10

SPONTANEITY OF CHEMICAL REACTIONS

SPONTANEOUS AND NON-SPONTANEOUS PROCESSES

- **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.

ENTROPY

- The **entropy** of an object is a measure of the amount of energy which is unavailable to do work. **Entropy** is also a measure of the number of possible arrangements the atoms in a system can have. In this sense, **entropy** is a measure of uncertainty or randomness.
- Ice melting, salt or sugar dissolving, making popcorn and boiling water for tea are processes with increasing entropy in your kitchen.
- **Formula of entropy:**

$$\Delta S_{sys} = \frac{(q_{rev})_{sys}}{\Delta T} = \frac{(\Delta H)_{sys}}{\Delta T}$$

- **Unit of Entropy = JK^{-1} mol^{-1}**

CRITERIA FOR SPONTANEOUS CHANGE: THE SECOND LAW OF THERMODYNAMICS

- For all the spontaneous processes totally entropy change must positive.

$$\Delta S_{total} = \Delta S_{sys} + \Delta S_{surr} > 0$$

ENTROPY CHANGE IN PHASE TRANSITIONS

- During the phase transition, the temperature remains constant
- At the temperature of phase transition, the transfer of heat is reversible
- Since we know that

For P = const, $q_{transition} = \Delta H_{transition}$

Ergo: $\Delta S_{transition} = \Delta H_{transition}/T_{transition}$

$\Delta S^0_{transition}$ – standard entropy of transition ($J\ mol^{-1}\ K^{-1}$).

THIRD LAW OF THERMODYNAMICS AND ABSOLUTE ENTROPY

- The entropy of a perfectly crystalline solid at absolute zero (0 K) is taken to be zero.

GIBBS ENERGY AND SPONTANEITY

- Gibbs Helmholtz Equation for determination of Spontaneity : **$\Delta G = \Delta H - T.\Delta S$**

(i) If ΔG = – ve, the process is spontaneous.

(ii) If ΔG =+ve, the process is nonspontaneous

(iii) If $\Delta G = 0$, the process is in equilibrium.

STANDARD GIBBS ENERGY CHANGE (ΔG^o) 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 $\Delta_r G°$.
- The standard Gibbs energy change ($\Delta_r G°$) is related to the equilibrium constant (K) of the reaction by the expression

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

- **Relation between Gibbs Energy Change and Equilibrium Constant :**

$$\Delta G^0 = -2.303\ RT \log K_c\ .$$

- **Heat capacity (C):** Amount of heat required to raise the temperature of a substance by 1°C to 1 K.

$$q = C\Delta T$$

- **Specific heat capacity (C_s):** Amount of heat required to raise the temperature of 1g of a substance by 1°C or 1K.

$$q = C_s \times m \times \Delta T$$

- **Molar Heat Capacity (C_m):** Amount of heat required to raise the temperature of 1 mole of a substance by 1°C or 1K.

$$q = C_m \times n \times \Delta T$$

- 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.
- **Entropy:** 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.

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

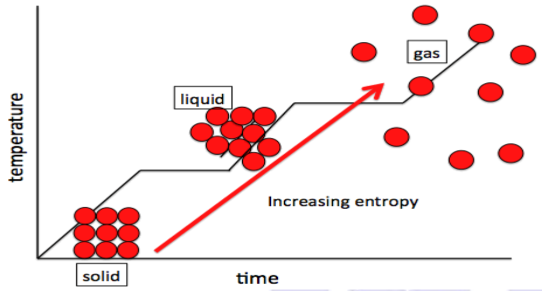


Fig. 10.1. **Entropy of any substance increases on heating.**

(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.

- **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 Δ S = 0 (at equilibrium)

- **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

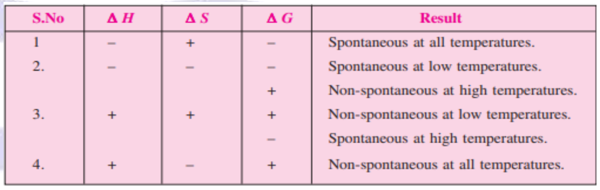
$$\Delta_r S_m^0 = \Sigma\, S_m^0 \text{ (products)} - \Sigma\, S_m^0 \text{ (reactants)}$$

- **Gibbs energy and spontaneity:**

$$\Delta G = -T \Delta S_{total}$$

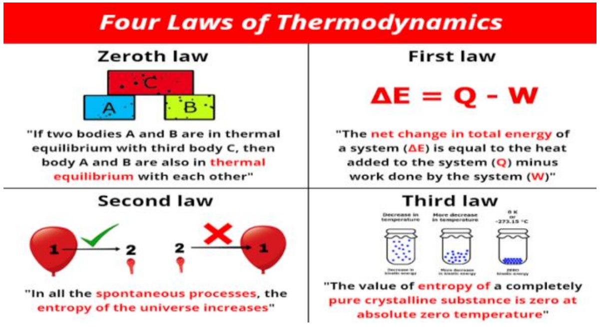
- $\Delta G < 0$ (negative), the process is spontaneous
- $\Delta G > 0$ (positive), the process is non-spontaneous
- $\Delta G = 0$ (zero), the process is at equilibrium

Table 10.2 Criterion for spontaneous change: ΔG = ΔH –TΔS



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.

- **Four Laws of Thermodynamics:**



"If two bodies A and B are in thermal equilibrium with third body C, then body A and B are also in thermal equilibrium with each other"

"The net change in total energy of a system (ΔE) is equal to the heat added to the system (Q) minus work done by the system (W)"

"In all the spontaneous processes, the entropy of the universe increases"

"The value of entropy of a completely pure crystalline substance is zero at absolute zero temperature"

Check Yourself

1. Third law of thermodynamics provides a method to evaluate which property?

(A) Absolute Energy

(B) Absolute Enthalpy

(C) Absolute Entropy

(D) Absolute Free Energy

2. One mole of which of the following has the highest entropy?

(A) Liquid Nitrogen (B) Hydrogen Gas

(C) Mercury (D) Diamond

3. The enthalpy of vaporisation of a substance is 8400 J mol-1 and its boiling point is –173°C. The entropy change for vaporisation is:

(A) 84 J mol-1K^{-1} (B) 21 J mol-1K^{-1}

(C) 49 J mol-1K^{-1} (D) 12 J mol-1K^{-1}

4. The species which by definition has ZERO standard molar enthalpy of formation at 298 K is

(A) $Br_{2(g)}$ (B) $Cl_{2(g)}$

(C) $H_2O_{(g)}$ (D) $CH_{4(g)}$

5. Which of the following is true for the reaction? **H_2O (l) ↔ $H_2O_{(g)}$** at 100° C and 1 atm pressure

(A) $\Delta S = 0$ (B) $\Delta H = T\,\Delta S$

(C) $\Delta H = \Delta U$ (D) $\Delta H = 0$

Stretch Yourself

1. Why is it advised to add ethylene glycol to water in a car radiator in hill station?

2. An aqueous solution of 2% non-volatile exerts a pressure of 1.004 Bar at the normal boiling point of the solvent. What is the molar mass of the solute?

3. Explain why does an azeotropic mixture distill without any change in composition?

Test Yourself

Question: Out of NH_3 and CO_2 which gas will be adsorbed more readily on the surface of activated charcoal and why?

Answer: NH_3 gas will be adsorbed more readily on activated charcoal. It has higher critical temperature than CO_2 and is an easily liquefiable gas. Its Van der Waals forces are stronger

Answers

Check Yourself

Answer: 1(C); 2(B); 3(A); 4(B); 5(A)

Stretch Yourself

1. NH_3 has higher critical temperature than CO_2, *i.e.,* NH_3 is more liquefiable than CO_2. Hence, NH_3 has greater intermolecular forces of attraction and hence will be adsorbed more readily.
2. Do it by yourself.
3. River water is a colloidal solution of clay and sea water contains a number of electrolytes. When river water meets the sea water, the electrolytes present in the sea water coagulate the colloidal solution of clay resulting in its deposition with the formation of delta.
4. Dialysis is a process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane
5. Hydrated ferric oxide sol $AlCl_3/Al^{3+}$