PART FIVE

IONIC EQUILIBRIA

The equilibrium established between the unionised molecules and the ions in the solution of weak electrolytes is known as ionic equilibrium (plural: ionic equilibria).

Acids, bases and salts

&

Solubility and solubility product

Chapter 15

ACIDS AND BASES

In our daily lives we use several acidic and basic chemicals. Some of the acidic chemicals are naturally derived like citric acid in fruits and some are synthetically derived like sulphuric acid. Acids and bases are very important for modern society. They exist everywhere in our body and in our surroundings; for example, vinegar (contains acetic acid), soft drinks (contains carbonic acid), buttermilk (contains lactic acid), soap (contains base).

CONCEPTS OF ACIDS AND BASES

The concept of acids and bases have been defined many times in different ways. Several scientists put various definitions to characterize the acids and bases in which some of the concepts are quite narrow and some are comprehensive. The earliest definitions were made on the basis of their taste and their effect on other substances.

Three important theories of the concept of acids and bases which we are going to discuss in this book are:

- Arrhenius theory
- Bronsted – Lowry theory
- Lewis theory

Arrhenius theory of acids and bases

Arrhenius proposed the concept of acid and base based on the theory of ionisation. It was the first modern approach to acid-base concept. This theory explains many phenomena like strength of acids and bases, salt hydrolysis and neutralisation.

According to **Arrhenius theory of acids and bases:**

Acids *are substances which produce hydrogen ions when dissolved in water.*

- Example of **Arrhenius acids** include compounds like HCl, H_2SO_4, HCN and CH_3COOH which give hydrogen ions (H^+) when dissolved in water (aqueous solution).

Bases *are substances which produce hydroxide ions when dissolved in water.*

- **Arrhenius bases** include compounds like NaOH and KOH which give hydroxide ions (OH^-) in aqueous solution.

Interpretation of Arrhenius theory

The following pieces of information can be deduced from the Arrhenius theory:

Information 1: For a substance to act as an acid, it must contain ionisable hydrogen.

Information 2: For a substance to act as a base, it must contain ionisable hydroxyl group.

Thus by combining the first two pieces, Arrhenius theory suggests that neutralisation happens because hydrogen ions and hydroxide ions react to produce water.

$$H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$$

Information 3: For a substance to act as an acid or a base, water must be present.

The necessity of water as a solvent medium for acid-base reaction, makes the Arrhenius theory of acids and bases to be also known as **water theory** of acids and bases.

Information 4: For a substance to act as an acid or a base, it must be soluble in water.

Advantages of the Arrhenius theory

Despite of its flaws, Arrhenius theory is still important in the following ways:

- It explains the properties of acids and bases in aqueous medium.
- It explains acid-base neutralisation of acid by reaction with base.
- It explains salt hydrolysis.
- It introduces the concept of acidity and basicity.

Disadvantages of the Arrhenius theory

The Arrhenius theory has the following drawbacks:

- It is only applicable to the acid – base behaviour in the aqueous medium (water) only.
- It does not provide any explanation to the acid – base behaviour in absence of water.
- It failed to explain why some compounds with hydrogen of oxidation state of +1 such as HCl dissolve in water to give acidic solution while others such as CH_4 do not.
- It failed to explain why some compounds such as NH_3 and Na_2CO_3 have basic characteristics although they have no hydroxyl (OH^-) group.

  e.g. $Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$

- It failed to explain why some compounds such as CO_2 have got acidic characteristics although they have no hydrogen (H) atom in their molecules.

  e.g. $2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$

- It does not explain acid-base characters for substances which are insoluble in water like aluminium hydroxide.

Acidity and basicity

Acidity of a base *is the number of moles of hydrogen protons (H^+) required by one mole of the base for its complete neutralisation.*

Examples:

1) One mole of NaOH needs one mole of H^+ to form water in neutralisation reaction and hence it is said to have acidity of 1, i.e. it is **monoacid**.
2) One mole of $Ca(OH)_2$ needs two moles and hence it has acidity of 2.
3) One mole $Al(OH)_3$ needs three moles and hence it has acidity of 3.

Basicity of an acid *is the number of hydroxyl ions required by one mole of the acid for its complete neutralisation.*

Examples:

1) One mole of HCl(aq) needs one mole of OH^- for its complete neutralisation and hence it is said to have basicity of 1, i.e. it is **monobasic**.
2) One mole of H_2SO_4 needs two moles and hence it has basicity of 2, i.e. it is **dibasic**.
3) One mole of H_3PO_3 needs three moles and hence it is **tribasic**.

Monoprotic and polyprotic acids

Depending on a number of ionisable hydrogen ions (protons) present in one molecule of an acid; acids can be classified into:

- Monoprotic and
- Polyprotic

Monoprotic acid *is an acid whose one molecule contains one ionisable hydrogen only like HCl.*

Polyprotic acid *is an acid whose one molecule contains more than one ionisable hydrogen.*

When one molecule of acid like H_2SO_4 contains two ionisable hydrogen, the acid is known as **diprotic.**

Diprotic acids undergo ionisation process in two steps. They may undergo one or two dissociation (ionisation) depending on the acidity of solution. For example, H_2SO_4 ionises in two steps according to the following equations:

$$H_2SO_4(aq) \longrightarrow HSO_4^- + H^+(aq)$$

Then; $$HSO_4^-(aq) \longrightarrow SO_4^{2-}(aq) + H^+(aq)$$

Bronsted – Lowry concept of acid and base

We have been previously learned an Arrhenius acid-base theory which provided a good start towards the acid-base chemistry but it has certain limitations. After this theory, Bronsted and Lowry proposed a different definition of acid-base that based on the abilities of compound to either donate or accept the protons. This theory is known as Bronsted-Lowry theory. This theory gives a more general and useful acid-base definition and applies to wide range of chemical reactions.

According to Bronsted – Lowry theory of acids and bases:

An **acid** *is any hydrogen containing specie which is capable of donating one or more hydrogen protons (H^+) to a base.*

- Thus the acid is a **proton donor**.

A **base** *is any specie which is capable of accepting one or more hydrogen protons (H^+) from an acid*

- Thus the base is a **proton acceptor**.

Acids and bases which are classified on the basis of Bronsted – Lowery theory are termed as **Bronsted acids and bases.**

e.g. $HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$

Interpretation of Bronsted-Lowry theory

The following pieces of information can be deduced from the Bronsted-Lowry theory:

Information 1: An acid must contain positively polarized hydrogen.

Information 2: For a substance to act as an acid there should be another substance to act as a base and vice versa. (You cannot have donor without acceptor and vice versa).

In other words, acids and bases are interdependent.
Information 3: Acid-base reactions involve transfer of hydrogen protons from acid to base.

The presence of hydrogen proton as a necessary component of acid-base reaction, makes the Bronsted-Lowry theory of acids and bases to be also known as **proton theory** of acids and bases.

Information 4: The extent of an acid – base reaction is governed not only by the proton donating ability of the acid, but also by the proton accepting ability of the base.

The relationship between the Bronsted – Lowry theory and the Arrhenius theory

The Bronsted – Lowry theory does not go against the Arrhenius theory in any way – it just adds to it as the following points explains:

- Hydroxide ions are still bases because they accept hydrogen ions (H^+) from acid and form water. $H^+ + OH^- \longrightarrow H_2O$
- An Acid produces hydrogen ions in solution because it reacts with the water molecules by giving proton to them. $H^+ + H_2O \longrightarrow H_3O^+$

Thus all Arrhenius acids and bases are Bronsted acids and bases but not all Bronsted acids and bases are Arrhenius acids and bases.

It is important to realize that: Whenever you talk about hydrogen ions in solution, H^+ (aq), what you are actually talking about are hydronium (sometime spelled hydroxonium) ions, H_3O^+.

i.e. $H^+ + H_2O \rightarrow H_3O^+$

The free hydrogen ions do not exist in aqueous solution.

Advantages of Bronsted – Lowry theory over Arrhenius theory

- It expands the list of potential acids and bases to include positive and negative ions as well as neutral molecules or ions with at least one pair of non-bonding electrons (lone pair).
- It explains the role of water in acid – base reaction (water accepts H^+ from acid to form H_3O^+).
- It expands to include solvent other than water and reactions which occur in the gas or solid phase e.g. $NH_3\,(g) + HCl\,(g) \rightarrow NH_4Cl(s)$
- It explains the difference in relative strength of a pair of acid and a pair of base.
- It can explain the **levelling effect of water**. *The fact that strong acids and bases will all have the same strength when dissolved in water*.
- It links acid and base into conjugate acid – base pair (This will be discussed later in this chapter).

Disadvantages of Bronsted – Lowry Concept

- It failed to explain why some compounds such as CO_2, SO_2 and $AlCl_3$ have acidic characters although they have not hydrogen atoms in their structures.
- It failed to explain the basic nature of oxides (basic oxides) like CaO and Na_2O.
- According to Bronsted-Lowry theory, same compound is act as acid in one reaction and act as base in other reaction. So, sometimes it is very difficult to predict the exact acid or base in a reaction.

Strong and Weak acids and bases

Bronsted – Lowry concept of acids and bases enable us to classify acids and bases into strong and weak. The classification is done due to their ability of donating or accepting hydrogen proton (H^+) which in turn affects degree of ionisation of the compounds in water.

A strong acid *is an acid that has high ability donating hydrogen proton to the base so that it undergoes essentially complete ionisation in water.*
Examples of strong acids are HCl, HNO_3 and H_2SO_4. The ionisation of these strong acids in water is a typical acid – base reaction. For better understanding of the concept considers HCl which ionises in water according to the following equation: HCl + $H_2O \rightarrow H_3O^+ + Cl^-$

In the above reaction (ionisation): the acid (HCl) loses a proton to the base. The equilibrium lies far towards the right (complete ionisation of HCl) because H_2O is stronger base (better proton acceptor) than Cl^- and HCl is stronger acid (better electron donor) than H_3O^+ and hence the reaction become irreversible.

A **weak acid** *is an acid which has low ability of donating hydrogen proton to the base so that only a small proportion of its molecules undergo ionisation in water.*
Carbonic acid (H_2CO_3) is a typical weak acid which ionises in water according to the following equation: $H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$

In the above reaction (ionisation): the equilibrium lies towards the non ionised side of the equation because H_3O^+ is the stronger acid than H_2CO_3 and HCO_3^- is stronger base than H_2O and hence large part of carbonic acid molecules remains unionised.

Another example of weak acid is CH_3COOH (Generally most of organic acids are weak).

Bases are classified as strong or weak depending on their affinity for hydrogen ions.

A strong base (such as OH^-) *is the base that has high affinity to hydrogen proton of an acid.*
A weak base (such as NH_3) *is the base that has low affinity to hydrogen proton of an acid.*

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

Ammonia **ammonium ion** **hydroxide ion (strong base than NH_3)**

(weak base) **(Stronger acid than H_2O)**

The student should note that:

The compound NH_4OH does not exist. We commonly write NH_4OH instead of solution of ammonia NH_3 (aq) just for simplicity of understanding some concept and not in actual sense.

Conjugate acids and bases

The concept of conjugate acids and bases is useful for comparison of acidity and basicity.

The **conjugate base of an acid** *is the ion or molecule that is formed when an acid loses its hydrogen ion.* For example, the chloride ion,Cl^-, is the conjugate base of HCl.
The **conjugate acid of a base** *is the product of the reaction of the base and a hydrogen ion.* We say the base has been protonated. Thus, the conjugate acid of NH_3 is NH_4^+.
In order to have better understanding of the concept of conjugate acid and base, consider an acid HA, and think of the reaction (ionisation of HA in water) as being reversible.

$HA + H_2O \rightleftharpoons H_3O^+ + A^-$

Thinking about forward reaction:

- The HA is an acid because it is donating proton (hydrogen ion) to the water.
- The water is base because it is accepting proton from the HA.

But there is also back (reverse) reaction between hydronium and A^- ion.

Thinking about backward reaction:

- The H_3O^+ is an acid because it is donating a hydrogen proton to the A^- ion.
- The A^- ion is a base because it is accepting a proton from the H_3O^+.

The reversible reaction contains two acids and two bases. We think them in pairs, called **conjugate pairs.**

One conjugate pair

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

Another conjugate pair

When the acid, HA, loses proton it forms a base, A^-. When the base, A^- accepts a proton back again, it obviously reforms the acid HA. These two are conjugate pair. Thus:

- If you are thinking about HA as an acid, then A^- is its conjugate base.
- If you are thinking about A^- as the base, then HA is its conjugate acid.

The water and hydronium ion is also a conjugate pair.

- Thinking of water as a base, the hydronium ion is its conjugate acid because it has the extra hydrogen ion which it can give away again.
- Thinking about the hydronium ion as an acid, then water is its conjugate base as the water can accept a hydrogen ion back again to reform the hydroxonium ion.

The reaction between ammonia and water is another example which may give conjugate pairs.

One Conjugate Pair

$$NH_3(g) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

Another conjugate pair

Definition of conjugate pair

These *are two species which differ from each other by the presence or absence of transferable hydrogen ion.*

Relative strengths of conjugate acid-base pairs

Acidic or basic strengths of conjugate acid or base can be derived from known basic or acidic strengths of base or acid respectively as follows:

- If an acid is a strong acid, its conjugate base is a weak base.

$$\underset{\substack{\textbf{Strong acid} \\ \textbf{(Loses } H^+ \textbf{ readily)}}}{HCl} + H_2O \rightarrow H_3O^+ + \underset{\substack{\textbf{Very weak base} \\ \textbf{(Has very little attraction to } H^+\textbf{)}}}{Cl^-}$$

- If an acid is weak, its conjugate base is a strong base.

$$\underset{\textbf{Weak acid}}{CH_3COOH} + H_2O \rightleftharpoons \underset{\textbf{Strong base}}{CH_3COO^-} + H_3O^+$$

$$\underset{\textbf{Very weak acid}}{2H_2O} \rightleftharpoons H_3O^+ + \underset{\textbf{Strong base}}{OH^-}$$

Similarly:

- If the base is strong, its conjugate acid is weak.
- If the base is weak, its conjugate acid is strong.

Thus, as the acid strengths of a series of compounds increase, the base strength of their conjugate bases decrease.

e.g. If acidic strengths of some conjugate acids follows the following trend:

$$\underrightarrow{H_2O,\ HCN,\ CH_3COOH,\ H_3PO_4,\ HCl}$$

Increasing acidity

Then the basic strengths of corresponding conjugate bases must follow the following order:

$$\underrightarrow{OH^-,\ CN^-,\ CH_3COO^-,\ H_2PO_4^-,\ Cl^-}$$

Decreasing basicity

Lewis concept of acids and bases

The Bronsted-Lowry theory which we have been previously studied was a good startup for acid-base chemistry. The Bronsted-Lowry concept was based on the transfer of proton from one chemical specie called acid to another called base. But this theory has its flaws too as we have seen. After Bronsted-Lowry theory, Lewis proposed a new acid-base theory which is based on their transfer of electrons (hence it is also known as electronic theory of acids and bases). This theory is more advanced and flexible than Bronsted-Lowry because it explains the acid-base behavior in that molecules which do not contain hydrogen or in non-aqueous medium.

According to Lewis theory of acids and bases:

- An **acid** *is any specie (charged or uncharged) that can accept a pair of electrons.* E.g. $H^+, BF_3,$ $AlCl_3$ and Ag^+. Thus Lewis acid in **an electron pair acceptor**.
- A **base** *is any specie (charged or uncharged) that can donate a pair of electrons.* E.g. OH^-, NH_3, F^- and CH_3COO^-. Thus Lewis base is **an electron pair donor**.

So the Lewis acid-base reaction leads to the formation of dative bond whereby all shared electrons come from the Lewis base. In other words, the acid-base reaction involves transfer electrons from base to acid.

Examples:

1) $H_3N + BF_3 \rightarrow H_3N - BF_3$
2) $CO_2 + OH^- \rightarrow HCO_3^-$

The reader should understand that:
The Lewis definition is the most general theory, having no requirements for solubility or protons. It expands the list of acids and bases by including the following:

1) All cations (like Na^+, Cu^{2+} and Fe^{3+}) which are regarded as Lewis acids.
2) All anions (like SO_4^{2-} and O^{2-}) which are regarded as Lewis bases.
3) The ion, molecule or an atom which has incomplete octet of electrons (for example, BF_3) are regarded as Lewis acids.
4) All molecules or atoms with lone pair like H_2O and NH_3 are regarded as Lewis bases.
5) The electron-rich pi (π) system like in benzene, ethene and ethyne are also considered as Lewis bases.
6) Molecules with multiple bonds between atoms of different electronegativities like NO_2 and CO_2 are regarded as Lewis acids.
7) All molecules with expanded octet like SF_4 and PCl_5 are regarded as Lewis acids.

Relationship between the Lewis theory and Bronsted – Lowry theory

All Bronsted Lowry acids and bases are also Lewis acids and bases but reverse is not true.

For bases: The Bronsted – Lowry theory says that some species are bases because they are combining with hydrogen ions. The reason they are combining with hydrogen ions is that they have lone pair of electrons (non-bonding electrons)-which is what the Lewis theory says. The two are entirely consistent. Thus all Bronsted bases are also Lewis bases.

For acids: Lewis acids are electron pair acceptors. Compounds like BF_3 are Lewis acids because they can accept lone pair from Lewis bases although on the Bronsted – Lowry theory, the BF_3 has nothing remotely acidic about it. This is an extension of the term acid well beyond any common use.

What about more obviously acid – base reactions – like for example, the reaction between ammonia and hydrogen chloride gas?

$$NH_3(g) + HCl(g) \rightarrow NH_4^+(g) + Cl^-(g)$$

What exactly accepting the lone pair of electron on the nitrogen? Most of students (even some textbooks) often misleads by writing as if the ammonia is donating its lone pair to hydrogen ion – a simple proton with no electrons around it. You don't usually get free hydrogen ions in chemical systems. They are so reactive that they are always attached to something else. They are not any uncombined hydrogen ions in HCl.

There is not any empty orbital anywhere on the HCl which can accept a pair of electrons. Why is then the HCl a Lewis acid?

Chlorine is more electronegative than hydrogen thus making the hydrogen chloride to be polar molecules with partial positive charge on hydrogen atom. ($^{\delta+}H - Cl^{\delta-}$). The lone pair on nitrogen is attracted to the slightly positive hydrogen atom. As it approaches it, the electrons in the $H - Cl$ bond are more repelled towards the chlorine. Eventually, a coordinate bond is formed between the nitrogen and hydrogen and the chlorine breaks away as a chloride ion as shown below:

$$\ddot{N}H_3 + {}^{\delta+}H - Cl^{\delta-} \longrightarrow NH_4^+ + Cl^-$$

Thus the whole HCl molecule is acting as a Lewis acid. It is accepting a pair of electrons from the ammonia and in the process it breaks up. **Lewis acids do not necessarily to have an existing empty orbital.**

Disadvantages of Lewis theory

- It fails to account for the relative strength of acids and bases because it is not based on ionisation.
- An acid – base reaction being an electron – transfer reaction, should be quite fast. However, many Lewis acid – base reactions are slow.
- It cannot explain the concept of relative strength of acids and bases.

Note: The main advantage of the Lewis theory is that it is much more general than other definitions.

Amphoteric and amphiprotic substances

Amphoteric substance *is the substance which can act as either an acid or a base.*

- Thus amphoteric substance can react with both acid and base depending on relative strength of the two; with stronger acid, amphoteric substance acts as a base while with stronger base, the substance acts as an acid.

A good example of amphoteric substance is water which is capable of accepting hydrogen proton to form H_3O^+ (hydronium ion) thus acting as the base and it is also capable of loosing hydrogen proton form OH^- (hydroxide ion) thus acting as the acid.

i.e. $H_3O^+ \xleftarrow{\text{water accepts proton as a base}} H_2O \xrightarrow{\text{water loses proton as an acid}} OH^-$

As an acid, water is capable of reacting with stronger base (than itself) like NH_3 and Cl^-.

$$H_2O + NH_3 \rightarrow NH_4^+ + OH^-$$
$$H_2O + Cl^- \rightarrow HCl + OH^-$$

As a base, water is capable of reacting with stronger acid (than itself) like HCl and HNO_3.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$
$$HNO_3 + H_2O \rightarrow H_3O^+ + NO_3^-$$

Some metal oxides like aluminium oxides (Al_2O_3) are also amphoteric – they reacts with both acids and bases.

Amphiprotic substance *is one which can both donate hydrogen protons and also accept them.*

- Again water is a good example of amphiprotic substance as explained earlier in the case of amphoteric substance.
- Another example is hydrogen sulphate ions (HSO_4^-) which can lose a hydrogen ion to form sulphate ions (SO_4^{2-}) or accept one to form sulphuric acid (H_2SO_4).

But as well as being amphiprotic, these compounds are also amphoteric as amphoteric means that they have reactions as both acids and bases. ***So what is the difference between the two terms?***

All amphiprotic substances are also amphoteric – but the reverse is not true. There are amphoteric substances which do not either donate or accept hydrogen ions when they act as acids or bases. According to Lewis theory, the acid – base reaction does not necessarily involve hydrogen ion. Some metal oxides like aluminium oxides are amphoteric. For example, they react as bases because the oxide ions accept hydrogen ions (protons) to make water. That is not a problem as far as the definition of amphiprotic is concerned –but the reaction as an acid is. The aluminium oxide does not contain any hydrogen to donate! But aluminium oxide is capable of accepting lone pair of hydroxide ions in empty orbital of aluminium ion of the oxide thus acting as Lewis acid.

WORKED EXAMPLES

Example 1

In each of the following indicate the acid / base conjugate pairs:

(i) $H_2SO_4 + HNO_3 \rightleftharpoons H_2NO_3^+ + HSO_4^-$
(ii) $[Fe(H_2O)_6]^{3+} + H_2O \rightleftharpoons [Fe(H_2O)_5OH^-]^{2+} + H_3O^+$
(iii) $NH_2^- + H_2O \rightleftharpoons NH_3 + OH^-$
(iv) $H_2O + CO_3^{2-} \rightleftharpoons HCO_3^- + OH^-$
(v) $HSO_3^- + H_2O \rightleftharpoons H_2SO_3 + OH^-$

Solution

(i) H_2SO_4 / HSO_4^- and $H_2NO_3^+/HNO_3$
(ii) $[Fe(H_2O)_6]^{3+}/[Fe(H_2O)_5OH^-]^{2+}$and H_3O^+/H_2O
(iii) $H_2O/OH^-$and NH_3/NH_2^-
(iv) $H_2O/OH^-$and HCO_3^-/CO_3^{2-}
(v) $H_2O/OH^-$and H_2SO_3/HSO_3^-

Example 2

In each of the following pairs of substances, write an equation to show how the pair reacts to form a conjugate acid – base pair.

(i) Hydrogen sulphate ion and hydroxide ion
(ii) Bicarbonate ion and water
(iii) Carbonic acid and water
(iv) Carbonate ion and water
(v) Hydrogen sulphate ion and water

Solution

(i) Hydroxide ion (which is conjugate base of weak acid, H_2O) is stronger base than hydrogen sulphate ion which is conjugate base of stronger acid, H_2SO_4. Thus OH^- is better proton acceptor in the reaction.

$$\underset{\textbf{Acid}}{HSO_4^-} + \underset{\textbf{Base}}{OH^-} \rightleftharpoons \underset{\textbf{Conjugate acid}}{H_2O} + \underset{\textbf{Conjugate base}}{SO_4^{2-}}$$

Where conjugate acid – base pairs are HSO_4^-/SO_4^{2-} and H_2O/OH^-

(ii) Bicarbonate ion being stronger base (than water) as it's conjugate acid, carbonic acid, is weaker acid than H_3O^+ (conjugate acid of H_2O), it must be proton acceptor in the reaction.

$$\underset{\textbf{Base}}{HCO_3^-} + \underset{\textbf{Acid}}{H_2O} \rightleftharpoons \underset{\textbf{Conjugate base}}{OH^-} + \underset{\textbf{Conjugate acid}}{H_2CO_3}$$

Where conjugate acid – base are $H_2O/OH^-$and H_2CO_3/HCO_3^-

(iii) Carbonic acid being stronger acid compared to water which is conjugate acid of very strong base,OH^-, it must be proton donor in the reaction.

$$\underset{\textbf{Acid}}{H_2CO_3} + \underset{\textbf{Base}}{H_2O} \rightleftharpoons \underset{\textbf{Conjugate acid}}{H_3O^+} + \underset{\textbf{Conjugate base}}{HCO_3^-}$$

Where conjugate acid – base pairs are H_2CO_3/HCO_3^- and H_3O^+/H_2O.

(iv) Carbonate ion having no hydrogen at all, it must be proton acceptor in the reaction.

$$\underset{\textbf{Base}}{CO_3^{2-}} + \underset{\textbf{Acid}}{H_2O} \rightleftharpoons \underset{\textbf{Conjugate acid}}{HCO_3^-} + \underset{\textbf{Conjugate base}}{OH^-}$$

Where conjugate acid – base pairs are $HCO_3^-/CO_3^{2-}$and H_2O/OH^-

(v) H_2O is stronger base than HSO_4^- whose conjugate acid, H_2SO_4 is stronger acid than H_3O^+ (conjugate acid of H_2O) and hence water is proton acceptor in the reaction.

$$\underset{\text{Acid}}{HSO_4^-} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+} + \underset{\text{Conjugate base}}{SO_4^{2-}}$$

Where conjugate acid – base pairs are HSO_4^-/SO_4^{2-} and H_3O^+/H_2O

Be careful: In writing chemical equation to show the formation of acid-base conjugate pairs, the reversibility sign ($\rightleftharpoons$ and not $\longrightarrow$) must be used.

ACID – BASE TITRATION

An **acid-base titration** *is the determination of the concentration of an acid or base by exactly neutralising the acid/base with an acid or base of known concentration.*

It makes use of **neutralisation reaction** that occurs between acids and bases and the knowledge of how acids and bases will react if their formulas are known.
The method of quantitative analysis which involves the experimental determination of volumes of solutions which react together completely is known as **titrimetric analysis**.

Some important definitions related to acid-base titration

Standard solution *is the solution of known concentration in the titration.* It is also known as **titrant** or **titrator**. An aqueous sodium carbonate is a good example of titrant which is commonly used in the experiment.

Analyte or **titrand** *is the solution of unknown concentration in the titration.*

Alkalimetry, (sometimes spelled **alkimetry**), *is the specialized analytic use of acid – base titration to determine the concentration of a basic substance.* Thus in alkalimetry, the analyte is the basic substance.

Acidimetry, (sometimes spelled **acidometry**), *is the specialized analytic use of acid – base titration to determine the concentration of an acidic substance.* Thus in acidimetry, the analyte is the acidic substance.

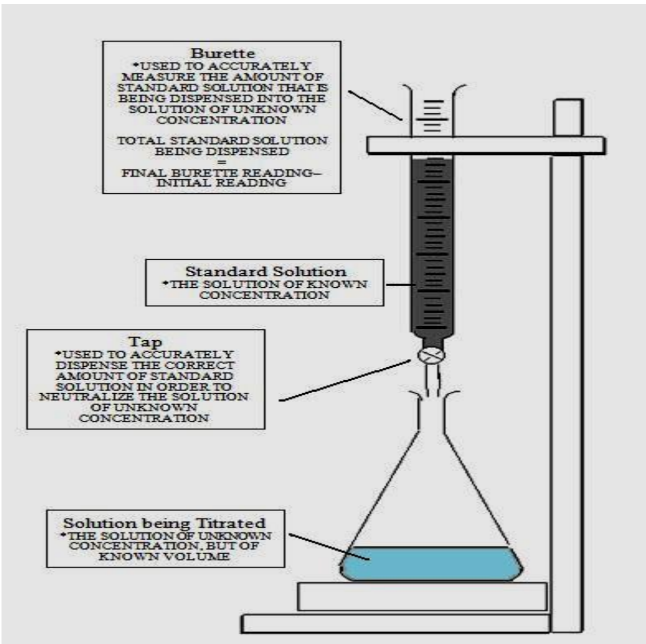


Figure 15.1 Titration diagram

Uses of acid – base titration

Acid – base titration is useful in:

- Determination of unknown concentration of acid or base
- Determination of percentage purity of chemicals

Acid – base indicators (pH indicator)

Acid-base indicators are used to detect pH of a solution. In theory, any substance that undergoes a reversible chemical change when pH changes can be used as an acid-base indicator. But in practice, a sharp change in some easily detectable property of the substance is required. Usually, the property is colour; but other properties such as odour can also change with pH. Almost any flower, fruit, or plant part that is red, blue, or purple can change color with pH. Carrots, rose petals, blue and red grapes, strawberries and red cabbage are good examples of common materials that can be used as acid-base indicators.

By definition:

An acid-base indicator *is an organic compound that changes colour with a change in pH.*

Working of acid-base indicators

Usually acid-base indicators operate as weak acid. To have better understanding of this, we are going to discuss three simple indicators, namely:

- Litmus
- Methyl orange (MO indicator)
- Phenolphthalein (POP indicator)

Litmus

Litmus is a weak acid. It has a seriously complicated molecule which we will simplify to HLit where the "H" is the hydrogen proton which can be given away to something else and the "Lit" is the rest of the weak acid molecule. Thus when the litmus (acid) is dissolved in water, the litmus being weak acid ionises according to the following equation:

$$\mathrm{HLit(aq)} \rightleftharpoons \mathrm{H^+(aq)} + \mathrm{Lit^-(aq)}$$

The un-ionised litmus (HLit) is **red**, whereas the ion ($\mathrm{Lit^-}$) is **blue.** ***Now, what would happen if hydroxide ions or some more hydrogen ions were added to the solution?***

Adding hydroxide ions:

In the equilibrium: $\underset{\textbf{Red}}{\mathrm{HLit\,(aq)}} \rightleftharpoons \mathrm{H^+\,(aq)} + \underset{\textbf{Blue}}{\mathrm{Lit^-\,(aq)}}$

Addition of hydroxide ions ($\mathrm{OH^-}$) is equivalent to removal of $\mathrm{H^+(aq)}$ because $\mathrm{OH^-}$ and $\mathrm{H^+}$ react together to form $\mathrm{H_2O}$. So according to be Le Chatelier's principle, the equilibrium will shift to the right and more $\mathrm{Lit^-}$(aq) are formed making the solution blue and hence **the litmus turns blue in basic solution**.

Adding hydrogen ions:

In the equilibrium: $\underset{\textbf{Red}}{\mathrm{HLit\,(aq)}} \rightleftharpoons \mathrm{H^+\,(aq)} + \underset{\textbf{Blue}}{\mathrm{Lit^-\,(aq)}}$

Addition of hydrogen ions ($\mathrm{H^+}$) increases its concentration. Thus according to Le Chatelier's principle, the equilibrium will shift to the left by forming more $\mathrm{HLit\ (aq)}$ - the unionised litmus. Hence the litmus turns **red in acidic solution.**

If the concentration of HLit and Lit^- are equal:

At some point during the movement of the position of equilibrium, the concentrations of the two colours will become equal. Thus the colour of the solution will be a mixture of the two (blue and red colourations) which is purple.

The reader should understand that:

The concentration of un-ionised indicator and that of ionised indicator not necessarily to be equal at pH of 7; among the common acid-base indicators, litmus is the only indicator which the 50/50 colour does occur at close to pH of 7 and this explains why the litmus is commonly used as test for acids and alkalis while other indicators do not. The pH at which the 50/50 colour occurs is determined by an equilibrium constant for the dissociation of the indicator which is known as **dissociation constant** for the indicator (and not by the neutrality of the solution).

Methyl Orange

Methyl orange is one of the indicators commonly used in titration. Again we will simplify its structure to HMeor where the "H" is the hydrogen proton which can be given away to something else and the "Meor" is the rest of the weak acid molecule. Thus the methyl orange ionises in solution according to the following equation:

$$\underset{\text{Red}}{\mathrm{HMeor(aq)}} \rightleftharpoons \mathrm{H^+(aq)} + \underset{\text{Yellow}}{\mathrm{Meor^-\,(aq)}}$$

Adding hydroxide ions:

Addition of hydroxide ions (OH^-) is equivalent to removal of $H^+(aq)$ because they react together to form H_2O. So according to Le Chatelier's principle, the equilibrium will shift to the right and more $Meor^-\,(aq)$ are formed making the solution yellow and hence **the methyl orange is yellow in alkaline solution.**

Adding hydrogen ions:

Addition of hydrogen ions (H^+) increase its concentration, thus according to Le Chatelier's principle, the equilibrium will shift to the left by forming more unionised HMeor. Hence **the methyl orange is red in acidic solution.**

It should be noted that:

In methyl orange case, the half – way stage where the mixture of red and yellow produces an orange colour happens at pH of 3.7 – nowhere near neutral!

Phenolphthalein

Phenolphthalein is another commonly used indicator for titrations, and is another weak acid.

$$\underset{\text{Colourless}}{\mathrm{H-phph\,(aq)}} \rightleftharpoons \mathrm{H^+\,(aq)} + \underset{\text{Bright pink}}{\mathrm{phph^-\,(aq)}}$$

In this case adding hydroxide ions removes the hydrogen ions from the equilibrium which shifts the position of equilibrium to the right to replace them – turning the indicator pink. Adding extra hydrogen ions shifts the position of equilibrium to the left and turns the indicator colourless. Hence **the phenolphthalein is pink in alkaline solution and it is colourless in acidic solution**. The half – way stage happens at pH of 9.3. Since a mixture of pink and colourless is simply paler pink, this is difficult to detect with any accuracy.

Dissociation constant for pH indicator

So far we have studied that the point at which the pH indicator changes its colour is determined by dissociation constant for the indicator and not necessary for that change to occur at $pH = 7$.

To have more understanding of this, consider the indicator, HIn (where **H** stands for ionisable hydrogen atom of the indicator and **In** stands for anionic part of the indicator) which ionises according to the following equation:

$$\underset{\textbf{Colour 1}}{HIn(aq)} \rightleftharpoons H^+(aq) + \underset{\textbf{Colour 2}}{In^-(aq)}$$

Where **colour 1** is the colour of un-ionised indicator. It is also known as **acid colour** because it is observed when the concentration of H^+ is relatively high.

And **colour 2** is the colour of ionised indicator. . It is also known as **base colour** because it is observed when the concentration of OH^- is relatively high.

Then from this equation of dissociation of the indicator, its equilibrium constant will be;

$$K_c = \frac{[H^+]\,[In^-]}{[HIn]}$$

But because this is the equilibrium constant for the dissociation of the indicator, to be more specific, we are going to call it K_{in} (where **in** stands for indicator).

That is; $\mathbf{K_{in} = \frac{[H^+]\,[In^-]}{[HIn]}}$

But it is clearly understood that the intensity of colour 1 will be equal to the intensity of colour 2 when $[HIn] = [In^-]$

Then from the equation, $K_{in} = \frac{[H^+]\,[In^-]}{[HIn]}$; when $[In^-] = [HIn]$; $K_{in} = [H^+]$

Thus the indicator starts to change its colour when the concentration of hydrogen ions is equal to the dissociation constant for the indicator.

When $\mathbf{[H^+] > K_{in}}$, **colour 1** is observed (position of equilibrium shifts to the left) and when $\mathbf{[H^+] < K_{in}}$, **colour 2** is observed.
Also from $[H^+] = K_{in}$ (when $[HIn] = [In^-]$)

$-\log[H^+] = -\log K_{in}$
Or $pH = pK_{in}$ ($-\log[H^+] = pH$ and likewise $-\log K_{in} = pK_{in}$)

Hence the indicator starts to change its colour when $\mathbf{pH = pK_{in}}$ and when:

- $\mathbf{pH < pK_{in}}$, **colour 1** is observed (By taking negative logarithm to both sides of the above relation, $\mathbf{[H^+] > K_{in}}$)
- $\mathbf{pH > pK_{in}}$, **colour 2** is observed (By taking negative logarithm to both sides of the above relation, $\mathbf{[H^+] < K_{in}}$)

And of course when $\mathbf{pH = pK_{in}}$, **colour mixture of colour 1 and colour 2** will be observed.

pH range of indicators

The end point of an indicator does not occur at a specific pH, rather than there is a range of pH within which the end point will occur. The exact values for the three indicators we have looked are:

Table 16.1 pH of common acid-base indicators

Indicator	pH at a half way of ionisation of the indicator i.e. at 50/50 colour mixture	pH range
Litmus	6.5	5 - 8
Methyl orange	3.7	3.1 – 4.4
Phenolphthalein	9.3	8.3 – 10.0

Choosing indicators for titrations

The point at which the indicator changes colour is called the **end point**.

A suitable indicator should be chosen, preferably one that will experience a change in colour (an end point) as close as possible to the **equivalence point** (**stoichiometric point**) of the reaction. That varies from titration to titration.
The **equivalence point of the reaction**, *the point at which equivalent amount of reactants have reacted in exactly equation proportion* will have a pH dependent on the relative strengths of the acid and base used.

The pH of the equivalence point can be estimated using the following rules:

- A strong acid will react with strong base to form a neutral (**pH = 7**) solution.
- A strong acid will react with a weak base to form an acidic (**pH < 7**) solution. Formation of the acidic solution is explained by the **cationic hydrolysis (cationic hydrolysis will be discussed in detail in chapter 19)** of the salt which is formed in the neutralisation reaction
- A weak acid will react with a strong base to form a basic (**pH > 7**) solution. Formation of basic solution is explained by **anionic hydrolysis (anionic hydrolysis will be discussed in detail in chapter 18)** of a salt which is formed in the neutralisation reaction.

When a weak acid reacts with a weak base, the equivalence point solution will be basic if the base is stronger and acidic if the acid is stronger (as result of the hydrolysis). If both are of equal strength, the hydrolysis will not occur and hence the equivalence point of the solution will be neutral. So in few words can say that: **It is difficult to get suitable indicator for titration of weak acids against weak bases because the titration is complicated by hydrolysis.**

However, even under presence of the suitable indicators**, weak acids are not often titrated against weak bases because the colour change shown with the indicator is often quick, and therefore very difficult for the observer to see the change in colour.**
Thus after above discussion, choice of suitable indicator different kinds of titration can be done as follows:

Methyl orange for the titration involving strong acid and weak base.
Reason for the choice: The end point of methyl orange indicator is found when the solution is acidic (pH range of $3.1 - 4.4$) while the solution at equivalence point of the reaction between strong acid and weak base is also acidic as the result of cationic hydrolysis of a salt formed in the neutralisation reaction.

Phenolphthalein indicator for the titration involving weak acid and strong base.
Reason for the choice: The end point of phenolphthalein indictor is found when the solution is basic (pH range of 8.3 – 10) while the solution at equivalence point of the reaction between weak acid and strong base is also basic as the result of anionic hydrolysis of a salt formed in the neutralisation reaction.

Any indicator (methyl orange or phenolphthalein) for the titration involving weak acid and strong base.

Reason for the choice: In strong acid – strong base titration, both the hydrogen ions and hydroxyl ions concentrations are very small (1×10^{-7}M) at the equivalence point. Consequently, the addition of single drop (negligible volume) of the base (or the acid) causes a large change in $[OH^-]$ or ($[H^+]$) in the pH of the solution and hence either of the two indicators may be used although neither of the two has end point at pH of 7.

It should be noted that: The litmus is always not used as indicator in acid–base titration because the litmus colour change happens over an unusually wide pH range ($5-8$). However, it is useful for detecting acids and alkalis in the laboratory because it changes colours around pH of 7.

Example 3

A certain acid – base indicator has K_a of 10^{-4} with pH range of 3.4 – 4.7. The colour of ionised indicator is yellow and that of unionised indicator is red. When a half of the indicator has been ionised, the colour of the indicator becomes orange.

(i) Calculate the pH at which the colour of the indicator is orange.
(ii) Is the indicator suitable test for acid and base? Explain.
(iii) Can the indicator be used to indicate the end point of the titration between strong acid and weak base or weak acid and strong a base? Give reasons for your choice.
(iv) What colour the indicator will show in 10^{-2} MHCl? Explain.

Solution

(i) Let HA be the acid –base indicator which is weak acid.

$$\underset{\text{Red}}{HA(aq)} \rightleftharpoons H^+(aq) + \underset{\text{Yellow}}{A^-(aq)}$$

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

Then $-\log[H^+] = -\log\left(\frac{K_a[HA]}{[A^-]}\right)$ or $-\log[H^+] = -\log K_a + \log\frac{[A^-]}{[HA]}$

Thus $pH = pK_a + \log\frac{[A^-]}{[HA]}$

The indicator become orange when a half indicator has been ionised, i.e. $[A^-] = [HA]$

Then $pK_a + \log\frac{[A^-]}{[HA]} = pK_a + \log 1 = pK_a$

So $pH = pK_a$ when $[A^-] = [HA]$

Substituting the given value of K_a gives $pH = -\log 10^{-4} = 4$

Hence the colour of indicator becomes yellow when pH is 4

(ii) **No**. For the given indicator, $[A^-] = [HA]$ occurs at pH which is not close 7; so it is possible for two acidic solutions with different pH (say pH of 3 and pH of 5) to give different colour with the indicator or for acidic solution with pH of above 4 to have the same colour as that basic solution (e.g. an acid solution with $pH = 5$ will give yellow colour like any basic solution which commonly have pH above 7).

(iii) The indicator is suitable for a titration between strong acid and weak base because at the **equivalence point** of the titration, the solution is acidic and the **end –point** (the point at which indicator changes its colour) of the indicator also occurs when the solution is acidic (pH range of $3.4-4.7$).

(iv) **Red colour**; pH of 10^{-2}MHCl $= -\log 10^{-2}M = 2$; at pH of 2, pH value is less than pK_a value, so the position of equilibrium will lie to the left hand side and hence the indicator will show red colour.

Calculations on acid – base titration

Example 4

1.400g of pure anhydrous sodium carbonate was made up into $250cm^3$ of aqueous solution. $25.0cm^3$ of this solution required $24.50cm^3$ of a certain sample of hydrochloric acid. Calculate the molarity of the acid and its concentration in gdm^{-3}. If the remaining acid occuipied $920cm^3$, how would it made exactly decimolar? Is the titration acidimetry or alkalimetry?

Solution

Mass Na_2CO_3 in $250cm^3$ of its solution 1.4g

Thus mass of Na_2CO_3 in $25cm^3$ of its solution = $\frac{1.4 \times 25}{250}$g

Using $n = \frac{m}{M_r}$;

Number of moles of Na_2CO_3 reacted in the titration $= \frac{1.4 \times 25}{250 \times 106}$ moles

Na_2CO_3 reacts with HCl according to the following equation:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

From which mole ratio of NaCl to HCl is 1: 2

Thus number of moles of HCl reacted = $\frac{1.4 \times 25 \times 2}{250 \times 106}$ moles = number of moles of HCl in $24.5cm^3$ of its solution

Using [ ] = $\frac{n}{v}$;

$$[HCl] = \frac{1.4 \times 25 \times 2 \times 1000}{250 \times 106 \times 24.5} M = 0.1078M$$

Molarity of the acid is 0.1078M

Mass concentration = Molarity × Molar mass $= 0.1078 \times 36.5gdm^{-3} = 3.9347gdm^{-3}$

Thus mass concentration of the acid is $3.9347gdm^{-3}$

By dilution principle: $M_cV_c = M_dV_d$

Where: M_c is the molarity of concentrated solution $= 0.1078M$

M_d is the molarity of diluted solution = 0.1M (decimolar)

V_c is the volume of concentrated solution = $920cm^3$

V_d is the volume of diluted solution

Then $V_d = \frac{M_cV_c}{M_d} = \frac{0.1078 \times 920}{0.1}cm^3 = 991.8cm^3$

Volume of distilled water added = $V_d - V_c = (991.8 - 920)cm^3 = 71.8cm^3$

Hence $71.8cm^3$ of distilled water must be added to $920cm^3$ of the acid solution in order to convert it to exactly 0.1M (decimolar).

The titration is **acidimetry**

Example 5

5.032g of dibasic organic acid, of anhydrous relative molecular mass 90, were made up to one dm^3 of aqueous solution. $25cm^3$ of this solution required $19.97cm^3$ of 0.10M Sodium hydroxide for neutralisation with phenolphthalein as indicator. Calculate the number of moles of water of crystallization per mole of the crystalline acid.

Solution

Let the formula of the organic acid be $H_2A.nH_2O$;

Then the acid will react with NaOH according to the following equation

$$H_2A.nH_2O + 2NaOH \rightarrow \quad Na_2A \ + \ (n+2)H_2O$$

From which mole ratio of $H_2A.nH_2O$ to NaOH is $1:2$

Number of moles of NaOH reacted = $\frac{19.97}{1000} \times 0.1 = 1.997 \times 10^{-3}$mol

Thus from the above mole ratio, number of moles of the acid in $25cm^3$ of the solution

$= \frac{1.997 \times 10^{-3}}{2}$ moles $= 9.985 \times 10^{-4}$moles

Then number of moles of the acid in $1dm^3$ $(1000cm^3)$

$= \frac{9.985 \times 10^{-4} \times 1000}{25}$moles $= 0.03994$moles

But 5.032g of the organic acid were used;

Then using $M_r = \frac{m}{n}$;

Molar mass of hydrated organic acid = $\frac{5.032g}{0.03994mol} = 126gmol^{-1}$

But relative molecular mass of anhydrous acid = 90;

Where $90 + 18n = 126$ or $n = 2$;

Hence number of moles of water of crystallization per mole of the crystalline acid is 2.

Example 6

1.6g of metallic oxide of type MO was dissolved in 100 cm^3 of 1M hydrochloric acid. The resulting liquid was made up to $500cm^3$ with distilled water. $25cm^3$ of the solution then required $21.02cm^3$ of 0.1020M sodium hydroxide for neutralisation. Calculate the mass of oxide reacting with 1 mole of hydrochloric acid and hence the molar mass of the oxide and the relative atomic mass of the metal.

Solution

After the reaction between MO and HCl, the resulting solution was neutralised by NaOH (alkaline solution). This suggests that the solution was acidic and hence HCl was in excess.

Number of moles of NaOH in $21.02cm^3$ of its solution

$= \frac{21.02}{1000} \times 0.1020$ moles $= 2.144 \times 10^{-3}$moles

NaOH reacts with HCl according to the following equation: $NaOH + HCl \rightarrow NaCl + H_2O$

From which mole ratio of NaOH to HCl is $1:1$

Thus number of moles of HCl in $25cm^3$ of its solution was also

2.144×10^{-3} moles $= 2.144 \times 10^{-3}$moles

Then number of moles of HCl in $500cm^3$ of its solution

$$= \frac{2.144 \times 10^{-3} \times 500}{25}\text{moles} = 0.04288$$

0.04288 moles is the amount of unreacted HCl in its reaction with MO

But total number of moles of HCl was $\frac{100}{1000} \times 1$moles $= 0.1$moles

Thus number of moles of HCl reacted = $(0.1 - 0.04288)$moles $= 0.05712$mol

And therefore, 0.05712 moles of HCl reacted with 1.6g of the oxide.

Whence 1mole of HCl reacted with $\frac{1.6}{0.05712}$g $= 28$g of the oxide

But HCl reacts with MO according to the following equation:

$2HCl + MO \rightarrow MCl_2 + H_2O$

From which 1mole of HCl reacts with 0.5 mole (28g) of MO

Thus mass of one mole of MO = $2 \times 28g = 56g$

Hence molar mass of MO is $56gmol^{-1}$

And relative atomic mass of M $= (56 - 16) = 40$

Example 7

3.000g of a mixture of sodium carbonate and sodium chloride were made up to $250cm^3$ of aqueous solution. $25cm^3$ of this solution required $21.00cm^3$ of 0.1050M hydrochloric acid (with methyl orange as indicator). Calculate the percentage by mass of sodium chloride in the mixture.

Solution

In the titration, sodium chloride is unchanged, while sodium carbonate reacts according to the following equation: $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

Using $n = MV$;

Number of moles of HCl used in the titration = $\frac{21}{1000} \times 0.1050$ moles

But mole ratio of HCl to Na_2CO_3 is $2:1$;

It follows that, number of moles of Na_2CO_3 used in the titration

$= \frac{21 \times 0.1050}{1000 \times 2}$ moles = number of moles of Na_2CO_3 in $25cm^3$ its solution

Thus number of moles of Na_2CO_3 in $250cm^3$ of its solution

$= \frac{21 \times 0.1050 \times 250}{1000 \times 2 \times 25}$ moles $= 0.011025$ moles

Using $m = nM_r$;

Mass of Na_2CO_3 in $250cm^3$ of an impure solution $= 106 \times 0.011025g = 1.16865g$

But total mass of sodium carbonate and sodium chloride = 3g.

Thus mass of NaCl in the mixture $= (3 - 1.16865)g = 1.83135g$

% NaCl $= \frac{m_{NaCl}}{m_T} \times 100\% = \frac{1.83135}{3} \times 100\% = 61.045\%$.

Hence percentage by mass of NaCl in the mixture is 61.045%

Example 8

1.34g of a sample of ammonium chloride was boiled with excess of sodium hydroxide solution. The ammonia evolved was absorbed in $50cm^3$of 0.5M sulphuric acid. The solution was then made up to $250cm^3$ with distilled water and $25cm^3$of it required $25.1cm^3$ of 0.1M sodium hydroxide for neutralisation. Calculate the percentage of ammonia (as NH_3) in the ammonium chloride.

Solution

Number of moles of NaOH in $25.1cm^3$ of its solution

$= \frac{25.1}{1000} \times 0.1$ moles $= 2.51 \times 10^{-3}$moles (Using $n = MV$)

NaOH reacts with H_2SO_4 according to the following equation

$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$

From which mole ratio of NaOH to H_2SO_4 is $2:1$

Thus number of moles of H_2SO_4 in $25cm^3$ of its solution

$$= \frac{2.51 \times 10^{-3}}{2} \text{ moles} = 1.255 \times 10^{-3}\text{moles}$$

Then number of moles of H_2SO_4 in $250cm^3$of its solution

$$= \frac{1.255 \times 10^{-3} \times 250}{25} \text{ moles} = 1.255 \times 10^{-2}\text{moles}$$

These are number of moles of unreacted H_2SO_4 in its reaction with NH_3.

But total number of moles H_2SO_4 before the reaction $= \frac{50}{1000} \times 0.5 \text{ moles} = 0.025 \text{ moles}$

Thus number of moles of H_2SO_4 which reacted in its reaction with NH_3

$= (0.025 - 1.255 \times 10^{-2})$ moles = 0.01245moles

H_2SO_4 reacts with NH_3 according to the following equation:

$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4$

Where mole ratio of NH_3 to H_2SO_4 is $2:1$;

Thus number of moles of NH_3 was (2×0.01245) moles $= 0.0249$moles

The ammonia (NH_3) was produced by the reaction between ammonium chloride (NH_4Cl) and sodium hydroxide according to the following equation:

$$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3$$

Using $m = nM_r$;

Mass of NH_3 in 1.34g of $NH_4Cl = 0.0249 \times 17g = 0.4233g$

Thus % $NH_3 = \frac{0.4233}{1.34} \times 100\% = 31.6\%$

Hence the percentage of NH_3 in the ammonium chloride is 31.6%

Note: Theoretically the percentage can be simply found by using the fact that; molar mass of NH_4Cl is $53.5gmol^{-1}$ out of which 17g is the mass of NH_3. Then using; $\%NH_3 = \frac{m_{NH_3}}{M_{NH_4Cl}} \times 100\% = \frac{17}{53.5} \times 100\% = 31.8\%$. However, this question requires finding the percentage practically and hence the 'shortcut' is not allowed.

Example 9

Hydrochloric acid was standardized in the following way: 1.010g of pure calcium carbonate was allowed to react with $50cm^3$ of the hydrochloric acid. The excess of the acid was neutralised by $24.6cm^3$ of a sodium hydroxide solution. $25cm^3$ of this sodium hydroxide solution needed $23.7cm^3$ of the hydrochloric acid solution for neutralisation. Calculate the molarity of the acid.

Solution

Let molarity of sodium hydroxide be M_b;

Then number of moles of NaOH in $24.6cm^3$ of its solution $= \frac{24.6}{1000}M_b = 0.0246M_b$

NaOH reacts with HCl according to the following equation:

$NaOH + HCl \rightarrow NaCl + H_2O$

From which mole ratio of NaOH to HCl is 1:1;

Thus number of moles of unreacted HCl was also $0.0246M_b$

Total number of HCl before its reaction with $CaCO_3 = \frac{50}{1000}M_a = 0.05M_a$

Where, M_a is the molarity of the hydrochloric acid.

Thus number of moles of HCl reacted with $CaCO_3$= $0.05M_a - 0.0246M_b$

But number of moles of $CaCO_3$ reacted with HCl = $\frac{1.010g}{100gmol^{-1}} = 0.01010$ mol

And $CaCO_3$ reacts with HCl according to the following equation

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + H_2O$$

From which mole ratio of $CaCO_3$ to HCl is 1:2.

Thus number of moles of HCl reacted = $2 \times 0.01010mol = 0.0202$ mol

And hence $0.05M_a - 0.0246M_b = 0.0202$ …………………(i)

But also, $25cm^3$ of NaOH reacts with $23.7cm^3$ of HCl:

Number of moles of NaOH $= \frac{25}{1000}M_b = 0.025M_b$

Number of moles of HCl $= \frac{23.7}{1000}M_a = 0.0237M_a$

From the equation of their reaction; mole ratio of NaOH to HCl is 1:1

It follows that, $0.025M_b = 0.0237M_a$

Or $M_b = 0.948M_a$…………………………………………… (ii)

Substituting (ii) to (i) gives $M_a = 0.757M$

Hence molarity of the acid is 0.757M

Example 10

$25cm^3$ of solution of sodium hydroxide and potassium hydroxide containing 5g of solid per dm^3 required $24.2cm^3$ of 0.1MHCl for neutralisation. Calculate the concentration of each compound in gdm^{-3} of solution.

Solution

Total mass of KOH and NaOH in $1dm^3$ $(1000cm^3)$ is 5g

Thus a mass of the mixture in $25cm^3 = \frac{25}{1000} \times 5g = 0.125g$

Let mass of KOH in $25cm^3$ be *x* in grams

And mass of NaOH in $25cm^3$ y in grams

Then x + y = 0.125 ………………………………………………..(i)

Number of moles of KOH in $25cm^3 = \frac{x}{56}$

Number of moles of NaOH in $25cm^3 = \frac{y}{40}$

KOH reacts with HCl according to the following equation:

$$KOH + HCl \rightarrow KCl + H_2O$$

From which mole ratio of KOH to HCl is 1: 1

Thus number of moles of HCl reacted with KOH was $\frac{x}{56}$

NaOH reacts with HCl according to the following equation:

$$NaOH + HCl \rightarrow NaOH + H_2O$$

From which mole ratio of NaOH to HCl is 1:1

Thus number of moles of HCl reacted with NaOH was $\frac{y}{40}$

But total volume of $24.2cm^3$ of 0.1MHCl was used for neutralisation of the two which give a total number of moles of $\frac{24.2}{1000} \times 0.1mol = 0.00242\ mol$

Whence $\frac{x}{56} + \frac{y}{40} = 0.00242$ ……………………………….(ii)

Solving (i) and (ii) simultaneously;

x = 0.0987 and y = 0.0263

Concentration in $gdm^{-3} = \frac{\text{Mass in g}}{\text{Volume of solution in dm}^3}$

Thus concentration of KOH $= \frac{0.0987 \times 1000}{25} gdm^{-3} = 3.948gdm^{-3}$

And concentration of NaOH $= \frac{0.0263 \times 1000}{25} gdm^{-3} = 1.052dgm^{-3}$

Titration by double indicator

Titration by using two different indicators can be used in:

- Estimation of a mixture of sodium hydroxide and sodium carbonate
- Estimation of a mixture of sodium carbonate and sodium hydrogencarbonate

Estimation of a mixture of sodium hydroxide and sodium carbonate by double indicators

The reaction between sodium hydroxide and hydrochloric acid occurs in a single stage according to the following equation:

$NaOH + HCl \longrightarrow NaCl + H_2O$……………………….… (i)

Or ionically $OH^- + H^+ \rightarrow H_2O$

Where NaOH and HCl being strong base and strong acid respectively, any indicator (**methyl orange** or **phenolphthalein**) can be used to determine the equivalence point of reaction (i).

The reaction between sodium carbonate and hydrochloric acid occurs in two stages, with the hydrogen carbonate ion as intermediate product.

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$ ………………….. (ii)

Then, $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$………………..…. (iii)

Or ionically, $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

$HCO_3^- + H^+ \rightarrow H_2O + CO_2$

Where:

- Na_2CO_3 and HCl being strong base and strong acid respectively, either methyl orange or phenolphthalein indicator can be used to determine the equivalence point of reaction (ii).
- $NaHCO_3$ being weak base and HCl being strong acid, only methyl orange indicator is suitable for determination of equivalence point of reaction (iii).
- Since mole ratio of Na_2CO_3 to HCl, $NaHCO_3$ to HCl as well as Na_2CO_3 to $NaHCO_3$ is 1:1, the amount (volume) of the acid (HCl) required for reaction (ii) and (iii) is the same.

Conclusion….!

- With **phenolphthalein** as indicator, the end point is registered at the completion of **reaction (i)** and **(ii)**.
- With **methyl orange** as an indicator, the end point is registered at the completion of **all three reactions**.
- Since the amount of acid required for reaction (ii) and (iii) is the same, and **the amount of acid used in the reaction (iii) is the difference between the titrations with methyl orange and**

phenolphthalein, it follows that twice this difference is the amount of acid which titrates the whole carbonate, Na_2CO_3, according to equation,

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$.

- The rest titrates the sodium hydroxide.

Estimation of a mixture of sodium carbonate and sodium hydrogen carbonate by double indicator

The same concept of the first case can be applied in this case as follows:

With **phenolphthalein as indicator**, the end point is given when all the carbonate is converted to hydrogen carbonate according to the following equation.

$Na_2CO_3 + HCl \rightarrow NaHCO_3 + NaCl$ ……………(i)

or ionically, $CO_3^{2-} + H^+ \rightarrow HCO_3^-$

With **methyl orange as indicator**, the end point is given when the original hydrogen carbonate and that produced in (i) as an intermediate product are both converted to CO_2 and H_2O according to the following equation:

Intermediate $NaHCO_3$ from (i), $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ ….(ii)

Original $NaHCO_3$ in the mixture, $NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$.... (iii)

Or ionically;

From (i), $HCO_3^- + H^+ \rightarrow H_2O + CO_2$

Original $HCO_3^- + H^+ \rightarrow H_2O + CO_2$

That is the end point with **methyl orange indicator is** obtained after completion of **all three reaction (i), (ii), (iii)** while that of **phenolphthalein indicator** is obtained after reaction (i) only.

Since the amount of acid required for reactions (i) and (ii) is the same, **twice the phenolphthalein titration is the amount of which titrates the carbonate,** Na_2CO_3, according to equation: $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

The rest titrates the original hydrogencarbonate ($NaHCO_3$) which was originally present in the mixture with Na_2CO_3.

Worked examples on the titration by double indicators

Example 11

$25cm^3$ of a solution containing sodium hydroxide and sodium carbonate required $21.5cm^3$ of 1MHCl with phenolphthalein as indicator and $27.85cm^3$ of the same with methyl orange as indicator. Calculate the concentration of each compound in gdm^{-3} of the solution.

Solution

Equations for reactions;

$NaOH + HCl \rightarrow NaCl + H_2O$……………………… (i)

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$…………………. (ii)

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ ……………. (iii)

Titre volume used in reaction (iii) = $(27.85 - 21.5)cm^3 = 6.35cm^3$

Thus the volume of acid required to titrate $Na_2CO_3 = 2 \times 6.35cm^3 = 12.7cm^3$

Whence, the acid required to titrate the sodium hydroxide in the same volume of solution = $(27.85 - 12.7)cm^3 = 15.15cm^3$

Number of moles of HCl reacted in (i) $= \frac{15.15}{1000} \times 1mol = 0.01515mol$

But from (i), mole ratio of NaOH to HCl is 1: 1

Then number of moles of NaOH reacted was also 0.01515 mol

Using; mass concentration in gdm^{-3} = [ ]M_r

Then mass concentration of NaOH = $\frac{0.01515\times1000\times40}{25}\text{gdm}^{-3} = 24.24\text{gdm}^{-3}$

Hence the concentration of sodium hydroxide solution was 24.24gdm^{-3}

The overall reaction equation between Na_2CO_3 and HCl is;

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

From which mole ratio of Na_2CO_3 to HCl is 1:2

But number of moles of HCl reacted with Na_2CO_3= $\frac{12.7}{1000} \times 1 \text{ mol} = 0.0127 \text{ mol}$

Thus number of moles of Na_2CO_3 reacted = $\frac{0.0127}{2}\text{mol} = 0.00635\text{mol}$

Then, $[Na_2CO_3] = \frac{0.00635\times1000}{25}\text{M} = 0.254\text{M}$

Using; mass concentration in gdm^{-3} = [ ]M_r $= 0.254 \times 106\text{gdm}^{-3} = 26.924\text{gdm}^{-3}$

Hence the mass concentration of solution of sodium carbonate was 26.924gdm^{-3}

Example 12

20cm^3 of a solution containing sodium hydroxide and sodium carbonate required 19.2cm^3 of 0.5MHCl with phenolphthalein as indicator. With methyl orange, a further 5.1cm^3 of the acid were needed. What is the concentration of each compound in the original solution, in grams of anhydrous solid per dm^3?

Solution

Equations for reactions:

$NaOH + HCl \rightarrow NaCl + H_2O$…………………………….. (i)

$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$ …..…………..…...… (ii)

$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2$ ……….......….. (iii)

From above equations:

The volume of acid required to titrate $Na_2CO_3 = 2 \times 5.1\text{cm}^3 = 10.2\text{cm}^3$

And the volume of acid required to titrate NaOH

= $(19.2 - 5.1)\text{cm}^3$ or $(19.2 + 5.1 - 10.2)\text{cm}^3 = 14.1\text{cm}^3$

Number of moles of HCl reacted with Na_2CO_3= $\frac{10.2}{1000} \times 0.5\text{mol} = 0.0051\text{mol}$

The overall reaction equation between Na_2CO_3 and HCl is

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

From which mole ratio of Na_2CO_3 to HCl is 1:2

Thus number of moles of Na_2CO_3 reacted = $\frac{0.0051\text{mol}}{2} = 0.00255\text{mol}$

And mass concentration of $Na_2CO_3 = \frac{0.00255\times106\times1000}{20}\text{gdm}^{-3}$= 13.515gdm^{-3}

Hence the concentration of anhydrous sodium carbonate was 13.515gdm^{-3}

Number of moles of HCl reacted with NaOH = $\frac{14.1}{1000} \times 0.5\text{mol} = 0.00705\text{mol}$

From (i), mole ratio of NaOH to HCl is 1:1

Thus number of moles of NaOH reacted was also 0.00705mol

And mass concentration of NaOH = $\frac{0.00705 \times 40 \times 1000}{20}$ $\mathrm{gdm^{-3}} = 14.1\mathrm{gdm^{-3}}$

Hence mass concentration of NaOH was $14.1\mathrm{gdm^{-3}}$

Example 13

Anhydrous sodium carbonate contaminated with sodium hydrogencarbonate was made up to $250\mathrm{cm^3}$ of solution. $25\mathrm{cm^3}$ of this solution required $11.2\mathrm{cm^3}$ of 1MHCl with phenolphthalein as indicator and $24.5\mathrm{cm^3}$ of the same acid with methyl orange as indicator. Calculate the percentage by mass of sodium hydrogen carbonate in the mixture.

Solution

Equations for reactions: $Na_2CO_3 + HCl \rightarrow NaHCO_3 + HCl$ ……………..……...…. (i)

From (i) $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$ ……………………………..…….. (ii)

Original $NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O$ ………………...……………...… (iii)

From above equation:

Volume of HCl required to titrate $Na_2CO_3 = 2 \times 11.2\mathrm{cm^3} = 22.4\mathrm{cm^3}$

Thus volume of HCl used to titrate original $NaHCO_3$ which was present in the mixture as impurity = $(24.5 - 22.4)\mathrm{cm^3} = 2.1\mathrm{cm^3}$

Number of moles of HCl reacted with $Na_2CO_3 = \frac{22.4}{1000} \times 1\mathrm{mol} = 0.0224$ mol

The overall reaction equation between Na_2CO_3 and HCl is

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

From which mole ratio of Na_2CO_3 to HCl is $1:2$

It follows that:

Number of moles of Na_2CO_3 in $25\mathrm{cm^3}$ reacted with HCl = $\frac{0.0224}{2} \times 0.0112\mathrm{mol}$

And mass of Na_2CO_3 in $25\mathrm{cm^3} = 0.0112\mathrm{mol} \times 106\mathrm{gmol^{-1}} = 1.1872\mathrm{g}$

Number o f moles of HCl reacted with the original $NaHCO_3 = \frac{2.1}{1000} \times 1\mathrm{mol} = 0.0021\mathrm{mol}$

From equation (iii), mole ratio of $NaHCO_3$ to HCl is $1:1$

Thus number of moles of the $NaHCO_3$ in $25\mathrm{cm^3}$ was also 0.0021mol

And mass of the original $NaHCO_3 = 0.0021 \times 84\mathrm{g} = 0.1764\mathrm{g}$

Total mass of Na_2CO_3 and its impurity ($NaHCO_3$) in $25\mathrm{cm^3}$

$= (1.1872 + 0.1764)\mathrm{g} = 1.3636$

Then % $NaHCO_3 = \frac{0.1764}{1.3636} \times 100\% = 12.9\%$

Hence the percentage by mass of $NaHCO_3$ in the mixture was 12.9%.

(In the above problem there in no necessity of using the $250\mathrm{cm^3}$; the important thing is to have mass of each component of mixture in any equal volume of solution)

Example 14

8.58g of impure sodium carbonate were made up to $250\mathrm{cm^3}$of aqueous solution. $25\mathrm{cm^3}$of this solution required $15\mathrm{cm^3}$ of 0.2MHCl for neutralisation with phenolphthalein (**POP**) as an indicator. Calculate percentage purity of the carbonate.

Solution

The reaction between sodium carbonate takes place in two stages as per equations:

$$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3 \ldots\ldots\ldots\ldots\ldots\ldots\text{(i)}$$

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2 \ldots\ldots\ldots\ldots\text{(ii)}$$

With POP indicator, the end point is registered after completion of reaction (i) only. Thus 15cm^3 is the volume of HCl used in reaction (i) only.

Since mole ratio of Na_2CO_3 to HCl, $NaHCO_3$ to HCl as well as Na_2CO_3 to $NaHCO_3$ is 1:1, the (volume) of the acid (HCl) required for reaction (i) and (ii) is the same.
Thus volume of HCl required to react with the whole carbonate (the volume at the end point if MO would be used) $= 2 \times 15\text{cm}^3 = 30\text{cm}^3$
And the overall reaction equation become (by taking (i) + (ii));

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + CO_2 + H_2O$$

From which mole ratio of Na_2CO_3 to HCl is 1:2

Number of moles of HCl required to react completely with the carbonate

$= \frac{30}{1000} \times 0.2 \text{ moles} = 6 \times 10^{-3}\text{moles}$

And from the mole ratio number of moles (in 25cm^3) of the carbonate $= \frac{6 \times 10^{-3}}{2} = 0.003\text{mol}$

So number of moles of the Na_2CO_3 in $250\text{cm}^3 = \frac{0.003 \times 250}{25}\text{mol} = 0.03\text{mol}$

Using $m = nM_r$;

Mass of Na_2CO_3 in $250\text{cm}^3 = 0.03\text{mol} \times 106\text{gmol}^{-1} = 3.18\text{g}$

But total mass of the impure sodium carbonate in 250cm^3 is 8.58g

Hence the percentage purity$= \frac{3.18}{8.58} \times 100\% = 37.06\%$

Alternative solution (By using equation (i) only)

Number of moles of HCl reacted at the end point with POP indicator

$$= \frac{15}{1000} \times 0.2 \text{ moles} = 3 \times 10^{-3}\text{moles}$$

But from (i); mole ratio of Na_2CO_3 to HCl is 1:1;

Therefore, number of moles of in 25cm^3 of Na_2CO_3 was also 3×10^{-3}

(On your own you may continue as in the first solution to get the same answer)

DIGGING DEEPER EXERCISE 15

EXERCISE 15A: BINDER QUESTIONS

Question 1

Classify each reactant as either a Bronsted-Lowry acid or base for the following reactions:

(a) $HCN + H_2O \longrightarrow CN^- + H_3O^+$

(b) $CH_3NH_2 + H_2O \longrightarrow CH_3NH_3^+ + OH^-$

Question 2

Write the formula for the following:

(a) Conjugate base of H_2SO_3 b) conjugate acid of CN^- c) conjugate acid of S^{2-} d) Conjugate base of HClO

(e) Conjugate acid of HCO_3^- f) conjugate base of NH_3 g) conjugate acid of $H_2PO_4^-$ h) conjugate base of H_3O^+

Question 3

Write conjugate acid and conjugate base of each of the following:

(i) OH^-
(ii) H_2O
(iii) NH_3
(iv) HCO_3^-

Question 4

Concentrated sulphuric acid reacts with sodium chloride as follows:

$$H_2SO_4 + Cl^- \rightleftharpoons HCl + HSO_4^-$$

(a) Identify the conjugate acid/base pairs in this reaction.
(b) What would be the observable result of this reaction?
(c) Explain why this reaction goes almost completely to the right despite the hydrochloric and sulphuric acids are strong acids.

Question 5

(a) What indicator should be used in titration of hydrochloric acid with ammonia solution?
(b) There is no suitable indicator for the titration of ethanoic acid with ammonia. Why this?

Question 6

Why an acid-base indicator changes color over a range of pH values rather than at a specific pH.

EXERCISE 15B: REAL QUESTIONS

Question 7

If someone in your family is suffering from a problem of acidity after overeating, which of the following substances would you suggest as a remedy? Lemon juice, vinegar or baking soda solution. Mention the property on the basis of which you will choose the remedy.

Question 8

Your friend, **Kipute** tested water from a pond and told you these results. When tested with phenolphthalein, it stays clear. When litmus paper is dipped in the pond water, the paper turns blue. What can you conclude from **Kipute's** result about pH of the pond water?

Question 9

You are given with two unknown solutions labelled **'A'** and **'B'**. Then you tested the two solutions and found that an aqueous solution **'A'** turns phenolphthalein solution pink. On addition of an aqueous solution **'B'** to **'A'** the pink colour disappears. What can you conclude about the nature of solution **'A'** and **'B'**?

Question 10

Mr. Akilikubwa added two drops of phenolphthalein to a solution of sodium hydroxide in a test tube.

(i) State the colour change he observed.
(ii) If he then added dilute HCl dropwise to the solution, what will be the colour change?
(iii) On adding few drops of NaOH solution to the above mixture, he found that the colour of the solution reappears. Why?

Question 11

Curry powder and tumeric are spices that contain a bright yellow pigment called curcumin and therefore they can be used natural acid-base indicators. The curcumin turns from yellow at pH 7.4 to red at pH 8.6.

(i) Can curry powder and tumeric be used in acid-base titrations? Give a reason to support your answer.
(ii) Can the spices be used to detect the equivalence point of the reaction between acetic acid solution and caustic soda solution? Explain.
(iii) *Natural indicators like curry powder and tumeric are less common in use in scientific settings such as laboratories than synthetic indicators like methyl orange and phenolphthalein.* Outline at least three reasons to justify this statement.

Question 12

Blueberry is the natural acid-base indicator whose colour change from blue (around pH $2.8 - 3.2$) to red in a strongly acidic solution. Based on this information alone answer the following questions:

(i) Can blueberries be used to detect acid and base? Rationalise your answer.
(ii) Can blueberries be used as an indicator in methanoic acid−potassium hydroxide titration? Explain.
(iii) Nowadays more research on the natural indicators are done so that uses of synthetic indicators can be reduced. Suggest any two possible reasons for this.

EXERCISE 15C: HOT QUESTIONS

Question 13

A solution of sodium hydroxide contained 0.25moldm^{-3}. Using phenolphthalein indicator, titration of 25cm^3 of this solution required 22.5cm^3 of a hydrochloric acid solution for complete neutralisation.

(a) Write the equation for the titration reaction.
(b) What apparatus would you use to measure out (i) the sodium hydroxide solution? (ii) the hydrochloric acid solution?
(c) What would you rinse your apparatus out with before doing the titration?
(d) What is the indicator colour change at the end-point?
(e) Calculate the moles of sodium hydroxide neutralised.
(f) Calculate the moles of hydrochloric acid neutralised.
(g) Calculate the concentration of the hydrochloric acid in mol/dm^3.

Question 14

A bulk solution of hydrochloric acid was standardized using pure anhydrous sodium carbonate (Na_2CO_3, a primary standard). 13.25 g of sodium carbonate was dissolved in about 150.0 cm^3 of deionised water in a beaker. The solution was then transferred, with appropriate washings, into a graduated flask, and the volume of water made up to 250cm^3, and thoroughly shaken (with stopper on!) to ensure complete mixing. 25.0 cm^3 of the sodium carbonate solution was pipetted into a conical flask and screened methyl orange indicator added. The aliquot required 24.65cm^3 of a hydrochloric acid solution, of unknown molarity, to completely neutralise it.

(a) Calculate the molarity of the prepared sodium carbonate solution.
(b) How many moles of sodium carbonate were titrated?
(c) How many moles of hydrochloric acid were used in the titration?
(d) What is the molarity of the hydrochloric acid?

Question 15

50.0 cm^3 sample of sulphuric acid was diluted to 1.00 dm^3. A sample of the diluted sulphuric acid was analysed by titrating with aqueous sodium hydroxide. In the titration, 25.0 cm^3 of 1.00M aqueous sodium hydroxide required 20.0 cm^3 of the diluted sulphuric acid for neutralisation.

(a) Calculate how many moles of sodium hydroxide were used in the titration?

(b) Calculate the concentration of the diluted acid.
(c) Calculate the concentration of the original concentrated sulphuric acid solution.

Question 16

Magnesium oxide is not very soluble in water, and is difficult to titrate directly. Its purity can be determined by use of a **'back titration'** method. 4.06 g of impure magnesium oxide was completely dissolved in 100 cm^3 of hydrochloric acid, of concentration 2.00M (in excess).

The excess acid required 19.7 cm^3 of sodium hydroxide (0.200M) for neutralisation.

This second titration is called a **'back-titration'**, and is used to determine the unreacted acid.

(a) Calculate the moles of hydrochloric acid added to the magnesium oxide.
(b) Calculate the moles of excess hydrochloric acid titrated.
(c) Calculate the moles of hydrochloric acid reacting with the magnesium oxide.
(d) Calculate the moles and mass of magnesium oxide that reacted with the initial hydrochloric acid.
(e) Hence the % purity of the magnesium oxide.
(f) What compounds could be present in the magnesium oxide that could lead to a false value of its purity? Explain.

Question 17

0.279g of an organic monobasic aromatic carboxylic acid, containing only the elements C, H and O, was dissolved in aqueous ethanol. A few drops of phenolphthalein indicator were added and the mixture titrated with 0.100M sodium hydroxide solution. It took 20.5 cm^3 of the alkali to obtain the first permanent pink.

(a) How many moles of sodium hydroxide were used in the titration?
(b) How many moles of the organic acid were titrated?
(c) Calculate the molecular mass of the acid.
(d) Suggest possible structures of the acid with your reasoning.

Question 18

A sample of sodium hydrogencarbonate was tested for purity using the following method. 0.400g of the solid was dissolved in 100.0 cm^3 of water and titrated with 0.20M hydrochloric acid using methyl orange indicator. 23.75cm^3 of acid was required for complete neutralisation.

(a) Calculate the moles of acid used in the titration and the moles of sodium hydrogencarbonate titrated.
(b) Calculate the mass of sodium hydrogen carbonate titrated and hence the purity of the sample.

Question 19

A 5.00g sample of dry mixture of potassium hydroxide, potassium carbonate, and potassium chloride is reacted with 0.100L of 2.0MHCl solution.

(a) A 249mL sample of dry CO_2 gas, measured at 22°C and 740mmHg, is obtained from the reaction. What is the percentage of potassium carbonate in the mixture?
(b) The excess HCL is found by titration to be chemically equivalent to 86.6mL of 1.5 MNaOH.calculate the percentages of:
    (i) Potassium hydroxide and
    (ii) Potassium chloride in the original mixture.

Question 20

A solution contains Na_2CO_3 and $NaHCO_3$. 10mL of this solution required 2mL of 0.1MH_2SO_4 for neutralisation using phenolphthalein as indicator. Methyl orange is then added when a further 2.5mL of 0.2MH_2SO_4 was required. Calculate the mass concentration of Na_2CO_3 and $NaHCO_3$ in solution.

Chapter 16

WEAK ELECTROLYTES

When some substances are dissolved in water, they undergo either a physical or a chemical change that yields ions in solution. These substances constitute an important class of compounds called **electrolytes**. Electrolytes can be acids, bases or salts as they all give ions when dissolved in water. These substances conduct electricity due to mobility of ions (cations and anions) they possess. In some cases, they conduct electricity even in their molten state too. Substances that do not yield ions when dissolved are called **non-electrolytes**. If the physical or chemical process that generates the ions is almost hundred percent efficient (all of the dissolved compound yields ions), then the substance is known as a **strong electrolyte**. If only a relatively small fraction of the dissolved substance ionises, it is called a **weak electrolyte**. Behaviour of weak electrolyte is well explained by Arrhenius theory of weak electrolyte.

ASSUMPTIONS OF ARRHENIUS THEORY

Assumption 1: A weak electrolyte is electrically neutral.

Assumptions 2: When dissolved in solution, the electrolyte tends to ionise yielding cations and anions.

Assumptions 3: The process of ionisation of the weak electrolyte in the solution is reversible. That is the ions formed after ionisation tends to recombine giving unionised molecule again.

e.g. (i) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^-(aq) + H_3O^+$

Or may be written as; $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$

(The reader should note that: in aqueous solution, the hydrogen proton, H^+ is always hydrated to give hydronium ions, H_3O^+, according to the equation, $H^+ + H_2O \rightarrow H_3O^+$, thus $H^+(aq)$ is equivalent to H_3O^+)

(ii) $NH_3 + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

(iii) $AgCl(s) + H_2O \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

Assumption 4: After ionisation, cations are attracted towards negative electrode while anions are attracted towards positive electrode.

Assumption 5: At any time of the ionisation process, there is a ratio of concentration of molecules ionised (dissociated) to form free ions to that of unionised (undissociated) molecule which is known as a degree of ionisation (dissociation).

That is: Degree of dissociation, $\alpha = \frac{\text{concentration of free ions}}{\text{Original concentration of molecules before dissociation,C}}$

Thus concentration of free ions $= \alpha C$

Application of Arrhenius theory in derivation of Ostwald's dilution law

Arrhenius theory can be applied in deriving Ostwald's dilution law as follows:

Consider a binary weak electrolyte, A^+B^- which ionises in aqueous solution according to the following equation:

	$AB + H_2O \rightleftharpoons$	$A^+(aq) +$	$B^-(aq)$
Initial number of moles before dissociation	1	0	0
At equilibrium (After dissociation)	$1-\alpha$	α	α
[ ] of each at the equilibrium	$(1-\alpha)C$	αC	αC

(The reader should recognise that: if the initial amount is 1mole then numerical value of number of moles dissociated must be equal to the degree of dissociation, α).

From the above equilibrium: $K_c = \frac{[A^+][B^-]}{[AB][H_2O]}$

The equilibrium constant expression can be rearranged as follows: $K_c[H_2O] = \frac{[A^+][B^-]}{[AB]}$

But for every dilute solution, $[H_2O]$ = constant.

Thus K_c $[H_2O]$ give another constant, K and the constant is known as **dissociation (or ionisation) constant.** So $\mathbf{K} = \frac{[\mathbf{A}^+][\mathbf{B}^-]}{[\mathbf{AB}]}$

From which $K = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha}$ (by substituting values of $[A^+]$, $[B^-]$ and $[AB]$ to the above equation of the equilibrium constant expression)

But weak electrolytes ionise only partially and most part of the molecules remain undissociated (unionised) thus α becomes too small and hence 1- α ≈ 1 **(The assumption is true if and only if $\boldsymbol{\alpha \leq 0.1}$; otherwise Ostwald's dilution law does not hold because when $\boldsymbol{\alpha >}$ 0.1, *the value of* α cannot be neglected compared to 1)**.

It follows that: $K = \alpha^2 C$

And hence $\boldsymbol{\alpha} = \sqrt{\frac{\mathbf{K}}{\mathbf{C}}}$

The result is known as **Ostwald dilution law** and the law states that: *The degree of dissociation of weak electrolyte varies inversely proportional to square root of its concentration.*

Also it should be remembered that, the reciprocal of concentration is known as **dilution.**
That is $\mathbf{1/C = V}$ **(Dilution)** = *Volume of solution in dm^3 (or L) which contains one mole of the solute*

Whence Ostwald dilution law can be rewritten as; $\boldsymbol{\alpha = \sqrt{KV}}$ where V is the dilution of the electrolyte

Thus according to Ostwald dilution law; **the degree of dissociation of a weak electrolyte increases with an increase of dilution of the electrolyte**.

Definition of dissociation constant

Quantitatively, **dissociation constant** may be defined as *an equilibrium constant which is given as a ratio of product of concentration of free ions to that of unionised molecules in a solution of weak electrolyte.*

Or qualitatively, the constant may be defined as *a factor (constant) which expresses the extent of ionisation of a weak electrolyte to give free ions when dissolved in aqueous solution.*

That is if the dissociation constant is large, it implies that there is more ionisation and if the constant is small, there is less ionisation.
So the significance of dissociation constant is to give the extent of ionisation of weak electrolyte yielding free ions which take part in the chemical reaction.

Don't forget this fact!

Ostwald's dilution law and hence the equation; $\alpha = \sqrt{\frac{K}{C}}$ is applicable if and only if the value of degree of dissociation, α is less than 0.1, i.e. It is negligible compared to 1 such that $1 - \alpha = 1$; otherwise the relationship: $K = \frac{\alpha^2 C}{1-\alpha}$, must be used as such.

DISSOCIATION CONSTANT FOR ACID AND BASE

Dissociation constant for acid, K_a

Consider a weak acid, HA which ionises partially in aqueous solution as follows;

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

	HA		H_3O^+	A^-
Initial number of moles before ionisation	1		0	0
At equilibrium (After ionisation)	$1-\alpha$		α	α
[ ] of each at equilibrium	$(1-\alpha)C$		αC	αC

Where C is the concentration of the acid before ionisation (dissociation)

From the above equilibrium: $K_c = \frac{[H_3O^+][A^-]}{[HA][H_2O]}$ Or $K_c[H_2O] = \frac{[H_3O^+][A^-]}{[HA]}$

But for very dilute solution, $[H_2O]$ is constant,

Thus $K_c[H_2O]$ gives another constant and the constant is known as **dissociation (or ionisation) constant for the acid, K_a**

Whence $\mathbf{K_a} = \frac{[\mathbf{H_3O^+}][\mathbf{A^-}]}{[\mathbf{HA}]}$

Substituting values of $[HA], [A^-]$ and $[H_3O^+]$ to the above dissociation constant expression gives: $K_a = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha}$

But for weak electrolyte, α is too small;

Thus 1 - α ≈ 1 and therefore $K_a = \alpha^2 C$

And hence $\boldsymbol{\alpha} = \sqrt{\frac{\mathbf{K_a}}{\mathbf{C}}}$

The final result is equivalent to **Ostwald's dilution law**

Definition of dissociation constant for acid, K_a

Quantitatively the constant may be defined as *the ratio of product of concentration of free ions to that of undissociated weak acid in aqueous solution*

Or qualitatively the constant may be defined as *the factor which expresses the extent to which the weak acid ionises to give hydrogen ions (H^+) in aqueous solution.*

Significance of dissociation constant for acid, K_a

Dissociation constant for acid, K_a, is important in determining the extent to which the acid tends to ionise in aqueous solution to give hydrogen ions (H^+) thus knowing acidic strength of the acid.

- If K_a of the one acid is large than that of another acid, then the acid become stronger acid.
- Generally if $K_a > 10^{-7}$ (At 25°C), the dilute solution is then acidic
- If K_a of one acid is smaller than that of another acid, the acid is then become weaker acid.
- Generally if $K_a < 10^{-7}$(At 25°C), the dilute solution is then basic (not acidic).
- K_a values for strong acids like HNO_3, H_2SO_4, HI and HCl are very large (Generally the acid is said to be strong if its $K_a > 10$).
- K_a values for weak acids like CH_3COOH and CH_3CH_2COOH are very small.
- Since K_a value for weak acid are very small, to avoid confusion which may arise in dealing with very small value; the values are always given as pK_a which is obtained by taking negative of common logarithm of K_a value

  That is $\mathbf{pK_a = -logK_a}$

Hence:

For strong acid; K_a is large and pK_a is small

For weak acid; K_a is small and pK_a is large

Generally:

For acidic dilute solution; $K_a > 10^{-7}$ and $pK_a < 7$ (At 25°C)

For basic dilute solution; $K_a < 10^{-7}$ and $pK_a > 7$ (At 25°C)

The reader should note that:

Dissociation constant (whether for acid or base) is equilibrium constant so it is temperature dependent like any other equilibrium constants.

Dissociation constant for base, K_b

Consider a weak base, B^-

	$B^- + H_2O$	$\rightleftharpoons$	$HB +$	OH^-
Initially	1		0	0
At equilibrium	$1-\alpha$		α	α
[ ] of each at equilibrium	$(1-\alpha)C$		αC	αC

Where C is the initial concentration of the base

From the above equilibrium: $K_c = \frac{[HB]\,[OH^-]}{[B^-]\,[H_2O]}$

From which: $K_c\,[H_2O] = \frac{[HB]\,[OH^-]}{[B^-]}$;

But for very dilute solution, $[H_2O]$ = constant.

Thus $K_c[H_2O]$ gives another constant which is known as **dissociation constant for the base K_b**

Whence $\mathbf{K_b} = \frac{[\mathbf{HB}][\mathbf{OH^-}]}{[\mathbf{B^-}]}$

Substituting values for $[HB], [OH^-]$ and $[B^-]$ gives: $K_b = \frac{\alpha C \times \alpha C}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha}$

But for very weak base, α is too small

Then 1 - α ≈ 1

If follows that, $K_b = \alpha^2 C$

And hence $\boldsymbol{\alpha} = \sqrt{\frac{\mathbf{K_b}}{\mathbf{C}}}$

The final result is equivalent to Ostwald's dilute law

Definition of dissociation constant for base, K_b

Quantitatively, the constant may be defined as *the equilibrium constant which is given as a ratio of the product of the concentration of free ions to that of undissociated weak base in aqueous solution.*

Or qualitatively, the constant may be defined *as the factor which expresses the extent to which a weak base tends to ionise in aqueous solution to give hydroxyl ions* (OH^-).

Significance of dissociation constant for base, K_b

Dissociation constant for base is important in determining the extent to which the base tends to ionise in aqueous solution to give hydroxyl ions (OH^-) thus knowing the basic strength of the base.

- If K_b of the base is large, then the base become strong and vice – versa.
- K_b values of strong bases like NaOH and KOH are very large.
- Generally if $K_b > 10^{-7}$, the dilute solution is then basic and if $K_b < 10^{-7}$, the dilute solution is then acidic for measurement taken at 25˚C.

To avoid confusion of dealing with small values of $K_b$for very weak bases like ammonia solution, the values are always given as pK_b which are obtained by taking negative of common logarithm of K_b value.
That is $\mathbf{pK_b = -logK_b}$

Hence:

For strong base; K_b is large and pK_b is small

For acidic base; K_b is small and pK_b is large

Generally:

For basic dilute solution: $K_b > 10^{-7}$ and $pK_b < 7$(At 25°C)

For acidic dilute solution; $K_b < 10^{-7}$ and $pK_b > 7$(At 25°C)

pH AND pOH FOR ACIDS AND BASES

pH (**p** stands for 'potential' and **H** stands for 'hydrogen') *is negative of common logarithm of hydronium ions* (H_3O^+) *concentration in very dilute solution.*

That is $\mathbf{pH = -log[H_3O^+]}$

Since H_3O^+ (hydronium ion) is formed when hydrogen proton is formed in water, i.e is the same as $H^+(aq)$;

Whence the above equation can be rewritten as follows: $\mathbf{pH = -log[H^+]}$

pH is also termed as the **hydrogen ion index**

pOH *is negative logarithm of hydroxyl ions* (OH^-) *concentration in very dilute solution*

That is $\mathbf{pOH = log[OH^-]}$

For Acids:

- If $[H^+]$ is large then the acid is strong acid and hence pH which is – $\log[H^+]$ become small for strong acid and vice – versa.
- Generally if $[H^+] > 10^{-7}$ mold m^{-3} then the dilute solution becomes acidic.

  So – log $[H^+] < -\log 10^{-7}$ and hence $\mathbf{pH < 7}$ **for acidic solution**

- If $[OH^-]$ is small then the solution is more acidic (less basic) and its **pOH** is large.
- Generally if $[OH^-] < 10^{-7}$ moldm^3, then the dilute solution become acidic.

  – log $[OH] > -\log 10^{-7}$ and hence $\mathbf{pOH > 7}$ **for acidic solution**

For bases:

- If $[OH^-]$ is large, then the base become strong and its pOH which is – log $[OH^-]$ become small and vise – versa.
- Generally if $[OH^-] > 10^{-7}$ moldm^3, the dilute solution is basic

  Then – log $[OH^-] < -\log 10^{-7}$ and hence $\mathbf{pOH < 7}$ **for basic solution**

- If $[H^+]$ is very small, then the solution is more basic (less acidic) and its pH is large.
- Generally if $[H^+] < 10^{-7}$ $moldm^{-3}$, then the dilute solution become basic

  So – log $[H^+] > -\log 10^{-7}$ and hence **pH** > 7 **for basic solution**

IONIC PRODUCT OF WATER

Water is very weak electrolyte and it is amphoteric. It undergoes **self-ionisation** partially yielding equal concentration of H_3O^+ and OH^- (The reaction is also known as **auto-ionisation of water).**

That is: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$ (or $2H_2O \rightleftharpoons H_3O^+ + OH^-$)

From which it is clearly understood that:

$[H_3O^+] = [OH^-]$ and the equality explains neutral character of water.

An introduction of an acid which ionises to give H^+ which combine with H_2O (In left hand side of the above equilibrium) to give H_3O^+ (which appears in right hand side of the above equilibrium) is equivalent to lowering the concentration of H_2O while concentration of H_3O^+ is increased. To restore the equilibrium more OH^- needs to combine with added H_3O^+ so to form water thus shifting the position of chemical equilibrium to the left making $[H_3O^+] > OH^-$.

Hence $[\mathbf{H_3O^+}] > [\mathbf{OH^-}]$ **for acidic solution**

By similar explanation, the addition of base in water makes $[H_3O^+] < [OH^-]$ when the new equilibrium is re-established and hence $[H_3O^+] < [OH^-]$ for basic solution.

It should be noted that: At standard conditions (25℃ and 1atm),

$[OH^-] = [H_3O^+] = 10^{-7}$ $moldm^{-3}$. This derives the following facts:

- $pH = pOH = -\log 10^{-7} = 7$ for pure water (neutral solution) at 25℃.
- For acidic solution, $[H_3O^+] > 10^{-7}$ $moldm^{-3}$ and hence its $pH < 7$ as mentioned earlier.
- For basic solution, $[H_3O^+] < 10^{-7} moldm^{-3}$ and hence its $pH > 7$

Derivation of ionic product of water

From the equation of self ionisation of water: $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

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

Rearranging the above equilibrium constant expression gives: $K_c [H_2O]^2 = [H_3O^+][OH^-]$

Since at given temperature, density of water is constant

So the concentration of pure water, $[H_2O]$, must be constant too.

Whence $K_c[H_2O]^2$ gives another constant which is known as the ionic product of water, K_w.

Hence $\mathbf{K_w} = [\mathbf{H_3O^+}]\,[\mathbf{OH^-}]$

But at 25℃, $[H_3O^+] = [OH^-] = 10^{-7}$ $moldm^{-3}$.

It follows that;

$K_w = 10^{-7}$ $mddm^{-3} \times 10^{-7}$ $moldm^{-3} = 10^{-14}$ mol^2dm^{-6} at 25℃ and **the product is always true even for non-neutral (acidic or basic solution) because like any other equilibrium constant, $\mathbf{K_w}$ is only temperature dependent and its value does not depend on the initial concentration of $\mathbf{H_3O^+}$ or $\mathbf{OH^-}$**. According to the equilibrium law, the equilibrium constant does not depend on the initial concentration of reagents present in the system, it is only temperature dependent.

Definition of ionic product of water, $\mathbf{K_w}$

Quantitatively, *it is the equilibrium constant which is given as the product of concentration hydronium ions (H_3O^+) and hydroxyl ions (OH^-) in self-ionisation of water at given temperature.*

That is; $K_W = [H_3O^+][OH^-]$

Qualitatively, *is the factor which expresses the ability of water to undergo self-ionisation yielding hydronium ions $[H_3O^+]$ and hydroxyl ions $[OH^-]$ at given temperature.*

Relationship between pH and pOH

From the ionic product of water: $K_w = [H_3O^+][OH^-]$

Taking – log both sides of the above K_w expression:

$-\log K_w = -\log[H_3O^+][OH^-]$
$-\log K_w = -\log[H_3O^+] + -\log[OH^-]$
But; $-\log K_w = pK_w$, $-\log[H_3O^+] = pH$ and $-\log[OH^-] = pOH$

Hence $\mathbf{pK_w = pH + pOH}$

But at 25°C, $K_w = 10^{-14}mol^2dm^{-6}$

It follows that $pK_w = -\log 10^{-14}mol^2dm^{-6} = 14$

Hence **at 25°C; $\mathbf{pH + pOH = 14}$**

RELATIONSHIP BETWEEN K_a and K_b FOR CONJUGATE PAIRS

Consider two dilute solutions; one with HA and another with A^- which are conjugate pairs;

For HA: $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

From which: $K_a = \frac{[H_3O^+][A^-]}{[HA]}$ ………………………………………. (i)

ForA^-: $A^- + H_2O \rightleftharpoons HA + OH^-$

From which; $K_b = \frac{[HA][OH^-]}{[A^-]}$ ………………………………………. (ii)

But from (ii); $[HA] = \frac{[A^-]K_b}{[OH^-]}$ ………………………………………….(iii)

Then substituting (iii) into (i): $K_a = \frac{[H_3O^+][A^-][OH^-]}{[A^-]K_b}$ or $K_aK_b = [H_3O^+][OH^-]$

But $[H_3O^+][OH^-] = K_W$

Hence $\mathbf{K_aK_b = K_w}$ **for conjugate pairs**

Introducing $-\log$ both sides in above equation:

$-\log K_aK_b = -\log K_w$ or $-\log K_a + -\log K_b = -\log K_w$

But $-\log K_a = pK_a, -\log K_b = pK_b$ and $-\log K_w = pK_w$

Hence $\mathbf{pK_a + pK_b = pK_w}$ **for conjugate pairs**

At 25°C, $K_w = 10^{-14}mol^2dm^{-6}$ and $\mathbf{pK_w} = 14$

Thus $\mathbf{K_aK_w = 10^{-14}mol^2dm^{-6}}$ and $\mathbf{pK_a + pK_b = 14}$

WORKED EXAMPLES

Example 1

Using ethanoic acid as the weak electrolyte, derive Ostwald's dilution law.

Solution

Ethanoic acid being weak electrolyte, (weak acid) ionises in aqueous solution according to the following equation:

	$CH_3COOH + H_2O$	$\rightleftharpoons$	$CH_3COO^- + H_3O^+$	
Number of moles before dissociation	1		0	0
Number of moles at equilibrium (After dissociation)	$1-\alpha$		α	α
[ ] of each at equilibrium	$(1-\alpha)C$		αC	αC

Where C is the concentration of ethanoic acid before dissociation and α is numerically equal to the degree of dissociation of the acid.

Then from the above equilibrium: $K_c = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH][H_2O]}$ or $K_c\,[H_2O] = \frac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]}$

But for every dilute solution, $[H_2O]$ is constant.

So $K_c\,[H_2O]$ gives another constant which is known as the dissociation constant for the acid, K_a.

Thus $K_a = \frac{[CH_3COO^-]\,[H_3O^+]}{[CH_3COOH]}$

But at equilibrium: $[CH_3COOH] = (1-\alpha)C$, $[CH_3COO^-] = \alpha C$ and $[H_3O^+] = \alpha C$

It follows that: $K_a = \frac{\alpha C \times \alpha C}{(1-\alpha)} = \frac{\alpha^2 C}{1-\alpha}$

For weak electrolyte (weak acid), α is to too small.

Therefore $1 - \alpha \approx 1$

Whence $K_a = \alpha^2 C$

And hence $\alpha = \sqrt{\frac{K_a}{C}}$ which is Ostwald's dilution law

Example 2

Calculate the degree of dissociation of CH_3COOH in (a) 0.5M (b) 0.125M (c) 0.031M. Comment on the value obtained ($K_a = 1.8 \times 10^{-5}$).

Solution

Using $\alpha = \sqrt{\frac{K_a}{C}}$

Where α is the degree of dissociation of the acid,

K_a is the dissociation constant for the acid,

C is the initial concentration of the acid before dissociation.

(a) $\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.5}} = 6 \times 10^{-3}$ or 0.6%

(b) $\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.125}} = 0.012$ or 1.2%

(c) $\alpha = \sqrt{\frac{1.8 \times 10^{-5}}{0.031}} = 0.024$ or 2.4%

Comment: Degree of dissociation increases as concentration of CH_3COOH decrease from (a) to (c), i.e. degree of dissociation increase with an increases of dilution of the acid.

Example 3

Show that figures below satisfy the dilution law:

Volume in dm^3 containing 1 mole	5.4	10.6	24.9	63.3
Degree of dissociation, α	0.0098	0.0138	0.0212	0.03375

Solution

If the solution obey Ostwald's dilution law; $\alpha = \sqrt{\frac{K}{C}}$

From which; $^{I}/_{C}$ = V (Volume in dm^3 containing 1 mole)

It follows that; $\alpha = \sqrt{KV}$

Rearranging the equation gives; $K = \frac{\alpha^2}{V}$ and its value should be constant for every given set of values of α and V if the solution obeys Ostwald's dilution law.

Volume of solution in dm^3 containing 1 mole, V	5.4	10.6	24.9	63.3
Degree of dissociation, α	0.0098	0.0138	0.0212	0.03375
$K = \frac{\alpha^2}{V}$	1.78×10^{-5}	1.8×10^{-5}	1.8×10^{-5}	1.8×10^{-5}

Hence the solution obeys Ostwald's dilution law as the value of $\frac{\alpha^2}{V}$ is almost the same which is equal to the dissociation constant.

Example 4

Calculate pH of 0.01MCH_3COOH ($K_a(CH_3COOH) = 1.8 \times 10^{-5}$).

Solution

$$[H^+] = \alpha C = C\sqrt{\frac{K_a}{C}} = \sqrt{CK_a}$$

$$pH = -\log\left[[H^+]\right] = -\log\sqrt{CK_a} = -\log\sqrt{0.01 \times 1.8 \times 10^{-5}} = 3.37$$

Hence pH of 0.01M CH_3COOH is 3.37

Example 5

Calculate the pH of:

(i) 0.01MHCl
(ii) 0.01MH_2SO_4
(iii) A solution prepared by dissolving 2.5g of H_2SO_4 in 250mL of water
(iv) If pH of solutions are determined experimentally, the results are often not exactly the same as the results obtained from calculations. Explain why the calculated pH of H_2SO_4 in ((ii) and (iii))

diverges more from the measured pH than the calculated pH of HCl. What should be given to improve the sulphuric acid calculations?

Solution

(i) Hydrochloric acid (HCl) being strong electrolyte (strong acid) ionises completely (its degree of dissociation is 100%) according to the following equation:

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$
From which mole ratio of HCl to H^+ is 1:1

And hence $[HCl] = [H^+] = 0.01M$

Then $pH = -\log[H^+] = -\log 0.01M = 2$

So the pH of 0.01MHCl is 2

(ii) Sulphuric acid (H_2SO_4) being strong electrolyte (strong acid) ionises completely by 100% according to the following equation: $H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$

From which mole ratio of H_2SO_4 to H^+ is 1: 2

And hence $[H^+] = 2[H_2SO_4] = 2 \times 0.01M = 0.02M$.

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

Then the required pH of the acid $= -\log 0.02M = 1.7$

Hence the pH of $0.01MH_2SO_4$ is 1.7

(iii) $[H_2SO_4] = \frac{m_{H_2SO_4}}{M_{H_2SO_4} \times V_{soln}} = \frac{2.5g}{98gmol^{-1} \times 0.25L} = 0.102M$

Equation for ionisation of H_2SO_4

$$\begin{array}{ll} H_2SO_4(aq) & \rightarrow 2H^+(aq) + SO_4^{2-}(aq) \\ 0.102M & \quad 2\times 0.102M = 0.204M \end{array}$$

Then $pH = -\log[H^+] = -\log 0.204M = 0.69$

Hence pH of the solution is 0.69

(iv) Sulphuric acid being diprotic acid (HCl is monoprotic) does not give all two hydrogen ions per molecule at once; it gives the ions in steps according to the following equations:
Step 1: $H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$

Step 2: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$

Since the second step involves the weak acid, HSO_4^-, the actual total $[H^+]$ is smaller than that used in the calculation making the calculated pH of sulphuric acid smaller than the measured pH. To reduce the difference, the dissociation constant (K_a) for HSO_4^- should be given.

Example 6

What is the pH of a 0.001M solution of H_2SO_4? $K_a(HSO_4^-) = 1.2 \times 10^{-2}$

Solution

Ionisation of H_2SO_4 takes place in the two steps:

Step 1: $H_2SO_4(aq) + H_2O(l) \longrightarrow H_3O^+(aq) + HSO_4^-(aq)$
0 0.001 0.001 ([ ] of each after ionisation)

Step 2: $HSO_4^-(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$
$0.001 - x$ x x ([ ] of each at equilibrium)

From the step 2;

$$K_a = \frac{[H_3O^+][SO_4^{2-}]}{[HSO_4^-]}$$

Where:

$K_a = 1.2 \times 10^{-2}$(Here the dissociation constant which is an equilibrium constant is not very small and lies between 10^{-3} and 10^3, thus there is appreciable concentration of both reactants and products, nothing is going to be neglected).

$[HSO_4^-] = 0.001 - x$

$[H_3O^+] = x + 0.001$

$[SO_4^{2-}] = x$

Substituting $1.2 \times 10^{-2} = \frac{(x+0.001)x}{0.001-x}$

From which; $x^2 + 0.013x - (1.2 \times 10^{-5}) = 0$

Solving above quadratic equation, gives $x = 8.6546 \times 10^{-4}$

Then $pH = -\log[H_3O^+] = -\log(x + 0.001) = -\log(8.6546 \times 10^{-4} + 0.001) = 2.73$

Hence the pH is 2.73

Example 7

Calculate pH of :

(a) 0.01M NaOH
(b) 0.01M NH_4OH ($K_b = 1.78 \times 10^{-5}$)

Solution

(a) NaOH being strong electrolyte (strong base), ionises completely in the solution according to the following equation: $NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

From which mole ratio of NaOH to OH^- is 1:1;

And hence $[NaOH] = [OH^-] = 0.01M$

It follows that; $pOH = -\log[OH^-] = -\log 0.01M = 2$

But from $pH + pOH = 14; pH = 14 - pOH = 14 - 2 = 12$

Hence pH of 0.01M NaOH is 12.

(b) NH_4OH being weak electrolyte (weak base), its degree of dissociation is given by Ostwald dilution law whereby: $\alpha = \sqrt{\frac{K_b}{C}}$

So by using the fact that; $[OH^-] = \alpha C$

It follows that: $[OH^-] = C\sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$

And $pOH = -\log[OH^-] = -\log\sqrt{0.01 \times 1.78 \times 10^{-5}} = 3.4$
Then $pH = 14 - pOH = 14 - 3.4 = 10.6$
Hence the pH of 0.01M NH_4OH is 10.6

Example 8

Calculate hydrogen ion index of 0.01M ammonia solution, given that; pK_a value of NH_4^+ is 9.301.

Solution

In this question we are given with pK_a value of NH_4^+ instead of more useful value of pK_b of its conjugate base, $NH_3(aq)$.

So since NH_4^+ and $NH_3(aq)$ is conjugate pair, their pK_a and pK_b respectively are related by the following equation:

$pK_a + pK_b = 14$

From which; $pK_b = 14 - pK_a = 14 - 9.301 = 4.699$

But $pK_b = -\log K_b$;

From which $K_b = \log^{-1}(-pK_b) = \log^{-1}(-4.699) = 2 \times 10^{-5}$

Thus K_b of $NH_3(aq)$ is 2×10^{-5}.

Then $[OH^-] = \alpha C = C\sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$;

Whence $pOH = -\log\sqrt{0.01 \times 2 \times 10^{-5}} = 3.35$

Hydrogen ion index is pH whose value is related to pOH by the following equation:

$pH = 14 - pOH$; then $pH = 14 - 3.35 = 10.65$

Hence the hydrogen ion index, pH of the ammonia solution is 10.65

Example 9

0.01M solution of methanoic acid had an osmotic pressure of $28350NM^{-2}$ at 25°C. Calculate the pH of the solution.

Solution

Expected osmotic pressure $= \frac{nRT}{V}$

But $\frac{n}{v} = [\quad]$; then the expected osmotic pressure = [ ]RT

But [ ] = 0.01mol/dm^3 $= \frac{0.01}{10^{-3}}mol/m^3 = 10mol/m^3$

So the expected osmotic pressure = $10 \times 8.314 \times 298Nm^{-2} = 24775.72Nm^{-2}$

But the observed osmotic pressure = $28350NM^{-2}$

Vant Hoff's factor, $i = \frac{\text{observed osmotic pressure}}{\text{expected osmotic pressure}} = \frac{28350}{24775.72} = 1.144$

One mole methanoic acid ionises (dissociates) to produce two moles of ions according to the following equation: $HCOOH \rightleftharpoons HCOO^- + H^+$; $N = 2$

Then $\alpha = \frac{i-1}{N-1} = \frac{1.144-1}{2-1} = 0.144$ or 14.4%

Using; $pH = -\log[H^+]$; but $[H^+] = \alpha C$;

Then $pH = -\log\alpha C = -\log(0.144 \times 0.01) = 2.84$

Hence, pH of 0.01M HCOOH is 2.84.

Example 10

Find pH of non – reacting mixture which is obtained by mixing two strong acidic solutions; one with pH of 1.8 and another of pH of 2.4 by taking $1dm^3$ of each solution.

Solution

From $pH = -\log[H^+]$; $[H^+] = \log^{-1}[-pH]$

For first solution: $[H^+] = \log^{-1}(-1.8) = 0.0158M$

For second solution: $[H^+] = \log^{-1}(-2.4) = 0.003981M$

Thus number of moles of H^+ taken from the first solution

$= 0.0158M \times 1dm^3 = 0.0158$ moles

And number of moles of H^+ taken from the second solution

$= 0.003981M \times 1dm^3 = 0.003981$moles

Total number of moles of H^+ in the mixture (0.0158 + 0.003981) moles = 0.019781 moles

$[H^+]$ in the mixture $= \frac{n_{Total}}{V_{Total}} = \frac{0.019781moles}{(1+1)dm^3} = 9.8905 \times 10^{-3}M$

$pH = -\log[H^+] = -\log(9.8905 \times 10^{-3}) = 2$

Hence pH of the mixture is 2

Example 11

500 cm^3 of 0.1MHCl is added to a 500 cm^3 of 0.1MCH_3COOH. Calculate following:

(i) CH_3COO^- concentration in the solution mixture.
(ii) pH of the solution mixture.

Dissociation constant (K_a) of CH_3COOH is 1.8×10^{-5}

Solution

$n_{HCl} = \frac{500}{1000} dm^3 \times 0.1moldm^{-3} = 0.05mol$

Then $[HCl] = \frac{n_{HCl}}{V_{soln}}$; where $V_{soln} = (500 + 500)cm^3 = 1000cm^3 = 1dm^3$

Substituting $[HCl] = \frac{0.05mol}{1dm^3} = 0.05M$

Also $n_{CH_3COOH} = \frac{500}{1000} dm^3 \times 0.1moldm^{-3} = 0.05mol$

Then $[CH_3COOH] = \frac{n_{CH_3COOH}}{V_{soln}} = \frac{0.05mol}{1dm^3} = 0.05M$

CH_3COOH being weak acid ionises partially according to the following equation:

$$CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

At equilibrium $\quad 0.05 - x \quad\quad x \quad\quad x$

HCl being strong acid ionises completely according to the following equation:

$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$

After ionisation $\quad 0 \quad\quad 0.05M \quad 0.05M$

Thus in $CH_3COOH|HCl$ mixture:

$[CH_3COOH] = 0.05 - x \approx 0.05$ (Amount the weak acid dissociated is too small compared to its original amount because the equilibrium constant (in this case, dissociation constant) is less than 10^{-3}).

$[CH_3COO^-] = x$

$[H^+] = x + 0.05M \approx 0.05M$ (With **equal** concentration of both HCl and CH_3COOH, $[H^+]$ from CH_3COOH which is the weak acid can be neglected compared to $[H^+]$ which comes from strong acid).

Then from the equation of ionisation of CH_3COOH;

$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH\ ]} = \frac{0.05x}{0.05} = 1.8 \times 10^{-5}$ or $x = 1.8 \times 10^{-5}$

Hence:

$[CH_3COO^-] = x = 1.8 \times 10^{-5}M$

And $pH = -\log[H^+] = -\log(0.05M) = 1.3$

Be aware with the fact that:

In this example, we were able to neglect $[H^+]$ coming from the weak acid because the two acids had equal concentration. If the concentration of weak acid is very large compared to that of strong acid, $[H^+]$ will be accounted by both acids. To have better understanding of this, study **example 12**.

Example 12

$500\ cm^3$ of 0.001MHCl is added to a $500\ cm^3$ of $0.1MCH_3COOH$. Calculate following:

(i) CH_3COO^- concentration in the solution mixture.
(ii) pH of the solution mixture.

Dissociation constant (K_a) of CH_3COOH is 1.8×10^{-5}

Solution

$n_{HCl} = \frac{500}{1000} dm^3 \times 0.001moldm^{-3} = 5 \times 10^{-4}mol$

Then $[HCl] = \frac{n_{HCl}}{V_{soln}}$; where $V_{soln} = (500 + 500)cm^3 = 1000cm^3 = 1dm^3$

Substituting $[HCl] = \frac{5\times10^{-4}mol}{1dm^3} = 5 \times 10^{-4}M$

Also $n_{CH_3COOH} = \frac{500}{1000} dm^3 \times 0.1moldm^{-3} = 0.05mol$

Then $[CH_3COOH] = \frac{n_{CH_3COOH}}{V_{soln}} = \frac{0.05mol}{1dm^3} = 0.05M$

CH_3COOH being weak acid ionises partially according to the following equation:

	$CH_3COOH(aq) \rightleftharpoons$	$CH_3COO^-(aq) +$	$H^+(aq)$
At equilibrium	$0.05 - x$	x	x

HCl being strong acid ionises completely according to the following equation:

	$HCl(aq) \rightarrow$	$H^+(aq) \quad +$	$Cl^-(aq)$
After ionisation	0	$5 \times 10^{-4}M$	$5 \times 10^{-4}M$

Thus in $CH_3COOH|HCl$ mixture:

$[CH_3COOH] = 0.05 - x \approx 0.05$ (Here the same reasoning of the previous example applies)

$[CH_3COO^-] = x$

$[H^+] = x + 5 \times 10^{-4}$ (In this case, $[H^+]$ from the weak acid cannot be neglected because the concentration of strong acid is very small compared to the concentration of weak acid).

Then from the equation of ionisation of CH_3COOH;

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

Substituting $1.8 \times 10^{-5} = \frac{x(x+5\times10^{-4})}{0.05}$

From which: $x^2 + 5 \times 10^{-4}x - 9 \times 10^{-7} = 0$

From the above quadratic equation; practical value of $x = 7.31 \times 10^{-4}$

Thus $[H^+] = x + 5 \times 10^{-4} = (7.31 \times 10^{-4} + 5 \times 10^{-4})M = 1.231 \times 10^{-3}M$

Hence:

$[CH_3COO^-] = x = 7.31 \times 10^{-4}M$

And $pH = -\log[H^+] = -\log(1.231 \times 10^{-3}M) = 2.9$

Example 13

Calculate pH of the following solution mixture of NaOH and HCl:

(a) $25cm^3$ of 0.1MNaOH is mixed with $50cm^3$ of 0.1MHCl
(b) $51cm^3$ of 0.1M NaOH is mixed with $50cm^3$ of 0.1MHCl

Solution

(a) NaOH reacts with HCl according to the following equation:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

From which mole ratio of NaOH to HCl is 1:1; so with equal concentration of NaOH and HCl, HCl having greater volume must be in excess.

That is $(50 - 25)cm^3 = 25cm^3$ of 0.1MHCl remain unreacted at the end of neutralisation reaction and hence the solution will be acidic.

Number of moles of unreacted HCl = $\frac{25}{1000} \times 0.1\text{moles} = 2.5 \times 10^{-3}\text{moles}$

And total volume of solution mixture = $(25 + 50)cm^3 = 75cm^3$

Then $[HCl] = \frac{n}{V} = \frac{2.5 \times 10^{-3}\text{moles}}{75 \times 10^{-3}dm^3} = 0.033M$

HCl being strong acid (strong electrolyte) ionises according to the following equation in the solution mixture: $HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

$0.033M \qquad 0.033M$

$pH = -\log[H^+] = -\log 0.033M = 1.5$

Hence the pH of the solution mixture is 1.5

(b) In this case, $(51 – 50)cm^3 = 1cm^3$ of 0.1MNaOH remain unreacted at the end of neutralisation reaction and hence the solution mixture will be acidic.

Number of moles of unreacted NaOH = $\frac{1}{1000} \times 0.1\text{mole} = 1 \times 10^{-4}\text{moles}$

And total volume of solution mixture = $(51 + 50)cm^3 = 101cm^3$

Then $[HCl] = \frac{n}{V} = \frac{1 \times 10^{-4}\text{moles}}{101 \times 10^{-3}dm^3} = 0.0009901M$

Then $pOH = -\log[OH^-] = -\log 0.0009901M = 3$

From $pH + pOH = 14$; $pH = 14 - pOH = 11$

Hence pH of the solution mixture is 11

Example 14

$100cm^3$ of 0.05M NaOH is mixed with $150cm^3$ of 0.04M HCl. Calculate pH of the solution mixture.

Solution

NaOH reacts with HCl according to the following equation:

$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$

From which mole ratio of NaOH to HCl is 1:1

But from given data:

Number of mole of HCl = $\frac{150}{1000} \times 0.04\text{moles} = 0.006\text{moles}$

Number of moles of NaOH = $\frac{100}{1000} \times 0.05\text{moles} = 0.005\text{moles}$

Thus HCl present in excess and the solution mixture is acidic.

Number of moles of HCl which remains unreacted

$= (0.006 - 0.005)\text{ moles} = 0.001\text{moles}$

Then $[\text{HCl}] = \frac{n_{\text{HCl}}}{V_{\text{mixture}}} = \frac{0.001\text{moles}}{(100+150)\times 10^{-3}\text{dm}^3} = 4\times 10^{-3}\text{M}$

Equation for ionisation of HCl;

$\text{HCl(aq)} \quad \rightarrow \quad \text{H}^+\text{(aq)} + \text{Cl}^-\text{(aq)}$

$4\times 10^{-3}\text{M} \qquad 4\times 10^{-3}\text{M}$

$\text{pH} = -\log[\text{H}^+] = -\log(4\times 10^{-3}) = 2.4$

Hence pH of the solution mixture is 2.4

Example 15

80cm^3 of 0.1M H_2SO_4 is mixed with 120cm^3 of 0.1MKOH. Calculate pH of the solution mixture.

Solution

H_2SO_4 reacts with KOH according to the following equation:

$$H_2SO_4 + 2KOH \rightarrow K_2SO_4 + 2H_2O$$

From which mole ratio of H_2SO_4 to KOH is $1:2$

Number of moles of $H_2SO_4 = \frac{80}{1000} \times 0.1\text{moles} = 8\times 10^{-3}\text{moles}$

Number of moles of KOH $= \frac{120}{1000} = \times 0.1\text{moles} = 1.2 \times 10^{-2}\text{moles}$

From the mole ratio:

1.2×10^{-2} moles of KOH needs $\frac{1.2\times 10^{-2}}{2}$ moles or 6×10^{-3} of H_2SO_4 for its complete neutralisation. Thus given amount of H_2SO_4 (8×10^{-3}) exceed the required amount and hence H_2SO_4 present in excess.

Number of moles of H_2SO_4 which remain unreacted

$= (8-6)\times 10^{-3}\text{ moles} = 2\times 10^{-3}\text{moles}$

Total volume of the solution mixture = $(80+120)\text{cm}^3 = 200\text{cm}^3$

Then $[H_2SO_4] = \frac{n_{H_2SO_4}}{V_{\text{mixture}}} = \frac{2\times 10^{-3}\text{moles}}{200\times 10^{-3}\text{dm}^3} = 0.01\text{M}$

H_2SO_4 ionises in the solution according to the following equation:

$H_2SO_4 \quad \rightarrow \quad 2H^+ + SO_4^{2-}$

0.01M $\qquad 2\times 0.01\text{M}$

$= 0.02\text{M}$

$\text{pH} = -\log[\text{H}^+] = -\log 0.02\text{M} = 1.7$

Hence pH of the solution mixture is 1.7.

Example 16

*x*cm^3 of a 0.01M solution of sulphuric acid were put into the volumetric flask of capacity 500cm^3. Into this solution, distilled water was added until the mark. The pH of the solution made was found to be 3. Calculate the volume *x* used to make the solution.

Solution

From $\mathrm{pH} = -\log[\mathrm{H^+}]$; $[\mathrm{H^+}] = \log^{-1}(-\mathrm{pH})$

Thus $[\mathrm{H^+}]$ in the diluted solution $= \log^{-1}(-3) = 10^{-3}\mathrm{M}$

H_2SO_4 ionises according to the following equation:

$$\mathrm{H_2SO_4} \longrightarrow \mathrm{SO_4^{2-}} + 2\mathrm{H^+}$$

From which mole ratio of H_2SO_4 to H^+ is 1:2

Thus concentration of diluted solution, $\mathrm{M_d}$ of $\mathrm{H_2SO_4} = \frac{10^{-3}\mathrm{M}}{2} = 5 \times 10^{-4}\mathrm{M}$

So $\mathrm{M_d} = 5 \times 10^{-4}\mathrm{M}, \mathrm{V_d} = 500\mathrm{cm^3}, \mathrm{M_c} = 0.01\mathrm{M}, \mathrm{V_c} = \mathrm{xcm^3}$.

By dilution principle; $\mathrm{M_cV_c} = \mathrm{M_dV_d}$

From which; $\mathrm{V_c} = \frac{\mathrm{M_dV_d}}{\mathrm{M_c}}$; thus $\mathrm{x} = \frac{5\times10^{-4}\times500}{0.01} = 25$

The value of *x* is 25

Example 17

Calculate how many cm^3 of:

(a) Hydrochloric acid of concentration $1\mathrm{mol/dm^3}$ is needed to change the pH of 1dm^3 of HCl of concentration 1.0×10^{-3} $\mathrm{mol/dm^3}$by 1 unit.

(b) NaOH of concentration 1moldm^{-3} is needed to change the pH of 1dm^3 of HCl of concentration of 1.0×10^{-3} $\mathrm{mol/dm^3}$by 1 unit.

Solution

(a) pH of 1×10^{-3} moldm^{-3} HCl $= -\log(1 \times 10^{-3}) = 3$.

On addition of the acid, pH value decreases; thus the new pH value $= 3 - 1 = 2$

So using $[\mathrm{H^+}] = \log^{-1}(-\mathrm{pH})$

The new $[\mathrm{H^+}] = \log^{-1}(-2) = 10^{-2}\mathrm{M}$

Let the volume needed be Vcm^3

Then number of moles of HCl added $= \frac{\mathrm{V}}{1000} \times 1 = 0.001\mathrm{V}$

Total number of moles of HCl in the mixture = 0.001V + 0.001

Total volume of the solution mixture $= (\mathrm{V} + 1000)\mathrm{cm^3} = \frac{(\mathrm{V}+1000)}{1000}\mathrm{dm^3}$

Thus $10^{-2} = \left(\frac{0.001\mathrm{V} + 0.001}{\mathrm{V} + 1000}\right) \times 1000$

Solving the above equation gives V = 9.09cm^3

Hence 9.09cm^3 of HCl is needed.

(b) pH of 1×10^{-3}MHCl $= -\log(1 \times 10^{-3}) = 3$

On addition of base, pH value increases; so the new pH value $= 3 + 1 = 4$

The new $[\mathrm{H}^+] = \log^{-1}(-4) = 10^{-4}\mathrm{M}$

The $[\mathrm{H}^+]$ decreases due to addition of OH^- from the alkaline solution which eliminates H^+ such that **number of moles of OH^- added = number of moles of H^+ eliminated.**

But number of moles of OH^- added in a litre of solution $= \frac{\mathrm{V}}{1000} \times 1 = 0.001\mathrm{V}$

Where V is the volume of the base in cm^3;

Then number of moles HCl in the mixture $= 0.001 - 0.001\mathrm{V}$

Total volume of the solution mixture $= (\mathrm{V} + 1000)\mathrm{cm}^3 = \left(\frac{\mathrm{V}+1000}{1000}\right)\mathrm{dm}^3$

Thus $10^{-4} = \left(\frac{0.001-0.001\mathrm{V}}{\mathrm{V}+1000}\right) \times 1000$

From which V = 0.9 cm^3

Hence 0.9 cm^3 of NaOH is required.

DIGGING DEEPER EXERCISE 16

EXERCISE 16A: BINDER QUESTIONS

Question 1

Calculate the pH for each of the solution with the following concentration:

(a) $[H^+] = 1 \times 10^{-3}M$ (b) $[H^+] = 1 \times 10^{-9}M$ (c) $[OH^-] = 1 \times 10^{-5}M$

Question 2

Solution "A" has a $[H^+] = 3.9 \times 10^{-5}M$. Solution "B" has a pH of 5.70. Which is more acidic? Which is more basic?

Question 3

Calculate the pH and pOH of a solution prepared by dissolving 0.93 g of HCl in enough water to give 0.40L of solution.

Question 4

A 1000mL solution of HCl has a pH of 1.30. How many grams of HCl are dissolved in the solution?

Question 5

How many times more acidic is a solution with pH $=$ 4.80 as compared to one with pH $=$ 6.33?

Question 6

Two solutions are mixed: 5.00 mL of 2.50 M HBr and 7.00 mL of 2.00 M LiOH. What is the final pH after mixing?

Question 8

(a) What feature of the ammonia molecule enables it to react as a base?
(b) Calculate the pH of a 0.100M solution of ammonia if its $K_b = 1.8 \times 10^{-5}M$

Question 9

100mL of a solution with pH of 2 is mixed with 300mL of another solution with pH of 7. What is the pH of the mixture?

Question 10

10mL of HCl solution was mixed with 20mL of NaOH solution that has pH 12. After mixing, the pH of the mixture was 7. What was the pH of the hydrochloric acid solution?

EXERCISE 16B: REAL QUESTIONS

Question 11

Why should temperature be specified when doing weak acid pH calculations?

Question 12

Kipute was asked to calculate pH of pure water at 100℃ and she found the **correct** answer to be 6. She then argued to you that; pure water is only neutral at 25℃ where its pH is 7. Do you agree or disagree with **Kipute's** argument? Explain.

Question 13

The antacid called "Milk of Magnesia" contains 800mg of $Mg(OH)_2$ per 2 teaspoons. The typical stomach pH is 1.420. How many mL of stomach acid (HCl) are neutralised by 2 Tablespoons of Milk of Magnesia? (1 Tablespoon = 3 teaspoon).

Question 14

White vinegar in a kitchen is a 5.0% by mass solution of acetic acid in water. If the density of white vinegar is 1.007 g/cm^3, what is the pH? $K_a(\text{acetic acid}) = 1.8 \times 10^{-5}$

Question 15

On another day, **Kipute** was asked to calculate pH of 10^{-2}MHCl and of 10^{-8}MHCl and she got 2 and 8 respectively by taking negative logarithm of each concentration. However, the second answer made her to doubt everything she learned about calculating pH of solutions. *"I'm certain that hydrochloric acid is acid; even its name is the confirmation of this. And without any doubt, pH of 8 that was found in my calculation is the pH of base, I'm confused indeed! Please do you have any explanation to this contradiction?"* She asked.

(i) By applying a knowledge of chemical equilibrium on self-ionisation of water, re-calculate the pH of 10^{-2}MHCl and show to Kipute that her simplification on the calculation of pH was correct in this case.
(ii) Explain to **Kipute**, how the simplification is incorrect in the case of 10^{-8}MHCl and hence calculate the correct pH value.

EXERCISE 16C: HOT QUESTIONS

Question 16

The equation to show auto-ionisation of water can be represented by using the following equation:

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

Give three pieces of information which can be deduced from the above equation:

Question 17

Propanoic acid dissociates in aqueous solution according to

$CH_3CH_2CO_2H + H_2O \rightleftharpoons CH_3CH_2CO_2^- + H_3O^+$;

(a) Write the expression for K_a for propanoic acid.
(b) Given that K_a for this reaction is 3.5×10^{-5}moldm^{-3} at 298 K, calculate the pH of a 0.100M solution of propanoic acid at this temperature.
(c) If the solution referred to in (ii) were to be diluted tenfold, it might be expected that the pH would rise by one unit. In fact, it rises by less than this. Explain.

Question 18

Water self-ionises: $2H_2O \rightleftharpoons H_3O^+ + OH^-$

At 0°C, $K_w = 1 \times 10^{-15}$mol^{2}dm^{-6} and at 100°C, $K_w = 5 \times 10^{-13}$mol^{2}dm^{-6}.

(a) Deduce with reasons whether the dissociation of water is exothermic or endothermic.
(b) The pH of a 1×10^{-2} moldm^{-3} solution of hydrochloric acid is 2 and that of 1×10^{-3}moldm^{-3} hydrochloric acid is 3. However the pH of a solution of 1×10^{-8} moldm^{-3} hydrochloric acid is **not** equal to 8. Suggest an explanation for this observation.

Question 19

Acids differ in the number of hydrogen ions that can be liberated from one molecule of the undissociated acid. Hydrochloric acid is a strong monobasic, or monoprotic acid, liberating one hydrogen ion per molecule. Sulphuric acid is a dibasic, or diprotic acid, its ionisation in aqueous solution being:

I: $H_2SO_4(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + HSO_4^-(aq)$ K_a = Very large

II: $HSO_4^-(aq) + H_2O(aq) \rightleftharpoons H_3O^+(aq) + SO_4^{2-}(aq)$ $K_a = 0.01$moldm^{-3}

K_a values are quoted for 25 °C.

(a) State the hydrogen ion concentration in 0.01moldm^{-3} hydrochloric acid, which is a strong acid, and hence find the pH of this solution.
(b) State the hydrogen ion concentration of 0.1moldm^{-3} sulphuric acid arising from the first stage of ionisation, **I**.
(c) A solution of sodium hydrogensulphate, $NaHSO_4$, of concentration 0.1 moldm^{-3}, ionises according to equation **II** above. Find the hydrogen ion concentration in this solution, and **hence** state what you would expect the hydrogen ion concentration in 0.1moldm^{-3}sulphuric acid to be.
(d) In fact the pH of 0.1 moldm^{-3}sulphuric acid is about 0.98. This indicates a hydrogen ion concentration of 0.105 moldm^{-3}. By considering the reactions, **I** and **II** in the presence of one another explain why this is so. You are not expected to perform any further calculations.

Question 20

Calculate the depression in freezing point of water when 10g of $CH_3CH_2CHClCOOH$ is added to 250g of water. $K_a = 1.4 \times 10^{-3}, K_f = 1.86$

Question 21

19.5g of CH_2FCOOH (fluoroacetic acid) is dissolved in 500g of water. The depression of freezing point of water observed is 1°C. Calculate the Van't Hoff factor and dissociation constant of fluoroacetic acid.

$K_f = 1.86$

Question 22

Calculate the fluoride ion concentration and pH of a solution that is 1M in HF and 0.01M in HCl.

$$K_a(HF) = 6.8 \times 10^{-4}$$

Question 23

30mL of a solution with pH of 2 is mixed with 20mL of another solution with pH of 13. What is the pH of the mixture?

Question 24

Consider the reaction of $Ba(OH)_2$ and HCl. You are mixing 2L of HCl solution that has pH of 1.52 and a solution of $Ba(OH)_2$ that has $pH = 13.3$. What volume of the $Ba(OH)_2$ solution is required to completely react with the HCl solution with no HCl or $Ba(OH)_2$ remaining?

Question 25

At a certain temperature, a 0.01M solution of sodium hydroxide has a pH of 11. Calculate a value for ionic product of water at this temperature.

Chapter 17
BUFFER SOLUTION

In everyday life, there are various systems which function properly under certain specified narrow range of pH. A constant pH is required for many biological and chemical reactions to proceed. In these systems, substances called **buffers** or **buffer solutions** are extremely useful to maintain pH. Literally *buffer* is something that lessens or absorbs the shock of an impact. Buffer solution lessens the impact of acid and base on the pH of the solution. So it can be defined as *the solution which can maintain its pH value on addition of small amount of acid or base.* That is, it is the solution whose pH value does not change significantly on addition of acid or base provided that **buffer capacity** is not exceeded. Because it controls pH of the solution, buffer solution is also known **pH buffer** or **hydrogen ion buffer**.

Examples of buffer solution are:

- **Acetate buffer solution** which is the mixture of ethanoic acid (acetic acid) and sodium ethanoate (sodium acetate) which is usually shortened as CH_3COOH/CH_3COONa buffer system.
- **Ammonium buffer solution** which is the mixture of ammonium hydroxide and ammonium chloride which is usually shortened as NH_4OH/NH_4Cl buffer system.
- A solution mixture of ammonium hydroxide and ammonium sulphate ($NH_4OH/((NH_4)_2SO_4$ buffer system).
- A solution mixture of hydrogen cyanide and sodium cyanide ($HCN/NaCN$ buffer system).

CHARACTERISTICS OF A BUFFER SOLUTION

Characteristics of a buffer solution include the following:

1) It has a definite pH.
2) Its pH remains the same on standing for a long time.
3) Its pH does not change on dilution.
4) Its pH changes negligibly by the addition of a small amount of acid or base.

TYPES OF BUFFER SOLUTION

Depending on their pH value, buffer solutions can be classified into two categories, namely:

- Acidic buffer solution
- Basic buffer solution

Acidic buffer solution

This is the buffer solution whose pH value is less than 7. It is used to maintain pH of the system which works properly in the acidic condition.

- It is prepared by mixing weak acid and its strong salt (the salt containing anion which is conjugate base of the acid and strong electropositive metal cation derived from strong base).

Examples of acidic buffer solution are:

- CH_3COOH/CH_3COOK buffer system
- CH_3COOH/CH_3COONa buffer system
- HCN/KCN buffer system
- $HCN/NaCN$ buffer system

Basic buffer solution

This is buffer solution whose pH value is greater than 7. It is used to maintain pH of the system which works properly in the basic condition.

- It is prepared by mixing a weak base and its strong salt (the salt containing its conjugate acid cation and strong electronegative anion derived from strong acid).

Examples of basic buffer solution are:

- NH_4OH/NH_4Cl buffer system
- $NH_4OH/(NH_4)_2SO_4$ buffer system

MECHANISM OF BUFFER SOLUTION TO CONTROL ITS pH VALUE

Acidic buffer solution mechanism

To understand this consider acetate buffer solution i.e. CH_3COOH/CH_3COONa buffer system which is acidic.

Determination of pH value of the buffer solution

- Before addition of strong salt (CH_3COONa), ethanoic acid being weak acid, ionises partially according to the following equation: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
- After addition of strong salt (CH_3COONa), the salt ionises completely according to the following equation: $CH_3COONa \rightarrow CH_3COO^- + Na^+$
- The ionisation of the strong salt is equivalent to an increase in concentration of CH_3COO^- which disturbs the position of the equilibrium of the ionisation of the weak acid through **common ion effect.**
- Thus more H^+ should combine with added CH_3COO^- to restore the equilibrium.
- The concentration of H^+ which remains after re-establishment of new equilibrium is the one which determine the pH of the buffer solution.

Definition of common ion effect

This *is the lowering in the dissociation of a weak electrolyte due to addition of a strong electrolyte which contains a cation or anion which is also found in the weak electrolyte.*

Addition of strong acid to the acidic buffer solution

- Consider strong acid like hydrochloric acid (HCl) is added to the buffer solution (our CH_3COOH/CH_3COONa buffer system)
- The strong acid (HCl) ionises completely in the solution according to the following equation:
  HCl (aq) $\rightarrow$ $H^+(aq) + Cl^-(aq)$
- The ionisation of HCl is equivalent to an increase of concentration of hydrogen ions (H^+) to the buffer solution. This disturbs the position of chemical equilibrium in the buffer solution.
- Thus more ethanoate ions (CH_3COO^-) should combine with added H^+ to restore the equilibrium.
- But the added H^+ are from strong acid which ionises completely; so ethanoate ions (CH_3COO^-) from the weak acid (CH_3COOH) are not enough to combine with added hydrogen ions from the strong acid.
- However presence of sodium ethanoate which ionises completely like HCl(aq) provides higher concentration of CH_3COO^- which are enough to combine with added H^+ from strong acid to re-establish the equilibrium and hence pH value of the buffer solution is maintained.

This resistance to change in pH on the addition of a strong acid is called as **reserve basicity** and is due to CH_3COO^- ions.
By definition: **reserve basicity** *is the resistance of a buffer solution to change in pH upon addition of a strong acid.*

Addition of strong base to the acidic buffer solution

Consider strong base like NaOH is added to the buffer solution:

- NaOH being strong base ionises completely according to the following equation:

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

- Hydroxyl ions (OH^-) produced in the above ionisation combine with hydrogen ions (H^+) in the buffer solution.
- This disturbs the position of chemical equilibrium in the buffer solution, so more ethanoic acid will ionise to give hydrogen ions so as to re-establish the equilibrium and hence the pH value of the buffer solution is maintained.

This resistance to change in pH on the addition of base is called **reserve acidity** and is due to CH_3COOH.
By definition: **reserve acidity** *is the resistance of a buffer solution to change in pH upon addition of a strong base.*

So what are uses of weak acid and strong salt in the buffer solution?

- The use of weak acid is to provide the dynamic system of the chemical equilibrium and to eliminate OH^- on addition of the strong base.
- The use of strong salt (CH_3COONa) is to provide enough concentration of anions (CH_3COO^-) to combine with H^+ on addition of the strong acid.

Basic buffer solution mechanism

To understand this consider ammonium buffer solution i.e. NH_4OH/NH_4Cl buffer system which is basic.

Determination of pH value of the solution

- Before addition of strong salt (NH_4Cl), NH_4OH being weak base ionises partially according to the following equation: $NH_4OH \rightleftharpoons NH_4^+ + OH^-$
- After addition of strong salt (NH_4Cl), the salt ionises completely according to the following equation: $NH_4Cl \rightarrow NH_4^+ + Cl^-$
- The ionisation of strong salt is equivalent to an increase of concentration of ammonium ions (NH_4^+) which disturbs the position of chemical equilibrium of the ionisation of NH_4OH through **common ion effect.**
- Thus more OH^- should combine with added (NH_4^+) to restore the equilibrium.
- To concentration of OH^- which remains after re-establishment of the new equilibrium is the one which determine the pOH which eventually determine pH of the buffer solution.

Addition of strong base to the basic buffer solution

Consider the strong base like NaOH is added to the buffer solution:

- The strong base ionises completely in the solution according to the following equation: $NaOH \rightarrow Na^+ + OH^-$
- The ionisation of NaOH is equivalent to an increase of concentration of hydroxyl ions (OH^-) to the buffer solution. This disturbs the position of chemical equilibrium in the buffer solution.
- Thus more ammonium ions (NH_4^+) should combine with added OH^- to restore the equilibrium.
- But the added OH^- are from strong base which ionises completely; so ammonium ions (NH_4^+)from the weak base (NH_4OH) are not enough to combine with added hydroxyl ions from the strong base.
- However presence of ammonium chloride which ionises completely like NaOH provides higher concentration of NH_4^+ which are enough to combine with added OH^- from the strong base to re-establish the equilibrium and hence pH value of the buffer solution is maintained.

In this case, the reserve acidity and is due to NH_4^+ ions in a solution.

Addition of strong acid to the basic buffer solution

Consider strong acid like HCl is added to the buffer solution

- HCl being strong acid ionises completely according to the following equation
$$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$$
- Hydrogen ions (H^+) produced in the above ionisation combine with hydroxyl ions, OH^- in the buffer solution. This disturbs the position of chemical equilibrium in the buffer solution.
- So more ammonium hydroxide will ionise to give hydroxyl ions so as to re-establish the equilibrium and hence the pH value of the buffer solution is maintained.

Here, the reserve basicity and is due to NH_4OH in the buffer solution.
So what are uses of weak base and strong salt in the buffer solution?

- The use of weak base is to provide the dynamic system of the chemical equilibrium and to eliminate H^+ on addition of the strong base.
- The use of strong salt (NH_4Cl) is to provide enough concentration of cations (NH_4^+) to combine with OH^- on addition of strong base.

EQUATION FOR CALCULATING pH OF ACIDIC BUFFER SOLUTION

Consider CH_3COOH/CH_3COONa buffer system which is acidic:

CH_3COOH being weak acid ionises according to the following equation:
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$
CH_3COONa being strong salt ionises according to the following equation:
$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$
From the equation of the ionisation of the weak acid: $K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$

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

Introducing –log both sides;

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

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

But $-\log[H^+] = pH$; $-\log K_a = pK_a$ and $-\log\frac{[CH_3COOH]}{[CH_3COO^-]} = \log\frac{[CH_3COO^-]}{[CH_3COOH]}$

Thus $\mathbf{pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}}$

Since CH_3COONa ionises completely while CH_3COOH ionises partially to give CH_3COO^-, it can be concluded that; approximately all CH_3COO^- are from CH_3COONa (salt).
And since mole ratio of CH_3COONa to CH_3COO^- is 1:1;
$[CH_3COO^-] = [CH_3COONa] = [Salt]$.
Hence for acidic buffer solution:

$$\mathbf{pH = pK_a + \log\frac{[salt]}{[Acid]}} \rightarrow \textbf{Henderson – Hasselbalch equation}$$

The above final formula applicable without any modification if and only if the mole ratio of salt to its anion is 1:1.

Note that the pH is determined by the ratio of concentrations, $\frac{[salt]}{[Acid]}$, but the buffering capacity of the solution can be increased by increasing the concentrations of both components in the same molar concentration ratio.

EQUATION FOR CALCULATING pH OF BASIC BUFFER SOLUTION

Consider NH_4OH/NH_4Cl buffer system which is basic:

NH_4OH being weak base ionises partially in the solution according to the following equation:

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

NH_4Cl being strong salt ionises completely in the solution according to the following equation:

$$NH_4Cl \rightarrow NH_4^+ + Cl^-$$

From the equation of ionisation of NH_4OH; $K_b = \frac{[NH_4^+][OH^+]}{[NH_4OH]}$

From which; $[OH^-] = \frac{K_b[NH_4OH]}{[NH_4^+]}$

Introducing –log both sides; $-\log[OH^-] = -\log\frac{K_b[NH_4OH]}{[NH_4^+]}$

Or $-\log[OH^-] = -\log K_b - \log\frac{[NH_4OH]}{[NH_4^+]}$

So $\mathbf{pOH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]}}$

Since NH_4Cl ionises completely while NH_4OH ionises only partially yielding NH_4^+; it may be assumed that the whole concentration of NH_4^+ is from NH_4Cl (salt).

Also since mole ratio of NH_4Cl to NH_4^+ is 1:1; $[NH_4^+] = [NH_4Cl] = [\text{salt}]$

Hence for basic buffer solution: $\mathbf{pOH = pK_b + \log\frac{[salt]}{[base]}}$

But $pH + pOH = 14$ or $pH = 14 - pOH$

Whence for basic buffer solution; $\mathbf{pH = 14 - \left(pK_b + \log\frac{[salt]}{[base]}\right)}$

Again the above final formula is applicable without any modification if and only if the mole ratio of the salt to its cation is 1:1. (Carefully study **Example 5** to understand how to deal with the situation when the ratio is not 1:1).

EFFICIENCY OF BUFFER SOLUTION

When a buffer solution can afford greater amount of strong acid or strong base without drastic change in its pH, then the buffer is said to work more efficiently. Also, when the buffer solution shows smaller change in the pH after adding given amount of strong acid or base, then the buffer is said to be more efficient. The two scenarios are related to **buffer capacity** and **buffer range** which are main determinant of efficiency of buffer solution.

Buffer capacity *is the relative ability of a buffer solution to resist pH change upon addition of acid or base*. Usually the change is counted as insignificant when does not exceed one unit. As a result, buffer capacity can also be defined *as the number of moles of acid or base required to change the pH of the buffer solution by one unit.*

Buffer capacity depends on the amounts of the weak acid (or base) and its conjugate base (or acid) that are in a buffer mixture. For example, 1L of a solution that is 1M in acetic acid and 1M in sodium acetate has a greater buffer capacity than 1L of a solution that is 0.1M in acetic acid and 0.1M in sodium acetate even though both solutions have the same pH. The first solution has more buffer capacity because it contains more acetic acid and acetate ion.

Buffer range i*s the pH range over which the buffer acts effectively.* For the buffer to be effective, the pH range must not diverge by more than 1 from the pK_a (or pK_b) value; i.e. It must lie between one pH unit above and below the pK_a (or pK_b) value.

Thus, $\mathbf{pH\ of\ the\ buffer = pK_a(\text{or } pK_b) \pm 1}$.

The closer the buffer pH is to the outer limits of the range, the less effective the buffer will be as it will be reaching the limits of its ability to counter acid or base; what does this imply? This implies that, it is best to have almost equal concentrations of weak acid or base and its conjugate base or acid so that the buffer pH is closer to the pK_a (or pK_b) value. To have better understanding of this consider Henderson – Hasselbalch equation for acetate buffer;

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

When $[CH_3COO^-] = [CH_3COOH]$; the above equation becomes;
$pH = pK_a + \log 1 = pK_a$
Hence the buffer solution is most effective when $\mathbf{[CH_3COO^-] = [CH_3COOH]}$ such that $\mathbf{pH = pK_a}$.
Another advantage of the equality in the concentration is that the buffer attains equal ability of eliminating both acid and base; that is, it attains equality in the reverse basicity and the reserve acidity.
So we can conclude that, buffer solution works more efficiently when the following conditions are met:

1) High concentrations of both of its components. (This ensures that high buffer capacity is achieved).
2) Equal concentrations of both of its components such that $pH = pK_a$. (A buffer solution has generally lost its usefulness when one component of the buffer pair is less than about 10% of the other).

CALCULATIONS INVOLVING BUFFER SOLUTION

Example 1

Taking the pK_a value of NH_4^+ as 9.301, calculate the change in hydroxide ion concentration produced by adding 10g of ammonium chloride to $1dm^3$ of 0.1M ammonia. Assume the salt is fully ionised.

Solution

Using $pK_a + pK_b = 14$

Then $pK_b = 14 - pK_a = 14 - 9.301 = 4.699$

But $pK_b = -\log K_b$

From which $K_b = \log^{-1}(-P^{K_b}) = \log^{-1}(-4.699) = 2 \times 10^{-5}$

Thus K_b of NH_4OH (conjugate base of NH_4^+) is 2×10^{-5}

Before addition of the salt:

From the equation of ionisation of NH_4OH in the solution: $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

But from the above equation of the ionisation; mole ratio of NH_4^+ to OH^- is 1: 1

Thus $[NH_4^+] = [OH^-]$

It follows that; $K_b = \frac{[OH^-]^2}{[NH_4OH]}$

So $[OH^-] = \sqrt{K_b[NH_4OH]} = \sqrt{2 \times 10^{-5} \times 0.1} = 1.414 \times 10^{-3}M$

Thus the $[OH^-]$ before addition of the salt is $1.414\times 10^{-3}M$

After addition of the salt $[NH_4Cl]$:

From $K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$

Since NH_4Cl is fully ionised, it may be assumed that the whole NH_4^+ comes from the salt (NH_4Cl). And since mole ratio of NH_4^+ to NH_4Cl in the ionisation of the salt is 1:1 $[NH_4^+] = [NH_4Cl]$

Whence $K_b = \frac{[NH_4Cl][OH^-]}{[NH_4OH]}$ or $[OH^-] = \frac{K_b[NH_4OH]}{[NH_4Cl]}$

But $[NH_4Cl] = \frac{m_{NH_4Cl}}{M_{NH_4Cl}\times V_{soln}} = \frac{10g}{53.5gmol^{-1}\times 1dm^3} = 0.1869M$

So $[OH^-] = \frac{2\times10^{-5}\times0.1}{0.1869}M = 1.07\times10^{-5}M$

Hence hydroxide ion concentration decreases from $1.414\times10^{-3}M$ to $1.07\times10^{-5}M$ after addition of the salt.

Example 2

The dissociation constant of ammonia is $1.8\times10^{-5}moldm^{-3}$. Calculate pH of decimolar ammonia solution. Also calculate the pH of the solution obtained by adding 2.5g of ammonium chloride to the $250cm^3$ of decimolar solution.

Solution

$[OH^-] = \alpha C$; where C = 0.1M (decimolar solution)

But from Ostwald's dilution law, $\alpha = \sqrt{\frac{K_b}{C}}$

Then $[OH^-] = C\sqrt{\frac{K_b}{C}} = \sqrt{CK_b}$

So $pOH = -\log[OH^-] = -\log\sqrt{CK_b} = -\log\sqrt{0.1\times1.8\times10^{-5}} = 2.87$

$pH = 14 - pOH = 14 - 2.87 = 11.13$

Thus pH of decimolar ammonia solution is 11.13

After addition of ammonium chloride to into ammonia solution, basic buffer solution whose pH is given by the equation below is formed; $pH = 14 - \left(pK_b + \log\frac{[salt]}{[base]}\right)$

But $[salt] = [NH_4Cl] = \frac{2.5}{53.5\times0.25} = 0.187M$

Then $pH = 14 - \left(-\log(1.8\times10^{-5}) + \log\left(\frac{0.187}{0.1}\right)\right) = 8.98$

Hence pH after addition of ammonium chloride is 8.98.

Example 3

Calculate the volume of 0.1MHCOONa that must be added to $1dm^3$ of 0.1MHCOOH to give a buffer solution of pH 3.5 (pK_a of HCOOH is 3.75).

Solution

The mixture of HCOOH and HCOONa is acidic buffer solution whose pH value is given by the following equation: $pH = pK_a + \log\frac{[salt]}{[acid]}$

But $[salt] = \frac{\text{number of moles of salt}}{\text{volume of buffer solution}}$

And $[Acid] = \frac{\text{number of moles of acid}}{\text{volume of buffer solution}}$

It follows that: $\frac{[salt]}{[acid]} = \frac{\text{number of moles of salt}}{\text{number of moles of acid}}$

Thus for acidic buffer solution:

$$\mathbf{pH = pK_a + \log\frac{\text{number of moles of salt}}{\text{number of moles of acid}}}$$

If V is the volume of the salt (HCOONa) required in dm^3

Then $3.5 = 3.75 + \log\frac{0.1V}{0.1\times1}$ (n = [ ]V)

From which; $V = 0.562dm^3$

Hence $0.562dm^3$ or $562cm^3$ of HCOONa is required.

Example 4

Calculate the mass of CH_3COONa that must be added to $1dm^3$ of a 0.1M CH_3COOH to produce a solution of pH 4? (K_a of CH_3COOH is 1.8×10^{-5})

Solution

CH_3COOH and CH_3COONa form acidic buffer solution whose pH is given by the following equation:

$$\mathrm{pH} = \mathrm{pK_a} + \log\frac{\text{Number of moles of salt }(CH_3COONa)}{\text{Number of moles of acid }(CH_3COOH)}$$

Using; $n = \frac{m}{M_r}$ and $n = [\quad]V$ and then substituting given values to the above equation gives:

$$4 = -\log(1.8 \times 10^{-5}) + \log\frac{\frac{m}{84}}{0.1 \times 1}$$

Where m is the mass of CH_3COONa in g

Solving above equation gives m = 1.512g

Hence the required mass of CH_3COONa is 1.512g

Example 5

Calculate the number of grams of ammonium sulphate which are to be added to $500cm^3$ of 0.176M ammonia solution to give a buffer solution of pH 9.42 (assume the volume of solution does not change on addition of ammonium sulphate. Given that pK_a of NH_4^+ is 9.243.

Solution

When ammonium sulphate is mixed with ammonia solution, basic buffer solution whose pH value is given by the equation below is formed.

$$\mathrm{pH} = 14 - \left(\mathrm{pK_b} + \log\frac{[NH_4^+]}{[NH_4OH]}\right) \text{ or } \mathrm{pH} = 14 - \mathrm{pK_b} - \log\frac{[NH_4^+]}{[NH_4OH]}$$

But NH_4^+ and NH_4OH are conjugate pair;

Thus $14 - \mathrm{pK_b} = \mathrm{pK_a}$ of NH_4^+ ($\mathrm{pK_a} + \mathrm{pK_b} = 14$ for conjugate pairs)

Therefore $\mathbf{pH = pK_a - \log\frac{[NH_4^+]}{[NH_4OH]}}$

Substituting the given values; $9.42 = 9.243 - \log\frac{[NH_4^+]}{0.176}$

From which, $[NH_4^+] = 0.117M$.

So number of mole of NH_4^+ in 1L of buffer solution is 0.117moles

Whence number of moles of NH_4^+ in $500cm^3$ (0.5L) of the solution

$$= 0.5 \times 0.117\text{moles} = 0.0585\text{moles}$$

The ammonium ions (NH_4^+) are from $(NH_4)_2SO_4$ (ammonium sulphate) which is fully ionised according to the following equation: $(NH_4)_2SO_4 \rightarrow 2NH_4^+ + SO_4^{2-}$

From which mole ratio of $(NH_4)_2SO_4$ to NH_4^+ is 1: 2

Thus $\frac{0.0585}{2}$moles $= 0.02925$mole of $(NH_4)_2SO_4$ is required to produce 0.0585moles of NH_4^+.

But molar mass of $(NH_4)_2SO_4$ is 132g/mol.

So by using $m = nM_r$;

Required mass of $(NH_4)_2SO_4$ is $0.02925 \times 132g = 3.861g$

Hence 3.861g of ammonium sulphate are required.

Example 6

Calculate pH of a solution formed by mixing 24.9cm^3 of 0.1MNaOH with 25cm^3 of 0.1M HCOOH(K_a of HCOOH is 1.6×10^{-4}).

Solution

HCOOH reacts with NaOH according to the following equation:

$$\text{HCOOH} + \text{NaOH} \rightarrow \text{HCOONa} + H_2O$$

From which mole ratio of HCOOH to NaOH is 1:1

Thus $(25 - 24.9)\text{cm}^3$ or $0.1\text{cm}^3$of 0.1MHCOOH remain uncreated at the end of chemical reaction.

Thus HCOOH is the reactant in excess while NaOH is limited reactant.

Number of moles of HCOONa formed after reaction= $\frac{24.9}{1000} \times 0.1\text{moles} = 2.49 \times 10^{-3}\text{moles}$

Number of moles of HCOOH which remain unreacted

$$= \frac{0.1}{1000} \times 0.1\text{moles} = 1 \times 10^{-5}\text{moles}$$

The formed HCOONa and unreacted HCOOH forms acidic buffer solution whose pH is given by the following equation: $\text{pH} = \text{pK}_a + \log\frac{\text{Number of moles of salt (HCOONa)}}{\text{Number of moles o f acid (HCOOH)}}$

By substituting the values: $\text{pH} = -\log(1.6 \times 10^{-4}) + \log\left(\frac{2.49\times10^{-3}}{1\times10^{-5}}\right) = 6.2$

Hence the pH was 6.2.

Example 7

Solution of unknown monobasic acid was titrated with the base and equivalent point reached when 36.12mL of 0.1MNaOH had been added. The 18.06mL of 0.1MHCl were added to the solution and the measured pH was found with pH meter to be 4.92. Calculate the dissociation constant of unknown acid.

Solution

Number of moles of NaOH added = $\frac{36.12}{1000} \times 0.1 = 3.612 \times 10^{-3}\text{mol}$

The acid, HA (monobasic acid) reacts with NaOH according to the following equation:

$$\text{HA} + \text{NaOH} \longrightarrow \text{NaA} + H_2O$$

From which mole ratio of NaOH to NaA is 1:1

Thus number of moles of NaA formed was also 3.612×10^{-3}moles

Number of moles of HCl added = $\frac{18.06}{1000} \times 0.1 = 1.806 \times 10^{-3}\text{mol}$

HCl reacts with NaA according to the following equation:

$$\text{NaA} + \text{HCl} \longrightarrow \text{NaCl} + \text{HA}$$

From which mole ratio of NaA to HCl is 1:1. So NaA is present in excess and $(3.612 \times 10^{-3} - 1.806 \times 10^{-3})$moles or 1.806×10^{-3}moles of it remain unreacted at the end of chemical reaction.

Also mole ratio of HCl (limited reactant) to HA is 1:1. Thus number of moles of HA formed was also 1.806×10^{-3}moles.

Hence at the end of the above reaction, there was:

- 1.806×10^{-3}moles of HA
- 1.806×10^{-3}moles of NaA

HA being weak acid and NaA being strong salt containing conjugate base (A^-) of the acid, their mixture gives acidic buffer solution whose pH is given by the following equation:

$$pH = pK_a + \log\frac{\text{Number of moles of salt (NaA)}}{\text{Number of moles o f acid (HA)}}$$

Substituting $4.92 = pK_a + \log\frac{1.806\times10^{-3}}{1.806\times10^{-3}}$; whence $pK_a = 4.92 = -\log K_a$

$K_a = \log^{-1}(-4.92) = 1.2\times10^{-5}$

Hence the dissociation constant for unknown acid is 1.2×10^{-5}.

Example 8

An CH_3COOH/CH_3COONa buffer containing 0.1M $CH_3\ COOH$ has a pH of 4.742;

(a) Determine concentration of CH_3COONa in this solution
(b) To $1dm^3$ of the buffer, 0.01moles of NaOH are added. Calculate the new pH
(c) To $1dm^3$ of the buffer, 0.01moles of HCl are added. What is the new pH ($K_a(CH_3COOH) = 1.8\times10^{-5}$)

Solution

CH_3COOH/CH_3COONa buffer is acidic whose pH is given by the following equation:

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

(a) Substituting given values: $4.742 = -\log(1.8\times10^{-5}) + \log\frac{[CH_3COO^-]}{1}$

From which; $[CH_3COO^-] = [CH_3COONa] = 0.99M$

(b) NaOH being strong base, ionises completely according to the following equation:

$$\underset{0.01\text{moles}}{NaOH} \rightarrow Na^+ + \underset{0.01\text{ moles}}{OH^-}$$

Introduction of OH^- shifts the position of chemical equilibrium of the buffer solution to the right as shown below

	CH_3COOH	$\rightleftharpoons$	CH_3COO^- +	H^+
Number of moles before addition of NaOH	$1dm^3 \times 1moldm^{-3}$ = 1mol		$1dm^3 \times 0.99moldm^{-3}$ = 0.99mol	
After addition of NaOH	$(1-0.01)$mol		$(0.99+0.01)$mol	

Thus at the new equilibrium:

$$[CH_3COOH] = \frac{(1-0.01)mol}{1dm^3} = 0.99M$$

$$[CH_3COO^-] = \frac{(0.99+0.01)mol}{1dm^3} = 1M$$

Then the new $pH = -\log(1.8\times10^{-5}) + \log\left(\frac{1}{0.99}\right) = 4.749$

Hence the new pH after addition of NaOH is 4.749

(c) HCl being strong acid, ionises completely according to the following equation:

$$HCl \rightarrow H^+ + Cl^-$$

An introduction of H^+ shifts the position of chemical equilibrium of the buffer solution to the left as shown below:

	CH_3COOH	$\rightleftharpoons$	$CH_3COO^- + H^+$
Before addition of HCl	1mol		0.99mol
After addition of HCl	$(1 + 0.01)$mol		$(0.99 - 0.01)$mol

Thus at the new equilibrium:

$$[CH_3COOH] = \frac{(1+0.01)\text{mol}}{1\text{dm}^3} = 1.01\text{M}$$

$$[CH_3COO^-] = \frac{(0.99-0.01\text{mol})}{1\text{dm}^3} = 0.98\text{M}$$

Then the new pH $= -\log(1.8 \times 10^{-5}) + \log\left(\frac{0.98}{1.01}\right) = 4.732$

Hence the new pH after addition of the acid is 4.732

APPLICATION OF BUFFER SOLUTIONS

Generally buffer solutions are useful in various systems which function properly under certain specified narrow range of pH. They have the following practical applications like:

- **Physiological uses in keeping correct pH for enzymes in various organisms** to work. For example, a buffer of carbonic acid and bicarbonate is present in **blood plasma** to maintain pH between 7.35 and 7.45.
- **Pharmaceutical uses** like in preparation of shampoo and baby lotion.
- **Industrial uses** like in fermentation processes and in setting the correct conditions for dyes and colouring fabrics.
- **Preparation of biological samples** that are used in research.
- **Chemical analysis and calibration of pH meters.**

DIGGING DEEPER EXERCISE 17

EXERCISE 17A: BINDER QUESTIONS

Question 1

How a buffer solution with pH of 3 manages to stabilise the pH against the addition of acid or base?

Question 2

It is known that, when water is added to acidic or basic solution, concentration of the solution and hence its pH changes. However, the change in pH is not witnessed when the dilution is done over a buffer solution.

(i) Why pH of a buffer solution does not change on dilution?
(ii) How the dilution affects buffer capacity?

Question 3

Does the pH of a solution increase, decrease, or stay the same when you add solid ammonium chloride to a solution of 0.10M NH_3?

Question 4

A buffer solution was prepared which had a concentration of 0.2moldm^{-3} in ethanoic acid and 0.1moldm^{-3} in sodium ethanoate. If the K_a for ethanoic acid is 1.74×10^{-5} moldm^{-3}, calculate the theoretical hydrogen ion concentration and pH of the buffer solution.

Question 5

What is the pH of a buffer solution made from dissolving 2.0g of benzoic acid and 5.0g of sodium benzoate in 250cm^3 of water? $K_a(\text{benzoic acid}) = 6.3 \times 10^{-5}\text{moldm}^{-3}$.

Question 6

Calculate the pH of a buffer made by mixing 100cm^3 of a 0.40 M sodium propanoate and 50cm^3 of 0.2Mpropanoic acid solutions. $K_a(\text{propanoic acid}) = 1.3 \times 10^{-5}\text{moldm}^{-3}$.

Question 7

Calculate the pH of buffer solution made by mixing together 100 cm^3 of 0.100M ethanoic acid and 50 cm^3 of 0.400M sodium ethanoate, given that K_a for ethanoic acid is 1.74×10^{-5} moldm^{-3}.

Question 8

What mass of sodium nitrite should be added to 1L of 1.5M nitrous acid so as to prepare buffer solution that can maintain a pH of 3.40 using? $K_a = 4.5 \times 10^{-5}$ for nitrous acid.

EXERCISE 17B: REAL QUESTIONS

Question 9

Buffers a crucial to physiology of human beings. Give three examples of buffers in the human body.

Question 10

Your friend **Kipute**, read the following statement from a chemistry book: **For buffer to be effective, it should possess equal concentrations of both of its components such that pH = $\mathbf{pK_a}$.** *"Hmmmh! Why do we study calculations of pH of buffers while in real life the pH will always be equal to pK_a? And why in the most of those calculations, the concentrations are different? What is the use of wasting our time and energy for applying Henderson-Hasselbalch equation while in real life only the pK_a value is required to know the pH?* She asked herself with small voice whispering inside her head.

If **Kipute** could ask those questions to you, what would be your response?

Question 11

You were given with four different acetate buffers. The concentration ratio, $[\textbf{Acetate}]:[\textbf{Acetic acid}]$ for each buffer was as follows:

Buffer 1: The ratio is $2:2$

Buffer 2: The ratio is $1:2$

Buffer 3: The ratio is $3:3$

Buffer 4: The ratio is $2:1$

(i) Which buffer has the highest pH?
(ii) Which buffer has the greatest capacity?
(iii) Should we add a small amount of strong acid or strong base to convert 1 to 2?
(iv) Should we add a small amount of strong acid or strong base to convert 3 to 4?
(v) Which buffers have the same pH?
(vi) Which buffer(s) works best?

In each case give a reason (s) to justify your answer.

Question 12

The laboratory technician, **Mr. Akilikubwa** was given a task to prepare the buffer solution which perform best at pH of 2. The following, are only acids present in the laboratory:

1. Acetic acid ($pK_a = 4.74$)
2. Chlorous acid ($pK_a = 1.95$)
3. Formic acid ($pK_a = 3.74$)

Advise **Mr. Akilikubwa** on the choice of the best acid to use.

Question 13

You have been provided with the following chemicals in the laboratory:

$$CH_3COOH, HCl, CH_3COONa, NaOH$$

(i) What a type of buffer solution can be made from given chemicals?
(ii) Give three possible pairs of chemicals which may act as buffer solution.
(iii) What amount should be taken for each component of pair in (ii) above to make the buffer work at best level.

EXERCISE 17C: HOT QUESTIONS

Question 14

Increasing temperature of a buffer system is said to decrease the buffer capacity. Explain why.

Question 15

By referring to the following Henderson – Hasselbalch equation, explain factors affecting pH of buffer solution.

$$pH = pK_a + \log\frac{[Salt]}{[Acid]}$$

Question 16

In what ratio by volume should a $0.3 moldm^{-3}$ of ethanoic acid be mixed with a $0.3 moldm^{-3}$ solution of sodium ethanoate to give a buffer solution of pH 5.6? K_a for ethanoic acid is 1.74×10^{-5} $moldm^{-3}$.

Question 17

You have 100mL of 1 M ammonia solution (pK_a=9.25). What volume of 1 M hydrochloric acid is needed to prepare buffer with pH=9.5?

Question 18

During a titration NaOH solution of concentration 0.100M was added to $30.0 cm^3$ of 0.100M propanoic acid.

(a) What property is shown by the reaction mixture when $15.0 cm^3$ of NaOH has been added to the propanoic acid?
(b) Calculate the pH of the reaction mixture at this stage. Propanoic acid has $K_a = 1.35 \times 10^{-5}$.

Question 19

A buffer solution of pH = 3.87 contains 7.40gdm^{-3} of propanoic acid together with a quantity of sodium propanoate. K_a for propanoic acid = $1.35 \times 10^{-5}\text{moldm}^{-3}$ at 298K.

(a) Calculate the concentration in gdm^{-3} of sodium propanoate, $C_2H_5CO_2Na$, in the solution, stating any assumptions made.
(b) If the sodium propanoate were to be replaced by anhydrous magnesium propanoate, calculate the concentration of magnesium propanoate in gdm^{-3}, required to give a buffer of the same pH.

Question 20

(a) Calculate the pH of 0.100moldm^{-3} sodium hydroxide solution at 25 ºC. The value of K_w at this temperature is $1 \times 10^{-14}\text{mol}^2\text{dm}^{-6}$.
(b) 100cm^3 of 0.100moldm^{-3} sodium hydroxide solution was added to 100cm^3 of 0.200moldm^{-3} ethanoic acid.
    (i) Find the concentration of ethanoic acid in the mixture.
    (ii) Calculate the concentration of sodium ethanoate in the mixture.
    (iii) Calculate the pH of the mixture at 25ºC; K_a for ethanoic acid at this temperature is 1.8×10^{-5} moldm^{-3}.
    (iv) State and explain what happens if a small amount of hydrochloric acid is added to this mixture?

Question 21

Calculate the pH in the solution formed by adding 10mL of 0.05M NaOH to 40mL of 0.0250M benzoic acid (C_6H_5COOH, $K_a = 6.3 \times 10^{-5}$).

Question 22

Calculate the pH in the solution formed by adding 10mL of 0.1M HCl to 20mL of 0.1M NH_3.

$$K_b(NH_3) = 1.8 \times 10^{-5}$$

Question 23

For acetic acid, $K_a = 1.76 \times 10^{-5}$ at 25°C.

(a) Calculate the pH in a solution prepared by dissolving 0.070mol of acetic acid and 0.035mol of sodium acetate in water and adjusting the volume to 500mL.
(b) Suppose 0.015mol of HCl is added to the buffer from part a. Calculate the pH of the solution that results (assume that the total solution volume remains 500mL).
(c) Suppose 0.015mol of HCl were added to 500.0 mL of pure water instead of the buffer solution in part a. Calculate the pH of the solution that results (again, assume that the total solution volume remains 500.0 mL).

Question 24

A sample of 1.25L of HCl gas at 21°C and 0.950atm is bubbled through 0.5L of 0.15M NH_3 solution. Calculate the pH of the resulting solution assuming that all the HCl dissolves and that the volume of the solution remains 0.5L. $K_b(NH_3) = 1.8 \times 10^{-5}$

Chapter 18
SALT HYDROLYSIS

Salts are ionic compounds that result from neutralisation reaction of an acid and a base. They are composed of related numbers of cations and anions so that the product is electrically neutral. These component ions can be inorganic, such as bromide ion (Br^-) and potassium ion (K^+) or organic, such as acetate(CH_3COO^-) and can be mono-atomic, such as chloride ion (Cl^-) or polyatomic, such as nitrate(NO_3^-) and ammonium ion (NH_4^+). They can also be simple ion, such as Ag^+ or complex ion, such as $[Cu(NH_3)_4]^+$

The ion-ion interactions between cations and anions of salt, are very strong making the physical state of salt to be solid.
So **salt** can simply be defined as *the compound which consists of ions in its solid state.* Thus salts consist of **cations** and **anions.**

- Always cations are **acidic** while anions are **basic**. If cation **is the conjugate** acid of weak base, then the cation is **strong acid** and if cation is **conjugate acid** of **strong base** then the cation is **weak acid.**
- On another hand, if anion is the **conjugate base** of **weak acid** then the anion is **strong base** and if the anion is **conjugate base** of **strong acid** then the anion is **weak base**.

Examples of strong acid cations are NH_4^+ and Al^{3+} as they are derived from NH_4OH and $Al(OH)_3$ respectively which are weak bases. Being strong acidic, NH_4^+ and Al^{3+} have high ability of holding OH^- (from base) to form NH_4OH and $Al(OH)_3$ molecules respectively and eventually to large extent NH_4OH and $Al(OH)_3$ exist as molecules and not as ions.

Examples of weak acid cations are Na^+ and K^+ as they are derived from NaOH and KOH respectively which are strong bases. Being weak acid, Na^+ and K^+ are unable (low ability) to hold OH^- (from base) to from NaOH and KOH molecules respectively and eventually the molecules do not exist as the two (NaOH and KOH) ionises completely to give their respective ions.

Examples of strong base anions are CH_3COO^- and CN^- as they are derived from CH_3COOH and HCN respectively which are weak acids. Being strong bases, CH_3COO^- and CN^- have high ability of holding H^+ (from acid) to from CH_3COOH and HCN molecules respectively and eventually to large extent CH_3COOH and HCN exist as molecules and not as ions.

Examples of weak base anions are Cl^- and NO_3^- as they are derived from HCl and HNO_3 respectively which are strong acids. Being weak acids Cl^- and NO_3^- are unable to hold H^+ (from acid) to form HCl and HNO_3 molecules respectively and eventually the molecules do not exist as the two (H Cl and HNO_3) ionises completely to give their respective ions.

Strong acid cation and strong base anion can attract (or be attracted by) OH^- and H^+ respectively from self ionisation of water thus reacting with the water in **salt hydrolysis**.

- Salts which contain strong acid cation or weak base anion have significant degree of covalent characters. These salts undergo salt hydrolysis in aqueous solution yielding acidic solution or basic solution according to the nature of the salt
- Generally, ability to hydrolyse in water is covalent character, i.e. salts (ionic compounds) with high degree of polarisation undergo salt hydrolysis (the greater degree of covalence, the higher ability to hydrolyse in water).

Definition of salt hydrolysis

Salt hydrolysis *is a chemical reaction in which the cation or anion or both of a salt react with water to produce acidity or alkalinity.*

CATIONIC AND ANIONIC SALT HYDROLYSIS

Salt hydrolysis can be classified into two main categories:

- Cationic salt hydrolysis
- Anionic salt hydrolysis

Cationic salt hydrolysis

This *is the chemical reaction between water and salt containing* ***strong acid cation*** *and* ***weak base anion*** *to give acidic solution.*

A good example of a salt which undergo cationic salt hydrolysis (or simply cationic hydrolysis) is ammonium chloride (NH_4Cl) in which NH_4^+ is strong acid cation while Cl^- is weak base anion. Salts which undergo cationic hydrolysis are known as **acidic salts.**

How acidic solution is formed after addition of NH_4Cl to water?

Before addition of the salt (NH_4Cl), water undergo self ionisation according to the following equation:
$H_2O(l) \rightleftharpoons H^+(aq) + OH^-(aq)$ ………………………….(i)

In which $[H^+] = [OH^-]$ and this explains for neutrality of the pure water.

Addition of the salt (NH_4Cl) to the water is equivalent to addition of NH_4^+ and Cl^- because NH_4Cl being strong salt ionises completely according to the following equation:

$$NH_4Cl \rightarrow NH_4^+ + Cl^- \text{…………………………………(ii)}$$

NH_4^+ being strong acid cation, combine with OH^- from self ionisation of water (from equation (i)) to form NH_4OH according to the following equation.

$$NH_4^+ + OH^- \rightarrow NH_4OH \text{………………………….(iii)}$$

While Cl^- being weak base anion is unable to combine with $H^+$from self ionisation of water (from equation (i)) i.e. $Cl^- + H^+ \rightarrow \text{No reaction}$

So concentration of hydroxyl ions (OH^-) is decreased while that of hydrogen ions (H^+) reamin unchanged thus shifting position of chemical equilibrium in self ionisation of water to the right and eventually the concentration of hydrogen ions become greater than that of hydroxyl ions i.e. $[H^+] > [OH^-]$ and hence the solution become acidic.

The overall reaction equation can simply be obtained through combining (i), (ii) and (iii) by taking (i) + (ii) + (iii) as follows:

$$H_2O + NH_4Cl + NH_4^+ + OH^- \rightarrow H^+ + OH^- + NH_4^+ + Cl^- + NH_4OH$$

Cancelling like terms gives the overall reaction equation which is:

$$\mathbf{NH_4Cl + H_2O \rightarrow NH_4OH + H^+ + Cl^-}$$

From the above overall reaction equation, it is clearly understood that only cation of the salt has undergone change and hence the name **cationic hydrolysis**.

The simplified overall reaction equation which shows changing species only is given below:

$$\mathbf{NH_4^+ + H_2O \rightarrow NH_4OH + H^+}$$

Where the formation of H^+ accounts for acidity of the solution.

Anionic salt hydrolysis

This *is the chemical reaction between water and salt containing* ***strong base*** *anion and* ***weak acid cation*** *to give basic solution.*

A good example of salt which undergo anionic salt hydrolysis (or simply **anionic hydrolysis**) is sodium ethanoate (CH_3COONa) in which CH_3COO^- is strong base anion while Na^+ is weak acid cation. Salts which undergo cationic hydrolysis are known as **basic salts.**

How basic solution is formed after addition of CH_3COONa to water?

Before addition of the salt(CH_3COONa), water undergo self ionisation according to the following equation:

$$H_2O \rightleftharpoons H^+(aq) + OH^-(aq)\text{...........................(i)}$$

In which $[H^+] = [OH^-]$ and hence the pure liquid is neutral.

Addition of the salt (CH_3COONa) to the water is equivalent to addition of CH_3COO^- and Na^+ because CH_3COONa being strong salt is fully ionised according to the following equation:

$$CH_3COONa \rightarrow CH_3COO^- + Na^+\text{.........................(ii)}$$

CH_3COO^- being strong base anion, combines with H^+ from self ionisation of water (equation (i)) to form CH_3COOH according to the following equation:

$$CH_3COO^- + H^+ \rightarrow CH_3COOH\text{.............................(iii)}$$

While Na^+ being weak acid cation, is unable to combine with OH^- from self ionisation of water (equation (i)) That is $Na^+ + OH^- \rightarrow \text{No reaction}$

So while concentration of hydrogen ions (H^+) is decreased, the hydroxyl ions concentration $[OH^-]$ remains unchanged thus shifting the position of chemical equilibrium in self-ionisation of water to the right and eventually the concentration of hydrogen ions become smaller than that of hydroxyl ions i.e. $[H^+] < [OH^-]$ and hence the solution become basic.

The overall reaction equation can simply be obtained through combining (i), (ii) and (iii) by taking (i) + (ii) + (iii) and cancelling like terms to give the following equation:

$$\mathbf{CH_3\,COONa + H_2O \rightarrow CH_3COOH + Na^+ + OH^-}$$

From the above overall reaction equation, it is clearly understood that only anionic part of the salt has undergone changes and hence the name anionic hydrolysis. The simplified overall reaction equation which shows changing species is given below as follows:

$$\mathbf{CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-}$$

Where formation of OH^- accounts for alkalinity (basicity) of the solution

What happen when very strong ionic salt like NaCl is mixed with water?

Nothing happen as far as salt hydrolysis is taken to an account.

NaCl being strong ionic salt, contains weak acid cation (Na^+) as well as weak base anion (Cl^-) both of which are unable to combine with OH^- and H^+ from self ionisation of water thus hydroxyl and hydrogen ions concentrations remain unchanged and hence the solution become neutral.
That is: $H_2O \rightleftharpoons H^+ + OH^-$ where $[H^+] = [OH^-]$ (in pure water)

NaCl being strong ionic salt ionises completely according to the following equation:

$$NaCl \rightarrow Na^+ + Cl^-$$

However both Na^+ and Cl^- being weak acid cation and weak base anion respectively are unable to combine with either OH^- or H^+ from the water ionisation thus maintaining neutrality of the solution and hence $\mathbf{NaCl + H_2O \rightarrow No\ reaction}$

The same kind of explanation applies for any other strong ionic salt like KCl, $CaCl_2$etc., which contain weak acid cation and weak base onion.

Salts which do not undergo hydrolysis such that they give neutral solution when dissolved in water are known as **neutral salts**.

What about salts which contain strong acid cation and strong base anion?

In this case both cation and anion are able to combine with OH^- and H^+ respectively from self ionisation of water and hence the solution may become neutral, acidic or basic depending on the difference in the strengths of bases and acids which are formed.

Examples:

- $CH_3COONH_4 + H_2O \rightarrow CH_3COOH + NH_4OH$
- $(NH_4)_2CO_3 + 2H_2O \rightarrow 2NH_4OH + H_2CO_3$
- $Al_2(CO_3)_3 + 6H_2O \rightarrow 2Al(OH)_3 + 3H_2CO_3$

Salts which contain strong acid cation and strong base anion are termed as **weak salts.**

EFFECTS OF SALT HYDROSIS ON PROPERTIES OF SALT SOLUTION

When a salt hydrolyse in water, properties of resulting solution are affected in the following ways:

Colouration of litmus paper
If the salt is introduced to the solution of the salt which undergoes cationic hydrolysis, the blue litmus paper turns red verifying that the solution is acidic as result of the hydrolysis. And if the salt undergoes anionic hydrolysis to give alkaline (basic) solution, the red litmus paper turns blue.

Evolvement of hydrogen gas
When strong electropositive metal is introduced to the solution of salt which undergoes cationic hydrolysis, the hydrogen gas is evolved verifying that the solution is acidic as result of the hydrolysis.

Evolvement of carbon dioxide gas
When carbonate or bicarbonate (hydrogen carbonate) is introduced to the solution which undergoes cationic hydrolysis, the carbon dioxide is evolved verifying that the solution is acidic as result of the hydrolysis

Electrolytic conduction
Usually covalent compounds or ionic compounds (including salts) with high degree of covalence characters as result of their high degree of polarisation are incapable of doing electrolytic conduction due to lack of enough concentration ions which are responsible for doing the conduction. The statement is always true in the molten state of the compound. However, in aqueous solution the compound may conduct electricity if they are capable of undergoing hydrolysis to give enough concentration of free ions which are responsible for doing electrolytic conduction.

Formation of precipitate
Two clear solutions may give a precipitate when they are mixed if one of the double decomposition products of the reaction between the two salts is capable of undergoing cationic hydrolysis to give the insoluble hydroxide which appears as the precipitate.

Worked examples

Example 1

Explain what will you **observe** when sodium carbonate is introduced in the solution containing iron (III) ions (Fe^{3+}).

Solution

Fe^{3+} being strong acid cation, undergo cationic hydrolysis in aqueous solution to give acidic solution which evolve carbon dioxide CO_2 gas from the carbonate and the gas appears as effervescence of colourless gas which turn lime water milky.

i.e. $Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$

Then $2H^+ + CO_3^{2-} \rightarrow CO_2 + H_2O$

Example 2

Hydrogen gas is evolved when magnesium is introduced into a beaker containing aqueous solution of ammonium chloride. Explain.

Solution

NH_4Cl contain strong acidic cation (NH_4^+) and weak basic anion (Cl^-) , so in aqueous solution it undergo cationic hydrolysis yielding acidic solution which is responsible of evolving hydrogen gas when magnesium (metal) is introduced in the solution.

That is $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$

Then $2H^+ + Mg \rightarrow Mg^{2+} + H_2$

Example 3

What will you **observe** when sodium metal is introduced into a beaker containing a solution of iron (III) chloride?

Solution

Bubbles of a gas which is recognised by its pop sound, i.e. hydrogen gas is evolved.

Example 4

What will you **observe** when blue litmus paper is dipped into a beaker containing aqueous solution of $AlCl_3$?

Solution

Blue litmus paper turns red

Example 5

What **happen** when sodium bicarbonate ($NaHCO_3$) is introduced in a beaker containing aqueous solution of $AlCl_3$?

Solution

In aqueous solution, $AlCl_3$ undergo cationic hydrolysis yielding acidic solution which reacts with $NaHCO_3$ to evolve carbon dioxide gas which appears as effervescence of colourless gas that turns lime water milky.

That is $\underset{\textbf{(From AlCl}_3\textbf{)}}{Al^{3+}} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

Then $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$

Example 6

Aqueous solution of $AlCl_3$ is acidic while that of CH_3COONa is basic. Explain.

Solution

$AlCl_3$ contains strong acidic cation, Al^{3+}, and weak basic anion, Cl^-, so in aqueous solution $AlCl_3$ undergo cationic hydrolysis yielding acidic solution while CH_3COONa contains strong basic anion, CH_3COO^-, and weak acidic cation, Na^+; so CH_3COONa undergo anionic hydrolysis yielding basic solution. i.e. $Al^{3+} + 3H_2O \rightarrow Al(OH)_3 + 3H^+$

Where presence of H^+ determines the acidity of solution of $AlCl_3$

While $CH_3COO^- + H_2O \rightarrow CH_3COOH + OH^-$

Where presence of OH^- determines the basicity of solution of CH_3COONa.

Example 7

$AlCl_3$ reacts chemically with water while NaCl does not. Explain.

Solution

$AlCl_3$ is the salt that contains strong acid cation, Al^{3+}, and weak base anion, Cl^-. So with water, the salt undergo cationic hydrolysis yielding acidic solution while NaCl being strongly ionic as it contains weak acid cation, Na^+, and weak base anion, Cl^-, does not hydrolyse in water.

i.e. $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3H^+ + 3Cl^-$
While $NaCl + H_2O \rightarrow \text{No reaction}$

Example 8

PCl_3 is covalent liquid but in aqueous solution it conducts electricity. Explain.

Solution

In aqueous solution, PCl_3 hydrolyse yielding enough concentration of H^+ and Cl^- to do electrolytic conduction.

i.e. $PCl_3 + H_2O \rightarrow POCl + 2H^+(aq) + 2Cl^-(aq)$

Then $POCl + 2H_2O \rightarrow H_3PO_3 + H^+(aq) + Cl^-(aq)$

Example 9

A precipitate of aluminium hydroxide is observed when a solution of aluminium sulphide is mixed with a solution of calcium chloride in the beaker. Explain.

Solution

After mixing the two solutions, aluminium chloride which is initially formed in the reaction of the two solutions is further undergoing cationic hydrolysis yielding insoluble aluminum hydroxide.

That is $Al_2S_3 + 3CaCl_2 \rightarrow 3CaS + 2AlCl_3$

Then $AlCl_3 + \underset{\text{(From the solution)}}{3H_2O} \rightarrow \underset{\text{insoluble}}{Al(OH)_3} + 3H^+ + 3Cl^-$

HYDROLYSIS CONSTANT FOR CATIONIC HYDROLYSIS

Consider ammonium chloride (NH_4Cl) which undergoes cationic hydrolysis according to the following equation: $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

From which, $K = \frac{[NH_4OH][H^+]}{[NH_4^+]\,[H_2O]}$ or $K\,[H_2O] = \frac{[NH_4OH]\,[H^+]}{[NH_4^+]}$

If $[H_2O]$ is constant, $K[H_2O]$ gives another constant which is known as hydrolysis constant, K_h.

Thus $K_h = \frac{[NH_4OH]\,[H^+]}{[NH_4^+]}$ ………………………………………………(i)

But the ammonium hydroxide (NH_4OH) produced in the hydrolysis ionises according to the following equation: $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

From which $K_b = \frac{[NH^+]\,[OH^-]}{[NH_4OH]}$

Or $\frac{[OH^-]}{K_b} = \frac{[NH_4OH]}{[NH_4^+]}$ ……………………………………………………(ii)

Substituting (ii) to (i) gives; $K_h = \frac{[OH^-]\,[H^+]}{K_b}$

But $[OH^-]\,[H^+] = K_w$

Hence for cationic hydrolysis, $K_h = \frac{K_w}{K_b}$

From K_h expression, it should be noted that: **$K_h = K_a$ of cation of the salt which is hydrolysed.**

HYDROLYSIS CONSTANT FOR ANIONIC HYDROLYSIS

Consider sodium ethanoate (CH_3COONa) which undergo anionic hydrolysis according to the following equation: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

From which, K = $\frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]\,[H_2O]}$ or $K\,[H_2O] = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]}$

If $[H_2O]$ is constant, $K[H_2O]$ gives another constant which is known as hydrolysis constant, K_h.

Thus $K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]}$ ………………………….………….(ii)

But ethanoic acid (CH_3COOH) produced in the hydrolysis ionises according to the following equation: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

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

Or $\frac{[H^+]}{K_a} = \frac{[CH_3COOH]}{[CH_3COO^-]}$ …………………………………………….(ii)

Substituting (ii) to (i) gives; $K_h = \frac{[H^+]\,[OH^-]}{K_a}$

But $[H^+]\,[OH^-] = K_w$

Hence for anionic hydrolysis, $K_h = \frac{K_W}{K_a}$

In this case $K_h = K_b$ for anion of the salt which is hydrolysed.

CONCENTRATION OF HYDROGEN IONS (H^+) IN CATIONIC HYDROLYSIS

Consider ammonium chloride (NH_4Cl) which undergoes cationic hydrolysis according to the following equation: $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$

From which $K_h = \frac{[NH_4OH]\,[H^+]}{[NH_4^+]}$

Where $[NH_4OH] = [H^+]$ (Their mole ratio is 1:1)

And $[NH_4^+] = [NH_4Cl] = [salt]$ (Their mole ratio is 1:1)

Then $K_h = \frac{[H^+]^2}{[Salt]}$ or $[H^+] = \sqrt{K_h[salt]}$

But $K_h = \frac{K_w}{K_b}$ (For cationic hydrolysis)

Hence for cationic hydrolysis $\mathbf{[H^+] = \sqrt{\frac{K_w}{K_b}\,[salt]}}$

The pH of the solution is found by taking negative logarithm of $[H^+]$ as usual,

i.e. $\mathbf{pH = -\log\sqrt{K_h[salt]}}$ **where** $\mathbf{K_h = \frac{K_w}{K_b}}$

CONCENTRATION OF HYDROGEN IONS (H^+) IN ANIONIC HYDROLYSIS

Consider sodium ethanoate (CH_3COONa) which undergoes anionic hydrolysis according to the following equation: $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

From which $K_h = \frac{[CH_3COOH]\,[OH^-]}{[CH_3COO^-]}$

Where $[CH_3COOH] = [OH^-]$ (Their mole ratio is 1:1)

And $[CH_3COO^-] = [CH_3COONa] = [salt]$ (Their mole ratio is 1:1)

Then $K_h = \frac{[OH^-]^2}{[salt]}$ or $[OH^-] = \sqrt{K_h\,[salt]}$

But for anionic hydrolysis, $K_h = \frac{K_w}{K_a}$

Thus $[OH^-] = \sqrt{\frac{K_w}{K_a}[salt]}$

But $[OH^-]\,[H^+] = K_w$; from which $[H^+] = \frac{K_w}{[OH^-]}$

If follows that, $[H^+] = \frac{K_w}{\sqrt{\frac{K_w}{K_a}[salt]}} = \sqrt{\frac{K_aK_w}{[salt]}}$

Hence for anionic hydrolysis; $[\mathbf{H^+}] = \sqrt{\frac{\mathbf{K_aK_w}}{\mathbf{[salt]}}}$

The pH of the solution is found by taking negative logarithm of $[H^+]$ as usual,

i.e. $\mathbf{pH = -log\sqrt{\frac{K_aK_w}{[salt]}}}$

Don't forget that:

- For cationic hydrolysis, $K_h = K_a$ of cation of the salt which is hydrolysed.
- For anionic hydrolysis, $K_h = K_b$ of anion of the salt which is hydrolysed.

Worked examples

Example 10

4.1g of CH_3COONa was dissolved in $500cm^3$ of water; calculate: $[CH_3COO^-], [H_3O^+], [OH^-]$ and pH of this solution.

Use $K_a(CH_3COOH) = 1.8 \times 10^{-5} moldm^{-3}$.

Solution

$$[CH_3COO^-] = [CH_3COONa] = \frac{\text{Mass concentration of } CH_3COONa \text{ in } gdm^{-3}}{\text{Molar mass of } CH_3COONa}$$

$$= \frac{4.1}{0.5 \times 82}M = 0.1M$$

Thus $[CH_3COO^-] = 0.1M$

CH_3COONa undergoes anionic hydrolysis to give the solution whose $[H_3O^+]$ is given by the following equation: $[H_3O^+] = \sqrt{\frac{K_ak_W}{[salt]}} = \sqrt{\frac{1.8 \times 10^{-5} \times 10^{-14}}{0.1}} = 1.34 \times 10^{-9}M$

Thus $[H_3O^+] = 1.34 \times 10^{-9}M$

From $[H_3O^+]\,[OH^-] = K_w = 10^{-14}$; $[OH^-] = \frac{10^{-14}}{1.34 \times 10^{-9}} = 7.46 \times 10^{-6}M$

Thus $[OH^-] = 7.46 \times 10^{-6}M$

$pH = -log[H_3O^+] = -log(1.34 \times 10^{-9}) = 8.87$

Hence:

$[CH_3COO^-] = 0.1M$, $[H_3O^+] = 1.34 \times 10^{-9}M$ $[OH^-] = 7.46 \times 10^{-6}M$

pH of the solution is 8.87

Example 11

0.3M solution of NH_4Br is present in aqueous solution. Assume complete dissociation of NH_4Br. Calculate: $[NH_4^+], [Br^-], [H_3O^+], [NH_3]$ and pH of the solution.

$$(K_a \text{ of } NH_4^+ \text{ is } 5.7 \times 10^{-10}\text{M})$$

Solution

NH_4Br is ionised according to the following equation: $NH_4Br \rightarrow NH_4^+ + Br^-$

From which mole ratio of NH_4Br to both NH_4^+ and Br^- is $1:1$;

Thus $[NH_4Br] = [NH_4^+] = [Br^-] = 0.3\text{M}$

NH_4Br undergoes cationic hydrolysis according to the following equation:

$$NH_4^+ + H_2O \rightleftharpoons NH_3(aq) + H_3O^+$$

($\mathbf{NH_3(aq)}$ is equivalent to $\mathbf{NH_4OH}$ and $\mathbf{H_3O^+}$ is equivalent to $\mathbf{H^+(aq)}$)

From which $[NH_3] = [H_3O^+] = \sqrt{K_h\,[\text{salt}]}$

But for cationic hydrolysis, $K_h = K_a$ of cation of the salt where in this case, K_a of NH_4^+.

If follows that $[NH_3] = [H_3O^+] = \sqrt{K_a[\text{salt}]} = \sqrt{5.7 \times 10^{-10} \times 0.3} = 1.3 \times 10^{-5}\text{M}$

And $\text{pH} = -\log[H_3O^+] = -\log(1.3 \times 10^{-5}) = 4.89$

Hence:

$[NH_4^+] = 0.3\text{M}$, $[Br^-] = 0.3\text{M}$, $[NH_3] = 1.3 \times 10^{-5}\text{M}$,

$[H_3O^+] = 1.3 \times 10^{-5}\text{M}$, pH of the solution is 4.89

Example 12

25cm^3 of $0.1\text{M}CH_3COOH$ is titrated against sodium hydroxide solution and 25cm^3 of the alkaline solution was found to be used at neutralisation point. Calculate pH of the solution at the end point of the neutralisation. Use K_a of $CH_3COOH = 1.8 \times 10^{-5}\text{M}$

Solution

CH_3COOH reacts with NaOH according to the following equation:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

From which mole ratio of CH_3COOH to CH_3COONa is $1:1$

Thus at neutralisation point:

Number of moles of CH_3COOH = Number of moles of CH_3COONa produced

$$= \frac{25}{1000} \times 0.1\text{moles} = 2.5 \times 10^{-3}\text{moles}$$

And $[CH_3COONa] = \frac{n}{v} = \frac{2.5\times10^{-3}\text{mol}}{(25+25)\times10^{-3}\text{dm}^3} = 0.05\text{M}$

The CH_3COONa which is produced, undergoes anionic hydrolysis to give basic solution whose pH is given by the following equation: $\text{pH} = -\log\sqrt{\frac{K_aK_w}{[\text{salt}]}} = -\log\sqrt{\frac{1.8\times10^{-5}\times10^{-14}}{0.05}} = 8.72$

Hence pH of the solution at neutralisation point is 8.72

Example 13

20cm^3 of $0.05\text{M}NaOH$ is titrated against $0.05\text{M}HCl$ and 20cm^3 of the acid was found to be used at neutralisation point. Calculate pH of the solution at the end point of the neutralisation.

Solution

Number of moles of NaOH used = $\frac{20}{1000} \times 0.05\text{moles} = 10^{-3}\text{moles}$

Number of moles of HCl used = $\frac{20}{1000} \times 0.05\text{moles} = 10^{-3}\text{moles}$

NaOH reacts with HCl according to the following equation: $NaOH + HCl \rightarrow NaCl + H_2O$

From which mole ratio of NaOH to HCl is 1:1.

Thus neither NaOH nor HCl is in excess as the given amounts of base and acid satisfy the mole ratio.

And because NaCl is incapable of undergoing salt hydrolysis; the solution remains neutral.

That is $[H_3O^+] = [OH^-] = 10^{-7}\text{moldm}^3$

It follows that pH $= -\log[H_3O^+] = -\log 10^{-7} = 7$

Hence pH of the solution at neutralisation point is 7

Example 14

100cm^3 of 0.01M HCOOH is titrated against 0.1M NaOH. Calculate the pH;

(a) Before the titration begin
(b) When 15cm^3 of NaOH solution has been added
(c) When 10cm^3 of NaOH solution has been added
(d) When 5cm^3 of NaOH solution has been added

$$(K_a \text{ of HCOOH} = 1.8 \times 10^{-4})$$

Solution

(a) $[H_3O^+] = \sqrt{K_aC}$

$\text{pH} = -\log[H_3O^+] = -\log\sqrt{K_aC} = -\log\sqrt{1.8 \times 10^{-4} \times 0.01} = 2.87$

Thus pH of the solution before titration was 2.87.

(b) Number of moles of HCOOH = $\frac{100}{1000} \times 0.01\text{moles} = 0.001\text{moles}$

Number of moles of NaOH = $\frac{15}{1000} \times 0.1\text{moles} = 0.0015\text{moles}$

Thus number of moles of unreacted NaOH $= (0.0015 - 0.001)$ moles $= 0.0005\text{moles}$

Total volume of solution = $(100 + 15)\text{cm}^3 = 115\text{cm}^3$

Thus [NaOH] after the reaction = $\frac{0.0005\text{mol}}{115\times10^{-3}\text{dm}^3} = 4.35 \times 10^{-3}\text{M}$

NaOH being strong base ionises according to the following equation:

$$\underset{4.35\times10^{-3}\text{M}}{NaOH} \rightarrow Na^+ + \underset{4.35\times10^{-3}\text{M}}{OH^-}$$

It follows that pOH $= -\log[OH^-] = -\log(4.35 \times 10^{-3}) = 2.36$

But pH = 14 − pOH; thus pH = 14 − 2.36 = 11.64

Hence pH of the solution after addition of 15cm^3 of NaOH was 11.64.

(c) Number of moles of NaOH $= \frac{10}{1000} \times 0.1\text{moles} = 0.001\text{moles}$

That is number of moles of NaOH = number of moles HCOOH which satisfy the required mole ratio and hence neither of the reactant is in excess.

But HCOONa produced in the reaction undergoes anionic hydrolysis to give solution whose pH is given by the following equation: $\text{pH} = -\log\sqrt{\frac{K_aK_w}{[\text{salt}]}}$

But $[\text{salt}] = [\text{HCOONa}] = \frac{0.001\text{moles}}{(100+10)\times10^{-3}\text{dm}^3} = 9.09 \times 10^{-3}\text{M}$

Therefore $\text{pH} = -\log\sqrt{\frac{1.8\times10^{-4}\times10^{-14}}{9.09\times10^{-3}}} = 7.85$

Hence pH of the solution after addition of $10\text{cm}^3$of NaOH was 7.85.

(d) Number of moles of HCOOH = $\frac{100}{1000} \times 0.01\text{moles} = 0.001\text{moles}$

Number of moles of NaOH = $\frac{5}{1000} \times 0.1\text{moles} = 0.0005\text{moles}$

Thus number of moles of unreacted HCOOH $= (0.001 - 0.0005)$ moles $= 0.0005$moles

Total volume of solution = $(100 + 5)\text{cm}^3 = 105\text{cm}^3$

Thus [HCOOH] after the reaction = $\frac{0.0005\text{mol}}{105\times10^{-3}\text{dm}^3} = 4.7619 \times 10^{-3}\text{M}$

But from the mole ratio and using the fact that NaOH is limited reactant;

Number of moles of HCOONa formed after the reaction= Number of moles of NaOH reacted

Thus number of moles of HCOONa produced was 0.0005moles

And [HCOONa] = $\frac{0.0005\text{mol}}{105\times10^{-3}\text{dm}^3} = 4.7619 \times 10^{-3}\text{M}$

The unreacted HCOOH and the produced HCOONa forms acidic buffer solution whose pH is given by the following equation:

$$\text{pH} = \text{pK}_\text{a} + \log\frac{[\text{HCOONa}]}{[\text{HCOOH}]}$$

Substituting $\text{pH} = -\log(1.8 \times 10^{-4}) + \log\frac{4.7619\times10^{-3}\text{M}}{4.7619\times10^{-3}\text{M}} = 3.74$

Hence pH of the solution after addition of $5\text{cm}^3$of NaOH was 3.74

DIGGING DEEPER EXERCISE 18

EXERCISE 18A: BINDER QUESTIONS

Question 1

Explain whether the following solutions will be acidic, basic or neutral at the equivalence point by indicating the major species that regulates the pH for each solution:

(i) A strong acid titrated with a strong base
(ii) A weak acid titrated with a strong base
(iii) A weak base titrated with a strong acid

Question 2

Predict if the following salts in water would be neutral, acidic, or basic:

a) KF b) $NaNO_3$ c) $NaClO_4$ d) NH_4Cl e) $FeCl_3$ f) Na_2CO_3

Question 3

Arrange the following solutions ascending order of their pH. Rationalise your arrangement.

$$0.01 MNaBr, 0.01 MKCN, 0.01 MNH_4Br$$

Question 4

Among the following, which compound has highest pH? Give a reason.

$$0.1MCH_3COONH_4, 0.1MNa_2CO_3, 0.1MNH_4Cl, 0.1MNaNO_3$$

Question 5

The hypothetical inorganic salt **CD** is made from strong base and weak acid. With reason and help of chemical equation, state whether an aqueous solution of CD is acidic, basic or neutral.

EXERCISE 18B: REAL QUESTIONS

Question 6

Although $AlCl_3$ is highly covalent in characters, its aqueous solution conducts electricity. Explain.

Question 7

Explain what happens when baking soda is introduced into an aqueous solution of NH_4Br?

Question 8

Explain what will you observed when a litmus paper is dipped into a solution of potassium cyanide.

Question 9

When sodium methanoate solution is added to the onion juice, the onion loses its smell; why?

Question 10

Kipute introduced magnesium into a solution ammonium sulphate. Immediately after that, she brought a burning candle near the solution and then the sound of small explosion was heard. Explain.

EXERCISE 18C: HOT QUESTIONS

Question 11

What is the pH of a 0.0500 M solution of ammonium chloride, NH_4Cl. $K_a = 5.65 \times 10^{-10}$ for NH_4^+

Question 12

What is the pH of a 0.100 M solution of methyl ammonium chloride (CH_3NH_3Cl). K_a of the methyl ammonium ion ($CH_3NH_3^+$) = 2.7×10^{-11}

Question 13

Calculate the pH of a 0.15 M solution of sodium acetate CH_3COONa. ($K_a = 1.8 \times 10^{-5}$)

Question 14

Given the pK_a for ammonium ion is 9.26, what is the pH of 1.00 L of solution which contains 5.45 g of NH_4Cl?

Question 15

Calculate the pH of a solution after 25.0mL of 0.1M hydrofluoric acid is titrated with 12.5mL of 0.200M lithium hydroxide. ($K_a = 6.8 \times 10^{-4}$ for hydrofluoric acid)

Question 16

When ammonium salts are dissolved in water, the following reaction occurs.

$$NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+$$

(a) Identify the acid/base conjugate pairs in this reaction by writing appropriate symbols under each of the species in the equation above.
(b) Write an expression for the dissociation constant, K_a, for NH_4^+(aq).
(c) Calculate the pH of a solution of ammonium chloride of concentration 0.100M at 298 K, the K_a value for NH_4^+ being 5.62×10^{-10}M at this temperature.
(d) How would you modify the solution of ammonium chloride in (c) to make it more resistant to changes in pH when small amounts of acid or base are added to it?

Chapter 19

SOLUBILITY AND SOLUBILITY PRODUCT

INTRODUCTION

In everyday life we are coming across to insoluble substances; from silver iodide, a solid that is recognised by its antiseptic properties, calcium carbonate, the active ingredient in many over-the-counter chewable antacids, magnesium hydroxide, the active ingredient in milk of magnesia to hydroxyapatite ($Ca_5(PO_4)_3OH$), the mineral which is a source of phosphate for fertilizers. These substances are not actually hundred percent insoluble in water (Remember, everything dissolve in the universal solvent called water, even if to very small extent which cannot be recognised by eyes!), they dissolve by very small amount; they are actually **sparingly soluble substances**. Because they dissolve only slightly to give free ions, they are weak electrolytes and thus they are also known as **sparingly soluble electrolytes.**

So **sparingly soluble electrolytes** *are substances (compounds) which dissolve only slightly in aqueous solution to give free ions.* They are approximately insoluble substances in a sense that very small portion of them go in solution as ions. Other examples of sparingly soluble substance are $AgCl$, $BaSO_4$ and $Al(OH)_3$.

When the sparingly soluble substance dissolves in a solvent, usually water, the dissociated ions are present in the solvent phase in the same proportions as they are found in the solid phase. In other words, the stoichiometry of the dissociation is preserved just like it is in any chemical reaction.

Consider A_nB_m to be sparingly soluble electrolyte which dissolves according to the following equation:
$A_nB_m(s) \rightleftharpoons nA^{m+}(aq) + mB^{n-}(aq)$

From which $K_c = \frac{[A^{m+}]^n [B^{n-}]^m}{[A_nB_m]}$ or $K_c [A_nB_m] = [A^{m+}]^n [B^{n-}]^m$

A_nB_m being solid and sparingly soluble, its concentration is invariable;

i.e. $[A_nB_m] = \text{constant}$

Thus $K_c [A_nB_m]$ gives another constant, which is known as **solubility product, K_{sp}**

Hence $\mathbf{K_{sp} = [A^{m+}]^n [B^{n-}]^m}$

Definitions of solubility and solubility product

Solubility

Generally, **solubility** *is the ability of a certain solute to be dissolved in a given solvent which is given as the amount of the substance dissolved in one litre of saturated solution at given temperature.*

- It can be expressed in g/L as **mass solubility** or mol/L as **molar solubility**.

Among the two methods, the former (g/L) is more common and when we speak about 'solubility' we always refer to the one expressed in g/L (in contrary to concentration which is commonly given in mol/L).

- **Molar solubility** *is the number of moles of a solute in one litre of a saturated solution*
- **Mass solubility** (commonly termed as simply, **solubility**) *is the number of grams of a solute in one litre of a saturated solution.*

Solubility product, K_{sp}

Solubility product *is an equilibrium constant which is given as the product of concentration of ions in a saturated solution of sparingly soluble electrolyte, each raised to the power of their stoichiometric coefficients in the balanced chemical equation.*

- If A_nB_m is the sparingly soluble substance its solubility product, K_{sp}, is given by $[A^{m+}]^n [B^{n-}]^m$ and its unit is $(moldm^{-3})^{n+m}$

- Like any other equilibrium constant, the value solubility product does not depend on concentration of ions present in solution, it is only temperature dependent.
- Solubility product is useful in comparing molar solubility of sparingly soluble substances with **the same number of ions per formula unit** like AgCl and ZnS or $Fe(OH)_2$ and $PbCl_2$ such that the greater the value the greater molar solubility of the salt. However solubility product cannot be used to compare molar solubility of two compounds with different formulas like ZnS and $Fe(OH)_2$ or AgCl and $PbCl_2$ which have different number of ions per formula unit. In this case it is necessary to calculate the solubility of each compound to know which compound is more soluble.

UNDERSTANDING SOLUBILITY AND SOLUBILITY PRODUCT

To build concrete foundation for understanding solubility and solubility product, it is important to have deeper understanding of the two terms. We are going to start with solubility.

Solubility

Imagine adding a small amount of table salt to a glass of water, stirring until all the salt has dissolved, and then adding a bit more. You can repeat this process until the salt amount that has been dissolved in the solution reaches its natural limit. You can be certain that you have reached this limit because, no matter how long you stir the solution, undissolved salt remains. The amount of salt that has been dissolved in the solution at this point is known as its solubility.

The solubility of a solute in a particular solvent is the maximum amount of solute that can be dissolved under given conditions when the dissolution process is at equilibrium.

When the solute amount in the solution is equal to its solubility, the solution is said to be **saturated** with that solute. If the solute amount is less than its solubility, the solution is said to be **unsaturated**.

Solutions may be prepared in which the solute amount exceeds its solubility. Such solutions are said to be **supersaturated**, and they are good examples of non-equilibrium states. For example, immediately after opening the container of the carbonated beverage, the beverage is supersaturated with carbon dioxide gas and if the container is left open, the carbon dioxide amount will decrease until it reaches its solubility (equilibrium).

Solubility product

When sparingly soluble electrolyte, say $Ca_3(PO_4)_2$ is dissolved in the solution, two processes occur:

First process: The electrolyte undergoes **dissolution** according to the following equation:

$$Ca_3(PO_4)_2(s) \longrightarrow 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Second process: The produced ions undergoes **precipitation** according to the following equation:

$$3Ca^{2+}(aq) + 2PO_4^{3-}(aq) \longrightarrow Ca_3(PO_4)_2(s)$$

Thus the two processes may be combined to get the following reversible process which represents the action of dissolving the given electrolyte in the aqueous solution.

$$Ca_3(PO_4)_2(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

The equilibrium of the above reversible process is achieved when *the rate of dissolution is equal to the rate of precipitation* and the equilibrium constant obtained under this constant is what we call solubility product. Now, why and how 'solubility' enters to the term of our equilibrium constant resulting to 'solubility product'? Is it solubility product the product (result of multiplication) of 'solubilities' as the name suggests? To answer these crucial questions, we are going to consider the following scenario:

Imagine certain mass of our electrolyte $Ca_3(PO_4)_2$ is added to **1L** of water. And assume that the mass is equivalent to **'a' moles** (after dividing the mass by molar mass of the electrolyte). Also assume that amount of the electrolyte has negligible volume such that the volume of solution remains to be **1L.**

Now, let **x** represents the amount of the electrolyte that dissolves into solution after any time, t. The dissolution process will continue and hence **x** will increase until the equilibrium is reached where the limit of the solvent to dissolve more solute has been reached and we can call this limit amount, **'s'** which by definition is actually the solubility of the electrolyte. This explanation can be summarised in the chemical equation as follows:

	$Ca_3(PO_4)_2(s) \rightleftharpoons$	$3Ca^{2+}(aq)$	$+ 2PO_4^{3-}(aq)$
Initially (at $t = 0$)	a	0	0
After any time, t (solution is still unsaturated)	$a - x$	3x	2x
At equilibrium (when solution is saturated, x becomes s)	$a - s$	3s	2s

Now, from the definition of solubility product, the constant is directly related to concentration of ions.
That is; $K_{sp} = [Ca^{2+}]^3\,[PO_4^{3-}]^2$
But $[Ca^{2+}] = 3s$ and $[PO_4^{3-}] = 2s$
Thus the K_{sp} can alternatively be written in terms of solubility (s) as follows:

$$K_{sp} = (3s)^3(2s)^2 = 108s^5$$

After that discussion, now you can understand the following conclusions which are very crucial in mastering solubility and solubility product:

- Solubility product is the multiple of **molar** solubility raised to certain powers.
- Solubility which is found directly from K_{sp} is the molar solubility, to convert it to mass solubility (which is the common method of representing solubility unless stated otherwise), it must be multiplied by molar mass of the electrolyte.
- Number of moles of undissolved electrolyte (precipitate) in a litre of the solution $= a - s$; it can be converted to the mass of precipitate in the litre of the solution by multiplying it by molar mass of the electrolyte. Another sub-conclusion which goes together with this is that, if $a > s$; the solution is **supersaturated** and there is a **formation of precipitate**.
- The limit of **forming or not forming the precipitate** is found when $a = s$ and the solution is **saturated** at this point.
- If $a < s$; the solubility equilibrium will not be achieved and the solution is **unsaturated** (**no formation of precipitate** at all).

Worked examples

Example 1

Given the following solubility in gdm^{-3} at 25^oC, obtain the corresponding K_{sp};

(i) $Al(OH)_3\ (1.35 \times 10^{-4})$
(ii) $CaF_2\ (1.47 \times 10^{-2})$

Solution

(i) Molar solubility of $Al(OH)_3 = \frac{1.35 \times 10^{-4}}{78}$ $moldm^{-3}$

$= 1.73 \times 10^{-6}$ $moldm^3$

Let molar solubility of $Al(OH)_3$ be s

Then $Al(OH)_3(s) \rightleftharpoons Al^{3+}(aq) + 3OH^-(aq)$

s 3s

And $K_{sp} = [Al^{3+}][OH^-]^3 = s\,(3s)^3 = 27s^4$

But $s = 1.73 \times 10^{-6}$ $moldm^{-3}$

Whence $K_{sp} = 27 \times (1.73 \times 10^{-6}\ moldm^{-3})^4$

$= 2.42 \times 10^{-22}\ mol^4\ dm^{-12}$

Hence the solubility product of $Al(OH)_3$ at 25^oC is $2.42 \times 10^{-22}\ mol^4\ dm^{-12}$

(ii) Molar solubility of $CaF_2 = \frac{1.47 \times 10^{-2}}{78}$ $moldm^{-3} = 1.88 \times 10^{-4}$ $moldm^{-3}$

Let molar solubility of CaF_2 be s

Then $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

s 2s

$K_{sp} = [Ca^{2+}][F^-]^2 = s(2s)^2 = 4s^3$

But $s = 1.88 \times 10^{-4}$ moldm^{-3}

Whence $K_{sp} = 4 \times (1.88 \times 10^{-4} \text{moldm}^{-3})^3 = 2.66 \times 10^{-11} \text{ mol}^3\text{dm}^{-9}$

Hence the solubility product of CaF_2 is $2.66 \times 10^{-11} \text{ mol}^3\text{dm}^{-9}$

Example 2

A 100cm^3 sample is removed from a water solution saturated in MgF_2 at 18^{o}C. The water is completely evaporated from sample and 7.6mg deposit of MgF_2(s) is obtained. What is the K_{sp} for MgF_2 at 18^{o}C?

Solution

The amount of deposit after evaporation, is the amount of MgF_2 originally dissolved in the solution

Thus mass solubility of MgF_2= $\frac{7.6\times10^{-3}}{0.1} = 7.6 \times 10^{-2}\text{gdm}^{-3}$

Then molar solubility of MgF_2= $\frac{7.6\times10^{-2}}{62} = 1.2258 \times 10^{-3}\text{M}$

MgF_2 dissolves in solution according to the following equation:

$$MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$$

s 2s

$K_{sp} = s \times (2s)^2 = 4s^3 = 4 \times (1.2258 \times 10^{-3})^3 = 7.37 \times 10^{-9}\text{M}^3$

Hence solubility product of magnesium fluoride is $7.37 \times 10^{-9}\text{M}^3$

Example 3

If hydroxyapatite is allowed to reach equilibrium in water, what is the concentration of calcium ion in the solution?

Given that: $K_{sp}(\text{hydroxyapatite}) = 2.34 \times 10^{-59}$

Ionic composition of hydroxyapatite = $Ca_5(PO_4)_3OH$

Solution

Let the solubility of hydroxyapatite be x in moldm^{-3}

$Ca_5(PO_4)_3OH\ (s) \rightleftharpoons 5\,Ca^{2+}(aQ) + 3PO_4^{3-}(aq) + OH^-(aq)$

5s 3s s

$K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[OH^-]$

Then $2.34 \times 10^{-59} = (5s)^5\,(3s)^3(s) = 84375s^9$

Or $s = \sqrt[9]{\frac{2.34 \times 10^{-59}}{84375}} = 8.67 \times 10^{-8}\text{M}$

But $[Ca^{2+}] = 5s = 5 \times 8.67 \times 10^{-8}\text{M} = 4.3 \times 10^{-7}\text{M}$

Hence concentration of calcium ions was $4.3 \times 10^{-7}\text{M}$

Example 4

What is the greatest mass of CaF_2 can be mixed with water to make a 5L solution without forming a precipitate? $K_{sp}(CaF_2) = 4 \times 10^{-11}\ mol^3dm^{-9}$

Solution

Let the solubility of CaF_2 in H_2O be s in $moldm^{-3}$

$$CaF_2(s) \rightleftharpoons \underset{s}{Ca^{2+}(aq)} + \underset{2s}{2\,F^-(aq)}$$

$K_{sp} = [Ca^{2+}]\,[F^-]^2$

Substituting $4 \times 10^{-11} = (s)\,(2s)^2 = 4s^3$

Or $\quad s = \sqrt[3]{\dfrac{4 \times 10^{-11}}{3}} = 2.3713 \times 10^{-4}\ moldm^{-3}$

Thus the solubility of CaF_2 in water is $2.3713 \times 10^{-4} moldm^{-3} \times 78g/mol = 0.018g/L$

So maximum mass of CaF_2 which can be dissolved in 1L of solution without forming precipitate is 0.018g.

In 5L of the solution, the mass will be $0.018g/L \times 5L = 0.09g$

Hence the mass is 0.09g

Example 5

What is the least mass of MgF_2 is required to form the precipitate when it is mixed with water to make a 2L solution? $K_{sp}(MgF_2) = 7.37 \times 10^{-9}\ mol^3dm^{-9}$

Solution

Let the solubility of MgF_2 in H_2O be s in $moldm^{-3}$

$$CaF_2(s) \rightleftharpoons \underset{s}{Ca^{2+}(aq)} + \underset{2s}{2\,F^-(aq)}$$

$K_{sp} = [Mg^{2+}]\,[F^-]^2$

Substituting $7.37 \times 10^{-9} = (s)\,(2s)^2 = 4s^3$

Or $\quad s = \sqrt[3]{\dfrac{7.37 \times 10^{-9}}{3}} = 1.3493 \times 10^{-3}\ moldm^{-3}$

Thus the solubility of CaF_2 in water is $1.3493 \times 10^{-3} moldm^{-3} \times 62g/mol = 0.084g/L$

So least mass of CaF_2 which can be dissolved in 1L of solution with just about starting to form precipitate is 0.084g.

In 2L of the solution, the mass will be $0.084g/L \times 2L = 0.168g$

Hence the mass is 0.168g

Example 6

The solubility product, K_{sp} of $CaSO_4 = 4 \times 10^{-4} mol^2dm^{-6}$. If 5g of calcium sulphate is mixed with water to make $500cm^3$ solution, calculate the mass of the precipitate in the solution.

Solution

Let the solubility of $CaSO_4$ in H_2O be s in $moldm^{-3}$

Then $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

$\qquad\qquad\qquad s \qquad\qquad s$

It follows that: $\quad K_{sp} = [Ca^{2+}][SO_4^{2-}]$

Substituting $4 \times 10^{-4} = s^2$ or $s = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2} moldm^{-3}$

Solubility in gdm^{-3} = solubility in $moldm^{-3}$ $\times$ molar mass

$$= 2 \times 10^{-2} \times 136\text{gdm}^{-3} = 2.72\text{gdm}^{-3}$$

Thus the saturated solution of $CaSO_4$ contains 2.72g of the sulphate in dm^3.

So maximum mass of $CaSO_4$ which can be dissolved in $500\text{cm}^3 = \frac{500}{1000}\text{dm}^3 \times 2.72\text{gdm}^{-3} = 1.36\text{g}$

But the given mass of 5g is greater than the limit mass of 1.36g.

Hence there is a formation of the precipitate whose mass is $(5 - 1.36)\text{g} = 3.64\text{g}$

Example 7

An aqueous solution of Na_2S is gradually added to a solution containing Ca^{2+}, Cu^{2+} and Ag^+each at concentration of 10^{-3}M. Determine $[S^{2-}]$ at which precipitation of each cations occurs.

Given that:

K_{sp} of CaS = $1 \times 10^{-28}\ \text{mol}^2\text{dm}^{-6}$

K_{sp} of CuS = $1 \times 10^{-36}\ \text{mol}^2\text{dm}^{-6}$

K_{sp} of Ag_2S = $1 \times 10^{-50}\ \text{mol}^3\text{dm}^{-9}$

Hence give the order of precipitation of given compounds.

Solution

(i) $CaS(s) \rightleftharpoons Ca^{2+}(aq) + S^{2-}(aq);\ K_{sp} = [Ca^{2+}][S^{2-}]$

From which $[S^{2-}]\ \frac{K_{sp}}{[Ca^{2+}]} = \frac{1 \times 10^{28}}{10^{-3}}\text{M} = 10^{-25}\text{M}$

(ii) $CuS(s) \rightleftharpoons Cu^{2+}(aq) + S^{2-}(aq);\ K_{sp} = [Cu^{2+}][S^{2-}]$

From which $[S^{2-}] = \frac{K_{sp}}{[Cu^{2+}]} = \frac{1 \times 10^{-36}}{10^{-3}}\text{M} = 10^{-33}\text{M}$

(iii) $Ag_2S(s) \rightleftharpoons 2Ag^+(aq) + S^{2-}(aq);\ K_{sp} = [Ag^+]^2[S^{2-}]$

From which $[S^{2-}] = \frac{K_{sp}}{[Ag^+]^2} = \frac{1 \times 10^{-50}}{(10^{-3})^2}\text{M} = 10^{-44}\text{M}$

The salt with least amount of $[S^{2-}]$ precipitates first and hence Ag_2S will precipitate first, followed by CuS and finally CaS will precipitate.

Differences between solubility and solubility product

Differences between solubility and solubility product are summarised in the table below.

Table 19.1 Differences between solubility and solubility product

	SOLUBILITY		SOLUBILITY PRODUCT
01	Definition	01	Definition
02	It is depressed by common ion effect	02	It does not be affected by concentration of ions present in the solution including common ion effect
03	It can be applied for both highly soluble and sparingly soluble substances	03	It is applied for sparingly soluble substance only. Its use is not common for highly soluble substance.
04	It is measured as the amount of solute dissolved in a litre of saturated solution.	04	It is deduced from measured solubility as the product of solubility (molar solubility) raised to the power of their stoichiometric coefficients
05	It is commonly given in g/L	06	It is always given in mol/L raised to certain powers

COMMON ION EFFECT IN SOLUBILITY

When strong electrolyte is introduced into saturated solution of sparingly soluble substance which contains the same (common) ion as that present in the strong electrolyte, the solubility of the sparingly soluble substance is depressed and the precipitate is formed.

For deeper understanding of the concept, consider solution of hydrochloric acid is introduced into a beaker containing saturated solution of silver chloride:

- Silver chloride (AgCl) being sparingly soluble, dissolves slightly in aqueous solution according to the following equation:
- $AgCl(s) \rightleftharpoons Ag^{+}(aq) + Cl^{-}(aq)$……………………….(i)
- Hydrochloric acid being strong electrolyte, dissolves completely in the solution according to the following equation: $HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$….(ii)
- Introduction of $Cl^{-}(aq)$ from HCl(aq) increases concentration of $Cl^{-}(aq)$ in (i) above; so according to Le Chatelier's principle the position of equilibrium will shift to the left by forming AgCl which appears as precipitate and hence the solubility of the silver chloride (sparingly soluble substance) is lowered.

It should be noted that:

The depression of solubility of sparingly soluble substance (as result of common ion effect) is a hundred percent correct if and only if the substance is incapable of forming complex with the common ion, how?

When the metallic cation of sparingly soluble substance is capable of forming complex ion which is always soluble in aqueous solution, the precipitate will be formed on small addition of the strong electrolyte only. When the electrolyte is added until in excess, the complex is formed and the precipitate appears to dissolve.
For example:
When small amount of sodium hydroxide which is strong electrolyte is added to a solution of lead(II) hydroxide ($Pb(OH)_2$) which is sparingly soluble electrolyte, the following happen:
Initially, the precipitate is formed due to common ion effect and when the sodium hydroxide in large amount (until in excess) the precipitate dissolves to give clear solution due to formation of complex ion, $[Pb(OH)_4]^{2-}$ which is soluble.

$$Pb(OH)_2 + 2OH^{-} \rightarrow [Pb(OH)_4]^{2-}$$

From NaOH	**Soluble**

Lead (II) chloride which is sparingly soluble electrolyte; is insoluble in dilute hydrochloric acid (when the strong electrolyte, HCl(aq) present in small amount) due to common ion effect. However the chloride of lead is soluble in concentrated hydrochloric acid (when the strong electrolyte present in large amount) due to formation of complex ion, $[PbCl_4]^{2-}$ which is soluble.

Worked examples

Example 8

The solubility product, K_{sp} of $CaSO_4 = 4 \times 10^{-4} mol^2 dm^{-6}$, calculate the solubility at the same temperature:

(i) In H_2O
(ii) In $0.10MNa_2SO_4$

Solution

(i) Let the solubility of $CaSO_4$ in H_2O be s in $moldm^{-3}$

Then $CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$

$$\qquad\qquad\quad s \qquad\qquad s$$

It follows that: $K_{sp} = [Ca^{2+}][SO_4^{2-}]$

Substituting $4 \times 10^{-4} = s^2$ or $s = \sqrt{4 \times 10^{-4}} = 2 \times 10^{-2} moldm^{-3}$

Solubility in gdm^{-3} = solubility in $moldm^{-3}$ × molar mass

$$= 2 \times 10^{-2} \times 136gdm^{-3} = 2.72gdm^{-3}$$

Hence the solubility of $CaSO_4$ in H_2O is $2.72gdm^{-3}$

(ii) Na_2SO_4 being strong electrolyte ionises completely according to the following equation:

$$\underset{0.1M}{Na_2SO_4} \rightarrow 2Na^+ + \underset{0.1M}{SO_4^{2-}}$$

So addition of Na_2SO_4 increases $[SO_4^{2-}]$, thus decreasing solubility of $CaSO_4$ by common ion effect

Let the new solubility of $CaSO_4$ be y
Then $[Ca^{2+}] = y$, $[SO_4^{2-}] = y + 0.1$

But since y comes from sparingly soluble electrolyte, its value (after common effect) can be neglected compared to 0.1 which comes from the strong electrolyte; i.e. y + 0.1 ≈ 0.1

- And since K_{sp} does not depend on concentration of ions present in the solution, it follows that:

$4 \times 10^{-4} = 0.1y$ or $y = 4 \times 10^{-3} moldm^{-3}$

Thus the solubility = $4 \times 10^{-3} \times 136gdm^{-3} = 0.544gdm^{-3}$

Hence the solubility of $CaSO_4$ in $0.1MNa_2SO_4$ is $0.544gdm^{-3}$

Interesting fact you have to understand!

A mother of solubility product and any other concept in ionic equilibria is the chemical equilibrium we studied in **chapter 4**. So whenever you feel any sort of doubt in your consideration about problems related to ionic equilibria including solubility product, return to our mother, chemical equilibrium and then make new consideration or solve the problem from the first principle. To get clearer picture of this, we are going to re-solve the second part of this question (ii) from the first principle.

Assume we are not sure about the effect of common ion effect on calculations involving solubility product.

But we know that at initial equilibrium (saturated solution **before** involving sodium sulphate); $[Ca^{2+}] = [SO_4^{2-}] = 2 \times 10^{-2} moldm^{-3} = \text{Solubility}, s$

The addition of sodium sulphate, will increase $[SO_4^{2-}]$ and the new $[SO_4^{2-}]$ will be $(2 \times 10^{-2} + 0.1)M$ or 0.12M.

The increase in $[SO_4^{2-}]$ will shift equilibrium position to the undissolved $CaSO_4$ side.

	$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) +$	$SO_4^{2-}(aq)$
Just after the addition of $0.1MNa_2SO_4$	0.02	0.12
After re-establishment of new equilibrium	$0.02 - x$	$0.12 - x$

Where new molar solubility $= [Ca^{2+}] = 0.02 - x$ (It cannot be deduced from $[SO_4^{2-}]$ because **not** all SO_4^{2-} came from the $CaSO_4$).

Then our equilibrium constant, $K_{sp} = [Ca^{2+}][SO_4^{2-}] = (0.02 - x)(0.12 - x) = 4 \times 10^{-4}$

From which; $x^2 - 0.14x + 2 \times 10^{-3} = 0$.

Solving above quadratic equation gives practical value of $x = 0.016$

Then new molar solubility $= 0.02 - x = 0.02 - 0.016 = 4 \times 10^{-3}M$ which will be converted to mass solubility to get the same answer of $0.544gdm^{-3}$.

In this particular problem, the alternative approach may seem tedious but you will find that the ability to connect with chemical equilibrium is very crucial in solving tricky problems involving solubility product.

Example 9

Calculate the solubility of CaF_2 in $moldm^{-3}$:

(i) In water
(ii) In 0.01MNaF
(iii) In IMHF

Given that: K_a of HF $= 5.6 \times 10^{-4}\ moldm^{-3}$

K_{sp} of $CaF_2 = 4 \times 10^{-11}\ mol^3dm^{-9}$

Solution

(i) Let the solubility of CaF_2 in H_2O be s in $moldm^{-3}$

$$\underset{}{CaF_2(s)} \rightleftharpoons \underset{s}{Ca^{2+}(aq)} + \underset{2s}{2F^-(aq)}$$

$K_{sp} = [Ca^{2+}][F^-]^2$

Substituting $4 \times 10^{-11} = (s)(2s)^2 = 4s^3$

Or $\quad s = \sqrt[3]{\dfrac{4 \times 10^{-11}}{3}} = 2.37 \times 10^{-4}\ moldm^{-3}$

Hence the solubility of CaF_2 in water is $2.37 \times 10^{-4} moldm^{-3}$

(ii) Let the solubility of CaF_2 in 0.01MNaF be y

Then $[Ca^{2+}] = y$

$[F^-] = 2y + 0.01 \approx 0.01M$

And $4 \times 10^{-11} = 0.01^2 y$ or $y = 4 \times 10^{-7} moldm^{-3}$

Hence the solubility of CaF_2 in 0.01NaF is $4 \times 10^{-7} moldm^{-3}$

(iii) $[F^-]$ from HF $= \sqrt{K_a[HF]}$

$= \sqrt{5.6 \times 10^{-4} \times 1} = 0.02M$

So if Z is the solubility of CaF_2 in 1MHF;

$[F^-] = 2Z + 0.02 \approx 0.02M$, $[Ca^{2+}] = Z$

And $4 \times 10^{-11} = (0.02)^2 \times Z$ or $Z = 1 \times 10^{-7}$ moldm^{-3}

Hence the solubility of CaF_2 in 1MHF is 1×10^{-7} moldm^{-3}

Example 10

If the solubility of barium ethanedioate of room temperature is 0.09gdm^{-3} of aqueous solution, calculate the solubility product of the salt. What mass of barium ethanedioate is precipitated by adding 2.68g of sodium ethanedioate (anhydrous) to 1dm^3 of saturated solution of barium ethanedioate at that temperature?

Solution

Molar mass of barium ethanedioate $(BaC_2O_4) = 225g/mol$

Molar solubility of the salt $= \frac{0.09}{225}$ moldm^{-3} $= 4 \times 10^{-4}$ moldm^{-3}

Thus $BaC_2O_4(s) \rightleftharpoons Ba^{2+}(aq) + C_2O_4^{2-}(aq)$

$\mathbf{4 \times 10^{-4} M}$ $\quad$ $\mathbf{4 \times 10^{-4} M}$

$K_{sp} = [Ba^{2+}][C_2O_4^{2-}] = (4 \times 10^{-4}M)^2 = 1.6 \times 10^{-7}M^2$

Hence solubility product of BaC_2O_4 is 1.6×10^{-7} mol^2 dm^{-6}.

Using $n = \frac{m}{M_r}$;

Number of moles of sodium ethanedioate $Na_2C_2O_4$added $= \frac{2.68}{134}$moles $= 0.02$moles

Being strong electrolyte, $Na_2C_2O_4$ ionises according to the following equation

$$Na_2C_2O_4 \rightarrow 2\,Na^+(aq) + C_2\,O_4^{2-}(aq)$$

2×0.02moles $\quad$ 0.02moles

$= 0.04$ moles

Let molar solubility of BaC_2O_4 after introduction of introduction of the strong electrolyte be x

Then $[Ba^{2+}] = x$, $[C_2\,O_4^{2-}] = x + 0.02 \approx 0.02$

It follows that; $1.6 \times 10^{-7} = 0.02x$ or $x = 8 \times 10^{-6}$

Then solubility of BaC_2O_4 in gdm^{-3} after introduction of $Na_2C_2O_4$

$$= 8 \times 10^{-6} \times 225\text{gdm}^{-3} = 1.8 \times 10^{-3}\ \text{gdm}^{-3}$$

Thus the solubility of BaC_2O_4 reduced from 9×10^{-2}gdm^{-3} to 1.8×10^{-3}gdm^{-3} after introducing $Na_2C_2O_4$ to the solution. The difference is the mass of BaC_2O_4 precipitated due to the common ion effect.

Hence mass BaC_2O_4 precipitated in 1dm^3 $= (9 \times 10^{-2} - 1.8 \times 10^{-3})$ or 8.82×10^{-2}g

IONIC PRODUCT OF SPARINGLY SOLUBLE SUBSTANCES

This *is the product of concentration of ions of sparingly soluble electrolyte, each raised to the power of their stoichiometric coefficients in the balanced equation at any concentration of the solution.*

Thus unlike solubility product, ionic product is applied in the solution which is not necessary to be saturated.
i.e. If A_nB_m is sparingly soluble substance which dissolves in a solution according to the following equation: $A_nB_m(s) \rightleftharpoons nA^{m+}(aq) + mB^{n-}(aq)$

$$Q_{sp} = [A^{m-}]_o^n [B^{n+}]_o^m$$

Where Q_{sp} the ionic product and subscripts in the molar concentration symbols insist that the concentration of ions (original concentration) not necessary to be that of saturated solution at equilibrium

Ionic product is useful in determining whether the solution of sparingly soluble substance is saturated or not by comparing its value to the solubility product (It is like comparison of reaction quotient, Q_c to equilibrium constant, K_c to determine whether the system is at equilibrium or not).

- If $\mathbf{Q_{sp} < K_{sp}}$, the solution is **unsaturated** and no precipitate is formed.
- If $\mathbf{Q_{sp} = K_{sp}}$, the solution is **saturated** and it is the margin of forming and not forming the precipitate i.e. if $Q_{sp} = K_{sp}$, the concentration of ions can be said as either minimum concentration for precipitate to be formed or maximum concentration of ions without forming the precipitate.
- It $\mathbf{Q_{sp} > K_{sp}}$, the solution is **supersaturated** and the precipitate is formed.

By definition:
Saturated solution *is the solution which cannot dissolve more solute without forming a precipitate at given temperature.*
Supersaturated solution *is the solution with more solute beyond its **saturated point**.* Where, **saturated point** *is the point at which a liquid cannot take up more of the solute at given temperature.*

Differences between ionic product and solubility product

Differences between ionic product and solubility product are summarised in the table below.

Table 19.2 Differences between ionic product and solubility product

	IONIC PRODUCT, Q_{sp}		**SOLUBILITY PRODUCT, K_{sp}**
01	Definition	01	Definition
02	Its value keeps changing with concentration	02	At constant temperature, its value is constant for a given electrolyte
03	It is applicable for solution at any concentration (saturated, unsaturated and supersaturated solution)	03	It is applicable for saturated solution only

Worked examples

Example 11

Will a precipitate form when $100cm^3$ of 8×10^{-3}M $Pb(NO_3)_2$ is added to $400cm^3$ of 5×10^{-3}M Na_2SO_4? The solubility product, K_{sp} of $PbSO_4 = 6.3 \times 10^{-7}M^2$.

Solution

$Pb(NO_3)_2$ which is highly soluble salt (strong electrolyte) ionises completely according to the following equation:

$$Pb(NO_3)_2(aq) \longrightarrow Pb^{2+}(aq) + 2NO_3^-(aq)$$

From which;

Number of moles of $Pb(NO_3)_2$ =Number of moles of $Pb^{2+} = \frac{100}{1000} \times 8 \times 10^{-3} = 8 \times 10^{-4}$mol

And thus $[Pb^{2+}]$ in the mixture $= \frac{8\times10^{-4}\text{mol}}{0.5\text{L}} = 1.6 \times 10^{-3}\text{M}$ $\quad (V_{soln} = (100 + 400)\text{cm}^3 = 0.5\text{L})$

Na_2SO_4 which is also strong electrolyte ionises according to the following equation:

$$Na_2SO_4(aq) \longrightarrow 2Na^+(aq) + SO_4^{2-}(aq)$$

Number of moles of Na_2SO_4 = Number of moles of $SO_4^{2-} = \frac{400}{1000} \times 5 \times 10^{-3} = 2 \times 10^{-3}$mol

And thus $[SO_4^{2-}]$ in the mixture $= \frac{2\times10^{-3}\text{mol}}{0.5\text{L}} = 4 \times 10^{-3}\text{M}$

Then $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

From which; $\quad Q_{sp} = [Pb^{2+}]_o[SO_4^{2-}]_o$

Substituting $Q_{sp} = (1.6 \times 10^{-3}\text{M}) \times (4 \times 10^{-3}\text{M}) = 6.4 \times 10^{-6}\text{M}^2 > K_{sp}$

Since $Q_{sp} > K_{sp}$; the precipitate will form.

Question 12

The solubility product of calcium sulphate is 6×10^{-5} mol^{2}dm^{-6} at room temperature. What mass of calcium sulphate would you expect to be precipitated if 125cm^3 of 1M sulphuric acid and 125cm^3 of 1M calcium chloride solution are mixed at room temperature? Assume simple summation of volumes and neglect any possible effect from the hydrochloric acid formed.

Solution

Before mixing

Number of moles of $H_2SO_4 = \frac{125}{1000} \times 1\text{mol} = 0.125\text{mol}$

Number of moles of $CaCl_2 = \frac{125}{1000} \times 1\text{mol} = 0.125\text{mol}$

In the solution mixture:

Total volume of solution = $(125 + 125)\text{cm}^3 = 250\text{cm}^3 = 0.25\text{L}$

H_2SO_4 being strong electrolyte ionises completely according to the following equation:

$$\begin{array}{ccccc} H_2SO_4 & \rightarrow & 2H^+ & + & SO_4^{2-} \\ 0.125\text{mol} & & & & 0.125\text{mol} \end{array}$$

Thus $[SO_4^{2-}] = \frac{0.125\text{mol}}{0.25\text{L}} = 0.5\text{M}$

$CaCl_2$ being strong electrolyte ionises completely according to the following equation:

$$\begin{array}{ccccc} CaCl_2 & \rightarrow & 2Cl^- & + & Ca^{2+} \\ 0.125\text{mol} & & & & 0.125\text{mol} \end{array}$$

Thus $[Ca^{2+}] = \frac{0.125\text{mol}}{0.25\text{L}} = 0.5\text{M}$

Checking whether precipitate will be formed or not:

$Q_{sp} = [Ca^{2+}]_o [SO_4^{2-}]_o = 0.5 \times 0.5\ M^2 = 0.25M^2$

By comparing the calculated ionic product, Q_{sp} with the given solubility product, it is clearly understood the $Q_{sp} > K_{sp}$ and hence the precipitate was formed.

Calculating the mass of the precipitate:

If s is the molar solubility of $CaSO_4$;

$K_{sp} = s^2$ or $s = \sqrt{K_{sp}} = \sqrt{6 \times 10^{-5}} = 7.746 \times 10^{-3}$ moldm^{-3}

Thus concentration of Ca^{2+} and SO_4^{2-} which appears uncombined in the solution was 7.746×10^{-3}M of each and the remaining amount which is $(0.5 - 0.007746)$ or 0.492254mol combines to form the precipitate of $CaSO_4$ in dm^3 according to the following equation:

$$Ca^{2+}(aq) + SO_4^{2-}(aq) \longrightarrow CaSO_4(s)$$

Thus 0.492254 moles of $CaSO_4$ would be formed in a litre of solution.

Therefore in 250mL; $\frac{0.492254 \times 250}{1000}$ moles $= 0.123$moles of $CaSO_4$ precipitate was formed
Using $m = nM_r$;

Mass of $CaSO_4$ formed $= 0.123 \times 136g = 16.73g$

Hence mass of $CaSO_4$ precipitate formed was 16.73g

Alternative solution

Calculating total amount of $CaSO_4$ that can be formed by the reaction between $CaCl_2$ and H_2SO_4:

$CaCl_2$ and H_2SO_4 reacts according to the following equation:

$$CaCl_2(aq) + H_2SO_4(aq) \longrightarrow CaSO_4(s) + 2HCl(g)$$

From which mole of $CaCl_2$ to H_2SO_4 is $1:1$

Since number of moles of H_2SO_4 = number of moles of $CaCl_2 = \frac{125}{1000} \times 1mol = 0.125mol$ (Given); nothing present in excess and hence number of moles of $CaSO_4$ formed was also 0.125mol.

Using $m = nM_r$;

Total mass of $CaSO_4$ formed $= 0.125 \times 136g = 17g$

Calculating the mass of precipitate

The $CaSO_4$ is sparingly soluble substance and thus it is in equilibrium with its ions according to the following equation:

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

Thus if s represents solubility of calcium sulphate; then $K_{sp} = [Ca^{2+}][SO_4^{2-}] = s^2$

From which; $s = \sqrt{K_{sp}} = \sqrt{6 \times 10^{-5}} = 7.746 \times 10^{-3}$ moldm^{-3}

Or $s = 7.746 \times 10^{-3}$ moldm$^{-3} \times 136g/mol = 1.0534g/L$

But total volume of solution $= (125 + 125)cm^3 = 250cm^3 = 0.25L$

Therefore, mass of $CaSO_4$ dissolved in 0.25L of the saturated solution is $1.0534g/L \times 0.25L = 0.26g$

Hence mass of the precipitate is $(17 - 0.26)g = 16.74g$

FACTORS AFFECTING SOLUBILITY OF SPARINGLY SOLUBLE ELECTROLYTES

Factors affecting solubility of sparingly soluble ionic compounds includes:

- Temperature
- Common ion effect (concentration)
- Complex formation
- pH of the solution

Temperature

Dissolving sparingly soluble substances in solution is endothermic process and hence (according to Le-Chatelier's principle) their solubility is found to increase with rise in temperature.

However:

- Dissolving some highly soluble substances like magnesium chloride is exothermic process; this makes their solubility to decrease as the temperature increases.
- In gases, solubility is found to decrease with an increase in temperature because at higher temperature, kinetic energy of gas molecules become higher thus making gas particles to escape from the solution.

Common ion effect

The solubility of sparingly soluble substances is found to decrease if there is common ion effect as explained earlier. If the excess common ions are added until the ionic product is greater than solubility product, the precipitate is formed. ***However, to ensure complete precipitation, the ion (if it is anion) must be only slightly excess, why?***

Reason: This is simply because in large excess of the common ion, there is complex formation which is soluble and hence the precipitate starts to dissolve.

Complex formation

If the salt can form complex ion (which are always soluble) then its solubility is found to increase in presence of large excess anions. For example; most of amphoteric hydroxide like $Al(OH)_3$ are soluble in strong alkaline solution like NaOH(aq) due to this reason of their ability of forming soluble complex.

pH of the solution

The pH affects solubility of sparingly soluble electrolyte which contains either strong acid cation (e.g. $PbSO_4$) or strong base anion (e.g. CaF_2). When the electrolyte contains cation from weak base (strong acid cation) or anion from weak acid (strong base anion), two things happen in relation to solubility.

First thing: When the electrolyte dissolved in water, its solubility becomes slightly higher than that predicted by solubility product.

To have better understanding of this, let us look at our two examples; $PbSO_4$ and CaF_2.

$$PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$$

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

In the above examples, Pb^{2+} and F^- being strong acid and strong base, they are capable of undergoing cationic hydrolysis and anionic hydrolysis respectively.

$$Pb^{2+} + 2H_2O \rightleftharpoons Pb(OH)_2 + 2H^+ \text{ (the equilibrium lies much to the left).}$$

$$F^- + H_2O \rightleftharpoons HF + OH^- \text{ (the equilibrium lies much to the left).}$$

The hydrolysis is therefore (by small extent) decreases concentration of ions (Pb^{2+} and F^-) and due to this equilibrium position shifts slightly to the ions side (in accordance with Le-Chatelier's principle) by dissolving more electrolyte.

However, the increase in solubility due to this (hydrolysis) is usually so small that we can ignore it. But when it comes to the acidic or basic solution, we cannot neglect this effect of acid-base characters of ions. Let us go to our 'second thing' to have better understanding of pH effect on solubility of sparingly soluble electrolytes.

Second thing: In acidic solution (solution with low pH), the strong base anion will react with the acid leading to significant decrease in the concentration of the anion. The same happens to strong acid cation when it is subjected to basic solution (solution with high pH).

$$F^- + H^+ \longrightarrow HF$$

$$Pb^+ + 2OH^- \longrightarrow Pb(OH)_2$$

According to Le-Chatelier's principle, the decrease in concentration of ions, shifts the equilibrium position to the ions side by dissolving more electrolyte. Consequently, *sparingly soluble electrolytes containing strong acid cation (acidic salts) are more soluble in basic solution (at high pH) whereas sparingly soluble electrolytes containing strong base anion (basic salts) are more soluble in in acidic solution (at low pH).*

You should be aware with the fact that, although HSO_4^- is anion, it behaves more as an acid and thus electrolytes containing HSO_4^- are more soluble in basic solution.

Also, **the reader should note that:** there are other factors which affect solubility of substances but not of sparingly soluble weak electrolyte. This includes:

- **Pressure** (Its effect is encountered for gases only whereby solubility of gases increases with an increase in pressure. It has no effect in solid and liquid).
- **Nature of solute and solvent** (Recall: like dissolves like).
- **Molecular weight** (Generally solubility decreases with an increase in molecular weight).

Worked examples

Example 13

Which of the following slightly soluble electrolytes will be more soluble in acidic solution than in water? For those where the solubility increases, write an equation for the net chemical reaction that occurs when a strong acid is present in solution. And for those where solubility does not increase, give a reason to support your choice.

(a) $Ni(OH)_2(s)$
(b) $CaCO_3$ (s)
(c) $BaF_2(s)$
(d) $AgCl(s)$

Solution

Only compounds whose anions are conjugate base of weak acid are basic, their solubility will be increased in the acidic solution. So the answer of each part is as follows:

(a) $Ni(OH)_2$ is more soluble in acidic solution because it contains OH^- which is strong base anion that reacts with strong acid according to the following equation:

$$Ni(OH)_2(s) + 2H^+(aq) \longrightarrow Ni^{2+}(aq) + 2H_2O(l)$$

(b) $CaCO_3$ is more soluble in acidic solution because it contains CO_3^- which is strong base anion that reacts with strong acid according to the following equation:

$$CaCO_3(s) + 2H^+(aq) \longrightarrow Ca^{2+}(aq) + CO_2(g) + H_2O(g)$$

(c) BaF_2 is more soluble in acidic solution because it contains F^- which is strong base anion that reacts with strong acid according to the following equation:

$$BaF_2(s) + 2H^+(aq) \longrightarrow Ba^{2+}(aq) + 2HF(aq)$$

(d) Solubility of AgCl in the acid will not increase because Cl^- being conjugate base of HCl which is very strong acid, it is very weak base and hence it cannot react with H^+ from the acid.

Example 14

The hypothetical ionic compound, A_2B_3 with molar mass of 200g/mol has solubility product of $4.32 \times 10^{-10}M^5$ and 9.72×10^{-4} at 20°C and 80°C respectively. If 5L of a saturated solution of A_2B_3 at 80°C is cooled to 20°C; what mass of the precipitate will be formed?

Solution

Assume s represents molar solubility of the compound.

Then

$$A_2B_3(s) \rightleftharpoons 2A^{3+}(aq) + 3B^{2-}(aq)$$

At equilibrium (when solution is saturated) $\quad 2s \quad 3s$

Then $K_{sp} = [A^{3+}]^2[B^{2-}]^3 = (2s)^2(3s)^3 = 108s^5$

From which $s = \sqrt[5]{\frac{K_{sp}}{108}}$

At 80°C; $s = \sqrt[5]{\frac{9.72\times10^{-4}}{108}} = 0.0979\text{mol/L} = 0.0979\text{mol/L} \times 200\text{g/mol} = 19.58\text{g/L}$

At 20°C; $s = \sqrt[5]{\frac{4.32\times10^{-10}}{108}} = 5.253 \times 10^{-3}\text{mol/L} = 5.253 \times 10^{-3}\text{mol/L} \times 200\text{g/mol} = 1.0506\text{g/L}$

Thus the solubility of the given compound decreases from 19.58g/L to 1.0506g/L when cooled from 80°C to 20°C. The difference is the mass of precipitate that will be formed in 1L of the solution.

Hence mass of the precipitate in 5L will be $(19.58 - 1.0506)\text{g/L} \times 5\text{L} = 92.647\text{g}$

The mass will be 92.647g.

Example 15

AgCl is a sparingly soluble electrolyte which ionises in aqueous solution according to the following equation:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq);\; K_{sp} = 1.8 \times 10^{-10}$$

The $Ag^+(aq)$ is capable of reacting with NH_3 to form complex ion according to the following equation:

$$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq);\; K = 1.7 \times 10^7$$

Use the above information to calculate an equilibrium constant for dissolution process of AgCl in ammonia solution and hence compare solubility of AgCl in the ammonia solution and the solubility in the water.

Solution

Given that:

$K_{sp} = 1.8 \times 10^{-10} = [Ag^+][Cl^-]$

And $K = 1.7 \times 10^7 = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$

Dissolution of AgCl in the ammonia solution can be represented by the following equation:

$AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$

From which; $K_c = \frac{[Ag(NH_3)_2^+][Cl^-]}{[NH_3]^2}$ ----------(i)

But from $K = \frac{[Ag(NH_3)_2^+]}{[Ag^+][NH_3]^2}$;

Or $K[Ag^+] = \frac{[Ag(NH_3)_2^+]}{[NH_3]^2}$ ------------------(ii)

Substituting (ii) in (i) gives:

$K_c = K[Ag^+][Cl^-] = K \times K_{sp} = 1.8 \times 10^{-10} \times 1.7 \times 10^7 = 3.06 \times 10^{-3}$

Hence the equilibrium constant is 3.06×10^{-3}.

Comment: The equilibrium constant of dissolution of AgCl in ammonia is much larger (17 million times) than that in water implying that solubility of AgCl in the ammonia solution is very high compared to that in water.

Example 16

The solubility product of calcium oxalate is $2 \times 10^{-9}\mathrm{M}^2$. How many times calcium oxalate is more soluble in the acidic solution with pH of 2 than in pure water?

Solution

In the pure water:

Let the solubility of CaC_2O_4 be s

$$CaC_2O_4\,(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$
$$\qquad\qquad\qquad s \qquad\qquad s$$

$K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = s^2$

$s = \sqrt{K_{sp}} = \sqrt{2 \times 10^{-9}\mathrm{M}^2} = 4.47 \times 10^{-5}\mathrm{M}$

In the acidic solution:

Using $[H^+] = \log^{-1}(-\mathrm{pH})$; the pH of 2 is equivalent to $\log^{-1}(-2)$ or 0.01M of H^+.

$C_2O_4^{2-}$ being strong base anion, combines with H^+ according to the following equation:

$$C_2O_4^{2-}(aq) + 2H^+(aq) \longrightarrow H_2C_2O_4(aq)$$

From which, mole ratio of $C_2O_4^{2-}$ to H^+ is $1:2$

Thus $[C_2O_4^{2-}]$ consumed in combining with $H^+ = \frac{[H^+]}{2} = \frac{0.01}{2}\mathrm{M} = 0.005\mathrm{M}$

The decrease in $[C_2O_4^{2-}]$ will shift the equilibrium position to free ions side and thus the solubility of CaC_2O_4 will increase from s to s′.

$$CaC_2O_4\,(s) \rightleftharpoons Ca^{2+}(aq) + C_2O_4^{2-}(aq)$$
$$\qquad\qquad\qquad s' \qquad\qquad s' - 0.005$$

Then $K_{sp} = [Ca^{2+}][C_2O_4^{2-}] = s'(s' - 0.005) = 2 \times 10^{-9}$

From which; $(s')^2 - 0.005s' - 2 \times 10^{-9} = 0$

Solving the above quadratic equation gives the practical value of $s' = 0.005$

Then $\frac{s'}{s} = \frac{0.005\mathrm{M}}{4.47\times10^{-5}\mathrm{M}} = 112$

Hence the solubility of calcium oxalate in the acidic solution is 112 times its solubility in the pure water.

APPLICATIONS OF SOLUBILITY PRODUCT

Solubility product is useful in:

1. Purification of common salt

Natural common salt consists of many insoluble and soluble impurities. Saturated solution of common salt is prepared and insoluble impurities are filtered off. Hydrogen chloride gas (HCl) is circulated through the saturated solution. HCl and NaCl dissociate into their respective ion, both giving Cl^- as anion.

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

2. Salting out of soap

Soap is a sodium salt of higher carboxylic acids with general molecular formula of $C_nH_{2n+1}COONa$. From the solution, soap is precipitated by the addition of concentrated solution of sodium chloride which ionises to give Na^+ which is also produced by the salt.

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

3. Manufacture of sodium bicarbonate (baking soda)

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

$$NH_4OH + CO_2 \rightarrow NH_4HCO_3$$

Then $NH_4HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl$,

$NaHCO_3$ is precipitated first because of its lower solubility product as compared to those of NH_4Cl, NH_4HCO_3 and NaCl.

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

4. Quantitative analysis

In quantitative analysis, solubility product is useful in estimation of:

barium as barium sulphate:

H_2SO_4 as precipitating agent is added to the aqueous solution of $BaCl_2$.

$$BaCl_2 + H_2SO_4 \rightarrow BaSO_4 + 2HCl$$

Precipitation of $BaSO_4$ takes place when its ionic product exceeds solubility product. H_2SO_4 is added in slight excess to ensure complete precipitation. Large excess of H_2SO_4 is harmful for complex formation.

silver as silver chloride:

NaCl solution is added to the silver nitrate solution, slight excess of NaCl is added to ensure complete precipitation.

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$$

Again, precipitation of AgCl takes place when ionic product of AgCl exceeds its solubility product.

In a similar manner; it is possible to estimate lead as lead chromate, calcium as calcium oxalate, etc.

Fractional precipitation

Fractional precipitation *is a technique that separates ions from solution based on their different solubility and hence different solubility products, K_{sp}.*

It is a technique of separating two or more ions from a solution by adding a reagent (common ion) that precipitates first one ion and then the second.

Let us suppose $0.1M Ba^{2+}$ and $0.1M Sr^{2+}$ in aqueous solution. K_2CrO_4 is added as **precipitating agent**. K_{sp} of $BaCrO_4$ is 1.2×10^{-10} and K_{sp} of $SrCrO_4$ is 3.5×10^{-5}:

$[CrO_4^{2-}]$ required to precipitate $BaCrO_4$

$$= \frac{K_{sp}}{[Ba^{2+}]} = \frac{1.2 \times 10^{-10}}{0.1} = \mathbf{1.2 \times 10^{-9} M}$$

$[CrO_4^{2-}]$ required to precipitate $SrCrO_4$

$$= \frac{K_{sp}}{[Sr^{2+}]} = \frac{3.5 \times 10^{-5}}{0.1} = \mathbf{3.5 \times 10^{-4} M}$$

Thus, $BaCrO_4$ will precipitate first because it requires low concentration of CrO_4^{2-} ions. On addition of chromate ions, $BaCrO_4$ starts precipitating when chromate ion concentration reaches $\mathbf{1.2 \times 10^{-9}M}$. When CrO_4^{2-} ion concentration reaches up to $\mathbf{3.5 \times 10^{-4}\ M}$, then $SrCrO_4$ also starts precipitating.

Remaining concentration of Ba^{2+} when $SrCrO_4$ starts precipitating

$$= \frac{K_{sp} \text{ of } BaCrO_4}{[CrO_4^{2-}] \text{ when } SrCrO_4 \text{starts precipitating}} = \frac{1.2 \times 10^{-10}}{3.5 \times 10^{-4}} = \mathbf{3.4 \times 10^{-7}M}$$

% of remaining concentration of Ba^{2+}

$$= \frac{[\text{Remaining } Ba^{2+}]}{[\text{Initial } Ba^{2+}]} \times 100\% = \frac{3.4 \times 10^{-7}}{0.1} \times 100\% = \mathbf{0.00034}\%$$

The resulting solution can be filtered and the Ba^{2+} isolated from the original solution as the chromate salt.

Definition of fractional precipitation:

Fractional precipitation is *the method for separating elements or compounds with similar solubility by a series of analytical precipitations, each one improving the purity of the desired element.*

Example 17

To a solution containing $0.1MCl^-$ and $0.01M\ CrO_4^{2-}$, a solution of $AgNO_3$ is added slowly.

(i) Which salt will precipitate first between AgCl and Ag_2CrO_4? Show clearly how you arrived to your answer.

(ii) Find the concentration of the ion that will precipitate first at the time the second ion will start precipitating. Use $K_{sp}(AgCl) = 2.72 \times 10^{-10}$ and $K_{sp}\ (Ag_2CrO_4) = 2.4 \times 10^{-12}$

Solution

(i) **For AgCl:**

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

From which $K_{sp} = [Ag^+][Cl^-]$ or $[Ag^+] = \frac{K_{sp}}{[Cl^-]}$

Thus minimum $[Ag^+]$ required to precipitate AgCl $= \frac{2.72\times10^{-10}}{0.1}M = 2.72 \times 10^{-9}M$

For Ag_2CrO_4:

$$Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$$

From which $K_{sp} = [Ag^+]^2[CrO_4^{2-}]$ or $[Ag^+] = \sqrt{\frac{K_{sp}}{[CrO_4^{2-}]}}$

Thus minimum $[Ag^+]$ required to precipitate $Ag_2CrO_4 = \sqrt{\frac{2.4\times10^{-12}}{0.01}}M = 1.55 \times 10^{-5}M$

Therefore AgCl will precipitate first because it requires lower concentration of Ag^+ ions. On addition of silver ions (from silver nitrate solution), AgCl starts precipitating when silver ion concentration reaches $2.72 \times 10^{-9}M$ while until concentration of silver ions reaches up to 1.55×10^{-4} M, Ag_2CrO_4 will also starts precipitating.

(ii) Remaining concentration of Cl^- when Ag_2CrO_4 starts precipitating

$$= \frac{K_{sp} \text{ of } AgCl}{[Ag^+] \text{ when } Ag_2CrO_4 \text{ starts precipitating}} = \frac{2.72 \times 10^{-10}}{1.55 \times 10^{-5}} = 1.75 \times 10^{-5}M$$

Hence the concentration of the ion that will precipitate first (Cl^-) at the time CrO_4^{2-} start to precipitate was $1.75 \times 10^{-5}M$.

MISCELLANEOUS WORKED EXAMPLES ON SOLUBILITY AND SOLUBILITY PRODUCT

Example 18

What is the minimum mass of sodium sulphate crystals that must be dissolved in 5L of 0.001M $Ca(NO_3)_2$ solution in order to initiate precipitation of calcium sulphate? $K_{sp}(CaSO_4) = 2.6 \times 10^{-5} M^2$

Solution

$Ca(NO_3)_2$ is highly soluble salt (strong electrolyte) which ionises completely according to the following equation;

$$Ca(NO_3)_2(aq) \longrightarrow Ca^{2+}(aq) + 2NO_3^-(aq)$$

$$0.001M \qquad\qquad 0.001M$$

Thus $[Ca(NO_3)_2] = [Ca^{2+}] = 0.001M$

Calcium sulphate being sparingly soluble electrolyte ionises according to the following equation;

$$CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)$$

The precipitate formation is initiated when ionic product is equal to solubility product.

Thus $K_{sp} = [Ca^{2+}][SO_4^{2-}]$ or $[SO_4^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{2.6\times10^{-5}M^2}{0.001M} = 2.6 \times 10^{-2}M$

So minimum $[SO_4^{2-}]$ required to initiate the precipitate is $2.6 \times 10^{-2}M$.

Na_2SO_4 is strong electrolyte and its formula suggests that for every mole of sodium sulphate there is one mole of sulphate ions. Thus, $[Na_2SO_4] = [SO_4^{2-}] = 2.6 \times 10^{-2}M$

Then mass of $Na_2SO_4 = [Na_2SO_4] \times V_{soln} \times M_r(Na_2SO_4)$

Substituting mass of $Na_2SO_4 = 2.6 \times 10^{-2} mol/L \times 5L \times 142 g/mol = 18.46g$

Hence the mass is 18.46g.

Example 19

A saturated solution of $Mg(OH)_2$ in contact with undissolved solid is prepared at 25 ºC. The pH of the solution is found to be 10.17. Calculate solubility product for this compound.

Solution

$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq); K_{sp} = [Mg^{2+}][OH^-]^2$

$[OH^-] = \log^{-1}(-pOH) = \log^{-1}\big(-(14 - pH)\big)$

$\quad = \log^{-1}(-(14 - 10.17)) = \log^{-1}(-3.83) = 1.4791 \times 10^{-4}M$

But from mole ratio of the equation for ionisation of $Mg(OH)_2$;

$$[Mg^{2+}] = \frac{[OH^-]}{2} = \frac{1.4791 \times 10^{-4}M}{2} = 7.3955 \times 10^{-5}M$$

$K_{sp} = (7.3955 \times 10^{-5}M)(1.4791 \times 10^{-4}M)^2 = 1.62 \times 10^{-12}M^3$

The solubility product is $1.62 \times 10^{-12}M^3$.

Example 20

If equal volume of 0.01M K_2SO_4 and 0.1M $Pb(NO_3)_2$ solutions are mixed;

(i) Will a precipitate form?
(ii) What are the concentrations of Pb^{2+} and SO_4^{2-} remaining in the solution?

Use $K_{sp}(PbSO_4) = 1.8 \times 10^{-8}$

Solution

(i) Let the volume of each solution taken in litres be V

Then:

Total volume of solution mixture will be $V + V = 2V$

$[\ K_2SO_4\ ]$ in the mixture $= \dfrac{0.01V}{2V} = 0.005M$

$[Pb(NO_3)_2\ ]$ in the mixture $= \dfrac{0.1V}{2V} = 0.05M$

As a general rule: *If equal volume of* ***two*** *solutions, concentration of each in the mixture will be halved.*

Then from, $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

$Q_{sp} = [Pb^{2+}]_o[SO_4^{2-}]_o = 0.005 \times 0.05 = 2.5 \times 10^{-4} > 1.8 \times 10^{-8}(K_{sp})$

Since $Q_{sp} > K_{sp}$, the precipitate will form.

(ii) $Pb(NO_3)_2$ reacts with K_2SO_4 (to precipitate $PbSO_4$) according to the following equation:

$$Pb(NO_3)_2(aq) + K_2SO_4(aq) \longrightarrow PbSO_4(s) + 2KNO_3(aq)$$

From which their mole ratio of 1:1. But the given amount of $Pb(NO_3)_2$ is greater than that of K_2SO_4. So $Pb(NO_3)_2$ was in excess.

Unreacted $[Pb(NO_3)_2\ ] = (0.05 - 0.005)M = 0.045M$

The unreacted $Pb(NO_3)_2$ being strong electrolyte ionises according to the following equation:

$$\begin{array}{lll} Pb(NO_3)_2(aq) & \longrightarrow Pb^{2+}(aq) & + 2NO_3^-(aq) \\ 0.045M & \quad 0.045M & \end{array}$$

So the unreacted will affect the dissolution of $PbSO_4$ by common ion effect and therefore if s is its solubility, then:

$[Pb^{2+}] = s + 0.045 \approx 0.045M$

$[SO_4^{2-}] = s$

It follows that; $K_{sp} = 0.045s = 1.8 \times 10^{-8}$ or $s = 4 \times 10^{-7}M$

Hence $[Pb^{2+}] = 0.045M$ and $[SO_4^{2-}] = 4 \times 10^{-7}M$

Alternative solution

You may find easier to solve the second part of the question from the 'first principle' as normal chemical equilibrium problem. Let us look how it is done!

We have found that just after mixing:

$[Pb(NO_3)_2\ ] = [Pb^{2+}] = 0.05M$

$[\ K_2SO_4\ ] = [SO_4^{2-}] = 0.005M$

Then the precipitation process will proceed until the equilibrium is achieved.

	$PbSO_4(s) \rightleftharpoons$	$Pb^{2+}(aq) +$	$SO_4^{2-}(aq)$
Just after mixing		0.05	0.005
At equilibrium		$0.05 - x$	$0.005 - x$

$K_{sp} = (0.05 - x)(0.005 - x) = 1.8 \times 10^{-8}$; $x^2 - 0.055x + 2.499982 \times 10^{-4} = 0$

Solving above quadratic equation, gives practical value of $x = 0.0049996$

Hence: $[Pb^{2+}] = 0.05 - x = (0.05 - 0.0049996)M = 0.045M$

And $[SO_4^{2-}] = 0.005 - x = (0.005 - 0.0049996)M = 4 \times 10^{-7}M$

Example 21

Lead chromate, $PbCrO_4$, is a yellow pigment used in paints. Suppose 0.5L of a $1 \times 10^{-5}M$ $(CH_3COO)_2Pb$ and 0.5L of a $1 \times 10^{-3}M$ K_2CrO_4 solution are mixed.

(i) Calculate the equilibrium concentration of Pb^{2+} ion remaining in the solution after $PbCrO_4$ precipitates.
(ii) What is the percentage of Pb^{2+} remaining in solution after the precipitation has occurred and hence state whether the precipitation of Pb^{2+} was complete or not.

Use $K_{sp}(PbCrO_4) = 1.8 \times 10^{-14}$

Solution

(i) Since equal volume (0.5L) of each solution was taken, their concentrations in the mixture will be halved. Thus:

$$[(CH_3COO)_2Pb] \text{ in the mixture} = \frac{1 \times 10^{-5}M}{2} = 5 \times 10^{-6}M$$

$$[K_2CrO_4\ ] \text{ in the mixture} = \frac{1 \times 10^{-3}M}{2} = 5 \times 10^{-4}M$$

$(CH_3COO)_2Pb$ reacts with K_2CrO_4 (to precipitate $PbCrO_4$) according to the following equation:

$$(CH_3COO)_2Pb(aq) + K_2CrO_4(aq) \longrightarrow PbCrO_4(s) + 2CH_3COOK(aq)$$

From which their mole ratio of 1:1. But the given amount of K_2CrO_4 is greater than that of $(CH_3COO)_2Pb$. So K_2CrO_4 was in excess.

Unreacted $[K_2CrO_4\ ] = (5 \times 10^{-4} - 5 \times 10^{-6})M = 4.95 \times 10^{-4}M$

The unreacted K_2CrO_4 being strong electrolyte ionises according to the following equation:

$$K_2CrO_4(aq) \longrightarrow 2K^+(aq) + CrO_4^{2-}(aq)$$

$$4.95 \times 10^{-4}M \qquad\qquad 4.95 \times 10^{-4}M$$

So the unreacted will affect the dissolution of $PbSO_4$ by common ion effect and because $PbCrO_4$ ionises according to the equation; $PbCrO_4(s) \rightleftharpoons Pb^{2+}(aq) + CrO_4^{2-}(aq)$; it follows that, if s is its solubility, then:

$[CrO_4^{2-}] = s + 4.95 \times 10^{-4}M \approx 4.95 \times 10^{-4}M$

$[Pb^{2+}] = s$

It follows that; $K_{sp} = 4.95 \times 10^{-4}s = 1.8 \times 10^{-14}$ or $s = 3.6363 \times 10^{-11}M$

Hence the equilibrium $[Pb^{2+}] = 3.6363 \times 10^{-11}M$

(ii) Original $[Pb^{2+}] = [(CH_3COO)_2Pb] = 5 \times 10^{-6}M$

Then %remained $= \frac{\text{remained } [Pb^{2+}]}{\text{original } [Pb^{2+}]} \times 100\% = \frac{3.6363 \times 10^{-11}M}{5 \times 10^{-6}M} \times 100\% = 0.00073\%$

The percentage of Pb^{2+} remaining is 0.00073% which is extremely small and hence the precipitation of Pb^{2+} was complete.

Example 22

A solution prepared by mixing 150mL of $1 \times 10^{-2}M$ $Mg(OH)_2$ and 250mL of $1 \times 10^{-1}M$ NaF. Calculate the concentration of Mg^{2+} and F^- at equilibrium with solid MgF_2. (K_{sp} at 298K is $6.4 \times 10^{-9}\ M^2$).

Solution

Number of moles of $Mg(OH)_2$ was $\frac{150}{1000} \times 1 \times 10^{-2}mol = 1.5 \times 10^{-3}mol$

Number of moles NaF was $\frac{250}{1000} \times 1 \times 10^{-1}mol = 2.5 \times 10^{-2}mol$

$Mg(OH)_2$ reacts with NaF according to the following equation:

$$Mg(OH)_2 + 2NaF \rightarrow MgF_2 + 2NaOH$$

From which mole ratio of $Mg(OH)_2$ to NaF is 1:2

Thus $1.5 \times 10^{-3}mol$ of $Mg(OH)_2$ reacted with $2 \times 1.5 \times 10^{-3}$or $3 \times 10^{-3}mol$ of NaF and $(2.5 \times 10^{-2} - 3 \times 10^{-3})$ moles or $2.2 \times 10^{-2}mol$ of NaF remain unreacted at the end of the reaction

Total volume of solution mixture = $(150 + 250)mL = 400mL$

Thus [NaF] after the reaction = $\frac{2.2 \times 10^{-2}}{400} \times 1000M = 0.055M$

NaF being strong electrolyte ionises according to the following equation

$$\underset{0.055M}{NaF} \rightarrow Na^+ + \underset{0.055M}{F^-}$$

So if x is the molar solubility of MgF_2 (which is formed in the double decomposition reaction) in 0.055M of unreacted NaF

$[Mg^{2+}] = x$

$[F^-] = 2x + 0.055 \approx 0.055$

And from: $MgF_2(s) \rightleftharpoons Mg^{2+}(aq) + 2F^-(aq)$; $K_{sp} = [Mg^{2+}]\,[F^-]^2$

Then $6.4 \times 10^{-9} = x\,(0.055)^2$ or $x = 2.1157 \times 10^{-6}\ moldm^{-3}$

Hence 2.1157×10^{-6} M of Mg^{2+} and 0.055M of F^- are at equilibrium with solid MgF_2.

Example 23

Calculate milligrams of precipitate of calcium fluoride that will formed when 1L of $2 \times 10^{-2}M$ NaF is mixed with 200mL of $1 \times 10^{-2}M$ $Ca(NO_3)_2$. Given that: $K_{sp}(CaF_2) = 3.9 \times 10^{-9}M^3$.

Solution

Calculating total mass of CaF_2 that can be formed by the reaction between NaF and $Ca(NO_3)_2$:

Number of moles of $Ca(NO_3)_2$ was $\frac{200}{1000} \times 1 \times 10^{-2}mol = 2 \times 10^{-3}mol$

Number of moles NaF was $1 \times 2 \times 10^{-2}mol = 2 \times 10^{-2}mol$

$Ca(NO_3)_2$ reacts with NaF according to the following equation:

$$Ca(NO_3)_2(aq) + 2NaF\,(aq) \rightarrow CaF_2(s) + 2NaNO_3(aq)$$

From which mole ratio of $Ca(NO_3)_2$ to NaF is 1: 2

Thus $2 \times 10^{-3}mol$ of $Ca(NO_3)_2$ reacted with $2 \times 2 \times 10^{-3}$ or $4 \times 10^{-3}mol$ of NaF and $(2 \times 10^{-2} - 4 \times 10^{-3})$ mol or 0.016mol of NaF remain unreacted at the end of the reaction.

So $Ca(NO_3)_2$ is the limited reactant and therefore it is going to determine the amount of CaF_2 produced.

From the same equation; mole ratio of $Ca(NO_3)_2$ to CaF_2 is 1:1.

Thus number of moles of CaF_2 produced =Number of moles of $Ca(NO_3)_2$ reacted = $2 \times 10^{-3}mol$

Using $m = nM_r$;

Total mass of CaF_2 produced just after reaction between $Ca(NO_3)_2$ and NaF

$$= 2 \times 10^{-3}\text{mol} \times 78\text{g/mol} = 0.156\text{g}$$

Calculating the mass of precipitate

Total volume of solution mixture = $(200 + 1000)\text{mL} = 1200\text{mL} = 1.2\text{L}$

Thus [NaF] after the reaction (concentration of unreacted NaF) = $\frac{0.016\text{mol}}{1.2\text{L}} = 0.01333\text{M}$

NaF being strong electrolyte ionises according to the following equation:

$$\underset{0.01333\text{M}}{\text{NaF}} \rightarrow \text{Na}^+ + \underset{0.01333\text{M}}{\text{F}^-}$$

So if s is the molar solubility of CaF_2, then:

$[Ca^{2+}] = s$

$[F^-] = 2s + 0.01333 \approx 0.01333\text{M}$

And from: $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$; $K_{sp} = [Ca^{2+}][F^-]^2$

Then $3.9 \times 10^{-9}\text{M}^3. = s\,(0.01333)^2$

Or $s = 2.1948 \times 10^{-7}\ \text{mol/L} = 2.1948 \times 10^{-5}\ \text{mol/L} \times 78\text{g/mol} = 0.001712\text{g/L}$

Thus mass of CaF_2 that dissolves in 1.2L of the solution= $0.001712\text{g/L} \times 1.2\text{L} = 0.002\text{g}$

Thus only 0.002g out of the total mass of 0.156g is dissolved in the solution and hence the solution is supersaturated and the mass of precipitate = $(0.156 - 0.002)\text{g} = 0.154\text{g} = 154\text{mg}$

There are 154 milligrams of precipitate of calcium fluoride.

Example 24

Below are data which can be used to compare solubility of AgBr in water and in ammonia solution.

$AgBr(s) \rightleftharpoons Ag^+(aq) + Br^-(aq)$; $K_{sp} = 3.3 \times 10^{-13}$
$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)$; $K = 1.7 \times 10^{+7}$

(i) How many grams of silver bromide, AgBr can be dissolved in 50 millilitres of water?
(ii) How many grams of silver bromide can be dissolved in 50millilitres of $10\text{M}NH_3(aq)$?
(iii) How many times is silver bromide more soluble in the ammonia solution than in water?

Solution

If s is the molar solubility of AgBr in water;

Then; $AgBr(s) \rightleftharpoons \underset{s}{Ag^+(aq)} + \underset{s}{Br^-(aq)}$

$K_{sp} = [Ag^+][Br^-] = s^2$

From which $s = \sqrt{K_{sp}} = \sqrt{3.33 \times 10^{-13}} = 5.744 \times 10^{-7}\text{M}$

The solubility of AgBr = Molar solubility × Molar mass

$$= 5.744 \times 10^{-7} \times 188\text{g/dm}^3 = 1.1 \times 10^{-4}\text{g/dm}^3$$

Thus mass of AgBr dissolved in 50mL = $\frac{50}{1000} \times 1.1 \times 10^{-4}\text{g} = 5.5 \times 10^{-6}\text{g}$

(i) Hence mass of AgBr dissolved in 50mL of water is 5.5×10^{-6}g.

$K_{sp} = [Ag^+][Br^-] = 3.3 \times 10^{-13}$ …… (i)

And $K = \frac{[Ag(NH_3)_2]^+}{[Ag^+][NH_3]^2} = 1.7 \times 10^7$……. (ii)

AgBr dissolves in $NH_3(aq)$ according to the following equation:

$$AgBr(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Br^-(aq)$$

At equilibrium $10 - 2s'$ $\quad s' \quad s'$

Where s is the molar solubility of AgBr in $NH_3(aq)$

Then $K_s = \frac{[Ag(NH_3)_2]^+[Br^-]}{[NH_3]^2} = \frac{(s')^2}{(10-2s')^2}$

But $K_{sp} \times K = \frac{[Ag(NH_3)_2]^+[Ag^+][Br^-]}{[Ag^+][NH_3]^2} = \frac{[Ag(NH_3)_2^+][Br^-]}{[NH_3]^2} = K_s$

Thus $K_s = K_{sp} \times K = 3.3 \times 10^{-13} \times 1.7 \times 10^7$

Then $\frac{(s')^2}{(10-2s')^2} = 5.61 \times 10^{-6}$

From which $(s')^2 + 2.244 \times 10^{-4}s' - 5.61 \times 10^{-6} = 0$; and $s' = 0.0236M$

Then mass solubility of AgBr in $NH_3(aq) = 0.0236 \times 188gdm^{-3} = 4.4368gdm^{-3}$

And mass of AgBr dissolved in 50mL $= \frac{50}{1000} \times 4.4368gdm^{-3} = 0.22g$

(i) Hence mass of AgBr dissolved in 50mL of ammonia solution is 0.22g.

(ii) Taking $\frac{\text{solubility of AgBr in ammonia}}{\text{solubility of AgBr in water}} = \frac{4.4368gdm^{-3}}{1.1\times10^{-4}g/dm^3} = 40335$

Hence the solubility of silver bromide in the given ammonia solution is about forty thousand times its solubility in water.

DIGGING DEEPER EXERCISE 19

EXERCISE 19A: BINDER QUESTIONS

Question 1

The solubility of $Zn(OH)_2$ is not the same in the following solutions as it is in pure water. In each case state whether the solubility is greater or less than that in water and briefly account for the change in solubility.

(a) 1-molar HCl
(b) 1-molar $Zn(NO_3)_2$
(c) 1-molar NaOH
(d) 1-molar NH_3

Question 2

One litre of water is able to dissolve 2.5×10^{-3}mol of PbF_2. What is the K_{sp} for PbF_2?

Question 3

What is the molar solubility of $Fe(OH)_3$ in a solution with a hydroxide ion concentration of 0.05M?

$K_{sp} = 1.6 \times 10^{-39}M^4$

Question 4

Will a precipitate of $CaSO_4$ form in a solution if the Ca^{2+} concentration is 0.0025M and the SO_4^{2-} concentration is 0.030M? For $CaSO_4$, $K_{sp} = 2.4 \times 10^{-5}M^2$.

Question 5

Will a precipitate of $PbSO_4$ form if 100mL of $1 \times 10^{-3}M\ Pb(NO_3)_2$ solution is added to 100mL of $2 \times 10^{-3}M\ MgSO_4$ solution? $K_{sp} = 6.3 \times 10^{-7}$

Question 6

For the equilibrium; $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$; $K_{sp} = 5 \times 10^{-10}mol^2dm^{-6}$.

(a) What is the molarity of calcium carbonate in a saturated solution at 298K?
(b) What is the solubility of calcium carbonate in $0.1moldm^{-3}$ sodium carbonate solution?

Question 7

A 50.0 mL sample of a saturated aqueous solution of lead bromide, $PbBr_2$, was evaporated to dryness. 0.422 g of solid $PbBr_2$ was obtained. Calculate the value of K_{sp} $(PbBr_2)$.

EXERCISE 19B: REAL QUESTIONS

Question 8

Silver bromide dissolves more in ammonia solution than in pure water. Explain the difference.

Question 9

Explain why addition of NH_3 or HNO_3 to a saturated solution of $Cu(OH)_2$ in contact with solid $Cu(OH)_2$ increases the solubility of the solid.

Question 10

Supersaturated solution of calcium sulphate in water are prepared by cooling its saturated solution. Supersaturated solution of carbon dioxide in water is prepared by heating its saturated solution. Explain the reasons for the difference in the two procedures.

Question 11

When hydrochloric acid solution is added to a supersaturated solution of calcium carbonate, the precipitate dissolves into clear solution but when it is added to a saturated solution of silver chloride, the solution becomes supersaturated accompanied with clear formation of precipitate. Explain.

Question 12

You were discussing the following question with your friend **Kipute**;

Two hypothetical salts, X_2Y and PQ, have the same molar solubility in water. If the solubility product for X_2Y is 1.08×10^{-7}, what is the solubility product for PQ?

In the discussion, **Kipute** argued that because the two compounds have the same molar solubility; the solubility product of PQ will be also 1.08×10^{-7}. With a reason, state whether you agree or disagree with **Kipute**. If you agree, explain clearly your reason and if you disagree, help **Kipute** to find the solubility product.

EXERCISE 19C: HOT QUESTIONS

Question 13

For the equilibrium; $\mathrm{CaSO_4(s) \rightleftharpoons Ca^{2+}(aq) + SO_4^{2-}(aq)}$; $\mathrm{K_{sp}} = 2 \times 10^{-5}\mathrm{mol^2dm^{-6}}$

(a) What is the solubility of calcium sulphate in a saturated solution of the salt in $\mathrm{gcm^{-3}}$?
(b) Assuming equal volumes of solutions are mixed, what is the minimum concentration of sodium sulphate $(\mathrm{Na_2SO_4})$ solution that when added to a $1 \times 10^{-4}\mathrm{moldm^{-3}}$ solution of calcium sulphate, will just begin to cause precipitation of calcium sulphate?

Question 14

What is the pH in a saturated solution of $\mathrm{Ca(OH)_2}$? $\mathrm{K_{sp}} = 5.5 \times 10^{-6}\mathrm{M^3}$

Question 15

A useful commercial source of magnesium is sea water, where $[\mathrm{Mg^{2+}(aq)}]$ is $0.054\mathrm{moldm^{-3}}$. The magnesium is precipitated from solution by adding calcium hydroxide.

$$\mathrm{Mg^{2+}(aq) + Ca(OH)_2 \longrightarrow Ca^{2+}(aq) + Mg(OH)_2(s)}$$

(a) Write an expression for the $\mathrm{K_{sp}}$ of $\mathrm{Mg(OH)_2}$, including its units.
(b) The numerical value for $\mathrm{K_{sp}}$ is 2×10^{-11}. Calculate $[\mathrm{Mg^{2+}(aq)}]$ in a saturated solution of $\mathrm{Mg(OH)_2}$.
(c) Hence calculate the maximum percentage of the original magnesium in the seawater that this method can extract.

Question 16

At 25ºC the solubility product constant, $\mathrm{K_{sp}}$, for strontium sulphate, $\mathrm{SrSO_4}$, is 7.6×10^{-7}. The solubility product constant for strontium fluoride, $\mathrm{SrF_2}$, is 7.9×10^{-10}.

(a) What is the molar solubility of $\mathrm{SrSO_4}$ in pure water at 25ºC?
(b) What is the molar solubility of $\mathrm{SrF_2}$ in pure water at 25ºC?
(c) An aqueous solution of $\mathrm{Sr(NO_3)_2}$ is added slowly to 1litre of a well-stirred solution containing 0.02mole $\mathrm{F^-}$ and 0.1mole $\mathrm{SO_4^{2-}}$ at 25ºC. (You may assume that the added $\mathrm{Sr(NO_3)_2}$ solution does not materially affect the total volume of the system.)
    (i) Which salt precipitates first?
    (ii) What is the concentration of strontium ion, $\mathrm{Sr^{2+}}$, in the solution when the first precipitate begins to form?
(d) As more $\mathrm{Sr(NO_3)_2}$ is added to the mixture in (c) a second precipitate begins to form. At that stage, what percent of the anion of the first precipitate remains in solution?

Question 17

A saturated solution of lead iodate in pure water has a lead ion concentration of 4×10^{-5} mole per litre at 25°C.

(a) Calculate the value for the solubility-product constant of $Pb(IO_3)_2$ at 25°C.
(b) Calculate the molar solubility of $Pb(IO_3)_2$ in a 0.10molar $Pb(NO_3)_2$ solution at 25°C.
(c) To 333millilitres of a 0.120-molar $Pb(NO_3)_2$ solution, 667 millilitres of 0.435-molar KIO_3 is added. Calculate the concentrations of Pb^{2+} and IO_3^- in the solution at equilibrium at 25°C.

Question 18

Barium ions are poisonous. Patients with digestive tract problems are sometimes given an X-ray after they have swallowed a 'barium meal', consisting of a suspension of $BaSO_4$ in water. The $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$ is too low to cause problems of toxicity.

(a) Write an expression for the solubility product, K_{sp}, for $BaSO_4$, including its units.
(b) The numerical value of K_{sp} is 1.3×10^{-10}. Calculate $[Ba^{2+}(aq)]$ in a saturated solution of $BaSO_4$.
(c) The numerical value of K_{sp} for $BaCO_3$ (5×10^{-10}) is not significantly higher than that for $BaSO_4$, but barium carbonate is very poisonous if ingested. Suggest a reason why this might be so.

EXAMINATION QUESTIONS FOR PART FIVE

Question 1

(a) Explain why the neutralisation reaction of a strong acid and a weak base gives an acidic solution.
(b) 0.16g of an acid, of relative molecular mass 118, was made up to $250cm^3$ of aqueous solution. $25cm^3$ of this solution required $27.1cm^3$ of 0.1M sodium hydroxide for neutralisation. Calculate the mass of acid reacting with 1 mole of sodium hydroxide and hence basicity of acid.

Question2

(a) Classify whether aqueous solutions of the following salts are acidic, basic or neutral:
$$FeCl_3, K_2CO_3, NH_4Br, KClO_4, KCl, HCOOK$$
(b) $100cm^3$ of vinegar at 15˚C were diluted to $250cm^3$ with distilled water. $25cm^3$of the diluted solution required $16.9cm^3$ of 0.5MNaOH for neutralisation with phenolphthalein as indicator. Assuming that all the acidity of vinegar is caused by ethanoic acid; calculate the percentage by mass of this acid in the original vinegar. (Density of vinegar at 15˚C is $1.02gcm^{-3}$).

Question 3

(a) Why do the salts of strong acid and strong base not hydrolyse in the solution?
(b) 8.58g of washing soda were made up to $250cm^3$of aqueous solution. $25cm^3$of this solution required $30cm^3$ of 0.2MHCl for neutralisation with methyl orange as indicator. Calculate *x* in the formula, $Na_2CO_3.xH_2O$, for washing soda.

Question 4

(a) Which of the following slightly soluble compounds has a solubility greater than that calculated from its solubility product because of hydrolysis of the anion present:
$$PbCO_3, CuI, KClO_4, AgCl, BaSO_4, CaF_2$$
(b) A potassium salt has the formula, $H_2C_2O_4.KHC_2O_4.xH_2O$
Calculate *x* from the following data. 1.923g of potassium salt was neutralised by $22.7cm^3$ of 1M NaOH, phenolphthalein as indicator.

Question 5

(a) Suggest at least three practical facts which make salt to dissolve slowly in water.
(b) 1.5g of a sample of limestone was dissolved in $50cm^3$ of 1M hydrochloric acid. The resulting solution was made up to $250cm^3$with distilled water. $25cm^3$of this solution required $21.05cm^3$of 0.1M sodium hydroxide for neutralisation. Assuming all the basic material in the rock to be calcium carbonate, calculate the percentage of calcium carbonate present.

Question 6

(a) Explain why NaCl cannot be a component in either an acidic or basic buffer.
(b) Calculate the relative molecular mass of the carbonate of divalent metal X and hence the relative atomic mass of X from the data: 1g of the anhydrous normal carbonate of X was added to $50cm^3$ of 1MHCl. The excess acid required $30cm^3$ of 1MNaOH for neutralisation.

Question 7

(a) Which solute combinations can make a buffer? Assume all are aqueous solutions.
$$HNO_3 \text{ and } KNO_3, NaHCO_3 \text{ and } Na_2CO_3, NH_4NO_3 \text{ and } NH_3, H_3PO_4 \text{ and } Na_3PO_4, HClO_4 \text{ and } NaClO_4$$
(b) Calculate the percentage of ammonium sulphate in a sample of this compound contaminated with sodium sulphate from the following data: 1.65g of the ammonium sulphate was made up to $250cm^3$ of aqueous solution. $25cm^3$of this solution were boiled with $50cm^3$ of 0.1 M NaOH and the excess alkali neutralised by $25.4cm^3$ of 0.1MHCl.

Question 8

(a) Why weak acid alone cannot act as buffer solution?
(b) $25cm^3$ of solution of sodium carbonate and sodium hydroxide required $18.6cm^3$ of 0.1M hydrochloric acid for the end point as determined by phenolphthalein as indicator. Another $25cm^3$ of the same solution required $22.7cm^3$ of 0.1M HCl, using methyl orange as indicator. Calculate the concentration of each in the original liquid in gdm^{-3}.

Question 9

Find pH of:

(i) 0.05M CH_3COOH (K_a (CH_3COOH) $= 1.8 \times 10^{-5}$M)
(ii) 0.05M HCl

Comment on difference in two values obtained.

Question 10

A 0.1M solution of aqueous ammonia is 1.4% dissociated at 25˚C;

(a) Calculate the dissociation constant of the base at this temperature, hence its pK_b
(b) Obtain a value for degree of dissociation of NH_3(aq) in 0.002M solution, hence its pH of the solution.

Question 11

(a) Why the mixture of sulphuric acid and salt containing its conjugate base like sodium hydrogensulphate is not a buffer solution?
(b) What is the degree of ionisation and pH of a 0.01M solution of ethanoic acid at 25˚ C if K_b for CH_3COO^- at this temperature is 5.025×10^{-10}.

Question 12

(a) Does temperature affect pH of buffer solution? Explain.
(b) The solubility benzoic acid in water at 0°C is $2.44 gdm^{-3}$; if the freezing point at standard pressure of a saturated solution of benzoic acid is -0.0392°C. Calculate the dissociation constant of the acid (Ebullioscopic constant of water is 1.86°C).

Question 13

(a) Is it possible for CH_3COONa and HCl to make a buffer? Explain.
(b) What is the condition for pH and pK_a of ethanoic acid (CH_3COOH) solution to be equal?

Question 14

(a) Explain briefly how do the buffer solutions resist the change in pH?
(b) Prove that $[H_3O^+]$ for any weak acid, H_nA is given by;
$[H_3O^+] = \sqrt[n+1]{nCK_a}$ where C is concentration of the acid.

Question 15

(a) The solubility product, K_{sp}, of AgCl has a value of 1.56×10^{-10} at 25°C and this value increases to 2.15×10^{-8} at 100°C. Explain why K_{sp} is higher at 100°C. Include reference to the relevant equilibrium equation in your answer.
(b) The dissociation constant of acetic (ethanoic acid) is 1.8×10^{-5}. Show that the pH of a solution containing 0.02 of a mole ethanoic acid and 0.2mole of a mole of sodium ethanoate per dm^3 is 5.7.

Question 16

(a) Explain clearly what is wrong with the following definition:
    (i) **Buffer solution**: *Is the solution which can maintain its pH value on addition of any amount of acid or base.*
    (ii) **Common ion effect**: *Is the depression in solubility of sparingly soluble substance after introducing strong electrolyte with the same ion as that present in sparingly soluble substance.*
(b) How many cm^3 of 0.1M HCOONa that must be added to $100 cm^3$ of 0.01M HCOOH to make a buffer solution of pH 5? (K_a value of HCOOH is 1.6×10^{-4}).

Question 17

(a) State Bronsted – Lowry theory of acids and bases and hence list down at least four advantages of the Bronsted – Lowry concept over the Arrhenius concept.
(b) What is the pH of a buffer solution by adding 100cm^3 of chloroethanoic acid ($CH_2Cl\ COOH$) of concentration 0.5M to 100cm^3 of 0.25MNaOH. (pK_a of $CH_2ClCOOH$ is 2.86).

Question 18

(a) What is the concentration hydronium ion(H_3O^+), of a dm^3 buffer solution that contains 0.1mole of hydrocyanic acid (HCN) and 0.8mole of sodium cyanide?
(b) If 0.1 mole of hydrochloric acid, HCl, is added to the buffer solution in (a) above, what will be the new $[H_3O^+]$.
(c) Calculate the pH of the buffer solution in (a) above if 0.02mole of sodium hydroxide (NaOH) id added to it. $K_a(HCN) = 4.93 \times 10^{-10}$.

Question 19

The K_{sp} of $Mg(OH)_2$ at 25°C is $1.1 \times 10^{-11} mol^3 dm^{-9}$

Calculate the solubility (in gdm^{-3}) of $Mg(OH)_2$

(i) In water
(ii) In 0.1MNaOH

Question 20

The solubility of Lead (II) sulphate at 20ºC is $0.4gdm^{-3}$:

(i) What is the solubility product?
(ii) Calculate the solubility in gdm^{-3} in a 0.01M of Na_2SO_4 solution. ($Pb = 207, S = 32,\ O = 16$).

Question 21

The solubility product of silver chloride at room temperature is $1 \times 10^{-10}\ mol^2\ dm^{-6}$. What is the maximum loss from a precipitate of silver chloride if it is washed with:

(a) One dm^3 of distilled water
(b) One dm^3 of 0.01MHCl (Ag = 108 and Cl = 35.5)

Question 22

(a) Anhydrous aluminium chloride does not conduct electricity but in aqueous solution conducts. Explain.
(b) How many grams of silver chloride will be precipitated if 5.85g of NaCl are added to a litre of saturated silver chloride solution? ($K_{sp}(AgCl) = 1.69 \times 10^{-10} mol^2 dm^{-6}$)

Question 23

If the dissociation constant for NaF and NH_3 are 1.5×10^{-11} and 1.77×10^{-5} respectively. Find the pH of:

(i) A 0.25M solution of NaF
(ii) A 0.01M solution of NH_3

Question 24

The solubility of $Fe(OH)_2$ in water at 25ºC is $0.6mgdm^{-3}$; calculate:

(a) The K_{sp} value o $Fe(OH)_2$
(b) The minimum pH required to precipitate Fe^{2+} so completely that no more than 1microgram (10^{-6}g) of Fe^{2+} remains in solution.

Question 25

To a solution containing $0.1MCa^{2+}$ and $0.1M\ Ba^{2+}$, Na_2SO_4 is added slowly. The solubility product of $CaSO_4$ and $BaSO_4$ are 2.4×10^{-5} and 1.1×10^{-10} respectively;

(a) Which will precipitate first, $CaSO_4$ or $BaSO_4$?Explain
(b) What is the $[SO_4^{2-}]$ at the instant the first solid precipitates
(c) Neglect dilution and calculate the $[Ba^{2+}]$ present when the first precipitate of $CaSO_4$occurs

Question 26

(a) Give the meaning of the following terms:
   (i) Solubility
   (ii) Saturated solution
   (iii) Saturated point
   (iv) Supersaturated solution
   (v) Fractional precipitation

(b) At room temperature, the solubility products of silver chloride and silver chromate are respectively $1 \times 10^{-10} mol^2\ dm^{-6}$ and $1 \times 10^{-12}\ mol^3 dm^{-9}$. What is the concentration in $moldm^{-3}$ of potassium chromate at the end point when used as indicator in titrating a chloride by silver nitrate?

Question 27

The following data are values for K_w at different temperature, in units of $mol^2 dm^{-6}$

Temperature (°C)	10	20	30
$K_w \times 10^{-14}$	0.293	0.681	1.471

(i) What is the pH of pure water at 30°C
(ii) What is the pH at equivalent point of titration of aqueous hydrochloric acid with potassium hydroxide at 10°C?

Question 28

For weak acid HA, $K_a = 1.0 \times 10^{-6} moldm^{-3}$. Given two solutions, one containing $0.1 moldm^{-3}$ of HA and other $0.1 moldm^{-3}$ of sodium hydroxide. Explain how would you make:

(i) A solution with pH = 6
(ii) A solution with pH = 5

Which of these solution would constitute the best buffer solution?

Question 29

(a) When excess magnesium hydroxide is added to water and shaken, a saturated solution is formed and the mixture reaches equilibrium;

$$Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$$

The solubility product, K_{sp} for this process is;

$$K_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2$$

   (i) Give a reason why the magnesium hydroxide is not included in the expression for K_{sp}.
   (ii) Derive units of K_{sp}

(b) Calculate concentration of calcium carbonate precipitate in gdm^{-3} if 0.1M of calcium chloride as added to equal volume of 0.1M of sodium carbonate solution. Given that: K_{sp} of $CaCO_3 = 1.69 \times 10^{-8}\ mol^2 dm^{-6}$

Question 30

(a) Explain how the value of solubility product of sparingly soluble substance varies with temperature change.
(b) Calculate the pH 1×10^{-9} MHCl.

Question 31

(a) Is it possible for neutral solution to have pH of less than 7? Explain your answer.
(b) The pH of a solution **A,** 0.15M solution of weak monoprotic acid, Hx is 2.69
   (i) Calculate $[H^+]$ in solution **A** and hence determine the value of K_a for Hx
   (ii) A $25\ cm^3$ sample of A is titrated with 0.25M NaOH. Calculate the pH of the titrated solution when Hx is exactly half neutralized and $[Hx] = [x^-]$

Question 32

(a) Classify the following species as Bronsted acid/Base. $S^{2-}, HCO_3^-, H_2O, NH_3$.

(b) The ionisation constant of NH_4^+ in water is 5.6×10^{-10}moldm^{-3} at 25°C. The rate constant for the reaction of NH_4^+ ions and OH^- ions to form NH_3 and water at 25°C is 3.4×10^{10}dm^{3}mol^{-1}sec^{-1}. Calculate the rate constant for the proton transfer from water to NH_3.

Question 33

(a) Explain the two components of the buffer solution.

(b) An unknown student taken an unknown weight of an unknown weak monobasic acid, dissolves it in an unknown amount of water, and titrates it with a strong monoacid base of unknown concentration. When he has added 10.00mL of base, he noticed that the concentration of $H_3O^+$is 1.0×10^{-5}M. He continues the titration until he reaches the equivalent point. At this time burette reads 22.22mL. What is the dissociation constant of acid?

ANSWERS TO DIGGING DEEPER EXERCISES

EXERCISE 15

1. a) $HCN(ACID) + H_2O(BASE) \longrightarrow CN^- + H_3O^+$

b) $CH_3NH_2(BASE) + H_2O(ACID) \longrightarrow CH_3NH_3^+ + OH^-$

2. a) HSO_3^- b) HCN c) HS^- d) ClO^- e) H_2CO_3 f) NH_2^- g) H_3PO_4 h) H_2O

3.

(i) Conjugate acid: H_2O; conjugate base: O^{2-}
(ii) Conjugate acid: H_3O^+; conjugate base: OH^-
(iii) Conjugate acid: NH_4^+; conjugate base: NH_2^-
(iv) Conjugate acid: H_2CO_3; conjugate base: CO_3^{2-}

4. (b) White fumes (c) HCl being gaseous is removed from the equilibrium system and thus the position of equilibrium shifts to the right.

5. Hint: Ammonia is the weak base, hydrochloric acid is the strong acid, and ethanoic acid is the weak acid.

6. Since the colour of the indicator depends upon the relative concentration of ionised indicator to that of unionised indicator, the colour change is gradual and does not occur suddenly at a specific pH value.

7. Acidity can be neutralised by a base. Hence, we should choose baking soda solution because it is a weak base and will react with excess acid produced in the stomach due to hyperacidity and will neutralise it.

8. The pH of the pond water lies between 7 and 8.3 exclusive.

9. As the aqueous solution of A turns phenolphthalein solution pink, hence A is basic in nature. On adding an acidic solution, the pink colour disappears indicating that B neutralises A. Hence, B is acidic in nature.

10. (i) On adding phenolphthalein to NaOH solution, the colour becomes pink.

(ii) On adding dilute HCl solution dropwise to the same test tube, the pink colour disappears and the solution again becomes colourless.

(iii) On again adding NaOH to the above mixture, pink colour reappears due to presence of unreacted NaOH which was in excess, thus making the solution basic.

11.

(i) Yes.

Reason: Because their **colour change** occurs at **narrow range**.

(ii) Yes.

Explanation:
The equivalence point of reaction between acetic acid (CH_3CH_2COOH) which is weak acid and caustic soda ($NaOH$) which is strong base occurs when the solution is basic. Since the end point of the given spices occurs at basic solution too, they are suitable indicators for the given reaction.

(iii) The following are the reasons for preferring synthetic indicators to natural indicators in scientific settings:
1) Precision

Natural indicators are generally less precise and less reliable than synthetic indicators.

2) Stability

Natural indicators are less stable and have shorter life than synthetic indicators.

3) Range

Natural indicators can be used to measure pH over narrower range than synthetic indicators.

4) Availability

Natural indicators may be more difficult to obtain and may vary in quality while synthetic indicators are more readily available and consistent.

12.

(i) No. For an indicator to be suitable for detecting acid and base, its end point must occur at pH that is close to 7. But for blueberry, the end point occurs at pH far below the neutral point (pH of 7). This means that it is possible for two acidic solutions (one with pH below the end point, e.g. pH of 2 and another with pH above the end point, e.g. pH of 4) to give different colours (of blue and red respectively) or one acidic solution and another basic solution, both with pH above the end point (e.g. the acid with pH of 4 and the base with pH of 10) to give the same colour of red and hence the indicator cannot detect acid and base with certainty.
(ii) No.

Explanation:
The equivalence point of reaction between methanoic acid which is weak acid and potassium hydroxide which is strong base occurs when the solution is basic. Thus the equivalence point diverges from the end point of blueberries which occurs at acidic solution and hence the indicator becomes unsuitable for the titration.

(iii) Possible reasons are:
1) To reduce environmental pollution accompanied with production and usage of synthetic indicators.
2) To avoid high cost of producing synthetic indicators.

13. (a) (i) pipette (ii) burette (b) Everything with distilled water(c) Pink to colourless, the first drop of excess acid removes the pink alkaline colour of phenolphthalein. (d) 0.00625mol(e) 0.00625mol HCl (f) 0.278 mol/dm^3

14. (a) 0.50M (b) 0.0125mol (c) 0.025mol (d) 1.014M

15. (a) 0.025mol (b) 0.625M (c) 12.5M

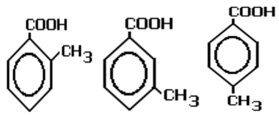
16. (a) 0.20mol (b) 0.00394 mol (c) 0.196 mol (d) 0.098mol, 3.92 g (e) 96.55% MgO

(f) $Mg(OH)_2$ from $MgO + H_2O$ and $MgCO_3$ from the original mineral source, both of these compounds react with acid and would lead to a false titration value.

17. (a) 0.00205mol (b) 0.00205 (c) 136g/mol

(d) The simplest aromatic carboxylic acid is benzoic acid C_6H_5COOH, $M_r = 122$

$136 - 122 = 14$, which suggests an 'extra' CH_2 (i.e. $-CH_3$ attached to the benzene ring instead of a H), so, since the COOH is attached to the ring, there are three possible positional/chain isomers of $CH_3C_6H_4COOH$ ($M_r = 136$) which are $2-, 3-$ or $4-$methylbenzoic acid.



18. (a) 0.00475mol (b) 0.399g, 99.75%

19. (a) 27.7% (b) (i) 56.2% (ii) 16.1%

20. 4.24g/L (Na_2CO_3) and 5.04g/L ($NaHCO_3$)

EXERCISE 16

1. (a) 3 (b) 9 (c) 9 (Hint for part (b): The concentration given is of H^+ and not for an acid)

2. A (pH = 4.41) is more acidic, B is more basic.

3. pH = 1.19, pOH = 12.81

4. 1.8g

5. 34

6. pH = 13.1

8. (a) Presence of lone pair on the N

(b) pH = 11.13

9. pH =2.6 (**Hint:** Treat the solution with pH of 7 as pure water, then use dilution principle to find $[H^+]$ in the mixture. Finally, the pH is easily found from the $[H^+]$ as usual).

10. 1.7

11. pH calculation involve K_a, K_b and K_w all of which are equilibrium constants whose values vary significantly as temperature change.

12. Disagree.

Explanation

The neutrality of water is due to the equality of concentration of hydronium ion and hydroxide ion in self-ionisation and not pH. The equality comes from stoichiometry of self-ionisation of water which is not affected by temperature change; so even at 100°C, $[H_3O^+] = [OH^-]$. Temperature affects the pH at which the equality occurs; at 25°C the equality occurs when the pH is 7 whereas at 100°C, the equality occurs when pH is 6.

13. 2200mL

14. pH = 2.4

15.

(i) Water undergoes self-ionisation according to the following equation:

$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$----------------------(i)

HCl dissolves in water according to the following equation:

$HCl + H_2O \longrightarrow H_3O^+ + Cl^-$----------------------------(ii)

So the introduction of HCl disturbs the equilibrium and thus the ionisation of water (in (i)) because it gives H_3O^+ which is also present in the equilibrium.

Therefore the increase in $[H_3O^+]$ by the acid is going to shift the equilibrium position to the left and hence the concentration of water ionised will decrease from 10^{-7}M to x.

So from water:

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

At equilibrium x x

And from HCl:

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

After ionisation: 0 $10^{-2}M$ $10^{-2}M$

Then by considering ions present in the equilibrium:

$[H_3O^+] = x + 10^{-2}$ and $[OH^-] = x$

It follows that: $K_w = [H_3O^+][OH^-]$

Substituting $10^{-14} = (x + 10^{-2})x$; $x^2 + 10^{-2}x - 10^{-14} = 0$

Solving above quadratic equation gives practical value of x which is 10^{-12}

So $[H_3O^+] = x + 10^{-2} = 10^{-12} + 10^{-2} = 10^{-2}M = [HCl]$

Here the contribution of water on $[H_3O^+]$ is extremely small, such that the whole $[H_3O^+]$ comes from HCl and hence it was correct for Kipute to ignore completely self-ionisation of water.

Then $pH = -\log[H_3O^+] = -\log 10^{-2}M = 2$

(ii) In 10^{-8}MHCl, the acid is very dilute and thus the $[H_3O^+]$ from the acid is comparable to that from water and hence it is incorrect to ignore self-ionisation of water which in turn leads to incorrect negligence of $[H_3O^+]$ from water.

Thus Total $[H_3O^+]$ = $[H_3O^+]$ from HCl + $[H_3O^+]$ from H_2O

Let $[H_3O^+]$ from H_2O = x

Then from ionisation of water, $[OH^-]$ is also x

And $[H_3O^+]$ total= $1 \times 10^{-8} + x$

Using; $K_w = [OH^-]\,[H_3O^+]$; $1 \times 10^{-14} = (1 \times 10^{-8} + x)x$

Or $x^2 + (1 \times 10^{-8})x - 1 \times 10^{-14} = 0$

Solving above equation gives $x = 9.5 \times 10^{-8}M$

So $[H_3O^+] = (1 \times 10^{-8} + 9.5 \times 10^{-8})M = 1.05 \times 10^{-7}M$

$pH = -\log[H_3O^+] = -\log(1.05 \times 10^{-7}) = 6.98$

Hence the pH of the solution is 6.98

16.

1) **Water is a weak electrolyte**. This is indicated by the reversibility sign (⇌) in the equation.
2) **Water is amphoteric.** This is indicated by presence of both H_3O^+ and OH^- in the equation.
3) **Water is neutral.** This is because mole ratio of H_3O^+ to OH^- is 1:1, implying that water gives equal concentration of H_3O^+ and OH^- in the ionisation.

17. (a) $K_a = \frac{[CH_3CH_2CO_2^-][H_3O^+]}{[CH_3CH_2CO_2H]}$ (b) pH = 2.73 (c) Concentration of H_3O^+ should decrease tenfold but the dilution will also move equilibrium to the right thus increasing degree of dissociation of the acid and hence the decrease of the concentration of H_3O^+ become less than expected.

18. (a) Endothermic because an increase in value of K_w as temperature increases suggest that position of equilibrium shift to the right as the temperature increases and hence according to Le-Chatelier's principle the reaction must be endothermic.

(b) $[H^+]$ from water itself become dominant and cannot be neglected and pH of the solution becomes very close to 7 (Just slight below 7).

19. (a) 0.01M, pH $= 2$ (b) 0.1M (c) 0.0316M, 0.1316M (d) $[H^+]$ of $0.105M < 0.1316M$ because reaction **II** suppress reaction **I** by common ion effect.

20. 0.65℃

21. Van't Hoff factor =1.0753; Dissociation constant $= 2.73 \times 10^{-3}$

22. $[F^-] = 0.02M$, $pH = 1.5$

23. pH=12.53 (**Hint:** The solution with pH of 2 is acidic while that of 13 is basic. So the question involves acid-base reaction. To solve; convert pH of 13 into corresponding $[OH^-]$, then use it with $[H^+]$ from the acidic solution to deduce the excess reactant. You will find that $[OH^-]$ was in excess; then continue to find pOH and hence pH of the mixture).

24. 302mL (or 0.302L)

25. $K_w = 1 \times 10^{-13}$

EXERCISE 17

1. The buffer solution consists of a weak acid and its conjugate base. If acid is added to the solution, it is consumed by the conjugate base and if base is added to the solution, it is consumed by the weak acid, keeping the pH almost constant.

2.

(i) Dilution decreases concentrations of both weak acid (or base) and its conjugate base (or acid) by the same factor and thus keeping their ratio in their molar concentration unchanged and hence the pH remains constant.

(ii) Dilution decreases concentrations of components of buffer solution and hence it decreases buffer capacity.

3. pH will decrease (more acidic solution), since the position of equilibrium will shift to unionised NH_3, resulting in lower $[OH^-]$.

4. pH = 4.46, $[H^+] = 3.5 \times 10^{-5}M$

5. pH = 4.53 **6.** pH = 5.48 **7.** pH = 5.06 **8.** 12g

9. The three buffer systems of the human body are:

1) Carbonic acid/bicarbonate buffer system,
2) Phosphate buffer system, and
3) Protein buffer system.

10.

In the real life it is difficult the acid with pK_a which exactly meet with our targeted pH of the buffer. So we have to adjust concentration ratio of the buffer components so as to achieve the intended pH. The adjustment we will demand us to apply the Henderson-Hasselbalch equation.

Furthermore, even if occasionally we can succeed to get the acid with pK_a that is exactly equal to the intended pH, an addition of strong acid or base to the buffer will alter the equality in concentration slightly and thus the pH will deviate slightly from the pK_a value and hence we will be demanded to perform pH calculation to know the new pH after the deviation.

11. The answers are:

(i) Buffer 4 because it has highest ratio.
(ii) Buffer 3 because it has highest concentration of acetate and acetic acid.
(iii) Strong acid because the addition of acid decreases pH and buffer 2 has smaller pH than buffer 1.
(iv) Strong base because the addition of base increases pH and buffer 4 has larger pH than buffer 3.
(v) Buffer 1 and buffer 3 because they have the same concentration ratio of their components.
(vi) Buffer 3 because has **highest and equal** concentrations of acetate and acetic acid.

12. The most efficient buffer is found when the pK_a value of the buffer solution is equal to the targeted pH. Among the given acids, chlorous acid has pK_a (1.95) which is closest to the target (pH of 2) and hence Mr. Akilikubwa should use chlorous acid.

13.

(i) Acidic buffer solution.
(ii) Possible buffers are:
 1) Mixture of CH_3COOH and CH_3COONa
 2) Mixture of CH_3COOH and NaOH
 3) Mixture of CH_3COONa and HCl
(iii) The amount of each should be as follows:
 1) For CH_3COOH | CH_3COONa mixture: The amount should be taken in such a way that **there is an equal concentration of the two components in the mixture.**
 2) For CH_3COOH | NaOH mixture: The amount should be taken in such a way that **the concentration of CH_3COOH in the mixture is twice the concentration of NaOH.**
 3) For CH_3COONa | HCl mixture: The amount should be taken in such a way that **the concentration of CH_3COONa in the mixture is twice the concentration of HCl**.

14. Dissociation constant of weak acid or weak base present in the buffer system tend to increase as the temperature increases. This means that the weak acid and base dissociate more at higher temperature leaving smaller concentration of undissociated acid or base which in turn decreases reserve acidity or reserve basicity respectively and hence buffer capacity is decreased.

15.

1) **Concentrations of salt and acid:** The pH will be high if the ratio, $\frac{[\text{Salt}]}{[\text{Acid}]}$ is high too. Thus if [Salt] is high compared to [Acid], the pH will be high whereas high [Acid] compared to [Salt] leads to low pH of the solution.
2) **The magnitude of K_a value:** The pH will be high if the magnitude of pK_a value is large. So if the **nature of acid** allows it to have large K_a value due to its high strength, the pK_a value will be small and hence its pH will be small as well. Also **high temperature**, makes K_a value high too and hence (as result of small value of pK_a) low pH.

16. Salt: acid = 6.93: 1 **17.** 36mL

18. (a) Acidic buffer (b) pH = 4.87

19. (a) 0.96gdm^{-3}. **Assumption:** Ionisation of the acid to give anions is negligible and hence all propanoate ions (anions) come from sodium propanoate (salt).(b) 0.85gdm^{-3}

20. (a) pH = 13 (b) (i) 0.05M (ii) 0.05M (iii) 4.74 (iv) The pH remain virtually constant because ethanoate ions from the salt react (combine) with added hydrogen ions and the solution mixture to become a buffer.

21. pH = 4.2 **23.** (a) pH = 4.45 (b) pH = 4.13 (c) pH = 1.52

22. pH = 9.26 **24.** pH = 8.97

EXERCISE 18

1.

(i) The solution would be **neutral** since the conjugate base of a strong acid is a weaker base than water, so the major species (conjugate base of strong acid and cation of strong base) remaining in solution are neutral.
(ii) The solution would be **basic** since the conjugate base of a weak acid is a stronger base than water, so it hydrolyses in water to produce hydroxide ions.
(iii) The solution would be **acidic** since the conjugate acid of a weak base being strong acidic hydrolyses in water to

produce H^+ ions.

2. a) basic b) neutral c) neutral d) acidic e) acidic f) basic

3. The pH of the given solutions is determined by hydrolysis. NaBr being strong ionic salt, does not hydrolyse in water and thus its pH is 7. KCN contains strong base anion and thus it undergoes anionic hydrolysis to give basic solution with pH which is above 7 while NH_4Br having strong acid cation undergoes cationic hydrolysis with pH which is below 7. Hence the arrangement is as follows:

$$\underset{\text{Increase in the pH of solutions}}{\overrightarrow{0.01MNH_4Br, 0.01MNaBr, 0.01MKCN}}$$

4. $0.1MNa_2CO_3$

Reason:

The basic salt has the highest pH and among the given salts only Na_2CO_3 is the basic salt.

5. Since the salt was made from strong base and weak acid, its cation (C^+) is weak acid while anion (D^-) is strong base. Thus the compound undergoes anionic hydrolysis to give basic solution as per equation;

$$D^- + H_2O \longrightarrow HD + OH^-$$

$$\text{Or } CD + H_2O \longrightarrow HD + C^+ + OH^-$$

6. In the aqueous solution, the salt having strong acid cation, undergoes cationic hydrolysis yielding enough concentration of free ions (H^+**(aq)** and Cl^-**(aq)** from HCl**(aq))** which are responsible for doing electrolytic conduction.

i.e. $AlCl_3 + 3H_2O \longrightarrow Al(OH)_3 + 3H^+(aq) + 3Cl^-(aq)$

7. In aqueous solution, NH_4^+ in the salt being strong acid cation, undergoes cationic hydrolysis yielding acidic solution which reacts with $NaHCO_3$ to evolve carbon dioxide gas which appears as effervescence of colourless gas that turns lime water milky.

That is $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$

(From NH_4Br**)**

Then $H^+ + HCO_3^- \rightarrow CO_2 + H_2O$

8. Potassium cyanide contains cyanide ion which is strong base anion (it is conjugate base of HCN which is weak acid) and therefore it undergoes anionic hydrolysis to give basic solution and hence the litmus paper turns blue.

$CN^- + H_2O \rightarrow HCN + OH^-$

9. Sodium methanoate contains methanoate ion which is strong base anion and thus it undergoes anionic hydrolysis to give basic solution and the onion is odourless in basic solution.

$HCOO^- + H_2O \rightarrow HCOOH + OH^-$

10. $(NH_4)_2SO_4$ contains strong acid cation (NH_4^+) and therefore in aqueous solution it undergoes cationic hydrolysis yielding acidic solution which is responsible of evolving hydrogen gas (which produced the 'pop' sound) when magnesium (metal) is introduced in the solution.

That is $NH_4^+ + H_2O \rightarrow NH_4OH + H^+$

Then $2H^+ + Mg \rightarrow Mg^{2+} + H_2$

11. pH $= 5.274$ **13.** pH $= 8.96$ **15.** pH $= 8$

12. pH $= 5.784$ **14.** pH $= 5.13$

16. (a) $NH_4^+ + H_2O \longrightarrow NH_3 + H_3O^+$

A1 **B2** **B1** **A2**

(b) $K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$ (c) pH = 5.1 (d) By adding ammonia solution to make basic buffer solution.

EXERCISE 19

1.

a) Greater: $Zn(OH)_2(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + 2H_2O(l)$

(b) Lower: increased $[Zn^{2+}]$ decreases the amount of dissolved $Zn(OH)_2$ by common ion effect.

(c) It depends on the relative amount of NaOH to that of $Zn(OH)_2$:

In small amount become lower due to common ion effect while when NaOH present in excess become greater due to formation of soluble complex.

$$(Zn(OH)_2(s) + 2OH^-(aq) \longrightarrow [Zn(OH)_4]^{2-}(aq))$$

(d) Greater: this is due to the formation of soluble complex;

$$Zn(OH)_2(s) + 4NH_3(aq) \longrightarrow [Zn(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

2. $K_{sp} = 6.25 \times 10^{-9} mol^3 dm^{-9}$ **3.** $1.28 \times 10^{-35} M$

4. $Q_{sp} = 7.5 \times 10^{-5} M^2$, so precipitate will form since $Q_{sp} > K_{sp}$

5. $Q_{sp} = 5 \times 10^{-7} M^2$, so no precipitate will form since $Q_{sp} < K_{sp}$

6. (a) $2.24 \times 10^{-5} moldm^{-3}$ (b) $5 \times 10^{-9} moldm^{-3}$ **7.** $4.87 \times 10^{-5} M^3$

8. AgBr being highly covalent in character as result of very large polarising power of Ag^+, does not dissolve in water which is polar solvent (it readily form yellow precipitate in water). However, in aqueous ammonia, it tends to form soluble complex which appears to dissolve.

$AgBr(s) + 2NH_3(aq) \rightarrow [Ag(NH_3)_2]^+ + Br^-$

Insoluble Soluble

9. $Cu(OH)_2$ contains strong base anion which is capable of reacting with the acid, HNO_3, to form soluble products. It also contain strong acid cation which is capable of reacting with Lewis base, NH_3, to form soluble complex.

$$Cu(OH)_2(s) + 2HNO_3(aq) \longrightarrow Cu(NO_3)_2(aq) + 2H_2O(l)$$

$$Cu(OH)_2(s) + 4NH_3(aq) \longrightarrow [Cu(NH_3)_4]^{2+}(aq) + 2OH^-(aq)$$

10. Calcium sulphate is sparingly soluble electrolyte whose solubility decreases as the temperature decreases because its dissolution is endothermic. So cooling its saturated solution, lowers its solubility and the solution becomes supersaturated.

On another hand, carbon dioxide is a gas whose solubility decreases as the temperature increases due to high kinetic energy of gas molecules which makes them to escape from the solution. So heating its saturated solution, lowers its solubility and the solution becomes supersaturated.

11. Carbonate ion in calcium is the conjugate base of weak acid and thus it is strong base. Consequently, calcium carbonate is basic salt that react with acids like hydrochloric acid to give clear solution.

$$CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$$

That is opposite to Cl^- which is the conjugate base of strong acid (HCl). Apart from that, the added hydrochloric acid being strong electrolyte with the same ion (Cl^-) as that present in AgCl, it decreases solubility of the silver chloride by common ion effect, leading to the formation of precipitate.

12. Disagree because the two compounds have different number of ions per formula unit; so their K_{sp} values will be different even if their molar solubility product is the same.

Calculation of the solubility product

$$\begin{array}{l} X_2Y(s) \rightleftharpoons 2X^+(aq) + Y^{2-}(aq) \\ \qquad\qquad\quad 2s \qquad\qquad s \end{array}$$

$K_{sp} = [X^+]^2[Y^{2-}] = s(2s)^2 = 4s^3$ or $s = \sqrt[3]{\frac{K_{sp}}{4}}$

Substituting $s = \sqrt[3]{\frac{1.08\times10^{-7}}{4}} = 3 \times 10^{-3} M$

Then;

$$\begin{array}{l} PQ(s) \rightleftharpoons P^+(aq) + Q^-(aq) \\ \qquad\qquad s \qquad\qquad s \end{array}$$

From which; $K_{sp} = [P^+][Q^-] = s^2 = (3 \times 10^{-3})^2 = 9 \times 10^{-6}$

The solubility product of PQ is 9×10^{-6}.

13. (a) $6.08 \times 10^{-4} gcm^{-3}$ (b) $0.8 moldm^{-3}$

14. pH = 12.35

15. (a) $K_{sp} = [Mg^{2+}][OH^-]^2$; Units: mol^3dm^{-9} (b) $1.7 \times 10^{-4}moldm^{-3}$ (c) 99.7%

16. (a) $8.7 \times 10^{-4}M$ (b) $5.8 \times 10^{-4}M$ (c) (i) SrF_2 precipitates first (Hint: solve for $[Sr^{2+}]$ required for precipitation of each salt then compare; whereby the salt with smaller value of the concentration precipitates first) (d) 50%

17. (a) $2.6 \times 10^{-13}M^3$ (b) $1.61 \times 10^{-6}M$ (c) $[IO_3^-] = 0.21M$, $[Pb^{2+}] = 5.8 \times 10^{-12}M$

18. (a) $K_{sp} = [Ba^{2+}][SO_4^{2-}]$; Units: mol^2dm^{-6} (b) $1.14 \times 10^{-5}moldm^{-3}$

(c) $BaCO_3$ can react with HCl in the stomach thus easily dissolves in it according to the following equation:

$$BaCO_3 + 2HCl \longrightarrow BaCl_2 + CO_2 + H_2O$$

SOLUTIONS TO EXAMINATION QUESTIONS

Question 1

(a) **Reason:**

The reaction produces acidic salt which undergoes cationic hydrolysis to give acidic solution.

Explanation

Anion which is the conjugate base of strong acid is the weak base while cation which is the conjugate acid of weak base is the strong acid. So the given reaction, gives a salt containing strong acid cation and weak base anion which undergoes cationic hydrolysis.

(b) Number of moles of base (NaOH) = $\frac{27.1}{1000} \times 0.1\text{mol} = 0.00271\text{mol}$

Thus 0.00271 mole of NaOH reacts with 0.16g of the acid

And $\frac{0.16\times1}{0.00271}\text{g} = 59\text{g of acid reacts with 1mole of NaOH}$

Whence 59g of the acid reacts with 1 mole of NaOH

But 59g is a half mole of acid (one mole of acid has mass of 118g), therefore 1 mole of the acid reacts with 2 moles of NaOH and hence the acid is dibasic.

Question 2

(a) Acidic salts: $FeCl_3$ and NH_4Br

Basic salts: K_2CO_3 and $HCOOK$

Neutral salts: $KClO_4$ and KCl

(b) Number of moles of NaOH in 16.9cm^3 of its solution

$$= \frac{16.9}{1000} \times 0.5 \text{ moles} = 8.45 \times 10^{-3}\text{moles}$$

NaOH reacts with CH_3COOH according to the following equation:

$$NaOH + CH_3COOH \rightleftharpoons CH_3COONa + H_2O$$

From which mole ratio of CH_3COOH to NaOH is 1:1

Thus number of moles of CH_3COOH (in 25cm^3) reacted was also 8.45×10^{-3} moles

It follows that: Number of moles of CH_3COOH in 250cm^3 of its solution (dilute solution formed by mixing 100cm^3 of vinegar and distilled water) = $\frac{8.45\times10^{-3}\times250}{25}$ moles $= 0.0845$moles

Thus number of moles of CH_3COOH in 100cm^3 of vinegar was 0.0845 moles.

Using $m = nM_r$;

Mass of ethanoic acid in 100cm^3 of vinegar = 0.0845 mol $\times$ $60\text{gmol}^{-1} = 5.07\text{g}$

Using mass = Volume $\times$ Density;

Total mass of vinegar in 100cm^3 of its volume = $100\text{cm}^3 \times 1.02\text{gcm}^{-3} = 102\text{g}$

Thus the percentage of $CH_3COOH = \frac{5.07}{102} \times 100\% = 4.97\%$

Hence the percentage by mass of the acid was 4.97%

Question 3

(a) Both cations and anions in salts coming from strong base and strong acid are weak acid and weak base respectively and hence they are incapable of combining with H^+ and OH^- from water, making solution of those salts neutral.

(b) Number of moles of HCl reacted with washing soda = $\frac{30}{1000} \times 0.2 \text{ moles} = 6 \times 10^{-3}\text{moles}$

HCl reacts with washing soda ($Na_2CO_3.xH_2O$) according to the following equation:

$$Na_2CO_3.xH_2O + 2HCl \rightarrow 2NaCl + CO_2 + (x+1)H_2O$$

From which mole ratio of washing soda to HCl is 1:2;

Thus number of moles (in 25cm^3) of washing soda reacted = $\frac{6\times10^{-3}}{2} = 0.003\text{mol}$

So number of moles of the soda in 250cm^3 = $\frac{0.003\times250}{25}\text{mol} = 0.03\text{mol}$

Using $M_r = \frac{m}{n}$;

Molar mass of washing soda = $\frac{8.58\text{g}}{0.03\text{mol}} = 286\text{mol}^{-1}$

It follows that: $(2 \times 23) + 12 + (16 \times 3) + 18x = 286$ or $x = 10$

Hence the value of *x* is 10

Question 4

(a) $PbCO_3$ and CaF_2

(b) The potassium salt is tribasic (presence of three H's) so the mole ratio of the salt to NaOH is 1:3

But number of moles of NaOH reacted = $\frac{22.7}{1000} \times 1\text{mol} = 0.0227\ \text{mol}$

Thus number of moles of the salt reacted = $\frac{0.0227}{3}\text{mol} = 0.00757\text{mol}$

Using $M_r = \frac{m}{n}$;

Molar mass of the salt = $\frac{1.923\text{g}}{0.00757\text{mol}} = 254\text{g/mol}$

Then $2 + 24 + 64 + 39 + 1 + 24 + 64 + 18x = 254$ or $x = 2$

Hence the value of *x* is 2.

Question 5

(a) Salt dissolve slowly in water if:

1) The water is cold.
2) The water already contains high concentration of salt.
3) The salt has not been finely ground.
4) The mixture of salt and water is not stirred.

(b) Since the resulting solution was neutralised by the base (NaOH), the solution was acidic and HCl was excess in its reaction with $CaCO_3$ of limestone.

Number of moles of NaOH reacted = $\frac{21.05}{1000} \times 0.1\text{mol} = 2.105 \times 10^{-3}\text{moles}$

NaOH reacts with HCl according to the following equation:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

From which mole ratio of NaOH to HCl is 1:1

Thus number of moles HCl in 25cm^3 to the solution is also 2.105×10^{-3}moles.

And number of moles of the unreacted HCl in the reaction with $CaCO_3$ was $\frac{2.105 \times 10^{-3} \times 250}{25}\ \text{mol} = 0.02105\text{mol}$.

But total number of moles of HCl before the reaction with $CaCO_3 = \frac{50}{1000} \times 1\text{mol} = 0.05\text{mol}$

Then number of moles of HCl reacted with $CaCO_3$= $(0.05 - 0.02105)\text{mol} = 0.02895\text{mol}$

$CaCO_3$ reacts with HCl according to the following equation:

$$2HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$$

From which mole ratio of HCl to $CaCO_3$ is 2:1

Thus number of moles of $CaCO_3$ reacted = $\frac{0.02895}{2}\text{mol} = 0.014475\text{mol}$

Using $m = nM_r$;

Mass of $CaCO_3$ in 1.5g of limestone = 0.014475 × 100g = 1.4475g

So % $CaCO_3 = \frac{1.4475}{1.5} \times 100\% = 96.5\%$

Hence the percentage of $CaCO_3$ present was 96.5%

Question 6

(a) NaCl contains weak acid cation and weak base anion as it is formed from strong base and strong acid. Consequently, neither Na^+ can react with base nor Cl^- can react with base and hence NaCl is incapable of eliminating added acid or base so to resist pH change which is the main purpose of buffer.

(b) Number of moles of NaOH reacted with excess acid = $\frac{30}{1000} \times 1\text{mol} = 0.03\text{mol}$

NaOH reacts with HCl according to the following equation:

$$NaOH + HCl \rightarrow NaCl + H_2O$$

From which mole ratio of NaOH to HCl is 1:1

Thus number of moles of excess acid was also 0.03mol

But number of moles of HCl before the reaction with carbonate = $\frac{50}{1000} \times 1\ \text{mol} = 0.05\ \text{mol}$

Thus number of moles of HCl reacted with the carbonate = $(0.05 - 0.03)\text{mol} = 0.02\ \text{mol}$

If X is divalent metal, the formula of its carbonate is XCO_3

The carbonate reacts with HCl according to the following equation:

$$2HCl + XCO_3 \rightarrow XCl_2 + CO_2 + H_2O$$

From which mole ratio of HCl to XCO_3 is 2:1

Therefore number of mole of XCO_3 reacted = $\frac{0.02}{2}$ mol $= 0.01$ mol

Using $M_r = \frac{m}{n}$;

Molar mass of the carbonate = $\frac{1g}{0.01mol} = 100g/mol$

The molecular mass of X is 100g/mol

Then $X + 12 + (16 \times 3) = 100$ or $X = 40$

Hence the relative atomic mass of X is 40

Question 7

(a) Combinations which gives buffer are:

$$NaHCO_3 \text{ and } Na_2CO_3, NH_4NO_3 \text{ and } NH_3$$

(b) Number of moles of HCl reacted with excess alkali = $\frac{25.4}{1000} \times 0.1 \text{ mol} = 0.00254\text{mol}$

NaOH reacts with HCl such that their mole is 1:1;

Thus number of moles of excess alkali (NaOH) was also 0.00254mol

But number of moles of NaOH before reaction with $(NH_4)_2SO_4 = \frac{50}{1000} \times 0.1\text{mol} = 0.005\text{mol}$

So number of moles of NaOH reacted with $(NH_4)_2SO_4$ = $(0.005 - 0.00254)\text{mol} = 0.00246\text{mol}$

NaOH reacts with $(NH_4)_2\ SO_4$ according to the following equation:

$$(NH_4)_2SO_4 \ + \ 2NaOH \ \rightarrow \ Na_2SO_4 \ + 2H_2O \ + 2NH_3$$

From which mole ratio of $(NH_4)_2SO_4$ to NaOH is $1:2$

Thus number of moles of $(NH_4)_2SO_4$ in $25cm^3$ reacted with NaOH = $\frac{0.00246}{2}$ mol $= 0.00123$ mol

So number of moles of $(NH_4)_2SO_4$ in $250cm^3$ = $\frac{0.00123 \times 250}{25}$ mol $= 0.0123$ mol

And mass of ammonium sulphate = $0.0123 \times 132g = 1.6236g$

$\%(NH_4)_2SO_4 = \frac{1.6236}{1.65} \times 100\% = 98.4\%$

Hence the percentage of ammonium sulphate is 98.4%.

Question 8

(a) It is incapable of producing enough concentration of conjugate base to eliminate added acid.

(b) From related equations of reactions of previous related problems:

Volume of acid required to titrate $Na_2CO_3 = 2(22.7 - 18.6)cm^3 = 8.2cm^3$

Volume of acid required to titrate NaOH = $(22.7 - 8.2)cm^3 = 14.5cm^3$

Number of moles of HCl reacted with $Na_2CO_3 = \frac{8.2}{1000} \times 0.1\text{mol} = 0.00082\text{mol}$

But mole ratio of Na_2CO_3 to HCl is $1:2$

Thus number of moles of Na_2CO_3 reacted $= \frac{0.00082\text{mol}}{2} = 0.00041\text{mol}$

Mass concentration of $Na_2CO_3 = \frac{0.00041 \times 1000 \times 106gdm^{-3}}{25} = 1.7384gdm^{-3}$

Hence mass concentration of sodium carbonate was $1.7384gdm^{-3}$

Number of moles of acid (HCl) reacted with NaOH = $\frac{14.5}{1000} \times 0.1\text{mol} = 0.00145\text{mol}$

But mole ratio of NaOH to HCl is 1:1

Thus number of moles of NaOH reacted was also 0.00145mol

And its mass concentration = $\frac{0.00145 \times 1000 \times 40}{25} gdm^{-3} = 2.32gdm^{-3}$

Hence mass concentration of sodium hydroxide was $2.32gdm^{-3}$

And mass concentration of sodium carbonate was $1.7384gdm^{-3}$

Question 9

(i) For CH_3COOH: $[H^+] = \alpha C = \sqrt{CK_a}$; $pH = -\log[H^+] = -\log\sqrt{0.05 \times 1.8 \times 10^{-5}} = 3$
Thus the pH of 0.05M CH_3COOH is 3

(ii) For HCl:

$$\underset{\mathbf{0.05M}}{HCl\,(aq)} \rightarrow \underset{\mathbf{0.05M}}{H^+(aq)} + Cl^-(aq)$$

$pH = -\log[H^+] = -\log 0.05 = 1.3$

Thus the pH of 0.05MHCl is 1.3

Comment: pH of HCl is smaller than that of CH_3COOH because HCl is stronger acid and ionises completely in the solution to give greater concentration of hydrogen ions.

Question 10

From Ostwald dilution's law; $\alpha = \sqrt{\frac{K_b}{C}}$

(a) From which; $K_b = \alpha^2 C = \left(\frac{1.4}{100}\right)^2 \times 0.1M = 1.96 \times 10^{-5}$

Thus the dissociation constant of the base is 1.96×10^{-5}

$pK_b = -\log K_b = -\log 1.96 \times 10^{-5} = 4.7$

Hence pK_b of the base is 4.7

(b) When C = 0.002M:

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.96 \times 10^{-5}}{0.002}} = 0.099 \text{ or } 9.9\%$$

Thus the degree of dissociation of $0.002MNH_3(aq)$ is 9.9%

$[OH^-] = \alpha C$; then $pOH = -\log[OH^-] = -\log(0.002 \times 0.099) = 3.7$

But $pH = 14 - pOH = 14 - 3.7 = 11.3$

Hence pH of the ammonia solution is 10.3.

Question 11

(a) Sulphuric acid being strong acid ionises completely in the aqueous solution and hence in such mixture there is no formation of dynamic equilibrium which is the fundamental requirement for buffer to function.

(b) CH_3COO^- is conjugate base of CH_3COOH; so their K_b and K_a respectively are related by the following equation:

$K_aK_b = 10^{-14}$

From which, K_a of $CH_3COOH = \frac{10^{-14}}{K_b \text{ of } CH_3COO^-} = \frac{10^{-14}}{5.025 \times 10^{-10}} = 1.99 \times 10^{-5}$

Then from Ostwald dilution law: $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{1.99\times10^{-5}}{0.01}} = 0.045 \text{ or } 4.5\%$

Thus the degree of ionisation of CH_3COOH is 4.5%

Using; $[H^+] = \alpha C$, then $pH = -\log[H^+] = -\log\alpha C = -\log(0.045 \times 0.01) = 3.35$

Hence pH of the solution is 3.35.

Question 12

(a) Yes, it affects.

Explanation

Both K_a and K_b values increase as temperature increases. This implies that pK_a and pK_b values decrease as temperature increases and hence the increase in temperature decreases pH of acidic buffer solution and increases pH of basic buffer solution.

(b) **"Solubility of benzoic acid in water at 0˚C is 2.44gdm^{-3}"** means **saturated solution** of benzoic acid in water contains 2.44g benzoic acid in $1dm^3$.

Taking density of water as $1g/cm^3$ or $1000g/dm^3$; mass of water in dm^3 of its volume is;

$\rho V = 1000gdm^{-3} \times 1dm^3 = 1000g$ or 1kg.

And molar mass of benzoic acid(C_6H_5COOH) is 122g/mol

Then number of moles of the acid in 1kg of the solvent (water) $= \frac{2.44g}{122gmol^{-1}} = 0.02mol$

Hence molality of the saturated solution of benzoic acid is 0.02mol/kg

Freezing point depression, ΔT of water in the solution = $0°C - (-0.0392°C)$ = 0.0392˚C

When there is dissociation of the solute in the solvent:

$$\Delta T = iK_fm \text{ or } i = \frac{\Delta T}{K_fm} = \frac{0.0392}{1.86 \times 0.02} = 1.054$$

But in the solution benzoic acid ionises according to the following equation:

$C_6H_5COOH(aq) \rightleftharpoons C_6H_5COO^-(aq) + H^+(aq)$; N = 2

Then $\alpha = \frac{i-1}{N-1} = \frac{1.054-1}{2-1} = 0.054 \text{ or } 5.4\%$

Thus the degree of dissociation of benzoic acid in the saturated is 0.054 or 5.4%

From Ostwald's dilution law: $\alpha = \sqrt{\frac{K_a}{C}}$

From which $K_a = \alpha^2 C$

But for very dilute solution of the water as a solvent: Molality = Molarity

Thus Molarity of saturated solution of the acid is 0.02M

Then $K_a = (0.054)^2 \times 0.02\ moldm^{-3} = 5.832 \times 10^{-5} moldm^{-3}$

Hence dissociation constant for the acid is $5.832 \times 10^{-5} moldm^{-3}$

Question 13

(a) It is possible.

Explanation

CH_3COONa reacts with HCl to give CH_3COOH. Thus when CH_3COONa present in excess, the unreacted CH_3COONa and the produced CH_3COOH will form acidic buffer solution.

$$CH_3COONa\ (Excess) + HCl \longrightarrow CH_3COOH + NaCl$$

(b) In the solution, ethanoic acid ionises according to the following equation:

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

From which: $K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]}$ or $[H_3O^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$

Introducing –log both sides; $-\log[H_3O^+] = -\log\frac{K_a[CH_3COOH]}{[CH_3COO^-]}$

Or $-\log[H_3O^+] = -\log K_a + -\log\frac{[CH_3COOH]}{[CH_3COO^-]}$

Thus $pH = pK_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$

When $[CH_3COO^-] = [CH_3COOH], \log\frac{[CH_3COO^-]}{[CH_3COOH]} = \log 1 = 0$ and therefore $pH = pK_a$

Hence pH of ethanoic acid solution will be equal to its pK_a, if the concentration of undissociated ethanoic acid is equal to the concentration of the dissociated acid i.e. if the acid has dissociated to 50%.

Question 14

(a) A buffer is a solution that contains either a large amount of weak acid and its conjugate base or a large amount of weak base and its conjugate acid.

Both of these buffers use the same principle such as: in a weak acid- conjugate base buffer solution, if an acid is added, the conjugate base neutralizes it. If a base is added to the buffer, then, the weak acid neutralizes it and vice-versa.

If at the end, the conjugate base/weak acid ratio does not change much, the value of the pH of the solution does not change much.

(b) H_nA being weak acid ionises according to the following equation:

$$H_nA + nH_2O \rightleftharpoons nH_3O^+ + A^{n-}$$

From which mole ratio of A^{n-} to H_3O^+ is 1: n;

Thus $[A^{n-}] = \frac{1}{n}[H_3O^+]$

And $K_a = \frac{[A^{n-}][H_3O^+]^n}{[H_nA]} = \frac{[H_3O^+][H_3O^+]^n}{n[H_nA]}$ or $K_a = \frac{[H_3O^+]^{n+1}}{n[H_nA]}$ or $[H_3O^+]^{n+1} = nK_a[H_nA]$

But $[H_nA] = C$; then $[H_3O^+]^{n+1} = nK_aC$

Hence $[H_3O^+] = \sqrt[n+1]{nCK_a}$

Question 15

(a) When sparingly soluble substance dissolves heat is absorbed from the surroundings. So the equilibrium reaction $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$ is endothermic. Being endothermic, the rise in temperature shifts position of equilibrium to the right by dissolving more AgCl(s) and this is reflected by the increase in value of K_{sp}.

(b) The mixture of ethanoic acid and sodium ethanoate is acidic of a buffer solution whose P^H value is given by the following equation: $P^H = P^{K_a} + \log\frac{[salt]}{[acid]}$

But $[Salt] = [CH_3COONa] = 0.2M$, $[Acid] = [CH_3COOH] = 0.02M$

And $pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = 4.7$; then $pH = 4.7 + \log\left(\frac{0.2}{0.02}\right) = 5.7$

Hence pH of the solution 5.7

Question 16

(a) (i) Buffer solution cannot maintain its pH value in any amount of acid/base. Buffer solution can only maintain its pH on addition of small amount of acid or base without exceeding its buffer capacity.

(ii) Basically common ion effect is the depression of ionization of weak electrolyte which is not necessary accompanied with depression in solubility. Adding strong electrolyte like HCl and NaOH in weak acid or weak base like CH_3COOH and NH_3 merely depress their ionization without affecting their solubility because their dissolution process is not based on ionisation. (Only for salts decrease in ionisation leads to decrease in solubility).

(b) Let the required volume in cm^3 be V

Then by using;

$pH = pK_a + \log\frac{\text{Number of moles of HCOONa (Salt)}}{\text{Number of moles of HCOOH (Acid)}}$; 5 = -log $1.6 \times 10^{-4} + \log\frac{0.1V}{100\times0.01}$

From which V = 160

Hence volume of HCOONa is $160cm^3$

Question 17

(a) Acid is any hydrogen containing specie which is capable of donating one or more hydrogen proton to a base.

Base is any specie which is capable of accepting one or more hydrogen proton from an acid.

Advantages of Bronsted-Lowry theory

1. It expands the list of potential acids and bases to include positive and negative ions as well as species with lone pair.
2. It explains the role of water in acid-base reaction where it accepts H^+ from acid to form H_3O^+.
3. It expands to include solvent other than water and reactions which occur in the gas or solid phase.
4. It explains the difference in relative strength of a pair of acid and a pair of base.

(b) Chloroethanoic acid reacts with NaOH according to the following equation:

$$CH_2ClCOOH + NaOH \rightarrow CH_2ClCOONa + H_2O$$

From which mole ratio of the acid to NaOH is 1:1

Number of moles of NaOH taken $= \frac{100}{1000} \times 0.25\text{moles} = 2.5 \times 10^{-2}\text{moles}$

Number of moles of $CH_2ClCOOH$ taken $= \frac{100}{1000} \times 0.5\text{moles} = 5 \times 10^{-2}\text{moles}$

Thus $CH_2ClCOOH$ is in excess and $(5 \times 10^{-2} - 2.5 \times 10^{-2})$ moles = 2.5×10^{-2}moles of it remain unreacted at the end of the reaction.

Number of moles of $CH_2ClCOONa$ formed is 2.5×10^{-2}moles

(NaOH is limited reactant, so amount of $CH_2Cl\ COONa$ formed is deduced from it).

So at the end of chemical reaction, there are 2.5×10^{-2}moles of formed $CH_2ClCOONa$ and

2.5×10^{-2}moles of unreacted $CH_2ClCOOH$.

The formed $CH_2ClCOONa$ and unreacted $CH_2ClCOOH$ forms acidic buffer solution whose pH value is given by the following equation: $pH = pK_a + \log\frac{\text{Number of moles of salt } (CH_2Cl\ COONa)}{\text{Number of moles of acid } (CH_2Cl\ COOH)}$

Substituting $pH = 2.86 + \log\left(\frac{2.5\times10^{-2}}{2.5\times10^{-2}}\right) = 2.86$

Hence pH of the buffer solution is 2.86.

Question 18

(a) $HCN + H_2O \rightleftharpoons H_3O^+ + CN^-; K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$

From which $[H_3O^+] = \frac{K_a[HCN]}{[CN^-]}$

Where$[CN^-] = [NaCN]$, because the salt is fully ionised while HCN being very weak acid is only partially ionised to give CN^-

Substituting $[H_3O^+] = \frac{4.93\times10^{-10}\times0.1}{0.8}M = 6.1625 \times 10^{-11}M$

Hence the concentration of H_3O^+ is $6.1625 \times 10^{-11}M$

Alternative solution

Using $pH = pK_a + \log\frac{[salt]}{[acid]}$; Where $[Salt] = [NaCN] = 0.8M$, $[Acid] = [HCN] = 0.1M$

And $pK_a = -\log K_a = -\log 4.93 \times 10^{-10} = 9.3$; So $pH = 9.3 + \log\frac{0.8}{0.1} = 10.2$

But $[H_3O^+] = \log^{-1}(-pH) = \log^{-1}(-10.2) = 6.31 \times 10^{-11}M$

Thus the concentration of H_3O^+ is $6.31 \times 10^{-11}M$

(b) After addition of 0.1mole of HCl:

$[CN^-] = \frac{(0.8-0.1)mol}{1dm^3} = 0.7M$ and $[HCN] = \frac{(0.1+0.1)mol}{1dm^3} = 0.2M$

Then from $[H_3O^+] = \frac{K_a[HCN]}{[CN^-]}$

Then new $[H_3O^+] = \frac{4.93\times10^{-10}\times0.2}{0.7}M = 1.41 \times 10^{-10}M$

After addition of 0.02mole of NaOH:

$[CN^-] = \frac{(0.8+0.02)mol}{1dm^3} = 0.82M$ and $[HCN] = \frac{(0.1-0.02)mol}{1dm^3} = 0.08M$

Using $pH = pK_a + \log\frac{[CN^-]}{[HCN]} = 9.3 + \log\left(\frac{0.82}{0.08}\right) = 10.31$

Hence the pH after addition of the NaOH is 10.31

Question 19

(i) Let the solubility of $Mg(OH)_2$ in water be s in $moldm^{-3}$

Then $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

$$\text{s} \qquad\qquad 2\text{s}$$

$K_{sp} = [Mg^{2+}][OH^-]^2$

Substituting $1.1 \times 10^{-11} = (s)(2s)^2 = 4s^3$

Or $s = \sqrt[3]{\frac{1.1 \times 10^{-11}}{4}} = 1.4 \times 10^{-4}$ moldm^{-3}

Solubility in gdm^{-3} $= 1.4 \times 10^{-4} \times 58$gdm^{-3} $= 8.12 \times 10^{-3}$gdm^{-3}

Thus the solubility of $Mg(OH)_2$ in H_2O is 8.12×10^{-3}gdm^{-3}

(ii) Let the solubility of $Mg(OH)_2$ in 0.1MNaOH be y in moldm^{-3}

Then $Mg(OH)_2(s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq)$

$$s' \qquad\qquad 2s' + 0.1 \approx 0.1$$

$K_{sp} = [Mg^{2+}][OH^-]^2$

Substituting $1.1 \times 10^{-11} = y \times 0.1^2$ or $y = 1.1 \times 10^{-9}$moldm^{-3}

Solubility in gdm^{-3} $= 1.1 \times 10^{-9} \times 58$gdm^{-3} $= 6.38 \times 10^{-8}$gdm^{-3}

Question 20

(i) Molar solubility of $PbSO_4 = \frac{\text{Solubility of } PbSO_4 \text{ in gdm}^{-3}}{\text{Molar mass of } PbSO_4}$

$= \frac{0.4}{303}$ moldm^{-3} $= 1.32 \times 10^{-3}$ moldm^{-3}

Then $PbSO_4(s) \rightleftharpoons Pb^{2+}(aq) + SO_4^{2-}(aq)$

From which $[Pb^{2+}] = [SO_4^{2-}] = 1.32 \times 10^{-3}$ moldm^{-3}

$K_{sp} = [Pb^{2+}]\,[SO_4^{2-}] = (1.32 \times 10^{-3}\ \text{moldm}^{-3})^2 = 1.7424 \times 10^{-6}\ \text{mol}^2\ \text{dm}^{-6}$

(ii) Hence the solubility product of $PbSO_4$ was 1.7424×10^{-6} mol^2 dm^{-6}

Let the solubility of $PbSO_4$in 0.01M Na_2SO_4 be s

Then $[Pb^{2+}] = s$

$[SO_4^{2-}] = s + 0.01 \approx 0.01$

Then $1.7424 \times 10^{-6} = 0.01s$ or $s = 1.7424 \times 10^{-4}$ moldm^{-3}

But solubility in gdm^{-3} = Molar solubility × Molar mass = $1.7424 \times 10^{-4} \times 303$gdm^{-3} = 0.053gdm^{-3}

Hence the solubility of $PbSO_4$ in 0.01MNa_2SO_4 is 0.053gdm^{-3}

Question 21

(a) Let the solubility of silver chloride in water be s in moldm^{-3}

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

$$s \qquad\qquad s$$

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

Then $1 \times 10^{-10} = s^2$ or $s = \sqrt{1 \times 10^{-10}} = 10^{-5}$ moldm^{-3}

Solubility AgCl in gdm^{-3} $= 10^{-5} \times 143.5$gdm^{-3} $= 1.435 \times 10^{-3}$ gdm^3

Thus maximum mass of AgCl which goes into solution as ions in 1dm^3

$= 1.435 \times 10^{-3}$ gdm^{-3} $\times$ 1dm^3 $= 1.435 \times 10^{-3}$g

Hence maximum loss from the precipitate is 1.435×10^{-3}g

(b) HCl being strong electrolyte, ionises according to the following equation:

$HCl(aq) \rightarrow H^+(aq) + Cl^-(aq)$

0.01mol $\qquad\qquad$ 0.01mol

Thus if s' is the molar solubility of AgCl in 0.01MHCl;

$[Ag^+] = s'$; $[Cl^-] = s' + 0.01 \approx 0.01$

Then $10^{-10} = 0.01s'$ or $s' = 10^{-8}$ moldm^{-3}

Solubility of AgCl in gdm^{-3} $= 10^{-8} \times 143.5 = 1.435 \times 10^{-6}$ gdm^{-3}

Thus, the maximum mass of AgCl which goes into the solution as dissolved ions in 1dm^3 of the solution

$= 1.435 \times 10^{-6}$ gdm^{-3} $\times$ 1dm^3 $= 1.435 \times 10^{-6}$g

Hence the mass of silver chloride lost by washing with 1dm^3 of 0.01MHCl is 1.435×10^{-6}g

Question 22

(a) In molten state (anhydrous form), $AlCl_3$ has no enough concentration of ions for doing electrolytic conduction as result of its high degree of polarisation. But in aqueous solution the salt undergoes cationic hydrolysis yielding enough concentration of free ions ($H^+(aq)$ and $Cl^-(aq)$) which are responsible for electrolytic conduction.

i.e. $AlCl_3 + 3H_2O \rightarrow Al(OH)_3 + 3H^+(aq) + 3Cl^-(aq)$

(b) If s is the solubility of AgCl in water (before addition of NaCl);

Then K_{sp} of AgCl $= [Ag^+][Cl^-] = s^2$

From which $x = \sqrt{K_{sp}} = \sqrt{1.69 \times 10^{-10}} = 1.3 \times 10^{-5}M = 1.3 \times 10^{-5} \times 143.5gdm^{-3}$

$= 1.8655 \times 10^{-3}gdm^{-3}$

Number of moles of NaCl in 5.85g of its mass $= \frac{5.85g}{58.5gmol^{-1}} = 0.1mol$

NaCl being strong electrolyte ionises completely according to the following equation:

$$\begin{array}{ccc} NaCl \rightarrow & Na^+ & + Cl^- \\ & 0.1mol & 0.1mol \end{array}$$

Then new: $[Cl^-] = s' + 0.1 \approx 0.1M$; $[Ag^+] = s'$

Where y is the solubility of AgCl after introducing AgCl to the solution

$K_{sp} = [Ag^+][Cl^-] = 0.1y = 1.69 \times 10^{-10}; y = 1.69 \times 10^{-9}M = 1.69 \times 10^{-9} \times 143.5gdm^{-3}$
$= 2.42515 \times 10^{-7}gdm^{-3}$

Thus the solubility of AgCl decreased from $1.8655 \times 10^{-3}gdm^{-3}$ to $2.42515 \times 10^{-7}gdm^{-3}$ after introducing 5.85g of NaCl. The difference is the mass of AgCl precipitate formed in a litre of solution.

That is$(1.8655 \times 10^{-3} - 2.42515 \times 10^{-7})g = 1.865 \times 10^{-3}g$ of AgCl precipitate was formed

Hence $1.865 \times 10^{-3}g$ of silver chloride will be precipitated in a litre of the solution

Question 23

In aqueous solution, NaF undergoes anionic salt hydrolysis according to the following equation: $NaF + H_2O \rightleftharpoons HF + NaOH$

The above equation can be written ionically as: $F^- + H_2O \rightleftharpoons HF + OH^-$

From which $K = \frac{[HF][OH^-]}{[F^-]}$

Where K stands for dissociation constant.

But $[HF] = [OH^-]$

Then $K = \frac{[OH^-]^2}{[F^-]}$

$[OH^-] = \sqrt{K[F^-]}$

Then $pOH = -\log[OH^-] = -\log\sqrt{K[F^-]}$

Where $[F^-] = [NaF] = 0.25M$(Since K is very small)

$pOH = -\log\sqrt{1.5 \times 10^{-11} \times 0.25} = 5.7$

Using $pH = 14 - pOH$ $(pH + pOH = 14)$

$= 14 - 5.7 = 8.3$

Hence the pH of 0.25M NaF is 8.3

In solution, NH_3 ionises according to the following equation:

$$\begin{array}{ccc} NH_3 + H_2O \rightleftharpoons & NH_4^+ & + OH^- \\ & \alpha c & \alpha c \end{array}$$

Where $[OH^-] = \alpha c$ and $pOH = -\log[OH^-]$

But from Ostwald's dilution law; $\alpha = \sqrt{\frac{K_b}{c}}$

Then $[OH^-] = C\sqrt{\frac{K_b}{c}} = \sqrt{CK_b}$

$pOH = -\log\sqrt{CK_b}$

where $K_b = 1.77 \times 10^{-5}$ and $C = 0.01M$

Substituting $pOH = -\log\sqrt{0.01 \times 1.77 \times 10^{-5}} = 3.34$

Then $pH = 14 - pOH$ $(pH + pOH = 14)$

$= 14 - 3.38 = 10.62$

Hence the pH of $0.01M\ NH_3(aq)$ is 10.62

Question 24

(a) Molar solubility of $Fe(OH)_2 = \frac{0.6 \times 10^{-3} gdm^{-3}}{90 gmol^{-1}} = 6.67 \times 10^{-6}$ moldm^{-3}

If s is the molar solubility of $Fe(OH)_2$

Then $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$

$\quad\quad\quad\quad\quad\quad\quad\quad s \quad\quad\quad 2s$

(b) From which $K_{sp} = [Fe^{2+}][OH^-]^{2-} = s(2s)^2 = 4s^3$

But s = 6.67×10^{-6} moldm^{-3}

Thus $K_{sp} = 4 \times (6.67 \times 10^{-6} \text{ moldm}^{-3})^3 = 1.19 \times 10^{15} \text{ mol}^3 \text{ dm}^{-9}$

There fore K_{sp} value of $Fe(OH)_2$ is $1.19 \times 10^{15} \text{ mol}^3\text{dm}^{-9}$

From $K_{sp} = [Fe^{2+}][OH^-]^2$; $[OH^-] = \sqrt{\frac{K_{sp}}{[Fe^{2+}]}}$

But $[Fe^{2+}] = \frac{10^{-6}}{56} M = 1.786 \times 10^{-8} M$

Then $[OH^-] = \sqrt{\frac{1.19 \times 10^{-15}}{1.786 \times 10^{-8}}} = 2.58 \times 10^{-4} M$

$pOH = -\log[OH^-] = -\log(2.58 \times 10^{-4}) = 3.6$

And pH = 14 – pOH = 14 – 3.6 = 10.4

Hence the minimum pH required is 10.4

Question 25

(a) Since the solubility product $BaSO_4$ is smaller than that of $CaSO_4$and the two compounds (salts) have similar formula with the same proportions of constituent then $BaSO_4$ will first precipitate.

(b) The first solid to precipitate is $BaSO_4$ whose K_{sp} is given by; $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

From which; $[SO_4^{2-}] = \frac{K_{sp}}{[Ba^{2+}]}$; but $[Ba^{2+}] = 0.1M$

Whence $[SO_4^{2-}]$ $\frac{1.1 \times 10^{-10}}{0.1} M = 1.1 \times 10^{-9} M$

Thus the molar concentration of SO_4^{2-} at the instant the first solid precipitate is $1.1 \times 10^{-9} M$

(c) For $CaSO_4$; $K_{sp} = [Ca^{2+}][SO_4^{2-}]$

From which $[SO_4^{2-}] = \frac{K_{sp}}{[Ca^{2+}]} = \frac{2.4 \times 10^{-5}}{0.1} = 2.4 \times 10^{-4} M$

But from $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

Thus $[SO_4^{2-}]$ when first precipitate of $CaSO_4$ occurs is $2.4 \times 10^{-4} M$

$$[Ba^{2+}] = \frac{K_{sp}}{[SO_4^{2-}]} = \frac{1.1 \times 10^{-10}}{2.4 \times 10^{-4}} = 4.58 \times 10^{-7} M$$

Hence concentration of Ba^{2+} present when the first precipitate of $CaSO_4$occurs is $4.58 \times 10^{-7} M$

Question 26

(a)

(i) Solubility is the ability of a certain solute to be dissolved in a given solvent which is given as the amount of substance dissolved in one litre of saturated solution at given temperature.
(ii) Saturated solution is the solution which cannot dissolve more solute without forming a precipitate at given temperature.
(iii) Saturated point is the point at which a liquid cannot take up more of the solute at given temperature.
(iv) Supersaturated solution is the solution with more solute beyond its saturated point.
(v) Fractional precipitation is the method for separating elements or compounds with similar solubility by a series of analytical precipitations, each one improving the purity of the desired element.

(b) Chloride, Cl^-, reacts with Ag^+ (from $AgNO_3$) according to the following equation:

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

The end point is obtained when $[Ag^+][Cl^-] = K_{sp}$ of AgCl at which $[Ag^+] = [Cl^-]$

Thus K_{sp} of AgCl = $[Ag^+]^2$

Using potassium chromate (K_2CrO_4) as an indicator, the end point is obtained when the precipitate of Ag_2CrO_4 (silver chromate) starts to form.

i.e. $Ag_2CrO_4(s) \rightleftharpoons 2Ag^+(aq) + CrO_4^{2-}(aq)$

From which K_{sp} of $Ag_2CrO_4 = [Ag^+]^2[CrO_4^{2-}]$

Taking; $\frac{K_{sp} \text{ of } Ag_2CrO_4}{K_{sp} \text{ of } AgCl} = \frac{[Ag^+]^2[CrO_4^{2-}]}{[Ag^+]^2}$

Substituting $[CrO_4^{2-}] = \frac{1 \times 10^{-12} \text{ mol}^3\text{dm}^{-9}}{1 \times 10^{-10} \text{ mol}^2\text{dm}^{-6}} = 10^{-2}$ moldm^{-3}

But potassium chromate (K_2CrO_4) ionises according to the following equation:

$$K_2CrO_4 \rightarrow 2K^+ + CrO_4^{2-}$$

From which mole ratio of K_2CrO_4 to CrO_4^{2-} is 1:1 and therefore; $[K_2CrO_4] = [CrO_4^{2-}]$

Hence the concentration of potassium chromate at the end point is 10^{-2} moldm^{-3}.

Question 27

(i) Water undergo self-ionization according to the following equation:

$2H_2O \rightleftharpoons H_3O^+ + OH^-$

Where $[OH^-] = [H_3O^+]$

Then $K_w = [OH^-][H_3O^+] = [H_3O^+]^2$; $[H_3O^+] = \sqrt{K_w}$

And $pH = -\log[H_3O^+] = -\log\sqrt{K_w}$

But at 30°C; $K_w = 1.471 \times 10^{-14}$

Substituting $pH = -\log\sqrt{1.471 \times 10^{-14}} = 6.9$

Hence the pH of water at 30°C is 6.9

(ii) Since both KOH and HCl are strong base and acid respectively, they give **neutral solution** at the equivalence point.

And for neutral solution; $[OH^-] = [H_3O^+]$

Then $K_w = [OH^-][H_3O^+] = [H_3O^+]^2$; $[H_3O^+] = \sqrt{K_w}$

And $pH = -\log[H_3O^+] = -\log\sqrt{K_w}$

Where at 10°C, $K_w = 0.293 \times 10^{-14}$

Substituting $pH = -\log\sqrt{0.293 \times 10^{-14}} = 7.3$

Hence the pH at equivalence point is 7.3.

Question 28

(i) HA reacts with NaOH according to the following equation: $HA + NaOH \rightarrow NaA + H_2O$

To make the solution with $pH = 6$ (acidic solution), the acid HA must be in excess.

But if the weak acid HA and produced NaA forms acidic buffer solution whose pH value is given by the following equation:

$pH = pK_a + \log\frac{[Salt]}{[Acid]}$; where $[Salt] = [NaA]$ and $[Acid] = [HA]$

Thus $pH = pK_a + \log\frac{[NaA]}{[HA]}$; $6 = 6 + \log\frac{[NaA]}{[HA]}$

From which $\frac{[NaA]}{[HA]} = \log^{-1}(0) = 1$

Whence $[NaA] = [HA]$ (after the reaction) for the solution to have pH of 6

Let volume of HA taken be V_{HA} and volume of NaOH taken to V_{NaOH}

Using $n = MV$; $n_{HA} = 0.1V_{HA}$ and $n_{NaOH} = 0.1V_{NaOH}$

Then from mole ratio of the reaction equation:

n_{NaA} produced $= 0.1V_{NaOH}$

n_{HA} unreacted $= 0.1V_{HA} - 0.1V_{NaOH}$

Using $[\ ] = \frac{n}{V}$ and $[HA]$ unreacted $= [NaA]$ produced

$$\frac{0.1V_{HA} - 0.1V_{NaOH}}{V_{HA} + V_{NaOH}} = \frac{0.1V_{NaOH}}{V_{HA} + V_{NaOH}}$$

From which; $0.1V_{HA} = 0.2V_{NaOH}$ or $V_{HA} = 2V_{NaOH}$

Hence to prepare the solution with pH of 6, the volume of HA solution mixed must be twice the volume of NaOH mixed.

(ii) Also from $pH = pK_a + \log\frac{[NaA]}{[HA]}$

If $pH = 5$; $5 = -\log(1 \times 10^{-6}) + \log\frac{[NaA]}{[HA]}$

$-1 = \log\frac{[NaA]}{[HA]}$; $\frac{[NaA]}{[HA]} = 0.1$

Whence after the reaction; $[NaA] = 0.1[HA]$; for the pH to be 5; n_{HA} mixed $= 0.1V_{HA}$

n_{NaOH} mixed $= 0.1V_{NaOH} = n_{NaA}$ produced (NaOH was limited reactant)

n_{HA} unreacted $= (0.1V_{HA} - 0.1V_{NaOH})$

But $[NaA]$ produced $= 0.1 \times [HA]$ unreacted

Thus $\frac{0.1V_{NaOH}}{V_{HA} + V_{NaOH}} = \left(\frac{0.1V_{HA} - 0.1V_{NaOH}}{V_{HA} + V_{NaOH}}\right) \times 0.1$

From which $V_{HA} = 11V_{NaOH}$

Hence to prepare the solution with pH of 5, the volume of HA solution mixed must be 11 times the volume of NaOH mixed

The best buffer solution is the solution with $pH = 6$ because at $pH = 6$, $[salt]([NaA]) = [Acid]([HA])$ making $pH = pK_a$ where the buffer becomes most efficient with maximum buffer range.

Question 29

(a)

(i) The concentration of solid $(Mg(OH)_2(s))$ is constant (unchanged).

(ii) From; $K_{sp} = [Mg^{2+}(aq)][OH^-(aq)]^2$

Units of K_{sp} = Units of $[Mg^{2+}(aq)] \times$ (Units of $[OH^-(aq)])^2$

Units of $K_{sp} = moldm^{-3} \times (moldm^{-3})^2 = mol^3dm^{-9}$

(b) Given that:

Volume of $CaCl_2$ = Volume of $Na_2CO_3 = Vdm^3$

Then using $n = MV$;

Number of moles of $CaCl_2 = 0.1V$ mol

Number of moles of $Na_2CO_3 = 0.1V$ mol

Na_2CO_3 reacts with $CaCl_2$ to give $CaCO_3$ according to the following equation:

$CaCl_2 + Na_2CO_3 \rightarrow CaCO_3 + 2NaCl$

From which mole ratio is 1:1 and because number of moles of $CaCl_2$ is equal to the number of moles of Na_2CO_3 (0.1V mol); nothing present in excess.

Also from the reaction equation; mole ratio of $CaCl_2$ (or Na_2CO_3) to $CaCO_3$ is $1:1$; thus number of moles of $CaCO_3$ produced was also 0.1V mol.

Using $[\ \ ] = \frac{n}{V}$;

Number of moles of $CaCO_3$ produced in 1 dm^3 of the solution $= \frac{0.1\text{ V mol}}{(V+V)dm^3} = 0.05\ moldm^{-3}$

Then using mass concentration in gdm^{-3} = Molar concentration $\times$ Molar mass

Mass of solid $CaCO_3$ produced (just before being dissolved in the solution)

$$= 0.05 \times 100 = 5\ gdm^{-3}$$

The produced $CaCO_3$ dissolves only slightly according to the following equation:

$$\underset{}{CaCO_3(s)} \rightleftharpoons \underset{s}{Ca^{2+}(aq)} + \underset{s}{CO_3^{2-}(aq)}$$

where s is the molar solubility of $CaCO_3$

Then using $K_{sp} = [Ca^{2+}][CO_3^{2-}] = s^2$

From which $s = \sqrt{K_{sp}} = \sqrt{1.69 \times 10^{-8}mol^2dm^{-6}} = 1.3 \times 10^{-4}moldm^{-3}$

Then using mass solubility = Molar solubility $\times$ Molar mass

Mass solubility of $CaCO_3 = 1.3 \times 10^{-4} \times 100 = 0.013\ gdm^{-3}$

And therefore mass of the precipitation in $1dm^{-3}$ of the solution $= (5 - 0.013)gdm^{-3} = 4.987gdm^{-3}$

Hence the mass concentration of $CaCO_3$ precipitate $4.987gdm^{-3}$

Question 30

(a) Since dissolving sparingly soluble substance is endothermic process, the value of solubility product increases with an increase in temperature.

(b) HCl ionises according to the following equation:

$$\underset{10^{-9}M}{HCl} \rightarrow \underset{10^{-9}M}{H^+} + Cl^-$$

If x moles of H_2O are ionised to its respective ions in $1dm^3$ of the solution;

$$H_2O \rightleftharpoons \underset{x + 10^{-9}}{H^+} + \underset{x}{OH^-}$$

Then $Kw = [H^+][OH^-] = 10^{-14} = (x + 10^{-9})x$

From which: $x^2 + 10^{-9}x - 10^{-14} = 0; x = 9.95 \times 10^{-8}$

Thus $[H^+] = (9.95 \times 10^{-8} + 10^{-9})M$

$= 1.005 \times 10^{-7}M$

And $pH = -\log[H^+] = -\log(1.005 \times 10^{-7})$

$= 6.9978$

Hence pH of the solution is 6.9978

Question 31

(a) Yes (It is possible).

Explanation:

For the solution to be neutral, $[H_3O^+]$ must just be equal to $[OH^-]$. Only at 25°C, the equality occurs when $[H_3O^+] = 10^{-7}M$ which inturn gives the value of pH of 7, because at 25°C, $K_W = 10^{-14}M^2$. However the K_w being an equilibrium constant, it is temperature dependent whose value increases with an increase in temperature. So at higher temperature than 25°C, the K_W value will be greater than 10^{-14} therefore making pH of neutral solution to be less than 7 (for example if $K_w = 10^{-12}M^2$, pH of the neutral solution will be 6).

(b) Using $pH = -\log[H^+]$

From which $[H^+] = \log^{-1}(pH) = \log^{-1}(-2.69) = 2.042 \times 10^{-3}M$

Hence $[H^+]$ is $\mathbf{2.042 \times 10^{-3}M}$

The equation to show ionisation of HX in solution:

$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq)$

From which $K_a = \frac{[H^+][X^-]}{[HX]}$

But $[H^+] = [X^-]$

Thus $K_a = \frac{[H^+]^2}{[HX]}$

Substituting $K_a = \frac{(2.042\times10^{-3}M)^2}{0.15M} = 2.78 \times 10^{-5}M$

Hence the value of K_a is $\mathbf{2.78 \times 10^{-5}M}$

HX reacts with NaOH according to the following equation:

$HX + NaOH \rightarrow NaX + H_2O$

Since only half of HX has neutralized, after the reaction there are following compounds;

HX (unreacted) and NaX (produced) in water (solution)

Since HX is weak acid, the mixture of HX and NaX (NaX is strong salt containing conjugate base of the weak acid, HX) forms acidic buffer solution whose pH value is given by the following equation:

$pH = pK_a + \log\frac{[X^-]}{[HX]}$

Where $[X^-] = [NaX] = [Salt]$

And $[HX] = [Acid]$ but $[X^-] = [HX]$

Thence $pH = pK_a = \log(2.78 \times 10^{-5}) = 4.56$

Hence the pH of the solution is 4.56

Question 32

(a) Bronsted acids: HCO_3^-, H_2O

Bronsted bases: $S^{2-}, HCO_3^-, H_2O, NH_3$

(b) Given that: $NH_4^+ + OH^- \rightleftharpoons NH_3 + H_2O$

From which $K_c = \frac{[NH_3]}{[NH_4^+][OH^-]} = 1\Big/\frac{[NH_4^+][OH^-]}{[NH_3]}$

But $\frac{[NH_4^+][OH^-]}{[NH_3]} = K_b(NH_3)$

Then $K_c = \frac{1}{K_b(NH_3)} = \frac{K_f}{K_r}$; From which: $K_r = K_f \times K_b(NH_3)$

Where;

K_r is the required rate constant of reverse reaction which involves proton transfer from water to NH_3

K_f is the rate constant of forward reaction $= 3.4 \times 10^{10}dm^3mol^{-1}sec^{-1}$

But because NH_4^+ and NH_3 form conjugate pair;

$K_a(NH_4^+)K_b(NH_3) = K_w = 10^{-14}mol^2dm^{-6}$

And ionisation constant of NH_4^+ in water is actually K_h (hydrolysis constant) of NH_4^+ which is equal to $k_a(NH_4^+)$

That is $K_a(NH_4^+) = 5.6 \times 10^{-10}$ $moldm^{-3}$

Thence from $K_aK_b = K_w = 10^{-14}mol^2dm^{-6}$

$K_b(NH_3) = \frac{10^{-14}mol^2dm^{-6}}{5.6\times10^{-10}\ moldm^{-3}} = 1.7857 \times 10^{-5}moldm^{-3}$

The substituting this value of $K_b(NH_3)$ and given value of K_f to $K_r = K_f \times K_b(NH_3)$

$K_r = 3.4 \times 10^{10}\cancel{dm^3mol^{-1}}sec^{-1} \times 1.7857 \times 10^{-5}\cancel{moldm^{-3}} = 6.1 \times 10^5 sec^{-1}$

Hence the rate constant is $6.1 \times 10^5 sec^{-1}$

Question 33

(a) **First component:** Weak electrolyte

Explanation:

This is either weak acid or weak base which is used to provide the dynamic system of the chemical equilibrium and to eliminate added base or added acid respectively.

Second component: Strong salt

Explanation:

The salt must contain either conjugate base of the acid or conjugate acid of the base of the first component. The strong salt which contain conjugate base of the weak acid, provides enough concentration of anions to combine with H^+ on addition of strong acid while strong salt which contain conjugate acid of the weak base provides enough concentration of cations to combine with OH^- on addition of strong acid.

(b) After adding 10mL of strong base, the solution was still acidic suggesting that the acid was excess.

The unreacted weak acid and produced salt forms **acidic buffer solution** whose pH is given by the following equation:

$pH = pKa + \log\frac{[Salt]}{[Acid]}$; $pH = pKa + \log\frac{\text{Number of moles of salt}}{\text{Number of moles of acid}}$

Where $pH = -\log[H_3O^+] = -\log 10^{-5} = 5$

If the base is monoacid, MOH, and the acid is monobasic, HA, then the reaction equation will be:

$HA + MOH \longrightarrow MA + H_2O$ (mole ratio is 1: 1 for all scenarios)

Number of moles of base in 10mL of its solution

= Number of moles of produced salt

$= \frac{10}{100} \times M_b (M_b \text{ is unknown concentration of base}) = 0.01M_b$

Volume of base used to neutralize the acid in the buffer solution

$= (22.22 - 10)mL = 12.22mL$

Number of moles of acid in the buffer = Number of moles of base used to neutralize it

$$= \frac{12.22}{1000} \times M_b = 0.01222M_b$$

Then from $pH = pKa + \log\frac{\text{Number of moles of salt}}{\text{Number of moles of acid}}$

$5 = pKa + \log\frac{0.01M_b}{0.01222M_b}$; From which $pKa = 5.087$

$Ka = \log^{-1}(-pKa) = \log^{-1}(-5.087) = 8.18 \times 10^{-6}$

Dissociation constant for the acid is 8.18×10^{-6}