**3.4Dissociation of Water (Ionic Product of water):**

The nature of water is ampholyte i.e., it can behave as an acid (donation of H+ ions) and base (Acceptance as H+ ions). This type of behavior is due to its ionization to form protons and hydroxyl ions.

The ionization of water is represented as:

H2O ⇌ H+ + OH-

By applying the law of ionic equilibrium, we get

K= [H+] [OH-]

[H2O]

Since dissociation of water takes place to a small extent, the concentration of undissociated water is nearly constant and is equal to 55.5 moles/litre.

Therefore, K= [H+] [OH-]

Constant

K x Constant = [H+] [OH-] OR

Kw = [H+] [OH-]

Where, Kw is the ionic product of water and defined as the product of the concentration of [H+] and [OH-] ions. The value of ionic product of water depends on temperature and found to be 1 x 10-14moles/litre at 25ºC.

**3.5 Dissociation of weak Acid:**

Consider an acid HA which when dissolved in water ionizes as below;

HA ⇌ H+ + A-

Applying the law of mass of action, to this equilibrium,

Ka= [H+] [A-]

[HA]

Where ka is the dissociation constant of the acid. Ka is directly proportional to H+ ion concentration, hence greater the dissociation constant of an acid, greater will be the H+ ion concentration in the solution of HA and hence more will be its acidity.

If c is the molarity of the acid and α is its degree of dissociation, then

HA ⇌ H+ + A-

Initial conc. C 0 0

Equilibrium conc. C (1- α) c α c α

At equilibrium,

Concentration of H+ = [H+] = c α

Concentration of A- = [A-] = c α

Concentration of HA = [HA] = C (1- α)

Substituting the concentration terms in equation

Ka = c α x c α/ C (1- α) = c α2/1- α

This equation is called as Ostwald dilution law equation. In case of weak acids, the degree of dissociation (α) is very small, therefore (1- α) taken as 1.

Therefore, ka = c α2

α =

since, [H+] = c α = C =

With the help of this equation, we can calculate hydrogen ion concentration of aqueous solution of acids whose dissociation constants are known.

**3.6 Dissociation of weak Base:**

Dissociation of a base can be represented as;

BOH ⇌ B+ + OH-

Initial conc. C 0 0

Equilibrium conc. C (1- α) c α c α

Kb = [B+] [OH-]

[BOH]

Kb== c α2/1- α

Where Kb is the dissociation constant, c is the molarity and α is the degree of dissociation of the base. Kb is a characteristic of the individual base, greater the value of kb, stronger will be the base.

In case of weak base, (1- α) is equal to 1.

Therefore, kb = c α2

α =

since, [OH-] = c α

[OH-] = c α = C =

**3.7 The pH Scale (Expressing Hydrogen ion concentration):**

In pure water concentration of H+ ions and concentration of OH- ions are equal. When small amount of acid is added in pure water then concentration of H+ ions increses than the concentration of OH- ions and solution becomes acidic. Simillarly, when small amount of alkali is added in pure water then concentratio of OH-ions increses and solution becomes alkaline or basic.

Thus H+ ions concentration is used to determine the acidity or alkalinity of solution.

pH is defined as the negative logarithm of to the base 10 of hydrogen ion concentration.

pH = -log10[H+]

similarly pOH of solution also used to indicate the hydroxyl ion concentration of solution. pOH is defined as negative logarithm to the base 10 of hydroxyl ion concentration.

pOH= -log10[OH-]

The ionic product of water Kw is also expressed in the form of logarithmic expression as,

pKw= -log Kw

since, Kw = [H+] [OH-]

= 1 x 10-14

taking logarothm of both sides of the equation and changing the signs os both sides of equation, we get

-log Kw = (-log [H+] ) + (-log [OH-])

pKw = pH + pOH = 14 at 25ºC.

the sum of pH and pOH is equal to 14 water and any aqueous solution at 25ºC.

similarly, the ionization constants of weak acids and weak bases are calculated by following expressions;

pKa = -log Ka and

pKb = -log Kb

**3.8 Common ion effect:**

It is defined as the suppression of dissociation of weak electrolyte by addition of strong electrolyte having some common ion is known as common ion effect.

E.g. degree of dissociation of ammonium hydroxide decreases in the presence of ammonium chloride,

NH4OH ⇌ NH4+ + OH-

NH4Cl → NH4+ + Cl-

Common ion

According to **Le-Chatelier principle**, because of the presence of common ion, degree of dissociation of NH4OH decreses.

Common ion effect is used in,

1. Purification of common salt

2. Salting out soap

3. Qualitative analysis

**3.9 Buffer Solution:**

**Solution which resists the change in pH value by addition of small amount of acid or base is called buffer solution.**

There are three types of buffer solutions; i) acidic buffer and ii) basic buffer iii) Neutral buffer.

**i) Acidic buffer:** acidic buffer is prepared by dissolving weak acid and its salt with strong base in water.

e.g. CH3COOH + CH3COONa

**ii) Basic Buffer**: basic buffer is prepared by dissolving weak base in its strong acid in water.

e.g. NH4OH + NH4Cl

**iii) Neutral Buffer:**

it is prepared by dissolving a salt of weak acid and weak base in water.

e.g. CH3COONH4

**3.9.1 Mechanism of Acidic Buffer:**

Consider the acidic buffer CH3COOH + CH3COONa which dissociates as

CH3COOH ⇌CH3COO- + H+

CH3COONa → CH3COO- + Na+

In this buffer solution, concentration of CH3COO- ions is large.

**i. when strong acid HCl is added to this buffer solution it dissociates completely as:**

HCl → H+ + Cl-

Here due to added H+ions, pH may change. But according to Le-Chatelier principle equilibrium shifts to the left i.e. H+ ions combine with CH3COO- ions to form undissociated CH3COOH and pH remains constant.

CH3COO- + H+ → CH3COOH

This resistance ton change in pH of buffer solution by addition of small amount of strong acid is called reserve basicity due to CH3COO- ions.

**ii) when strong base NaOH is added in this buffer solution it dissociates completely as:**

NaOH → Na+ + OH-

Her due to added OH- ions pH may change but OH- ions combine with CH3COOH to form CH3COO- ions.

CH3COOH + OH- → CH3COO- + H2O

Thus OH- ions are neutralized and pH of buffer solution do not change.

This resistance to change in pH of buffer solution by addition of small amount of strong base is called reserve acidity due to CH3COOH.

**3.9.2 Mechanism of Basic Buffer:**

Consider basic buffer NH4OH + NH4Cl is dissolved in water, then components of buffer dissociates as:

NH4OH ⇌ NH4+ + OH-

NH4Cl →NH4+ + Cl-

In this buffer solution concentration of NH4+ ions is large.

**i) when strong acid HCl is added in this buffer solution it disssociates completely as,**

HCl → H+ + Cl-

Here due to H+ ions, pH may change but NH4OH from buffer combines with H+ ions i.e. H+ ions are neutralised and pH do not changes.

NH4OH + H+ → NH4+ + H2O

This resistance to change in pH of buffer solution by addition of small amount of strong acid is called reserve basicity due toNH4OH.

**ii) When strong base (NaOH) is added in this buffer solution itdissociates completely as:**

NaOH → Na+ + OH-

Here due to OH- ions pH may change but OH- ions combine with NH4+ ions to form undissociated NH4OH and pH do notchange.

NH4+ + OH-→ NH4OH

This resistance to change in pH of buffer solution by addition of small amount of strong base is called reserve acidity due toNH4 ions.

**3.9.3 Henderson-Hasselbalch Equation for buffer solution:**

The equimolar mixture of weak acid its salt (acidic buffer) in aqueous solution they dissociate as:

HA ⇌ H+(aq) +A-(aq) (1)

Weak base equilibrium lies to the left due to common ion effect, hence [HA] = [acid]

NaA →Na+ + A- (2)

Applying law at equilibrium to equation (1) as:

Ka = [H+] [A-]/[HA] (3)

Therefore, [A-] = [Salt ], and salt is completely dissociated, hence equation (3) becomes,

Ka = [H+] [NaA]/[HA] = [H+][Salt]/[Acid] (4)

By rearranging equation (4), we get

[H+] = Ka[Acid]/[Base] (5)

By taking negative logarithm of both side of equation (5), we get

-log[H+] = -logKa – log [Acid]/[Base]

pH=PKa + log [salt]/[acid] (6)

This equation is known as Henderson – Hasselbalch equation of acidic buffer used to calculate the pH buffer solution.

Similarly, to calculate pOHof basic buffer theHenderson – Hasselbalch equation is as follows.

pOH= PKb + log [Salt]/[Acid] (7)

**3.9.4Properties of Buffer Solution:**

i. The pH of buffer solution is definite.

ii. The pH of buffer solution does not change when solution is stored for longer time.

iii. The pH of buffer solution does not change by addition of small quantity of acid or base.

iv. The pH of buffer solution does not change when diluted with water.

**3.9.5Applications of Buffer Solution:**

1. Buffer solution present in human blood maintains pH of bloodabout 7.4.

2. Buffer solution present in milk maintains constant pH of milk.

3. Buffer solutions are used as preservatives for food material like;

jams, jellies.

4. Buffer solutions are used for precipitation of basic radicals in qualitative analysis.

5. Buffer solutions are used in different processes in industries like paper industry, leather industry.

**Example:**Calculate the pH and pOH of 0.001 M H2SO4 solution

Solution: the concentration of H2SO4 solution is 0.001 M

H2SO4 is completely dissociated therfore hydrogen ion in solution i.e. [H+] = 0.001 mol lit -1

pH = -log [H+] = - log 0.001 = 3

∴pOH = 14 – pH = 14-3 = 11

**3.10 Hydrolysis of Salt:**

**The reaction between salt and water to produce acidic or basic solution is called as hydrolysis**.

i.e. salt + water ⇌ Acid + Base

BA + H2O ⇌ HA + BOH

**3.10.1 Types of salts:**

Salts are classified into four types depending upon hydrolysis reaction.

1. salts of strong acid and strong base:

e.g. NaCl, NaNO3, Na2SO4, KCl, KNO3, K2SO4, etc.

2. salts of strong acid and weak base:

e.g. CuSO4, FeCl3, NH4Cl, NH4NO3, etc.

3. salt of weak acid and strong base:

e.g. HCOONa, HCOOK, CH3COONa, CH3COOK, Na2CO3, etc.

4. salt of weak acid and weak base:

e.g. HCOONH4, CH3COONH4, (NH4)2CO3, etc.

**3.11Hydrolysis of different types of salts:**

**3.11.1 Hydrolysis ofsalts of strong acid and strong base:**

This types of salts does not undergo hydrolysis. e.g. sodium chloride (NaCl) is dissolved in water.

NaCl + H2O ⇌ NaOH + HCl

Strong Base Strong Acid

By ionic theory, NaCl, HCl dissociates completely because they are strong electrolytes.

Na+ + Cl- + H2O ⇌ Na+ + OH- + H+ + Cl-

By cancelling common ions

H2O ⇌ H+ + OH-

In The aqueous solution of this salt, cation or anion of salt do not react with water. Therefore, solution contains equal concentration of H+ ions and OH- ions and solution remains neutral (pH= 7).

Hence this type of salts does not undergo hydrolysis.

**3.11.2 Hydrolysis of salts of strong acid and weak base:**

When this type of salts (e.g. NH4Cl) is dissolved in water.

NH4Cl + H2O ⇌ NH4OH + HCl

Weak base strong acid

By ionic theory, the salt NH4Cl and strong acid HCl dissociates completely.

NH4+ + Cl- + H2O ⇌ NH4OH + H+ Cl-

By cancelling common ions

NH4+ + H2O ⇌ NH4OH + H+

In this salt solution excess H+ ions are present and solution remains acidic (pH <7).

Salts liker CuSO4, FeCl3 when dissolved in water, forms turbid solutions.

Hydrolysis of CuSO4 takes place as

CuSO4 + 2H2O ⇌ Cu(OH)2 + H2SO4.

By ionic theory the salt CuSO4 and strong acid H2SO4 dissociate completely as

Cu++ + SO4-- + 2H2O ⇌ Cu(OH)2 + 2H+ + SO4—

By cancelling common ions

Cu++ + 2H2O ⇌ Cu(OH)2 + 2H+

In this solution, insoluble weak base Cu(OH)2 is formed, therefore solution becomes turbid.

When small quantity of sulphuric acid is added in the above solution it reacts with Cu(OH)2 and favours reverse reaction then the solution of CuSO4 becomes clear.

Cu(OH)2 + H2SO4→ CuSO4 + 2H2O

**3.11.3Hydrolysis of salts of weak acid and strong base:**

When this type of salts (e.g. CH3COONa) is dissolved in water.

CH3COONa + H2O ⇌ CH3COOH + NaOH

weak acid strong base

By ionic theory salt CH3COONa and strong base dissociate completely as:

CH3COO- + Na+ + H2O ⇌ CH3COOH + Na+ OH-

By cancelling common ions:

CH3COO- + H2O ⇌ CH3COOH + OH-

In this salt solution excess, OH- ions are present and therefore solution remains basic (pH >7).

**3.11.4Hydrolysis of salts of weak acid and weak base:**

When this type of salt (e.g. CH3COONH4) is added in water.

CH3COONH4 + H2O ⇌ CH3COOH + NH4OH

Weak acid weak base

By ionic theory only the salt CH3COONH4 dissociates completly as:

CH3COO- + NH4+ + H2O ⇌ CH3COOH + NH4OH

In this salt solution neither H+ ions nor OH- ions are present and therefore solution remains neutral (pH = 7).

However solution of this type of salt is slightly acidic or slightly basic and it depents uopn strnth odf weak acid or weak base.

**3.12 Degree of Hydrolysis:**

The fraction of toatal numberof moles of the salt hydrolysed at equilibrium at a given temperature is called degree of hydrolysis.

It is denited by symbol ‘h’.

Degree of hydrolysis (h) = number of moles of salt hudrolysed at equlibrium/total number of moles dissolved

Percentage hydrolysis = 100 x h

**Degree of hydrolysis of salts depends upon,**

1. Nature of salt
2. Temperature and
3. Concentration of solution

**3.12.1 Hydrolysis constant:**

The equlibrium constant obtained by applying law of mass action to the hydrolysis reaction is called hydrolysis constant.

It is denoted by symbol ‘Kh’.

Consider hydrolysis reaction for the salt BA

BA + H2O ⇌ BOH + HA

Base Acid

By applying law of mass action

K= [BOH] [HA]

[BA][H2O]

Where K = Equilibrium constant and [H2O] = constant

∴ K = [BOH] [HA]

[BA] xConstant

K x Constant = [BOH] [HA]

[BA]

Kh = [BOH] [HA]

[BA]

Where Khis hydrolysis constant or hydrolytic constant

**3.13 Derivation of relation between degree of hydrolysis and hydrolysis constant for different types of salts**

**3.13.1 For the salts of strong acid and weak base:**

Consider one mole of salt BA is dissolved in V dm3 of solution and ‘h’ is degree of hydrolysis then hydrolysis reaction is

BA + H2O ⇌ BOH + HA

Weak Base Strong Acid

By ionic theory

B+ + A- + H2O ⇌ BOH + H+ + A-

By cancelling common ions

B+ + H2O ⇌ BOH + H+

1 - 0 0 ----(Initial moles)

1-h - h h ---(moles at equilibrium)

1-h/v - h/v h/v (moles per dm3 at equilibrium)

By applying law of mass action

K= [BOH] [H+]

[B+][H2O]

K x [H2O] = [BOH] [H+]

[B+]

[H2O] = Constant and K x [H2O] = Kh

Or Kh = [BOH] [H+]

[B+]

Substituting values,

Kh =

If degree of hydrolysis (h) is very small then (1-h) ≈1

∴ Kh = h2/V

Or h2 = Kh x V

h =

h ∝

But 1/V = C

∴ Kh = h2C

H2 = Kh/C

h =

h ∝

thus, the degree of hydrolysis of salt of strong acid and weak base is (a) directly proportional to the square root of dilution (volume) and (b) inversely proportional to the square root of concentration.

**3.12.2 For the salt of weak acid and strong base:**

Consider one mole of salt BA is dissolved in V dm3 of solution and ‘h’ is degree of hydrolysis then hydrolysis reaction is

BA + H2O ⇌ BOH + HA

Strong base weakacid

By ionic theory

B + A- + H2O ⇌ B+ + OH- + HA

By cancelling common ions

A- + H2O ⇌ OH- + HA

1 - 0 0 (initial mole)

1-h - h h (moles at equilibrium)

- (moles per dm3 at equilibrium)

By applying law of mass action;

K= [OH-] [HA]

[A-][H2O]

K x [H2O] = [OH-] [HA]

[A]

[H2O] = Constant and K x [HO] = Kh

Or Kh = [OH-] [HA]

[A-]

Substituting values, we get,

Kh =

If degree of hydrolysis (h) is very small then (1-h) ≈1

∴Kh = h2/V

Or h2 = Kh x V

h =

h ∝

But 1/V = C

∴Kh = h2C

h2 = Kh/C

h =

h ∝

thus, the degree of hydrolysis of salt of weak acid and strong base is a) directly proportional to the square root of dilution (volume) and b) inversely proportional to the square root of concentration.

**3.12.3 For the salts of weak acid and weak base:**

Consider salt BA (WAWB) is dissolved in water then hydrolysis reaction is

BA + H2O ⇌ BOH + HA

Weak base weak acid

By ionic theory

B+ + A- +H2O ⇌ BOH + HA

By applying law of mass action

K =

K x [H2O] =

Water is present in large quantity therefore its concentration is taken as constant.

K x Constant =

Kh = ----------------------(1)

Where Kh is hydrolysis constant

In the same aqueous salt solution three more equilibria are present.

1. For water

H2O ⇌ H+ + OH-

∴ Kw = [H+] [OH-]-----------------(2)

Where Kw is ionic product of water.

1. For weak acid

HA ⇌ H+ + A-

∴ Ka = ---------------------(3)

Where Ka = dissociation constant for acid

1. For weak base

BOH ⇌ B+ + OH-

∴Kb = -------------------(4)

Where Kb is dissociation constant for base

Dividing equation 2 by 3 and 4 we get

=

= ------------------------(5)

But from equation 1 Kh =

Comparing equation 1 and 5 we get

Kh =

Thus, for the salt of weak acid and weak base the hydrolysis constant Kh is equal to the ratio of ionic product of water Kw to the dissociation constant of weak acid Ka and weak base Kb.

**3.12.4 For the salt of Strong acid and strong base:**

This types of salts does not undergo hydrolysis. e.g. sodium chloride (NaCl) is dissolved in water.

NaCl + H2O ⇌ NaOH + HCl

Strong Base Strong Acid

By ionic theory, NaCl, HCl dissociates completely because they are strong electrolytes.

Na+ + Cl- + H2O ⇌ Na+ + OH- + H+ + Cl-

By cancelling common ions

H2O ⇌ H+ + OH-

In The aqueous solution of this salt, cation or anion of salt do not react with water. Therefore, solution contains equal concentration of H+ ions and OH- ions and solution remains neutral (pH= 7).

Hence this type of salts does not undergo hydrolysis.

Consider salt BA (WASB) is dissolved in water then hydrolysis reaction is

BA + H2O ⇌ BOH + HA

Strong base weak acid

By ionic theory

B+ + A- + H2O ⇌ B+ + OH- + HA

By applying law of mass action,

K =

K x [H2O] =

Water is present in large quantity therefore its concentration is taken as constant.

K x Constant =

Kh = -------------- (1)

Where Kh = hydrolysis constant

In the same aqueous solution two more equilibria are present.

1. For water

H2O ⇌ H+ + OH-

∴ Kw = [H+] [OH-]-------------- (2)

Where Kw is ionic product of water.

1. For weak acid

HA ⇌ H+ + A-

∴ Ka = -------------(3)

Where Ka = dissociation constant for acid

Dividing equation 2 by 3 we get

=

∴= --------------(4)

But from equation (1) Kh =

Comparing equation 1 and 4 we get,

Kh =

Thus, for the salt of weak acid and strong base the hydrolysis constant (Kh) is equal to the ratio of ionic product of water (Kw) to the dissociation constant of weak acid (Ka).

**Problems:**

**1.Calcualte hydrolysis constant and degree of hydrolysis of ammonium chloride in 0.02M solution**.

[Given Kw = 1 x 10 -14, Kb = 1.8 x 10-5]

**Solution**

Given

Kw = 1 x 10 -14

Kb = 1.8 x 10-5

C = 0.02 M

Kh=?

h =?

Ammonium chloride is a salt

It is a salt of strong acid and weak base type.

**Formula**: Kh = and h =

Kh =

= x 10-9

Kh = 0.5555 x 10-9

Kh = 5.555 x 10-10

h = =

h = 1.66 x 10-14

**2. Calculate hydrolysis constant and degree of hydrolysis of 0.25 M solution of sodium acetate.**

[Given: Kw = 1 x 10-14, Ka = 1.69 x 10-5]

**Solution:**

Given: Kw = 1 x 10-14

Ka = 1.69 x 10-5

C = 0.25M

Kh =?

h =?

Salt of sodium acetate (CH3COONa)

It is a salt of weak acid and strong base type

**Formula:**

Kh = and h =

Kh =

Kh =

Kh = 5.91 x 10-10

h = =

h = 4.862 x 10-5.

**3. Calculate the hydrolysis constant and dissociation constant of ammonium hydroxide if degree of hydrolysis of ammonium acetate is 4.921 x 10-4 in 0.01 M solution.**

[Given ionic product of water is 1 x 10-14 and dissociation constant of acetic acid is 1.66 x 10-5 at 298k]

**Solution:**

Given: Kw = 1 x 10-14

Ka = 1.66 x 10-5

C = 0.01 M

h = 4.921 x 10-4

Kh =?

Salt of ammonium acetate (CH3COONH4)

It is salt of weak acid and weak base type.

**Formula:**

Kh = and h =

∴Kh = h2 = (4.921 x 10-4)2

Kh = 2.421 x 10-7

Kh =

Kb =

= 1 x 10-14

1.66 x 10-5x 2.421 x 10-7

Kb = 2.488 x 10-3