Thermochemistry

BASICS Section - 1

In this chapter, we will study the heat changes that take place when a chemical process occurs. Heat (a form of energy) is either evolved or absorbed in the course of a chemical reaction. The study of energetics considers the relationship between thermodynamical functions: heat (q), work (W) and internal energy (U or E).

1. Definitions :

System :

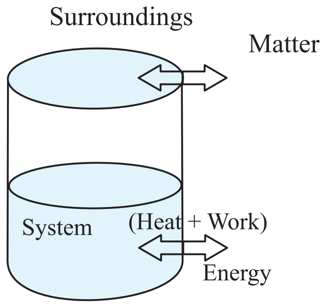
A small portion of the universe with-in which we confine our study of energy changes is called as a *system*.

Surroundings :

The remainder of the universe (i.e., apart from the system), which can interact with the system is called as *surroundings*.

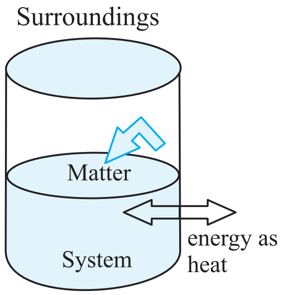
Open System :

This type of system can exchange matter as well as energy with surroundings. The boundary is not sealed and not insulated. Sodium reacting with water in an open beaker is an example of open system.



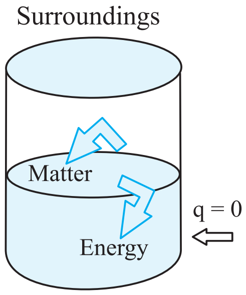
Closed System :

This type of system can exchange energy in the form of heat, work or radiations but not matter with its surroundings. The boundary between system and surroundings is sealed but not insulated. For example, liquid in contact with vapour in a sealed forms a closed system. Heat can be transferred through the walls of the tube to the surroundings but total amount of matter remains the same as vapours cannot escape.



Isolated System :

This type of system has no interaction with its surroundings. Neither matter nor energy can be exchanged with surroundings. A substance contained in an ideal thermos-flask is an example of an isolated system.



2. Thermodynamic Properties :

(i) Intensive Properties :

The properties which do not depend upon the quantity of matter present in the system are called *Intensive properties*. Pressure, temperature, specific heat, surface tension, refractive index, viscosity, melting point, boiling point, volume per mole (molar volume), concentration, color, potential, electrical field, electrical resistivity, specific energy, etc, are examples of intensive properties of the system.

(ii) Extensive Properties :

The properties whose magnitude depends upon the quantity of matter present in the system are called *Extensive properties.* Internal energy, total moles, volume, enthalpy, entropy, Gibbs energy, length, mass, electrical resistance etc. are examples of extensive properties.

3. Internal Energy (U) :

All the possible forms of energy that are associated with a system are referred to as *internal energy*. It includes kinetic energy due to all kinds of motion of the particles of the system, and their potential energy due to intermolecular forces (interaction). It is impossible to measure the exact value of the internal energy of a system. It can be measured when the system changes its state i.e. as change in internal energy (ΔU).

The internal energy change of a system depends upon the state of the system and not on how the system achieved the particular state. Such a thermodynamic function is called as *state function*. Other examples are: temperature, pressure, volume, enthalpy, entropy, Gibbs energy etc.

If U_1 is the internal energy of a system in state 1, and U_2 in the state 2, then the change in the internal energy of the system (ΔU) is given by : $\Delta U = U_2 - U_1$

As stated above, ΔU is independent of the process which takes the system from state 1 *to state* 2.

4. First Law of Thermodynamics :

Energy can neither be created nor destroyed, although it can be transformed from one form to another.

If we supply an amount of heat (= q) to the system in state 1, the system does a work w and goes to achieve the state 2. The heat supplied to the system gets converted into two parts :

(a) Work done by the system

(b) Change in internal energy of the system.

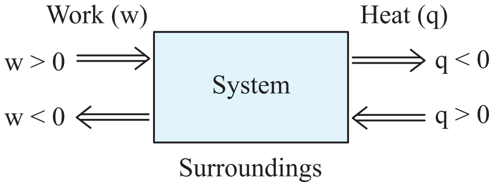
From Law of Conservation of Energy, we have :

$$q = \Delta U + (-w) \qquad \text{....(i)}$$

This equation is known as *First Law of Thermodynamics*.

5. Sign Convention :

- w is positive, when the work is done on the system.
- w is negative, when the work is done by the system.
- q is positive, when the heat is supplied to the system.
- q is negative, when the heat is lost by the system.



6. Enthalpy :

It is a thermodynamic function (H) defined to study heat changes in chemical reactions. It is also known as *heat content* of the system defined as :

$H = U + PV$ where P : Pressure V : Volume

If the change of state takes place at constant pressure, q is denoted as q_p (heat transfer at constant pressure). It is also known as *change in enthalpy* of the system, represented as

$\Delta H = q_p$ (H : Enthalpy of the system).

In such a process, volume of the system will change and work done is given as :

$w = -P\Delta V$ ΔV : change in volume

$\Rightarrow$ $q_p = \Delta U + P\Delta V$ [Using first law of thermodynamics]

or $q_p = U_2 - U_1 + P(V_2 - V_1)$

or $q_p = (U_2 + PV_2) - (U_1 + PV_1)$

or $q_p = H_2 - H_1 = \Delta H$ where $H_1 = U_1 + PV_1$ = enthalpy of the system in state 1

and $H_2 = U_2 + PV_2$ = enthalpy of the system in state 2

Enthalpy change like internal energy change is a *state function.*

Heat change in all chemical reactions is studied as enthalpy change of the reaction ($\Delta_r H$). System in state 1 is taken as *system of reactants* and in state 2 is taken as *system of products*. Enthalpy change (Heat change) accompanying the reaction is given as :

$\Delta_r H$ = Enthalpy of products – Enthalpy of reactants = $\Sigma(H_{\text{products}}) - \Sigma(H_{\text{reactants}})$

If the change of state takes place at constant volume, q is denoted as q_v (heat transfer at constant volume).

$\Delta U = q_v$

7. Exothermic and Endothermic reactions :

(a) Exothermic reactions :

Chemical reactions in which heat is evolved are known as exothermic reactions.

For example : $2\,Mg\,(s) + O_2\,(g) \longrightarrow 2\,MgO\,(g)$

$N_2\,(g) + 3H_2\,(g) \longrightarrow 2\,NH_3\,(g)$

Both of the above reactions are exothermic reactions because heat is evolved in them.

In general, an exothermic reaction is represented as : Reactants $\longrightarrow$ Products + heat

Here enthalpy (or heat content) of reactants is partially transferred to the enthalpy of the products and partially evolved as heat.

If H_R : enthalpy of reactants and H_P : enthalpy of products

Clearly, $H_P < H_R$ $\Rightarrow$ $\Delta_r H < 0$ $[\Delta_r H = H_P - H_R]$

i.e. for exothermic reaction, $\Delta_r H$ (reaction enthalpy) will bear a –ve sign (evolution of heat)

Note : In exothermic reaction, for some time (i.e. during the change) temperature of the products will rise above room temperature. But, very soon the heat is lost to surroundings and the same temperature is maintained.

(b) Endothermic Reactions :

Chemical reactions in which the heat is absorbed from the surroundings are known as *endothermic reactions*.

For example : $N_2(g) + O_2(g) \longrightarrow 2\,NO(g)$

$H_2(g) + I_2(g) \longrightarrow 2\,HI(g)$

Both of the above reactions are endothermic reactions because in them heat is absorbed from the surroundings.

In general, an endothermic reaction can be expressed as : Reactants + heat $\longrightarrow$ Products

Here, enthalpy of products is derived from enthalpy of reactants plus the absorbed heat.

Clearly $H_P > H_R$

$\Rightarrow \quad \Delta_r H > 0 \qquad [\Delta_r H = H_P - H_R]$

i.e. for endothermic reactions, $\Delta_r H$ (reaction enthalpy) will bear a +ve sign (absorption of heat)

Note : In endothermic reactions, (unlike exothermic reactions), temperature of the reacting mixture falls during the change. But very soon, heat is absorbed from the surrounding and same temperature is restored.

8. Enthalpy Change at Standard Conditions :

$\Delta_r H$ depends upon the conditions under which a reaction is performed. So to compare enthalpy changes of various reactions, they are performed at standard conditions.

Standard conditions for temperature and pressure are 298 K (or 25°*C*) and 1.0 atm pressure. Any enthalpy change measured under these conditions is known as *Standard Enthalpy change* or *Standard Heat of reaction* and it is denoted as $\Delta_r H^\ominus$.

It is also important to specify the states of all reactants and products in a reaction.['*s*' for solids, '*l*' for liquids, '*g*' for gases (or free atoms), '*aq*' for solution in water].

A chemical reaction which clearly informs about the heat change accompanying it (i.e. exothermic or endothermic) and the physical state of all reactants and products is known as *Thermochemical Equation*.

For example : $C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$; $\Delta_r H_1 = -385.2$ kJ (Exothermic)

$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \longrightarrow NO(g)$; $\Delta_r H = +90.25$ kJ (Endothermic)

Note : $\Delta_r H$ is the reaction enthalpy for a reaction in any form (i.e. stoichiometric coefficients) e.g. refer to the reaction below :

$2C(s) + O_2(g) \longrightarrow 2\,CO(g)$; $\Delta_r H_2 = -770.4$ kJ (Exothermic)

Here, $\Delta_r H_2 = 2\,\Delta_r H_1$

9. Enthalpy of a Compound :

To define the enthalpy of a compound, it is taken that the enthalpy of an element in its most stable state at standard conditions is zero.

Standard states of some elements :

C : Graphite ; S : Rhombic ; Br as $Br_2(\ell)$; I as $I_2(s)$; H as $H_2(g)$; Cl as $Cl_2(g)$; N as $N_2(g)$; O as $O_2(g)$;

P : White (Exception : Red Phosphorus is more stable than White Phosphorus)

e.g. $H^\ominus_{Cl_2(g)} = 0$; $H^\ominus_{H_2(g)} = 0$; $H^\ominus_{O_2(g)} = 0$; $H^\ominus_{Br_2(\ell)} = 0$; $H^\ominus_{I_2(s)} = 0$

Consider the following thermochemical equations at 25°C and 1 atm.

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) \longrightarrow HCl(g)$$

It represents formation of HCl at standard conditions i.e. $\Delta_f H^\ominus = \Delta H$ of given reaction

From definition : $\Delta_r H = \Sigma (H_{products}) - \Sigma (H_{reactants}) = \Sigma a_i (H)_{m,\ products} - \Sigma b_i (H)_{m,\ reactants}$

[H_m is the molar enthalpy of the compound and a_i &b_i the stoichiomeric coefficients of products and reactants respectively]

$\Rightarrow \quad \Delta_r H^{\ominus} = \Delta_f H^{\ominus} = H^{\ominus}{}_{HCl} - \left(\frac{1}{2} H^{\ominus}{}_{H_2} + \frac{1}{2} H^{\ominus}{}_{Cl_2}\right)$ [see definition of $\Delta_f H^{\ominus}$ in Section - 2]

$\Rightarrow \quad \Delta_f H^{\ominus} = H^{\ominus}{}_{HCl} - 0$ [Enthalpy of elements in standard state = 0]

$\Rightarrow \quad H^{\ominus}_{(HCl)} = \Delta_f H^{\ominus}_{(HCl)}$

Hence the enthalpy of a compound is the standard heat of formation of the compound OR *enthalpy of a compound is often taken as standard enthalpy of formation of that compound.*

Enthalpy of a compound A at standard conditions = $\Delta_f H^{\ominus}$ of A

Note : By convention, $\Delta_f H^{\ominus}\ (H^+ (aq)) = 0$

Illustration - 1 *How much heat is evolved by the preparation of* 100 *gm of iron by the following reaction ?*

$$2\,Al\,(s) + Fe_2O_3\,(s) \longrightarrow 2\,Fe(s) + Al_2O_3\,(s)\ ; \qquad \Delta_r H = -202.6\ kcal/mol$$

SOLUTION :

From thermochemical reaction, it is clear that 202.6 kcal of heat is involved when two moles of *Fe* (iron) is formed.

$\Rightarrow \quad$ 2 moles of Fe $\equiv$ 202.6 kcal $\quad \Rightarrow \quad$ 1 mole of Fe $\equiv$ 101.3 kcal

$\Rightarrow \quad$ 100/56 mole of Fe $\equiv 101.3 \times 100/56 = 180.9$ kcal

Heat of Reaction Section - 2

The heat of a reaction can be assigned special names in the following manner :

(a) Standard Heat of Formation ($\Delta_f H^{\ominus}$) :

The heat evolved or absorbed when one mol of any compound is formed from its elements in their standard states. It is usually denoted by $\Delta_f H^{\ominus}$. $\Delta_f H^{\ominus}$ can be given –ve or +ve sign, depending upon whether formation is exothermic or endothermic.

$$C(s,\ graphite) + 2\,H_2\,(g) \longrightarrow CH_4\,(g) \quad ; \qquad \Delta_f H^{\ominus} = -74.3\ kJ/mol$$

$$\frac{1}{2} H_2\,(g) + \frac{1}{2} I_2\,(s) \longrightarrow HI\,(g) \quad ; \qquad \Delta_f H^{\ominus} = 25.92\ kJ/mol$$

Note : To write chemical equations for formation, balance the reaction for one mole of compound whose formation is to be studied.

(b) Standard Heat of Combustion ($\Delta_c H^{\ominus}$) :

The heat evolved (or enthalpy change) when one mole of any substance is completely burnt in excess of oxygen.

$\Delta_c H^{\ominus}$ will always bear –ve sign for it being enthalpy change of an exothermic reaction.

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(\ell)\ ; \qquad \Delta_c H^{\ominus} = -212\ kcal/mol$$

$$C(s,\ graphite) + O_2(g) \longrightarrow CO_2\,(g) \quad ; \qquad \Delta_c H^{\ominus} = -94\ kcal/mol$$

Note : To write chemical equations for combustion, balance the reaction for one mole of compound whose combustion is to be studied.