CHAPTER 5

CHEMICAL THERMODYNAMICS

That branch of science which deals with the study of heat exchange within chemical reaction

5.1.0 INTRODUCTION

Chemical thermodynamics (کیمیائی حرحرکیات) is that branch of science which deals with the quantitative relationship between the heat of chemical reaction and the other forms of energy. Its main objective with reference to the chemistry are as follows.

(i) It tells us whether a chemical reaction occurs under the given set of conditions. In other words, it tells us the feasibility (امکان) of the chemical reaction.

(ii) Chemical thermodynamics (کیمیائی حرحرکیات) helps us to predict (پیشن گوئی کرنا) the yield of products obtained in a chemical reaction and it tells us the possible extent (ممکنہ حد) to which the chemical reactions take place before attaining equilibrium.

(iii) With the help of chemical thermodynamics, we can explain the processes like lowering of vapour pressure (بخارات کے دباؤ کا کم ہونا), elevation of boiling point (B.P کا بڑھنا), depression of freezing point (F.P کا کم ہونا), distribution law and phase rule.

5.1.1 Limitation of Chemical Thermodynamics:

Chemical thermodynamic has the following limitations (حدود و قیود):

(i) Thermodynamic deals with the properties like temperature, pressure etc., if the matter is in the bulk. It deals with macroscopic (بغیر خوردبین دیکھے جانے والی) quantities and not microscopic (خوردبینی والی). This means that we study the large groups of atoms, molecules or ions.

(ii) No doubt, it tells us the feasibility of a process, but does not tell us about the rate (رفتار) at which the reaction completes (مکمل ہوتا ہے).

(iii) Thermodynamic is concerned (تعلق رکھتی ہے) with initial and final states of a system but not with route (راستہ) by which the reaction is taking place (ہو رہا ہے).

5.1.2 Important Terms in Chemical Thermodynamics:

System and Surrounding: Any part of universe which is under observation. System,

"A material or a collection of materials which is under study is called a system." The system can be very big or small, so we can say that the part of a universe (کائنات), which is chosen for the study of effect of temperature, pressure etc., is called a system. The remaining portion of the universe, included in the system is called surrounding (گردوپیش). All the part of universe which is outside system is called surrounding

Open System:

"If the exchange of both matter and energy takes place with the surroundings, then it is open system." For example, a hot liquid placed in open vessel cools down with the passage of time.

This is due to the loss of heat in the surrounding and spreading of the vapour (بخارات کا بکھرنا) of the liquid with the surrounding.

Closed System:

"If the exchange of only energy with the surrounding takes place then it is called the closed system." For examples, if you have a hot liquid in closed container then water vapours can not escape to the surrounding, but epergy is dissipated (ضائع ہونا) in the air, if the walls of the vessels are conducting (گرمی کو گزرنے دینے والے).

Isolated System:

"If there in no exchange of matter and energy with the surroundings, then it is called isolated system." Place some hot liquid closed, then neither matter nor energy can take place between the system and surrounding.

Macroscopic System:

"A system which contains a large amount of substance is a macroscopic system." (خوردبین کے بغیر دیکھا جاسکنے والا) In other words, there are many particles which may be atoms, ions and molecules. The property which is associated (منسلک ہے) with the collective behaviour (مجموعی تاثر) of particles in a macroscopic system is called macroscopic property. The properties like pressure, temperature, volume, surface tension, viscosity, density, refractive index, melting point and boiling point are macroscopic properties of the substances.

State of a System:

"A condition of the system, when various macroscopic properties like pressure, temperature, volume etc. of a system have definite values is called state of a system." When there happen changes in the system, then there may be initial state or final states. The four most common macroscopic properties of a system are

(i) Composition of the substance
(ii) Pressure
(ii) Volume
(iv) Temperature

If these four properties of a system are fixed, then all other physical properties are automatically (خودبخود) fixed.

Phase

کسی چیز یا مقدار کی وہ کیفیت یا پوزیشن جو تغیریات کے ایک سلسلے سے بار بار گزرنے کے بعد اس میں پیدا ہوتی ہے۔

5.1.3 Thermodynamic Equilibrium (تھرموڈائنامک توازن یا حرحرکیات میں توازن):

"When the macroscopic properties of the system in various phases, do not undergo any change with time, then the system is said to be in thermodynamic equilibrium."

There are three different types of equilibria which should exist simultaneously.

(i) **Thermal Equilibrium:**

"If there is no flow of heat from one portion of system to another, then the system is said to be in thermal equilibrium."

(ii) **Mechanical Equilibrium (میکانکی توازن):**

"If there is no flow of matter from one portion of the system to another, then it is mechanical equilibrium." In other words, you can say that there is no macroscopic movement of matter within the system from system to the surrounding. This is possible when the pressure within the system is kept constant.

the system, with ... equilibrium.

5.1.4 Different Types of Processes (مختلف قسم کے عملیات):

Processes are of four types in thermodynamics.

(i) Isothermal (ii) Adiabatic
(iii) Isochoric (iv) Isobaric.

Process

عملیات کا ایک ایسا سلسلہ جو ایک خاص نتیجہ حاصل کرنے کے لئے کیے جاتے ہیں۔

(i) Isothermal Process (مستقل درجہ حرارت):

"If the temperature remains constant throughout the process, then it called an isothermal process." Heat can flow from the system to the surrounding and vice versa, in order to keep the temperature of the system constant.

(ii) Adiabatic Process (حرارت ناگزار پراسیس):

"If there is no heat flow from the system to the surrounding or vice versa, then it is adiabatic process." In adiabatic processes, the system is completely insulated from the surroundings.

(iii) Isochoric Process (جسامت کی تبدیلی کے بغیر پراسیس):

"If there is no volume change in the system, then it is called isochoric process."

(iv) Isobaric Process (دباؤ کی تبدیلی کے بغیر پراسیس):

"If the pressure of the system is kept constant, then it is isobaric process."

5.1.5 Internal Energy of a System (کسی سسٹم کی اندرونی توانائی):

Substances exist because they possess energy (چیزوں کا وجود دنیا میں اس لئے ہے کہ ان کے پاس توانائی ہوتی ہے). When different process happen, then evolution or absorption of energy takes place. The actual value of the energy of a substance depends upon the nature of the substance. The reason is that the arrangement of atoms and electrons within the molecules are different for different substances. The internal energy also depends upon **pressure**, **temperature** and the **composition of the substance** (کسی چیز کی ترکیب).

It is not possible to find the absolute value (مطلق قیمت) of internal energy possessed by any system. The reason is that the internal energy is due to **translational** (جگہ بدلنے والی), **rotational** (گھومنے والی) and vibrational (ارتعاش والی) kinetic energies and they cannot be measured. Actually, we simply measure the change of internal energy, when the reaction take place. It is represented by ΔE.

$$\Delta E = E_2 - E_1$$

or $$\Delta E = E_p - E_r$$

Where, E_1 and E_2 are the internal energies in the initial and final states respectively. E_p and E_r are the internal energies of products and reactants respectively. If E_r is greater than E_p, then the heat is evolved during the chemical reaction and ΔE is negative.

If E_p is greater than E_r, then ΔE is positive and the energy is absorbed.

$E_2 > E_1$ ΔE = + ve, $E_p > \Delta E$ ΔE = +ve.

then in turn they have equality

and second laws of thermodynamics, that is why it is called zeroth law of thermodynamics.

5.2.2 First Law of Thermodynamics:

First law of thermodynamics can be defined in various forms as follows.

(i) *"Energy can neither be created nor destroyed although it may be converted from one form to the other."*

(ii) *"The total energy of an isolated system remains constant, although it may undergo transformation from one form to the other."*

(iii) *"Whenever certain quantity of some form of energy disappears* (غائب ہوتی ہے), *then equivalent amount* (برابر کی مقدار) *of some other form of energy must appear."*

5.2.3 Mathematical Statement of First Law of Thermodynamics:

Let us have a gaseous system and we supply heat 'q' calories to the system. A part of this q is used to increase the internal energy of the system and a part may produce some mechanical work. Suppose ΔE is the increase in the internal energy of the system and 'W' is the work done, then

$$q = (\Delta E + W) \quad \ldots\ldots (1)$$

Work done by system = -ve
Work done on system = +ve

It can be rearranged as,

$$\Delta E = q - W \quad \ldots\ldots (2)$$

If the changes are very very small, then

$$dE = \delta q - \delta W \quad \ldots\ldots (3)$$

If the work done is written as PdV, then

$$dE = \delta q - PdV \quad \ldots\ldots (4)$$

$\Rightarrow$ if $W = -ve$ then $\Delta E = q_v - (-W) = q_v + W = q_v + P\Delta V$

Be Careful

One has to be very careful to handle all the equation from (1) to (4), when we use latest SI convention. According to this the work done by the system is negative, so first law can be written as,

$$\Delta E = q + W$$

5.2.4 Enthalpy (کسی مادے کی مجموعی حرارت یا تپش کی مقدار):

Enthalpy is the heat content (پاس رکھی جانے والی حرارت) of the system. Internal energy E, pressure P, and volume 'V' are the functions (تفاعل) of state. So, (E + PV) is also a state function. This thermodynamic quantity (E + PV) is called the heat content or enthalpy (H) of the system.

$$H = E + PV \quad \ldots\ldots (1)$$

Enthalpy change for any system is the heat supplied to the system at constant pressure.

$$q_p = \Delta H$$

مستقل دباؤ قائم کرکے جو گرمی دی جاتی ہے وہ Change of Enthalpy کی تبدیلی کہلاتی ہے۔

$\Delta H = \Delta E + \Delta(PV) \Rightarrow \Delta H = \Delta E + P\Delta V + V\Delta P$

The value of ΔH in term of ΔE and $P\Delta V$ is as follows,

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

$$\Delta H = \Delta E + P\Delta V \quad \ldots\ldots (3)$$

According to this equation, the enthalpy change of a process is sum of the increase in the internal energy of the system and pressure volume work done.