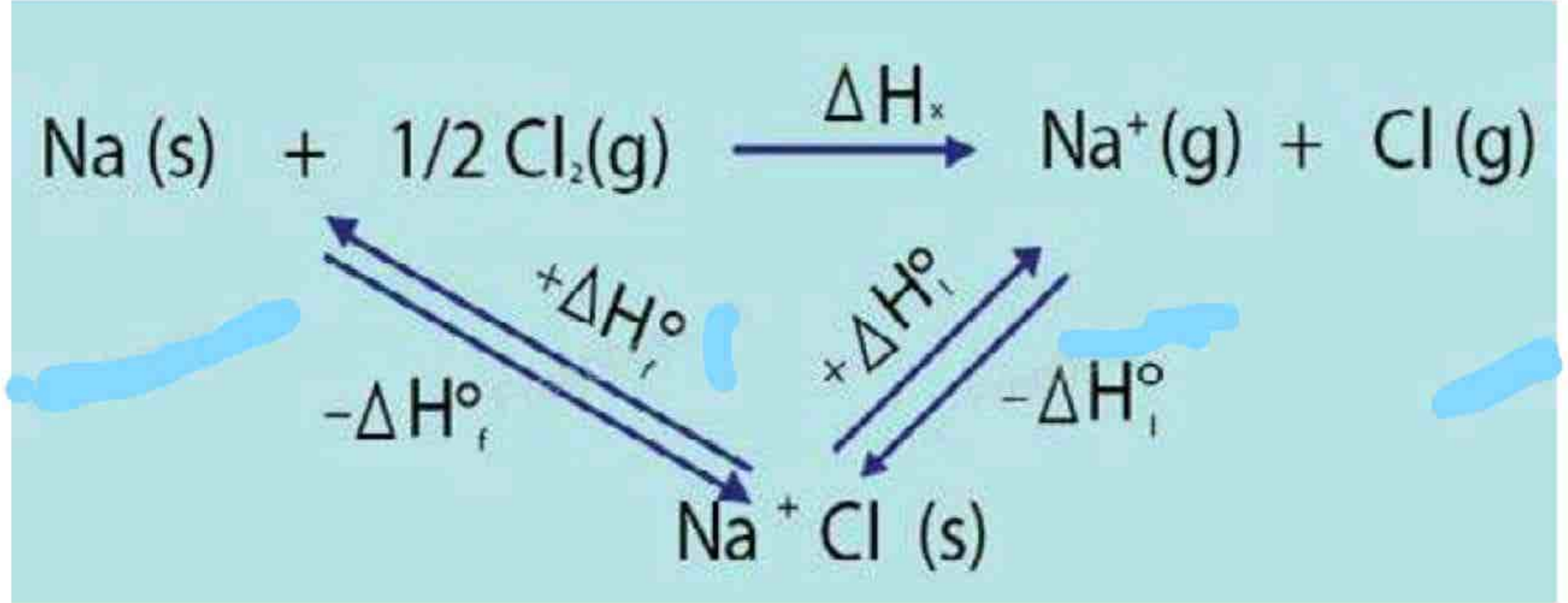
It enables us, to calculate the lattice energies of binary ionic compounds such as M^+X^-.

The lattice energy of an ionic crystal is the enthalpy of formation of one mole of the ionic compound from gaseous ions under standard conditions.

$$Na^+_{(g)} + Cl^-_{(g)} \rightarrow Na^+Cl^-_{(s)} \qquad \Delta H^\circ_{Latt} = -787\ kJ\ mol^{-1}$$

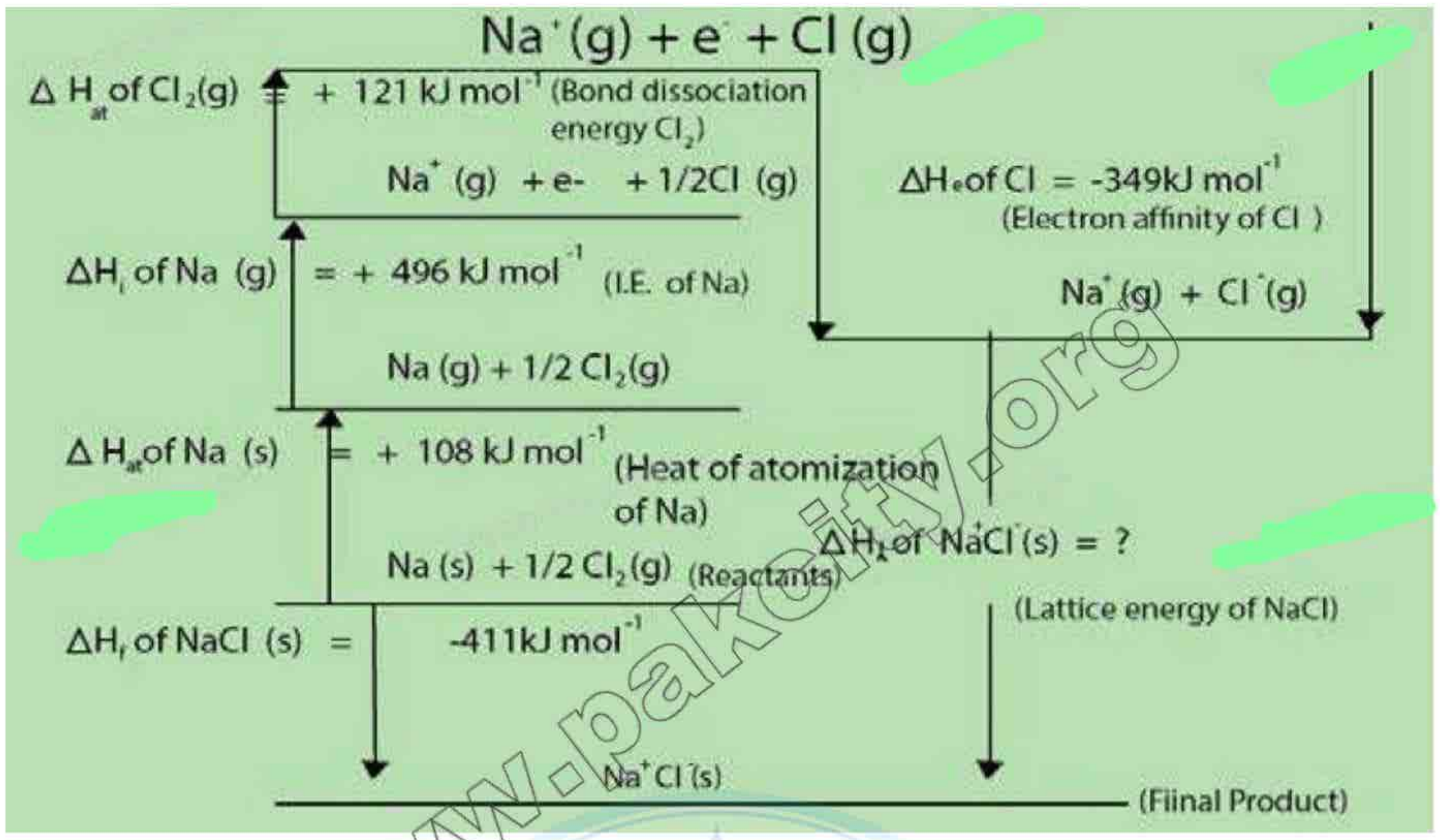
Lattice energies cannot be determined directly but values can be obtained indirectly by means of an energy cycle.

Energy triangle



ΔH°_f can be measured conveniently in a calorimeter.
ΔH°_l can be obtained if ΔH_x, which is the total energy involved in changing sodium and chlorine from their normal physical states to gaseous ions, can be calculated.

Born-Haber Cycle



$$\Delta H_x = \Delta H_{at(Na)} + \Delta H_{i(Na)} + \Delta H_{at(Cl)} + \Delta H_{e(Cl)}$$

Atomization and Ionization

$$Na_{(s)} \rightarrow Na_{(g)} \qquad \Delta H_{at} = 108 kJ\ mol^{-1}$$

$$Na_{(g)} \rightarrow Na_{(g)} + 1e^- \qquad \Delta H_i = 496 kJ\ mol^{-1}$$

Atomization of chlorine

$$\frac{1}{2}Cl_{2(g)} \rightarrow Cl_{(g)} \qquad \Delta H_{at} = 121\ kJ\ mol^{-1}$$

Absorption of electron by chlorine

$$Cl_{(g)} + e^- \rightarrow Cl^-_{(g)} \qquad \Delta H_e = -349\ kJ\ mol^{-1}$$

$$\Delta H_x = (108+496+121-349) = 376 \text{ kJ mol}^{-1}$$

Lattice energy for sodium chloride

$$\Delta H^\circ_f = \Delta H^\circ_\ell + \Delta H_x$$

$$\Delta H^\circ_\ell = \Delta H^\circ_f - \Delta H_x$$

$$\mathbf{\Delta H_\ell = -411-376 = -787 \text{ KJ/mol}}$$

It gives idea of the force of attraction between Na^+ and Cl^- ions in crystalline sodium chloride.

Important long questions from past papers

12. Define Enthalpy and prove that $\Delta H = q_p$
13. State and explain Hess's law of constant heat summation.
14. State 1st law of thermodynamics. Prove that $\Delta E = q_v$
15. Define Enthalpy of reaction. How is it measured by Glass Calorimeter?
16. What is molar heat of combustion? How is it measured by bomb calorimeter?

All definitions (any four) may come for long question.