IMPORTANT POINTS (EQUILIBRIUM)

- Equilibrium state: When rate of formation of a product in a process is in competition with rate of formation of reactants, the state is then named as "Equilibrium state".

- Equilibrium in physical processes: solid ⇄ liquid ⇄ gas

\[ \text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_2\text{O}_{(vap)} \]

- Law of chemical equilibrium: At a given temperature, the product of concentrations of the reaction products raised to the respective stoichiometric coefficients in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the Equilibrium Law or Law of Chemical Equilibrium.

\[ \frac{[C]^c [D]^d}{[A]^a [B]^b} \]

- Chemical equation

\[ \text{aA + bB} \leftrightharpoons \text{cC + dD} \]

\[ K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \]

- Equilibrium constant

\[ K'c = \frac{1}{K_c} \]

\[ K''c = (K_c)^b \]

Concentrations or partial pressure of pure solids or liquids do not appear in the expression of the equilibrium constant. In the reaction,

\[ \text{Ag}_2\text{O}(s) + 2\text{HNO}_3(aq) \rightleftharpoons 2\text{AgNO}_3(aq) + \text{H}_2\text{O}(l) \]

\[ K_c = \frac{[\text{AgNO}_3]^2}{[\text{HNO}_3]^2} \]

- If \( Q_c > K_c \), the reaction will proceed in the direction of reactants (reverse reaction). If \( Q_c < K_c \), the reaction will proceed in the direction of the products (forward reaction).

- \( K_p \) is equilibrium constant in terms of partial pressure of gaseous reactants and products.

- \( K_c \) is equilibrium constant in terms of molar concentration of gaseous reactants and products.

- \( K_p = K_c (RT)^\Delta n \) here \( R \) is gas constant, \( T \) is temperature at which the process is carried out & \( \Delta n \) is no. of moles of gaseous product minus no. of moles of gaseous reactants.

- If \( K_c > 10^3 \), \( K_c \) is very high i.e. the reaction proceeds nearly to completion.

- If \( K_c < 10^3 \), \( K_c \) is very small i.e. the reaction proceeds rarely.

- If \( K_c \) is in the range of \( 10^3 \) to \( 10^5 \), i.e. reactants and products are just in equilibrium.

- \( \Delta G^0 = -RT \ln K \) or \( \Delta G^0 = -2.303RT \log K \)

- Factors affecting equilibrium constant: temperature, pressure, catalyst and molar concentration of reactants and products.
- **Le Chatelier’s principle**: It states that a change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

- Arrhenius acids are the substances that ionize in water to form $\text{H}^+$.
- Arrhenius bases are the substances that ionize in water to form $\text{OH}^-$.
- Lewis acids are lone pair (of e-) accepters while Lewis bases are lone pair donators.
- Proton donor are acids while proton accepters are bases (Bronsted-Lowry concept).
- The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. If Brönsted acid is a strong acid then its conjugate base is a weak base and vice versa.

- **Ionic product of water** $K_w = [\text{H}^+][\text{OH}^-]$
- $\text{pH} = -\log [\text{H}^+]$; here $[\text{H}^+]$ is molar concentration of hydrogen ion.
- $\text{pH} + \text{pOH} = 14$
- $\text{p}K_a + \text{p}K_b = 14$
- $K_a \times K_b = K_w = \text{ionic product of water} = 1 \times 10^{-14}$

- Buffer solution: The solutions which resist change in pH on dilution or with the addition of small amounts of acid or alkali are called Buffer Solutions.
- **Common ion effect**: It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.
- Hydrolysis of Salts: process of interaction between water and cations/anions or both of salts is called hydrolysis.
- The cations (e.g., $\text{Na}^+$, $\text{K}^+$, $\text{Ca}^{2+}$, $\text{Ba}^{2+}$, etc.) of strong bases and anions (e.g., $\text{Cl}^-$, $\text{Br}^-$, $\text{NO}_3^-$, $\text{ClO}_4^-$, etc.) of strong acids simply get hydrated but do not hydrolyse, and therefore the solutions of salts formed from strong acids and bases are neutral i.e., their pH is 7.
- Salts of weak acid and strong base e.g., $\text{CH}_3\text{COONa}$ are basic in nature.
- Salts of strong acid and weak base e.g., $\text{NH}_4\text{Cl}$, are acidic.
- Salts of weak acid and weak base, e.g., $\text{CH}_3\text{COONH}_4$. The pH is determined by the formula $\text{pH} = 7 + \frac{1}{2} (\text{p}K_a - \text{p}K_b)$
- **Solubility product**: product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.
1. Equilibrium constant helps in predicting the direction in which a given reaction will proceed at any stage.

   a) In which one of the following conditions a chemical reaction Proceeds in the forward direction?

   i) \( Q_C < K_C \)
   ii) \( Q_C > K_C \)
   iii) \( Q_C = 1/K_C \)
   iv) \( Q_C = -K_C \)

   b) Write whether the following statement is true or false:

   "High value of equilibrium constant suggests high concentration of the reactants in the equilibrium mixture".

   c) State the Le-Chatliers principle. Applying this principle, explain the effect of pressure in the following equilibrium.

   \[ \text{CO}(g) + 3 \text{H}_2(g) \rightarrow \text{CH}_4(g) + \text{H}_2\text{O}(g) \] (3)

2. a) i) Give the Arrhenius concept about acids and bases.
    ii) Give one example each for Arrhenius acid and base.

   b) i) Write the expression for equilibrium constant \( K_p \) for the following equilibrium.

   \[ 2\text{NOCl}(g) \rightarrow 2\text{NO}(g) + \text{Cl}_2(g) \]

   ii) Find the value of \( K_c \) for the above equilibrium if the value of \( K_p \) is \( 1.8 \times 10^{-2} \text{ atm} \) at 600 K. (\( R = 0.0821 \text{ Latm K}^{-1}\text{mol}^{-1} \))

3. Le-Chatlier’s principle makes a qualitative prediction about the change in conditions on equilibrium.

   a) State Le-Chatlier’s principle.
   b) \( \text{N}_2(g) + \text{O}_2(g) \rightarrow 2\text{NO}(g) \). What is the effect of pressure on the above equilibrium?
   c) The species \( \text{HCO}_3^- \) and \( \text{HSO}_4^- \) can act both as Bronsted acids and bases. Write the corresponding conjugate acid and conjugate base of the above species.

4. a) Write an equation for equilibrium constant in terms of concentration (\( K_c \)) for the equilibrium reaction given below.

   \[ \text{Ag}_2\text{O}(s) + 2\text{HNO}_3(aq) \rightarrow 2\text{AgNO}_3(aq) + \text{H}_2\text{O}(l) \] (1)

   b) What are buffer solutions? Give an example for a buffer solution.
c) The concentration of H+ ion in a sample of soft drink is 3.8 x 10^-3M. Determine its pH.

5. a) What is conjugate acid – base pair? Illustrate with an example.
   b) Define the pH scale. The pH of a soft drink is 2.42. Give the nature of the solution.
   c) An aqueous solution of CuSO4 is acidic while that of Na2SO4 is neutral. Explain.

6. Equilibrium is possible only in a closed system at a given temperature.
   a) Write the expression for equilibrium constant, Kc for the reaction
      
      4 NH3(g) + 5 O2(g) \rightarrow 4 NO(g) + 6 H2O(l)

   b) What happens to the value of the equilibrium constant (Kc) when the above reaction is reversed?

7. Weak acids are partially ionized in aqueous solutions.
   a) The ionization constants of some acids are given below:
      
      Acid Ionisation constant (K_a)
      Formic acid (HCOOH) 1.8 x 10^{-4}
      Hypochlorous acid (HClO) 3.0 x 10^{-8}
      Nitrous acid (HNO2) 4.5 x 10^{-4}
      Hydrocyanic acid (HCN) 4.9 x 10^{-10}

   Arrange the above acids in the increasing order of their acid strength.

   b) Calculate the pH of a 0.01 M acetic acid solution with the degree of ionization 0.045.

8. Salts can be classified into different categories on the basis of their solubility.
   a) Identify the solubility range of sparingly soluble salts from the following:
      
      (Between 0.01 M and 0.1 M, less than 0.01 M, greater than 0.1 M).
   b) Calculate the solubility (S) of CaSO4 at 298 K, if its solubility product constant (Ksp) at this
      temperature is 9 x 10^{-6}.

9. a) During a class room discussion one of your friends argues that equilibrium constant is
    not altered with change in temperature. What is your view towards this argument? Justify.

   b) Dissociation of CaCO3 in a closed vessel is given as CaCO3(s) \rightarrow CaO(s) + CO2(g)
      
      i) Write an expression for Kc

      ii) Explain the effect of increase in pressure on the above reaction. Name the principle
          behind this.

10. Le-Chatlier’s principle helps to explain the effect of change in conditions on equilibrium.
    Discuss the effect of pressure in the following equilibrium on the basis of Le-Chatlier’s
    principle:

        CO(g) + 3 H2(g) \rightarrow CH4(g) + H2O(g)

11. The behaviour of acids and bases can be explained by using different concepts.
a) Select the Lewis acid from the following: (NH\textsubscript{3}, OH\textsuperscript{—}, BCl\textsubscript{3}, Cl\textsuperscript{—})

b) What are conjugate acid – base pairs? Illustrate using a suitable example.

12. The pH of a salt solution depends on the hydrolysis of its ions.
   a) Out of the following, which can produce an acidic solution in water?
      (CH\textsubscript{3}COONa, NH\textsubscript{4}Cl, CH\textsubscript{3}COONH\textsubscript{4}, NaCl) (1)
   b) Explain the phenomenon of common ion effect with a suitable example.

13. The principal goal of chemical synthesis is to maximize the conversion of reactants into products. Le-Chatlier’s principle can be applied to achieve this goal.
   a) State Le-Chatlier’s principle.
   b) Predict the conditions to be applied to maximize the production of ammonia in the following reaction.
      \[ \text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightarrow 2 \text{NH}_3(\text{g}); \Delta H = -92.38 \text{ kJ/mol} \] (3)
   c) Comment on the effect of increasing pressure in the reaction, \[ 2 \text{SO}_3(\text{g}) \rightarrow 2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) \]

14. Common ion effect is a phenomenon based on Le-Chatlier’s principle.
   a) Illustrate the common ion effect with an example.
   b) If the concentration of hydrogen ion in a soft drink is 3 x 10\textsuperscript{—3} M, calculate its pH.
   c) Identify the Lewis acids from the following: OH\textsuperscript{—}, BCl\textsubscript{3}, NH\textsubscript{3}, H\textsuperscript{+}

15. Lowry-Bronsted concept of acid and bases is based on the exchange of H\textsuperscript{+} during a reaction.
   a) Illustrate with an example of the conjugate acid – base pair.
   b) Explain the Lewis concept of acids and bases.
   c) According to Lewis theory, classify the following into acids and bases:
      H\textsubscript{2}O, NH\textsubscript{3}, AlCl\textsubscript{3}, OH\textsuperscript{—}

16. When some sodium acetate is added to a solution of acetic acid, the concentration of unionized acetic acid increases.
   a) What is the phenomenon involved? Substantiate.
   b) Consider the equilibrium, AgCl(s) \rightarrow Ag+(aq) + Cl\textsuperscript{—}(aq)

The solubility of AgCl is 1.06 x 10\textsuperscript{—5} mol/L at 298K. Find out its K\textsubscript{sp} at this temperature.
   c) What happens to the value of solubility and solubility product when HCl is passed through AgCl solution?

17. The aqueous solutions of the ionic compounds NaCl, CH\textsubscript{3}COONa and NH\textsubscript{4}Cl show different pH.
   a) Identify the acidic, basic and neutral solutions among these.
   b) Justify your answer.

18. CaCO\textsubscript{3}(s) \rightarrow CaO(s) + CO\textsubscript{2}(g)
a) Write down the expression for Kp.
b) What is the relation between Kp and Kc in the above reaction?

19. PCl5(g) → PCl3(g) + Cl2(g)
   a) What happens to Kp of the above system if more chlorine is added to the system in equilibrium.
   b) Give the relation between Kp and Kc in the above system.