

K_1 and K_2 are equilibrium constants at temperature T_1 and T_2 , ΔH° = enthalpy of reaction.

- **Reaction quotient** : Ratio at any stage of reaction other than the equilibrium is called reaction quotient or concentration quotient. It is represented as Q_c or Q_p or simply Q . Thus, for the reaction,
 $aA + bB \rightleftharpoons xX + yY$

$$Q = \frac{[X]^x [Y]^y}{[A]^a [B]^b}$$

Few important results can be drawn from reaction quotient (Q)

- If $Q = K$, the reaction is in equilibrium.
- If $Q < K$, the reaction proceeds in forward direction (i.e., from left to right).
- If $Q > K$, the reaction proceeds in backward direction (i.e., from right to left).

LE CHATELIER'S PRINCIPLE

- The law states that if any kind of change in concentration, temperature or pressure is imposed on the system in equilibrium, then equilibrium shifts in a direction that tends to undo the effect of the change imposed.
- **Effect of change in concentration** : In a reaction at equilibrium, if concentration of any reactant or product is increased, the equilibrium shifts in a direction where it will be consumed. The increase in concentration of reactant or decrease in concentration of products shifts the equilibrium in forward direction whereas increase in concentration of products and decrease in concentration of reactants shifts the equilibrium in backward direction.

- **Effect of change in temperature**: In a reaction at equilibrium if temperature is increased, reaction will proceed in the direction in which some heat can be destroyed i.e., absorbed so that temperature of the system remains constant. It means increase in temperature supports the endothermic reaction where heat is absorbed. Decrease in temperature favours exothermic reaction in which heat is liberated.
- **Effect of change in pressure** : In a reaction at equilibrium if pressure is increased, then according to Le Chatelier's principle, the equilibrium will shift in a direction in which the pressure decreases. This implies that equilibrium will shift in a direction which produces smaller number of moles, since pressure is directly proportional to the number of moles.
- **Effect of catalyst** : It does not effect the equilibrium position. It only helps in attaining the equilibrium state quickly.
- **Effect of adding inert gas**
 - > If inert gas is added at *constant volume* to the reaction at equilibrium, the equilibrium will not be changed/disturbed, because at constant volume addition of an inert gas will not change the molar concentration of the reactants and products.
 - > If inert gas is added at *constant pressure* to the reaction at equilibrium, the volume of reaction mixture increases and equilibrium will shift in the direction in which there is increase in the number of moles of the gas. If number of moles on either side of equilibrium are same, there will be no effect of adding an inert gas on the state of equilibrium.

Summary of factors affecting equilibrium

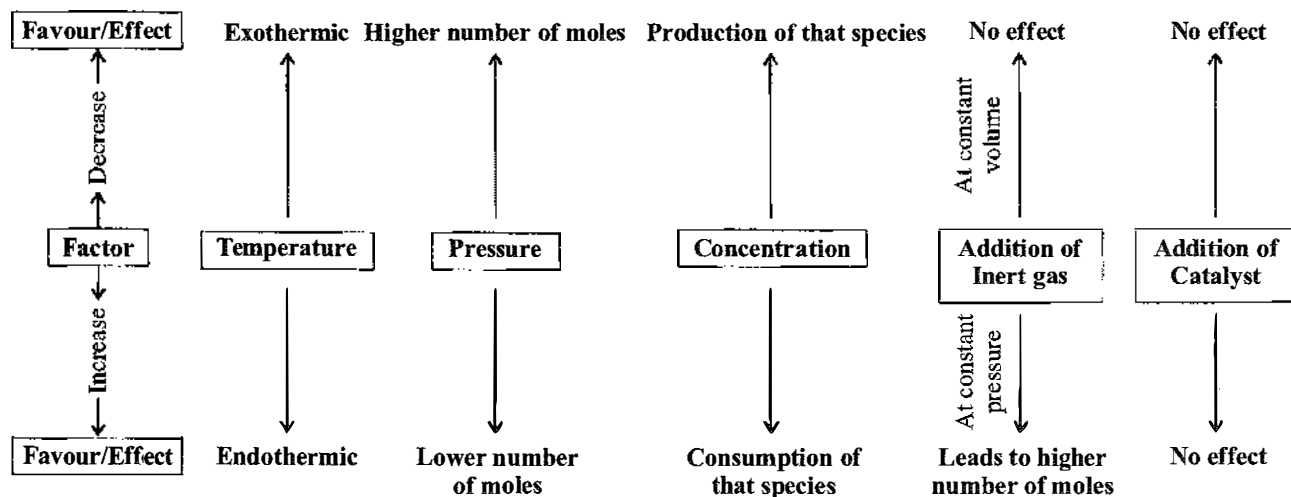
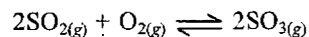


Illustration 3

For the exothermic formation of sulphur trioxide from sulphur dioxide and oxygen in the gas phase:



$K_p = 40.5 \text{ atm}^{-1}$ at 900 K and $\Delta_r H = -198 \text{ kJ mol}^{-1}$

- (i) Write the expression for the equilibrium constant for the reaction.

Equilibrium

- (ii) At room temperature (≈ 300 K) will K_p be greater than, less than or equal to K_p at 900 K.
- (iii) How will the equilibrium be affected if the volume of the vessel containing the three gases is reduced, keeping the temperature constant. What happens?
- (iv) What is the effect of adding 1 mole of $\text{He}_{(g)}$ to a flask containing SO_2 , O_2 and SO_3 at equilibrium at constant volume?

Soln.: (i) The equilibrium constant for this reaction is written in terms of the partial pressure of the reactants and products. So,

$$K_p = \frac{p_{\text{SO}_3(g)}^2}{p_{\text{SO}_2(g)}^2 \times p_{\text{O}_2(g)}}$$

(ii) This reaction is exothermic. So, its equilibrium constant should increase with the lowering of temperature

($d \ln K/dT = \Delta_r H^\circ/RT^2$). Therefore, the value of K_p at 300 K will be greater than the value at 900 K.

(iii) When the volume of the vessel is reduced, the volume of the reaction mixture will decrease. As a result, pressure of the gaseous mixture will increase. According to the Le Chatelier's principle, the system will move in a direction so as to decrease the number of moles of the gaseous substances in the system. The number of moles decrease in going from reactants to the product side. Therefore, a decrease in the volume of the reacting system will shift the equilibrium to the right. That is, more $\text{SO}_3(g)$ will be formed from the reactants.

(iv) Addition of helium to the reaction mixture at equilibrium under constant volume has no effect on the equilibrium.

IONIC EQUILIBRIUM

Acids and Bases

Concept	Acid	Base
• Arrhenius concept (1884)	A substance which gives H^+ ion when dissolved in water. e.g., HCl , H_2SO_4 , HNO_3	A substance which gives OH^- ions when dissolved in water. e.g., KOH , NaOH , Ca(OH)_2
• Bronsted-Lowry concept (1923)	Proton donors e.g., CH_3COOH , HCl , HNO_3	Proton acceptors e.g., NH_3 , Cl^- , CO_3^{2-}
• Lewis concept (1939)	Electron acceptor e.g., H^+ , SO_3 , SO_2 , AlCl_3 , Ag^+	Electron donor e.g., O_2^- , NH_3 , $\text{H}_2\ddot{\text{O}}$

Illustration 4

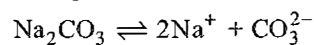
Classify the following as acid or base and also mention the concept on the basis of which these are so.

- (i) $\text{HCl}_{(aq)}$ (ii) $\text{Na}_2\text{CO}_{3(aq)}$ (iii) $\text{CO}_{2(g)}$
 (iv) H_2O (v) NH_4^+

Soln.: (i) $\text{HCl}_{(aq)}$: Acid according to Arrhenius concept and Bronsted-Lowry concept



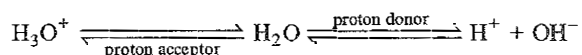
(ii) $\text{Na}_2\text{CO}_{3(aq)}$: Base according to Bronsted-Lowry concept



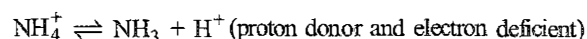
(iii) $\text{CO}_{2(g)}$: Acid according to Lewis concept.

In case of CO_2 ($\text{O}=\text{C}=\text{O}$), double bond exists between carbon and oxygen. Since oxygen is more electronegative than carbon, a slight positive charge is induced on carbon and hence it can accept an electron pair.

(iv) H_2O : Both acid and base i.e., amphoteric according to Arrhenius concept and Bronsted-Lowry concept



(v) NH_4^+ : Acid according to Arrhenius, Bronsted-Lowry and Lewis concept.

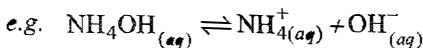


Electrolytes

- When an ionic compound is dissolved in water or melted, it gets split into its ions. The process is known as **ionization** or **dissociation**. Since the ions have either positive or negative charge, the aqueous solution of such compounds can conduct electricity.
- A compound whose aqueous solution or melt conducts electricity is known as **electrolyte**, whereas **non-electrolyte** is the compound whose neither aqueous solution nor melt conducts electricity.
- **Strong and weak electrolytes**: Electrolytes which dissociate almost completely into ions in aqueous solution are known as strong electrolytes, e.g., NaCl , HCl , NaOH , H_2SO_4 , etc. They are very good conductors of electricity. They have degree of dissociation nearly one i.e., $\alpha \approx 1$.

Whereas those electrolytes which dissociate only partially into ions in aqueous solution are known as weak electrolytes, e.g., CH_3COOH , NH_4OH , etc.

They have conductivity smaller than that of strong electrolytes. Their value of degree of dissociation is much smaller than one i.e., $\alpha \ll 1$. An equilibrium is set up in case of partially ionized weak electrolytes between ions and unionized electrolyte.



- **Degree of ionisation (α)**: The fraction of total number of molecules dissociated into ions at a particular temperature is known as degree of ionisation or degree of dissociation. It is denoted by α .

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{Total number of moles}}$$

Degree of ionisation depends on temperature and increases with increase in temperature.