

EQUILIBRIUM

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CONCEPTS (Chemical Equilibrium)

C1 Reaction is set to be equilibrium reaction where the rate of the forward reaction is equal to the rate of backward reaction. Chemical equilibrium at a given temperature there is a constancy of certain observable properties such as pressure, concentration and density. Chemical equilibrium can be approach from another side. A catalyst can hasten the approach of equilibrium but does not alter the state of equilibrium. Chemical equilibrium is dynamic in nature.

C2A Expression of equilibrium constant K_c and K_p :

Expression of K_c for $aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} . \text{ If any component in solid state or in excess its conc. is 1.}$$

$$K_p = \frac{[P_D]^d [P_C]^c}{[P_A]^a [P_B]^b} , P \rightarrow \text{partial pressure can be expressed as } P_A = \frac{nRT}{V} , P_A = P_T X_A$$

$X_A \rightarrow$ mole fraction

$P_T \rightarrow$ Total pressure

Practice Problems :

- K_p for the equilibrium, $FeO(s) + CO(g) \rightleftharpoons Fe(s) + CO_2(g)$ at $1000^\circ C$ is 0.4. If $CO(g)$ at a pressure of 1 atm and excess $FeO(s)$ are placed in a container at $1000^\circ C$, the pressures of $CO_2(g)$ when equilibrium is attained is
 (a) 0.714 atm (b) 2.745 atm (c) 3.222 atm (d) 4.202 atm
- One mole of hydrogen iodide is heated in a closed container of 2 litre. At equilibrium half mole of hydrogen iodide has dissociated. The equilibrium constant is
 (a) 1.0 (b) 0.5 (c) 0.25 (d) 0.75
- When S in the form of S_8 is heated at $90^\circ K$, the initial pressure of 1 atmosphere falls by 29% at equilibrium. This is because of the conversion of some gaseous S_8 to gaseous S_2 . The K_p for the reaction is
 (a) 2.55 atm^3 (b) 1 atm^3 (c) 5 atm^3 (d) 9.55 atm^3
- The equilibrium constant for the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$ at $1000K$ is 3.5. What would the partial pressure of oxygen gas have to be to give equal moles of SO_2 and SO_3 ?
 (a) 0.29 atm (b) 3.5 atm (c) 0.53 atm (d) 1.87 atm
- For the reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. The equilibrium constant $K_p = 2.9 \times 10^{-5} \text{ atm}^3$. The total pressure of gases at equilibrium when 1.0 mole of reactant was heated will be
 (a) 0.0194 atm (b) 0.0388 atm (c) 0.0580 atm (d) 0.0667 atm
- For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the relation connecting the degree of dissociation (α) of $N_2O_4(g)$ with equilibrium constant K_p is
 (a) $\alpha = \frac{K_p / p}{4 + K_p / p}$ (b) $\alpha = \frac{K_p}{4 + K_p}$
 (c) $\alpha = \left(\frac{K_p / P}{4 + K_p / P} \right)^{1/2}$ (d) $\alpha = \left(\frac{K_p / P}{4 + K_p} \right)^{1/2}$
- At temperature, T , a compound $AB_2(g)$ dissociates according to the reaction

$2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$ with a degree of dissociation x , which is small compared with unity. The expression of K_p , in terms of x and the total pressure, P is

- (a) $\frac{Px^3}{2}$ (b) $\frac{Px^2}{3}$ (c) $\frac{Px^3}{3}$ (d) $\frac{Px^2}{2}$

[Answers : (1) a (2) c (3) a (4) a (5) c (6) c (7) a]

C2B RELATION BETWEEN K_p AND K_c

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

Δn_g = moles of gaseous product - moles of gaseous reactants.

Practice Problems :

1. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at $500^\circ C$, the value of K_p is 1.44×10^{-5} when partial pressure is measured in atmosphere. The corresponding value of K_c , with concentration in mole litre⁻¹, is

- (a) $1.44 \times 10^{-5}/(0.082 \times 500)^{-2}$ (b) $1.44 \times 10^{-5}/(8.314 \times 733)^{-2}$
 (c) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$ (d) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

[Answers : (1) d]

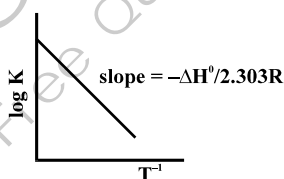
C3 FACTORS AFFECTING EQUILIBRIUM CONSTANT

1. Methods of representing the equation :

$N_2 + 3H_2 \rightleftharpoons 2NH_3$, K_c , on reversing the reaction new equilibrium constant $K'_C = \frac{1}{K_C}$

2. If a reaction is multiplied by coefficient 'n' then $K'_C = (K_C)^n$ and if reaction is divided by coefficient n then $K'_C = (K_C)^{1/n}$.

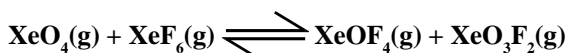
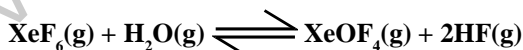
3. Effect of temperature : $K_{eq} = A_0 e^{-\Delta H/RT}$, $\log \frac{K_2}{K_1} = \frac{\Delta H}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$



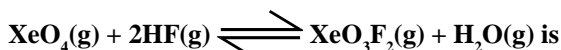
4. On adding two equilibrium reactions having equilibrium constant K_1 and K_2 then $K_3 = K_1 \times K_2$.
 5. On subtracting two equilibrium reactions then $K_3 = K_1/K_2$.

Practice Problems :

1. If K_1 and K_2 are the respective equilibrium constants for the two reactions,



The equilibrium constant for the reaction,



- (a) $K_1 K_2$ (b) K_1/K_2^2 (c) K_2/K_1 (d) K_1/K_2

2. Determine K_c for the reaction $1/2N_2(g) + 1/2O_2(g) + 1/2Br_2(g) \rightleftharpoons NOBr(g)$ from the following information (at 298 K)



- (a) 6.45×10^{-16} (b) 9.03×10^{-16} (c) 3×10^{-8} (d) 1.7×10^{-4}
3. For the reaction $2NO_2(g) + 1/2 O_2(g) \rightleftharpoons N_2O_5(g)$ if the equilibrium constant is K_p , then the equilibrium constant for the reaction.

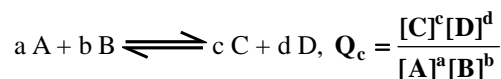


- (a) K_p^2 (b) $2/K_p$ (c) $1/K_p^2$ (d) $1/\sqrt{K_p}$

[Answers : (1) c (2) b (3) c]

C4 REACTION QUOTIENT (Q_c)

It is an expression that has the same form as the equilibrium constant expression, but all concentration values are not necessarily those at equilibrium.



- i) If $Q_c > K_c$, backward reaction takes place
 ii) If $Q_c < K_c$, forward reaction takes place
 iii) If $Q_c = K_c$, the reaction mixture is at equilibrium

Practice Problems :

1. At a certain temperature, K_c for $SO_{2(g)} + NO_{2(g)} \rightleftharpoons SO_{3(g)} + NO_{(g)}$ is 16. If we take one mole of each of all the four gases in one litre container, what would be the equilibrium concentrations of NO and NO_2 are respectively

- (a) 0.6, 0.4 (b) 1.6, 0.6 (c) 1.6, 0.4 (d) 0.4, 0.6

[Answers : (1) c]

C5 THERMODYNAMICS OF CHEMICAL EQUILIBRIUM

Spontaneous or natural process is a process that occurs in a system left to itself once started; no action from outside the system is necessary to make the process continued.

Gibbs Free Energy Change and Spontaneity :

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

For a process occurring at constant T and P, if

- (i) $\Delta G < 0$ (negative) the process is spontaneous
 (ii) $\Delta G > 0$ (positive) the process is nonspontaneous
 (iii) $\Delta G = 0$ (zero) the process is at equilibrium

Relation of ΔG^0 to the equilibrium constant K :

$$\Delta G^0 = -2.303 RT \log K$$

C6 LE-CHATELIER'S PRINCIPLE

It states that "When a system at equilibrium is subjected to some stress (such as a change in concentration, temperature, pressure) then the equilibrium adjusted itself in such a way so as to nullify the effects of the stress". With the help of this principle it is possible to predict favourable conditions for the reactions.

CONCLUSIONS

- If endothermic reaction $K_{eq} \uparrow, T \uparrow$ and $K_{eq} \downarrow, T \downarrow$
 - In exothermic reaction $K_{eq} \downarrow, T \uparrow$ and $K_{eq} \uparrow, T \downarrow$
 - If $P \uparrow$ reaction will move to that side where $V \downarrow$ i.e. where no. of mole of gaseous components is less.
 - If concentration of reactant decreases then reaction takes place in backward reaction.
- By change of conc. pressure, volume, value of K_p and K_c does not change it only changes with temperature.

Addition of an Inert Gas at Constant Volume or at Constant Pressure :

- At Constant Volume :** The addition of an inert gas at constant volume has no effect. It only increase the total pressure but does not alter the partial pressure of various species.
- At Constant Pressure :** The addition of an inert gas at constant pressure will favour the direction of reaction where total no. of moles at equilibrium show an increase.

Practice Problems :

- The equilibrium constant for the reaction, $Br_2 \rightleftharpoons 2Br$ at 500 K and 700 K and 1×10^{-10} and 1×10^{-5} respectively. The reaction is
 (a) Endothermic (b) Exothermic (c) Fast (d) Slow
- For an equilibrium reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$, $\Delta H = +ve$, an increase in temperature would cause
 (a) an increase in the value of K_{eq}
 (b) a decrease in the value of K_{eq}
 (c) no change in the value of K_{eq}
 (d) a change in K_{eq} which cannot be qualitatively predicated
- Given the following reaction at equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
 Some inert gas is added at constant volume. Predict which of the following facts will be affected ?
 (a) More of $NH_3(g)$ is produced
 (b) Less of $NH_3(g)$ is produced
 (c) No effect on the degree of advancement of the produced reaction at equilibrium
 (d) K_p of the reaction is increased.
- Predict which of the following facts for the equilibrium reaction $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ holds good ?
 (a) K_p of the reaction is changed with increase in pressure of the system
 (b) K_p of the reaction remains unaffected with increase in pressure of the system
 (c) More of $NH_3(g)$ is decreased with increase in pressure
 (d) Less of $H_2(g)$ is formed as compared to $N_2(g)$
- The oxidation of SO_2 by O_2 to SO_3 is an exothermic reaction. The yield of SO_3 will be maximum if
 (a) temperature is increased and pressure is kept constant
 (b) temperature is reduced and pressure is increased
 (c) both temperature and pressure are increased
 (d) both temperature and pressure are reduced
- For a chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of $X_3Y(g)$ at equilibrium is affected by
 (a) temperature and pressure (b) temperature only
 (c) pressure only (d) temperature, pressure & catalyst

7. When $\text{NaNO}_3(\text{s})$ is heated in a closed vessel, oxygen is liberated and $\text{NaNO}_2(\text{s})$ is left behind. At equilibrium
- addition of NaNO_2 favours reverse reaction
 - addition of NaNO_3 favours forward reaction
 - increasing temperature favours forward reaction
 - increasing pressure favours reverse reaction
8. For the gas phase reaction $\text{C}_2\text{H}_4 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H}_6$ $\Delta H = -136.8 \text{ kJ mol}^{-1}$ carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by
- increasing the temperature
 - decreasing the pressure
 - removing some H_2
 - all of above
9. PCl_5 is 50% dissociated into PCl_3 and Cl_2 at 1 atmosphere. It will be 40% dissociated at
- 1.75 atm
 - 1.84 atm
 - 2.00 atm
 - 1.25 atm
- [Answers : (1) a (2) a (3) c (4) b (5) b (6) a (7) c (8) d (9) a]

CONCEPTS (Ionic Equilibrium)

C1A Ionic equilibrium is the study of equilibrium among ions in the aqueous solution. The process of splitting of a molecules into its ions is known as ionization.

C1B There are two types of electrolytes :

- strong electrolyte : are converted into ions element completely.
- weak electrolyte : dissociation is incomplete. In aqueous solution of these compounds only slight amount of electrolyte ionises and there exist an equilibrium between ionized molecules and unionized molecules. for e.g.
 - weak acids : CH_3COOH , HCN etc.
 - weak bases : NH_4OH , $\text{C}_5\text{H}_5\text{N}$ etc.
 - weak salts : AgCl , PbCl_2 , AgCrO_4 , MnS , H_2S etc.

C1C STRENGTH OF ACIDS AND BASES AND pH SCALE

Acidic strength means the tendency of an acid to give H^+ ions in water and basic strength means the tendency of a base to give OH^- ions in water. So more the tendency to give H^+ or OH^- ions more will be the acidic or basic strength of acid or base.

$$\text{pH} = -\log[\text{H}^+]$$

$$\text{pOH} = -\log[\text{OH}^-]$$

When $[\text{H}^+]$ of a solution is more than $[\text{OH}^-]$ the solution is called to be acidic. When $[\text{H}^+]$ of a solution is less than $[\text{OH}^-]$ the solution is called to be basic. If $[\text{H}^+]$ and $[\text{OH}^-]$ of a solution are equal the solution is called neutral.

C2A SELF IONISATION OF WATER

Pure water act as a very weak electrolyte i.e. it gets ionised very weakly to give H^+ and OH^- ions, that is $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$. Now, applying law of chemical equilibrium.

$K_w = [\text{H}^+] \times [\text{OH}^-]$ where K_w is ionic product of water which is constant at constant temperature. The value of K_w is approximately 10^{-14} at 298 K.

Therefore, $[\text{H}^+] [\text{OH}^-] = 10^{-14}$ at 298 K

As water gives equal amount of H^+ and OH^- , we can say

$$[\text{H}^+] [\text{H}^+] = 10^{-14}, [\text{H}^+] = 10^{-7}, \text{pH} = 7$$

For pure water $[\text{H}^+]$ is always equal to $[\text{OH}^-]$ so it is called neutral. For acidic or basic solution the $[\text{H}^+]$ and $[\text{OH}^-]$ are not equal but their product is always equal to K_w at that temperature.

Practice Problems :1. Water has $pK_w = 13.26$ at 50°C . Its pH will be

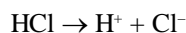
- (a) 6.0 (b) 7.0 (c) 6.63 (d) 13.26

[Answers : (1) c]

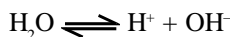
C2B COMMON ION EFFECT

If to an ionic equilibrium, we add any ion which appears in the equilibrium reaction, the equilibrium will shift in a direction opposite to that in which that ion appears.

So dissociation of weak acid and bases is suppressed in presence of strong acids and bases respectively. Similarly the solubility of salts decreases in presence of any common ion of that salt.

C2C DETERMINATION OF pH OF ACIDS AND BASES(i) **Strong Acid :** A strong acid is that which ionises completely to give maximum H^+ ions. For e.g.

Let the concentration of HCl is c . So the $[\text{H}^+]$ coming from acid is also c , but some $[\text{H}^+]$ is also coming due to self ionisation of water (say x)



$$\text{Now pH} = -\log [\text{H}^+]_{\text{total}} = -\log([\text{H}^+]_{\text{acid}} + [\text{H}^+]_{\text{water}})$$

$$\text{But } [\text{H}^+]_{\text{total}} [\text{OH}^-]_{\text{total}} = K_w$$

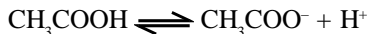
$$(c + x)(x) = K_w$$

If we know c and K_w we can calculate x .

$$\text{Now pH} = -\log(c + x)$$

But in most of the cases if c is more than 10^{-6} , the value of x will be negligible and we can take

$$\text{pH} = -\log c \quad (\text{as } x \ll c)$$

(ii) **Weak acids :** Weak acids are those which dissociates partially in water at equilibrium as

The equilibrium constant is called K_a (dissociation constant)

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

Let the $[\text{H}^+]$ coming from water is x and the degree of dissociation of weak acid is α .



initial	c	0	0
at equilibrium	$c - c\alpha$	$c\alpha$	$c\alpha$



$$K_a = \frac{\alpha \times (c\alpha + x)}{1 - \alpha} \quad \dots(i)$$

$$K_w = (c\alpha + x)(x) \quad \dots(ii)$$

Now if we know c , K_a and K_w we can calculate α and x .

$$\text{pH} = -\log [\text{H}^+]_{\text{total}} = -\log(c\alpha + x)$$

$[\text{H}^+]_{\text{water}}$ is very less (i.e. $c\alpha$ is more than 10^{-6})

$$K_a = \frac{c\alpha^2}{1 - \alpha} \quad \text{pH} = -\log(c\alpha)$$

If $\alpha \ll 1$ then $1 - \alpha \approx 1$ (i.e., if α is less than 0.1)

$$K_a = c\alpha^2 \quad \text{or} \quad \alpha = \sqrt{\frac{K_a}{c}}$$

$$\text{pH} = -\log c\alpha = -\log \left(c \times \sqrt{\frac{K_a}{c}} \right) = -\log \sqrt{K_a c}$$

pH OF BASES

The pH of bases can also be calculated as we have done for acids. In case of a base, instead of H^+ we take OH^- ions, instead of K_a we take K_b and instead of pH we calculate pOH. Then pH can be calculated as $\text{pH} = 14 - \text{pOH}$.

NOTE :

- Strong acid – $[\text{H}^+] = \text{Normality}$
- Strong Base – $[\text{OH}^-] = \text{Normality}$
- pH of mixture of strong acids / strong bases : We calculate the normality of final solution.
- pH of mixture of strong acids and strong bases : we calculate normality of final solution.
 - If equivalents of acids $>$ eq. of base. Final solution will be acidic and normality = $[\text{H}^+]$
 - If eq. of base $>$ eq. of acid. Final solution will be alkaline and normality = $[\text{OH}^-]$
 - If eq. of acid = eq. of base, final solution will be neutral and $\text{pH} = 7$ at 25°C .
- pH of weak monobasic acid or weak monoacidic base $[\text{H}^+] = \sqrt{K_a \times C}$ $[\text{OH}^-] = \sqrt{K_b \times C}$

Here $\alpha = \sqrt{K_a / C}$

- Note :
- In above formula for α , we have assumed α is very small compared to one and hence neglected compared to one.
 - In case when we use above formula and $\alpha > 0.1$, we do not apply above approximation and if $\alpha \leq 0.1$, approximation is valid.

Practice Problems :

- The pH of a solution obtained by dissolving 5×10^{-4} moles of $\text{Ca}(\text{OH})_2$ (strong electrolyte) to 100 ml solution at 298 K will be
 (a) 11 (b) 12 (c) 9.8 (d) 2
- Consider the reaction $\text{A}^- + \text{H}_3\text{O}^+ \rightleftharpoons \text{HA} + \text{H}_2\text{O}$. The K_a value for acid HA is 1.0×10^{-6} . What is the value of K for this reaction.
 (a) 1.0×10^6 (b) 1.0×10^{-8} (c) 1.0×10^8 (d) 1.0×10^{-6}
- The ionisation constant of HCO_2H is 1.8×10^{-4} . What is the percent ionization of a 0.001 M solution ?
 (a) 66% (b) 42% (c) 34% (d) 58%
- The pH of a 10^{-10} M NaOH solution is nearest to
 (a) 10 (b) 7 (c) 4 (d) -10

[Answers : (1) b (2) a (3) c (4) b]

C3 SALT HYDROLYSIS

Reaction in which cation or anion of the salt react with water to convert water acidic or basic in nature, is known as salt hydrolysis.

- | | | |
|--|---|--|
| <ol style="list-style-type: none"> Salt of a Strong Acid and Weak Base e.g. NH_4Cl
 $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4\text{OH} + \text{H}^+$
 i) $K_H = K_w / K_b$
 ii) $h = \sqrt{\frac{K_H}{c}}$ | <ol style="list-style-type: none"> Salt of Weak acid and Strong Base e.g. CH_3COONa
 $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{OH}^-$
 i) $K_H = K_w / K_a$ | <ol style="list-style-type: none"> Salt of Weak acid and Weak Base e.g. $\text{CH}_3\text{COONH}_4$
 $\text{NH}_4^+ + \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COOH} + \text{NH}_4\text{OH}$
 i) $K_H = K_w / K_a \cdot K_b$ |
|--|---|--|

iii)	$[H^+] = Ch$	ii)	$h = \sqrt{\frac{K_H}{c}}$	ii)	$h = \sqrt{K_H}$
iv)	$[H^+] = \sqrt{\frac{K_w \times c}{K_b}}$	iii)	$[H^+] = \sqrt{\frac{K_w \times K_a}{c}}$	iii)	$[H^+] = hK_a, [OH^-] = hK_b$
v)	$pH = (1/2)$	iv)	$pH = 1/2$	iv)	$[H^+] = \sqrt{\frac{K_w K_a}{K_b}}$
vi)	$[pK_w - \log c - pK_b]$. their solution is acidic $pH < 7$	v)	$(pK_w + \log c + pK_b)$ their solution is basic $pH > 7$	v)	$pH = 1/2 [pK_w + pK_a - pK_b]$ vi) solution is acidic if $K_a > K_b$ solution is basic if $K_b > K_a$. solution is neutral if $K_a = K_b$

NOTE :

- All the formulae for salt hydrolysis are for univalent salts. The term 'c' in the above equations however represents the concentration of ion that undergoes hydrolysis.
- In all the formulae mentioned above we have neglected h compared to one.

Practice Problems :

- pH of 0.01 M HS^- will be :

(a)	$pH = 7 + \frac{pK_a}{2} + \frac{\log c}{2}$	(b)	$pH = 7 - \frac{pK_b}{2} + \frac{\log c}{2}$
(c)	$pH = \frac{pK_1 + pK_2}{2}$	(d)	$pH = 7 + \left(\frac{pK_a - pK_b}{2} \right)$

- The degree of hydrolysis of anilinium acetate is
 - independent of initial concentration
 - directly proportional to initial concentration
 - inversely proportional to initial concentration
 - inversely proportional to square root of initial concentration
- The compound whose 0.1 M solution is basic is

(a) Ammonium acetate	(b) Ammonium chloride
(c) Ammonium sulphate	(d) Sodium acetate
- Which of the following when mixed, will give a solution with pH greater than 7 ?
 - 0.1 M HCl + 0.2 M NaCl
 - 100 ml of 0.2 M H_2SO_4 + 100 ml of 0.3 M NaOH
 - 100 ml of 0.1 M CH_3COOH + 100 ml of 0.1 M KOH
 - 25 ml of 0.1 M HNO_3 + 25 ml of 0.1 M NH_3

5. The correct order of increasing $[H_3O^+]$ in the following aqueous solutions is

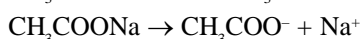
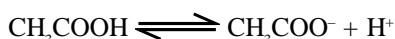
- (a) $0.01 M H_2S < 0.01 M H_2SO_4 < 0.01 M NaCl < 0.01 M NaNO_2$
 (b) $0.01 M NaCl < 0.01 M NaNO_2 < 0.01 M H_2S < 0.01 M H_2SO_4$
 (c) $0.01 M NaNO_2 < 0.01 M NaCl < 0.01 M H_2S < 0.01 M H_2SO_4$
 (d) $0.01 M H_2S < 0.01 M NaNO_2 < 0.01 M NaCl < 0.01 M H_2SO_4$

[Answers : (1) a (2) a (3) d (4) c (5) c]

C4 BUFFER SOLUTION

There are three types of buffers :

(i) **Acidic buffer** : This consists of solution of a weak acid and its conjugate base (i.e., its salt with weak or strong base). Let us consider an acid buffer containing acetic acid and sodium acetate (conjugate base is CH_3COO^-)

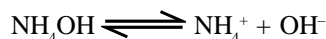
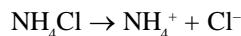


Now due to the presence of CH_3COO^- ions of salt the dissociation of CH_3COOH is suppressed due to common ion effect of CH_3COO^- ions. So we can assume that the total $[CH_3COO^-]$ is almost equal to (CH_3COO^-) from salt.

$$K_a = \frac{[CH_3COO^-]_{total}[H^+]_{total}}{[CH_3COOH]}, \quad [H^+] = K_a \frac{[CH_3COOH]}{[CH_3COO^-]}$$

$$pH = pK_a + \log \frac{[CH_3COO^-]}{[CH_3COOH]}, \quad pH = pK_a + \log \frac{[Salt]}{[Acid]}$$

(ii) **Basic buffer** : It is a solution of a weak base and its conjugate acid (salt with weak or strong acid). Let us consider a buffer containing NH_4OH and NH_4Cl

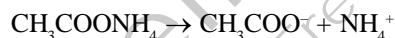


The buffer action may be explained as in the case of acid buffer. The pH is given by

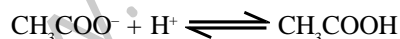
$$pOH = pK_b + \log \frac{[Salt]}{[Base]}$$

$$pH = 14 - pOH$$

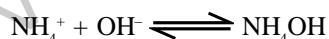
(iii) **Salt buffer** : A solution of a salt of weak acid with weak base (CH_3COONH_4) also act as a buffer.



When an acid is added to it, the H^+ combine with CH_3COO^- to give CH_3COOH .



When a base is added, the OH^- combine with NH_4^+ to give NH_4OH .



The pH of this type of solution has been discussed already in the case of hydrolysis of such salts.

Practice Problems :

- The pH of mixture of $CH_3COONa + CH_3COOH$ after adding water shows.....value.
 (a) Increased (b) Decreased (c) Constant (d) All
- A certain buffer solution contains equal concentration of X^- and HX . The K_b for X^- is 10^{-10} . The pH of the buffer is
 (a) 4 (b) 7 (c) 10 (d) 14

3. One litre of a buffer solution containing 0.01 M NH_4Cl and 0.1 M NH_4OH having pK_b of 5 has pH of
 (a) 9 (b) 10 (c) 4 (d) 6
 [Answers : (1) c (2) a (3) b]

C5 SOLUBILITY PRODUCT

Insoluble substances like AgCl , BaSO_4 , PbCl_2 , etc., are in fact not completely insoluble when present in an aqueous medium. A very small amount of these dissolves and is present as ions. Further, there exists an equilibrium between the undissolved and the dissolved salt. For AgCl , the equilibrium equation may be written as,



$[\text{AgCl}]$ is assumed to be constant because of the fact that very little of this solid dissolved in aqueous solution (by definition)

$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

NOTE :

- Let the solubility of salt of weak acid and strong base is s_1 in pure water, s_2 in basic buffer and s_3 in acidic buffer then
 $s_3 > s_1 > s_2$
- For Precipitation, $K_{sp} < K_{ip}$ [K_{ip} is the ionic product]

Practice Problems :

- K_{sp} of CaSO_4 is 4×10^{-12} . CaSO_4 is precipitated on mixing equal volumes of the following solutions :
 (a) 3×10^{-6} M CaCl_2 and 3×10^{-6} M $(\text{NH}_4)_2\text{SO}_4$
 (b) 4×10^{-6} M CaCl_2 and 3×10^{-6} M $(\text{NH}_4)_2\text{SO}_4$
 (c) 6×10^{-6} M CaCl_2 and 3×10^{-6} M $(\text{NH}_4)_2\text{SO}_4$
 (d) In all cases.
- The precipitate of Ag_2CrO_4 ($K_{sp} = 1.9 \times 10^{-12}$) is obtained when equal volumes of the following are mixed
 (a) 10^{-4} M Ag^+ + 10^{-4} M CrO_4^{2-} (b) 10^{-2} M Ag^+ + 10^{-3} M CrO_4^{2-}
 (c) 10^{-5} M Ag^+ + 10^{-3} M CrO_4^{2-} (d) 10^{-4} M Ag^+ + 10^{-5} M CrO_4^{2-}
- M(OH)_x has ($K_{sp} 4 \times 10^{-12}$) and solubility 10^{-4} M. Then the value of x is
 (a) 1 (b) 2 (c) 3 (d) - 4

[Answers : (1) d (2) b (3) b]