

# Chemical Thermodynamics - I

## BASICS

## Section - 1

### Internal Energy :

When we talk about our chemical system losing or gaining energy, we need to introduce a quantity which represents the total energy of the system. It may be chemical, electrical, mechanical or any other type of energy you may think of, the sum of all these is the energy of the system. In thermodynamics, we call it the **internal energy**,  $U$  of the system, which may change, when

- heat passes into or out of the system,
- work is done on or by the system,
- matter enters or leaves the system.

Let us consider the general case in which a change of state is brought about both by doing work and by transfer of heat. We write change in internal energy for this case as :  $\Delta U = q + w$  .....(i)

For a given change in state,  $q$  and  $w$  can vary depending on how the change is carried out. However,  $q + w = \Delta U$  will depend only on initial and final state. It will be independent of the way the change is carried out. If there is no transfer of energy as heat or as work (**isolated system**) i.e., if  $w = 0$  and  $q = 0$ , then  $\Delta U = 0$ .

The equation,  $\Delta U = q + w$  is mathematical statement of the first law of thermodynamics, which states that *the energy of an isolated system is constant*.

Many chemical reactions involve the generation of gases capable of doing mechanical work or the generation of heat. It is important for us to quantify these changes and relate them to the changes in the internal energy. Let us see how!

### Pressure-Volume work :

For understanding pressure-volume work, let us consider a cylinder which contains one mole of an ideal gas fitted with a frictionless piston. Total volume of the gas is  $V_i$  and pressure of the gas inside is  $p$ . If external pressure is  $p_{ex}$  which is greater than  $p$ , piston is moved inward till the pressure inside becomes equal to  $p_{ex}$ . Let this change be achieved in a single step and the final volume be  $V_f$ .

During this compression, suppose piston moves a distance, and its cross-sectional area of the piston is  $A$  (figure shown).

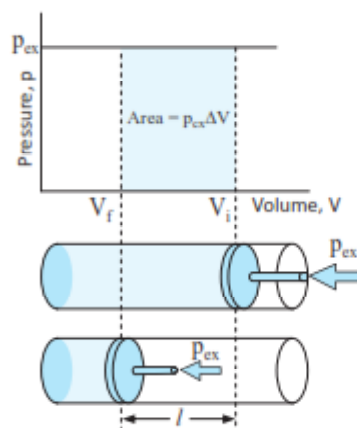


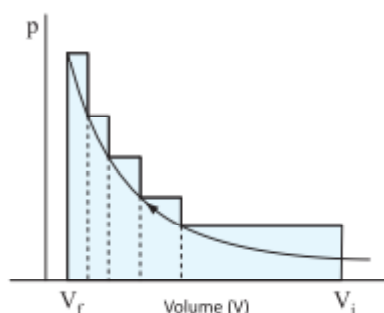
Figure : Work done on an ideal gas in a cylinder when it is compressed by a constant external pressure,  $p_{ex}$  (in single step) is equal to the shaded area.

We also know,  $\text{pressure} = \frac{\text{force}}{\text{area}}$  Therefore, force on the piston =  $p_{\text{ex}} \cdot A$

If  $w$  is the work done on the system by movement of the piston then

$$w = \text{force} \times \text{distance} = p_{\text{ex}} \cdot A \cdot l = p_{\text{ex}} \cdot (-\Delta V) = -p_{\text{ex}} \Delta V = -p_{\text{ex}} (V_f - V_i) \quad \dots\text{(ii)}$$

The negative sign of this expression is required to obtain conventional sign for  $w$ , which will be positive. It indicates that in case of compression work is done on the system. Here  $(V_f - V_i)$  will be negative and negative multiplied by negative will be positive.



**Figure :** pV-plot when pressure is not constant and changes in finite steps during compression from initial volume,  $V_i$  to final volume,  $V_f$ . Work done on the gas is represented by the shaded area.

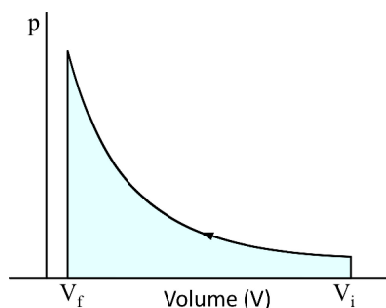
If the pressure is not constant at every stage of compression, but changes in number of finite steps, work done on the gas will be summed over all the steps and will be equal to  $-\sum p \Delta V$ .

If the pressure is not constant but changes during the process such that it is always infinitesimally greater than the pressure of the gas, then, at each stage of compression, the volume decreases by an infinitesimal amount,  $dV$ . In such a case we can calculate the work done on the gas by the relation

$$w = - \int_{V_i}^{V_f} p_{\text{ex}} dV \quad \dots\text{(iii)}$$

Here,  $p_{\text{ex}}$  at each stage is equal to  $(p_{\text{in}} + dp)$  in case of compression. In an expansion process under similar conditions, the external pressure is always less than the pressure of the system i.e.,  $p_{\text{ex}} = (p_{\text{in}} - dp)$ . In general case we can write,  $p_{\text{ex}} = (p_{\text{in}} \pm dp)$ . Such processes are called **reversible processes**.

A process or change is said to be reversible, if a change is brought out in such a way that the process could, at any moment, be reversed by an infinitesimal change. A reversible process proceeds infinitely slowly by a series of equilibrium state such that system and the surroundings are always in near equilibrium with each other. Processes other than reversible are known as **irreversible processes**.



**Figure :** pV-plot when pressure is not constant and changes in infinite steps (reversible conditions) during compression from initial volume,  $V_i$  to final volume,  $V_f$ . Work done on the gas is represented by the shaded area.

In chemistry, we face problems that can be solved if we relate the work term to the internal pressure of the system. We can relate work to internal pressure of the system under reversible conditions by writing equation (iii) as follows:

$$w_{\text{rev}} = - \int_{V_i}^{V_f} p_{\text{ex}} dV$$

Since  $dp \times dV$  is very small we can write

$$w_{\text{rev}} = - \int_{V_i}^{V_f} p_{\text{in}} dV$$

Now, the pressure of the gas ( $p_{\text{in}}$  which we can write as  $p$  now) can be expressed in terms of its volume through ideal gas equation. For  $n$  mol of an ideal gas i.e.,  $pV = nRT$

$$\Rightarrow p = \frac{nRT}{V}$$

Therefore, at constant temperature (isothermal process),

$$w_{\text{rev}} = - \int_{V_i}^{V_f} nRT \frac{dV}{V} = -2.303 nRT \log \frac{V_f}{V_i}$$

**Free Expansion:** Expansion of a gas in vacuum ( $p_{\text{ex}} = 0$ ) is called free expansion. No work is done during free expansion of an ideal gas whether the process is reversible or irreversible (equation (ii) and (iii)).

Now, we can write equation (i) in number of ways depending on the type of processes.

Let us substitute  $w = -p_{\text{ex}} \Delta V$  from equation (ii) in equation (i), and we get :

$$\Delta U = q - p_{\text{ex}} \Delta V$$

If a process is carried out at constant volume ( $\Delta V = 0$ ), then

$$\Delta U = q_v$$

the subscript  $v$  in  $q_v$  denotes that heat is supplied at constant volume.

**Isothermal and free expansion of an ideal gas :**

For isothermal ( $T = \text{constant}$ ) expansion of an ideal gas into vacuum :  $w = 0$  since  $p_{\text{ex}} = 0$ . Also, Joule determined experimentally that  $q = 0$  ; therefore,  $\Delta U = 0$ .

Equation  $\Delta U = q + w$  can be expressed for isothermal irreversible and reversible changes as follows:

1. For isothermal irreversible change  $q = -w = p_{\text{ex}} (V_f - V_i)$
2. For isothermal reversible change  $q = -w = nRT \ln \frac{V_f}{V_i} = 2.303 nRT \log \frac{V_f}{V_i}$
3. For adiabatic change,  $q = 0$ ,  $\Delta U = w_{\text{ad}}$
4. For isochoric process :  $-w = 0$
5. For isobaric process :  $-w = P_{\text{gas}} \Delta V$

**Note :** ➤ In many cases, an irreversible process can be easily recognized by using the fact that the process involving constant external pressure is an irreversible process.

➤ In a reversible process, an equilibrium exists (known as quasi-equilibrium) at every stage of the process.

➤ Work done by system in a reversible expansion process will always be greater than that in irreversible expansion process.

**Heat Capacity :****Heat Capacity (C) :**Heat required to raise the temperature of a system by  $1^\circ\text{C}$  or  $1\text{ K}$ .**Units :** J/K; kJ/K**Specific Heat Capacity (c) :**Heat required to raise the temperature of a 1gm of a system by  $1^\circ\text{C}$  or  $1\text{ K}$ .**Units :** J/g/K; kJ/Kg/K**Molar Heat Capacity ( $C_m$ ) :**Heat required to raise the temperature of a 1 mole of a system by  $1^\circ\text{C}$  or  $1\text{ K}$ .**Units :** J/mole/K; kJ/mole/K

Mathematically, the above quantities are defined as :

$$q = C \times \Delta T; \quad q = n \times C_m \times \Delta T; \quad q = m \times c \times \Delta T$$

where

$q$  = amount of heat absorbed by the system;  $\Delta T$  = Rise in the temperature;

$m$  = mass of the system;

$n$  = moles of the system

**Note:** Molar heat capacity has 2 forms :  $C_p$  (at constant pressure) and  $C_v$  (at constant volume) defined as :

$$C_p = \left( \frac{q}{\Delta T} \right)_p = \left( \frac{\Delta H}{\Delta T} \right)_p ; \quad C_v = \left( \frac{q}{\Delta T} \right)_v = \left( \frac{\Delta U}{\Delta T} \right)_v \quad [\because \Delta H = q_p ; \Delta U = q_v]$$

The subscript after the brackets in the above equation denotes the parameter kept constant during the process.

i.e.  $\left( \frac{\Delta H}{\Delta T} \right)_p$  denotes change in Enthalpy per unit change in Temperature keeping Pressure constant.

In terms of *differentials* :

$$C_p = \left( \frac{dq}{dT} \right)_p = \left( \frac{dH}{dT} \right)_p ; \quad C_v = \left( \frac{dq}{dT} \right)_v = \left( \frac{dU}{dT} \right)_v \quad [\because dH = dq_p ; dU = dq_v]$$

$$\text{Also, } C_p - C_v = R ; \quad \frac{C_p}{C_v} = \gamma$$

### Determination of $w$ , $q$ , $\Delta H$ and $\Delta U$ for a process and a reaction :

Clearly, we need to create 4 equations to solve 4 variables ( $w$ ,  $q$ ,  $\Delta H$  and  $\Delta U$ ) as follows :

Whether it is a process or a reaction, the first equation will always be applicable :

$$q = \Delta U + (-w) \quad \dots (i) \quad [\text{From First law of Thermodynamics}]$$

Calculating  $\Delta H$  and  $\Delta U$  will be different in case of a process and a reaction and explained as follows :

#### (i) For a process :

$$\Delta H = nC_p \Delta T \quad \dots (ii) \quad [\text{From definition of } C_p]$$

$$\text{or } \Delta H = \int_{T_1}^{T_2} nC_p dT \quad [\text{When } C_p \text{ is also a function of Temperature}]$$

$$\Delta U = nC_v \Delta T \quad \dots (iii) \quad [\text{From definition of } C_v]$$

$$\text{or } \Delta U = \int_{T_1}^{T_2} nC_v dT \quad [\text{When } C_v \text{ is also a function of Temperature}]$$

$$\text{Also, } \Delta H = \Delta U + \Delta(PV) \quad \text{or} \quad dH = dU + dPV + VdP \quad [\because H = U + PV]$$

$$\text{Many a times, we also write : } \Delta(PV) = P_2 V_2 - P_1 V_1 = \Delta(nRT = nR\Delta T)$$

#### (ii) For a reaction :

For a reaction,  $\Delta H$  is the most important parameter and can be calculated as :

$$\Delta H = \sum H_{\text{Products}} - \sum H_{\text{Reactants}} \quad \dots (ii)$$

$$\text{Also, } \Delta_r H = \Delta_r U + P\Delta V \quad [\text{As Chemical reactions occur at constant pressure and constant temperature}]$$

$$\text{or } \Delta_r H = \Delta_r U + \Delta n_g RT \quad \dots \text{ (iii)}$$

Thus, to get the interconversion between  $\Delta_r H$  and  $\Delta_r U$ , we must need to write down the balanced chemical reaction with states of all the reactants and products and then calculate the change in the number of gaseous moles.

The fourth variable can be calculated based on the process / situation as explained in the illustrations below :

**Illustration - 1** Calculate  $w$ ,  $q$ ,  $\Delta H$  and  $\Delta U$  for an ideal gas expanding in vacuum (i) isothermally (ii) adiabatically

**SOLUTION :**

- |      |                           |   |                                     |
|------|---------------------------|---|-------------------------------------|
| (i)  | $w = 0$                   | [As $P_{\text{Ext.}} = 0$ ]                       |                                     |
|      | $\Delta H = \Delta U = 0$ | [As $T = \text{constant}$ for isothermal process] |                                     |
|      | $q = 0$                   | [Using First law of Thermodynamics]               |                                     |
| (ii) | $q = 0$                   | [Adiabatic Process]                               |                                     |
|      | $w = 0$                   | [As $P_{\text{Ext.}} = 0$ ]                       |                                     |
|      | $\Delta U = 0$            | [Using First law of Thermodynamics]               | $\Rightarrow T \text{ is constant}$ |
|      | $\Delta H = 0$            | [As $T = \text{constant}$ ]                       |                                     |

**Note:** For an ideal gas,  $U = U(T)$  and  $H = H(T)$  but for real gas,  $U = U(T, V)$  and  $H = H(T, P)$

**Illustration - 2** Five mole of an ideal gas at 293 K are expanded isothermally from an initial pressure 0.4 kPa to a final pressure of 0.1 kPa against a constant external pressure of 0.1 kPa.

(a) Calculate  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$ .

(b) Calculate the corresponding value of  $q$ ,  $w$ ,  $\Delta U$  and  $\Delta H$  if the above process is carried out reversibly.

**SOLUTION :**

(a) For an isothermal expansion against a constant pressure, we have:

$$\begin{aligned}
 -w &= P_{\text{Ext}} (V_2 - V_1) \\
 &= P_{\text{Ext}} \left( \frac{nRT}{P_2} - \frac{nRT}{P_1} \right) = P_{\text{Ext}} nRT \left( \frac{1}{P_1} - \frac{1}{P_2} \right) \Rightarrow w = -9135 \text{ J}
 \end{aligned}$$

Since temperature is constant:  $\Delta U = 0$ ,  $\Delta H = 0$

$$q = -w = 9135 \text{ J} \quad [\text{Using First law of Thermodynamics}]$$

(b) For isothermal reversible expansion :

$$-w = 2.303 nRT \log_{10} \frac{P_1}{P_2} = 2.303 \times 5 \times 8.314 \times 293 \log_{10} \frac{0.4}{0.1} \Rightarrow w = -16888 \text{ J}$$

Since temperature is constant :  $\Delta U = 0$ ;  $\Delta H = 0$ ,  
 $q = -w = 16888 \text{ J}$  [Using First Law of Thermodynamics]

**Illustration - 3** The magnitude of enthalpy changes for reversible adiabatic expansion of a gas from volume  $V_1$  to  $V_2$  (in L) is  $\Delta H_1$  and for irreversible adiabatic expansion for the same expansion is  $\Delta H_2$ . Then :  
 (A)  $\Delta H_1 > \Delta H_2$  (B)  $\Delta H_1 < \Delta H_2$  (C)  $\Delta H_1 = \Delta H_2$  (D)  $\Delta H_1 = \Delta U_1$  and  $\Delta H_2 = \Delta U_2$   
 where  $\Delta U_1$  and  $\Delta U_2$  are the changes in magnitudes for internal energy of gas in the two expansions.

**SOLUTION : (A)**

We know that work done in a reversible expansion process is always greater than in an irreversible expansion process.

Using First Law of Thermodynamics :  $q = 0 = \Delta U + (-w)$

Thus, decrease in  $U$  will be larger in reversible adiabatic than irreversible adiabatic expansion and since

$\Delta U = nC_V\Delta T$ , we can conclude that  $\Delta T$  in reversible adiabatic expansion will be greater than in irreversible adiabatic expansion.

Now,  $\Delta H_1 = nC_p\Delta T_1$ , and  $\Delta H_2 = nC_p\Delta T_2 \Rightarrow \Delta H_1 > \Delta H_2$

## SPONTANEITY

## Section - 2

The first law of thermodynamics tells us about the relationship between the heat absorbed and the work performed on or by a system. It puts no restrictions on the direction of heat flow. However, the flow of heat is unidirectional from higher temperature to lower temperature. In fact, all naturally occurring processes whether chemical or physical will tend to proceed spontaneously in one direction only. For example, a gas expanding to fill the available volume, burning carbon in dioxygen giving carbon dioxide.

### Second Law of Thermodynamics :

*It is impossible to construct a machine that is able to convey heat by a process from a colder to a hotter body unless work is done on the machine by some outside agency.*

Second law of Thermodynamics also helps in predicting the spontaneity of a reaction/process.

A process which proceeds of its own accord without any outside help is termed as a spontaneous process. To understand the concept of spontaneity, we first need to understand the most important factor involved which is **Entropy** ( $S$ ) and is explained below :

### 1. Entropy ( $S$ ) :

Entropy is a thermodynamic state quantity which is a measure of **randomness** or **disorder** of the system. More is the randomness in the system, more is the entropy of the system.

(i) Entropy is a state function and depends only on initial and final states of the system.

- (ii) Whenever heat is added to the system, it increases molecular motions causing increased randomness in the system. The distribution of heat also depends on the temperature at which heat is added to the system.

Entropy change of the system for a reversible process is mathematically defined as :

$$dS = \frac{dq_{\text{Rev}}}{T} \quad \text{or} \quad \Delta S = \int \frac{dq_{\text{Rev}}}{T} = \left( \frac{q_{\text{Rev}}}{T} \right) \quad [\text{when the heat is absorbed reversibly at constant } T]$$

If heat is absorbed, then  $\Delta S$  is positive (increase in entropy). If heat is released, then  $\Delta S$  is negative (decrease in entropy). Also, for the same amount of heat absorbed, increase in entropy will be more at lower temperature than at higher temperature.

- (iii) If the temperature of a system increases, entropy increases. If the temperature of a system decreases, entropy decreases.
- (iv) For a fixed volume system, entropy increases if the number of molecules is increased in the system and vice – versa.
- (v) For a system with fixed number of molecules, entropy increases as volume increases and vice – versa.
- (vi) Entropy of a system increases with change in the state of a system as :  $S(s) \longrightarrow S(l) \longrightarrow S(g)$
- (vii) Entropy of more complex molecules is larger than those of simpler molecules as in more complex molecules there are more ways of arranging atoms in 3D (i.e. more randomness).  
e.g.  $S_{\text{propane}} > S_{\text{ethane}}$ .
- (viii) Entropy of compounds with similar molecular masses increases (with increase) in their sizes.  
e.g.  $S_{\text{Ar}} < S_{\text{CO}_2} < S_{\text{C}_3\text{H}_8}$
- (ix) Entropies of ionic solids becomes larger as the attraction amongst the ions become weaker.  
e.g.  $S_{\text{NaF}} > S_{\text{MgO}}$  as in  $\text{MgO}$ , +2 and –2 charges result in greater attraction.
- (x) Harder substances have smaller entropies than softer substances.  
e.g.  $S_{\text{C(diamond)}} < S_{\text{C(graphite)}} < S_{\text{Fe}} < S_{\text{Al}} < S_{\text{Na}}$
- (xi) All spontaneous processes are irreversible processes or vice - versa.
- (xii) When a system is in equilibrium, the entropy is maximum, and the change to entropy,  $\Delta S = 0$ .

For both reversible and irreversible expansion for an ideal gas, under isothermal conditions,  $\Delta U = 0$ , but  $\Delta S_{\text{Total}}$  is not zero for irreversible process. Thus,  $\Delta U$  does not discriminate between reversible and irreversible process, whereas  $\Delta S$  does.



## 2. Criteria for Spontaneity :

First law of thermodynamics is basically the law of conservation of energy. It has no restriction on the way energy can flow. Thus, energy can flow from higher to lower temperature or lower to higher temperature, as per first law of thermodynamics. But, natural processes tend to flow only in one direction (known as direction of spontaneity).

It has been observed that in most of the spontaneous processes/reactions, there is a decrease in energy which seems to be the criteria for spontaneity but it is not the only criteria, Evaporation of water is an endothermic reaction yet it spontaneous.

There are two criterias which decide the direction of spontaneity :

- (a) Decrease in energy                      (b) Increase in entropy

In other words, a chemical reaction or process tends to follow the direction of minimum energy and maximum randomness, i.e. reaction will be more probable to occur if it is exothermic or there is an increase in entropy. A reaction will occur if the value of  $\Delta H$  is negative and the value of  $\Delta S$  is positive. But the endothermic reactions in which  $\Delta H$  is positive, also take place. There are also reactions in which there is decrease in entropy, i.e.,  $\Delta S$  is negative but still they occur. It is, thus, clear that for the spontaneity of a reaction both  $\Delta H$  and  $\Delta S$  should be considered simultaneously.

Thus, for processes which do not involve a heat change, increase in entropy is the only criteria. It should be noted that the criterias for the prediction of direction of spontaneity have been derived through mere observations. No process/reaction has been found to violate these.

### Illustrating the Concept:

Consider the adiabatic expansion of an ideal gas in vacuum. This system is an isolated system (as no exchange of energy and mass between system and surroundings). So, direction of spontaneity is expansion process because expansion will cause an increase in the entropy of the system.

## 3. Finding the direction of spontaneity :

For spontaneity, Second Law of Thermodynamics defines the following statements:

- (i) In an isolated system, direction of increase in entropy of the system is the direction of spontaneity.  
 (ii) In a non-isolated system, direction of increase in total entropy i.e.  $\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$ , is the direction of spontaneity.

$$\Rightarrow \text{For a reaction/process to be spontaneous: } \Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}} > 0$$

To focus on the system for thermodynamic analysis,  $\Delta S_{\text{Surroundings}}$  is defined and eliminated as :

- (a) For a reaction :

$$\begin{aligned} \Delta S_{\text{Surroundings}} &= \frac{q_{\text{Surroundings}}}{T} = \frac{-q_{\text{System}}}{T} \\ \Delta S_{\text{Surroundings}} &= \frac{-\Delta H_{\text{System}}}{T} \quad [\text{Chemical reactions occur at constant T and P}] \\ \Rightarrow \Delta S_{\text{Total}} &= \Delta S_{\text{System}} - \frac{\Delta H_{\text{System}}}{T} \Rightarrow -T\Delta S_{\text{Total}} = \Delta H_{\text{System}} - T\Delta S_{\text{System}} \end{aligned}$$

**(b) For a process:**

$$\Delta S_{\text{Surroundings}} = \frac{q_{\text{Surroundings}}}{T} = \frac{-q_{\text{System}}}{T}$$

$$\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}} \quad [\text{In a short while, we will learn to calculate } \Delta S_{\text{System}}]$$

Also, a new thermodynamic function, **Gibbs energy** 'G' is introduced to check the spontaneity of the reaction directly and is defined as :

$$G = H - TS$$

$$\Rightarrow \Delta G = \Delta H - \Delta(TS) \quad \text{or} \quad dG = dH - TdS - SdT$$

Thus, for a reaction taking place at a certain temperature, we can also define spontaneity of a reaction in terms of change in Gibbs energy as :  $\Delta G_{\text{System}} = -T \Delta S_{\text{Total}} = \Delta H_{\text{System}} - T \Delta S_{\text{System}}$

**(i)** If  $\Delta S_{\text{Total}} > 0 \Rightarrow \Delta G_{\text{System}} < 0$  [Spontaneous]

**(ii)** If  $\Delta S_{\text{Total}} < 0 \Rightarrow \Delta G_{\text{System}} > 0$  [Non-spontaneous]

**(iii)** If  $\Delta S_{\text{Total}} = 0 \Rightarrow \Delta G_{\text{System}} = 0$  [At Equilibrium]

The free energy of a reaction is the chemical analogue of 'potential energy' of mechanical systems. A body moves in the direction in which there is decrease in potential energy. Similarly, in chemical system, the substance moves in a direction in which there is decrease in free energy, i.e.,  $\Delta G$  is negative.

For any system in which a reaction/process taking place,  $\Delta G = 0$  denotes the attainment of equilibrium. In other words, a reaction/process proceeds till its entropy has become maximum i.e. no further change in entropy is possible. A very famous example is the mixing of two ideal gases which happens till the new system has become homogenous (because in that state only it will have maximum entropy).

Calculation of Gibbs energy is very important in finding out the direction of spontaneity and is widely, mostly and mainly used in chemical reactions. We will discuss more on this in the upcoming portions of this chapter.

**Case (i) :** 
$$\left. \begin{array}{l} \Delta S_{\text{System}} > 0 \\ \Delta S_{\text{Surroundings}} > 0 \end{array} \right\} \Rightarrow \Delta S_{\text{Total}} > 0$$

**Case (ii) :** 
$$\left. \begin{array}{l} \Delta S_{\text{System}} < 0 \\ \Delta S_{\text{Surroundings}} > 0 \end{array} \right\} \Rightarrow \Delta S_{\text{Total}} > 0 \text{ or } < 0$$

**Case (iii) :** 
$$\left. \begin{array}{l} \Delta S_{\text{System}} > 0 \\ \Delta S_{\text{Surroundings}} < 0 \end{array} \right\} \Rightarrow \Delta S_{\text{Total}} > 0 \text{ or } < 0$$

**Case (iv) :** 
$$\left. \begin{array}{l} \Delta S_{\text{System}} < 0 \\ \Delta S_{\text{Surroundings}} < 0 \end{array} \right\} \Rightarrow \Delta S_{\text{Total}} < 0$$

Clearly, **Case (i)** is always spontaneous since change in total entropy is always positive i.e. total entropy is increasing. **Case (ii)** and **(iii)** may or may not be spontaneous. **Case (iv)** is always non-spontaneous since change in total entropy is always negative i.e. total entropy is decreasing.

#### 4. Calculating entropy change in phase change :

When a substance changes phase (e.g., solid to liquid), there is a change in entropy associated with it (even though temperature is constant at phase change).

(a) **Melting :** 
$$\Delta S_{\text{melting}} = \frac{\Delta H_{\text{melting}}}{T_{\text{melting}}} = \text{Entropy change due to melting (takes place at constant temperature)}$$

e.g. Entropy change for 1 kg ice at its melting point :

$$\Rightarrow \Delta S_{\text{melting}} = \frac{\left(\frac{1000}{18}\right) \times 6 \times 1000}{273} = 1220.8 \text{ J / K}$$

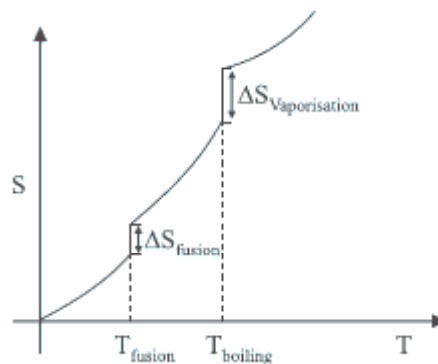
[ Enthalpy of fusion of water = 6 kJ/mole ]

(b) **Vaporisation :** 
$$\Delta S_{\text{vaporisation}} = \frac{\Delta H_{\text{vaporisation}}}{T_{\text{boiling}}}$$

e.g. Entropy change for 1 kg water at its boiling point :

$$\Delta S_{\text{vaporisation}} = \frac{\left(\frac{1000}{18}\right) \times 44 \times 1000}{373} = 6552.8 \text{ J / K}$$

[ Enthalpy of vaporisation of water = 44 kJ/mole ]



(c) **Allotropic Transition :** 
$$\Delta S_{\text{Transition}} = \frac{\Delta H_{\text{Transition}}}{T_{\text{Transition}}}$$

e.g. Transition of 1 mole of Sulphur from Rhombic to Monoclinic :

$$\Delta S_{\text{transition}} = \frac{402}{368.5} = 1.09 \text{ JK}^{-1} \text{ mol}^{-1}$$

[ Enthalpy of transition from rhombic to monoclinic Sulphur = 402 J mole<sup>-1</sup> and T<sub>transition</sub> = 368.5 K ]

### Entropy of a substance :

First of all, we need to know an important law helpful the entropy of a substance i.e. Third Law of Thermodynamics. As per Third Law of Thermodynamic (also known as Nernst heat theorem) :

- (a) All substance have same heat capacities at  $0^\circ \text{K}$ .
- (b) Heat capacity of every substance is zero at  $0 \text{ K}$ .
- (c) Entropy of a perfectly crystalline substance is zero at  $0 \text{ K}$ .

This law provides an absolute reference point for the determination of entropy. The entropy determined relative to this point is the absolute entropy.

### Entropy change of a reaction :

To calculate  $\Delta S_{\text{system}}$  for a reaction at say  $T \text{ (K)}$ , simply balance the reaction and use the following formula:

$$\Delta S_{\text{System}} = \Delta_r S = \sum S_{\text{Products}} - \sum S_{\text{Reactants}} \quad \text{and} \quad \Delta S_{\text{Surroundings}} = \frac{q_{\text{Surr.}}}{T_{\text{Surr.}}} = \frac{-q_{\text{Sys.}}}{T_{\text{Surr.}}} = \frac{-\Delta H_{\text{Sys.}}}{T_{\text{Surr.}}}$$

as chemical reactions occur at constant  $T$  and  $P$ .

At standard conditions :

$$\Delta_r S^\ominus = \sum S_P^\ominus - \sum S_R^\ominus$$

**Note:** Every reactant/product will have a non-zero Entropy for  $T$  above  $0 \text{ K}$ .

### Variation of Spontaneity of a reaction with temperature :

We can have an idea of the spontaneity of reaction with temperature using :

$$\Delta G = \underbrace{\Delta H}_{\substack{\text{Enthalpy} \\ \text{Factor}}} - T \underbrace{\Delta S}_{\substack{\text{Entropy} \\ \text{Factor}}}$$

In general,  $|\Delta H| \gg |T\Delta S|$ . Clearly, Entropy factor increases as  $T$  increase and decreases as  $T$  decreases. For an exothermic reaction proceeding with a decrease in entropy,  $\Delta G$  is in general, negative i.e. spontaneous reaction.

For an endothermic reaction proceeding with an increase in entropy,  $\Delta G$  is in general, positive i.e. non-spontaneous reaction.

Thus, in general, exothermic reactions are spontaneous at room temperature and may tend to become non-spontaneous (if  $\Delta S_{\text{system}} < 0$ ) at higher temperatures. In general, endothermic reactions are non-spontaneous at room temperature and may tend to become spontaneous (if  $\Delta S > 0$ ) at higher temperatures.

Thus, we need to calculate :  $\Delta S_{\text{Total}} = \Delta S_{\text{System}} + \Delta S_{\text{Surroundings}}$  for the reaction/process and if it comes out to be  $> 0$  then that direction will be spontaneous.

- Note:** ➤ The decrease in Gibbs energy is a measure of the maximum useful work that can be obtained from a system. The Gibbs energy is the *maximum* amount of non-expansion work that can be extracted from a system and this maximum can be attained only in a completely reversible process.
- We can have a rough idea of temperature about which there is a spontaneity change for a reaction and is given by :

$$T_{\text{Switch}} = \frac{\Delta H_{\text{System}}^{\ominus}}{\Delta S_{\text{System}}^{\ominus}} \quad \text{Here, we have assumed that } \Delta H_{\text{System}}^{\ominus} \text{ and } \Delta S_{\text{System}}^{\ominus} \text{ doesn't vary with}$$

temperature just to get an idea of  $T_{\text{Switch}}$

$\Delta_r H^{\ominus}$	$\Delta_r S^{\ominus}$	$\Delta_r G^{\ominus}$	Description
–	+	– (at low T)	Reaction spontaneous at all temperature
–	–	– (at low T)	Reaction spontaneous at low temperature
–	–	+ (at high T)	Reaction nonspontaneous at high temperature
+	+	+ (at low T)	Reaction nonspontaneous at low temperature
+	+	– (at high T)	Reaction spontaneous at high temperature
+	–	+ (at all T)	Reaction nonspontaneous at all temperature

**Illustration - 4** Assuming  $\Delta_r H^{\ominus}$  and  $\Delta_r S^{\ominus}$  to be independent of temperature, at what temperature will the reaction given below becomes spontaneous?



**SOLUTION :**

First calculate  $\Delta_r S^{\ominus}$  for the given reaction as follows :

$$\Delta_r S^{\ominus} = \sum S_P^{\ominus} - \sum S_R^{\ominus} = 2S_{\text{NO}}^{\ominus} - S_{\text{N}_2}^{\ominus} - S_{\text{O}_2}^{\ominus} = 2 \times 210.5 - 191.4 - 204.9 = 24.7 \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{Using: } \Delta_r G^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus} = 180.8 - 298 \times 24.7 \times 10^{-3} = 173.4 \text{ kJ mol}^{-1}$$

Clearly, the given endothermic reaction is non-spontaneous at room temperature. So, we need to increase the temperature to make the reaction spontaneous.

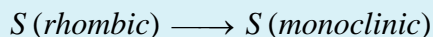
$$\Rightarrow \Delta_r G^{\ominus} = 180.8 - (T \times 24.7 \times 10^{-3}) \text{ kJ mol}^{-1}$$

For spontaneity, put  $\Delta_r G^{\ominus} = 0$  to get :

$$T_{\text{Switch}} = \frac{\Delta_r H_{\text{System}}^{\ominus}}{\Delta_r S_{\text{System}}^{\ominus}} \Rightarrow T_{\text{switch}} = \frac{180.8 \times 10^3}{24.7} \approx 7320 \text{ K}$$

The reaction becomes spontaneous above a temperature of 7320K.

**Illustration - 5** Sulphur exists in more than one solid form. The stable form at room temperature is rhombic sulphur. But above room temperature the following reaction occurs :



If  $\Delta_r H = 276.144 \text{ J}$  at 298 K and 1 atm and  $\Delta_r G = 75.312 \text{ J}$

- (a) Calculate  $\Delta_r S$  at 298 K
- (b) Assume that  $\Delta_r H$  and  $\Delta_r S$  do not vary significantly with temperature, calculate  $T_{\text{eq}}$ , the temperature at which rhombic and monoclinic sulphur exist in equilibrium with each other.

**SOLUTION :**

- (a) Since  $\Delta_r G = \Delta_r H - T\Delta_r S$

$$\Rightarrow \Delta_r S = \frac{\Delta_r H - \Delta_r G}{T} = \frac{276.144 - 75.312}{298} = 0.674 \text{ J K}^{-1}$$

- (b) Under equilibrium condition  $\Delta_r G = 0$

$$\Rightarrow \Delta_r H - T_{\text{eq}} \Delta_r S = 0 \Rightarrow T_{\text{eq}} = \frac{\Delta_r H}{\Delta_r S} = \frac{276.144}{0.674} = 409.7 \text{ K}$$

### Free energy change of a reaction :

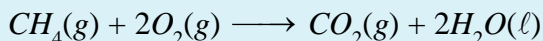
$\Delta_r G$  for a reaction can be calculated using following two methods :

- (i) Using :  $\Delta_r G = \Delta_r H - T\Delta_r S$
- (ii) Using :  $\Delta_r G = \sum G_{\text{Products}} - \sum G_{\text{Reactants}}$

Take note of the followings while calculating Gibbs energy change for a reaction :

- (a) Chemical reaction in which a compound in its standard state is formed from its elements in their standard states, the Gibbs energy change is the **Standard Gibbs energy of formation**,  $\Delta_f G^{\ominus}$ .
- (b)  $\Delta_f G^{\ominus} = 0$  for an element in its standard state.
- (c)  $\Delta_f G^{\ominus} = \sum G_{\text{products}}^{\ominus} - \sum G_{\text{reactants}}^{\ominus} = \Delta_r H^{\ominus} - T\Delta_r S^{\ominus}$
- (d)  $\Delta_r G$  is an extensive property.
- (e)  $\Delta_r G$  changes sign when a process is reversed. [ It can be treated in a similar manner as with  $\Delta_r H$  ]

**Illustration - 6** Compute the Gibbs energy change of the reaction at 27°C for the combustion of methane.



$$\Delta_f H^\ominus \text{ (in kJ mol}^{-1}\text{)} \quad -74.8 \quad \text{—} \quad -393.5 \quad -285.8$$

$$S_m^\ominus \text{ (in J K}^{-1} \text{ mol}^{-1}\text{)} \quad 186 \quad 205 \quad 214 \quad 70$$

**SOLUTION :**

$$\Delta_r H^\ominus = \Delta_f H^\ominus_{(\text{CO}_2)} + 2\Delta_f H^\ominus_{(\text{H}_2\text{O})} - \Delta_f H^\ominus_{(\text{CH}_4)} = -393.5 + 2 \times (-285.8) - (-74.8) = -890 \text{ kJ mol}^{-1}$$

$$\Delta_r S^\ominus = S^\ominus_{(\text{CO}_2)} + 2S^\ominus_{(\text{H}_2\text{O})} - S^\ominus_{(\text{CH}_4)} - 2S^\ominus_{(\text{O}_2)} = 214 + 2 \times 70 - 186 - 2 \times 205 = -242 \text{ J/K/mol}$$

$$\Delta_r G = \Delta_r H^\ominus - T\Delta_r S^\ominus = -890 - 300 \times (-242 \times 10^{-3}) = -890 + 72.6 = -817.4 \text{ kJ mol}^{-1}$$

**Illustration - 7** Show that the reaction  $\text{CO}(\text{g}) + (1/2)\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g})$  at 300 K, is spontaneous and exothermic, when the standard entropy change is  $-0.094 \text{ kJ mol}^{-1} \text{ K}^{-1}$ . The standard Gibbs free energies of formation for  $\text{CO}_2$  and  $\text{CO}$  are  $-394.4$  and  $-137.2 \text{ kJ mol}^{-1}$ , respectively.

**SOLUTION :**

$$\text{For the given reaction, we have : } \text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) \quad \Delta_r S^\ominus = -0.094 \text{ kJ K}^{-1} \text{ mol}^{-1}$$

The free-energy change of the reaction is :

$$\begin{aligned} \Delta_r G^\ominus &= \Delta_f G^\ominus_{\text{CO}_2} - \Delta_f G^\ominus_{\text{CO}} - \frac{1}{2} \Delta_f G^\ominus_{\text{O}_2} \\ &= (-394.4 + 137.2) \text{ kJ mol}^{-1} = -257.2 \text{ kJ mol}^{-1} \quad [\because \Delta_f G^\ominus_{\text{O}_2} = 0] \end{aligned}$$

Since  $\Delta_r G^\ominus$  is negative, the reaction is spontaneous. The enthalpy change of the reaction is:

$$= 8.314 \text{ J mol}^{-1} \text{ K}^{-1} = [-257.2 + (300)(-0.094)] \text{ kJ mol}^{-1} = -285.4 \text{ kJ mol}^{-1}$$

Since  $\Delta_r H^\ominus$  is negative, the reaction is exothermic.

### Gibbs energy and Equilibrium Constant:

We can relate  $\Delta_r G$  for a reaction under any set of conditions to its value for standard conditions, that is, to  $\Delta_r G^\ominus$  by:

$$\Delta_r G = \Delta_r G^\ominus + 2.303 RT \log_{10} Q \text{ where } Q \text{ is reaction quotient.}$$

If a system is at equilibrium,  $\Delta_r G^\ominus = 0$ . Thus from the above equation :

$$\Delta_r G^\ominus = -2.303 RT \log_{10} K_{eq} \quad \text{where } K_{eq} \text{ is thermodynamic equilibrium constant.}$$

Magnitude of  $\Delta_r G^\ominus$  determines the value of  $K_{eq}$ . Consider three cases:

- (i)  $K_{eq} \gg 1$  : Reaction proceeds mainly in forward direction and is almost complete  
( $X_{\text{Products}} \approx 1$ ;  $X_{\text{Reactants}} \approx 0$ )
- (ii)  $K_{eq} \ll 1$  : Reaction does not “wish” to proceed in forward direction ( $X_{\text{Products}} \approx 0$ ;  $X_{\text{Reactants}} \approx 1$ )
- (iii)  $K_{eq} \approx 1$  : Both products and reactants exist in appreciable amounts, at equilibrium.

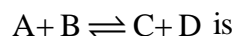
We have seen how a knowledge of the sign and magnitude of the free energy change of a chemical reaction allows:

1. Prediction of the spontaneity of the chemical reaction.
2. Prediction of the useful work that could be extracted from it.

So far we have considered free energy changes in irreversible reactions. Let us now examine the free energy changes in reversible reactions.

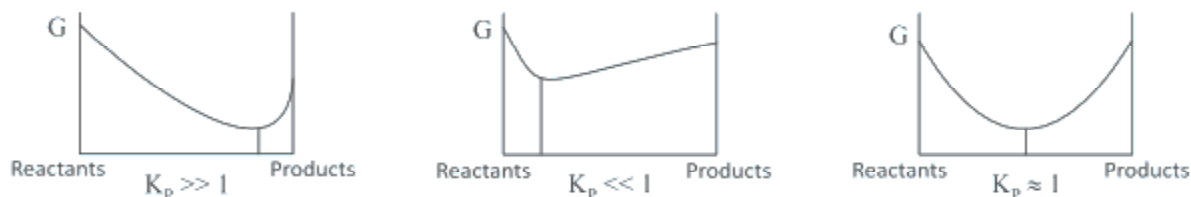
‘Reversible’ under strict thermodynamic sense is a special way of carrying out a process such that system is all times in perfect equilibrium with its surroundings. When applied to a chemical reaction the term ‘reversible’ indicates that a given reaction can proceed in either direction simultaneously, so that a **dynamic** equilibrium is set up. This means that the reactions in both the directions should proceed with a decrease in free energy, which seems impossible. It is possible only if at equilibrium the free energy of the system is minimum. If it is not, the system would spontaneously change to configuration of lower free energy.

So, the criterion for equilibrium



$$\Delta_r G = 0$$

### Variation of Gibbs Energy and Equilibrium Constant :



**Note :**

- Equilibrium is the point of minimum in the above diagrams.
- If we move away from the point of minimum, there will be an increase in Gibbs energy which is non-spontaneous.



**Equilibrium constant vs. Temperature :**

For a reaction :  $\Delta_r G = \Delta_r H - T \Delta_r S$

At standard conditions :  $\Delta_r G^\ominus = \Delta_r H^\ominus + T \Delta_r S^\ominus$

When the reaction reaches equilibrium at temperature T, we have :  $\Delta_r G^\ominus = -RT \ln K_{eq}$

Thus, we have at temperature  $T_1$  :  $-RT_1 \ln (K_{eq})_1 = \Delta_r H^\ominus - T_1 \Delta_r S^\ominus$

and at temperature  $T_2$  :  $-RT_2 \ln (K_{eq})_2 = \Delta_r H^\ominus - T_2 \Delta_r S^\ominus$

Solve to get :  $\ln \frac{(K_{eq})_2}{(K_{eq})_1} = \frac{\Delta_r H^\ominus}{R} - \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

**Illustration - 8** A certain gas is expanded from (1L, 10 atm) to (4 L, 5 atm) against a constant external pressure of 1 atm. If the initial temperature of gas is 300 K and heat capacity for the process is 50 J / °C, the enthalpy change during the process : ( Use : 1 L atm  $\approx$  100 J )

- (A) 15 kJ      (B) 15.7 kJ      (C) 14.3 kJ      (D) 14.7 kJ

**SOLUTION : (B)**

Use :  $\Delta H = \Delta U + \Delta(PV) = \Delta U + (P_2 V_2 - P_1 V_1)$

Calculate  $\Delta U$  as follows :

(i) Use :  $\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \Rightarrow \frac{10 \times 1}{300} = \frac{5 \times 4}{T_2} \Rightarrow T_2 = 600 \text{ K}$

(ii)  $q = C \Delta T = 50 \times (600 - 300) = 15 \text{ kJ}$

(iii)  $-w = P_{\text{Ext}} \Delta V = (4 - 1) = 3 \text{ L atm} \equiv 0.3 \text{ kJ}$

(iv)  $q = \Delta U + (-w) \Rightarrow 15 = \Delta U + 0.3 \Rightarrow \Delta U = 14.7 \text{ kJ}$

$\Rightarrow \Delta H = 14.7 + (5 \times 4 - 10 \times 1) \times 100 \times 10^{-3} = 15.7 \text{ kJ}$

**Illustration - 9** For the reaction :  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ Calculate  $\Delta_r G$  of the system in a mixture of 5 mol of  $N_2O_4(g)$  and 5 mol of  $NO_2(g)$  at 298 K at a total pressure of 20 atm. Use the following data in  $\text{kJ mol}^{-1}$  :  $\Delta_f G^\ominus(NO_2, g) = 50$  ;  $\Delta_f G^\ominus(N_2O_4, g) = 100$ **SOLUTION :**We need to calculate  $\Delta_r G$ . Use :  $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$ So, first calculate  $\Delta_r G^\ominus$  using :  $\Delta_r G^\ominus = \sum G^\ominus_{\text{Products}} - \sum G^\ominus_{\text{Reactants}}$ 

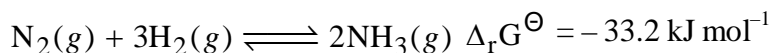
$$= \sum (\Delta_f G^\ominus)_{\text{Products}} - \sum (\Delta_f G^\ominus)_{\text{Reactants}}$$

$$[\because \text{At standard conditions : } G^\ominus_{\text{compound}} = \Delta_f G^\ominus_{\text{compound}}]$$

$$= 2 \times \Delta_f G^\ominus(NO_2, g) - \Delta_f G^\ominus(N_2O_4, g) = 2 \times 50 - 100 = 0$$

$$\text{and } \Delta_r G = \Delta_r G^\ominus + RT \ln Q = 0 + 8.314 \times 298 \ln \left( \frac{10^2}{10} \right) = 5.70 \text{ kJ mol}^{-1}$$

$$\left[ \because Q = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{\left( \frac{5}{10} \times 20 \right)^2}{\left( \frac{5}{10} \times 20 \right)} \right]$$

**Note:**  $\Delta_f G^\ominus$  of an element in its standard state is zero.**Illustration - 10** Calculate  $\Delta_r G$  at 298 K for the following reaction if the reaction mixture consists of 1 atm of  $N_2$ , 3 atm of  $H_2$  and 1 atm of  $NH_3$ .  $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ;  $\Delta_r G^\ominus = -33.32 \text{ kJ}$ **SOLUTION :**Using :  $\Delta_r G = \Delta_r G^\ominus + RT \ln Q$ 

$$\text{where } Q = \frac{p_{NH_3}^2}{p_{N_2} p_{H_2}^3} = \frac{1^2}{1 \times 3^3} = \frac{1}{27} ; T = 298 \text{ K} ; R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$\Rightarrow \Delta_r G = -33.2 + (8.314 \times 10^{-3}) \times 298 \times 2.303 \log_{10} \frac{1}{27} = -33.2 - 8.16 = -41.36 \text{ kJ mol}^{-1}$$

**Illustration - 11** The temperature dependence of equilibrium constant of a reaction is given by :

$$\ln K_{eq} = 4.8 - \frac{2059}{T} \text{ Find } \Delta_r G^\ominus, \Delta_r H^\ominus, \Delta_r S^\ominus.$$

**SOLUTION :**

Compare  $\ln K_{eq} = 4.8 - \frac{2059}{T}$  with  $\ln K_{eq} = \frac{\Delta_r S^\ominus}{R} - \frac{\Delta_r H^\ominus}{RT}$

We have :  $\frac{\Delta_r S^\ominus}{R} = 4.8 \Rightarrow \Delta_r S^\ominus = 4.8 \times 8.314 \text{ J/K} = 39.9 \text{ J/K}$

$\frac{\Delta_r H^\ominus}{R} = 2059 \Rightarrow \Delta_r H^\ominus = 2059 \times 8.314 \text{ J/K} = 17.12 \text{ kJ /K}$

and  $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus = 17.12 - 298 \times 39.9 \times 10^{-3} = 5.31 \text{ kJ/K}$

**Illustration - 12**  $K_a$  for acetic acid at  $27^\circ\text{C}$  is  $2.0 \times 10^{-5}$  and at  $77^\circ\text{C}$ ,  $K_a$  is  $2.5 \times 10^{-5}$ . What are  $\Delta H^\ominus$  and  $\Delta S^\ominus$  for the ionization of acetic acid ?

**SOLUTION :**

Using :  $\ell n \frac{(K_{eq})_2}{(K_{eq})_1} = \frac{\Delta_r H^\ominus}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$

$\Rightarrow \ell n \left( \frac{2.5 \times 10^{-5}}{2.0 \times 10^{-5}} \right) = \frac{\Delta_r H^\ominus}{8.314} \times \left( \frac{1}{300} - \frac{1}{350} \right)$

$\Rightarrow \Delta_r H^\ominus = 3.89 \text{ kJ mol}^{-1}$

Also,  $\Delta_r G^\ominus = -RT \ell n K_{eq}$

$\Rightarrow \Delta_r G^\ominus = -8.314 \times 298 \times \ell n (2.0 \times 10^{-5}) = 26.81 \text{ kJ mole}^{-1}$

[Taking  $(K_{eq})_{25^\circ\text{C}} \approx (K_{eq})_{27^\circ\text{C}}$ ]

Using :  $\Delta_r G^\ominus = \Delta_r H^\ominus - T\Delta_r S^\ominus$

$\Rightarrow 26.81 = 3.89 - (298 \times 10^{-3}) \times \Delta_r S^\ominus \Rightarrow \Delta_r S^\ominus = 76.9 \text{ J mole}^{-1} \text{ K}^{-1}$

**NOW ATTEMPT IN-CHAPTER EXERCISE**

**THEN ATTEMPT OBJECTIVE WORKSHEET TO COMPLETE THIS EBOOK**

## My Chapter Notes



Vidyamandir Classes

