

MODULE - 4

Chemical Energetics



Notes



10

SPONTANEITY OF CHEMICAL REACTIONS

We have studied about the first law of thermodynamics in lesson 09. 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 us 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 can be converted from one form 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 elsewhere. In this lesson you shall learn to predict whether a given process or a chemical reaction can occur spontaneously or not.



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 entropy criterion for a spontaneous process $\Delta S_{universe} > 0$ and at equilibrium $\Delta S_{universe} = 0$
- state the second law of thermodynamics.



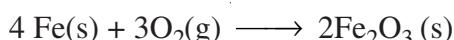
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- state the third law of thermodynamics;
- state the relationship between G, H and S ;
- derive the relation $\Delta G_{\text{system}} = T \Delta S_{\text{system}}$;
- state Gibbs energy criterion for spontaneous process
 $\Delta G < 0$ for a spontaneous process
 $\Delta G = 0$ at equilibrium
 $\Delta G > 0$ for a non-spontaneous process
- define standard Gibbs energy of formation of a substance;
- relate the standard Gibbs energy change with the equilibrium constant and
- solve numerical problems.

10.1 SPONTANEOUS AND NON-SPONTANEOUS PROCESSES

We know that hot water kept in a container cools down by losing heat to the surroundings. On the other hand, water at room temperature cannot become hot by gaining heat from the surroundings. It can be made hot by heating it over a gas burner. The cooling down of hot water is an example of a spontaneous process. Heating of water (at room temperature) is an example of a non-spontaneous process because an outside agency (gas burner) has been used.

A spontaneous process is a process that occurs in a system by itself; once started, no action from outside the system (outside agency) is necessary to make the process continue. A **non-spontaneous process** will not take place unless some external action is continuously applied. Let us consider another example, we know that when iron objects are exposed to moist atmosphere, rusting of iron takes place. Although the rusting of iron is a slow process but it always takes place in the same direction. We say that the rusting of iron is a spontaneous process. During rusting of iron, iron is oxidised to iron (III) oxide.



The reverse of the above reaction is also possible but it is non-spontaneous. An external agency has to be used to reduce iron (III) oxide to iron.

From our discussion it can be concluded that

- if a process is spontaneous, the reverse process is non-spontaneous.
- all the spontaneous processes and most of the non-spontaneous processes are possible.
- spontaneous processes occur naturally whereas non-spontaneous processes require the help of an outside agency to occur.

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10.2 ENTROPY

In fig 10.1(a) the bulb 'I' contains 1 mol of an ideal gas 'A' at a pressure of 1 bar and the bulb II contains 1 mol of another ideal gas 'B' at 1 bar. The two bulbs are joined together through a valve.

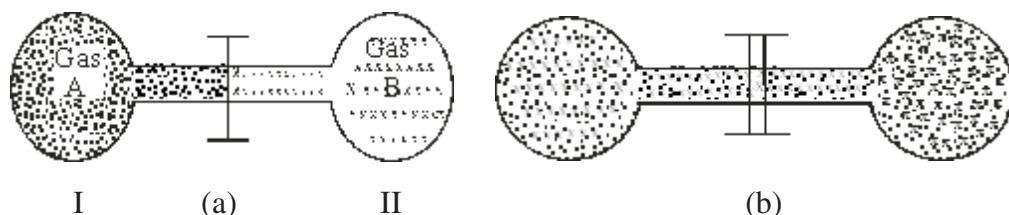


Fig 10.1

When the valve between the two bulbs is opened [Fig 10.1 (b)], the two gases mix spontaneously. The mixing of gases continues until the partial pressure of each gas becomes equal to 0.5 bar in each bulb i.e., the equilibrium is attained. We know from experience that the process cannot be reversed spontaneously - the gases do not unmix on their own. What is the driving force behind this process?

We know that the internal energy (U) 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, $\Delta U = \Delta H = 0$ 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 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,

- the crystalline state is the most ordered state, hence its entropy is the lowest.
- the gaseous state is the most disordered state, hence its entropy is the maximum, and
- the disorder in the liquid state is intermediate between the solid and the gaseous state.

Entropy of any substance increases on heating. In a chemical reaction, entropy increases if there is an increase in number of moles of gases during the reaction and *vice-versa*.

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

$$\Delta S = \frac{q_{\text{rev}}}{T} \quad (10.1)$$

where q_{rev} is the heat supplied reversibly at a constant temperature T .

10.3 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 properties? Let us see whether these changes in properties can be used as a criterion for determining the spontaneity of a process or not.

- (i) We know that most of the processes which occur spontaneously are exothermic. 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 ice is more ordered than the liquid water and therefore the entropy must decrease. The answer to this question is that we must consider simultaneously two entropy changes:
 - (a) the entropy change of the system itself, and
 - (b) the entropy change of the surroundings

$$\Delta S_{\text{total}} = \Delta S_{\text{univ}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}} > 0 \quad (10.2)$$

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

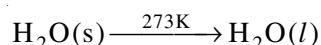
According to *the second law of thermodynamics all spontaneous or natural processes produce an increase in entropy of the universe.*

Thus, for a spontaneous process when a system is at equilibrium, the entropy is maximum, and the change in entropy is zero

$$\Delta S = 0 \text{ (at equilibrium)} \quad (10.3)$$

10.4 ENTROPY CHANGE IN PHASE TRANSITIONS

When a solid melts and produces liquid, the process occurs at the melting point of the solid. For example, ice melts at 273 K and produces water at the same temperature.



The heat involved in the process of melting a solid is called enthalpy of fusion ($\Delta_{\text{fus}}H$). Therefore, the entropy of fusion ($\Delta_{\text{fus}}S$) is given by

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T} \quad (\because q_{\text{rev}} \text{ at const } p = \Delta_{\text{fus}}H)$$

where T is the melting point of the solid.



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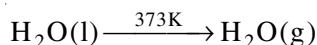
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Similarly, for the equilibrium



$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T}, \quad (T \text{ is the boiling point of the liquid.})$$

Example 10.1: 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: $\text{H}_2\text{O(l)} \xrightleftharpoons{373\text{ K}} \text{H}_2\text{O(g)}$

$$\Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T}$$

$$\Delta_{\text{vap}}H = 40.8 \text{ kJ mol}^{-1} = 40.8 \times 10^3 \text{ J mol}^{-1}$$
$$T = 373 \text{ K}$$

$$\Delta_{\text{vap}}S = \frac{40.8 \times 10^3 \text{ J mol}^{-1}}{373 \text{ K}} = 109 \text{ J K}^{-1} \text{ mol}^{-1}$$



INTEXT QUESTIONS 10.1

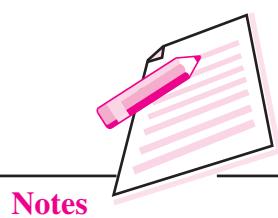
1. The enthalpy change for the transition of ice to liquid water at 273 K is 6.02 kJ mol⁻¹. Calculate the entropy change for the process.
2. Arrange the following systems in the order of increasing randomness,
 - (i) 1 mol of gas A
 - (ii) 1 mol of solid A
 - (iii) 1 mol of liquid A
3. Indicate whether you would expect the entropy of the system to increase or decrease
 - (a) $2\text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2\text{SO}_3(\text{g})$
 - (b) $\text{N}_2(\text{g}) + 3\text{H}_2(\text{g}) \rightarrow 2\text{NH}_3(\text{g})$
 - (c) $\text{O}_2(\text{g}) \rightarrow 2\text{O(g)}$

10.5 THIRD LAW OF THERMODYNAMICS AND ABSOLUTE ENTROPY

When temperature of a substance is increased, the translational, vibrational and rotational motions become more vigorous. It leads to greater disorder and as a

result the entropy of the substance increases. Thus, on increasing the temperature of a substance the entropy of a substance increases. It decreases on decreasing the temperature of a substance.

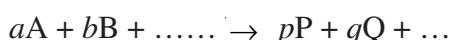
The entropy of a pure and perfectly crystalline solid at absolute zero temperature is zero. This is known as the **Third law of thermodynamics**. This third law of thermodynamics helps us to calculate the absolute value of molar entropies (S_m^0) of substances at different temperatures. The standard molar entropies of some substances at 298 K are given in Table 10.1.

**Notes****Table 10.1 : Standard molar entropies ($S_m^0/J\text{ K}^{-1}\text{ mol}^{-1}$) at 298 K**

Solids	Entropy	Liquids	Entropy	Gases	Entropy
C (graphite)	5.7	H ₂ O	69.9	H ₂	130.7
C (diamond)	2.4	Hg	76.0	O ₂	205.1
Fe	27.3	C ₂ H ₅ OH	160.7	N ₂	191.6
Pb	64.8	C ₆ H ₆	173.3	CO ₂	213.7
Cu	33.1	CH ₃ COOH	159.8	NO ₂	240.1
Al	96.2			N ₂ O ₄	304.3
C ₁₂ H ₂₂ O ₁₁	360.8			NH ₃	192.3
CaCO ₃	92.9			CH ₄	186.2

Entropy Change for a Reaction

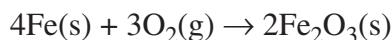
The absolute entropies can be used for calculating standard entropies changes accompanying chemical reaction. It can be determined by subtracting the standard entropies of reactants from those of products. Thus, for a general reaction



$$\Delta S_m^0 = [pS_m^0(P) + qS_m^0(Q) + \dots] - [aS_m^0(A) + bS_m^0(B) + \dots]$$

$$\Delta_r S_m^0 = \sum S_m^0(\text{products}) - \sum S_m^0(\text{reactants})$$

Example 10.2 : Calculate the entropy change, $\Delta_r S_m^0$ for the following reaction at 298K.



Given that the standard molar entropies of Fe(s), O₂(g), and Fe₂O₃(s) at 298 K are 27.3, 205.0 and 87.4 J K⁻¹ mol⁻¹ respectively.

Solution : 4Fe(s) + 3O₂(g) → 2Fe₂O₃(s)

$$\Delta_r S^0 = \sum v_P S_m^0(\text{products}) - \sum v_R S_m^0(\text{reactants})$$

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$$\begin{aligned}\Delta_r S^\circ &= 2S_m^\circ(\text{Fe}_2\text{O}_3) - [4S_m^\circ(\text{Fe}) + 3S_m^\circ(\text{O}_2)] \\ &= [2 \times 87.4 - (4 \times 27.3 + 3 \times 205.0)] \text{ J K}^{-1} \text{ mol}^{-1} \\ &= -549.4 \text{ J K}^{-1} \text{ mol}^{-1}\end{aligned}$$

10.6 GIBBS ENERGY AND SPONTANEITY

We can use the expression

$$\Delta S_{\text{univ}} = \Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} > 0 \quad (10.4)$$

as our basic criterion for a spontaneous change. But it is very difficult to apply it because we have to evaluate the total entropy change i.e. the entropy change of system plus that of surroundings. This is a tedious process as it is difficult to figure out all the interactions between the system and the surroundings. For a system which is not isolated from its surroundings.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}} \quad (10.5)$$

At constant temperature and pressure if q_p is the heat given out by the system to the surroundings, $-q_p$ is the heat gained by the surroundings we can write

$$\Delta S_{\text{surrounding}} = \frac{-q_p}{T} = -\frac{\Delta H_{\text{system}}}{T} \quad (10.6)$$

(since $q_p = \Delta H$ at constant pressure)

Substituting Eq. 10.6 in Eq. 10.5, we get

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

$$T \Delta S_{\text{total}} = T \Delta S_{\text{system}} - \Delta H_{\text{system}}$$

$$\text{or} \quad -T \Delta S_{\text{total}} = \Delta H_{\text{system}} - T \Delta S_{\text{system}} \quad (10.7)$$

Now, let us define another thermodynamic property, Gibbs energy. It is defined by the equation

$$G = H - TS \quad (10.8)$$

For a change in Gibbs energy, we write

$$\Delta G = \Delta H - \Delta(TS)$$

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

For a change at constant temperature, $\Delta T = 0$,

$$\text{Therefore} \quad \Delta G = \Delta H - T \Delta S \quad (10.9)$$

Spontaneity of Chemical Reactions

Since H , T and S are state functions, it follows that G is also a state function. Comparing equations 10.7 and 10.9, we find that

$$\Delta G = -T \Delta S_{\text{total}} \quad (10.10)$$

We have seen that if ΔS_{total} is positive, the change will be spontaneous. Equations 10.10 can be used to predict the spontaneity of a process based on the value of ΔG .

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

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

$\Delta G > 0$ (positive), the process is non-spontaneous

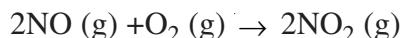
$\Delta G = 0$ (zero), the process is at equilibrium

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 ΔH , and (ii) the entropy factor ΔS . Based on the signs of ΔH and ΔS there are four possibilities for ΔG . These possibilities are outlined in table 10.2

Table 10.2 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.
			+	Non-spontaneous at high temperatures.
3.	+	+	+	Non-spontaneous at low temperatures.
			-	Spontaneous at high temperatures.
4.	+	-	+	Non-spontaneous at all temperatures.

Example 10.3 : For the reaction



Calculate $\Delta_r G$ at 700 K when enthalpy and entropy changes ($\Delta_r H$ and $\Delta_r S$) are respectively $-113.0 \text{ kJ mol}^{-1}$ and $-145 \text{ JK}^{-1} \text{ mol}^{-1}$

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

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

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$$\begin{aligned}\Delta G &= (-113.0 \text{ kJ mol}^{-1}) - (700 \text{ K}) (-145 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\ &= (-113.0 \text{ kJ mol}^{-1}) + (101.5 \text{ kJ mol}^{-1}) \\ &= -11.5 \text{ kJ mol}^{-1}\end{aligned}$$



INTEXT QUESTIONS 10.2

1. Determine whether the following reaction
 $\text{CCl}_4(\text{l}) + \text{H}_2(\text{g}) \rightarrow \text{HCl}(\text{g}) + \text{CHCl}_3(\text{l})$ is spontaneous at 298 K if $\Delta_f H = 91.35 \text{ kJ mol}^{-1}$ and $\Delta_f S = 41.5 \text{ JK}^{-1} \text{ mol}^{-1}$ for this reaction.
2. Which of the following conditions would predict a process that is always spontaneous?
 - (i) $\Delta H > 0, \Delta S > 0$
 - (ii) $\Delta H > 0, \Delta S < 0$
 - (iii) $\Delta H < 0, \Delta S > 0$
 - (iv) $\Delta H < 0, \Delta S < 0$

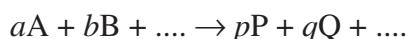
10.7 STANDARD GIBBS ENERGY CHANGE (ΔG°) AND EQUILIBRIUM CONSTANT (K)

The standard Gibbs energy change is defined as the change in Gibbs energy for the process in which the reactants in their standard states are converted into the products in their standard states. It is denoted by the symbol $\Delta_r G^\circ$.

The value of $\Delta_r G^\circ$ can be found from the standard Gibbs energy of formation of substances.

The standard Gibbs energy of formation of a compound is defined as the change in Gibbs 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 Gibbs energy of formation of an element in its standard state is taken as zero.

Thus for a reaction



$$\Delta_r G^\circ = (p \Delta_f G_p^\circ + q \Delta_f G_q^\circ + \dots) - (a \Delta_f G_A^\circ + b \Delta_f G_B^\circ + \dots)$$

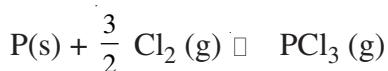
$$\Delta_r G^\circ = \sum v_R \Delta_f G^\circ (\text{products}) - \sum v_R \Delta_f G^\circ (\text{reactants})$$

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The standard Gibbs energy change ($\Delta_r G^\circ$) is related to the equilibrium constant (K) of the reaction by the expression

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

Example 10.4 : The equilibrium constant of the reaction



is 2.00×10^{24} at 500 K. Calculate the value of $\Delta_r G^\circ$.

Solution : Given that

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

$$T = 500 \text{ K}$$

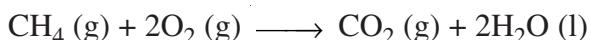
$$\Delta_r G^\circ = -2.303 RT \log K$$

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

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

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

Example 10.5 : Calculate the standard Gibbs energy change for the reaction



at 298K. The standard Gibbs energies of formation of CH₄, CO₂ and H₂O at 298K are – 50.8 kJ mol⁻¹, –394.4 kJ mol⁻¹, and –237.2 kJ mol⁻¹ respectively.

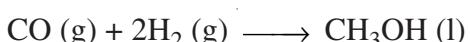
Solution : CH₄(g) + 2O₂(g) → CO₂(g) + 2H₂O(l)

$$\begin{aligned}\Delta_r G^\circ &= \Delta_f G^\circ(CO_2) + 2 \Delta_f G^\circ(H_2O) - \Delta_f G^\circ(CH_4) - 2\Delta_f G^\circ(O_2) \\ &= -394.4 + 2 \times (-237.2) - (-50.8) - 2 \times 0 \\ &= -394.4 - 474.4 + 50.8 \\ &= -818 \text{ kJ mol}^{-1}\end{aligned}$$



INTEXT QUESTIONS 10.3

- What is the relationship between the standard Gibbs energy change and the equilibrium constant of the reaction?
- The standard Gibbs energy change for the reaction



at 298 K is – 24.8 kJ mol⁻¹. What is the value of the equilibrium constant at 298 K?

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WHAT YOU HAVE LEARNT

- All spontaneous processes lead to an increase in disorder or randomness
- The thermodynamic function related to disorder in a system is called entropy, S .
- According to the second law of thermodynamics for a spontaneous change the total entropy change of the system and the surroundings must increase.
- Absolute entropies of different substances can be calculated with the help of the third law of thermodynamics which states that the entropy of a pure and perfectly crystalline solid is zero at absolute zero temperature.
- Gibbs 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 Gibbs energy, i.e., $\Delta G < 0$.

At equilibrium $\Delta G = 0$

The standard Gibbs energy change is related to the equilibrium constant of the reaction by the expression

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

- The standard Gibb's energy change is given by

$$\Delta_r G^\circ = \sum v_p \Delta_f G^0 \text{ (products)} - \sum v_R \Delta_f G^0 \text{ (reactants)}$$



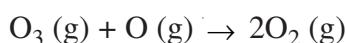
TERMINAL EXERCISE

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) $O_2(g, 300\text{ K}) \rightarrow O_2(g, 500\text{ K})$
3. Define entropy.
4. Explain why entropy is not a good criteria for determining the spontaneity of a process?

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

6. For the reaction



$\Delta_rH = -391.9 \text{ kJ mol}^{-1}$ and $\Delta_rS = 10.3 \text{ J K}^{-1} \text{ mol}^{-1}$ at 298 K. Calculate Δ_rG at this temperature and state whether the reaction is spontaneous or not.

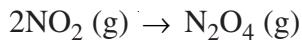
7. What happens to Δ_rG during

(a) a spontaneous process

(b) a non-spontaneous process

(c) a process at equilibrium

8. Calculate Δ_rG° at 298 K for the reaction



Given $\Delta_rH = -57.20 \text{ kJ mol}^{-1}$ and $\Delta_rS = -175.8 \text{ J K}^{-1} \text{ mol}^{-1}$

Is this reaction spontaneous?

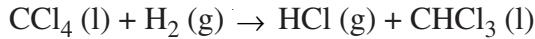
9. The standard Gibbs energies of formation at 298 K are $-202.85 \text{ kJ mol}^{-1}$ for $\text{NH}_4\text{Cl}(\text{s})$, $-16.45 \text{ kJ mol}^{-1}$ for $\text{NH}_3(\text{g})$ and $-95.3 \text{ kJ mol}^{-1}$ for $\text{HCl}(\text{g})$

(a) What is Δ_rG° for the reaction



(b) Calculate the equilibrium constant for this decomposition.

10. For the following reaction



$\Delta_rG^\circ = -103.7 \text{ kJ mol}^{-1}$ at 298 K. Calculate the equilibrium constant for this reaction.



ANSWERS TO INTEXT QUESTIONS

10.1

$$1. \quad \Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T} = \frac{6.02 \text{ kJ mol}^{-1}}{273 \text{ K}} = \frac{6.02 \times 10^3 \text{ J mol}^{-1}}{273 \text{ K}}$$
$$= 22.0 \text{ J mol}^{-1} \text{ K}^{-1}$$

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2. 1 mol of solid, 1 mol of liquid, 1 mol of gas.
3. Decrease (b) Decrease (c) Increase

10.2

1. $\Delta G = -103.7 \text{ kJ}$. Therefer the reaction is spontaneous.
2. (iii)

10.3

1. $\Delta G^\circ = -2.303 RT \log K$
2. 2.2×10^4

MODULE - V

CHEMICAL DYNAMICS

- 11. Chemical Equilibrium
- 12. Ionic Equilibrium
- 13. Electrochemistry
- 14. Chemical Kinetics
- 15. Adsorption and Catalysis

