9

SPONTANEITY OF CHEMICAL REACTIONS

9.1 INTRODUCTION

We have studied about the first law of thermodynamics in lesson 8. According to this law the processes occur in such a way that the total energy of the universe remains constant. But it does not tell whether a specified change or a process including a chemical reaction can occur spontaneously i.e., whether it is feasible or not. For example, the first law does not deny the possibility that a metal bar having a uniform temperature can spontaneously become warmer at one end and cooler at the other. But it is known from experience that such a change does not occur without expenditure of energy from an external source.

The first law also states that energy from one form can be converted into an equivalent amount of energy of another form. But it does not tell that heat energy cannot be completely converted into an equivalent amount of work without producing some changes eleswhere. In this lesson we shall learn to predict whether a given process or a chemical reaction can occur spontaneously or not.

9.2 OBJECTIVES

After reading this lesson you will be able to

- define entropy
- recognise that entropy change in a system is given by

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

- state that for a spontaneous process $\Delta S_{univ} > 0$ and at equilibrium $\Delta S = 0$
- state the relationship between G, H and S
- derive the relation $\Delta G_{syst} = -T\,\Delta S_{univ}$
- recognise that

  $\Delta G < 0$ for a spontaneous process

  $\Delta G = 0$ at equilibrium

  $\Delta G > 0$ for a non spontaneous process. 9.1

- define standard free energy of formation of a subtance
- calculate the standard free energy change of a reaction
- relate the standard free energy change with the equilibrium constant
- solve numerical problems

9.3 ENTROPY

In Fig 9.1 the bulb A contains 1mol. of an ideal gas 'A' at a pressure of 1.00 atm and the bulb B contains 1mol. of another ideal gas 'B' at 1.00 atm. The two bulbs are joined together through a valve.

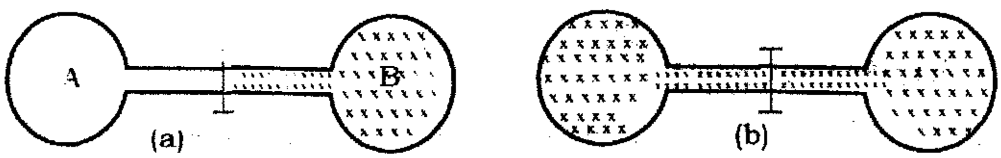

Fig 9.1

When the valve between the two bulbs is opened [Fig 9.1 (b)], the two gases mix spontaneously. The mixing of gases continues until the partial pressure of each gas becomes equal to 0.5 atm in each bulb i.e., the equilbrium is attained. We know from experience that the process cannot be reversed spontaneously – the gases do not unmix. What is the driving force behind this process ?

We know that the internal energy (E) and enthalpy (H) of an ideal gas depend only upon the temperature of the gas and not upon its pressure or volume. Since there are no intermolecular forces in ideal gases. $\Delta E = \Delta H = 0$ when ideal gases mix at constant temperature. Thus energy change is not the driving force behind the spontaneous mixing of ideal gases. The driving force is simply the tendency of the molecules of the two gases to achieve the maximum state of mixing, i.e., disorder. The thermodynamic property related to the disorder of the system is called *entropy*. It is denoted by the symbol S

The entropy is the measure of disorder or randomness in a system. The greater the disorder in a system, the greater is the entropy of the system.

For a given substance

(i) the crystalline state is the most ordered state. hence its entropy is the lowest.

(ii) the gaseous state is the most disordered state, hence its entropy is the maximum, and

(iii) the disorder in the liquid state is intermediate between the solid and the gaseous state.

When *a system* changes from one state to another, the change of entropy ΔS is given by

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

Where $q_{rev.}$ is the heat supplied reversibly at temperature T.

9.4 CRITERIA FOR SPONTANEOUS CHANGE : THE SECOND LAW OF THERMODYNAMICS

So far we have studied about internal energy, enthalpy and entropy Can we define the spontaneity of a process in terms of these changes ? You will see that we still have not found a single criteria that alone will tell us whether a process is spontaneous. For example :

(i) We know that most of the reactions which occur spontaneously are exothermic. But water kept in a container at room temperature evaporates spontaneously. It is an endothermic process. Thus enthalpy change cannot be used as a criteria for spontaneous change.

(ii) Can we use the increase of entropy as a criteria for the spontaneous change ? Then how do we explain the spontaneous freezing of water at $-10°C$? We know that crystalline is more ordered then the liquid water and therefore the entropy must decrease. The answer to this question is that we must consider simultaneously three entropy changes :

(a) the entropy change of the system itself

(b) the entropy change of the surroundings, and

(c) the entropy change of the universe.

$$\Delta S_{Total} = \Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} \quad 9.2$$

The equation is one of the many forms of the second law of thermodynamics.

According to the second law of thermodynamics **all spontaneous or natural processes produce an increase in entropy of the universe.**

Thus for a spontaneous process

$$\Delta S_{Total} = \Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0 \quad 9.3$$

When a system is at equilibrium, the entropy is at maximum i.e., the change in entropy is zero,

$$\Delta S = 0 \text{ (at equilibrium)} \quad 9.4$$

9.5 ENTROPY CHANGE IN PHASE TRANSITIONS

When a solid melts, there is an equlibrium between the solid and the liquid at the freezing point.

$$H_2O(s, 273k) \rightleftharpoons H_2O\ (l, 273k)$$

The heat involved at the freezing point is called heat of fusion (ΔH_{fus}). Therefor the entropy of fusion (ΔS_{fus}) is given by

$$\Delta S_{fus} = \frac{\Delta H_{fus}}{T} = \quad (\because q_{rev} \text{ at const. } p = \Delta H_{fus})$$

Similarly for the equlibrium

$$H_2O(l, 373\ k) \rightleftharpoons H_2O(g, 373\ k)$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

Example 9.1 : The enthalpy change for the transition of liquid water to steam at 373 K is 40.8 kJ mol^{-1}. Calculate the entropy change for the process.

Solution : $H_2O(l, 373K) \rightleftharpoons H_2O(g, 373k)$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T}$$

ΔH_{vap} = 40.8 kJ mol^{-1} = 40.8×10^3 J mol^{-1}

T = 373 K

$$\Delta S_{vap} = \frac{40.8 \times 10^3\ J\ mol^{-1}}{373\ K} = 109\ J\ mol^{-1}\ K^{-1}$$

INTEXT QUESTIONS 9.1

1 The enthalpy change for the transition of ice to liquid water at 273 K is 6.02 k mol^{-1}. Calculate the entropy change for the process.

....

2. Arrange the following systems in the order of increasing randomness,

(i) 1 mol of gas A

(ii) 1 mol of solid A

(iii) 1 mol of liquid A

....

3. Indicate whether you would expect the entropy of the system to increase or decrease

(a) $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$

(b) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

(c) $O_2(g) \rightarrow 2O(g)$

....

9.6 GIBBS FREE ENERGY AND SPONTANEITY

We can use the expressior

$$\Delta S_{Total} = \Delta S_{univ} = \Delta S_{system} + \Delta S_{surroundings} > 0 \qquad 9.5$$

as our basic criterio:. ·or a spontaneous change. But it is very difficult to apply because we have to evaluate the total entropy change. This is a tedious process as we cannot figure out all the interactions between the system and the surroundings. Thus for a system which is not isolated from its surroundings.

$$\Delta S_{Total} = \Delta S_{system} + \Delta S_{surroundings} \qquad 9.6$$

At constant temperature and pressure if ΔH is the heat given out by the system to the surroundings, we write

$$\Delta S_{surroundings} = \frac{-q_p}{T} = \frac{\Delta H_{system}}{T} \qquad 9.7$$

(Sin.·e q_p = ΔH at constant pres·:·re)

Substituting Eq. 9.7 in Eq. 9.6, we get

$$\Delta S_{Tota} = \Delta S_{system} - \frac{\Delta H_{system}}{T}$$

$$T\Delta S_{Total} = T\Delta S_{system} - \Delta H_{system}$$

or $$-T\Delta S_{Total} = \Delta H_{system} - T\Delta S_{system} \qquad 9.8$$

The Gibbs free energy, G, is defined by the equation

$$G = H - TS \qquad 9.9$$

For a change in free energy, we write

$$\Delta G = \Delta H - T\Delta S - S\Delta T$$

For a ...ange at consta.:t temperature, we write

$$\Delta G = \Delta H - T\Delta S \qquad 9.10$$

Since *H*, *T* and *S* are state functions, it follows that *G* is also a state function.

Comparing equations 9.8 and 9.10, we find that

$$\Delta G = -T\Delta S_{Total} \qquad 9.11$$

We have seen that if ΔS_{Total} is positive, the change will be spontaneous. Equation 9.11 can be used to predict the spontaneity of a change based on the value of ΔG.

The use of Gibbs free energy has the advantage that it refers to system only. Thus for a process occuring at constant temperature and pressure, if

$\Delta G < 0$ (negative), the process is spontaneous

$\Delta G > 0$ (positive), the process is nonspontaneous

$\Delta G = 0$ (zero), the process is at equilibrium

In deciding the spontaneity of a chemical reaction, the equation

$\Delta G = \Delta H - T\Delta S$ takes into account two factors (i) the energy factor and (ii) the entropy factor. Based on the signs of ΔH and ΔS there are four possibilities for ΔG. These possibilities are outlined in the table 9.1

Table 9.1 Criterion for spontaneous change : $\Delta G = \Delta H - T\Delta S$

S.No.	ΔH	ΔS	ΔG	Result
1.	–	+	–	Spontaneous at all temperatures.
2.	–	–	{ –	Spontaneous at low temperatures.
			+	Nonspontaneous at high temperatures.
3.	+	+	{ +	Nonspontaneous at low temperatures.
			–	Spontaneous at high temperatures.
4.	+	–	+	Nonspontaneous at all temperatures.

Example 9.2 : For the reaction

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

Calculate ΔG at 700K when enthalpy and entropy changes (ΔH and ΔS) are respectively – 113.0 kJ mol^{-1} and – 145 kJ mol^{-1}.

Solution : Given that

$$\Delta H = -113.0 \text{ kJ mol}^{-1}$$

$$\Delta S = -145 \text{ Jk}^{-1} \text{ mol}^{-1} = -145 \times 10^{3} \text{ kJ K}^{-1} \text{ mol}^{-1}$$

$$T = 700 \text{ K}$$

Substituting the values in

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G = (-113.0 \text{ kJ mol}^{-1}) - (700\text{K})(-145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})$$

$$= (-113.0 \text{ kJ mol}^{-1}) + (101.5 \text{ kJ mol}^{-1})$$

$$= -11.5 \text{ kJ mol}^{-1}$$

INTEXT QUESTIONS 9.2

1. Determine whether the following reaction

$$CCl_4(l) + H_2(g) \rightarrow HCl(g) + CHCl_3(l)$$

is spontane s at 25° C. At 25° C $\Delta H = 91.35$ kJ and 41.5Jl fo his reaction.

....

2. Which of the following conditions would predict a process that is always spontaneous

(i) $\Delta H > 0$, $\Delta S > 0$

....

(ii) $\Delta H > 0$, ΔS 0

....

(iii) $\Delta H < 0$, $\Delta S > 0$

....

(iv) $\Delta H < 0$, $\Delta S < 0$

....

9.7 STANDARD FREE ENERGY CHANGE (ΔG^o) AND EQUILIBRIUM CONSTANT (K)

The standard free energy change is defined as the free energy change for the process in which the reactants in their standard states are converted in to the products in the standard states. It is denoted by the symbol ΔG^o.

The value o: ΔG^o can be found from the standard free energy of formation of substances.

The standard free energy of formation of a compound is defined the change in free energy when 1 mole of the compound is formed from its constituent elements in their standard states. Like the standard enthalpy of formation of an element, the standard free energy of formation of an element in its standard state is taken as zero.

Thus for a reaction

$$aA + bB + ---- \rightarrow lL + mM + ----$$

$$\Delta G^o = (l\Delta G^o_L + m\Delta G^o_M + ----) - (a\Delta G^o_A + b\Delta G^o_B + ----)$$

$$\Delta G^o = \Sigma\Delta G^o\ (\text{Products}) - \Sigma\Delta G^o\ (\text{Reactants})$$

The standard free energy change (ΔG°) is related to the equilibrium constant (K) of the reaction by the expression

$$\Delta G^\circ = -RT\ln K = -2.303\ RT\log K$$

Example 9.3 : The equilbrium constant of the reaction

$$P(s) + \tfrac{3}{2}\ Cl_2(g) \rightleftharpoons PCl_3(g)$$

is 2.00×10^{24} at 500 K. Calculate the value of ΔG°.

Solution : Given that

$K = 2.00 \times 10^{24}$

$T = 500K$

$\Delta G^\circ = -2.303\ RT\log K$

$= -2.303 \times (8.314\ J\ mol^{-1}K^{-1})\ (500\ K)\log 2.0 \times 10^{24}$

$= -2.303 \times (8.314\ J\ mol^{-1}K^{-1})\ (500\ K) \times 24.30$

$= -232.6\ kJ\ mol^{-1}$

Example 9.4 : Calculate the standard free energy change for the reaction

$$CH_4(g) + O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

at 25° C. The standard free energies of formation of CH_4, CO_2 and H_2O at 25° C are -50.8 kJ mol^{-1}, -394.4 kJ mol^{-1}. and -237.2 kJ mol^{-1} respectively.

Solution : $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta G^\circ = \Delta G_f^\circ(CO_2) + 2\Delta G_f^\circ(H_2O) - \Delta G_f^\circ(CH_4) - 2\Delta G_f^\circ(O_2)$

$= -394.4 + 2 \times (-237.2) - (-50.8) - 2 \times 0$

$= -394.4 - 474.4 + 50.8$

$= -818\ kJ\ mol^{-1}$

INTEXT QUESTIONS 9.3

1. What is the relationship between the standard free energy change and the equilibrium constant of the reaction ?

....

2. The standard free energy change for the reaction

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(l)$$

at 25°C is —24.8 kJ mol^{-1}. What is the value of the equilibrium constant at 25° C ?

....

9.8 WHAT YOU HAVE LEARNT

- All spontaneous processes lead to an increase in disorder or ran domness.
- The thermodynamic function related to disorder in a system is called entropy, S.
- For a spontaneous change the total entropy change of the system and the surroundings must increase.
- Gibbs free energy is defined as $G = H - TS$
- At a constant temperature, the change in Gibbs free energy is related to enthalpy and entropy changes by the expression

  $\Delta G = \Delta H - T\Delta S$
- For a spontaneous change, there must be a decrease in free energy, i.e., $\Delta G < 0$.

  At equilibrium $\Delta G = 0$
- The standard free energy change (ΔG°) of the reaction is given by

  $\Delta G^\circ = \Sigma \Delta G^\circ_f$ (Products) — $\Sigma \Delta G^\circ_f$ (reactants)
- The standard free energy change is related to the equilibrium constant of the reaction by the expression

  $\Delta G^\circ = -2.303\ RT \log K$

9.9 TERMINAL EXERCISE

1. What do you call the measure of disorder or randomness in a system ?

   ....

2. Predict the sign of ΔS for each of the following processes.

   (i) $H_2(g) \rightarrow 2H(g)$

   ....

   (ii) $O_2(g, 5\ atm) \rightarrow O_2\ (g, 1\ atm)$

   ....

3. Define entropy .

   ....

4. Explain why entropy is not a good criteria for determining the spontaneity of a process ?

   ....

5. What is the relationship between the enthalpy and the entropy change for a system at equilibrium ?

   ....

6. For the rection

$O_3(g) + O(g) \rightarrow 2O_2(g)$

ΔH = — 391.9 kJ and ΔS = 10.3 J K^{-1} at 25° C. Calculate ΔG at this temperature and state whether the reaction is spontaneous or not.

....

7. Characterize ΔG for

(a) a spontaneous process

....

(b) a nonspontaneous process

....

(c) a process at equilibrium

....

8. Calculate ΔG° at 25° C for the reaction

$2NO_2(g) \rightarrow N_2O_4(g)$

Given ΔH° = – 57.20 kJ and ΔS° = – 175.8 J K^{-1}

Is this reaction spontaneous ?

....

9. The standard free energies of formation at 25° C are – 202.85 kJ mol^{-1} for $NH_4Cl(s)$, – 16.45 kJ mol^{-1} for $NH_3(g)$, and – 95.3 kJ mol^{-1} for HCl(g).

(a) What is ΔG° for the reaction

$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl\ (g)$

....

(b) Calculate the equilibrium constant for this decomposition.

....

10. For the following reaction

$CCl_4(l) + H_2\ (g) \rightleftharpoons HCl\ (g) + CHCl_3\ (l)$

Δ G° = – 103.7 kJ at 25°C. Calculate the equilibrium constant for this reaction.

....

....

CHECK YOUR ANSWERS

INTEXT QUESTIONS 9.1

1. $$\Delta S_{fus} = \frac{\Delta H_{fus}}{T} = \frac{6.02\ \text{kJ mol}^{-1}}{273\ \text{K}} = \frac{6.02 \times 10^3\ \text{J mol}^{-1}}{273\ \text{K}}$$

$$= 22\ 0\ \text{J mol}^{-1}\ \text{K}^{-1}$$

2. 1 mol of solid A, 1 mol of liquid A, 1 mol of gas A

3. (a) Decrease (b) Decrease (c) Increase

INTEXT QUESTIONS 9.2

1. $\Delta G = -103.7$ kJ. The negative value of ΔG indicates that the reaction is spontaneous.

2. (iii)

INTEXT QUESTIONS 9.3

1. $\Delta G^\circ = -2.303\ RT \log K$

2. 2.2×10^4

TERMINAL EXERCISE

1. Entropy

2. (i) Positive (ii) Positive

3. The measure of disorder or randomness in a system.

4. This is because we have to calculate the total entropy change of the system and the surroundings. Such a criteria is inconvenient.

5. $\Delta H = T\Delta S$

6. $\Delta G = \Delta H - T\Delta S$

   $\Delta H = -391.9$ kJ $= -391.9 \times 10^3$ J

   $\Delta S = 10.3$ J K^{-1}

   $T = 25^\circ$ C $= (25 + 237)$ K $= 298$ K

   Substituting the value, we get

   $\Delta G = -391.9 \times 10^3$ J $- (10.3$ J K$^{-1}) \times (298$ K$)$

   $= -395.0$ kJ

   Thus the reaction is spontaneous

7. (a) $\Delta G < 0$ (b) $\Delta G > 0$ (c) $\Delta G = 0$