

ACIDS AND BASES

Topic-3

Hydrolysis of salts, buffer solutions and common ion effect and its applications and uses

VERY SHORT ANSWER QUESTIONS

1. What is Buffer solution?

Ans: A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called the **buffer solution**. It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

2. Give one example each of acid and base buffer solution?

Ans: Acid buffer solution is formed by mixing a weak acid with its salt with a strong base,

eg;



(ii) Base buffer solution is formed by mixing a weak base with its salt with a strong acid,

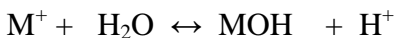
e.g;



3. Explain the hydrolysis of salt?

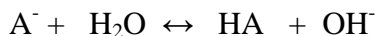
Ans: When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as **salt hydrolysis**. It is defined as **a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity**.

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.



Weak base

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.



Weak acid

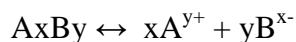
4. What is solubility product of a salt?

Ans: The equilibrium for a saturated solution of any sparingly soluble salt may be expressed as:



Thus, **solubility product**, $K_s = [A^{y+}]^x[B^{x-}]^y$

Let 's' mole per litre be the **solubility** of the salt, then



$$x s \quad y s$$

So
$$K_s = [x s]^x [y s]^y$$

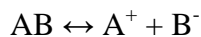
$$= x^x \cdot y^y (s)^{x+y}$$

SHORT ANSWER QUESTIONS

1. What is a common ion effect? Illustrate?

Ans: COMMON ION EFFECT:

Let AB to the weak electrolyte. Considering its dissociation,



and applying law of mass action we have

$$K = \frac{[A^+][B^-]}{[AB]}$$

The equilibrium constant, K , has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution. It will increase the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increase, i.e., the equilibrium will shift to the left hand side.

In other words, the degree of dissociation of an electrolyte (weak) is suppressed by the addition of another electrolyte (strong) containing a common ion. This is termed as common ion effect. Acetic acid is a weak electrolyte and its ionization is suppressed in presence of a strong acid (H^+ ion as common ion) or a strong salt like sodium acetate (acetate ion as common ion). Similarly, the addition of NH_4Cl or $NaOH$ to NH_4OH solution will suppress the dissociation of NH_4OH due to common ion either NH_4^+ or OH^- .

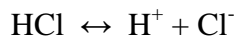
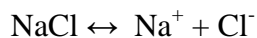
As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

2. Give any two applications of solubility product?

Applications of solubility product

(i) Purification of common salt

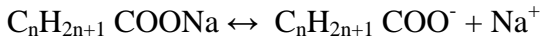
Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and $NaCl$ dissociate into their respective ions as:



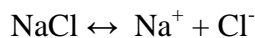
The concentration of Cl^- ions increases considerably in solution due to ionization HCl . Hence, the ionic product $[Na^+][Cl^-]$ exceeds the solubility product of sodium chloride and, therefore, pure sodium chloride precipitates out from solution.

(ii) Salting out of soap

Soap is a sodium salt of higher acids. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride. Soap and sodium chloride are present in the form of ions.



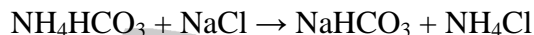
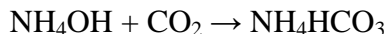
Soap



Thus, the concentration of Na^+ ions increases considerably on addition of $NaCl$ solution. Hence, the ionic product $[C_nH_{2n+1}COO^-][Na^+]$ exceeds the solubility product of soap and, therefore, soap precipitates out from the solution.

(iii) Manufacture of sodium bicarbonate (baking soda):

In Solvay's soda process. CO_2 gas is passed through ammonical brine to precipitate out $NaHCO_3$.



$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl , NH_3HCO_3 and $NaCl$.

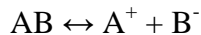
Thus, baking soda ($NaHCO_3$) can be quantitatively estimated.

LONG ANSWER QUESTIONS

1. Explain the concept of Common ion effect?

COMMON ION EFFECT:

Let AB be the weak electrolyte. Considering its dissociation,



and applying law of mass action we have

$$K = \frac{[A^+][B^-]}{[AB]}$$

The equilibrium constant, K , has a definite value at any given temperature. If now another electrolyte furnishing the A^+ and B^- ions be added to the above solution. It will increase the concentration of either A^+ ions or B^- ions (whichever has been added) and in order that K may remain constant, the concentration of AB must increase, i.e., the equilibrium will shift to the left hand side.

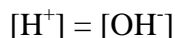
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As a result of common ion effect, the concentration of the ion not in common in two electrolytes, is decreased. The use of this phenomenon is made in qualitative analysis to adjust concentration of S^{2-} ions in second group and OH^- ion concentration in third group of analysis.

2. Explain the concept of Hydrolysis of salt?

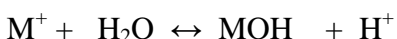
Ans: Salt Hydrolysis:

Pure water is a weak electrolyte and neutral in nature, i.e., H^+ ion concentration is exactly equal to OH^- ion concentration



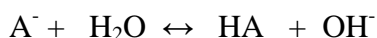
When this condition is disturbed by decreasing the concentration of either of the two ions, the neutral nature changes into acidic or basic. When $[H^+] > [OH^-]$, the water becomes acidic and when $[H^+] < [OH^-]$, the water acquires basic nature. This is exactly the change which occurs during the phenomenon known as **salt hydrolysis**. It is defined as **a reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity**.

Salts are strong electrolytes. When dissolved in water, they dissociate almost completely into ions. In some salts, cations are more reactive in comparison to anions and these react with water to produce H^+ ions. Thus, the solution acquires acidic nature.



Weak base

In other salts, anions may be more reactive in comparison to cations and these react with water to produce OH^- ions. Thus, the solution becomes basic.



Weak acid

The process of **salt hydrolysis** is actually the reverse of neutralization.



If acid is stronger than base, the solution is acidic and in case base is stronger than acid, the solution is alkaline. When both the acid and the base are either strong or weak, the solution is generally neutral in nature.

As the nature of the cation or the anion of the salt determines whether its solution will be acidic or basic, it is proper to divide the salts into four categories.

(i) Salt of a strong acid and a weak base.

Examples: FeCl₃, CuCl₂, AlCl₃, NH₄Cl, CuSO₄, etc.

(ii) Salt of a strong base and a weak acid.

Examples: CH₃COONa, NaCN, NaHCO₃, Na₂CO₃, etc.

(iii) Salt of a weak acid and a weak base.

Examples: CH₃COONH₄, (NH₄)₂CO₃, NH₄HCO₃, etc.

(iv) Salt of a strong acid and a strong base.

Examples: NaCl, K₂SO₄, NaNO₃, NaBr, etc.

3. Explain the hydrolysis of salt of strong acid and weak base?

Ans:

Salt of a strong acid and a weak base:

The solution of such a salt is acidic in nature. The cation of the salt which has come from **weak base** is reactive. It reacts with water to form a **weak base** and H⁺ ions.



Weak base

Consider, for example, NH₄Cl. It ionises in water completely into NH₄⁺ and Cl⁻ ions. ions react with water to form a **weak base** (NH₄OH) and H⁺ ions.



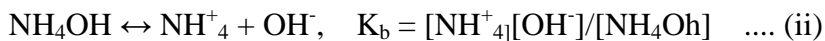
Thus, hydrogen ion concentration increases and the solution becomes acidic.

Applying law of mass action,

$$K_h = \frac{[H^+][NH_4OH]}{[NH_4^+]} = \frac{(Cx.Cx)}{C(1-x)} = \frac{(x^2 C)}{(1-x)} \quad \dots (i)$$

where C is the concentration of salt and x the degree of hydrolysis.

Other equilibria which exist in solution are



From eqs. (ii) and (iii)

$$K_w/K_b = \frac{[H^+][NH_4OH]}{[NH_4^+]} = K_h \quad \dots (iv)$$

$$[H^+] = \frac{K_w}{K_b} \times \frac{[NH_4OH]}{[NH_4^+]}$$

$$\log [H^+] = \log K_w - \log K_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$-pH = -pK_w + pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$pK_w - pH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

$$pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$$

Relation between Hydrolysis constant and Degree of hydrolysis

The extent to which **hydrolysis** proceeds is expressed as the degree of **hydrolysis** and is defined as the fraction of one mole of the salt that is hydrolysed when the equilibrium has been attained. It is generally expressed as *h* or *x*.

$$h = \frac{\text{(Amount of salt hydrolysed)}}{\text{(Total salt taken)}}$$

Considering again eq. (i),

$$K_h = \frac{x^2 C}{(1-x)} \quad \text{or} \quad K_h = \frac{h^2 C}{(1-h)}$$

When *h* is very small $(1-h) \rightarrow 1$,

$$K_h = h^2 \times C$$

$$\text{or } h = \sqrt{\frac{K_h}{C}}$$

$$= \sqrt{\frac{K_w}{K_b} \times C}$$

$$[H^+] = h \times C = \sqrt{\frac{C \times K_h}{K_b}}$$

$$\log [H^+] = 1/2 \log K_w + 1/2 \log C - 1/2 \log K_b$$

$$pH = 1/2 pK_w - 1/2 \log C - 1/2 pK_b$$

$$= 7 - 1/2 pK_b - 1/2 \log C$$

4. Explain the concept of hydrolysis of salt of weak acid and strong base?

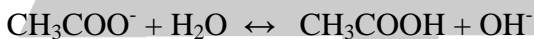
Salt of a weak acid and a Strong base:

The solution of such a salt is basic in nature. The anion of the salt is reactive. It reacts with water to form a **weak acid** and OH⁻ ions.



Weak acid

Consider, for example, the salt CH₃COONa. It ionises in water completely to give CH₃COO⁻ and Na⁺ ions. CH₃COO⁻ ions react with water to form a **weak acid**, CH₃COOH and OH⁻ ions.

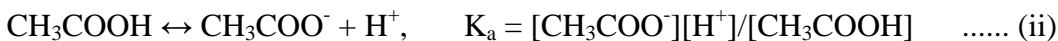


Thus, OH⁻ ion concentration increases, the solution becomes alkaline.

Applying law of mass action,

$$K_h = [CH_3COOH][OH^-]/[CH_3CO^-] = (Cx \times Cx)/C(1-x) = (Cx^2)/(1-x) \dots\dots (i)$$

Other equations present in the solution are:



From eqs. (ii) and (iii),

$$\log [OH^-] = \log K_w - \log K_a + \log [salt]/[acid]$$

$$-pOH = -pK_w + pK_a + \log [salt]/[acid]$$

$$pK_w - pOH = pK_a + \log [salt]/[acid]$$

$$pH = pK_a + \log [salt]/[acid]$$

Considering eq. (i) again,

$$K_h = cx^2/(1-x) \quad \text{or} \quad K_h = Ch^2/(1-h)$$

When h is very small, $(1-h) \rightarrow 1$

$$\text{or} \quad h^2 = K_h/C$$

$$\text{or} \quad h = \sqrt{K_h/C}$$

$$[\text{OH}^-] = h \times C = \sqrt{CK_h} = \sqrt{C \cdot K_w/K_a}$$

$$[\text{H}^+] = K_w/[\text{OH}^-]$$

$$= K_w/\sqrt{C \cdot K_w/K_a} = \sqrt{K_a \cdot K_w}/K_c$$

$$-\log [\text{H}^+] = -1/2 \log K_w - 1/2 \log K_a + 1/2 \log C$$

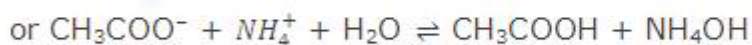
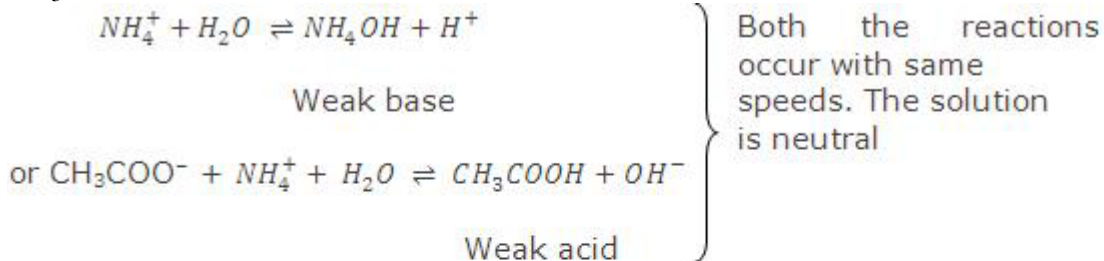
$$\text{pH} = 1/2 \text{p}K_w + 1/2 \text{p}K_a + 1/2 \log C$$

$$= 7 + 1/2 \text{p}K_a + 1/2 \log C.$$

5. Explain the concept of hydrolysis of salt of weak acid and weak base?

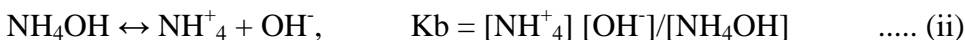
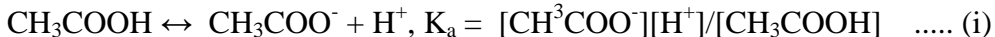
Salt of a weak acid and a weak base:

Maximum **hydrolysis** occurs in the case of such a salt as both the cation and anion are reactive and react with water to produce H^+ and OH^- ions. The solution is generally neutral but it can be either slightly acidic or slightly alkaline if both the reactions take place with slightly different rates. Consider, for example, the salt $\text{CH}_3\text{COONH}_4$. It gives CH_3COO^- and NH_4^+ ions in solution. Both react with water.



$$K_h = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]}$$

Other equilibria which exist in solution are:



From Eqs. (i), (ii) and (iii),

$$K_h = K_w/K_a \cdot K_b = \frac{[\text{CH}_3\text{COOH}][\text{NH}_4\text{OH}]}{[\text{CH}_3\text{COO}^-][\text{NH}_4^+]} \dots (iv)$$

Let C be the concentration and h be the degree of **hydrolysis**

$$K_h = h^2/(1-h)^2$$

When h is small, $(1-h) \rightarrow 1$.

$$K_h = h^2$$

$$h = \sqrt{K_h} = \sqrt{K_w/K_a \cdot K_b}$$

$$[\text{H}^+] K_a \times h$$

$$= K_a \times \sqrt{K_w/K_a \cdot K_b}$$

$$= \sqrt{K_w \cdot K_a/K_b}$$

$$-\log [\text{H}^+] = -1/2 \log K_a - 1/2 \log K_w + 1/2 \log K_b$$

$$\text{pH} = 1/2 \text{p}K_a + 1/2 \text{p}K_w - 1/2 \text{p}K_b$$

$$= 7 + 1/2 \text{p}K_a - 1/2 \text{p}K_b$$

When $\text{p}K_a = \text{p}K_b$, $\text{pH} = 7$, i.e., solution will be neutral in nature.

When $\text{p}K_a > \text{p}K_b$. The solution will be alkaline as the acid will be slightly weaker than base and pH value will be more than 7. In case $\text{p}K_a < \text{p}K_b$, the solution will be acidic as the acid is relatively stronger than base and pH will be less than 7

6. Explain the concept of buffer solutions and its preparation?

BUFFER SOLUTIONS:

For several purposes, we need solutions which should have constant pH. Many reactions, particularly the biochemical reactions, are to be carried out at a constant pH. But it is

observed that solutions and even pure water ($\text{pH} = 7$) cannot retain the constant pH for long. If the solution comes in contact with air, it will absorb CO_2 and becomes more acidic. If the solution is stored in a glass bottle, alkaline impurities dissolve from glass and the solution becomes alkaline.

A solution whose pH is not altered to any great extent by the addition of small quantities of either an acid (H^+ ions) or a base (OH^- ions) is called the **buffer solution**. It can also be defined as a solution of **reserve acidity** or **alkalinity** which resists change of pH upon the addition of small amount of acid or alkali.

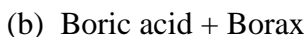
General characteristics of a buffer solution

- (i) It has a definite pH, i.e., it has reserve acidity or alkalinity.
- (ii) Its pH does not change on standing for long.
- (iii) Its pH does not change on dilution.
- (iv) Its pH is slightly changed by the addition of small quantity of an acid or a base.

Buffer solutions can be obtained:

- (i) by mixing a weak acid with its salt with a strong base,

e.g;



- (ii) by mixing a weak base with its salt with a strong acid,

e.g;



(iii) by a solution of ampholyte. The ampholytes or amphoteric electrolytes are the substances which show properties of both an acid and a base. Proteins and amino acids are the examples of such electrolytes.

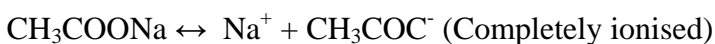
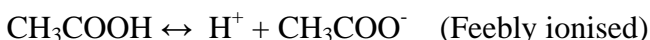
(iv) by a mixture of an acid salt and a normal salt of a polybasic acid, e.g., $\text{Na}_2\text{HPO}_4 + \text{Na}_3\text{PO}_4$, or a salt of weak acid and a weak base, such as $\text{CH}_3\text{COONH}_4$.

The first and second type is also called acidic and basic buffers respectively.

Explanation of buffer action

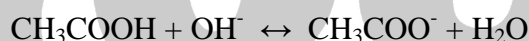
(i) Acidic buffer:

Consider the case of the solution of acetic acid containing sodium acetate. Acetic acid is feebly ionised while sodium acetate is almost completely ionised. The mixture thus contains CH_3COOH molecules, CH_3COO^- ions, Na^+ ions, H^+ ions and OH^- ions. Thus, we have the following equilibria in solution:



When a drop of strong acid, say HCl, is added, the H^+ ions furnished by HCl combine with CH_3COO^- ions to form feebly ionised CH_3COOH whose ionisation is further suppressed due to common ion effect. Thus, there will be a very slight effect in the overall H^+ ion concentration or pH value.

When a drop of NaOH is added, it will react with free acid to form undissociated water molecules.



Thus, OH^- ions furnished by a base are removed and pH of the solution is practically unaltered.

(ii) Basic buffer:

Consider the case of the solution containing NH_4OH and its salt NH_4Cl . The solution will have NH_4OH molecule, ions, Cl^- ions, OH^- ions and H^+ ions

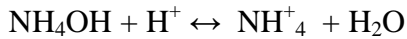


When a drop of NaOH is added, the added OH^- ion combine with NH_4^+ ions to form feebly ionised NH_4OH whose ionisation is further suppressed due to common ion effect. Thus pH is not disturbed considerably.



(From strong base)

When a drop of HCl is added, the added H^+ ions combine with NH_4OH to form undissociated water molecules.



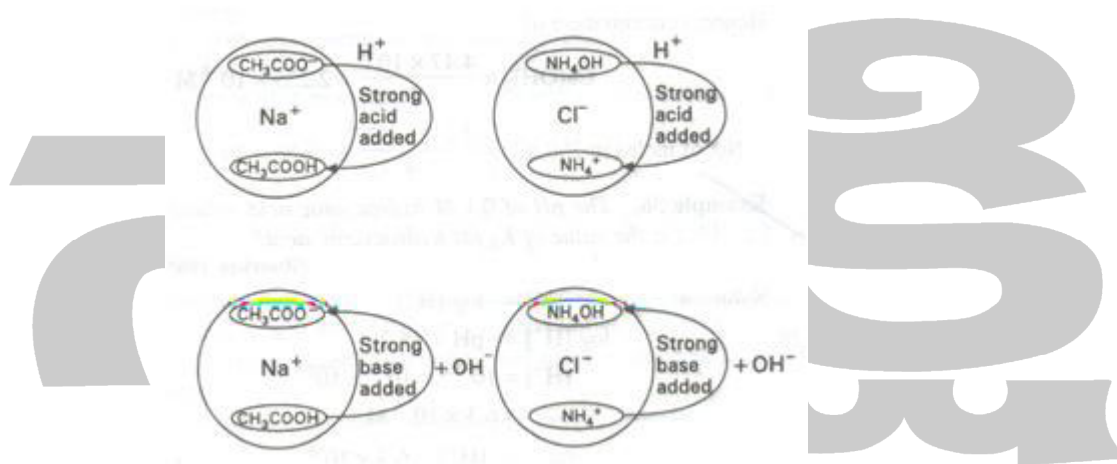
(From strong acid)

Thus pH of the buffer is practically unaffected.

Diagrammatic Representation of Buffer Action

Acid Buffer ($CH_3COOH + CH_3COONa$)

Base Buffer ($NH_4OH + NH_4Cl$)



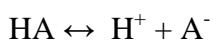
7. Explain the Henderson's equation of P^H of buffer?

Ans:

Henderson's Equation (pH of a buffer):

(i) Acidic buffer:

It consists of a mixture of weak acid and its salt (strong electrolyte). The ionisation of the weak acid, HA, can be shown by the equation



Applying law of mass action,

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

It can be assumed that concentration of A^- ions from complete ionisation of the salt BA is too large to be compared with concentration of A^- ions from the acid HA .



Thus, $[HA]$ = Initial concentration of the acid as it is feebly ionised in presence of common ion

and $[A^-]$ = Initial concentration of the salt as it is completely ionised.

$$\text{So } [H^+] = K_a \cdot \frac{[\text{Acid}]}{[\text{Salt}]} \quad \dots\dots \text{(iii)}$$

Taking logarithm and reversing sign,

$$-\log [H^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\text{or } \text{pH} = \log \frac{[\text{Salt}]}{[\text{Acid}]} - \log K_a$$

$$\text{or } \text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \quad \dots\dots \text{(iv)}$$

This is known as Henderson's equation.

When $\frac{[\text{Salt}]}{[\text{Acid}]} = 10$, then

$$\text{pH} = 1 + \text{p}K_a$$

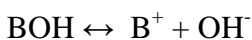
and when $\frac{[\text{Salt}]}{[\text{Acid}]} = 1$, then

$$\text{pH} = \text{p}K_a - 1$$

So weak acid may be used for preparing buffer solutions having pH values lying within the ranges $\text{p}K_a + 1$ and $\text{p}K_a - 1$. The acetic acid has a $\text{p}K_a$ of about 4.8; it may, therefore, be used for making buffer solutions with pH values lying roughly within the ranges 3.8 to 5.8.

(ii) Basic offer:

It consists of a weak base and its salt with strong acid. Ionization of a weak base, BOH , can be represented by the equation.



Applying law of mass action,

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad \dots\dots (i)$$

$$\text{or } [OH^-] = K_b \frac{[BOH]}{[B^+]} \quad \dots\dots (ii)$$

As the salt is completely ionized, it can be assumed that whole of B^+ ion concentration comes from the salt and contribution of weak base to B^+ ions can be ignored.



$$\text{So } [OH^-] = K_b \frac{[\text{Base}]}{[\text{Salt}]} \quad \dots (iii)$$

$$\text{or } pOH = \log \frac{[\text{Salt}]}{[\text{Base}]} - \log K_b$$

$$\text{or } pOH = pK_b + \log \frac{[\text{Salt}]}{[\text{Base}]} \quad \dots\dots (iv)$$

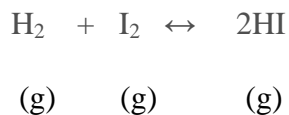
Knowing pOH, pH can be calculated by the application of the formula.

$$pH + pOH = 14$$

NUMERICALS

The value of K_p , if the value of K_c is 2×10^{-3} for $H_2(g) + I_2(g) \leftrightarrow 2HI(g)$ at $27^\circ C$

Sol: $K_p = K_c [RT]^{\Delta n}$



$$\Delta n = [(\text{no. of moles of gaseous products}) - (\text{no. of moles of gaseous reactants})]$$

$$= [2 - (1+1)]$$

$$= 2 - 2$$

$$\Delta n = 0$$

If $\Delta n = 0$ then, $K_p = K_c$

$$\text{Given } K_c = 2 \times 10^{-3}$$

$$\therefore K_p = 2 \times 10^{-3}$$

4. How many grams of NaOH are present per litre if the pH of NaOH solution is 10 ?

Sol: ∴ The Ph Value of NaOH is = 10
∴ $pOH = 14 - 10 = 4$ ($pH + pOH = 14$)
∴ $[OH] = 10^{-4} N$
∴ Normality (N) = $10^{-4} N$
∴ Weight of NaOH = Normality x eq. wt
= $10^{-4} \times 40$
= 4×10^{-3} grams

5. What is the P^H of 0.1 M NaOH ?

Sol: Molarity of NaOH = $0.1 = 10^{-1}$
Since $NaOH \rightarrow Na^+ + OH^-$

∴ $[OH] = 10^{-1}$

$p^{OH} = -\log [10^{-1}] = 1$

$p^{OH} = 1$

$p^H = 14 - p^{OH}$

= $14 - 1$

= 13

6. Find the pH of 0.05 M Ba (OH)₂ aqueous solution?

Sol: Since $Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$

∴ $[OH^-] = 2[Ba(OH)_2]$

$$\begin{aligned}
 &= 2 \times 5 \times 10^{-2} \\
 [\text{OH}^-] &= 10 \times 10^{-2} = 10^{-1} \\
 \text{p}^{\text{OH}} &= -\log [\text{OH}^-] \\
 &= -\log [10^{-1}] \\
 \text{pOH} &= 1 \\
 \text{p}^{\text{OH}} &= 14 - \text{p}^{\text{H}} \\
 &= 14 - 1 \\
 \text{p}^{\text{H}} &= 13
 \end{aligned}$$

7. Find the p^H of 10⁻⁸ M HCL solution?

Sol: The given acid solution is very dilute. Hence the H⁺ obtained from the acid and water must be taken into consideration.

H⁺ Ion concentration of acid is 10⁻⁸ M

H⁺ Ion concentration of water is 10⁻⁷ M

Total [H⁺] = 10⁻⁸ + 10⁻⁷ = 1.1 × 10⁻⁷ or 1.1 × 10⁻⁷ M

$$\therefore \text{p}^{\text{H}} = -\log 1.1 \times 10^{-7}$$

$$= 7 - \log 1.1 = 7 - 0.0414 = 6.9586$$

8. 0.1825% HCL solution would have a p^H of -----?

Sol: 0.1825% HCL solution means 100 ml solution contain 0.1825 g. of HCL

$$\text{Normality (N)} = \frac{W}{EW} \times \frac{1000}{V} \times \frac{0.1825}{36.5} \times \frac{1000}{100} = 0.05\text{N}$$

$$\therefore [\text{H}^+] = 0.05\text{N}$$

$$\therefore p^H = -\log [H^+] = -\log [0.05] = -\log [5 \times 10^{-2}] = 2 - \log 5 = 2 - 0.692$$

$$\therefore p^H = 1.308$$

9. The p^H of solution is 5.4 . What is the hydrogen ion concentration?

Sol: $p^H = -\log [H^+]$

$$\Rightarrow [H^+] = 10^{-p^H}$$

$$= 10^{-5.4}$$

$$= 10^{-6+0.6}$$

$$= \text{Antilog } (0.6) \times 10^{-6}$$

$$= 3.981 \times 10^{-6} \text{ moles/litre}$$

10. 50 ml of 0.2 NH_2SO_4 were added to 100 ml of 0.2 N HNO_3 . Then the solution is diluted to 300 ml. What is the p^H of the solution?

Sol: $N = [H^+] = \frac{(50 \times 0.2) + (100 \times 0.2)}{300}$

$$= \frac{10 + 20}{300}$$

$$= \frac{30}{300} = 0.1 \text{ N}$$

$$[H^+] = 0.1 \text{ N} = 10^{-1} \text{ N}$$

$$p^H = -\log [H^+]$$

$$= -\log [10^{-1}]$$

$$= 1$$

$$\therefore p^H = 1$$

11 At a certain temperature, the ionic product of H_2O is 9.55×10^{-14} moles²/lit². Then what is the of the p^H solution?

Sol: Since $K_w = [H^+] [OH^-]$

$$K_w = 9.55 \times 10^{-14} \text{ moles}^2/\text{lit}^2$$

$$[H^+] [OH^-] = 9.55 \times 10^{-14} \text{ moles}^2/\text{lit}^2$$

$$\therefore [H^+] = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7} \text{ moles}^2/\text{lit}^2$$

$$p^H = -\log [H^+] = -\log [3.09 \times 10^{-7}]$$

$$= -[\log 3.09 + \log 10^{-7}]$$

$$= -[0.49 - 7]$$

$$p^H = 7 - 0.49 = 6.51$$

12. The K_a for a 0.2M $CH_3 COOH$ is 2×10^{-5} what is its p^H ? (Assume $CH_3 COOH$ as a strong acid)

Sol: Given that $CH_3 COOH$ is strong acid. So, complete ionisation takes place.



$$0.2M \qquad \qquad 0.2M$$

$$[H^+] = 0.2 M = 2 \times 10^{-1} M$$

$$p^H = -\log [H^+] = -[2 \times 10^{-1}] = 1 - \log 2 = 1 - 0.3010 = 0.6990$$

13. Find the p^H of 0.5 M NH_4OH solution. K_b for NH_4OH is 2×10^{-5} (If NH_4OH is assumed as a strong base.)?

Sol: Given that NH_4OH is strong base. So, complete ionisation takes place.



$$0.5 \text{ M} \quad 0.5 \text{ M}$$

$$[\text{OH}^-] = 0.5 \text{ M} = 5 \times 10^{-1} \text{ M}$$

$$\text{pOH} = -\log [\text{OH}^-] = -\log [5 \times 10^{-1}] = 1 - \log 5 = 1 - 0.6989 = 0.3011$$

$$\text{p}^{\text{H}} = 14 - \text{pOH} = 14 - 0.311 = 13.69$$

14. What is the pH of HCl solution containing 3.65g in 250 ml?

$$\text{Sol: Molarity of HCl} = \frac{\text{Weight of HCl}}{\text{Molecular weight}} \times \frac{1000}{250}$$

$$= \frac{3.65}{36.5} \times \frac{1000}{250} = 0.4 \text{ M}$$

Since HCl is strong acid $[\text{H}^+] = 0.4 \text{ M}$

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

$$= -\log [0.4]$$

$$= -\log [4 \times 10^{-1}]$$

$$= 1 - \log 4$$

$$= 1 - 0.6020$$

$$= 0.398 (\approx 0.4)$$

15. A litre of buffer solution contains 0.1 mole of acetic and 1 mole of sodium acetate. Find its p^{H} if pK_a at $\text{CH}_3\text{COOH} = 4.8$. ?

$$\text{Sol: For an acid buffer } \text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$\begin{aligned}
 \text{p}^{\text{H}} &= 4.8 + \log \frac{1}{0.1} \\
 &= 4.8 + \log 10 \\
 \text{p}^{\text{H}} &= 4.8 + 1 \\
 \Rightarrow \text{p}^{\text{H}} &= 5.8
 \end{aligned}$$

16. 20ml of 0.2 M CH₃ COOH and 20 ml of 0.4M sodium acetate were mixed together to form a buffer. What is the p^H? (CH₃ COOH has pK_a of 4.8)

Sol: For an acid buffer $\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$

$$\text{p}^{\text{H}} = \text{pK}_a + \log x \frac{20 \times 0.4}{20 \times 0.2}$$

$$\begin{aligned}
 \Rightarrow \text{p}^{\text{H}} &= 4.8 + \log 2 \\
 &= 4.8 + 0.3010 \\
 &= 5.1
 \end{aligned}$$

17. Find the hydrolysis constant at 0.1M sodium acetate K_a of CH₃ COOH = 2 x 10⁻⁵.

Sol: The hydrolysis constant $K_h = \frac{K_w}{K_a}$

$$\Rightarrow K_h = \frac{1 \times 10^{-14}}{2 \times 10^{-5}}$$

$$2 \times 10^{-5}$$

$$\Rightarrow K_h = 0.5 \times 10^{-9}$$

$$\Rightarrow K_h = 5 \times 10^{-10}$$

18. What is the p^H of a buffer formed by mixing 20 ml of 0.1 M NH_4Cl and 2 ml of 0.1 M NH_3 ? pK_b for $NH_4OH = 4.8$.

Sol: For a basic buffer $pH = pK_w \left\{ pK_b + \log \frac{[\text{salt}]}{[\text{acid}]} \right\}$

$$pH = 14 - 4.8 - \log x \frac{20 \times 0.1}{2 \times 0.1}$$

$$= 14 - 4.8 - \log \frac{0.090}{0.0090}$$

$$= 9.2 - \log 10$$

$$= 9.2 - 1$$

$$= 8.2$$

19. The hydrolysis constant for NH_4Cl solution is 0.5×10^{-9} . Then what is the dissociation constant of the base ?

Sol: The hydrolysis constant $K_h = \frac{K_w}{K_a}$

$$\Rightarrow K_b = \frac{K_w}{K_h}$$

$$= \frac{1 \times 10^{-14}}{0.5 \times 10^{-9}}$$

$$K_a = 2 \times 10^{-5}$$

Dissociation constant of NH_4OH is 2×10^{-5}

20. The dissociation constants of NH_4OH and CH_3COOH are 2×10^{-5} and 1.8×10^{-5} respectively. Find the hydrolysis constant of ammonium acetate?

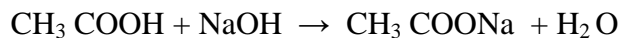
Sol: Since ammonium acetate is a salt of weak acid and weak base $K_h = \frac{K_w}{K_a K_b}$

$$K_h = \frac{1 \times 10^{-14}}{2 \times 10^{-5} \times 1.8 \times 10^{-5}}$$
$$= \frac{1 \times 10^{-14}}{2 \times 1.8 \times 10^{-10}}$$
$$= 0.277 \times 10^{-4}$$

$$K_h = 2.77 \times 10^{-5}$$

21. 50 ml of 1 M CH_3COOH solution, when added to 50 ml of 0.5 M NaOH gives a solution with pH value 'X'. Find the value of 'X' ($\text{p}K_a$ of $\text{CH}_3\text{COOH} = 4.8$)

Sol: Acetic acid reacts with sodium hydroxide to form sodium acetate.



$$\text{No. of millimoles of } \text{CH}_3\text{COOH} = 50 \times 1 = 50$$

$$\text{No. of millimoles of } \text{NaOH} = 50 \times 0.5 = 25$$

$$\text{No. of millimoles of } \text{CH}_3\text{COOH} \text{ remained unreacted} = 50 - 25 = 25$$

Total Vol. of solution = 50 + 50 = 100ml

No. of millimoles of CH_3COONa formed = 25

$$\therefore \text{Molarity of } \text{CH}_3\text{COONa} = \frac{25}{100} = .25\text{M}$$

$$\text{Molarity of } \text{CH}_3\text{COOH} = \frac{25}{100} = .25\text{M}$$

$$\text{pH} = \text{pK}_a + \log \frac{[\text{salt}]}{[\text{acid}]}$$

$$= 4.8 + \log \frac{.25}{.25} = 4.8 + \log (1)$$

$$\therefore \text{pH of solution} = 4.8 + 0 = 4.8$$

22. What is the pH of solution formed by mixing 50ml 1 M HCl and 50ml 0.1M NaOH?

Sol: $N_a V_a = 50 \times 1 = 50$

$$N_b V_b = 50 \times 0.1 = 5$$

$$\therefore N_a V_a > N_b V_b$$

$$[\text{H}^+] = \frac{N_a V_a - N_b V_b}{V_a + V_b} = \frac{50 - 5}{100} = \frac{45}{100}$$

$$[\text{H}^+] = 4.5 \times 10^{-1}$$

$$\begin{aligned} \text{pH} &= -\log [\text{H}^+] = -\log [4.5 \times 10^{-1}] \\ &= 1 - \log 4.5 \\ &= 0.35 \end{aligned}$$

23. 0.005 M monobasic acid has a pH of 5. What is the degree of dissociation?

Sol: $\text{pH} = 5$

$$\therefore [\text{H}^+] = 10^{-5}$$

Concentration (C) = 0.005 M = 5×10^{-3} M

$$[\text{H}^+] = C \alpha$$

α = degree of dissociation per mole = ?

$$\therefore \alpha = \frac{[\text{H}^+]}{C} = \frac{[\text{H}^+]}{5 \times 10^{-3}} = \frac{10^{-5}}{5 \times 10^{-3}} = \frac{1}{5} \times 10^{-2} = 0.2 \times 10^{-2}$$

Percentage of degree of dissociation = $0.02 \times 10^{-2} \times 100 = 0.2 \%$