CHAPTER # 8
ACIDS, BASES AND SALTS

Introduction:

Acids:

Acids were first recognized as substances that taste sour.

Vinegar tastes sour because it is a dilute solution of acetic acid. Citric acid is responsible for the sour taste of a lemon.

Bases:

Bases, sometimes called alkalies are characterized by their bitter taste and slippery feel.

Commercial preparations for unclogging drains are highly basic.

Salt:

A salt is an ionic substance that results from the neutralization of an acid and a base.

Importance:

Acid-base chemistry is important in a wide variety of everyday applications. The influence of acids on living things has assumed special importance in recent years due to the phenomenon of acid rain.

Q1. What do you know about the terms?

i. mineral acids ii organic acids

Ans: Acids:

Acids were first recognized as substances that taste sour.

The acids classified into

(i) Mineral acids (ii) organic acids.

Organic acids:

The organic acids are much weaker and less convenient mineral acids. The organic acids are mostly found in vegetables, fruit and other stuffs. Some common organic acids and their appearance in different categories are as follows:

Organic acids	Where it is found
Lactic acid	Sour Milk
Citric acid	Citrus fruits like lemons, oranges
Formic acid	Insect bites
Tartaric acid	Grape juice
Maleic acid	Apples and pears

Mineral acids:

The mineral acids are much stronger acids. e.g. HCl, H_2SO_4, HNO_3

Q2. Explain acid and bases in terms of their reaction with water.

Ans: Acid in aqueous solution:

The presence of water is essential for the formation of H^+. Acid produce H^+ ion in water which is the indication of their acidic nature.

Example:

HCl is covalent in nature and does not form H^{+1} ions. However it forms H_3O^+ ions (which is hydrated proton) in the presence of H_2O.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Base in aqueous solution:

Bases form a class of chemical substances including metal oxides and hydroxides. A soluble base is called an alkali and forms OH^{-1} ions when dissolved in H_2O. In general the bases on hydrolysis produce alkali.

$$CaO + H_2O \rightarrow Ca(OH)_2$$

Here CaO is a base where as $Ca(OH)_2$ is an alkali.

Importance:

Alkalies are important in soap and detergent manufacture. Caustic soda (NaOH) is used for this purpose.

Q3. Write different properties of acids and bases.

Ans: Properties of acids:

Following are the different properties of acids.

i. Acids turn blue litmus red

ii. They react with carbonates to evolve carbon dioxide

iii. They have sour taste.

iv. **Examples:** HCl, H_2SO_4, HNO_3

Properties of bases:

i. Bases turn red litmus blue.

ii. They have slippery touch.

iii. They have bitter taste.

iv. Examples: sodium hydroxide (NaOH), calcium hydroxide [$Ca(OH)_2$].

Q4. Define basic oxides and acidic oxides. Explain them with the help of examples.

Ans: Basic oxides:

The oxides which dissolve in water to form bases are called basic oxides.

Example:

There are certain oxides of metals, like sodium oxide (Na_2O) and calcium oxide (CaO) which react with water to furnish bases sodium hydroxide (NaOH) and calcium hydroxide [$Ca(OH)_2$].

$$Na_2O_{(s)} + H_2O_{(l)} \longrightarrow 2NaOH_{(aq)}$$

$$CaO_{(s)} + H_2O_{(l)} \longrightarrow Ca(OH)_{2(aq)}$$

Thus, these oxides are basic in nature.

Acidic oxides:

The oxides which dissolve in water to form acids are called acidic oxides.

Example:

Non-metal oxides like carbon dioxide (CO_2) sulphur dioxide (SO_2) and nitrogen pentaoxide (N_2O_5) when react with water yield carbonic acid (H_2CO_3) sulphurous acid (H_2SO_3) and nitric acid (HNO_3). Such oxides are thus acidic in nature.

$$CO_{2(g)} + H_2O_{(l)} \longrightarrow H_2CO_{3(aq)}$$

$$SO_{2(g)} + H_2O_{(l)} \longrightarrow H_2SO_{3(aq)}$$

Note:

In addition to oxides, certain salts are also acidic and basic in nature e.g. ammonium chloride (NH_4Cl) is acidic because when dissolved in water it furnishes an acidic solution; potassium carbonate (K_2CO_3) is basic since it yields a basic solution in water. $NH_4Cl + HOH \rightarrow NH_4OH + HCl$.

$$N_2O_{5(g)} + H_2O_{(l)} \longrightarrow 2HNO_{3(aq)}$$

Q5. Define amphoteric oxides and give its examples.

Ans: There are certain oxides which are on the border line of being acidic or basic. These oxides which tend to be insoluble in water, are soluble in both acids and bases are called amphoteric oxides. In character that is both acidic and basic.

Example:

Aluminium oxide (Al_2O_3) is amphoteric and it reacts with both acidic and basic solutions:

$$\text{(basic) } Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$$

$$\text{(acidic) } Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)}$$

Also, chromium trioxide is amphoteric since it reacts with both acids and bases.

$$\text{(basic) } Cr_2O_{3(s)} + 6HNO_{3(aq)} \longrightarrow 2Cr(NO_3)_{3(aq)} + 3H_2O_{(l)}$$

$$\text{(acidic) } Cr_2O_{3(s)} + 6KOH_{(aq)} \longrightarrow 2K_3CrO_{3(aq)} + 3H_2O_{(l)}$$

Q6. Define Salt, and also explain its types.

Ans: Salts:

The substance obtained as a result of neutralization of acids and bases are called salts

A salt is of three types (1) Neutral salt (2) Acidic salt (3) Basic salt.

1. Neutral Salt:

It is obtained by the neutralisation of a strong acid and a strong base.

e.g. $HCl + NaOH \longrightarrow NaCl + H_2O$

HCl	NaOH	NaCl
Strong acid	Strong base	Neutral

2. Acid salt:

It is obtained by the neutralisation of a strong acid with a weak base.

e.g. $2HCl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O$

2HCl	Ca(OH)₂	CaCl₂
Strong acid	Weak base	Neutral

3. Basic salt:

It is obtained by the neutralisation of a strong base with a weak acid.

e.g. $2NaOH + H_2CO_3 \longrightarrow Na_2CO_3 + 2H_2O$

2NaOH	H₂CO₃	Na₂CO₃
Strong base	Weak acid	Neutral

Q7. Write a detailed note on the relative strength of acids and bases.

Ans: Strength of Acids:

Different Bronsted acids donate proton to different extents.

The ability of an acid to donate proton is called 'strength of acid' or the 'acid strength'.

An acid which can donate proton to a higher degree than another acid is said to be relatively strong acid.

Example:

Hydrochloric acid is a relatively stronger acid than acetic acid. Also, acetic acid is relatively stronger than water.

Strength of bases:

The bases also differ in their ability to accept proton.

A base which can accept proton to higher degree than another base is a relatively stronger base.

Example:

Thus ammonia is a relatively stronger base than water because ammonia can accept a proton to a higher degree than water.

Q8. Define pH and explain different types of solutions on the bases of pH.

Ans: pH:

Since the concentration of $[H^+]$ and $[OH^-]$ are usually very small numbers and inconvenient to work with, a more practical measure called pH was proposed and defined as:

It means that pH of a solution is given by the negative logarithm of the $[H^+]$ concentration (in mol/dm^3).

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

No units:

However it must be kept in mind that pH being a logarithmic value, does not have any units,

Conditions:

The pH concept implies that at 25°C, the different types of solutions will show the following behaviours:

Acid solution: $[H^+] > 1.0 \times 10^{-7}$ M, $pH < 7.00$

Basic solution: $[H^+] < 1.0 \times 10^{-7}$M, $pH > 7.00$

Neutral solution: $[H^+] = 1.0 \times 10^{-7}$ M, $pH = 7.00$

A scale analogous to the pH can be devised using the negative logarithm of the H^+ concentration.

Q9. Define pOH and prove that: pH + pOH = 14

Ans: pOH:

The negative logarithm of OH^- ions concentration (in mol dm^{-3}) is called pOH.

pH + pOH = 14

As $K_w = [H^+][OH^-]$

$1.0 \times 10^{-14} = [H^+][OH^-]$

Taking log of both sides

$\log(1.0 \times 10^{-14}) = \log \times [H^+] + \log [OH^-]$

$-14 = \log [H^+] + \log [OH^-]$

$14 = -\log [H^+] - \log [OH^-]$

$$14 = \left(-\log\left[H^+\right]\right) + \left(-\log\left[OH^-\right]\right)$$

$$14 = pH + pOH$$

This equation provides another way to express the relationship between the $[H^+]$ and $[OH^-]$ concentrations.

Q10. The concentration of $[OH^-]$ ion in a household ammonia solution is 0.005M. Calculate the concentration of $[H^+]$ in it.

Solution:

$$[OH^-] = 0.005\ M$$

$$K_w = [H^+][OH^-]$$

$$1.0 \times 10^{-14} = [H^+] \times 0.005$$

$$[H^+] = \frac{1.0 \times 10^{-14}}{0.005}$$

$$= 2.0 \times 10^{-12}\ M$$

Q11. Calculate the pH of 0.001 M aqueous hydrochloric acid solution.

Solution:

Hydrochloric acid ionises in water completely therefore,

$$\underset{0.001\ M}{HCl} + H_2O \longrightarrow \underset{0.001\ M}{H_3O^+} + Cl^-$$

$[H_3O^+]$ is in fact the same as $[H^+]$

Therefore $[H^+] = 0.001$ M

$$pH = -\log(0.001)$$
$$= -\log 10^{-3}$$
$$= 3.00$$

Therefore, the pH of 0.001 M aqueous hydrochloric acid is 3.00

Q12. Calculate the pH of 0.062 M NaOH solution.

Solution:

$$\underset{0.062M}{NaOH_{(aq)}} \longrightarrow \underset{0.062M}{Na^+_{(aq)}} + \underset{0.062M}{OH^-_{(aq)}}$$

$$pOH = -\log[OH^-]$$
$$= -\log[0.062]$$
$$= 1.21$$

Now $pH + pOH = 14$

$$pH = 14 - pOH$$
$$= 14 - 1.21$$
$$= 12.79$$

Activity for Students

Example 4:

What is the pH of a solution containing 1.95g pure H_2SO_4 per dm^3 of solution? (Ans: pH = 1.4)

Solution:

Mass of H_2SO_4 = 1.95g

Molecular mass of H_2SO_4 = 98g mole^{-1}

Number of moles of H_2SO_4 = $\frac{1.95}{98}$ = 0.02 moles

The ionization of H_2SO_4 in water is given below

$$H_2SO_4 + 2H_2O \rightarrow 2H_3O^+ + SO^-_4$$

0.02 moles 2 × 0.02 moles

$[H_3O^+]$ is in fact the hydrated proton $[H^+]$

Therefore $[H^+] = 2 \times 0.02 = 0.04$ M

$$pH = -\log(0.04)$$
$$= 1.40$$

Activity for Students

Calculate the fourth parameter when given three of four parameters–molarity of base, volume of base, molality of acid, volume of acid–used in a titration experiment, assuming a strong acid and strong base reaction.

(Analysing)

Solution:

Titration:

"It is defined as a method to find the volume of the standard solution required to react completely with known volume of another solution under analysis".

Procedure:

Acid-base titrations are conducted using burettes and volumetric pipettes. Generally acid solution is placed with the burette.

A fixed volume of base is placed into a conical flask along with a few drops of the appropriate acid-base indicator.

Acid from the burette is added to the base until the indicator changes colour. This change of colour indicates the **end point** of titration.

Phenolphthalein as an indicator:

In the neutralization of a strong acid with a strong base, phenolphthalein is used as an indicator. It imparts pink colour to the base solution. At the end point, solution just becomes colourless.

The molarity of the acid solution under test is determined with the help of the following equation:

$$M_1 V_1 = M_2 V_2$$

Where M_1 = Molarity of the base

V_1 = Volume of the base taken in flask

M_2 = Molarity of the acid

V_2 = Volume of acid used from the burette

Thus by knowing the three parameters, the fourth can be calculated.

Activity for Students

Perform acid-base titrations to calculate molarity and strength of given sample solutions.

Solution:

Take strong acid (HCl) and strong base (NaOH) solutions. Molarity of NaOH is known and that of HCl is to be determined. For titration purposes phenolphthalein is used as an indicator. HCl is taken in the burette while 10 ml of NaOH in the burette. The disappearance of pink colour gives the end point.

According to molarity concept

$$M_1 V_1 = M_2 V_2$$

$$\text{HCl} = \text{NaOH}$$

$$M_1 \times 10 = \frac{1}{10} \times 10 \quad \text{or} \quad M_1 = \frac{1}{10} = 0.1\ \text{m}$$

Thus molality of the given solution is 0.1m.

Strength dm^{-3} = molality x molar mass

$$= \frac{1}{10} \times 36.5 = 3.65\text{g dm}^{-3}$$

Activity for Students

In a titration it is found that 25 cm^3 of 0.12M NaOH is neutralized with 30 cm^3 of HCl of unknown concentration. Calculate concentration and strength of HCl solution.

Solution:

$$HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O$$

$$n_1 = 1 \qquad n_2 = 1$$

$$\text{HCl} \qquad \text{NaOH}$$

$$\frac{M_1 V_1}{n_1} = \frac{M_2 V_2}{n_2}$$

$$\frac{M_1 \times 30}{1} = \frac{0.12 \times 25}{1}$$

$$M_1 = 0.1\text{M}$$

Thus Molarity of HCl solution is 0.1M.

Strength of solution = Molarity × Molar mass

Strength of HCl solution = 0.1 × 36.5 = 3.65g dm^3

Q13. What is acid dissociation constant? How it is related to pK_a. Write equation to elaborate.

Ans: Strong and Weak Acids:

i. According to the Bronsted-Lowery definition an acid is a proton donor species. Different acids have a tendency to donate proton but this tendency is different.

ii. An acid may donate proton to very high degree, a high degree or to small degree or very small degree. Depending on this ability of donation of proton, an acid is regarded as strong acid or a weak acid.

iii. Strong acids donate proton to a greater degree than the weak acids. The strength of an acid is generally expressed in terms of the acid ionisation constant, K_a.

iv. The extent of ionisation and the acid dissociation constant K_a can be used to distinguish between strong and weak acids.

Derivation of acid dissociation constant K_a:

Consider the case of ionisation of a general acid HX in water. In this aqueous solution, the established equilibrium may be represented as follows:

$$HX_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \overline{X}_{(aq)}$$

The equilibrium constant K for this ionisation process may be written as follows:

$$K = \frac{[H_3O^+][\overline{X}]}{[HX][H_2O]}$$

$$\text{or} \qquad K\,[H_2O] = \frac{[H_3O^+][\overline{X}]}{[HX]}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, K $[H_2O]$ is another constant and is designated as K_a thus,

$$K\,[H_2O] = K_a = \frac{[H_3O^+][\overline{X}]}{[HX]}$$

K_a is termed as the acid dissociation constant. It is a measure of the extent to which an acid is ionized or dissociated at the equilibrium state.

"The greater the value of K_a, the stronger is the acid".

K_a is temperature dependent:

It must be kept in mind that the acid dissociation constant, K_a, is dependent on temperature. Therefore, the value of K_a should be mentioned along with the temperature at which K_a was determined. Dissociation constant, K_a, of acetic acid in water at 25°C is 1.8×10^{-5}. The comparison of K_a Values of different acids provides a method to compare their strengths.

pK_a:

The value of K_a are usually inconvenient numbers, therefore, for convenience these values are converted to pK_a values. The relationship between K_a and pK_a is as follows:

$$pK_a = -\log K_a$$

Conclusion:

Since pK_a refers to the negative logarithm of K_a. Thus smaller the value pK_a stronger shall be the acid because smaller pK_a value corresponds to a greater K_a value. In table 8.2 are listed the ionisation constants and pK_a values of some common acids in water at 25°C.

Table: Ionisation constants and pK_a of Acids

Name of Acid	Formula	K_a	pK_a
Perchloric acid	$HClO_4$	1.0×10^{10}	-10.0
Hydroiodic acid	HI	1.0×10^{10}	-10.0
Hydrobromic acid	HBr	1.0×10^{9}	-9.0
Hydrochloric acid	HCl	1.0×10^{7}	-7.0
Sulphuric acid	H_2SO_4	1.0×10^{3}	-3.0
Hydrofluoric acid	HF	1.0×10^{-4}	+3.1
Formic acid	HCOOH	1.0×10^{-4}	+3.7
Benzoic acid	C_6H_5COOH	1.0×10^{-5}	+4.5
Acetic acid	$CH_3.COOH$	1.0×10^{-5}	+4.7
Phenol	$C_6H_5.OH$	1.0×10^{-10}	+9.3
Water	H_2O	1.0×10^{-18}	+16.0

The K_a and pK_a and given in Table 8.2 show that perchloric acid ($HClO_4$) is the strongest among all the acids given in the table. Also, water is the weakest acid among all acids listed in it.

Q14. Calculate concentration of H^+ ions of a solution that contains 1.0M HF ($K_a = 7.2 \times 10^{4}$)

Solution:

$$HF_{(aq)} \rightleftharpoons H^+_{(aq)} + F^-_{(aq)}$$

Initial conc. 1.0M 0 0

Eq. conc. (moles dm^{-3}) $1.0 - x$ x x

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

$$7.2 \times 10^{-4} = \frac{x.x}{1.0 - x}$$

Since x is very small as compared to 1.0, the term in the denominator can be approximated as follows:

$$1.0 - x = 1.0$$

$$7.2 \times 10^{-4} = \frac{x^2}{1}$$

$$x = 0.268M$$

$$[H^+] = 0.268M$$

Q15. The pH of a 0.1M solution of an acid is 2.85. Calculate the ionisation constant, K_a of the acid.

Solution:

Using the pH value, the equilibrium concentration of the acid and the conjugate base can be calculated. These concentrations may then be used to calculate K_a.

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

$$2.85 = -\log[H^+]$$

Taking antilog "of" both side $[H^+]$ turns out to be 1.4 × 10^{-3}M.

Now equilibrium is considered:

$$\text{Acid}_{(aq)} \rightleftharpoons H^+_{(aq)} + \text{conjugate base}_{(aq)}$$

	Acid	H^+	conjugate base
Before equilibrium	0.100M	0.000	0.000
Change	0.0014M	0.0014M	0.0014M
At equilibrium	0.0986M	0.0014M	0.0014M

$$K_a = \frac{[H^+]\ [\text{conjugate base}]}{[\text{acid}]}$$

$$= \frac{(0.0014)\ (0.0014)}{0.0986}$$

$$= 2.0 \times 10^{-5}$$

Thus the ionisation constant, K_a is 2.0×10^{-5}

Q16. What is base dissociation constant? How it is related to pK_b. Write equation to elaborate.

Ans: Strong and Weak Bases:

The strength of a base is the ability to accept a proton form a solvent. Hydroxides of alkali metals such as sodium hydroxide and potassium hydroxide are strong bases and ionise completely in aqueous solution.

$$NaOH_{(aq)} \longrightarrow Na^+_{(aq)} + OH^-_{(aq)}$$

$$KOH_{(aq)} \longrightarrow K^+_{(aq)} + OH^-_{(aq)}$$

The OH^- ion thus formed is a Bronsted base because it can accept proton H^+

$$OH^- + H^+ \longrightarrow H_2O$$

The ability of a base to accept a proton from an acid, usually water, is termed as strength of the base.

The extent of ionisation and the base dissociation constant K_b is use to distinguish between strong and weak bases.

Derivation of base dissociation constant K_b:

Consider a base B, an equilibrium reaction with water can be represented by the following equation:

$$B + H_2O_{(aq)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, K $[H_2O]$ is another constant and is designated as K_b thus,

$$K_b = \frac{[BH^+]\ [OH^-]}{[B]}$$

K_b value will be large if degree of ionisation of the base B is high i.e. if the base B is strong. The Value of K_b will be small for a weak base B.

pK_b:

For convenience, a parameter pK_b has been devised to express K_b value in convenient numbers. Thus, pK_b is defined as the negative logarithm of K_b.

$$pK_b = -\log K_b$$

Table: $K_b$and pK_bValues of Some Common Bases:

Name of Base	Formula	K_b	pK_b
Diethlyamine	$(C_2H_5)_2\,NH$	9.6×10^{-4}	3.02
Ethylamine	$C_2H_5\,NH_2$	5.6×10^{-4}	3.25
Methylamine	$CH_3\,NH_2$	4.5×10^{-4}	3.34
Ammonia	NH_3	1.7×10^{-5}	4.76
Pyridine	$C_5H_5\,N$	5.6×10^{-9}	8.25
Aniline	$C_6H_5\,NH_2$	4.3×10^{-10}	9.37

Conclusion:

According to these values ammonia is a stronger base than pyridine and aniline but weaker than methylamine and ethylamine. Also, diethyl amine is a strongest base among all those listed in the table.

Q17. Prove that $K_a \times K_b = K_w$

Ans: Relationship of K_a and K_b:

$$K_a \times K_b = K_w$$

This relationship can be proved by considering the ionisation of an acid HA and writing equation for its K_a

$$HA_{(aq)} \rightleftharpoons H+_{(aq)} + A^-_{(aq)}$$

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

The equilibrium for the conjugate base is

$$A^-_{(aq)} + H_2O_{(l)} \rightleftharpoons HA_{(aq)} + \overline{OH}_{(aq)}$$

$$K_b = \frac{[HA]\,[OH^-]}{[A^-]}$$

Multiplying the expression for K_a and K_b.

$$K_a\,K_b = \frac{[H^+]\,[A]}{[HA]} \times \frac{[HA]\,[OH^-]}{[A^-]}$$

Thus $K_a\,K_b = [H^+]\,[OH^-] = K_w$

This result leads to an important conclusion that if the value of K_a is known K_b can be calculated since K_a, $\times$ K_b, = K_w

$$K_a = \frac{K_w}{K_b}$$

and $$K_b = \frac{K_w}{K_a}$$

Conclusion:

Since K_w is constant at a given temperature, it may be deduced that K_a is inversely proportional to K_b.

$$K_a \propto \frac{1}{K_b}$$

Thus, stronger the acid, weaker is its conjugate base. It can also be said that stronger a base, weaker is its conjugate acid.

Example:

Ammonia is a weaker base (pK_b = + 4.76) than diethylamine (pK_b = 3.02), therefore the conjugate acid of ammonia is stronger acid than the conjugate acid of diethylamine. Similarly, the conjugate base of a weak acid, water (pK_a = + 6.00) is a stronger base than the conjugate base of stronger acid, hydrochloric acid (pK_a = -7.00). Thus, hydroxide ion (OH^-) is a stronger base than the chloride ion (Cl).

Q18. Prove that $pK_a + pK_b = 14$ at 25°C

Solution: $K_a \times K_b = K_w$

Taking log on both sides

$\log (K_a \times K_b) = \log K_w$

$\log K_a + \log K_b = \log K_w$

On changing the signs from plus to minus in the above equation

$(-\log K_a) + (-\log K_b) = (-\log K_w)$

Note that in terms of pK_a& pK_b the equation becomes

$pK_a + pK_b = pK_w$

As $pK_w = 14$ at 25°C

$pK_a + pK_b = 14$ at 25°C

Q19. The pK_a of acetic acid at 25°C is +4.76. Calculate the pKb of the conjugate base of acetic acid.

Solution:

$pK_a + pK_b = 14.00$

pK_a of acetic acid is given as + 4.76

$4.76 + pK_b = 14$ or $pK_b = 9.24$

Example 8 (b):

The pK_a of acetic acid at 25°C is + 4.76. Calculate the pK_b of the conjugate base of acetic acid.

Solution:

$pK_a + pK_b = 14.00$

pK_a of acetic acid is given as + 4.76

$4.76 + pK_b = 14$

Solution:

$pK_a + pK_b = 14.00$

pK_a of pyridine $= + 8.25$

therefore $pK_a + 8.25 = + 14.00$

and $pK_a = + 14.00 - 8.25$

$= + 5.75$

Therefore, the pK_a of the conjugate acid of pyridine turns out to be +5.75 one of the important conclusion of the equation $K_a \times K_b = K_w$ is

Activity for Students

What is the percentage ionisation of acetic acid in a solution in which 0.1 M of it has been dissolved per dm^3 of the solution

$$K_a = 1.8 \times 10^{-5}$$

Hint: $$\text{Percentage ionisation} = \frac{\text{concentration of ionised acid}}{\text{original concentration}} \times 100$$

(**Ans**: 1.3%)

Solution:

	CH_3OOOH	$\rightleftharpoons$	CH_3COOH^-	$+ H^+$
Initial Conc. (mol/dm^3)	0.1		0	0
Equilibrium Conc. (mol/dm^3)	$0.1 - x \approx 0.1$ (since acid is weak)		x	x

K_a for acetic acid is given by

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$K_a = \frac{(x)(x)}{0.1} = 1.8 \times 10^{-5}$$

$$x^2 = 0.1\,(1.8 \times 10^{-5})$$

$$x^2 = 1.8 \times 10^{-6})$$

Taking square root on both sides

$$x = 1.3 \times 10^{-3} \textit{moles}$$

$$\textit{Hence } [H^+] = x = 1.3 \times 10^{-3} \textit{ moles}$$

$$\%\ \textit{ionization} = \frac{\textit{Amount of acid ionized}}{\textit{Amount of acid initially available}} \times 100$$

$$\%\ \textit{ionization} = \frac{1.3 \times 10^{-3}}{0.1} \times 100 = 1.3\%$$

Activity for Students

Calculate the $[H_3O^+]$, given the K_a and molar concentration of weak acid.

Solution:

When water is added to a weak acid, it is partially dissociated. Thus an equilibrium is established between the dissociated and un-dissociated molecule,

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

$$K = \frac{[H_3O^+]\ [X^-]}{[HX] \times [H_2O]} \quad \text{Law of Mass action}$$

The quantities written within brackets indicate activities of reactants and products. As water is always in excess, therefore, its concentration remains almost constant.

The above equation is further written as:

$$K\,[H_2O] = \frac{[H_3O^+]\,[X^-]}{[HX]}$$

$$K_a = \frac{[H_3O^+]\,[X^-]}{[HX]}$$

Where K_a is called dissociation constant of the weak acid.

or $K_a\,[HX] = [H_3O^+]\,[X^-]$ or

$$[H_3O^+] = \frac{K_a\,[HX]}{[X^-]}$$

Thus $[H_3O^+]$ can be calculated if K_a [HX] and $[H^-]$ are known.

Activity for Students

Calculate the K_a for the system, given the equilibrium concentrations of a weak acid and the $[H_3O^+]$ in the solution.

Solution:

In the equation,

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

$$K \quad \frac{[H_3O^+] \times [X^-]}{[HX] \times [H_2O]}$$

$$K\,[H_2O] = \frac{[H_3O^+]\,[X^-]}{[HX]}$$

$$K_a = \frac{[H_3O^+]\,[X^-]}{[HX]} \text{ where } K\,[H_2O] = K_a$$

Thus K_a, the ionisation constant of weak acid can be calculated if $[H_3O^+]$, $[X^-]$ and $[HX]$ are known $[H_3O^+]$, $[X^-]$ and the activities of H_3O^+, X^- and HX respectively.

Example 10:

(a) Calculate the pH of an acetic acid-sodium acetate buffer solution containing 1.0 moles of each component.

(b) What will be the pH of this solution after addition of 0.01 mole of hydrochloric acid gas to $1dm^3$ volume? Assume that the volume of solution remains unchanged on addition hydrochloric acid. (Ka for acetic acid is 1.8×10^{-5}.

(c) The pH of the buffer solutions can be calculated by assuming the equilibrium concentration of both the acid and its conjugate base as starting concentration.

Thus $[CH_3CO_2H] = 1.0M$ $[CH_3COO] = 1.0M$

For acetic acid dissociation

$$K_a = \frac{[CH_3COO]\,[H^+]}{[CH_3CO_2H]} = 1.8 \times 10^{-5}$$

$$1.8 \times 10^{-5} \quad \frac{[1.0]\,[H^+]}{[1.0]}$$

Thus, the pH of buffer solution is 4.745

(d) After HCl addition:

$$HCl_{(aq)} \longrightarrow H^+_{(aq)} + Cl_{(aq)}$$

0.01 mole 0.01 mole 0.01 mole

Initially, there were 1.0 mole of CH_3COOH and 1.0 mole of CH_3COO^- present per dm^3 of the solution. After addition of hydrochloric acid 0.01 mole of CH_3COO^- ions are combined with the H^+ ions formed from dissociation of 0.01 mole of added hydrochloric acid. This can be written as:

$$CH_3COO^-_{(aq)} + H^+_{(aq)} \longrightarrow CH_3CO_2H_{(aq)}$$

0.01 mole 0.01 mole 0.01 mole

Thus, the numbers of moles of acetic acid and acetate ions, after addition of hydrochloric acid are:

$$CH_3CO_2H : (1.0+0.01)\text{ mole} = 1.01\text{ mole}$$

$$CH_3CO\overline{O} : (1.0-0.01)\text{ mole} = 0.99\text{ mole}$$

The equilibrium equation for this new situation can be written

$$K_a = \frac{[CH_3COO\overline{O}]\,[H^+]}{[CH_3CO_2H]}$$

or

$$[H^+] = \frac{Ka[CH_3CO_2H]}{CH_3.COO}$$

$$[H^+] = \frac{1.8 \times 10^{-5}\,(1.01)}{0.99}$$

$$pH = -\log(2.2 \times 10^{-5}) = 4.736$$

Notice there is a slight change in pH from 4.745 to 4.736, that is only a difference of 0.009. Thus a buffer does a very good job in limiting the change in pH to a very small amount.

Q20. What are buffer solutions? Elaborate with suitable examples, their significance in acid-base reactions. Write three common applications of buffer solutions.

Ans: Definition:

Those solutions which resist the change in their pH when a small amount of an acid or a base is added them, are called buffer solutions. They have a specific constant value of pH.

Buffer Capacity:

A buffer solution is that which tends to maintain its pH when small amount of an acid or alkali is added to that. The property of such a solution is called buffer action and the capability to maintain constant pH as buffer capacity.

Constitution of buffer:

A buffer solution contains a weak dissociating acid and the salt of that acid with a strong base.

e.g. **(1)** H_2CO_3 + Na HCO_3
H_3PO_4 + Na H_2PO_4
$CH_3COOH + CH_3COONa$

(2) A solution containing a weak base e.g. NH_4OH and its salt with a strong acid like NH_4Cl can also act as a buffer.

Equations to explain buffer solution:

Let us take a buffer solution H_2CO_3 + $NaHCO_3$. If HCl is added to it, the reaction will be

$$NaHCO_3 + HCl \rightarrow NaCl + H_2CO_3.$$

The addition of HCl will result only a little change in the original pH of the buffer solution. In the same way if NaOH is added to this buffer solution, it reacts with H_2CO_3 as follows:

$$NaOH + H_2CO_3 \rightarrow NaHCO_3 + H_2O$$

Since $NaHCO_3$ is a much weaker base than NaOH, the resulting rise in pH will be quite small.

Composition of a buffer solution:

The composition can be expressed in two ways:

(1) **Acidic buffers:**
By mixing a weak acid and a salt of it with a strong base. Such solutions give acidic buffers with pH less than 7. e.g. CH_3COOH + CH_3COONa.

(2) **Basic buffers:**
By mixing a weak base and a salt of it with a strong acid. Such solutions will give basic buffers with pH more than 7. e.g. NH_4OH + NH_4Cl.

Buffer Action:

(i) Let us take a buffer solution of CH_3COOH and CH_3COONa. Common ion effect helps us to understand how will buffer work. CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH3COONa, a strong electrolyte is added to CH_3COOH solution, the dissociation of CH_3COOH is suppressed due to common effect of CH_3COO^-.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

Addition of strong acid:

Suppose we add a few drops of HCl to it. Its H ions are used up by CH_3COO^- and the equilibrium is **shifted towards left**.

Thus the addition of HCl will not change the pH of the buffer solution.

(ii) **Addition of strong base:**
In the same buffer solution, if a strong base is added it is neutralised by the acid.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$H^+ + OH^- \longrightarrow H_2O$$

Thus the addition of NaOH will not change value of pH.

Applications of buffer solutions:

(i) Buffer solutions play an important role in several industrial processes. For example, they are used in the manufacture of photographic materials, leather and dyes

(ii) They are also used in the process of electroplating and analytical procedures.

(iii) The buffer solutions are also used for calibration of pH meters.

(iv) In nature, many biological systems depends upon buffer action to preserve a constant pH e.g. The pH of human blood is maintained between 7.35 to 7.45. The pH of tears is also maintained at 7.40 whereas the stomach juices are known to have pH preserved at 1.65 – 1.75. Milk and egg white (protein) show their pH as 6.7 – 6.8 and 8.0 – 8.1 respectively.

(v) Buffers are used to maintain the pH of culture media for the growth of bacteria in bacteriological applications.

Q21. List some important facts about buffer solutions.

Ans: Some important facts about buffer solutions are as follows:

(i) Buffer solution can be prepared by combining, in aqueous solution, a weak acid and its conjugate base or a weak base and its conjugate acid.

(ii) A buffer solution resists change in its pH even if a small amount of strong acid or a base is added to it.

(iii) A buffer solution maintains the stability of its pH by shifting their equilibrium to consume added H^+ ion or to replace H_3O^+ ions which have reacted with the added OH^- ions.

(iv) An aqueous solution of a strong acid and its conjugate base (as its soluble salt) cannot act as a buffer solution. Since the strong acid is completely ionized already, addition of small amount of base (OH^- ions) will consume the H_3O^+ ions which cannot be replaced and the pH of the solution will change. If a small amount of strong acid is added to this solution, the equilibrium will not shift to the left because the acid already present is a strong acid. Also a solution of strong base and its conjugate acid do not form a buffer solution due to similar reasons.

(v) Some common examples of buffers are acetic acid/sodium acetate buffer, phosphoric acid/potassium dihydrogen phosphate buffer and formic acid/sodium format buffer.

Q22. What is the pH of buffer if concentration of CH_3COOH is 0.1 M dm^{-3} and CH_3COONa is 1.0 M dm^{-3} pK_a for CH_3COOH is 4.76?

Solution:

Concentration of CH_3COOH = 0.1 M dm^{-3}

Concentration of CH_3COONa = 1.0 M dm^{-3}

The formula to determine pH value is

$$pH = pK_a + \log \frac{\text{salt (i.e. } CH_3COONa)}{\text{acid (i.e. } CH_3COOH)}$$

$$pH = 4.76 + \log\left(\frac{1.0}{0.1}\right)$$

$$pH = 4.76 + \log 10 \quad \left(\frac{1.0}{0.1} = \frac{10}{1}\right)$$

$$pH = 4.76 + 1.00 \quad (\log 10 = 1)$$

$$pH = 5.76$$

Activity for Students

Example 12:

Calculate the pH of a buffer solution in which 0.11 Molar CH_3COONa and 0.09 Molar CH_3COOH solutions are present.

K_a for CH_3COOH is 1.8×10^{-5} **(Ans: 4.83)**

Solution:

K_a of acetic acid $= 1.8 \times 10^{-5}$

$pK_a = -\log K_a$

$pK_a = -\log(1.8 \times 10^{-4})$

$pK_a = 4.745$

$[CH_3COOH] = 0.09\ M$

$[CH_3COONa] = 0.11\ M$

$$pH = pK_a + \log\frac{[salt](i.e. CH_3COON_a)}{[acid](i.e. CH_3COOH)}$$

$$pH = 4.745 + \log\left(\frac{0.11}{0.09}\right)$$

$$pH = 4.745 + 0.087$$

$$pH = 4.832$$

Q23. Briefly describe the concept of salt hydrolysis.

Ans: Salt Hydrolysis (Major Concept):

"The reaction of cations and anions of salts with water is called hydrolysis." Consider the following observations:

(i) Aqueous solution of NH_4Cl turns blue litmus red.

(ii) Aqueous solution of K_2CO_3 turns red litmus blue.

(iii) Aqueous solution of NaCl has no action on litmus solutions.

Explanation:

These observations can be explained on the basis of Bronsted-Lowry acid-base theory. When a salt (MX) is dissolved in water, it splits up into its M^+ and X^- ions. These ions may react with water and give following reactions:

$$M^+ + H - OH_{(l)} \rightleftharpoons MOH_{(aq)} + H^+_{(aq)}$$

$$\overset{-}{X}_{(aq)} + H - OH_{(l)} \rightleftharpoons HX_{(aq)} + OH_{(aq)}$$

Since H^+ and OH^- ions are produced in these reactions, the solution of the salt may be acidic or basic. In salts anions are derived from acids and cations from bases. The anions of weak acids are strong conjugate bases. Such anions react with water producing basic solutions

Examples:

$$CH_3COO^{-1},\ CN^{-1},\ HCO_3^{-1}, CO_3^{-2}\ \text{etc.}$$

$$CH_3COO^{-1}_{(aq)} + H-OH_{(l)} \rightleftharpoons CH_3COOH_{(aq)} + OH^-_{(aq)}$$

$$CN^-_{(aq)} + H-OH_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-_{(aq)}$$

$$CO^{-2}_{3(aq)} + 2H-OH_{(l)} \rightleftharpoons H_2CO_{3(aq)} + 2OH^-_{(aq)}$$

Anions like Cl^-, NO_3^-, SO_4^{-2}, are so weak conjugate bases that, they do not react with water. Cations of weak bases are strong conjugate acids. Such cations react with water producing acidic solutions.

Examples:

$$Cu^{+2},\ Al^{+3},\ NH_4^+,\ \text{etc.}$$

$$Cu^{+2}_{(aq)} + 2H-OH_{(l)} \rightleftharpoons Cu(OH)_{2(aq)} + 2H^+_{(aq)}$$

$$NH^+_{4(aq)} + H-OH_{(l)} \rightleftharpoons NH_{3(aq)} + H_3O^+_{(aq)}$$

Cations like Na^+ K^+, Ca^{+2}, Mg^{+2} etc. are so weak conjugate acids that they do not react with water.

These reactions are called hydrolysis reactions.

Types of salts:

There are four types of salts on the basis of their reactivity with water:

1. Salts of strong acids and strong bases do not hydrolyse (pH = 7).

Examples: NaCl, Na_2SO_4, KNO_3 etc.

2. Salts of weak acids and strong bases hydrolyse producing basis solutions (pH>7).

Examples: CH_3COONa, NaCN, Na_2S etc.

3. Salts of strong acids and weak bases hydrolyse producing acidic solutions. (pH < 7).

Examples: $CuSO_4$, NH_4Cl, NH_4NO_3 etc.

4. Salts of weak acids and weak bases hydrolyse, but the resulting solution is either neutral, acidic or basic. This depends upon the relative values of K_a and K_b of cations and anions of the salt.

The important aspects of the salt hydrolysis, discussed above, are summarised in Table 8.5.

Table 8.5: Summarised discussed as above

Salt Type		**Common Example**	**Ions which impart Hydrolysis**	**Solution pH (Nature)**
Acid	**Base**			
Strong	Strong	NaCl, K Br	None	= 7.0 (Neutral)
Strong	Weak	NH_4NO_3, NH_4Cl	Cations	< 7.0 (Acidic)
Weak	Strong	NaCN, K_2CO_3	Anions	> 7.0 (Basic)
Weak	Weak	NH_4CN, NH_4NO_2	Anions & Cations	May be equal, smaller or greater than 7.0

Q24. Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic.

Ans:

The salts of weak acids and strong bases hydrolyse producing basic solution. Here the value of pH is greater than 7. For examples CH_3COONa, Na_2S etc. The equation is

$$CH_3COONa + HOH \longrightarrow \underset{\text{weak acid}}{\underline{CH_3COOH}} + \underset{\text{strong base}}{\underline{NaOH}}$$

$$Na_2S + 2HOH \longrightarrow H_2S + 2NaOH$$

The salts of strong acids and weak bases hydrolyse producing acidic solution. Here the value of pH is lesser than 7. For example $CuSO_4$, NH_4Cl etc. The equation is

$$CuSO_4 + 2HOH \longrightarrow \underset{\text{weak bases}}{\underline{Cu(OH)_2}} + \underset{\text{strong acid}}{\underline{H_2SO_4}}$$

$$NH_4Cl + HOH \longrightarrow \underset{\text{weak bases}}{\underline{NH_4OH}} + \underset{\text{strong acid}}{\underline{HCl}}$$

The concept of hydrolysis can be used to explain why the solution of a salt is not necessarily neutral.

The salts of strong acids and strong bases are neutral because the value of pH = 7. They in hydrolysis give strong acids and strong bases. e.g. NaCl, Na_2SO_4 etc.

$$NaCl + HOH \longrightarrow \underset{\text{strong base}}{\underline{NaOH}} + \underset{\text{strong acid}}{\underline{HCl}}$$

$$NH_2SO_4 + 2HOH \longrightarrow \underset{\text{strong base}}{\underline{2NaOH}} + \underset{\text{strong acid}}{\underline{H_2SO_4}}$$

However salts of weak acids and strong bases and salts of strong acids and weak bases show acidic or basic behaviour.

Salts of weak acids and weak bases hydrolyse, but the resulting solution is neutral, acidic or basic. This depends upon the relative values of K_a and K_b of cations and anions of the salt.

Q25. How Hydrolysis is different from hydration?

Ans: Hydrolysis is different from hydration In hydrolysis H – OH bond is broken whereas in hydration water molecule adds up to a substance without bond breakage.

Activity for Students

Calculate concentrations of ions of slightly soluble salts using concept of solubility product.

Ans: Solubility Product:

The product of the molar concentration of positive and negative ions in saturated solution in equilibrium with solid salt is called solubility product.

Explanation:

When a sparingly soluble electrolyte is dissolved in water to form a saturated solution, an equilibrium is established between the dissociated and un-dissociated salt e.g. $PbSO_4$

$$PbSO_4 \rightleftharpoons Pb_{(aq)} + SO^{2}_{(aq)}$$

$$K_c = \frac{[Pb^{2}] \times [SO^{2}_{4}]}{[PbSO_4]} \quad \text{Law of mass action}$$

The rate of change of concentration of $PbSO_4$ is so small, that it almost remains constant.

$$K_C \times [PbSO_4] = [Pb^{+2}] \times [SO^{2}_{4}] \quad \text{or}$$

$$K_{SP} = [Pb^{+2}] \times [SO^{2}_{4}] \text{ where } K_C\ [PbSO_4] = K_{SP}$$

Where K_{SP} is called as solubility product.

The product of the molar concentration of positive and negative ions in saturated solution in equilibrium with solid salt is called solubility product.

Q26. Example 13: The solubility of PbF_2 at 25°C is 0.64g dm^{-3} calculate K_{SP} of PbF_2.

Solution:

Mass of PbF_2 = 0 64g dm^{-3}

(Molar) Mass of PbF_2 = 245.2g $mole^{-1}$

(At wt of Pb = 207.2, F = 19).

$$\text{No of moles of } PbF_2 = \frac{\text{Mass of } PbF_2}{\text{Molar mass of } PbF_2}$$

$$= \frac{0.64g\ dm}{245.2g\ Mole^{-1}}$$

$$= 2.6 \times 10^{-3}\ Mole\ dm^{-3}$$

Now from the equation

$$2.6 \times 10^{-3}\ M\ dm \rightleftharpoons 2.6 \times 10^{-3}\ M + 2 \times 2.6 \times 10^{-3}\ M$$

$$K_{SP} = [Pb^{+2}] \times [F^{-1}]^2$$

$$= 2.6 \times 10^{-3} \times [2 \times 2.6 \times 10^{-3}]^2$$

Activity for Students

The solubility of CaF_2 in H_2O at 25°C is found to be 2.05 × 10^{-4} M dm^{-3}. What is the value of K_{SP} at this temperature? (Ans: K_{SP} = 8.405 × 10^{-12})

Solution:

Solubility of CaF_2 = 2.05×10^{-4} mole dm^{-3}

According to Balanced chemical eq.

	$CaF_{2\,(aq)}$	$\rightleftharpoons$	$Ca^{2+}_{(aq)}$	+	$2F_{(aq)}$
At initial stage (mol/dm^3)	2.05×10^{-4}		0		0

After solubility 0 2.05×10^{-4} $2 \times 2.05 \times 10^{-4}$
(At eq. mol/dm^3)
Hence

$$[C_a^{2+}] = 2.05 \times 10^{-4} mole\ dm^{-3}$$
$$[F^-] = 2 \times 2.05 \times 10^{-4} = 4.1 \times 10^{-4}\ mole\ dm^{-3}$$

Therefore

$$KSP = [C_a^{2+}] = F^-]^2$$
$$KSP = [2.05 \times 10^{-4} mole\ dm^{-3}][4.1 \times 10^{-4} mole\ dm^{-3}]^2$$
$$KSP = 3.446 \times 10^{-11} mole^3\ dm^{-9}$$

EXERCISE

MULTIPLE CHOICE QUESTIONS

1 **Encircle the correct answer in each case:**

i. **Water cannot act as:**
(a) Lewis acid (b) Lewis base
(c) Bronsted acid (d) Bronsted base

ii. **pH of 0.01M HCl solution is:**
(a) 10^{-2} (b) 10^{+2} (c) 2.0 (d). 1.0

iii. **An aqueous solution of ammonium chloride is:**
(a) Basic (b) Acidic (c) Neutral (d) Amphotric

iv. **An aqueous solution of which compound is basic:**
(a) Ammonium nitrate (b) Calcium chloride
(c) Ammonium acetate (d) Potassium carbonate

v. **Which statement about acids is not correct? An acid:**
(a) Contains hydrogen ions in solution.
(b) Contains oxygen.
(c) Has a pH of less than 7.
(d) Gives off carbon dioxide from a carbonate.

vi. **If a liquid has a pH of 7.**
(a) It must be colourless.
(b) It has boiling point of 100°C.
(c) It must be a solution.
(d) It must be neutral.

vii. **When air is bubbled through pure water, the pH is lowered from 7.0 to 5.6, which gas in the air is responsible for this change.**
(a) Argon (b) Carbon dioxide (c) Nitrogen (d) Oxygen.

After solubility 0 2.05×10^{-4} $2 \times 2.05 \times 10^{-4}$
(At eq. mol/dm^3)

Hence

$$[C_a^{2+}] = 2.05 \times 10^{-4} mole\ dm^{-3}$$
$$[F^-] = 2 \times 2.05 \times 10^{-4} = 4.1 \times 10^{-4}\ mole\ dm^{-3}$$

Therefore

$$KSP = [C_a^{2+}][F^-]^2$$
$$KSP = [2.05 \times 10^{-4} mole\ dm^{-3}][4.1 \times 10^{-4} mole\ dm^{-3}]^2$$
$$KSP = 3.446 \times 10^{-11} mole^3\ dm^{-9}$$

EXERCISE

MULTIPLE CHOICE QUESTIONS

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i. Water cannot act as:

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(a) Argon (b) Carbon dioxide (c) Nitrogen (d) Oxygen.

viii. Which of the following oxides is classified incorrectly:

(a)	Zinc oxide (ZnO)	amphoteric
(b)	Carbon dioxide (CO_2)	acidic
(c)	Carbon monoxide	neutral
(d)	Lead oxide (PbO)	basic

ix. If 25cm^3 of 1 mol.dm^{-3} nitric acid is added to 50cm^3 of 0.5 potassium hydroxide solution, what would be the pH of the resulting solution

(a) 5 (b) 7 (c) 9 (d) 14

x. If dry citric acid crystals are placed on dry litmus paper they will

(a) turn yellow (b) turn green

(c) turn red (d) remains unchanged

xi. A base is a substance which will neutralise an acid which of these substances is not a base:

(a) Aqueous ammonia (b) Copper oxide

(c) Potasium chloride (d) Sodium carbonate

xii. A strong acid:

(a) Is always partially ionised when in solution.

(b) Is always fully ionised when in solution.

(c) Always decomposes carbonates.

(d) Always contains oxygen.

xiii. Which one of the following oxides dissolves in water to form acidic solution:

(a) MgO (b) Na_2O (c) SO_2 (d) SiO_2

xiv. When crystals of copper sulphate are heated, the colour changes from blue to white. This is caused by:

(a) Loss of water only

(b) Loss of water and SO_2.

(c) Reaction with CO_2 in the air.

(d) Loss of water, sulphur dioxide and oxygen.

xv. The oxide of a metal was found to react with HCl along aqueous NaOH solution. Which of the following is the best description of the oxide?

(a) Acidic (b) Amphoteric (c) Basic (d) Neutral

xvi. Which one of the following statements must be true of an acid salt?

(a) It can only be formed from a weak acid.

(b) It is the only salt formed from a dibasic acid.

(c) It is the salt of a non-metal.

(d) It contains hydrogen that is replaceable by a metal.

xvii. One mole of each of the following compounds was dissolved in water to make one dm^3 of solution. Which of the solution would have the lowest pH value?

(a) NH_3 (b) CH_3COOH (c) NaCl (d) NaOH (e) H_2SO_4

xviii. Which salt could be obtained as the insoluble product of a reaction between a dilute acid and an aqueous salt?

(a) $BaSO_4$ (b) $CuSO_4$ (c) $MgSO_4$ (d) $AgNO_3$ (e) $ZnCl_2$

xix. Which one of the following oxides react with aqueous NaOH to give a salt.

(a) Calcium oxide (b) Copper oxide (c) Iron oxide
(d) Magnesium oxide (c) Zinc oxide

xx. Which one of the following salts cannot be prepared by a reaction between a dilute acid and a metal?

(a) $CaCl_2$ (b) $CuCl_2$ (c) $FeCl_2$ (d) $MgSO_4$ (e) $ZnSO_4$

Answers

i. a	**ii. c**	**iii. b**	**iv. d**	**v. b**	**vi. d**	**vii. b**
viii. d	**ix. b**	**x. d**	**xi. c**	**xii. b**	**xiii. c**	**xiv. a**
xv. b	**xvi. d**	**xvii. e**	**xviii. a**	**xix. c**	**xx. b**	

Q.2 (i) What are acidic, basic and amphoteric substances? Give one example of each substance.

Ans: J. Bronsted and T.Lowry, independently, elaborate acid base concept by defining them in a different manner.

According to these definitions,

A Bronsted acid is a proton donor

A Bronsted base is a proton acceptor

Acidic substance:

A substance which can donate a proton is called acidic substance. According to the following equation hydrochloric acid is a Bronsted acid since it donates a proton to water.

$$HCl_{(g)} + H_2O_{(l)} \longrightarrow H_3O^{+}_{(aq)} + Cl^{-}_{(aq)}$$

Acid Base

Since water accepts a proton, it is a Bronsted base. After accepting a proton, water is converted to hydroxonium ion (H_3O^+). The hydroxonium ion is infact a **hydrated proton**.

Basic substances:

Those substances which can accept a proton are called basic substances. Thus, in the following equation, water is a Bronsted base since it accepts a proton from sulphuric acid.

$$H_2SO_{4(l)} + H_2O_{(l)} \longrightarrow H_3O^{+}_{(aq)} + HSO^{-}_{4(aq)}$$

Acid Base

Also, in the equation below, ammonia accepts a proton from water. Therefore, ammonia is a base and water is a acid here.

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

Base Acid

Amphoteric substance:

There are some substances which are on the border line of acids and bases these substances are called amphoteric substances. They show properties of both acids and bases.

Example:

Aluminium oxide (Al_2O_3) is amphoteric and it reacts with both acidic and basic solutions:

$$\text{(basic) } Al_2O_{3(s)} + 6HCl_{(aq)} \longrightarrow 2AlCl_{3(aq)} + 3H_2O_{(l)}$$

$$\text{(acidic) } Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)}$$

Also, chromium trioxide is amphoteric since it reacts with both acids and bases.

$$\text{(basic) } Cr_2O_{3(s)} + 6HNO_{3(aq)} \longrightarrow 2Cr(NO_3)_{3(aq)} + 3H_2O_{(l)}$$

$$\text{(acidic) } Cr_2O_{3(s)} + 6KOH_{(aq)} \longrightarrow 2K_3CrO_{3(aq)} + 3H_2O_{(l)}$$

(ii) Elaborate with equations two compounds which are amphoteric in nature.

Ans: Amphoteric substance:

There are some substances which are on the border line of acids and bases these substances are called amphoteric substances. They show properties of both acids and bases.

Example:

Aluminium oxide (Al_2O_3) is amphoteric and it reacts with both acidic and basic solutions:

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$$\text{(acidic) } Al_2O_{3(s)} + 2NaOH_{(aq)} \longrightarrow 2NaAlO_{2(aq)} + H_2O_{(l)}$$

Also, chromium trioxide is amphoteric since it reacts with both acids and bases.

$$\text{(basic) } Cr_2O_{3(s)} + 6HNO_{3(aq)} \longrightarrow 2Cr(NO_3)_{3(aq)} + 3H_2O_{(l)}$$

$$\text{(acidic) } Cr_2O_{3(s)} + 6KOH_{(aq)} \longrightarrow 2K_3CrO_{3(aq)} + 3H_2O_{(l)}$$

(iii) What is Bronsted - Lowry acid-base theory? Give examples.

Ans: Bronsted Lowery Concepts for Acids and Bases:

J Bronsted and T.Lowry, independently, elaborate acid base concept by defining them in a different manner.

According to these definitions,

A Bronsted acid is a proton donor.

A Bronsted base is a proton acceptor.

Definition of proton:

In this respect, a proton is defined as the nucleus of a hydrogen atom (H^+) and it has nothing to do with the protons in a carbon atom, or a sodium atom or any other atom.

Bronsted acid:

Hydrochloric acid is a Bronsted acid since it donates a proton to water according to the following equation.

$$\underset{\text{Acid}}{HCl_{(g)}} + \underset{\text{Base}}{H_2O_{(l)}} \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)}$$

Since water accepts a proton, it is a Bronsted base. After accepting a proton, water is converted to hydroxonium ion (H_3O^+). The hydroxonium ion is infact a **hydrated proton**.

Example:

Some more common Bronsted acids are sulphuric acid (H_2SO_4), phosphoric acid (H_3PO_4) and acetic acid (CH_3CO_2H) etc.

Bronsted bases:

The Bronsted bases have been defined as those species which accept a proton. Thus, in the following equation, water is a Bronsted base since it accepts a proton from sulphuric acid.

$$H_2SO_{4(l)} + H_2O_{(l)} \longrightarrow H_3O^+_{(aq)} + HSO^-_{4(aq)}$$

Acid Base

Also, in the equation below, ammonia accepts a proton from water. Therefore, ammonia is a Bronsted base and water is a Bronsted acid here:

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$$

Base Acid

(iv) What are conjugate acid-base pairs? Explain with examples.

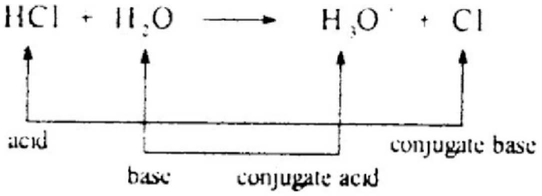
Ans: Conjugate acids:

Conjugate acid is a species which is formed as a result of acceptance of proton by a base. Every Bronsted acid has a conjugate base.

Conjugate bases:

Conjugate base is a species which is left behind after donation of a proton from the acid.

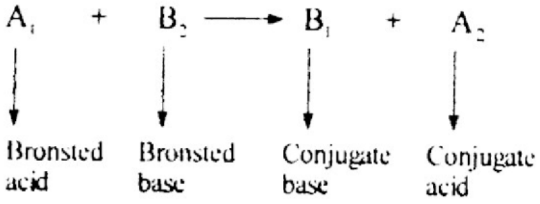
e.g. Ionisation of HCl in water



$$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$$

Conjugate Acid – Base Pairs (Major Concepts):

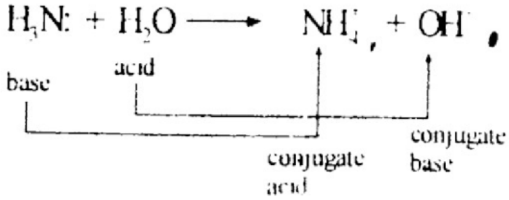
In an acid-base reaction, an acid yields a base (conjugate) and base after accepting proton yields a conjugate acid. The acid-base reaction is represented as



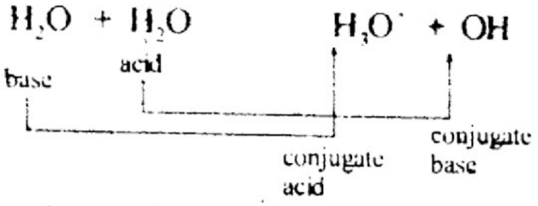
$$A_1 + B_2 \longrightarrow B_1 + A_2$$

The conjugate acid-base pairs are species on opposite sides of an equation that differ by a proton.

The weaker acids have strong conjugate base pairs and stronger acids have weaker conjugate bases e.g.



$$H_3N: + H_2O \longrightarrow NH_4^+ + OH^-$$

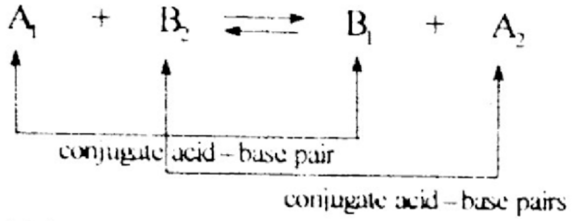


$$H_2O + H_2O \qquad H_3O^+ + OH$$

The water is amphoteric in nature i.e. it is acidic as well as basic in nature.

General notation:

The general notation of conjugate acid-base pair is



$$A_1 + B_2 \rightleftharpoons B_1 + A_2$$

Each acid has a conjugate base and each base has a conjugate acid.

Particular Examples of Conjugate Acid-Base Pairs:

$$\underline{A_1} + \underline{B_2} \qquad \underline{B_1} + \underline{A_2}$$

$$HCl + H_2O \rightleftharpoons Cl^{-1} + H_3O^{+1}$$

$$HCl + NH_3 \rightleftharpoons Cl^{-1} + NH^{+1}_4$$

$$HNO_3 + H_2O \rightleftharpoons NO^{-1}_3 + H_3O^{+1}$$

$$NH^{+1}_4 + H_2O \rightleftharpoons NH_3 + H_3O^{+1}$$

$$H_2O + H_2O \rightleftharpoons OH^{-1} + H_3O^{+1}$$

$$H_2O + CO^{-2}_3 \rightleftharpoons OH^{-1} + HCO^{-1}_3$$

$$HClO_4 + H_2O \rightleftharpoons ClO^{-1}_4 + H_3O^{+1}$$

A_1 B_1 and B_2 A_2 are known as conjugate acid-base pairs.

(v) How preservatives are used in food products and allergic reactions in people.

Ans: Preservatives:

Preservatives are used to preserve food from bacteria They are chemicals that inhibit the growth of bacteria and fungi. It prevents decomposition of food from microbial growth or by chemical changes.

Most commonly used preservatives are

i. Benzoates in bakery products.
ii. Nitrates in meat products.
iii. Sulphites in drinks.
iv. Potassium bromated.
v. Ammonium sulfate
vi. Benzoic acid and Parabens.
vii. Nitrates and Nitrites.

Allergic reactions in people:

The preservatives can cause severe allergic reactions in people. They increase the rate of cancer, childhood illness and auto-immune diseases sulphites can cause wheezing, chest tightness and coughing. Benzoates may cause urticaria, asthma etc.

(vi) Define Lewis acid and Lewis bases. Give one example in each case.

Ans: Lewis Definitions of Acid And Base (MajorConcept):

G.N Lewis, in 1932, put forward his acid-base theory on the basis of electron pair.

Base:

According to Lewis definition, a base is a substance that donates a pair of electrons.

Acid:

According to Lewis definition, an acid is a substance which can accept a pair of electrons.

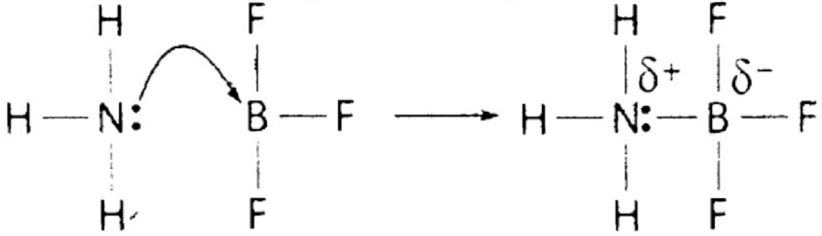
Example:

The hydroxide ion (OH^-) is a Lewis base because it donates a pair of electron and the proton (H^+) is a Lewis acid-since it accepts a pair of electrons.

$$H^+ + :\ddot{\underset{\cdot\cdot}{O}}^- — H \longrightarrow H — \ddot{\underset{\cdot\cdot}{O}} — H$$

Significance:

The significance of the Lewis acid-base concept is that it is much more general than other concepts. It may include such acid-base reactions which are not covered by the Bronsted–Lowery theory. One such example is the reaction between ammonia and boron trifluoride (BF_3) illustrated by the following equation:



The vacant, unhybridized 2p orbital of boron atom in boron trifluoride accepts the electron pair from ammonia. Thus in this reaction ammonia is a Lewis-base and boron trifluoride is a Lewis acid although no proton transfer is observed here.

Some common Lewis acids and bases are listed in the table.

Some common Lewis Acids and Bases:

Lewis Acids		Lewis Bases	
Name	**Formula**	**Name**	**Formula**
Proton	H^+	Hydroxide ion	OH^-
Boron trifluoride	BF_3	Ammonia	NH_3
Aluminium chloride	$Al\,Cl_3$	Carbon monoxide	CO
Silver cation	Ag^+	Water	H_2O
Carbon dioxide	$O = C = O$	Cyanide ion	$^-C \equiv N$

Conclusion:

According to this table Lewis acids have the ability to accept electron pair where as the Lewis bases are capable of donating electron pair.

(vii) Classify each of the following as Bronsted acid or Bronsted base.

(i) HCO^{-1}_3 (ii) HBr (iii) CH_3COO^{-1}

Ans:

Bronsted acid	Bronsted base
i. A Bronsted acid is a proton donor	**i.** A Bronsted base is a proton acceptor
HBr: It is a Bronsted acid as it donates a proton to water $HBr + H_2O \longrightarrow H_3O^+ + Br^{-1}$	**HCO^{-1}_3:** It is a Bronsted base because it accepts from water $HCO_3^{-1} + H_2O \longrightarrow H_2CO_3 + OH^{-1}$
	CH_3COO^{-1}: It is a Bronsted base as it accepts a proton from water. $CH_3COO^{-1} + H_2O \longrightarrow CH_3COOH + OH^{-1}$

(viii) Explain gastric acidity and use of anti-acid drug.

Ans: Human stomach produces HCl. It helps us to digest food. Production of excess HCl by stomach is called gastric acidity. It is generally caused by eating spicy foods.

Anti-acid drug:

This problem can be deduced by taking anti-acidic drugs like Milk of Magnesia ($Mg(OH)_2$) or the medicines in which sodium bicarbonate ($NaHCO_3$) and $Al(OH)_3$ are present. These bases react with acid to neutralize it. In this way acidity can be remove by taking anti-acidic drugs. These are generally present in a single medicinal preparation.

(ix) Write briefly about the ionization of water.

Ans: Auto Ionization of Water:

Water is a unique compound due to its ability to accept or donate proton under different environments. It has been mentioned earlier that water acts as a Bronsted acid in presence of ammonia, and as a Bronsted base in presence of hydrochloric acid. In fact, Water itself undergoes ionization to a small extent as shown in the following equation:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH$$

This reaction is regarded as auto ionization of water.

Explanation:

Here, a molecule of water (which is acting as an acid) donates a proton to another molecule of water (which is acting as a-base) and two species, a hydronium ion and a hydroxide ion, are formed.

In this equation, there are two acid-base conjugate pairs; the first one is water-hydroxide ion (acid-conjugate base) and the second water hydronium ion (base conjugate acid).

In fact, there is an equilibrium between water molecules (on the left side of the equation) and the hydronium ions and hydroxide ions on the right side of the equation).

Equilibrium constant (K):

The equilibrium constant (K) for this equilibrium can be expressed by the following equation.

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

In this equation $[H_3O^+]$ $[OH^-]$ and $[H_2O]$ arc the concentration of hydronium ion, hydroxide ion and water at equilibrium stage.

Large excess of water:

Since water is a solvent, the concentration of water, $[H_2O]$ is in large excess, therefore it remains constant. The above equation may be re-written as:

$$K[H_2O]^2 = [H_3O^+][OH^-]$$

Ion-product constant of water:

The term $K[H_2O]^2$ is the product of two constants, K and $[H_2O]$. Therefore this term is another constant represented by K_w in the following equation where

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

K_w is termed as the ion-product constant of water. Since $[H_3O^+]$ is the concentration of hydrated protons at equilibrium, the above equation corresponds to: $K_w = [H^+][OH^-]$

Applications:

In pure water at 25°C, the concentration of H^+ and OH^- are equal and found to be 1.0×10^{-7} M each. Thus:

$$K_w = [1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

It has been noted that whether in pure water or in a solution of dissolved species, the following relationship always holds.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

(x) Define pH what are the values of pH for acidic, basic and neutral solutions.

Ans: pH:

Since the concentration of $[H^+]$ and $[OH^-]$ are usually very small numbers and inconvenient to work with, a more practical measure called pH was proposed and defined as:

It means that pH of a solution is given by the negative logarithm of the $[H^+]$ concentration (in mol/dm^3).

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

No units:

However it must be kept in mind that pH being a logarithmic value, does not have any units,

Conditions:

The pH concept implies that at 25°C, the different types of solutions will show the following behaviours:

Acid solution: $[H^+] > 1.0 \times 10^{-7}$ M, $pH < 7.00$

Basic solution: $[H^+] < 1.0 \times 10^{-7}$M, $pH > 7.00$

Neutral solution: $[H^+] = 1.0 \times 10^{-7}$ M, pH = 7.00

(xi) Define K_a and pK_a and their applications,

Ans: **K_a:**

K_a is termed as the acid dissociation constant. It is a measure of the extent to which an acid is ionized or dissociated at the equilibrium state.

$$K\,[H_2O] = K_a = \frac{[H_3O^+]\,[\overline{X}]}{[HX]}$$

pK_a:

The negative logarithm of K_a value is called pK_a. The relationship between K_a and pK_a is as follows:

$$pK_a = -\log K_a$$

Applications:

- **i.** pK_a value is also used to determine the strength of acid.
- **ii.** Smaller the value pK_a value, stronger will be the acid and vice versa. It is because smaller pK_a value means greater K_a value.
- **iii.** The K_a values are also used to determine the percentage dissociation of an acid.
- **iv.** The greater the value of K_a, the stronger is the acid and vice versa.

$$pK_a \propto \frac{1}{K_a}$$

(xii) Explain curdling of milk with lemon juice,

Ans:

- **i.** Milk is actually made up of a lot of different components, the main ones being protein, fat, and water.
- **ii.** When it comes to curdling, we're mainly concerned with one specific milk protein called casein.
- **iii.** Normally, little groupings of casein float around in the milk without bonding to anything.
- **iv.** These groupings (technically called micelles) have a negative charge, which makes them repel other groupings of casein and keeps the casein evenly dispersed in the milk.
- **v.** When milk becomes too acidic, like when we add lemon juice or when it goes sour, the negative charge on the casein groupings becomes neutralized.
- **vi.** Now instead of pushing each other apart, the casein starts to clump together.
- **vii.** Eventually large enough clumps are formed that we can actually see the separation, and then we have curdled milk.

(xiii) What are K_b and pK_a and their applications.

Ans: **K_b:**

Base dissociation constant is known as K_b. The extent of ionisation and the base dissociation constant K_b is use to distinguish between strong and weak bases.

Derivation of base dissociation constant K_b:

Consider a base B, an equilibrium reaction with water can be represented by the following equation:

$$B + H_2O_{(aq)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, K [H_2O] is another constant and is designated as K_b thus,

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

K_b value will be large if degree of ionisation of the base B is high i.e. if the base B is strong. The Value of K_b will be small for a weak base B.

pK_b:

pK_b is defined as the negative logarithm of K_b.

$$pK_b = -\log K_b$$

Applications:

i. pK_b also measures the strength of a base.

ii. Smaller the value pK_b, value, stronger will be the base and vice versa. It is because smaller pK_b value means greater K_b value.

$$pK_b \propto \frac{1}{K_b}$$

iii. K_b values are used to determine the strength of different bases.

iv. The greater the value of K_b, the stronger is the base.

(xiv) What is an iodised salt? What is its use in practical life.

Ans: Iodised Salt:

A mixture of sodium chloride (NaCl) that contain some amount of NaI (Sodium Iodide) or KI (Potassium Iodide) is called iodized salt.

Use in practical life:

i. Improved Thyroid Function:

Body needs iodine for the thyroid to produce a couple of essential hormones called thyroxine and triodothyronine. These hormones help to regulate the metabolism and the growth and development of the body. Moreover the deficiency of iodized salt can cause a disease called goiter. In this disease throat swells up due to enlargement of thyroid gland

ii. Improved Brain Function:

Iodized salt can improve the functions of the brain, such as memory, concentration and the ability to learn. An iodine deficiency can lower the IQ by as much as 15 points.

iii. Fights Depression:

Depression and feelings of anxiety and frustration may be the result of an iodine deficiency. Iodized salt can help to ensure that you are getting enough iodine to prevent these emotional feelings from occurring.

iv. Weight Control:

Iodine is important for regulating the metabolism. When it is too high, you may not be able to gain a healthy weight, and if it is too low, you may gain weight, or be unable to lose it. Additionally, iodized salt can increase your energy levels so that you will exercise more.

v. Improved Appearance:

It can help to cure dry and flaky skin, and improve the growth of your hair and nails. It also plays a role in developing and maintaining healthy teeth.

vi. Removes Toxins:

Iodized salt can help to remove harmful metals such as lead and mercury as well as other harmful toxins from our body. This can help to restore a healthy pH level in your body.

vii. Heart Health:

Iodized salt can help to create hormones which regulate the heart rate and blood pressure. It can also help the body to burn extra fat deposits that contribute to heart disease.

(xv) What is the relationship between K_a and K_b.

Ans: As we know that

$$K_a \times K_b = K_w$$

$$K_a = \frac{K_w}{K_b}$$

and $$K_b = \frac{K_w}{K_a}$$

Conclusion:

Since K_w is constant at a given temperature, it may be deduced that K_a is inversely proportional to K_b.

$$K_a \propto \frac{1}{K_b}$$

Thus, stronger the acid, weaker is its conjugate base. It can also be said that stronger a base, weaker is its conjugate acid.

(xvi) Calculate concentrations of ions of slightly soluble salts.

Ans: Slightly soluble salts are partially ionized on dissolving in water.

The product of the equilibrium concentrations of ions, each raised to a power which is the coefficient of the ion in the balanced equation is called solubility product.

For example:

When AgCl is mixed with water. Following equilibrium is established.

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

Mathematically:

K_C for this equilibrium can be written as

$$K_c = \frac{[Ag^+][Cl^-]}{[AgCl]}$$

Since CaF_2 is slightly soluble salt its concentration almost remains constant. Therefore,

$$K_C[AgCl] = [Ag^+][Cl^-]$$

$$K_{SP} = [Ag^+][Cl^-]$$

Where K_{SP} is a constant known as the solubility product constant.

Therefore the value **of concentrations of ions of slightly soluble salts** can be determine by using the value of K_{SP}.

(xvii) Give two examples of a buffer solution.

Ans: A buffer solution contains a weak dissociating acid and the salt of that acid with a strong base.

Examples of a buffer solution:

(i) $H_2CO_3 + NaHCO_3$
$H_3PO_4 + NaH_2PO_4$
$CH_3COOH + CH_3COONa$

(ii) A solution containing a weak base e.g. NH_4OH and its salt with a strong acid like NH_4Cl can also act as a buffer.

(xviii) Perform acid-base titrations to calculate molarity and strength of a given sample solution.

Ans: Consider a titration process in which 25 cm^3 of 0.12M NaOH is neutralized with 30 cm^3 of HCl of unknown concentration. Calculate concentration and strength of HCl solution.

Solution: $HCl_{(aq)} + NaOH_{(aq)} \longrightarrow NaCl_{(aq)} + H_2O$

$$n_1 = 1 \qquad n_2 = 1$$

$$\underset{HCl}{\frac{M_1 V_1}{n_1}} = \underset{NaOH}{\frac{M_2 V_2}{n_2}}$$

$$\frac{M_1 \times 30}{1} = \frac{0.12 \times 25}{1}$$

$$M_1 = 0.1M$$

Thus Molarity of HCl solution is 0.1M.

Strength of solution = Molarity × Molar mass

Strength of HCl solution = $0.1 \times 36.5 = 3.65 g\ dm^3$

(xix) Write two acidic, two basic and two neutral salts.

Ans: Acidic Salts:

Salt formed by the reaction between strong acid and weak base is called "Acidic salt" these salts have pH is more than 7.

Examples: $CuSO_4$, NH_4Cl, NH_4NO_3 etc.

Basic Salts:

Salt formed by the reaction between strong base and weak acid is called " basic salt" these salts have pH less than 7.

Examples: CH_3COONa, NaCN, Na_2S etc.

Neutral Salts:

A salt which is formed by the neutralization of strong acid and strong base is called neutral salts. They have pH = 7.

Examples: NaCl, Na_2SO_4, KNO_3 etc.

(xx) Use the concept of hydrolysis to explain why aqueous solutions of some salts are acidic or basic.

Ans: Hydrolysis:

The reaction of cations and anions of salts with water is called hydrolysis.

Acidic Salts:

Those salts which produce strong acid and weak base on hydrolysis are called acidic salts. The solution becomes acidic due to the presence of strong acid and the hydrolysis is called acidic hydrolysis.

Examples: $CuSO_4$, NH_4Cl, NH_4NO_3 etc.

$$CuSO_4 + H_2O \longrightarrow \underset{\textit{(Weak base)}}{Cu(OH)_2} + \underset{\textit{(Strong acid)}}{H_2SO_4}$$

$$NH_4Cl + H_2O \longrightarrow \underset{\textit{(Strong acid)}}{HCl} + \underset{\textit{(Weak base)}}{NH_4OH}$$

$$NH_4NO_3 + H_2O \longrightarrow \underset{\textit{(Strong acid)}}{HNO_3} + \underset{\textit{(Weak base)}}{NH_4OH}$$

Basic Salts:

Those salts which produce weak acid and strong base on hydrolysis are called basic salts. The solution becomes basic due to the presence of strong base and the hydrolysis is called basic hydrolysis.

Examples:

CH_3COONa, $NaHCO_3$, Na_2S etc.

$$CH_3COONa + H_2O \longrightarrow \underset{\textit{(Weak acid)}}{CH_3COOH} + \underset{\textit{(Strong bane)}}{NaOH}$$

$$NaHCO_3 + H_2O \longrightarrow \underset{\textit{(Weak acid)}}{H_2CO_3} + \underset{\textit{(Strong bane)}}{NaOH}$$

Q3. Elaborate the ionisation equation of water. How does it lead to the ion-product, constant of water? Describe an important application of the ion-product of water.

Ans: Auto Ionization of Water:

Water is a unique compound due to its ability to accept or donate proton under different environments. It has been mentioned earlier that water acts as a Bronsted acid in presence of ammonia, and as a Bronsted base in presence of hydrochloric acid. In fact, Water itself undergoes ionization to a small extent as shown in the following equation:

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

This reaction is regarded as auto ionization of water.

Explanation:

Here, a molecule of water (which is acting as an acid) donates a proton to another molecule of water (which is acting as a-base) and two species, a hydronium ion and a hydroxide ion, are formed.

Acid-base conjugate pairs:

In this equation, there are two acid-base conjugate pairs; the first one is water-hydroxide ion (acid-conjugate base) and the second water hydronium ion (base conjugate acid).

In fact, there is equilibrium between water molecules (on the left side of the equation) and the hydronium ions and hydroxide ions on the right side of the equation).

Equilibrium constant (K):

The equilibrium constant (K) for this equilibrium can be expressed by the following equation.

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

In this equation $[H_3O^+][OH^-]$ and $[H_2O]$ arc the concentration of hydronium ion, hydroxide ion and water at equilibrium stage.

Large excess of water:

Since water is a solvent, the concentration of water, $[H_2O]$ is in large excess, therefore it remains constant. The above equation may be re-written as:

$$K[H_2O]^2 = [H_3O^+][OH^-]$$

Ion-product constant of water:

The term $K[H_2O]^2$ is the product of two constants, K and $[H_2O]$. Therefore this term is another constant represented by K_w in the following equation where

$$K[H_2O]^2 = K_w = [H_3O^+][OH^-]$$

K_w is termed as the ion-product constant of water. Since $[H_3O^+]$ is the concentration of hydrated protons at equilibrium, the above equation corresponds to:

$$K_w = [H^+][OH^-]$$

In pure water at 25°C, the concentration of H^+ and OH^- are equal and found to be 1.0×10^{-7} M each. Thus:

$$K_w = [1.0 \times 10^{-7}][1.0 \times 10^{-7}] = 1.0 \times 10^{-14}$$

It has been noted that whether in pure water or in a solution of dissolved species, the following relationship always holds.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Conditions:

Whenever $[H^+] = [OH^-]$, the aqueous solution is found to be neutral, neither acidic nor basic.

$[H^+] > [OH^-]$ Acidic solution

$[OH^-] > [H^+]$. Basic solution

K_w is temperature dependent:

It is to be noted that, because K_w is an equilibrium constant, it is temperature dependent thus, at 40 °C $K_w = 3.8 \times 10^{-14}$ which corresponds to

$$[H^{+1}] = 1.9 \times 10^{-7}\text{ M and }[OH^{-1}] = 1.9 \times 10^{-7}\text{ M as }[H^+] = [OH^-]$$

Application:

i. pH scale is based on the ionic product of water.

ii. It tells us about the behavior of water.

pH:

Since the concentration of $[H^+]$ and $[OH^-]$ are usually very small numbers and inconvenient to work with, a more practical measure called pH was proposed and defined as:

It means that pH of a solution is given by the negative logarithm of the $[H^+]$ concentration (in mol/dm^3).

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

No units: However it must be kept in mind that pH being a logarithmic value, does not have any units,

Conditions:

The pH concept implies that at 25°C, the different types of solutions will show the following behaviours:

Acid solution: $[H^+] > 1.0 \times 10^{-7}$ M, $pH < 7.00$

Basic solution: $[H^+] < 1.0 \times 10^{-7}$M, $pH > 7.00$

Neutral solution: $[H^+] = 1.0 \times 10^{-7}$ M, $pH = 7.00$

A scale analogous to the pH can be devised using the negative logarithm of the H^+ concentration.

Q.4 What are buffer solutions? Elaborate with suitable examples, their significance in acid-base reactions. Write three common applications of buffer solutions.

Ans: Definition:

Those solutions which resist the change in their pH when a small amount of an acid or a base is added them, are called buffer solutions. They have a specific constant value of pH.

Constitution of buffer:

A buffer solution contains a weak dissociating acid and the salt of that acid with a strong base

e.g. (1) H_2CO_3 + Na HCO_3
H_3PO_4 + Na H_2PO_4
CH_3COOH + CH_3COONa

(2) A solution containing a weak base e.g. NH_4OH and its salt with a strong acid like NH_4Cl can also act as a buffer

Significance:

It resists the change in the pH of a solution even when a small amount of a strong acid and base is added in the solution

Buffer action:

Let us take a buffer solution of CH_3COOH and CH_3COONa. Common ion effect helps us to understand how will buffer work. CH_3COOH being a weak electrolyte undergoes very little dissociation. When CH3COONa, a strong electrolyte is added to CH_3COOH solution, the dissociation of CH_3COOH is suppressed due to common effect of CH_3COO^-.

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$$

Addition of strong acid:

Suppose we add a few drops of HCl to it. Its H ions are used up by CH_3COO^- and the equilibrium is **shifted towards left**.

Thus the addition of HCl will not change the pH of the buffer solution.

Addition of strong base:

In the same buffer solution, if a strong base is added it is neutralised by the acid.

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

$$NaOH \rightleftharpoons Na^+ + OH^-$$

$$H^+ + OH^- \longrightarrow H_2O$$

Thus the addition of NaOH will not change value of pH.

Applications of buffer solutions:

(i) Buffer solutions play an important role in several industrial processes. For example, they are used in the manufacture of photographic materials, leather and dyes

(ii) They are also used in the process of electroplating and analytical procedures.

(iii) The buffer solutions are also used for calibration of pH meters.

Q.5 Write detailed notes on each of the followings:

(a) Conjugate acid base pairs (b) pK_a

(c) pK_b (d) Relative strength of acids.

Ans: (a) Conjugate acid base pairs

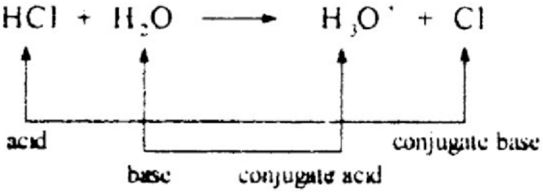
Conjugate acids:

Conjugate acid is a species which is formed as a result of acceptance of proton by a base. Every Bronsted acid has a conjugate base.

Conjugate bases:

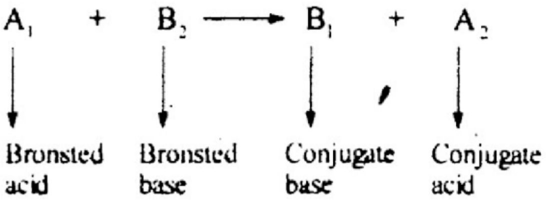
Conjugate base is a species which is left behind after donation of a proton from the acid.

e.g. Ionisation of HCl in water



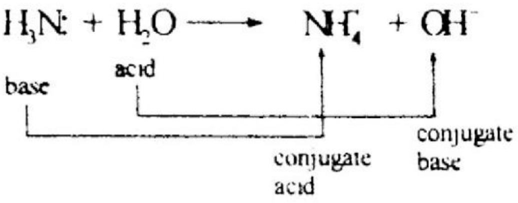
Conjugate Acid – Base Pairs (Major Concepts):

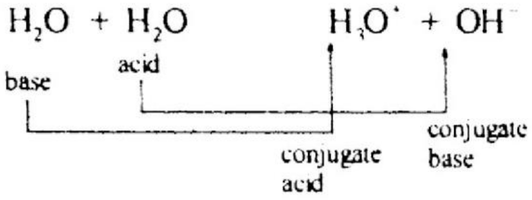
In an acid-base reaction, an acid yields a base (conjugate) and base after accepting proton yields a conjugate acid. The acid-base reaction is represented as



The conjugate acid-base pairs are species on opposite sides of an equation that differ by a proton.

The weaker acids have strong conjugate base pairs and stronger acids have weaker conjugate bases e.g.

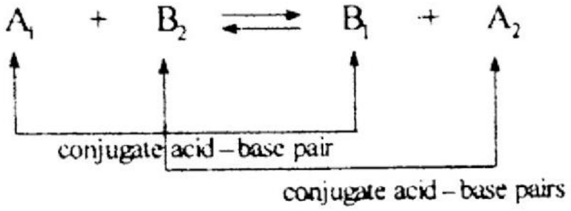




The water is amphoteric in nature i.e. it is acidic as well as basic in nature.

General notation:

The general notation of conjugate acid-base pair is



Each acid has a conjugate base and each base has a conjugate acid.

Particular Examples of Conjugate Acid-Base Pairs:

$$\underline{A_1} + \underline{B_2} \qquad \underline{B_1} + \underline{A_2}$$

$$HCl + H_2O \rightleftharpoons Cl^{-1} + H_3O^{+1}$$

$$HCl + NH_3 \rightleftharpoons Cl^{-1} + NH^{+1}_4$$

$$HNO_3 + H_2O \rightleftharpoons NO^{-1}_3 + H_3O^{+1}$$

$$NH^{+1}_4 + H_2O \rightleftharpoons NH_3 + H_3O^{+1}$$

$$H_2O + H_2O \rightleftharpoons OH^{-1} + H_3O^{+1}$$

$$H_2O + CO^{-2}_3 \rightleftharpoons OH^{-1} + HCO^{-1}_3$$

$$HClO_4 + H_2O \rightleftharpoons ClO^{-1}_4 + H_3O^{+1}$$

(b) pK_a

The value of K_a are usually inconvenient numbers, therefore, for convenience these values are converted to pK_a values. The relationship between K_a and pK_a is as follows:

$$pK_a = -\log K_a$$

Conclusion:

Since pK_a refers to the negative logarithm of K_a. Thus smaller the value pK_a stronger shall be the acid because smaller pK_a value corresponds to a greater K_a value.

(c) pK_b

For convenience, a parameter pK_b has been devised to express K_b value in convenient numbers. Thus, pK_b is defined as the negative logarithm of K_b.

$$pK_b = -\log K_b$$

Table: K_b and pK_b Values of Some Common Bases:

Name of Base	Formula	K_b	pK_b
Diethlyamine	$(C_2H_5)_2\ NH$	9.6×10^{-4}	3.02
Ethylamine	$C_2H_5\ NH_2$	5.6×10^{-4}	3.25
Methylamine	$CH_3\ NH_2$	4.5×10^{-4}	3.34
Ammonia	NH_3	1.7×10^{-5}	4.76
Pyridine	$C_5H_5\ N$	5.6×10^{-9}	8.25
Aniline	$C_6H_5\ NH_2$	4.3×10^{-10}	9.37

Conclusion:

According to these values ammonia is a stronger base than pyridine and aniline but weaker than methylamine and ethylamine. Also, diethyl amine is a strongest base among all those listed in the table.

(d) Relative strength of acids

Different Bronsted acids donate proton to different extents.

The ability of an acid to donate proton is called 'strength of acid' or the 'acid strength'.

An acid which can donate proton to a higher degree than another acid is said to be relatively strong acid.

Example:

Hydrochloric acid is a relatively stronger acid than acetic acid. Also, acetic acid is relatively stronger than water.

Q.6 What is hydrolysis? Discuss in detail, the behaviour of each of the following salts in their aqueous solutions.

(a) K_2CO_3 (b) NH_4Cl (c) $NaNO_3$

Ans: Hydrolysis:

"The reaction of cations and anions of salts with water is called hydrolysis."

Example:

When a salt (MX) is dissolved in water, it splits up into its M^+ and X^- ions. These ions may react with water and give following reactions:

$$M^+ + H - OH_{(l)} \rightleftharpoons MOH_{(aq)} + H^+_{(aq)}$$

$$\overline{X}_{(aq)} + H - OH_{(l)} \rightleftharpoons HX_{(aq)} + OH^-_{(aq)}$$

Since H^+ and OH^- ions are produced in these reactions, the solution of the salt may be acidic or basic. In salts anions are derived from acids and cations from bases. The anions of weak acids are strong conjugate bases. Such anions react with water producing basic solutions.

Hydrolysis of some salts.

(a) K_2CO_3

$$K_2CO_3 + 2H_2O \rightleftharpoons \underset{\textit{Strong base}}{2KOH} + \underset{\textit{Weak acid}}{H_2CO_3}$$

As strong base and weak acid is produce therefore the solution become basic.

(b) NH_4Cl

$$NH_4Cl + H_2O \rightleftharpoons \underset{\textit{Weak base}}{NH_4OH} + \underset{\textit{Strong acid}}{HCl}$$

As strong acid and weak bases produce therefore the solution become acidic.

(c) $NaNO_3$

$$NaNO_3 + H_2O \rightleftharpoons \underset{\textit{Strong acid}}{HNO_3} + \underset{\textit{Weak base}}{NaOH}$$

Since strong base and strong acid is produce therefore, they do not hydrolyze with water and the solution will remain neutral.

Q.7 (a) Calculate the pH of formic acid-sodium format buffer solution containing 1.0 mole of each component. (Ans: 3.7447)

(b) What will be the pH of the solution after addition of 0.10 mole of hydrochloric acid gas to 1.01dm volume of the .buffer solution in part (a) Assume that the volume of solution remains unchanged on addition of hydrochloric acid (K_a for formic acid is 1.8×10^{-4}) (Ans: 3.6997)

Solution: Let the volume of buffer solution is 1 dm^3

[HCOONa] $= 1.0$ mole dm^{-3}

[HCOOH] $= 1.0$ mole dm^{-3}

K_a for formic acid $= 1.8 \times 10^{-4}$

pK_a for formic acid $= -\log(1.8 \times 10^{-4})$

pK_a $= 3.745$

Using Handerson's equation.

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

$$pH = pK_a + \log\frac{[HCOONa]}{[HCOOH]}$$

$$pH = 3.745 + \log\frac{[1.0]}{[1.0]}$$

$$pH = 3.745 + 0$$

$$pH = 3.745$$

(b) What will be the pH of the solution after addition of 0.10 mole of hydrochloric acid gas to 1.01dm volume of the .buffer solution in part (a) Assume that the volume of solution remains unchanged on addition of hydrochloric acid (K_a for formic acid is 1.8×10^{-4})

Solution:

As HCl is a strong acid it ionizes completely. Thus, it means that 0.1 moles of H^+ ions produces: These H^+ ions react with 0.1 moles of $HCOO^-$ ions. Hence, out of 1.0 moles of salt (HCOONa), 0.9 moles (1.0-0.1 = 0.9) of salt are left behind.

As the equilibrium is shifted towards the left therefore the concentration of acid (HCOOH) is increased from 1.0 moles to 1.1 moles (1.0 + 0.1 = 1.1).

New concentrations of salt and acid:

Number of moles of HCOONa = 0.9 moles

Number of moles of HCOOH = 1.1 moles

Since volume of the buffer solution is 1.01 dm^3, therefore, the molar concentrations will be

$$[HCOONa] = \frac{0.9}{1.01} = 0.891 \text{ mole } dm^{-3}$$

$[HCOOH] = \frac{1.1}{1.01} = 1.089$ mole dm^{-3}

K_a of formic acid $= 1.84 \times 10^{-4}$

$pK_a = -\log K_a$

$= -log\left(1.84 \times 10^{-4}\right) = 3.745$

Using Handerson's eq. pH of buffer will be

$pH = pK_a + \log \frac{[salt]}{[acid]}$

$pH = pK_a + \log \frac{[HCOONa]}{[HCOOH]}$

$pH = 3.745 + \log \frac{[0.891]}{[1.089]}$

$pH = 3.745 - 0.0872$

$pH = 3.658$

Q.8 (a) Calculate the H^+ ion concentration of an aqueous solution having pH 10.6. (Ans: 2.5×10^{-11} moles/dm^3)

(b) An aqueous solution contains 1.0×10^{-9} moles/dm of hydronium ions. Calculate the pOH of these solutions. (Ans: 5.0)

Solution: (a)

pH = 10.6

$[H^+]$ = ?

As $pH = -\log [H^+]$

$10.6 = -\log [H^+]$

$\log [H^+] = -10.6$

Taking antilog on both sides

$[H^+] = \text{antilog} (-10.6)$

$[H^+] = 2.51 \times 10^{-11}$

(b) Hydronium ion (H_3O^+) is actually the hydrated proton.

Therefore

$[H^+] = 1.0 \times 10^{-9}$

pOH = ?

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

$pH = -\log[1.0 \times 10^{-9}]$

$pH = -\log(10^{-9})$

$pH = -\log (10)$

$pH = 9 \times 1 = 9$

As, pH + pOH = 14

9 + pOH = 14

pOH = 14 - 9

pOH = 5

Q.9 (a) What is acid dissociation constant? How is it related to pK_a. Write equation to elaborate.

(b) Define and briefly describe the levelling effect of water in acid-base reactions.

Solution:

(a) What is acid dissociation constant? How is it related to pK_a. Write equation to elaborate.

Ans: Acid dissociation constant:

Consider the case of ionisation of a general acid HX in water In this aqueous solution, the established equilibrium may be represented as follows:

$$HX_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + \overline{X}_{(aq)}$$

The equilibrium constant K for this ionisation process may be written as follows.

$$K = \frac{[H_3O^+][\overline{X}]}{[HX][H_2O]}$$

or $$K\,[H_2O] = \frac{[H_3O^+][\overline{X}]}{[HX]}$$

Since water is a solvent, it is present in excess and therefore its concentration may be regarded as constant. Thus, K $[H_2O]$ is another constant and is designated as K_a thus,

$$K\,[H_2O] = K_a = \frac{[H_3O^+][\overline{X}]}{[HX]}$$

K_a is termed as the acid dissociation constant. It is a measure of the extent to which an acid is ionized or dissociated at the equilibrium state.

"The greater the value of K_a, the stronger is the acid".

Relationship between pK_a and K_a:

The value of K_a are usually inconvenient numbers, therefore, for convenience these values are converted to pK_a values. The relationship between K_a and pK_a is as follows:

$$pK_a = -\log K_a$$

Conclusion:

Since pK_a refers to the negative logarithm of K_a. Thus smaller the value pK_a stronger shall be the acid because smaller pK_a value corresponds to a greater K_a value.

(b) Define and briefly describe the levelling effect of water in acid-base reactions.

The Levelling Effect:

Whenever acid react with water hydroxonium ion (H_3O^+) will produce which is acidic in nature and is form in each case. The equal behavior of water, levels the strength of the acids and this leveling of strength is called leveling effect.

Explanation:

The reaction between any stronger acid and water produce hydroxonium ion (H_3O^+) and water goes completely to the right.

Strong acids like perchloric acid, hydrochloric acid, nitric acid and Sulphuric acid in water appear to be of equal strength. Thus, water as a base, is unable to differentiate among the relative acid strength of acids stronger than hydroxonium ion. Such inability of any solvent to differentiate among the relative strength of all acids is termed as the levelling effect. Because the solvent is said to level the strength of all the acids, making them appear identical.

[illegible] effect of water compensated:

The leveling effect of water can be compensated for, if a more weakly basic solvent like acetic acid is employed in place of water. Since acetic acid is a much weaker base than water, it is not easily protonated. Thus, appreciable differences in proton donation of acids are observed in acetic acid (solvent).
The relative acid strength is
$HCl > HI > HBr > H_2SO_4 > HNO_3$
It may be pointed out that all these acids are of identical strength in water (solvent) due to the levelling effect.

e.g. $HCl + H_2O \longrightarrow H_3O^+ + Cl^-$

$$HI + H_2O \longrightarrow H_3O^+ + I^-$$

$$HBr + H_2O \longrightarrow H_3O^+ + Br^-$$

$$H_2SO_4 + H_2O \longrightarrow H_3O^+ + HSO^-_4$$

$$HNO_3 + H_2O \longrightarrow H_3O^+ + NO_3$$

Hydroxonium ion (H_3O^+), which is acidic in nature, is formed in each case. The equal behaviour of such ions formed levels the strength of the acid.

Q.10 (a) What is hydrolysis? Write the equations of hydrolysis equilibrium for each of the followings:
(i) Li^+ (ii) NH^+_4 (iii) CN^-
(b) Write a unique property of a buffer solution. What types of acids are required to prepare buffer solutions? Name two such acids.

Ans: (a)

"The reaction of cations and anions of salts with water is called hydrolysis."

Explanation:

These observations can be explained on the basis of Bronsted-Lowry acid-[illegible] theory. When a salt (MX) is dissolved in water, it splits up into its M^+ and X^- [illegible]. These ions may react with water and give following reactions:

$$M^+ + H-OH_{(l)} \rightleftharpoons MOH_{(aq)} + H^+_{(aq)}$$

$$\overline{X}_{(aq)} + H-OH_{(l)} \rightleftharpoons HX_{(aq)} + OH^-_{(aq)}$$

Since H^+ and OH^- ions are produced in these reactions, the solution of the [illegible] may be acidic or basic. In salts anions are derived from acids and cations from bases. The anions of weak acids are strong conjugate bases. Such anions react with water producing basic solutions

Examples:

CH_3COO^{-1}, CN^{-1}, HCO^{-1}_3, CO^{-2}_3 etc.

[illegible]tions:

(i) **Li^+** $Li^+ + H_2O \rightleftharpoons LiOH + H^+$
(ii) **NH^+_4** $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$
(iii) **CN^-** $CN^- + H_2O \rightleftharpoons HCN + OH^-$
([illegible])

Unique property of a buffer solution:

They resist the change in their pH when a small amount of an acid or a base is added them. They have a specific constant value of pH.

Constitution of buffer:

A buffer solution contains a **weak dissociating acid** and the salt of that acid with a strong base

e.g. H_2CO_3 + Na HCO_3
$H_3 PO_4$ + Na $H_2 PO_4$
CH_3COOH + CH_3COONa