Equilibrium

FAST TRACK : QUICK REVISION

- **Equilibrium :** It is a state in a process when two opposing processes (forward and reverse) occur simultaneously at the same rate. The free energy change at equilibrium state is zero *i.e.*, $\Delta G = 0$.

- **Equilibrium constant :** For a general reaction :

    $a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$

    $K_c = \dfrac{[\text{C}]^c [\text{D}]^d}{[\text{A}]^a [\text{B}]^b}$ and $K_p = \dfrac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$

- **Relationship between K_p and K_c :**

    $K_p = K_c (RT)^{\Delta n_g}$

    $\Delta n_g = n_p(g) - n_r(g)$

- Magnitude of equilibrium constant depends upon the way in which a reaction is written :

Chemical equation	Equilibrium constant
$a\text{A} + b\text{B} \rightleftharpoons c\text{C} + d\text{D}$	K
$c\text{C} + d\text{D} \rightleftharpoons a\text{A} + b\text{B}$	$K_1 = \dfrac{1}{K}$
$na\text{A} + nb\text{B} \rightleftharpoons nc\text{C} + nd\text{D}$	$K_2 = K^n$
$\dfrac{1}{n}a\text{A} + \dfrac{1}{n}b\text{B} \rightleftharpoons \dfrac{1}{n}c\text{C} + \dfrac{1}{n}d\text{D}$	$K_3 = K^{1/n}$

- **Predicting the direction of reaction :**

  If $Q_c = K_c \Rightarrow$ The reaction is in a state of equilibrium.

  $Q_c > K_c \Rightarrow$ The reaction proceeds in reverse direction.

  $Q_c < K_c \Rightarrow$ The reaction proceeds in forward direction.

- **Ostwald's dilution law :** Degree of dissociation of weak electrolyte,

  $$\alpha = \sqrt{\frac{K}{C}}$$

- **Ionic Product of water (K_w) = $[H_3O^+]$ $[OH^-]$ = 10^{-14} at 298K**

- **Le-Chatelier's Principle :** When a system of equilibrium is subjected to a change in temperature, pressure or concentration, the equilibrium shifts itself in such a way so as to undo or nullify the effect of change.

- **Outcomes of Le-Chatelier's Principle**

Change at equilibrium	Shift in equilibrium
Increase in temperature	Endothermic direction
Decrease in temperature	Exothermic direction
Increase in pressure	Towards lesser gaseous moles
Decrease in pressure	Towards greater gaseous moles
Increase in Conc. of reactants	Forward direction
Increase in Conc. of products	Reverse direction

- **Conjugate Acid or Base : Acid-base pair which differ by H^+ ion.**

  Species $- H^+$ = Conjugate base

  Species $+ H^+$ = Conjugate acid

- **pH of solution :**

  $pH = -\log [H_3O^+]$ or $[H^+] = 10^{-pH}$, $pOH = -\log [OH^-]$

  $pH + pOH = pK_w = 14$ at 298K

- **Common ion effect** : The depression of ionisation of weak electrolyte by the presence of common ion from a strong electrolyte is called common ion effect. For example degree of dissociation of NH_4OH decreases in the presence of strong electrolyte NH_4Cl.

- **Hydrolysis of salts and pH of their solutions :** Hydrolysis of salt is defined as the reaction of cation or anion with water as a result of which the pH of water changes.

  1. Salts of strong and strong bases (*e.g.*, NaCl) do not hydrolyse. The solution pH will be 7.

  2. Salts of weak acids and strong bases (*e.g.*, CH_3COONa) hydrolyse, pH >7 (The anion acts as a base).
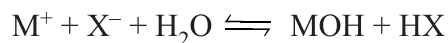
$$X^- \ + \ H_2O \ \rightleftharpoons \ HX \ + \ OH^-$$
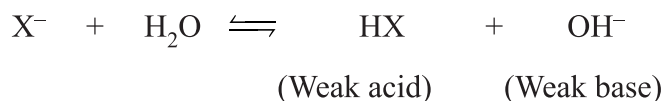
$$\text{(Weak acid)} \qquad \text{(Weak base)}$$

$$pH \ = \ 7 + \frac{1}{2} \ (pK_a + \log C)$$

  3. Salt of strong acids and weak bases (*e.g.*, NH_4Cl) hydrolyse, pH < 7. (The cation acts as an acid).

$$M^+ + H_2O \rightleftharpoons MOH + H^+$$
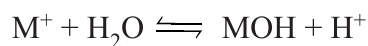
$$pH \ = \ 7 - \frac{1}{2} \ (pK_b + \log C)$$

  4. Salt of weak acids and weak base (*e.g.*, CH_3COONH_4) hydrolyse. The cation acts as an acid and anion as a base but whether the solution is acidic or basic depends upon the relative values of K_a and K_b for these **ions.**

$$M^+ + X^- + H_2O \rightleftharpoons MOH + HX$$

$$pH = 7 + \frac{1}{2} \ (pK_a - pK_b)$$

- **Buffer solutions :** The solutions, which resist the change in pH on dilution or addition of small amounts of acid or base, are called buffer solutions.

- **Basic buffer :** Solution of weak base and its salt with strong acid, For *e.g.*, $NH_4OH + NH_4Cl$

- **Acidic buffer :** Solution of weak acid and its salt with strong base, For *e.g.*, $CH_3COOH + CH_3COONa$.

- **Henderson Hasselbalch Equation for the pH of Buffer solution—**

$$pH = pK_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \qquad \text{(for acidic buffer)}$$

$$pOH = pK_a + \log \frac{[\text{Salt}]}{[\text{Base}]} \qquad \text{(for basic buffer)}$$

- **Solubility Product (K_{sp}) :** The equilibrium constant that represent the equilibrium between undissolved salt (solute) and its ions in a saturated solution is called solubility product constant (K_{sp}).

  For $A_xB_y \xrightleftharpoons{aq} xA^{y+} + yB^{x-}$
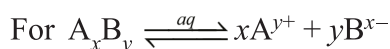
  $$K_{sp} = [A^{y+}]^x [B^{x-}]^y = (xs)^x (ys)^y = x^x \cdot y^x \cdot s^{(x+y)}$$

  where s = Molar solubility

  If ionic product $< K_{sp}$; salt remain dissolve.

  If ionic product $> K_{sp}$; salt will be precipitated.

- **Relationship between solubility (s) and solubility product (K_{sp}).**
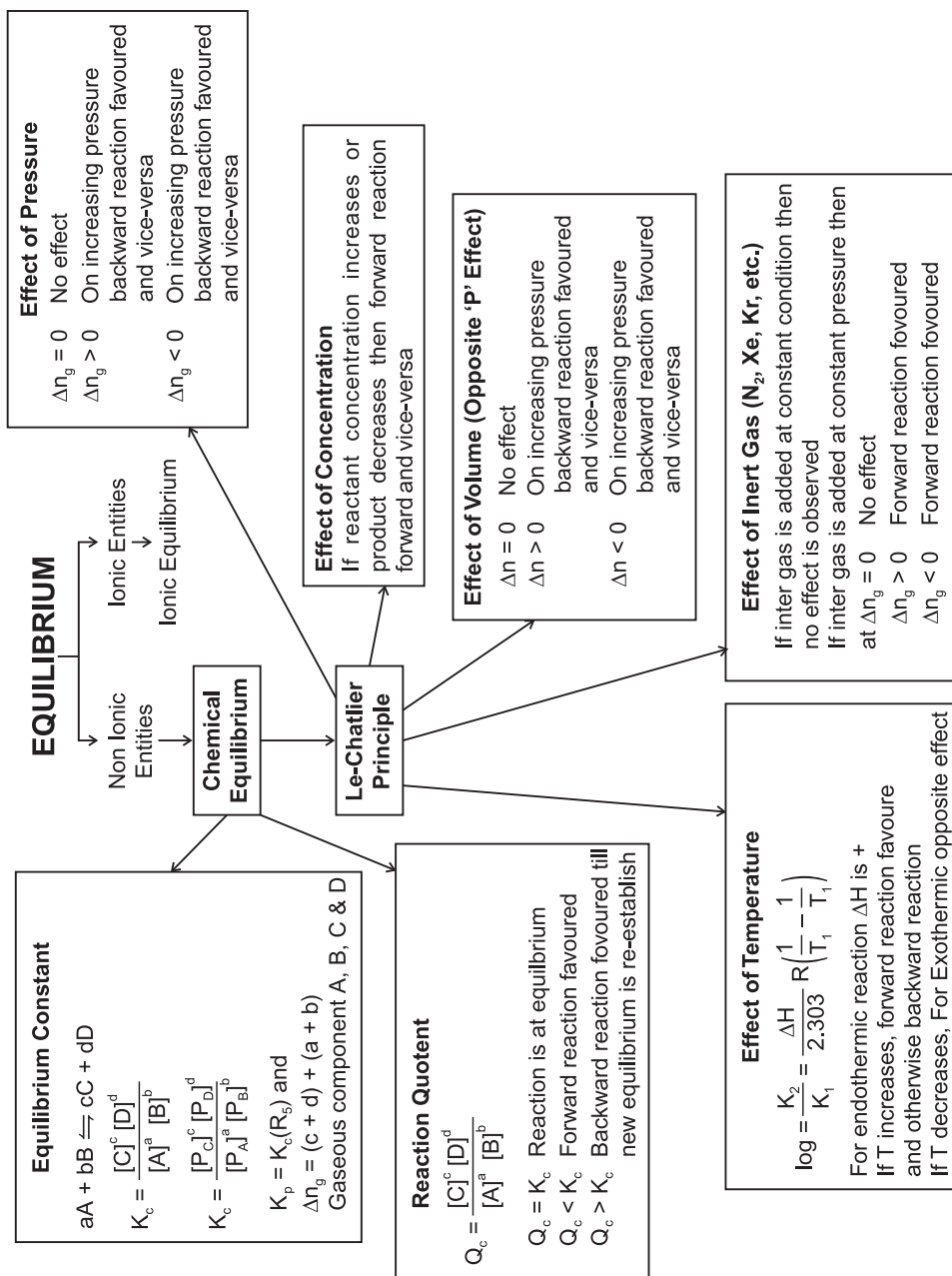
  $$K_{sp} = x^x \cdot y^y \cdot s^{x+y}$$

  For binary salts (*e.g.*, AgCl, AgBr, AgI) $\qquad\qquad K_{sp} = s^2$

  For Ternary salts (*e.g.*, PbI$_2$) $\qquad\qquad K_{sp} = 4s^3$

MIND MAP : EQUILIBRIUM

EQUILIBRIUM

Non Ionic Entities → **Chemical Equilibrium**

Ionic Entities → Ionic Equilibrium

Chemical Equilibrium → **Le-Chatlier Principle**

Equilibrium Constant

$aA + bB \rightleftharpoons cC + dD$

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

$$K_c = \frac{[P_C]^c [P_D]^d}{[P_A]^a [P_B]^b}$$

$K_p = K_c (R_5)$ and

$\Delta n_g = (c + d) + (a + b)$

Gaseous component A, B, C & D

Reaction Quotent

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

$Q_c = K_c$ Reaction is at equilbrium

$Q_c < K_c$ Forward reaction favoured

$Q_c > K_c$ Backward reaction favoured till new equilibrium is re-establish

Effect of Pressure

$\Delta n_g = 0$ No effect

$\Delta n_g > 0$ On increasing pressure backward reaction favoured and vice-versa

$\Delta n_g < 0$ On increasing pressure backward reaction favoured and vice-versa

Effect of Concentration

If reactant concentration increases or product decreases then forward reaction forward and vice-versa

Effect of Volume (Opposite 'P' Effect)

$\Delta n = 0$ No effect

$\Delta n > 0$ On increasing pressure backward reaction favoured and vice-versa

$\Delta n < 0$ On increasing pressure backward reaction favoured and vice-versa

Effect of Inert Gas (N₂, Xe, Kr, etc.)

If inter gas is added at constant condition then no effect is observed

If inter gas is added at constant pressure then

at $\Delta n_g = 0$ No effect

$\Delta n_g > 0$ Forward reaction fovoured

$\Delta n_g < 0$ Forward reaction fovoured

Effect of Temperature

$$\log = \frac{K_2}{K_1} = \frac{\Delta H}{2.303} R \left(\frac{1}{T_1} - \frac{1}{T_1} \right)$$

For endothermic reaction ΔH is +

If T increases, forward reaction favoure and otherwise backward reaction

If T decreases, For Exothermic opposite effect

IONIC EQUILIBRIUM

1 — ACID / BASE

Arrhenius Concept
H^+ Donar – Acid (Hcl)
OH^- Donar – Base (NaOH)

Bronsted Lowry Concept
H^+ Donar (Acid)
H^+ Acceptor (Base)

Lewis Concept
Lone Pair Donar – Base (NH_3)
Lone Pair Acceptor – Acid ($AlCl_3$)

2 — WEAK ACID / BASE

- $K = \dfrac{K\alpha^2}{C}$ $\alpha = \sqrt{\dfrac{K\alpha}{C}}$ $= \sqrt{Ka.c}$
  (dilute sol.)
- $[H^+] = [c\alpha]$
- $[OH^-] = [c\alpha]$
- $pH = \dfrac{1}{2}[pKa - logC]$

3 — pH, pOH

- $pH = -log\,[H_3O^+]_{total}$
- $[H_3O^+] = 10^{-pH}$
- $pOH = -log\,[OH^-]_{total}$
- $pH + pOH = 14\ (298K)$

4 — SOLUBILITY PRODUCT

A_xB_y Salt solution has solubility 'S' M
$A_xB_y \rightleftharpoons xA^{4-}_{(aq.)} + yB^{x-}_{(aq.)}$

$K_{sp} = x^x.y^y[S]^{x+y}$
$A_xB_y = K_{sp} = 1^1.2^2.S^{1+2} = 4S^3$
$A_2b_3 = K_{sp} = 2^2.3^3.S^{2+3} = 108.S^3$

5 — BUFFER SOLUTIONS

Acid Buffer ($CH_3COOH + CH_3COONa$)
$[H^+] = \dfrac{K_a.[Acid]}{[Salt]}$

$pH = pk_a + log\ \dfrac{Salt}{Acid}$

Basic Buffer ($NH_4OH + NH_4Cl$)
$[OH^-] = \dfrac{K_b.[Acid]}{[Salt]}$

$pOH = pk_b + log\ \dfrac{[Salt]}{[Acid]}$

6 — SALT HYDROLYSIS

Acid Salt (NH_4Cl) : $K_H = \dfrac{K_w}{K_b}$ $pH = 7 - \dfrac{1}{2}\,[pk_a + logC]$

$h = \sqrt{K_w/K_b.c}$

Basic Salt (CH_3COONa) : $K_H = \dfrac{K_w}{K_a}$ $pH = 7 + \dfrac{1}{2}\,[pk_a + logC]$

$h = \sqrt{K_w/K_b.c}$

Mixed Salt (CH_3COONH_4) : $K_H = \dfrac{K_w}{K_a.K_b}$, $\dfrac{h}{1-h} = \sqrt{K_H}$

$h = \sqrt{\dfrac{K_w}{K_aK_b}} = \sqrt{K_H}$

$pH = 7 + \dfrac{1}{2}\,[pk_a - pk_b]$

K_H = Hydrolysis constant

h = Degree of Hydrolysis

PASSAGE -1

According to Arrehenius theory, acids are substances that dissociates in water to give hydrogen ions and bases are substances that produce hydroxyl ions.

Bronsted-Lowry gave a more general definition of acids and bases. According to Bronsted-Lowry theory , acid is a substance that is capable of donating a hydrogen ion and bases are substance which are capable of accepting of a hydrogen ion.

According to Lewis Acids and Bases , an acid is a species which accepts electron pair and base which donates an electron pair

Answer the following questions

1. Which of the following acts as both Bronsted acid as well as Bronsted base

    (A) HCO_3 (B) O_2

    (C) HS^- (D) HPO_3^{2-}

2. Arrange the following in order of increasing basic strength

    OH^-; CH_3COO^-, Cl^-, $C_2H_5O^-$

3. Define lewis acid, Give example.

4. All Arrhenius acid are Bronsted acid but Arrhenius bases are not Bronsted base. Explain.

<center>OR</center>

    Classify the following as lewis acid and lewis base and show hot they acts as such

    (A) $AlCl_3$ (B) H_2O

ANS. 1. HCO_3^-, HS^- 2. $Cl^- < CH_3COO^- < OH^- < C_2H_5O^-$ 3. Definition

4. all Arrhenius acid gives H^+ in aqueous solution while Bronsted acids also gives H^+ and hence all Arrhenius acids are Bronsted acids but Arrhenius base given OH^- in aqueous solution while Bronsted bases accept H^+.

OR

AlCl$_3$: lewis acid as it accept electron pair

H$_2$O : Lewis base as it can donate lone pair of electron present on oxygen atom.

PASSAGE -2

Common Ion effect is the phenomenon in which weak acid or weak base dissociation is suppressed due to the presence of the common ion provided by the strong electrolyte . For example the dissociation of CH$_3$COOH is suppressed by the addition of the CH$_3$COONa. Similarly the dissociation of NH$_4$OH is suppressed due to presence of NH$_4$Cl.This occurs due to the Le-Chatlier's principle .

Due to common ion effect there is decrease in solubility of an ionic precipitate by addition to the solution of a soluble compound with an ion common with then precipitate. In water treatment process highly soluble sodium carbonate salt is added to precipitate out sparingly soluble salt calcium carbonate. Salting out process used in manufacturing soap is also benefit from the common ion effect. Common ion effect also help in maintaining pH of a buffer solution.

Answer the following questions:

1. What is common ion effect?

2. Why salt is added to soap during soap formation.

3. Name the principle common ion is based on.

4. Both cation of 2th and 4th group are precipitated as sulphides, but 4th group radicals do no get precipitated when H$_2$S is passed through solution for 2nd group why.
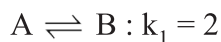
Or

3rd group radicals are precipitated as hydroxides by addition of NH$_4$OH in presence of NH$_4$Cl, what is the role of NH$_4$Cl.

1. For the hypothetical reactions, the equilibrium constant (k) values are given

   $A \rightleftharpoons B : k_1 = 2$

   $B \rightleftharpoons C : K_2 = 4$

   $C \rightleftharpoons D : K_3 = 8$
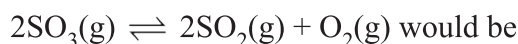
   The equilibrium constant (K) for the reaction $A \rightleftharpoons D$ is

   (a) 48   (b) 24   (c) 12   (d) 64

2. The equilibrium constant for the reaction

   $SO_2(g) + \dfrac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$ is 5×10^{-2} atm$^{-1/2}$

   The equilibrium constant for the reaction

   $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ would be
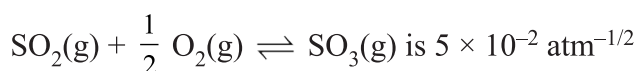
   (a) 100 atm   (b) 25×10^{-4} atm   (c) 400 atm   (d) 125×19^{-6} atm$^{-3/2}$

3. $A(g) + 3B(g) \rightleftharpoons 4C(g)$ initial concentration of A is equal to that of B. The equilibrium concentrations of A and C are equal. What is the equilibrium constant for

   $4C(g) \rightleftharpoons A(g) + 3B(g)$

   (a) 4   (b) 1/8   (c) 64   (d) 16

4. The equilibrium reaction that is not affected by volume change at constant temperature is

   (a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$ (b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

   (c) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (d) $H_2(l) + CO_2(g) \rightleftharpoons H_2CO_3(l)$

5. For the reaction $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$, the value of K_c/K_p is equal to

   (a) RT   (b) $(RT)^2$ (c) 1/RT   (d) 1.0

6. At 90°C pure water has $K_w = 10^{-12}$. The solution with pH value 6.5 is

   (a) Acidic   (b) Basic   (c) Amphoteric   (d) Data insufficient

7. 40 ml of 0.1 M NH_4OH is mixed with 20 mL of 0.1 M HCl. What is the pH of the mixture? (pK_b of ammonia solution = 4.74)

    (a) 4.74   (b) 2.26   (c) 9.26   (d) 5

8. Identify Bronsted Lowry Acids in the reaction

    $$[Al(H_2O)_6]^{3+} + HCO_3^- \rightleftharpoons [Al(H_2O)_5(OH)]^{2+} + H_2CO_3$$
    $\quad$ (X) $\qquad$ (Y) $\qquad\qquad$ (P) $\qquad\qquad$ (Q)

    (a) X, Y   (b) Y, P   (c) P, Q   (d) X, Q

9. The pK_a of weak acid HA is 4.80 and pK_b of a weak base BOH is 4.78. The pH of an aqueous solutions of corresponding salt BA will be

    (a) 7.01   (b) 4.79   (c) 9.22   (d) 10.0

10 If 'p' M is the solubility of $KAl(SO_4)_2$, then K_{sp} is equal to

    (a) p^3 (b) $4p^4$ (c) p^4 (d) $4p^3$

TRUE AND FALSE TYPE QUESTIONS

1. Equilibrium state can be achieved if a reversible reaction is carried out in closed or open container.

2. For a reaction $2A(g) \rightleftharpoons B(g)$ $Q_c > K$ if 'A' is added maintaining $Q_c > K$, the reaction will move in backward direction.

3. For the reaction at equilibrium

    $$CaCO_3 \rightleftharpoons CaO(s) + CO_2(g)$$

    What CaO(s) is removed reaction moves in forward direction.

4. For a reaction $aA + bB \rightleftharpoons cC + dD$ at equilibrium $\Delta G^0 = 0$ always.

5. For a reaction at equilibrium $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

    $K = 4$, the value of $\dfrac{K_b[HCl]^2}{K_f[H_2][Cl_2]}$ is 1.

6. For the electrolyte A_2B if K_{sp} is solubility product then its solubling 'S' M is $[K_{sp}]^{1/3} \div 4$.

7. HCO_3^- is conjugate base of H_2CO_3.

8. H_2O can act as acid as well as base.

9. The pH of buffer solution remain same when any amount of dilution is done.

10. For a salt AB_2(s) solution if Ionic product (I.P) > K_{sp}, then precipitation will take place.

Ans. 1. False   2. True   3. False   4. False   5. True

      6. True   7. True   8. True   9. False   10. True

FILL IN THE BLANKS

1. At equilibrium rate of forward reaction is always equal to ....

2. K_p & K_c are .... for reaction at equilibrium of type $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$.

3. If K_c for reaction $CH_3COOH(l) + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$ is 4. Then Q_c and K_c are .... at equilibrium.

4. If A+B $-70J/mol \rightleftharpoons$ D, reaction temperature is increased then reaction moves in .... direction.

5. Presence of catalyst will ...... the equilibrium constant.

6. The conjugate acid of H_2O is ....

7. On dilution, the degree of dissociation of acetic acid will ....

8. The presence of NH_4Cl in NH_4OH solution will .... the degree of dissociation of NH_4OH.

9. If Ionic product (IP) < K_{sp} for a salt solution of AB, then addition of AB further .... lead to precipitation initially.

10. K_p is always equal to K_c if Δn_g is ....

Ans. 1. rate of backward reaction, 2. equal, 3. equal, 4. backward direction forward, 5. not change, 6. H_3O^+, 7. increase, 8. decrease, 9. will not, 10. zero.

MATCH THE COLUMNS

I. Match the reaction in Column I with the parameters in Column II and unit (M=Molarity) of K eq in Column III

S.N.	Column I	Column II	Column III
1.	$N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$, ΔH= -ve	(a) T increase then K increase	(p) M^0
2.	$2N_2(g)+2O_2(g)\rightleftharpoons 4NO(g)$, ΔH= +ve	(b) T increase then K decrease	(q) M^{2-}
3.	$2X(g)\rightleftharpoons Y(g)$, ΔH= +Ve	(c) P has not effect	(r) M^{-1}
4.	$PCl_5(g)\rightleftharpoons PCl_3(g)+Cl_2(g)$, ΔH= +ve	(d) Equilibrium move forward On addition of Xe Gas	(s) M

II. Match the parameter in Column I with the pH expression in Column II and examples in Column III

S.N.	Column I	Column II-pH	Column III
1.	Salt of weak acid and weak base	(a) $7 + 0.5(pka + logC)$	(p) NH_4Cl
2.	Salt of weak acid and strong base	(b) $7 + 0.5(pka - pkb)$	(q) $NaCl$
3	Salt of strong acid and strong base	(c) $7 - 0.5(pkb + logC)$	(r) CH_3COONa
4.	Salt of strong acid and weak base	(d) $0.5 (pkw)$	(s) CH_3COONH_4

ANS. :

MATCH-I : 1. b, q   2. c, p   3. a, r   4. d, s

MATCH-II : 1. b, s   2. a, r   3. d, q   4. c, p

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ASSERTION - REASON TYPE QUESTION

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Each question contains statement-1 (assertion) and Statement-2 (Reason) Examine the statements carefully and mark the correct answer according to the instruction given below :

A. If both the statements are true and statement -2 is the correct explanation of statement-I

B. If both the statements are true but statement-2 is not the correct explanation of statement-I

C. If statement-I is true and statement-2 is false

D. If statement-I is false and statement-2 is true.

1. Statement-1 : The endothermic reactions are favoured at lower temperature and the exothermic reactions are favoured at higher temperature.
   Statement-2 : when a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of change.

2. Statement-1 : The melting point of ice decreases with increase of pressure
   Statement-2 : Ice contracts on melting.

3. Statement -1 : The gas phase reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$ shifts to the right on increasing pressure.
   Statement-2 : When pressure increase, equilibrium shifts towards more number of moles.

4. Statement-1 : The chemical equilibrium is not static but dynamic in nature.
   Statement-2: The chemical equilibrium is a state in which two opposing process are proceeding at the same rate.

5. Statement-1 : The catalyst does not change the equilibrium constant.
   Statement-2 : Because for the catalysed reaction and uncatalysed reaction ΔH remains same and equilibrium constant depends on ΔH.

6. Statement-1 : If water is heated to 59°C, the pH will increase.
   Statement-2 : K_w increases with increase in temperature.

7. Statement-1: Addition of HCl(aq.) to CH_3COOH (aq.) decrease the ionisation of CH_3COOH (aq.).
   Statement-2 : Due to common ion effect H^+, ionisation of CH_3COOH decreases.

8. Statement-1: Sparingly soluble salts AB and XY_2 with the same solubility product, will have different solubility.
   Statement 2: Solubility of sparingly soluble salts depends upon solubility product.

9. Statement-1 : The ionisation constants of weak diprotic acid are in the order of $Ka_1 > Ka_2$.
   Statement-2 : Removal of H^+ from anion is difficult as compared to neutral atom.

10. Statement-1 : In a titration of weak acid with strong base, the pH at the half equivalence point is pK_a.
    Statement-2 : At half equivalence point, it will form acidic buffer at its maximum capacity where [Acid] = [Salt].

Ans.: 1. D, 2. A, 3. C, 4. A, 5. A, 6. D, 7. A, 8. B, 9. A, 10. A

ONE WORD ANSWER TYPE QUESTIONS

1. What is sum of pH + pOH at 25ºC?   [**Ans.** 14]
2. Write the Henderson Hasselbalch equation for acidic buffer
   $$\textbf{Ans. } pH = pka + 10g \frac{[SALT]}{[ACID]}$$
3. How is degree of dissociation related with concentration terms and Ka, for weak electrolyte.   **Ans**. $\alpha = \sqrt{Ka/c}$
4. How NH_3 is defined as Lewis base?
                          [**Ans.** It contain Lone paid of electrons]
5. How are K_p and K_c related?   [**Ans.** $K_p = K_c (RT)^{\Delta n}$]
6. How does K affected for endothermic reaction if temperature is increased?
   [**Ans.** K get decreased]

7. What is the effect of catalyst on K? [**Ans.** K remains unaffected]

8. How is pH scale affected by increasing temperature?

[**Ans.** pH scale gets contracted]

9. What is the conjugate base of HCO_3^- ? [**Ans.** CO_3^{2-}]

10. What is the nature of CH_3COOH in conc. HCl solution?

[**Ans.** Bronsted Base]

1-MARK QUESTIONS

1. Define physical equilibrium. Give an example also.

2. Fizz is observed when soda water bottle is opened. Why ?

3. Justify the statement : 'Both physical and chemical equilibrium are dynamic in nature'

4. State Law of Chemical equilibrium.

5. In a reversible reaction, the two substances are in equilibrium. If the concentration of each one is reduced to half, then what is the effect on the equilibrium constant ?

6. K_1 and K_2 are equilibrium constant for reactions (1) and (2)
   (i) $N_2(g) + O_2(g) \rightleftharpoons 2\ NO(g)$

   (ii) $NO(g) \rightleftharpoons 1/2\ N_2(g) + 1/2\ O_2(g)$

   Calculate the relation between K_1 and K_2.

7. Write the equilibrium constant expression for the following reaction :

   $3\ Fe(s) + 4\ H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4\ H_2(g)$

8. Classify the equilibrium as homogeneous or heterogeneous :

 $CH_3COOC_2H_5(aq.) + H_2O(1) \rightleftharpoons CH_3COOH(aq.) + C_2H_5OH\ (aq.)$
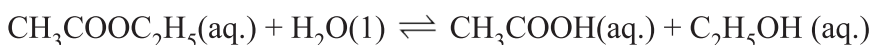
9. $K_p = \dfrac{(P_{NH_3})}{(P_{H_2})^{3/2}(P_{N_2})^{1/2}}$

   Write the balanced chemical equation corresponding to the above expression.

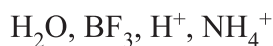10. Give the direction in which the reaction would proceed if $Q_c > K_c$.

11. $Hb(s) + O_2(g) \rightleftharpoons HbO_2(s)$

    Predict the direction in which equilibrium gets shifted if partial pressure of $O_2(g)$ is lowered.

12. Discuss the position of equilibrium if the following reaction is carried out in the presence of catalyst.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
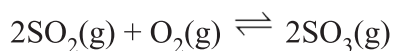
13. Which of the following are Lewis acids ?

H_2O, BF_3, H^+, NH_4^+

14. Write the conjugate acids for the following Bronsted bases.

C_6H_5OH, H_2O

15. Write the conjugate bases for the following Bronsted acids.

H_2O, CH_3COOH.

16. Which of the following are Lewis acids ?

(a) H_2O (b) $AlCl_3$ (c) NH_4^+

17. Define Ostwald's dilution law.

18. SO_3^{2-} is Bronsted base or acid and why ?

19. Why pH of our blood remains almost constant at 7.4 though we quite often eat spicy food ?

20. pH of black coffee is 5.0 at 25ºC. Is black coffee acidic or basic ? [**Ans.** Acidic]

21. What will be the value of $(pK_a + pK_b)$ at 25ºC.

22. What will be the pH of 1 M KNO_3 solutions at 25ºC?

23. $CaCl_2(s) + H_2O(l) \rightleftharpoons CaCl_2(aq.) + Heat$

Discuss the solubility of $CaCl_2$ if temperature is increased.

24. Why does the solubility of CO_2 decrease with rise in temperature ?

25. The solubility of $A_2 X_3$ is y mol dm^{-3}. Calculate its solubility product.

26. Write the K_{sp} expression for $Al(OH)_3$.

27. What is the condition for precipitation of a salt ?

28. Pridict whether the solution is acidic, basic or natural when NH_4NO_3 undergo hydrolysis.

29. Explain why pure NaCl precipitates out when HCl gas is passed through the solution of NaCl ?

30. Give the Henderson's Hasselbalch equation for an acidic buffer solution.

31. On which of the factors the equilibrium depend : Temperature, nature of reactant and product, initial concentration and pressure of the reactants.

32. Arrange the following in increasing acidic strength HCl, HBr, HF, HI

[**Ans.** HF < HCl < HBr < HI]

33. Arrange the following in increasing Lewis base strength

NH_3, BiH_3, PH_3, AsH_3, SbH_3

[**Ans.** BiH_3 < SbH_3 < ASH_3 < PH_3 < NH_3]

34. Arrange following in increasing pH value

0.1M CH_3COOH, 0.1 M NaCl, 0.1MHCl, 0.1MNaOH, 0.1MNH_4OH

[**Ans.** 0.1MHCl < 0.1M CH_3COOH < 0.1M NaCl < 0.1 NH_4OH < 0.1M NaOH]

35. Arrange following in increasing order of degree of hydrolysis.

0.1M NH_4OH, 0.01 M NH_4OH, 10^{-5} M NH_4OH, 10^{-3} M NH_4OH, 10^{-6} M NH_4OH

[**Ans.** 0.1M NH_4OH < 10^{-2} M NH_4OH, 10^{-3}M NH_4OH < 10^{-5}MNH_4OH < 10^{-6} M NH_4OH]

36. Arrange following in increasing order of acidic strength

CH_3COOH, HCOOH, CH_3CH_2COOH, C_6H_5COOH, CH_2COOH

[**Ans.** CH_3COOH < C_6H_5COOH < HCOOH < CH_2FCOOH]

37. Arrange the basic strength of following

F^-, Br^-, Cl^-, I^-

[**Ans.** I^- < Br^- < Cl^- < F^-]

38. Arrange the following in increasing base strength

CH_3^-, NH_2^-, OH^-, F^-

[**Ans.** F^- < OH^- < NH_2 < CH_3^-]

<div align="center">

2-MARKS QUESTIONS

</div>

1. Calculate pH of 0.001M CH_3COOH having 3% dissociation.

[**Ans.** 4.5229]

2. The equilibrium constant for

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is K, then calculate equilibrium constant for $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$. [**Ans.** $\sqrt{K}$]

3. For the reversible reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 500°C, the value of Kp is 1.44×10^{-5} atn^{-2}. Find the K_c value.

[**Ans.** $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$]

4. The equilibrium constant at 298 K for the reaction $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1M each, then equilibrium concentration of D will be [**Ans.** 1.818]

5. For the reaction

$NH_4COO\ NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

If equilibrium pressure is 3 atm. Find the value of Kp [**Ans.** 4]

6. A buffer solution with pH 9 is to be prepared by mixing NH_4Cl that should be added to one litre of 1.0m NH_4OH kb 1.8×10^{-5}

[**Ans.** NH_4Cl = 1.8 M]

7. Calculate the solubility of silver chloride in water at room temperature if the K_{sp} of AgCl is 1.6×10^{-10}. [**Ans.** 1.26×10^{-5}M]

8. Calculate the molar solubility of $Ni(OH)_2$ in 0.10m NaOH. The ionic product of $Ni(OH)_2$ is 2.0×10^{-15}. [**Ans.** 2.0×10^{-13}M]

9. Calculate the pH of 10^{-8} M HCl solution. [**Ans.** 6.96]

10. How many grams of NaOH must be dissolved in IL of the solution to give it a pH value of 12? [**Ans.** 0.4g]

3-MARKS QUESTIONS

1. The equilibrium constant for the reaction $H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g)$ at 1024 K is 1.6×10^5. Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024K. [**Ans.** 10 bar]

2. For the reaction $2BrCl(g) \rightleftharpoons Br_2(g) + Cl_2(g)$ K_c is 32 at 500 K. If initially pure BrCl is present at a concentration of 3.30×10^{-3} M, what is its molar concentration in the mixture at equilibrium? [**Ans.** 3.0×10^{-4} M]

3. When 0.02M HCl solution is added to 0.01M $Pb(NO_3)_2$, will a precipitate of $PbCl_2$ be formed or not. $K_{sp} = 1.6 \times 10^{-5}$ [**Ans:** No]

4. Find the value of Kc for the reaction

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_2(g)$ $K_p = 3.4$ bar^{-1} at 1000°C
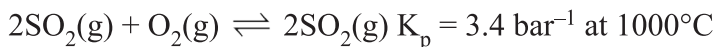
[**Ans.** 359.24]

5. Ammonium hydrogen sulphide dissociate according to equation

$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

If the observed pressure at equilibrium is 1.12 atm at 380K. What is Kp for the reaction [**Ans.** 0.3136]

6. How much of 0.3M NH_4OH should be mixed with 30 mL of 0.2m solution of NH_4Cl to give a buffer solution of pH 10. pk_b for NH_4OH is 4.75.

[**Ans.** V = 112.5 mL]

7. Predict whether a precipitate will be formed or not on mixing 20 mL of 0.001 N NaCl solution with 80 mL of 0.01 M $AgNO_3$ solution. K_{sp} for AgCl is 1.5×10^{-10}. [**Ans.** Yes, ppt will formed.]

8. The values of Ksp of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6.0×10^{-17} respectively. Which salt is more soluble. Explain

[**Ans.** $S_{Ni(OH)_2} = 7.93 \times 10^{-6}M : S_{(Ag\,CN)} = 7.8 \times 10^{-9}M . Ni(OH)_2$

is more soluble]

9. The ionization constant of propanoic acid is 1.32×10^{-5}. Calculate the degree of ionization if its solution is 0.05 M. What will be its degree of ionization if the solution is 0.01 M in HCl solution.
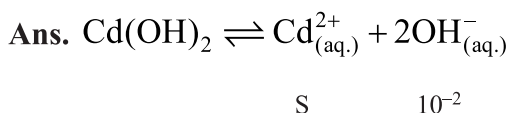
[**Ans.** 1.62×10^{-2}, 1.32×10^{-3}]

10. Calculate the pH of a solution obtained by mixing 50ml of 0.2M HCl with 49.9 mL of 0.2m NaOH solution. [**Ans.** 3.699]

1. The molar solubility of $Cd(OH)_2$ is 1.84×10^{-5}M. Calculate the expected solubility of $Cd(OH)_2$ in a buffer solution of pH = 12.

    Ans. $Cd(OH)_2 \rightleftharpoons Cd^{2+}_{(aq.)} + 2OH^-_{(aq.)}$

    $\qquad\qquad\qquad$ S $\qquad\qquad$ 10^{-2}

 $2.49 \times 10^{-14} = S(10^{-2})^2 \qquad \therefore S = 2.49 \times 10^{-10}M$

2. An aqueous solution contains an unknown concentration of Ba^{2+}. When 50 ml of a 1M solution of Na_2SO_4 is added. $BaSO_4$ just begins to precipitate. The final volume is 500ml. The solubility product of $BaSO_4$ is 1×10^{-10}. Find the original concentration.

    Ans. $K_{sp} = \left[Ba^{2+}\right]\left[SO_4^{2-}\right] = \left[Ba^{2+}\right]\left[\dfrac{50 \times 1}{500}\right] = 10^{-9} \times 500$

    $\qquad Ba^{2+} = 10^{-9} M$

    $\qquad 10^{-9} \times 500 = 450 \times M \qquad \therefore M = 1.11 \times 10^{-9}M$

3. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS^- from H_2S is 1.0×10^{-7} and that of S^{2-} from $4S^-$ ions is 1.2×10^{-13}, then find the concentration of S^{-2} ions in aqueous solution.

    Ans. $\qquad H_2S(aq.) \quad \rightleftharpoons \quad 2H^+ \quad + \quad S^{2-}$
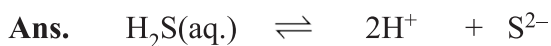
    $\qquad\qquad (0.1 - x) \qquad\quad (2x + 0.29) \qquad x$

    $\qquad K_a = K_{a_1} \times K_{a_2} = 1.2 \times 10^{-20}$

    $\qquad 1.2 \times 10^{-20} = \dfrac{(0.2)^2\left[S^{2-}\right]}{0.1}, [S^{2-}] = 3 \times 10^{-20}$

4. How many litres of water must be added to 1 litre of an aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?

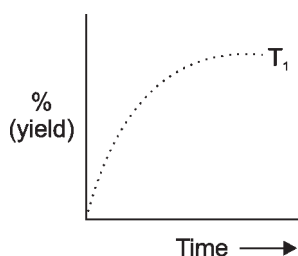   **Ans.** $0.1 \times 1 = (1 + v)(0.01) \Rightarrow v = 9L$

5. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. Find the pH of the buffer.

Ans. $k_a \cdot k_b = 10^{-14}$ $\therefore k_a = \dfrac{10^{-14}}{10^{-10}} = 10^{-4}$

$$pH = pka + \log\dfrac{[x^-]}{[Hx]}$$

$\therefore pH = 4 + \log\dfrac{1}{1} = 4$ $\therefore pH = 4$

6. The % yield of Ammonia as a function of time in the reaction $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H < O$ at (P, T) is given below:

If this reaction is conducted at $T_2 > T_1$, then plot the % yield of NH_3 as a function of time on same graph

Ans. Initially on increasing temperature the rate of reaction increases, however since the reaction is exothermic therefore % yield of NH_3 get decreased overall after a certain interval of time.
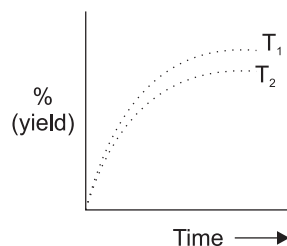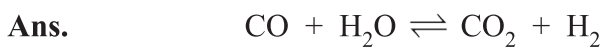

7. Consider the reaction $NH_4COONH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$ at a certain temperature, the equilibrium pressure of the system is 0.318 atm. Find K_p of the decomposition of ammonium carbonate.

Ans. $P_{total} = 3P$ $\therefore P = 0.318/3 = 0.106$

$Kp = 4P^3 = 4.76 \times 10^{-3}$

8. The equilibrium constant for the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ is 5. How many moles of CO_2 must be added to 1 litre container already containing 3 moles each of CO and H_2O to make 2M equilibrium concentration of CO?

Ans. $\qquad$ $CO + H_2O \rightleftharpoons CO_2 + H_2$

$\qquad$ **t = 0** $\quad$ 3 $\qquad$ 2 $\qquad$ x $\qquad$ 0

$\quad$ **At equilibrium** $\quad$ 2 $\qquad$ 2 $\qquad$ x+1 $\qquad$ 1

$$\therefore \ S = \frac{x+1}{4} \Rightarrow x = 19$$

9. At constant temperature, the equilibrium constant K_p

$N_2O_4 \rightleftharpoons 2NO_2$ is given by

$$k_p = \frac{4x^2 P}{1-x} \qquad \text{where, } P = \text{Pressure and } X = \text{Extent of reaction}$$

How does the value of K_p change on following changes

(a) 'P' increases

(b) X changes

(c) 'P' decreases

Ans. K_p is equilibrium constant which does not change on changing the P, x. K_p depends on temperature.

10. When two reactants A and B are mixed to give product 'c' and 'p' the reaction quotient 'Q' at the initial stages of the reaction will be?

Ans. In the beginning of the reaction Q = 0. As the reaction proceeds in the forward direction Q starts increasing.

At chemical equilibrium Q = K

UNIT TEST-I

Time Allowed: 1 Hr.   **Maximum Marks : 20**

General Instructions:

(i)   All questions are compulsory.

(ii) Maximum marks carried by each question are indicated against it.

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1. What is the pH 10^{-3} M HCl solution ?   [1]

    (a) 1   (b) 11   (c) 3   (d) 14

2. Which one can act as Arrhenius Acid ?   [1]

    (a) NH_3 (b) H_2O (c) HCl   (d) C_6H_5OH

3. Write the conjugate base of CH_3COOH, H_2O.   [1]

4. Write the relation between K_p and K_c.   [1]

5. What is the nature of following reaction   [1]

    Exothermic or endothermic

    $A + B - 70J \longrightarrow C$

6. The pka of CH_3COOH and pkb of NH_4OH are 4.76 and 4.75 respectively. Calculate the pH of CH_3COONH_4.   [2]

7. What is a buffer solution. Calculate the pH of the solution obtained by adding 4mol of CH_3COOH with 3 mol of NaOH in 1 litre container. [2]

    pka, CH_3COOH = 4.74 log2 = 0.3010 log3 = 0.4771

8. Calculate the molar solubility of $Ni(OH)_2$ in 0.1M KOH solution. The K_{sp} for $Ni(OH)_2$ is 2.0×10^{-15}.   [3]

9. K_p = 0.04 atm at 899 K for the equilibrium shown below. What is the equilibrium concentration of H_2 when it is placed in a flask at 4.0 atm pressure and allowed to come to equilibrium.   [3]

    $C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$

10. The first ionization constant of H_2S is 9.1×10^{-4}. Calculate the concentration of HS^{-1} in its 0.1 M solution. How will this concentration be effected if the solution is 0.1 M HCl also? If the second dissociation constant of H_2S is 1.2×10^{-12}. Calculate the concentration of S^{2-} in both conditions.   [5]

UNIT TEST-II

Time Allowed: 1 Hr.   **Maximum Marks : 20**

General Instructions:

(i) All questions are compulsory.

(ii) Maximum marks carried by each question are indicated against it.

1. What is the pH 10^{-8} MHCl solution ?   [1]

    (a) pH>7   (b) pH<7

    (c) pH=7   (d) Cannot be defined

2. What is the conjugate acid for the NH_3?   [1]

    (a) NH_2^- (b) NH^{2-}

    (c) N^{3-} (d) NH_4^+

3. Define Lewis acid and base with one example each.   [1]

In following questions a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and Reason both are correct statement and reason is correct explanation for assertion.

(b) Assertion and Reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

4. **Assertion :** HI is stronger acid than HCl   [1]

    Reason : Size of I is more than Cl and hence H-I bond strength is less than HCl.

5. **Assertion :** BF_3 is Lewis acid and NH_3 is Lewis base.   [1]

    Reason : NH_3 is short of octet and BF_3 molecule contain lone pair of electron.

6. Arrange the following in increasing acidic strength. Give reason also

   CH_4, NH_3, H_2O, HF [2]

7. K_c for the reaction $SO_2 + 0.5O_2 \rightarrow SO_3$ at 600°C is 61.7. Calculate K_p.   [2]

8. 25.4 ml of hydrogen and 20.4 ml of iodine when heated in a closed container, produced 30.8 mL of HI at equilibrium. Calculate the degree of dissociation of HI at same temperature.   [3]

9. Define common ion effect. The solubility of CaF_2 in water at T K is 2×10^{-4} moles/L. Calculate (i) K_{sp}, and (ii) Solubility in 0.01 M NaF solution.   [3]

10. (i) What is a buffer solution? What are its types?

    (ii) Derive the Henderson-Hasselbalch equation for an Acidic buffer with the help of relevant example.

    (ii) 8g of NaOH was dissolved in one litre of a solution containing one mole of CH_3COOH and one mole of CH_3COONa. Find the pH of the resulting solution. (The pK_a of CH_3COOH is 4.74).   [5]

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