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## Assignment - 2

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Q: Definition of Enthalpy, Entropy, Free energy, formulas explanation of these three in a system with an example.

Ans:

### Enthalpy

Before discussing on enthalpy, we should make a brief statement on internal energy ( $E$ ). Internal energy is actually the sum of all possible types of energies (translational Energy; Rotational Energy; Vibrational Energy of molecules; Electronic Energy; nuclear energy etc) associated with the atoms and molecules of a given substance. #

It is established that the heat change during a chemical reaction that occurs at constant temperature and constant volume can be measured in terms of the change in the internal energy of the system. However it is not always possible to carry out reactions at constant volume in laboratories. When a reaction is carried out at a constant pressure, there may be a change in the volume of the reacting system. The change in the volume involves some work either done by the system (in case of increase in volume) or done on the system (in case of decrease in volume). Thus, the amount of heat exchanged with the surroundings at constant pressure is not the same as that at constant volume. (because at constant volume there is no change in volume and therefore no work is done.) In order to study the heat exchanges at constant pressure, enthalpy is introduced. It is represented by  $H$  and is regarded as the total heat content of a system at constant pressure. Thus, the sum of internal energy and pressure-volume energy of a system, under a particular set of conditions, is referred to as enthalpy of a system. Mathematically,

$$H = E + PV$$

—①



where  $E$  = internal energy of system  
 $P \& V$  = pressure and volume of the system.

Enthalpy is a state function. Therefore, change in enthalpy ( $\Delta H$ ) depends only upon the initial and final states of the system; i.e.,

$$\Delta H = H_{\text{final state}} - H_{\text{initial state}}.$$

For a chemical reaction occurring at constant temperature and pressure, the change in enthalpy is equal to the difference of enthalpies of products and reactants. i.e.

$$\Delta H = H_{\text{Products}} - H_{\text{Reactants}}$$

$$\text{or } \Delta H = H_p - H_R \quad \text{--- (II)}$$

From the definition of  $H$ , change in enthalpy is:

$$\begin{aligned} \Delta H &= \Delta E + \Delta(PV) \\ &= \Delta E + P\Delta V + V\Delta P \end{aligned} \quad \text{--- (III)}$$

At constant pressure, (i.e.  $\Delta P = 0$ ),

$$\Delta H = \Delta E + P\Delta V \quad \text{--- (IV)}$$

According to 1st law of thermodynamics,

$$\Delta E = q + w.$$

If work done is work of expansion,  $w = -P\Delta V$

$$\text{So } \Delta E = q - P\Delta V$$

Substituting value of  $E$  in equation (IV), we have,

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

$$\Rightarrow \Delta H = q_p \quad \text{where } q_p \text{ is heat exchange occurring at constant pressure.}$$



Therefore,  $\Delta H$  is regarded as a measure of heat evolved or absorbed in a process occurring at constant pressure.

## Entropy

We know that a spontaneous change of a system is associated with an increase in randomness or disorder. In order to measure the disorder or randomness of a system, a thermodynamic function called 'Entropy' was introduced. It is a state function and is represented by  $S$ . For a reversible change, the change in entropy  $\Delta S$  is :-

$$\Delta S = \frac{q_{rev}}{t}$$

where  $q_{rev}$  is the heat supplied isothermally and reversibly to the system at temperature  $T$ .  $\therefore$  Entropy is a state function,  $\Delta S$  depends only upon the initial and final states of the system and not upon the path by which the system transits. Thus;

$$\Delta S = S_{\text{final state}} - S_{\text{initial state}}.$$

and for chemical reactions,

$$\Delta S = S_{\text{products}} - S_{\text{reactants}} \quad \text{--- (1)}$$

The absolute entropy of a system at  $25^\circ\text{C}$  and  $1\text{ atm}$  is called standard entropy of system and is represented by  $S^\circ$ .

Units of Entropy :  $\text{J K}^{-1} \text{ mole}^{-1}$  (SI system)

**Physical Significance of Entropy :** For a given substance, the entropy of a system is minimum for crystalline solid state while maximum for the gaseous state. The liquid state possesses the intermediate value. Thus,

$$S_{\text{gas}} > S_{\text{liquid}} > S_{\text{crystalline solid}}.$$



From thermodynamic point of view, the system and the surroundings constitute universe. Therefore, for a spontaneous change, the total change in entropy is equal to the change in entropy of the universe. Hence,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$
$$= \Delta S_{\text{universe}} > 0$$

The mathematical condition for entropy to be maximum, is that the change in entropy ( $\Delta S$ ) is zero.   
  $\therefore$  there are several conditions <sup>for chemical reactions</sup>. They are:

- i) If  $\Delta S_{\text{total}}$  is +ve (i.e.  $\Delta S_{\text{total}} > 0$ ) the process is spontaneous in direction as mentioned i.e. eq. of reaction
- ii) If  $\Delta S_{\text{total}}$  is zero (i.e.  $\Delta S_{\text{total}} = 0$ ), the process is at equilibrium.
- iii) If  $\Delta S_{\text{total}}$  is -ve (i.e.  $\Delta S_{\text{total}} < 0$ ), the process is non spontaneous i.e. it is spontaneous in reverse direction.

### Free Energy (Gibbs Free Energy)

From the entropy concept, a spontaneous process proceeds in the direction in which  $\Delta S_{\text{system}}$  is maximum. We know that neither a -ve value of  $\Delta H$  nor a +ve value of  $\Delta S_{\text{system}}$  alone can be taken as the sole criterion for the spontaneity of a process. However as suggested by the second law of thermodynamics,

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

The determination of  $\Delta S_{\text{total}}$  requires the determination of



$\Delta S_{\text{surroundings}}$ , which is not always possible. Hence, a new thermodynamic function known as Gibbs free energy was introduced to explain the spontaneity of a process. Mathematically, Gibbs free energy is given by,

$$G = H - TS \quad \text{--- (i)}$$

where  $H$  represents the enthalpy of a system,  $S$  is the entropy of the system and  $T$  represents the temperature of the system on Kelvin scale.

Thus the maximum amount of energy available to a system during a process for doing useful work under constant temperature and pressure conditions is called Gibbs free energy. Now,

$$\Delta G = \Delta H - T \Delta S \quad \text{--- (ii)}$$

Equation (ii) represents the free energy change in a process occurring at constant temperature and constant pressure.

This equation is referred to as Gibbs-Helmholtz equation. This equation is very helpful in predicting the spontaneity of a process. The change in Gibbs free energy, i.e.  $\Delta G$  is regarded as the sole criterion to discuss the spontaneity of a process. The criterion can be summarized as follows:

- (a) When  $\Delta G$  is -ve ( $\Delta G < 0$ ), the process is spontaneous.
- (b) When  $\Delta G$  is +ve ( $\Delta G > 0$ ), the process is non-spontaneous.
- (c) When  $\Delta G = 0$ , the process is at equilibrium.

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