REVISION

CHEMISTRY TECHNIQUES

DOMINIC MAGUT

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PREFACE

Even seasoned academicians also admit that exams and exam times are the most horrible times in academic life. .Nobody goes into exams expecting to fail, we all want to pass. However, passing in exams is not a walk in the park. Passing exams requires effort.

> ***"A winning effort begins with preparation." -Joe Gibbs.***

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We endeavor to continue enriching the contents of these books, so that they become the most comprehensive revision guides for students. This cannot be achieved without your input as a reader, we therefore look forward to the comments, suggestions and criticism from the readers. Constructive suggestions and feedback from users would be highly appreciated, gratefully acknowledged and suitably incorporated.

Best wishes

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CHAPTER ONE

MATTER

1. *State four differences between a physical and a chemical change*

Chemical change is a process that causes a substance to change into a new substance with a new chemical formula.

chemical reaction is a process involving the breaking or making of interatomic bonds and the transformation of a substance (or substances) into another. Chemical changes cause a substance to change into an entirely substance with a new chemical formula. Chemical changes are also known as chemical reactions. The "ingredients" of a reaction are called reactants, and the end results are called products.

physical change is a process that does not cause a substance to become a fundamentally different substance. Physical changes only change the appearance of a substance, not its chemical composition.

2. *Differences Between Physical and Chemical Change*

Physical Change	***Chemical Change***
When a substance undergoes a physical change, its composition remains the same despite its molecules being rearranged.	*When a substance undergoes a chemical change, its molecular composition is changed entirely. Thus, chemical changes involve the formation of new substances.*
Physical change is a temporary change.	*A chemical change is a permanent change.*
A Physical change affects only physical properties i.e. shape, size, etc.	*Chemical change both physical and chemical properties of the substance including its composition*
A physical change involves very little to no absorption of energy.	*During a chemical reaction, absorption and evolution of energy take place.*

Some examples of physical change are freezing of water, melting of wax, boiling of water, etc.	*A few examples of chemical change are digestion of food, burning of coal, rusting, etc.*
Generally, physical changes do not involve the production of energy.	*Chemical changes usually involve the production of energy (which can be in the form of heat, light, sound, etc.)*
In a physical change, no new substance is formed.	*A chemical change is always accompanied by one or more new substance(s).*
Physical change is easily reversible i.e original substance can be recovered.	*Chemical changes are irreversible i.e. original substance cannot be recovered.*

3. Discuss the criteria for determining purity of a substance

a) Physical Comparison With a Pure Standard

One of the simplest ways to check the purity of any substance is to compare the substance with a certified pure sample. Even physical comparisons can reveal a lot about the purity of a sample. Visual comparison can reveal the presence of any large impurities, such as dirt or other differently colored impurities. If the substance is nontoxic, a smell test can be used to compare it with the pure sample. Any dissimilar odors indicate the presence of at least one impurity. If the substance is edible, a taste test can be conducted. A difference between the taste of the substance and the taste of the pure sample hints at the presence of impurities.

b) Melting and Boiling Point Determination

The physical properties of a substance can be used to establish its purity. These properties include the melting point and boiling point. Different substances tend to have different melting and boiling points, and any pure substance will have a specific melting and boiling point. However, the presence of impurities will cause a lower melting point as well as a change in boiling point.

c) Colorimetric Methods

There are many colorimetric methods for determining whether a substance is pure or if there are impurities present. These usually involve the use of a chemical for detecting the presence of common impurities, which will turn the chemical a certain color. These methods are simple and are usually designed to determine the presence of impurities, not to determine the *amount or the percent purity of the substance. One common use of such colorimetric methods is in forensics, where color tests are frequently used to identify illegal drugs as well as to determine their purity.*

d) ***Color*** *is one of the more useful properties for identifying substances without doing any chemical or physical tests. A violet vapor, for example, is characteristic of iodine. A red/brown gas could well be bromine or nitrogen dioxide (NO2) A characteristic yellow/brown color in water may be indicative of organically bound iron.*

The human eye responds to colors of electromagnetic radiation ranging in wavelength from about 400 nanometers (nm) to somewhat over 700 nm. Within this wavelength range humans see light; immediately below 400 nm is ultraviolet radiation, and somewhat above 700 nm is infrared radiation. Light with a mixture of wavelengths throughout the visible region, such as sunlight, appears white to the eye. Light over narrower wavelength regions has the following colors: 400–450 nm, blue; 490– 550 nm, green; 550–580 nm, yellow; 580–650 nm, orange, 650 nm–upper limit of visible region, red. Solutions are colored because of the light they absorb.

Red, orange, and yellow solutions absorb violet and blue light; purple solutions absorb green and yellow light; and blue and green solutions absorb orange and red light. Solutions that do not absorb light are colorless (clear); solids that do not absorb light are white

e) Density

The density is a much used criterion of the purity of liquid substances. It can be measured relatively easily and with high precision. If the density differs by more than 0.02 per cent from reliable published data , the substance cannot be considered to be pure.

f) Refractive Index

The refractive index is the most simply and quickly measurable constant of liquid substances ,and a very small amount of the substance is sufficient for its determination. This criterion of purity is therefore used whenever possible. For precise work in the field of phase equilibria we require that the refractive index should not differ from the literature values for the substance by more than ± 1 in the fourth place.

g) ***Specific Gravity***

Often densities are expressed by means of specific gravity defined as the ratio of the density of a substance to that of a standard substance. For solids and liquids, the standard substance is usually water; for gases it is usually air. For example, the density of ethanol (ethyl alcohol) at 20°C is 0.7895 g/ml.

The specific gravity of ethanol at 20°C referred to water at 4°C is given by

Specific gravity $= \frac{\underline{\text{density of ethanol}}}{\text{Density of water}} = \frac{\underline{0.7895}\text{ g/ml}}{1.000\text{ g/ml}} = 0.7895$

i.

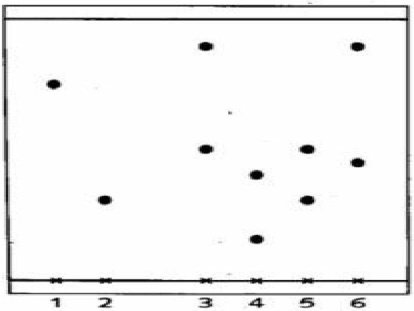
For an exact value of specific gravity, the temperatures of the substances should be specified. In this case the notation of specific gravity of ethanol at 20˚/4˚ C shows that the specific gravity is the ratio of the density of ethanol at 20˚C to that of water at 4˚C

h) Viscosity

The viscosity is suitable criterion of purity particularly with substances that polymerize easily. It is very difficult to determine the absolute value of the viscosity with a precision greater than 1 per cent

Paper chromatography*: (To separate substances) a drop of the substance is placed at the centre of a piece of filter paper and allowed to dry. Three or four more drops are added to it. Water is dripped on, drip by drip, so the ink spreads creating different coloured circles.*

Paper + rings = ***chromatogram****.*



Rings are created because different substances travel at different rates. (To identify substances) Spots of substances placed onto a pencilled line (as ink would separate) which is called the ***origin****, and labelled. Paper goes in solvent, and solvent travels up paper, then paper is taken out. There are spots which have travelled different distances.*

*–**Interpreting** simple chromatograms:*

Number of rings/dots = number of substances

If two dots travel the same distance up the paper they are the same

You can calculate the ***Rf value*** *to identify a substance, given by the formula:*

Rf value = distance moved by substance / distance moved by solvent

To make colourless substances visible you use a ***locating agent****: 1. Dry paper in oven 2. Spray it with locating agent 3. Heat it for 10 minutes in oven.*

The ***stationary phase*** *is the material on which the separation takes place (e.g. the paper). The* ***mobile phase*** *consists of the mixture you want to separate, dissolved in a solvent.*

i) Analytical Methods for Testing Purity

The most accurate means of determining the purity of a substance is through the use of analytical methods. These methods, widely used in different industries, mostly involve chemical analysis, which can pinpoint the presence, identity and amount of impurities in the sample. The most simple chemical methods include gravimetry and titration. There are also the more advanced light-based or spectroscopic methods, such as UV-VIS spectroscopy, nuclear magnetic resonance and infrared spectroscopy. Chromatographic methods, such as gas chromatography and liquid chromatography, can also be used. Other methods used in testing the purity include mass spectroscopy, capillary electrophoresis, optical rotation and particle size analysis..

CHAPTER TWO

PERIODIC TABLE

1. Figure 2 is a section of the periodic table. Study it and answer the questions that follow. The letters do not represent the actual symbols of elements.

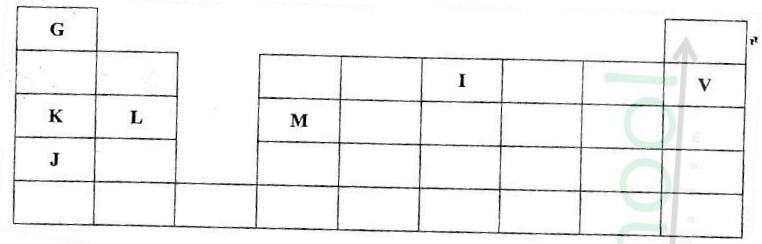


Figure 2

(a) (i) ***Select elements which belong to the same chemical family.***
K and J

(ii) Write the formulae of ions for elements in the same period. *KL and M*

(b) The First ionisation energies of two elements K and M at random are 577 kJ/mol and 494 kJ/mol

i) Write equations for the 1st ionisation energies for elements K and M and indicate their energies.

$K_{(g)} \rightarrow K^{+}_{(g)} + e$ $\Delta H_{IE} = 494kJ/mol$

$M_{(g)} \rightarrow M^{+}_{(g)} + e$ $\Delta H_{IE} = 577kJ/mol$

ii) Explain why the ionization energy for M is higher than that of K
Across the period ,sizes of atoms decreases and therefore more energy is required to remove an electron from an atom in its gaseous state hence the 1st ionization energy for M will be greater than that of K

(iii) ***Write the formula of the compound formed when L and I react.***
L_3I_2

(iv) ***Give one use of elemcnt V.***
Being an inert gas ,V can be used in fluorescent tubes and bulbs

(c) ***How do the reactivity of elements J and K compare? Explain.***

J is more reactive than K because of the increase in the atomic size . This is because the size of atoms increases as you go down the group and so does their reactivity

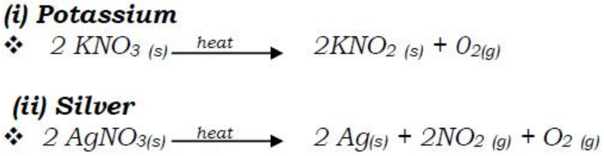
(d) ***(i) Elements L and M form chlorides. Complete the following table by writing the formulae of each chloride and state the nature of the solutions.***

Elements	Formula of chloride	Nature of chloride solution
L	LCl_2	Neutral
M	MC_3 or M_2Cl_6	Acidic

(ii) ***The chloride of element M vapourises easily while its oxide has a high melting point. Explain.***

Chloride of M vaporizes easily because of its weak van der wall forces between its dimers , its oxides have high melting points because of its strong ionic bonds which are very difficult to break

2. (a) Write an equation to show the effect of heat on the nitrate of:
(i)Potassium
(ii)Silver



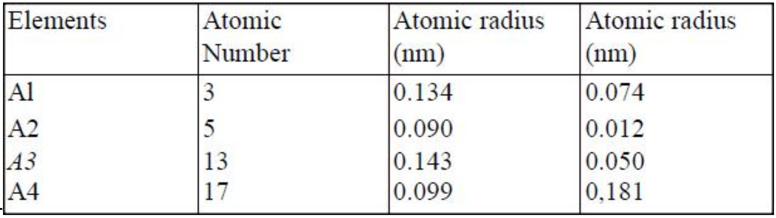
(i) Potassium

- $2\,KNO_{3\,(s)} \xrightarrow{heat} 2KNO_{2\,(s)} + O_{2(g)}$

(ii) Silver

- $2\,AgNO_{3(s)} \xrightarrow{heat} 2\,Ag_{(s)} + 2NO_{2\,(g)} + O_{2\,(g)}$

(b) The table below gives information about elements Ai, A2, A3, and A4



Elements	Atomic Number	Atomic radius (nm)	Atomic radius (nm)
A1	3	0.134	0.074
A2	5	0.090	0.012
A3	13	0.143	0.050
A4	17	0.099	0,181

i) ***In which period of the periodic table is element A2? Give a reason.***

Period 2, because it has two energy levels

(ii) ***Explain why the atomic radius of:***
I. Ai is greater than that of A2;

A2 has greater atomic number than AI, it also has greater nuclear charge and more protons than A1, Therefore , you would expect a greater nuclear pull on A2 than on A1 hence a reduction in its atomic size

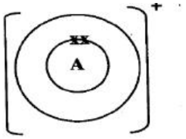
II. A4 is smaller than its ionic radius.

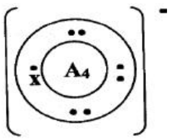
A4 gains electrons, this incoming electrons are usually repelled by existing electrons which causes them to move far away from the nucleaus hence the reason for their increased electron cloud

(iii) ***Select the element which is in the same group as A3.***

A2

(iv) ***Using dots (•) and crosses(x) to represent outermost electrons, draw a diagramto show the bonding in the compound formed when Ai reacts with A4.***





Define term 'relative atomic mass'

The relative atomic mass of an element is defined as the weight in grams of the number of atoms of the element contained in 12.00 g of carbon-12. Every atom has its own unique ***relative atomic mass (RAM)*** *based on a* ***standard*** *comparison or relative* ***scale*** *e.g. it has been based on hydrogen H = 1 amu and oxygen O = 16 amu in the past (amu = relative atomic mass unit).*

o *The relative atomic mass of an element takes into account the different masses of the isotopes of that element and the abundance of the isotopes in the naturally occurring element (meaning the percentage of each isotope present).*

o *Relative atomic mass is defined and explained below, and examples of how to calculate it from data.*

- *The **relative atomic mass** scale is now based on an isotope of **carbon**, namely, **carbon-12**, nuclide symbol* ${}^{12}_{6}C$ ***, which is given the arbitrary value of 12.0000 amu** by international agreement.*

To calculate the relative atomic mass of chlorine, the average mass of one atom of chlorine is found by considering 100 atoms of chlorine.

a. ***Calculating the relative atomic mass of bromine*** ${}^{79}_{35}Br$ ***and*** ${}^{81}_{35}Br$

- *bromine consists of two isotopes, **50%** ^{79}**Br** and **50%** ^{81}**Br**, calculate the A_r of bromine from the mass numbers (top left numbers).*
- *Think of the calculation in terms of '100 atoms'*
- $A_r = [\ (50 \times 79) + (50 \times 81)\ ] / 100 = 80$
- *So the relative atomic mass of bromine is 80 or **RAM or** $A_r(Br)$ **=** __**80**__*
- ***Note the full working shown.** Yes, ok, you can do it in your head BUT many students ignore the %'s and just average all the isotopic masses (mass numbers) given, in this case bromine-79 and bromine-81.*
- *The element bromine is the only case I know where averaging the isotopic masses actually works! so beware!*
- ***Calculating the relative atomic mass of chlorine based on the*** ${}^{35}_{17}Cl$ ***and*** ${}^{37}_{17}Cl$ ***isotopes***
- *Chlorine consists of two isotopes, **75% chlorine-35** and **25% chlorine-37**, so using these two mass numbers ...*
- *... again think of the data based on 100 atoms, so 75 have a mass of 35 and 25 atoms have a mass of 37.*
- *The average mass =* $[\ (75 \times 35) + (25 \times 37)\ ] / 100 = \mathbf{35.5}$
- *So the relative atomic mass of chlorine is 35.5 or **RAM or** $A_r(Cl)$ **=** __**35.5**__*
- *Note:* ^{35}***Cl** and* ^{37}***Cl** are the most common isotopes of chlorine, but, there are tiny percentages of other chlorine isotopes which are usually ignored at GCSE/IGCSE and Advanced GCE AS/A2 A level.*

3. Why do elements potassium and sodium have similar chemical properties?

Both elements, sodium (Na) and potassium (K) lie in the Group 1 column of the Periodic Table , which contains the members of the Alkali Metals family. Members within a family, or column, of elements tend to have similar chemical properties.

4. ***Element A has atomic mass 23 and element B has atomic mass 7 and also have 12neutorns and 4 neutrons respectively.***

a. Write the electronic arrangement of A and B

A= 2.8.1
B= 2.1

b. Which element has higher ionization energy? Explain

Strong attraction of the outermost energy level electron to the nucleus make it difficult to remove This is due to smaller atomic radius compared to A
Or - Outermost electrons are closer to the nucleus hence higher force of attraction

5. The table below shows the relative atomic masses and the percentage abundance of isotope M_1 and M_2 of element M.

	Relative atomic mass	***% abundance***
M_1	***62.93***	***69.09***
M_2	***64.93***	***30.91***

Calculate the relative atomic mass of element M

$$R.A.M = \frac{(62.93 \times 69.09) + (64.93 \times 3091)}{100}$$

$$= \frac{4347.834 + 2006.99}{100}$$

$= 63.5482$

≈ 63.5

Element V has two isotopes. Two thirds of V and one third of V . What is the relative atomic mass of element V?

$$R.A.M = \frac{(33 \times 2) + (30 \times 1)}{3}$$

$$\frac{99}{3} = 33$$

6. The following refers to element Y

Isotope	***A***	***B***	***C***
Isotope mass	***54***	***56***	***57***

Given that isotope C contains 31 neutrons in its nucleus find the number of protons in isotope B

Number of electrons of C = 57 − 31 = 26
Number of electrons of B is the same as for C = No. of Protons
B = 26 protons

7. The table below shows the relative atomic masses and the percentage abundance of the isotopes L_1 and L_2 of element L.

	Relative atomic mass	***% abundance***
L_1	***62.93***	***69.09***
L_2	***64.93***	***30.91***

Calculate the relative atomic mass of element K.

$$\frac{69.09}{100} \times 62.93 + \frac{30.91}{100} \times 64.93$$

$43.4783 + 20.0698$

$= 63.548$

8. An element M has two isotopes M and M . The relative atomic mass of the naturally occurring is 63.55. Calculate the percentage of each isotope

$$\frac{63x + 65(100 - x)}{100} = 63.55$$

$63x + 6500 - 65x = 6355$

$2x = 6355 - 6500$

$2x = -145$

$x = 72.5$

% abundance of $^{63}M = 72.5\%$

$^{65}M = 27.5\%$

9. An oxide of element G has the formula as G_2O_3

State the valency of element G

Valency of G is 3

In which group f the periodic table is element G?

G is a group 3 element

10. The table below gives information about the ions T^+ and Z^{2-}

Ion	**T^+**	**Z^{2-}**
Electron arrangement	2.8	2.8.8
Number of neutrons	12	16

How many protons are there in the nucleus of ?

i. *Element T? 11 protons*

i. *Element Z? 16 protons*

Determine the relative formula mass of the compound formed between T and Z

Formula of compound = T_2Z

Mass number of T = 11+ 12 = 23

Mass number of Z = 16+16 = 32

Formula Mass of T_2Z = (23x2) + 32 = 78

State two conditions under which the compound would conduct electricity

i) *When molten*

ii) *When in aqueous solution*

2. Carbon and silicon belong to the same group of the periodic table, yet Carbon (IV) oxide is a gas while silicon (IV) oxide is a solid with a high melting point. Explain this difference

Silicon (IV) Oxide has giant atomic structure with strong covalent bond holding the atom together. These require a lot of energy to break, hence it has high melting point. Carbon (IV) Oxide has simple molecular structure with weakVan Der Waals forces holding the molecules together which require little energy to break, hence sublimes at low temperature and is a gas at room temperature and pressure

11. ***An ion of oxygen is larger than oxygen atom. Explain***

The oxide ions has 2 extra electrons that causes greater electron repulsion than in oxygen atom

12. Explain why the ionic radius of non-metallic element is greater than its atomic radius

When a non metal gains electrons to become a negative ion the radius increases. The number of protons remains the same so the pull on the electrons is the same. However as the number of electrons increases with the extra electrons the average pull on the electrons is less. The decreased pull causes the distance from the nucleus to increase.

CHAPTER THREE

CHEMICAL BONDS

1.Define

a. electron affinity

The energy released when an electron is added to neutral gaseous atom, is known as electron affinity.

b. cations and anions

When an atom loses electron it becomes cation, and when an atom gains electrons it becomes anion.

c. coordinate bond

A coordinate bond is a type of covalent bond formed by the donation of a lone pair of electrons by one atom.

2 List four properties of ionic and covalent compounds

Ionic Bond

✓ *The transfer of electrons from one atom to another leads to the formation of the chemical bond. This bond is known as an ionic bond.*

✓ *An ionic bond is formed in two scenarios:*

✓ *When one of the atoms donates electrons to achieve the inert gas electron configuration for the completion of octet resulting in stability.,*

✓ *When the other atom needs electrons to achieve the inert gas electron configuration.*

✓ *So, when a metal reacts with a non-metal, transfer of electrons takes place from metal atoms to the non-metal atoms, and thus an ionic bond is formed.*

✓ *The strong force of attraction developed between the oppositely charged ions is known as an ionic bond. Examples of ionic bonds are sodium chloride, magnesium chloride and magnesium oxide, etc.*

✓ *Ionic compounds are held strongly by the electrostatic force of attraction because oppositely charged ions are present.*

✓

b.Properties Of Ionic Compounds

✓ *Physical properties of ionic compounds:*

○ *Ionic compounds are solids and are hard to break due to the strong force of attraction between the positive and negative ions.*

○ *However, they break into pieces when pressure is applied. So they are considered brittle.*

✓ *Melting and boiling points of ionic compounds:*

○ *A large amount of energy is required to break the ionic bonds between the atoms.*

○ *So, they have high melting and boiling points.*

✓ *Solubility of ionic compounds:*

○ *Ionic compounds are generally soluble in polar solvents such as water but the solubility tends to decrease in non-polar solvents such as petrol, gasoline etc.*

✓ *Conduction of Electricity:*

○ *Although ionic compounds do not conduct electricity in the solid state because movement of ions is not possible.*

○ *But they are good conductors in a molten state because electrostatic forces of attraction between the ions are overcome by the heat released.*

c.Covalent Bond

- *Whenever a non-metal combine with another non-metal, sharing of electrons takes place between their atoms, which leads to the formation of a covalent bond. A covalent bond can also be formed between two atoms of the same non-metal.*

Covalent compounds are formed by the sharing of electrons between atoms. Such compounds are known as covalent compounds.

d.Properties Of Ionic Compounds

✓ *They are usually crystalline solids.*

✓ *They have high melting points and high boiling points.*

✓ *They are usually soluble in water but insoluble in organic solvents.*

✓ *They conduct electricity when dissolved in water or when melted.*

3. Differences Between Ionic Compounds And Covalent Compounds

Ionic compounds	***Covalent compounds***
They are usually crystalline solids.	*They are usually liquids or gases. Only some of them are solids.*
They have high melting points and boiling points. That is, ionic compounds are non-volatile.	*They have usually low melting points and boiling points. That is, covalent compounds are usually volatile.*
They conduct electricity when dissolved n water or melted.	*They do not conduct electricity.*
They are usually soluble in	*They are usually insoluble in water*

water.	*(except, glucose, sugar, urea, etc.).*
They are insoluble in organic solvents (like alcohol, ether, acetone, etc.).	*They are soluble in organic solvents.*

4. **What property determines the polarity of a covalent bond?**

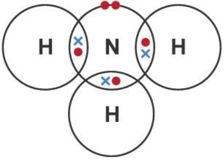
Polarity in a bond results from an uneven sharing of electrons. An extreme example is an ionic bond, in which an electron is almost fully transferred from one atom to another due to the second atom's electron affinity.

In order to generate an uneven pull on shared electrons, the atoms involved in the bond must have significantly differing electronegativities. This will cause one atom to pull electrons closer to its nucleus, away from the other atom involved.

Molecular and electronic geometry can affect the polarity of a compound, but do not directly affect polarity of a single given bond. Atomic radius does not play a significant role in polarity.

5. Ammonia is an important compound used by industry and agriculture.

- ***a) Describe, in terms of outer shell electrons, the bonding in a molecule of ammonia. You should include a suitable diagram showing outer shell electrons in your answer.***
    - ✓ *three single bonds from nitrogen to hydrogen atoms*
    - ✓ *non-bonded pair of electrons left on nitrogen*



b) Explain why ammonia is a gas at room temperature.

- ✓ *Because of weak forces between ammonia molecules*
- ✓ *molecules have sufficient energy at room temperature to overcome these forces*

6. Lithium chloride is a solid with a high melting point. It conducts electricity only when molten or in solution. Describe the bonding present in lithium chloride and explain the properties given above.

- ✓ *lithium atom loses an electron*
- ✓ *it becomes a positive ion*
- ✓ *chlorine atom gains an electron*
- ✓ *it becomes a negative chloride ion*

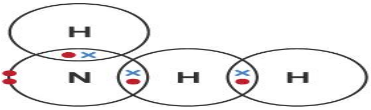
✓ *diagram showing transfer of electrons from lithium to chlorine*
✓ *strong force of attraction between oppositely charged ions*
✓ *high melting point due to strong bonds between ions*
✓ *conducts electricity when molten or in solution as charged ions are free to move*
✓ *does not conduct when solid as ions are not free to move*

7. ***Ammonia, NH_3, is a compound that contains the elements nitrogen and hydrogen. The electronic structure for each element is given below.***

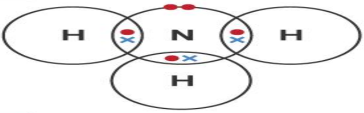
N = 2, 5   H = 2, 1

State which of the following dot and cross diagrams represents the bonding in a molecule of ammonia.

A



B



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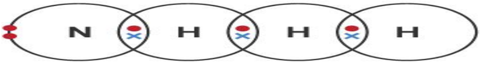


CHAPTER FOUR

HYDROCARBONS

1. ***Define each of the following terms***

a) Hydrocarbons

A hydrocarbon is any of a class of organic chemicals made up of only the elements carbon (C) and hydrogen (H). The carbon atoms join together to form the framework of the compound, and the hydrogen atoms attach to them in many different configurations.

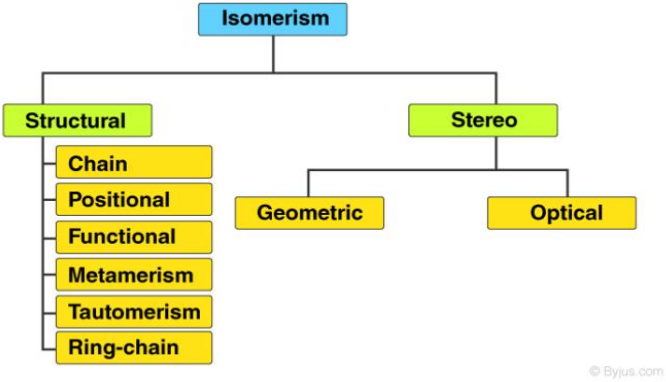
b. Isomerism

Isomerism is the phenomenon in which more than one compounds have the same chemical formula but different chemical structures. Chemical compounds that have identical chemical formulae but differ in properties and the arrangement of atoms in the molecule are called isomers.

Describe the various types of isomers

i. Isomerism Types

There are two primary types of isomerism, which can be further categorized into different subtypes. These primary types are ***Structural Isomerism*** *and* ***Stereoisomerism****. The classification of different types of isomers is illustrated below.*



ii. Structural Isomerism

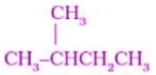
Structural isomerism is commonly referred to as constitutional isomerism. The functional groups and the atoms in the molecules of these isomers are linked in different ways. Different structural isomers are assigned different IUPAC names since they may or may not contain the same functional group.

iii. *Chain Isomerism*

- *It is also known as skeletal isomerism.*
- *The components of these isomers display differently branched structures.*
- *Commonly, chain isomers differ in the branching of carbon*
- *An example of chain isomerism can be observed in the compound* C_5H_{12}*, as illustrated below.*

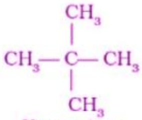
$CH_3CH_2CH_2CH_2CH_3$

Pentane



$CH_3CH(CH_3)CH_2CH_3$

Isopentane
(2-Methylbutane)

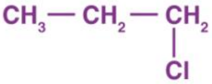


$C(CH_3)_4$

Neopentane
(2,2-Dimethylpropane)

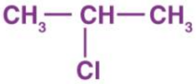
iv. *Position Isomerism*

- *The positions of the functional groups or substituent atoms are different in position isomers.*
- *Typically, this isomerism involves the attachment of the functional groups to different carbon atoms in the carbon chain.*
- *An example of this type of isomerism can be observed in the compounds having the formula* C_3H_7Cl*.*



$CH_3-CH_2-CH_2Cl$

1-Chloropropane



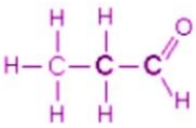
$CH_3-CH(Cl)-CH_3$

2-Chloropropane

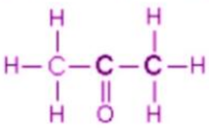
v. *Functional Isomerism*

- *It is also known as functional group isomerism.*
- *As the name suggests, it refers to the compounds that have the same chemical formula but different functional groups attached to them.*
- *An example of functional isomerism can be observed in the compound* C_3H_6O*.*

propanal



propanone (acetone)



Vi. Metamerism

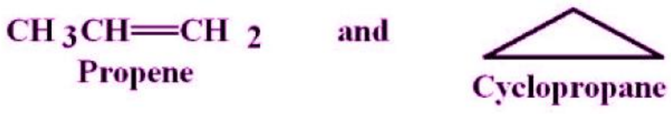
- *This type of isomerism arises due to the presence of different alkyl chains on each side of the functional group.*
- *It is a rare type of isomerism and is generally limited to molecules that contain a divalent atom (such as sulfur or oxygen), surrounded by alkyl groups.*
- *Example:* $C_4H_{10}O$ *can be represented as ethoxyethane* ($C_2H_5OC_2H_5$) *and methoxy-propane* ($CH_3OC_3H_7$).

vi. Tautomerism

- *A tautomer of a compound refers to the isomer of the compound which only differs in the position of protons and electrons.*
- *Typically, the tautomers of a compound exist together in equilibrium and easily interchange.*
- *It occurs via an intramolecular proton transfer.*
- *An important example of this phenomenon is Keto-enol tautomerism.*

vii. Ring-Chain Isomerism

- *In ring-chain isomerism, one of the isomers has an open-chain structure whereas the other has a ring structure.*
- *They generally contain a different number of pi bonds.*
- *A great example of this type of isomerism can be observed in* C_3H_6. *Propene and cyclopropane are the resulting isomers, as illustrated below.*



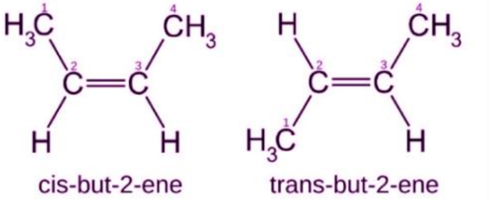
viii. Stereoisomerism

This type of isomerism arises in compounds having the same chemical formula but different orientations of the atoms belonging to the molecule in three-dimensional space. The compounds that exhibit stereoisomerism are often referred to as stereoisomers. This phenomenon can be further categorized into two subtypes. Both these subtypes are briefly described in this subsection.

ix. Geometric Isomerism

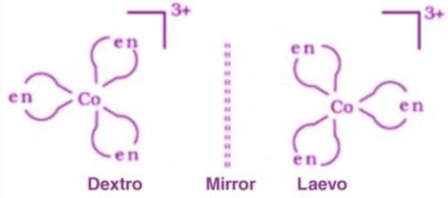
- *It is popularly known as cis-trans isomerism.*
- *These isomers have different spatial arrangements of atoms in three-dimensional space.*

- *An illustration describing the geometric isomerism observed in the acyclic But-2-ene molecule is provided below.*



x. Optical Isomerism

- *Compounds that exhibit optical isomerism feature similar bonds but different spatial arrangements of atoms forming non-superimposable mirror images.*
- *These optical isomers are also known as enantiomers.*
- *Enantiomers differ from each other in their optical activities.*
- *Dextro enantiomers rotate the plane of polarized light to the right whereas laevo enantiomers rotate it to the left, as illustrated below.*



Xi. Ionization Isomerism

The compound which give different ions in the solution, although they have same composition, are called ionization isomers and this property is known as ionization isomerism. Compounds which gives different ions in solution although they have same composition are called ionization isomerism. This form of isomerism arises when the counter ion in a complex salt is itself a potential ligand and can displace a ligand which can then become the counter ion.

One example of ionisation isomerism is [Co(NH3)5SO4]Br and [Co(NH3)5Br]SO4.

We can prepare these ionisation isomers in the following method.

$[CoBr(NH_3)_5]SO_4 \rightarrow [CoBr(NH_3)_5]^{2+} + SO_4^{2-}$ = Red−Violet

$[CoSO_4(NH_3)_5]Br \rightarrow [CoSO_4^{2-}(NH_3)_5]^{+} + Br^{-}$ = Red

CHAPTER FIVE

CHEMICAL EQUILIBRIUM

1.a. Define chemical equilibrium

Chemical equilibrium refers to the state of a system in which the concentration of the reactant and the concentration of the products do not change with time and the system does not display any further change in properties.

2.Explain types of chemical equilibrium

There are two types of chemical equilibrium:

a. Homogenous Chemical Equilibrium

In this type, the reactants and the products of chemical equilibrium are all in the same phase. Homogenous equilibrium can be further divided into two types: Reactions in which the number of molecules of the products is equal to the number of molecules of the reactants. For example,

$H_2 (g) + I_2 (g) \rightleftharpoons 2HI (g)$

$N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$

Reactions in which the number of molecules of the products is not equal to the total number of reactant molecules. For example,

$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g)$

$COCl_2 (g) \rightleftharpoons CO (g) + Cl_2 (g)$

Heterogeneous Chemical Equilibrium

In this type, the reactants and the products of chemical equilibrium are present in different phases. A few examples of heterogeneous equilibrium are listed below.

$CO_2 (g) + C (s) \rightleftharpoons 2CO (g)$

$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (g)$

Thus, the different types of chemical equilibrium are based on the phase of the reactants and products.

4. For an equilibrium reaction, what effect does reversing the reactants and products have on the value of the equilibrium constant?

By reversing the reactants and products for an equilibrium reaction, the equilibrium constant becomes: $K'=1K$ $K'=1K$.

5. ***Which of the following equilibriums are homogeneous and which are heterogeneous?***

a. $2HF(g) \rightleftharpoons H2(g)+F2(g)$

This equilibrium is homogenous as all substances are in the same state.

b. $C(s)+2H2(g) \rightleftharpoons CH4(g)$

This equilibrium is heterogeneous as not all substances are in the same state.

c. $H2C{=}CH2(g)+H2(g) \rightleftharpoons C2H6(g)$

d. This equilibrium is homogeneous as all substances are in the same state.

e. $2Hg(l)+O2(g) \rightleftharpoons 2HgO(s)$

This equilibrium is heterogeneous as not all substances are in the same state.

6. ***Classify each equilibrium system as either homogeneous or heterogeneous.***

a. $NH4CO2NH2(s) \rightleftharpoons 2NH3(g)+CO2(g)$ *This equilibrium is heterogeneous as not all substances are in the same state.*

b. $C(s)+O2(g) \rightleftharpoons CO2(g)$

This equilibrium is heterogeneous as not all substances are in the same state.

c. $2Mg(s)+O2(g) \rightleftharpoons 2MgO(s)$

d. This equilibrium is heterogeneous as not all substances are in the same state.

e. $AgCl(s) \rightleftharpoons Ag^{+}(aq)+Cl^{-}(aq)$

This equilibrium is heterogeneous as not all substances are in the same state.

7. ***If an equilibrium reaction is endothermic, what happens to the equilibrium constant if the temperature of the reaction is increased? if the temperature is decreased?***

. According to Le Chatelier's principle, equilibrium will shift in the direction to counteract the effect of a constraint (such as concentration of a reactant, pressure, and temperature). Thus, in an endothermic reaction, the equilibrium shifts to the right-hand side when the temperature is increased which increases the equilibrium constant and the equilibrium shifts to the left-hand side when the temperature is decreased which decreases the equilibrium constant.

8. ***Industrial production of NO by the reaction***

N2(g)+O2(g)⇌2NO(g)

is carried out at elevated temperatures to drive the reaction toward the formation of the product. After sufficient product has formed, the reaction mixture is quickly cooled. Why?

After sufficient industrial production of NO by the reaction of $N2(g)+O2(g)\rightleftharpoons 2NO(g)$ at elevated temperatures to drive the reaction toward the formation of the product, the reaction mixture is cooled quickly because it quenches the reaction and prevents the system from reverting to the low-temperature equilibrium composition that favors the reactants.

9. ***How would you differentiate between a system that has reached chemical equilibrium and one that is reacting so slowly that changes in concentration are difficult to observe?***

To differentiate between a system that has reached equilibrium and one that is reacting slowly that changes in concentrations are difficult to observe we can use Le Chatelier's principle to observe any shifts in the reaction upon addition of a constraint (such as concentration, pressure, or temperature).

10. ***What is the relationship between the equilibrium constant, the concentration of each component of the system, and the rate constants for the forward and reverse reactions?***

The relationship between the equilibrium constant, the concentration of each component of a system, and the rate constants for the forward and reverse reactions considering a reaction of a general form:

$$aA+bB\rightleftharpoons cC+dD \quad \text{is} \quad K=\frac{[C]^c[D]^d}{[A]^a[B]^b}=\frac{kf}{Kr}$$

11. ***Consider the reaction $2H_2 + O_2 \rightleftharpoons 2H_2O$. State the correct the expression for the equilibrium constant for this reaction?***

$$K_c = \frac{[H_2O]^2}{[H_2]^2[O_2]}$$

12. ***Nitrogen oxides are air pollutants produced by the reaction of nitrogen and oxygen at high temperatures. At 2000°C, the value of the equilibrium constant K_C for the reaction,***

$$N_2 (g) + O_2 (g) \rightleftharpoons 2\ NO\ (g), \text{ is } 4.1 \times 10^{-4}.$$

Calculate the equilibrium concentration of NO (g) in air at 1.00 atm pressure and 2000°C. The equilibrium concentrations of N_2 and O_2 at this pressure and temperature are 0.036 M and 0.0089 M, respectively.

We are given all of the equilibrium concentrations except that of NO. Thus, we can solve for the missing equilibrium concentration by rearranging the equation for the equilibrium constant.

$$
\begin{aligned}
K_C &= \frac{[NO]^2}{[N_2][O_2]} \\
[NO]^2 &= K_C [N_2][O_2] \\
[NO] &= \sqrt{K_C [N_2][O_2]} \\
&= \sqrt{(4.1 \times 10^{-4})(0.036)(0.0089)} \\
&= \sqrt{1.31 \times 10^{-7}} \\
&= 3.6 \times 10^{-4}
\end{aligned}
$$

Thus [NO] is 3.6×10^{-4} mol/L at equilibrium under these conditions.
We can check our answer by substituting all equilibrium concentrations into the expression for the reaction quotient, Q_C, to see whether it is equal to the equilibrium constant, and thus confirm that the system is indeed at equilibrium.

$$
\begin{aligned}
Q_C &= \frac{[NO]^2}{[N_2][O_2]} \\
&= \frac{(3.6 \times 10^{-4})^2}{(0.036)(0.0089)} \\
Q_C &= 4.0 \times 10^{-4} = K_C
\end{aligned}
$$

The answer checks; our calculated value gives the equilibrium constant within the error associated with the significant figures in the problem.

13. Why is Chemical Equilibrium called Dynamic Equilibrium

The stage at which the rate of the forward reaction is equal to the rate of backward reaction is called an equilibrium stage. At this point, the number of reactant molecules converting into products and product molecules into reactants are the same. The same equilibrium can be carried out with the same reactants anywhere with similar conditions with continuous interchanging of molecules hence chemical equilibrium is dynamic.

14. State the following as used in chemical equilibria

a) Henry's law

Was first formulated in 1803 by the English physician and chemist William Henry . It states that the weight of a gas dissolved by a liquid is proportional to the pressure of the gas upon the liquid. The law, holds true only for dilute solutions and low gas pressures.

b) Le chateliers's principle

Le chatelier's principle states that changes in the temperature, pressure, volume, or concentration of a system will result in predictable and opposing changes in the system in order to achieve a new equilibrium state.
Le Chatelier's principle is an observation about chemical equilibria of reactions. It States that If the concentration of a reaction species is increased (at constant T and V), the equilibrium system will shift in the

direction that reduces the concentration of that species. Le Châtelier's principle can be used to predict the effect that a stress like changing concentration has on a reaction system at equilibrium.

15. State four factor which affect chemical equilibrium

According to Le-Chatelier's principle, if there is any change in the factors affecting the equilibrium conditions, the system will counteract or reduce the effect of the overall transformation. This principle applies to both chemical and physical equilibrium.

There are several factors like temperature, pressure and concentration of the system which affect equilibrium. Some important factors affecting chemical equilibrium are discussed below.

a) Change in Concentration:

The concentration of the reactants or products added is relieved by the reaction which consumes the substance which is added. The concentration of reactants or products removed is relieved by the reaction which is in the direction that replenishes the substance which is removed. When the concentration of the reactant or product is changed, there is a change in the composition of the mixture in chemical equilibrium.

b) Change in Pressure:

Change in pressure happens due to the change in the volume. If there is a change in pressure it can affect the gaseous reaction as the total number of gaseous reactants and products are now different. According to Le Chatelier's principle, in heterogeneous chemical equilibrium, the change of pressure in both liquids and solids can be ignored because the volume is independent of pressure.

c) Change in Temperature:

The effect of temperature on chemical equilibrium depends upon the sign of ΔH *of the reaction and follows Le-Chatelier's Principle. As temperature increases the equilibrium constant of an exothermic reaction decreases. In an endothermic reaction the equilibrium constant increases with an increase in temperature.*

Along with the equilibrium constant, the rate of reaction is also affected by the change in temperature. As per Le Chatelier's principle, the equilibrium shifts towards the reactant side when the temperature increases in case of exothermic reactions, for endothermic reactions the equilibrium shifts towards the product side with an increase in temperature.

Effect of a Catalyst:

A catalyst does not affect the chemical equilibrium. It only speeds up a reaction. In fact, catalyst equally speeds up the forward as well as the reverse reaction. This results in the reaction reaching its equilibrium faster.

The same amount of reactants and products will be present at equilibrium in a catalysed or a non-catalysed reaction. The presence of a catalyst only facilitates the reaction to proceed through a lower-energy transition state of reactants to products.

d) Effect of Addition of an Inert Gas:

When an inert gas like argon is added to a constant volume it does not take part in the reaction so the equilibrium remains undisturbed. If the gas added is a reactant or product involved in the reaction then the reaction quotient will change.

16. Ammonia is manufactured according to the following equation

N2 + 3H2 ⇔ 2NH3 ΔH= -92KJMol-1
(g) (g) (g)

Explain what happens to the yield of ammonia when; a) Temp increases, b) Press increases c) Catalyst changes

Ammonia is made in the Haber Process (3H2(g) + N2(g)<-> 2NH3(g)). Using Le Chetelier's Principal, what happens to the equilibrium yield of ammonia when...:

Le Chetelier's Principal gives us a guide to work out what will happen when we change the conditons of a reaction in dynamic equilibrium. It states that if the dynamic equilibiurm is disturbed, the equilibrium position will change in order to counteract the change that has occured.

A) When we increase the temperature of the system, the reaction with the greatest surface area, or the one which produces the most moles of gas, is more favourable. Hence the equilibrium position will shift towards the reverse reaction in the Haber process and the equilibrium yield of ammonia will decrease.

B) Increasing the pressure has an opposite effect to an increase in the temperature in that it favours the reaction which produces the least moles of gas. Since the forward reaction produces 2 moles from 4 moles, the number of moles of gas is decreasing hence the forward reaction is favoured when the pressure increases. The equilibrium yield of ammonia will therefore increase.

C) A catalyst is a compound, usually a metal such as Fe or Pd, that provides the reaction with an alternative reaction pathway with a lower activation energy. Hence it increases the rate of the reaction. A catalyst has NO EFFECT on the equilibrium position hence the equilibrium yield of ammonia does not change (though the rate at which the reaction reaches equilibrium might).

CHAPTER SIX

SAMPLES AND SAMPLING TECHNIQUES

1. Define the term sample

A sample refers to a smaller, manageable version of a larger group. It is a subset containing the characteristics of a larger population.

2. Why are samples important in analytical chemistry?

Using whole populations for research comes with challenges, which is why samples are used.

Researchers may have problems gaining ready access to entire populations. And because of the nature of some studies, researchers may have difficulties getting the results they need in a timely fashion. This is why people who conduct studies use samples.

Using a smaller number of people who represent the entire population can still produce valid results while cutting back on time and resources.

Samples and sampling methods are widely used in a variety of settings where research is conducted.

It is also a time-convenient and a cost-effective method and hence forms the basis of any research design. Samples used by researchers should closely resemble the population. All the participants in the sample should share the same characteristics and qualities.

3. Qualities of a good sample

A sample should represent the population as a whole and not reflect any bias toward a specific attribute. Samples are used in statistical testing when population sizes are too large for the test to include all possible members or observations.

4. Distinguish between sample and sampling

Whereas a sample is a smaller, manageable version of a larger group. It is a subset containing the characteristics of a larger population, sampling is the actual process of selecting certain members or a subset of the population to make statistical inferences from them and to estimate characteristics of the whole population.

5. State and explain various types of samples

***Grab sample**: A grab sample is a discrete sample which is collected at a specific location at a certain point in time. If the environmental medium varies spatially or temporally, then a single grab sample is not representative and more samples need to be collected.*

Composite sample: *A composite sample is made by thoroughly mixing several grab samples. The whole composite may be measured or random samples from the composites may be withdrawn and measured.*

A composite sample may be made up of samples taken at different locations, or at different points in time. Composite samples represent an average of several measurements and no information about the variability among the original samples is obtained.

A composite of samples which all contain about the same concentration of analyte can give a result which is not different from that obtained with a composite made up of samples containing both much higher and much lower concentrations.

During compositing, information about the variability, patterns, and trends is lost. When these factors are not critical, compositing can be quite effective. When the sampling medium is very heterogeneous, a composite sample is more representative than a single grab sample. For example, in a study of the exposure to tobacco smoke in an indoor environment, a several hour composite sample will provide more reliable information than several grab samples.

Composite samples may be used to reduce the analytical cost by reducing the number of samples. A composite of several separate samples may be analyzed and if the pollutant of interest is detected, then the individual samples may be analyzed individually. This approach can be useful for screening many samples. A common practice, for example, in clinical laboratories screening samples for drug abuse among athletes is to analyze a composite of about ten samples. If the composite produces a positive result, then the individual samples are tested

6. Outline methods of sampling

Sampling techniques can broadly be classified into two categories namely;

1. *Probability sampling*
2. *Non probability sampling*

Non-probability Sampling:

Non probability sampling method is reliant on a researcher's ability to select members at random. This sampling method is not a fixed or pre-defined selection process which makes it difficult for all elements of a population to have equal opportunities to be included in a sample.

Probability Sampling Methods

Probability sampling is a sampling method that selects random members of a population by setting a few selection criteria. These selection parameters *allow every member to have the equal opportunities to be a part of various samples.*

Probability Sampling is a sampling technique in which sample from a larger population are chosen using a method based on the theory of probability. This sampling method considers every member of the population and forms samples on the basis of a fixed process. It gets rid of bias in the population and gives a fair chance to all members to be included in the sample.

There are 4 types of probability sampling technique:

a) Simple Random Sampling:

It is one of the best probability sampling techniques that helps in saving time and resources. It is a trustworthy method of obtaining information where every single member of a population is chosen randomly, merely by chance and each individual has the exact same probability of being chosen to be a part of a sample.

b) Cluster Sampling:

Cluster sampling is a method where the researchers divide the entire population into sections or clusters that represent a population. Clusters are identified and included in a sample on the basis of defining demographic parameters such as age, location, sex etc. which makes it extremely easy for a survey creator to derive effective inference from the feedback.

For example, if the government of the Kenya wishes to evaluate the number of students TVET institutions they can divide it into clusters on the basis of national polytechnics, technical institutes, vocational institutions etc. This way of conducting a survey will be more effective as the results will be organized into institutions and provides insightful student data.

c) Systematic Sampling:

Using systematic sampling method, members of a sample are chosen at regular intervals of a population. It requires selection of a starting point for the sample and sample size that can be repeated at regular intervals. This type of sampling method has a predefined interval and hence this sampling technique is the least time-consuming.

For example, a researcher intends to collect a systematic sample of 500 people in a population of 5000. Each element of the population will be numbered from 1-5000 and every 10th individual will be chosen to be a part of the sample (Total population/ Sample Size = 5000/500 = 10).

d) Stratified Random Sampling:

Stratified Random sampling is a method where the population can be divided into smaller groups, that don't overlap but represent the entire population together. While sampling, these groups can be organized and then draw a sample from each group separately.

7. Why is sample preparation important in sampling?

Sample preparation refers to the ways in which a sample is treated prior to its analyses.

Sample preparation is a very important step because most samples collected may not be in a form that is suitable for subsequent analytical techniques due presence of impurities, size ,form and ability to dissolve in the solvents and to be detected or be responsive with the reagents and analytical instruments to be used . Also the original form of the analytic in the sample may at that time of sampling not be homogenic, concentrated enough or fully separated from its matrix so as to be responsive to the subsequent analytic procedures

8. Outline steps involved in sample preparation

Sample preparation could involve:

a) Size reduction

Sample reduction involves the processes and procedures done to achieve fine sized particles with increased surface area to enable subsequent dissolution in appropriate solvents and medias

b) Making sample homogeneous

The material within the sample selected from the population is usually heterogeneous. For this reason, it is usually necessary to make samples homogeneous before they are analyzed, otherwise it would be difficult to select a representative laboratory sample from the sample

c) Dissolution.

Most subsequent analytical procedures require the sample to be dissolved appropriate solvents whether aqueous or organic

d) Chemical digestion with acid or alkali,

Digestion is a process where the precipitate is re-dissolved and precipitated out of a cleaner environment (solution). The precipitate obtained in the separation step is placed into a volatile electrolyte solution and heated. Large particles are broken up to speed up digestion. This "solution" is often heated to increase the kinetic rates of dissolution and precipitation. Since the solid is in dynamic equilibrium with the solution, in time, all material will cycle from solid to solution and back. Observation does not speed up the chemical kinetics, so we take a cola break during digestion. The *solution is cooled after digesting for an hour or more. The precipitate is now refiltered.*

(c) Sample extraction,

(d) Sample clean up

(e) Sample pre-concentration.

9. Distinguish between sampling bias and sampling errors

The difference is that a sampling error is a specific instance of inaccurately sampling, such that the estimate does not represent the population, while a sampling bias is a consistent error that affects multiple samples.

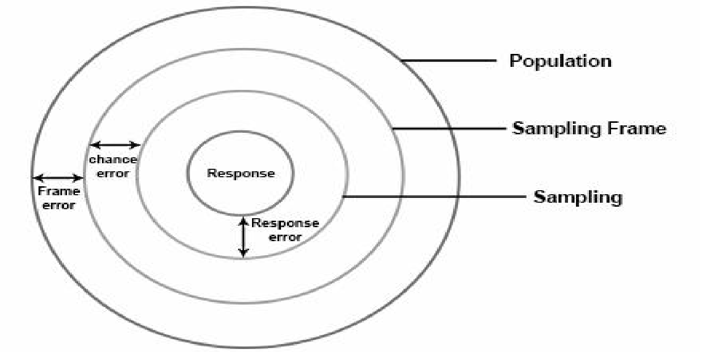
Sampling bias occurs when some members of a population are systematically more likely to be selected in a sample than others.

Sampling bias limits the generalizability of findings because it is a threat to external validity, specifically population validity. In other words, findings from biased samples can only be generalized to populations that share characteristics with the sample.

Sampling bias can occur in both probability and non-probability sampling.

Sampling error is defined as the amount of inaccuracy in estimating some value, which occurs due to considering a small section of the population, called the sample, instead of the whole population. It is also called an error. Sample surveys take into account the study of a tiny segment of a population, so, there is always a particular amount of inaccuracy in the information obtained. This inaccuracy can be defined as error variance or sampling error.

The concept of sampling error can be understood from the followingdiagram



:

From the above diagram

Sampling Error = (Response Error) + (Frame Error) + (Chance Error)

Sampling Error Formula

The measure of the sampling error can be calculated for particular sample size and design. This measure is termed as the correctness of the sampling plan. Sampling error is also due to the concept called sampling bias. This error is considered a systematic error.

The formula to find the sampling error is given as follows:

If N is the sample size and SE is the sampling error, then

Sampling Error, S. E = (1/√ N) 100

Assume that the size of the population is 1000, out of which 600 are men, and 400 are women, select 100 members.

Stratum	***Size***	***Sample for each Stratum***
1	$N_1 = 600$	$n_1 = (100\times600)/1000$ $= 60$
2	$N_2 = 400$	$n_2 = (100\times400)/1000 = 40$
	$N = 600+400$ $= 1000$	$n = 60 + 40 = 100$

10.Describe how to Reduce Sampling Error?

There are two methods by which this sampling error can be reduced. The methods are

1. *Increasing sample size*
2. *Stratification*

Increasing Sample Size

From a population, we can select any sample of any size. The size depends on the experiment and the situation. If the size of the sample increases, the chance of occurrence of the sampling error will be less. There will be no error if the sample size and the population size coincide. Hence, sampling error is in inverse proportion to the sample size.

Stratification

If all the population units are homogeneous or the population has the same characteristic feature, it's very easy to get a sample. The sample can be taken as a representative of the entire population. But if the population is not homogeneous (i.e population with the different *characteristic features); it is impossible to get a perfect sample. In such conditions, to get a better representative, the sample design is altered. The population is classified into different groups called strata, that contain similar units. From each of these strata, a sub-sample is selected in a random manner. Thus, all the groups are defined in the sample, the sampling error is reduced. Hence, the sub-sample size from each stratum is in proportion with the stratum size.*

11. State any four causes of bias in sampling

A common cause of sampling bias lies in the design of the study or in the data collection procedure, both of which may favor or disfavor collecting data from certain classes or individuals or in certain conditions. Sampling bias is also particularly prominent whenever researchers adopt sampling strategies based on judgment or convenience, in which the criterion used to select samples is somehow related to the variables of interest.

12.State and explain any three causes of loss of analytes in samples during sampling

Materials may be lost from a sample during laboratory preparation through the following ways

1. Losses as Dust or Particulates- small suspended particles in the residue may be readily by any air flow over the sample by air generated by changes in temperature. This can be prevented by storing the samples in covered containers

2. Losses Through Volatilization- The loss of volatile elements during heating is minimized by heating without exceeding the boiling point of the volatile compound and by also carrying out reactions in a properly constructed sealed vessel

3. Losses due to reactions between sample and container or reactions with other reagents initially used in the container, similarly, the internal surface area of a container, whether used for sample preparation or storage, may cause loss of analyte. Scratches and abrasions increase the surface area, and their geometry make loss of analyte likely.

13. Outline any for sources of contamination of samples in the laboratory

Possible sources of contamination include:

1. *Moisture and airborne contamination from the immediate environment*
2. *Reagents contaminations due to inherent impurities*
3. *Glassware/equipment contamination used in collecting , processing and storage of the samples*
4. *Contamination of Facilities e.g. processing lines , benches , rooms etc.*

5. Cross-contamination between high- and low-activity samples during storage and handling of samples.

14. Describe ways of preventing sample contamination

✓ *Many biological samples contain active enzymes they can cause changes in the properties of the food prior to analysis, e.g., proteases, cellulases, lipases, etc. If the action of one of these enzymes alters the characteristics of the compound being analyzed then it will lead to erroneous data and it should therefore be inactivated or eliminated. Freezing, drying, heat treatment and chemical preservatives (or a combination) are often used to control enzyme activity, with the method used depending on the type of food being analyzed and the purpose of the analysis.*

✓ *Ensuring proper storage conditions. Exposure to light, elevated temperatures, oxygen or pro-oxidants can increase the rate at which these reactions proceed. Consequently, it is usually necessary to store samples that have high unsaturated lipid contents under nitrogen or some other inert gas, in dark rooms or covered bottles and in refrigerated temperatures. Providing that they do not interfere with the analysis antioxidants may be added to retard oxidation.*

✓ *Microbial Growth and Contamination. Microorganisms are present naturally in biological materials and if they are not controlled, they can alter the composition of the sample to be analyzed. Freezing, drying, heat treatment and chemical preservatives (or a combination) are often used to control the growth of microbes in foods.*

✓ *Physical Changes. A number of physical changes may occur in a sample, e.g., water may be lost due to evaporation or gained due to condensation; fat or ice may melt or crystallize; structural properties may be disturbed. Physical changes can be minimized by controlling the temperature of the sample, and the forces that it experiences.*

✓ *Ensuring clean and hygienic environment for sample handling, storage and processing including using appropriate gloves , labcoats etc together with ensuring scrupulous cleanness of glassware, surfaces and other apparatus and equipment used. It also important to ensure availability of separate places for holding and processing samples so as to prevent their cross contamination.*

15.Outline steps involved in developing a sampling plan

*To do a successful environmental study it is necessary to have a 'plan of action', referred to as **a sampling plan**. Sampling plan will be different for each of these purposes.*

The first step is to clearly define the problem being studied and identify the environmental "population" of interest. Some of the major steps involved in the development of a successful study are as follows:

a) Clearly outline the goal of the study. Decide what hypothesis is to be tested and what data should be generated to obtain statistically significant information.
b) Identify the environmental population or area of interest.
c) Obtain information about the physical environment. Weather patterns, for instance, are important if air samples are to be taken.
d) Research the site history.
e) Carry out a literature search and examine data from similar studies previously carried out. This can provide information about trends and variability in the data. In the absence of previous data, a pilot study may be necessary to generate preliminary information on which to base a more detailed study.
f) Identify the measurement procedures to be used, because these affect the way samples are collected and handled.
g) Develop an appropriate field sampling design. Decide how many samples are to be collected and delimit the time and area to be covered by the study.
h) Determine the frequency of samples to be taken, both in time and space, depending upon the project objectives. Decide if, for example, 24 hour integrated samples will be collected or individual samples will be taken every few hours.
i) Develop a plan to insure and document the quality of each of the processes involved in the study: sampling, laboratory analysis, contamination control, etc.
j) Once the sampling and analysis are complete, assess the uncertainty of the measurements.
k) Perform statistical analysis on the data. Determine mean concentrations, variability, and trends with time and location.
l) Evaluate whether study objectives have been achieved. If not, additional work may be necessary to provide the needed information.

17. State factors to consider when designing a sampling plan

- ✓ *The purpose for the sample*
- ✓ *The nature of sample*
- ✓ *The resources required*
- ✓ *The time required*
- ✓ *The technical expertise needed*

17. Justify the following sample treatment procedures

a. Drying

Many of the samples received in the laboratories are wet. They must be dried before they can be crushed or pulverized for analysis. Laboratory staff uses drying procedures that avoid contamination and ensure that the drying temperature is suitable for your sample and the analysis that you want to perform on it.

a. Grinding

Grinding is usually required to decrease the particle size of solid samples.however, crushing should not introduce extrenous particles and impurities or alter the composition of the samples. A serious contamination error can arise during grinding and crushing due to mechanical wear and abrasion of the grinding surfaces.

Grinding must be continued until every particle has been passed if the screened sample is to have the same composition as it had before grinding and screening.

18. State any four sample storage methods

Methods of preservation are intended to retard biological and chemical degradation of compounds and complexes, and reduce volatility of constituents. No single preservation method is entirely satisfactory; choose the preservation with regard to the analyses being made..

Because a preservation method for one analysis may interfere with the preservation for another, samples for multiple determinations may need to be split and preserved separately. Use chemical preservation only when it is shown not to interfere with the method of analysis

Following collection and during transportation, samples should be kept at 6^{o}C or on ice. Samples requiring preservation should be preserved as soon as possible after collection to maintain the integrity of the sample.

In the laboratories, samples may be stored in dark rooms, in clean tightly closed or canned bottles, cool and dry rooms or in the fridges. Some may require to be stored in closed vessels with desiccants to absorb any moisture from the surrounding environment that may interfere with the samples

To minimize the potential for volatilization or biodegradation between sampling and analysis, keep the sample as cool as possible without freezing. Analyze the samples as quickly as possible upon arrival at the laboratory. If immediate analysis is not possible, storage at 2-4o C is recommended for most samples.

All samples must be properly stored from the time they arrive at the laboratory to disposal. Samples are refrigerated at 4°C prior to analysis unless method SOPs indicate other storage conditions.
Nature of Sample Changes: Some analyses are more likely than others to be affected by storage before analysis.
Temperature, pH, and dissolved oxygen are best determined in the field. Temperature changes quickly and pH may change significantly in a matter of minutes. Dissolved gases (oxygen, carbon dioxide) may be lost very quickly. With the changes in the pH-alkalinity-carbon dioxide balance, calcium carbonate may precipitate and cause a decrease in the values for calcium and total hardness.

In general, the shorter the time that elapses between the collection of a sample and its analysis, the more reliable the analytical results. However, it is impossible to state exactly how much time may be allowed between sample collection and analysis. Changes occurring in the sample depend on the character of the sample, the analysis to be made, and the conditions of storage. Changes caused by the growth of microorganisms are greatly retarded by keeping the sample in the dark and at a low temperature.

20.Explain methods used in sampling gases

The methods are: 1. Gravity Sedimentation Methods 2. Inertial Methods 3. Filtration 4. Precipitation.

1. Gravity Sedimentation Methods:

a. Sedimentation from still air:

The method was invented by Alvarez and Castro (1952) who constructed a simple box for the study of airborne fungi, it has two hinged slides and a covered tray at the bottom for inserting a microscopic slide or petridish. During air sampling the hinged slides are raised horizontally and wind is allowed to blow through the box.
The slides are then closed and the entrapped spores are sedimented under gravity. Here sampling is discontinuous and a small volume of air being sampled at a time. An improved form of this model was later described by Ogden (1974).

2. Inertial Methods:

In this method the particles may be retained on filters, on flat surface or on liquids. Air sample may be drawn through a jet tube or apparatus may move the trapping surface through the air.

3. Filtration:

In this method, the particle is removed from the air by suction. The air is allowed to pass through fibrous or porous medium that sieves the particles. In such a case filters with smooth surface like molecular membranes are suitable for the microscopic examination of the entrapped particles.

4. Precipitation:

i) Electrostatic precipitation:

It is very useful for small particles. Air is drawn through the sampling unit and the particles are charged near the entrance and then attracted to an electrode of opposite charge inside the instrument.

ii) Thermal precipitation:

These are similar to electrostatic precipitations through the electrostatic charges. From the air which flows through the sampler the particles are driven away from a hot surface to a cooler one.

21. Discuss storage methods of chemical samples in the laboratory

All chemicals handled in the laboratory must be considered as hazardous and therefore a risk. The inherent hazards of chemicals can be reduced by minimizing the quantity of chemicals on hand. However, when chemicals must be used, proper storage and handling can reduce or eliminate associated risks.

All chemical storage areas and cabinets should be inspected at least annually and any unwanted or expired chemicals should be removed. Safe chemical handling requires routine inspections of chemical storage areas and maintenance of stringent inventory control.

Typical storage considerations may include temperature, ignition control, ventilation, segregation and identification. Proper segregation is necessary to prevent incompatible materials from inadvertently coming into contact. A physical barrier and/or distance is effective for proper segregation.

22. Discuss methods for safe chemical storage:

✓ *Ensure all containers of hazardous chemicals are properly labeled with the identity of the hazardous chemical(s) and appropriate hazard warnings.*

✓ *Segregate all incompatible chemicals for proper storage of chemicals by hazard class. In other words, store like chemicals together and away from other groups of chemicals that might cause reactions if mixed.*

✓ *Do not store chemicals alphabetically except within a grouping of compatible chemicals.*

✓ *Flammable materials should be stored in an approved, dedicated flammable materials storage cabinet or storage room if the volume exceeds ten gallons. Keep cabinet doors closed.*

✓ Chemicals should be stored no higher than eye level and never on the top shelf of a storage unit. Do not overcrowd shelves. Each shelf should have an anti-roll lip.

✓ Avoid storing chemicals on the floor (even temporarily) or extending into traffic aisles.

✓ Liquids should be stored in unbreakable or double-contained packaging, or the storage cabinet should have the capacity to hold the contents if the container breaks.

✓ Store acids in a dedicated acid cabinet. Nitric acid may be stored there also but only if it is kept isolated from all other acids.

✓ Store highly toxic or controlled materials in a locked, dedicated poison cabinet.

✓ Volatile or highly odorous chemical shall be stored in a ventilated cabinet. Chemical fume hoods shall not be used for storage as containers block proper air flow in the hood and reduce available work space.

✓ All chemicals should be labeled and dated upon receipt in the lab and on opening. This is especially important for peroxide-forming chemicals such as ethers, dioxane, isopropanol, and tetrahydrofuran. Solutions should be labeled and dated when prepared.

✓ Look for unusual conditions in chemical storage areas, such as:

- *Improper storage of chemicals*
- *Leaking or deteriorating containers*
- *Spilled chemicals*
- *Temperature extremes (too hot or cold in storage area)*
- *Lack of or low lighting levels*
- *Blocked exits or aisles*
- *Doors blocked open, lack of security*
- *Trash accumulation*
- *Open lights or matches*
- *Fire equipment blocked, broken or missing*
- *Lack of information or warning signs ("Flammable liquids", "Acids", "Corrosives", "Poisons", etc.)*

✓ First aid supplies, emergency phone numbers, eyewash and emergency shower equipment, fire extinguishers, spill cleanup supplies and personal protective equipment should be readily available and personnel trained in their use.

✓ Chemicals stored in explosion-proof refrigerators or cold rooms shall be sealed and labeled with the name of the person who stored the material in addition to all other required hazard warnings.

✓ Only compressed gas cylinders that are in use and secured in place shall be kept in the laboratory. All others, including empties, shall be sent to the compressed gas cylinder storage area for the particular facility.

✓ Keep all stored chemicals, especially flammable liquids, away from heat and direct sunlight.

Packaging

After sampling, the sample containers must be checked for leaks. The outer surface of packages must be clean and dry. If leaks occur, caps and stoppers should be reinforced or replaced. Another inspection should then be carried out, and if leaks persist fresh samples should be taken. Preferably use another sample container.

The sample containers used for the packaging of volatile liquid samples should be filled to approximately 90 % of their total holding capacity. Warning signs, markings and symbols indicating potential hazards should be placed on packages holding samples of hazardous goods/compounds.

Sealing

Depending on your national regulations the sample container should be sealed in an appropriate manner for the type of container used, to prevent unauthorised or inappropriate handling of samples (and ensure the integrity of the contents). The seal must be firmly attached and stable in order to prevent damage during sample storage or transport, and to safeguard the chain of evidence.

Marking

The markings on labels must be clearly legible and permanent in order to prevent deletion or substitution/alteration during storage, handling and transport.In the case of retail sale packages, the customs label should not cover the commercial labels of the original product (trademark, manufacturer, contents, expiry date, etc.). It is recommended that you place retail packages in a polythene bag and fix the labels and seals to the bag.Health and safety regulations must be observed.

Documents accompanying final samples

The accompanying documents must be kept in line with rules laid down by the customs administration. This depends on the local situation. In some Member States only digital documents are used; they are sent by email to the customs laboratory or using integrated information systems. Copies of other relevant documents concerning the nature of the goods may also be enclosed (SDS, technical specifications, quality/compliance certificates, etc.).

23. Storage of samples

Storage conditions are determined by the characteristics and properties of samples taken. Storage conditions should ensure that the sample is not altered in any way that might affect the parameters to be analysed.

Health and safety regulations must be observed.

In general, samples should be stored in a clean, dry, dark, cool and sufficiently ventilated room.

- *Foodstuff samples must be stored separately from other samples. Perishable goods must be stored in refrigerators or freezers and the storage temperature must be monitored regularly. If frozen, samples should be maintained at below -18 °C and the storage temperature should be monitored.*
- *Flammable substances must be stored in accordance with the fire safety regulations.*

If the customs office cannot provide these facilities and the sample cannot be transferred to the customs laboratory immediately, an alternative external storage place should be sought that fulfils the conditions for safeguarding the quality and identity of the samples.

It is recommended that each customs office appoint an officer to manage the sample storage facility. Their job description should also include the following tasks:

- *accepting samples for storage and transport for analysis, and record keeping;*
- *monitoring the sample storage deadlines;*
- *organising sample disposal after expiry of these dates;*
- *ensuring that the storage conditions for the samples are met at all times.*

For certain products specific conditions are appropriate. Some examples are given below, but you should refer to the specific sampling procedure for more details.

Product	***Conditions***
Light sensitive samples	*Storage in a dark place.*
Samples giving off poisonous or unpleasant smells.	*Possible storage in a fume hood or in a room with sufficient mechanical ventilation.*
Mineral oils, highly inflammable and other	*See SDS. Storage in a safety cupboard, when possible. If no information*

dangerous samples	*available, ask laboratory for storage conditions.*
Samples susceptible to decay	*Storage in a freezer or refrigerator; depends of character of the product. If in doubt, consult the laboratory.*
Samples of very perishable goods	*Foodstuff samples must be stored separately from other samples. Perishable goods must be stored in refrigerators or frozen in consultation with laboratory. Indicate on Sample form that freezing was done by customs officer. Frozen samples must be maintained at below -18 °C and the storage temperature should be monitored regularly.*
Samples of chilled products	*Foodstuff samples must be stored separately from other samples. Chilled samples must be maintained at approx. 4 °C and the storage temperature should be monitored regularly.*
Samples of frozen products	*Foodstuff samples must be stored separately from other samples. Frozen samples must be maintained at below -18 °C and the storage temperature should be monitored regularly.*
Samples of retail packing of food products and of medicines and pharmaceutical products.	*Storage at conditions labelled on packing, but not above approx. 30 °C or as indicated on the package.*

Transport

The transport conditions must guarantee the integrity and characteristics of the samples being transported. The type of transport will depend on the nature of the samples (e.g. dangerous good or special temperature *requirements), the quantities, the urgency and frequency with which they occur.There are several methods for transporting samples to the customs laboratory.*

Transport	***Remarks***
By post and regular delivery services	*Can only be used for samples without special storage conditions.* *Some delivery services may also transport certain dangerous samples. Each service may have special requirements regarding quantities, packaging and labelling.*
By specially equipped transport, e.g. for transporting chemical samples or frozen goods	*Samples of all types can be transported by this method provided there is no risk of cross-contamination. Samples with special storage conditions can best be sent by this method. For samples with dangerous properties, check the contractor's requirements regarding quantities, packaging and labelling.*
By courier	*Samples of all types can be transported by this method provided the samples are suitably packed and there is no risk of cross-contamination. For samples with dangerous properties, check the contractor's requirements regarding quantities, packaging and labelling. The courier may also have restrictions on what they will accept. It can be practical to use a courier for regular transport operations or urgent deliveries.*
By customs officers themselves	*Delivery direct to the customs laboratory. The regulations regarding the transport of dangerous substances (ADR), must be observed, unless the samples are transported under circumstances that permit exemptions from ADR.*

CHAPTER SEVEN

SEPARATION EXTRACTION AND PURIFICATION

1a. Describe the advantages of vacuum filtration over gravity filtration

Vacuum filtration is typically a fast and efficient way of filtering. Gravity filtration relies on downwark sucking through filter paper by gravity,therefore the gravitation pull exerted by the gravity may not be sufficient enough to cause diltration of relatively courseparticles to pass through the filter paper.

In a vacuum filtration, the solution to be filtered is drawn through the filter paper by applying a vacuum to a filter flask with a side arm adaptor (also known as a Buchner flask). This exert relative high sucking presure which causes sucking or filtration of substances through filter paper to be more faster and more efficient

2. Describe any two reasons for using an oil bath instead of water bath in determining the melting point of a substance

Oil baths are much like water baths, but use silicone or mineral oils is used in order to enable temperatures hotter than the boiling point of water.

Silicone oil baths can be heated to 250°C, while mineral oil baths can be heated to 300°C. Mineral oil is composed of mixtures of long-chain alkanes, and so is combustible.

Silicon oil provide a relatively uniform and sustained heat distribution that can be maintained over a longer period that water bath

a. Explain the importance of using the most minimum amounts of solvent to disolve solid during crystalization process

If too much solvent is added, the solution will not be saturated upon cooling and no crystals will form. Therefore, the solvent is heated to its boiling point and then slowly added to completely dissolve the solute

b. State two reasons for slow cooling of hot filtrate during recrystalization

✓ *The slower the cooling process, the less chance of trapping impurities in the developing crystal lattice.*

✓ *Slow cooling often leads to purer crystals.*

c. Outline the procedure used in vacuum distillation

Vacuum distillation is a special method of separating compounds at pressure lower than the standard atmospheric pressure.

Under this condition, the compounds boil below their normal boiling temperature. Hence, vacuum distillation is best suited for separation of *compounds with higher boiling points (more than 392°F), which tend to decompose at their boiling temperature.*

Vacuum distillation can be conducted without heating the mixture, as is usually followed in other distillation types.

For the separation of some aromatic compounds, vacuum distillation is used along with steam distillation. When vacuum distillation is combined with fractional distillation method, components of a mixture get separated very easily.

24. Describe two conditions that a compound must meet to be successfully separated by steam distillation

Steam distillation is used for the purification of mixtures in which the components are heat sensitive; for example, organic compounds.

In this process, steam is introduced to the apparatus and the temperature of the compounds are depressed, by vaporizing them at lower temperature. This way, the heat sensitive compounds are separated before decomposition. The vapors are collected and condensed in the same way as other distillation types. The resultant liquid consists of two part, water and compound, which is then purified by using simple distillation..

The process requires some initial training and skill to operate the equipment. It also requires periodic maintenance. Steam distillation is widely used for large-scale separation of essential oils, fats, waxes, and perfumes.

3. Two solvents are equally suitable for recrystalization process. State two preferences in choosing one of them

The solvent should have a high temperature coefficient.

The solvent must not dissolve the compound at low temperatures, but must dissolve the compound at high temperatures. The solute must dissolve in order to rid its lattice of impurities, but must not remain dissolved at room temperature.

b.) using a solvent that dissolves impurities readily or not at all. If the solvent dissolves the impurities readily (even at room temperature) then the impurities will not become trapped in the developing crystal lattice, but will remain dissolved in the solvent. If the impurities do not dissolve (even at elevated temperatures) then they can be easily removed by gravity filtration.

c.) The solvent should not react with the solute. As mentioned earlier, recrystallization does not chemically alter a molecule. No chemical bonds must be broken in the solute molecule. The crystal lattice is dissolved at elevated temperatures, but this only involves overcoming the intermolecular attractive forces.

d.) The solvent should be nonflammable, inexpensive and volatile. Solvents with low boiling points (i.e., volatile) can be easily removed from the resultant crystals by simply allowing the solvent to evaporate.

4. State three advantages of Soxhlet extraction as a method of separating mixtures

✓ *Only minimum amount of solvent is used*

✓ *Instead of many portions of warm solvent being passed through the sample, just one batch of solvent is recycled.*

✓ *The non-soluble portion of the extracted solid remains in the thimble, and is easier to discard*

✓ *After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound.*

5. ***Describe how a Soxhlet apparatus works***

The solvent is heated to reflux. The solvent vapour travels up a distillation arm, and floods into the chamber housing the thimble of solid.

The condenser ensures that any solvent vapour cools, and drips back down into the chamber housing the solid material.

The chamber containing the solid material slowly fills with warm solvent. Some of the desired compound dissolves in the warm solvent.

When the Soxhlet chamber is almost full, the chamber is emptied by the siphon.

The solvent is returned to the distillation flask. The thimble ensures that the rapid motion of the solvent does not transport any solid material to the still pot.

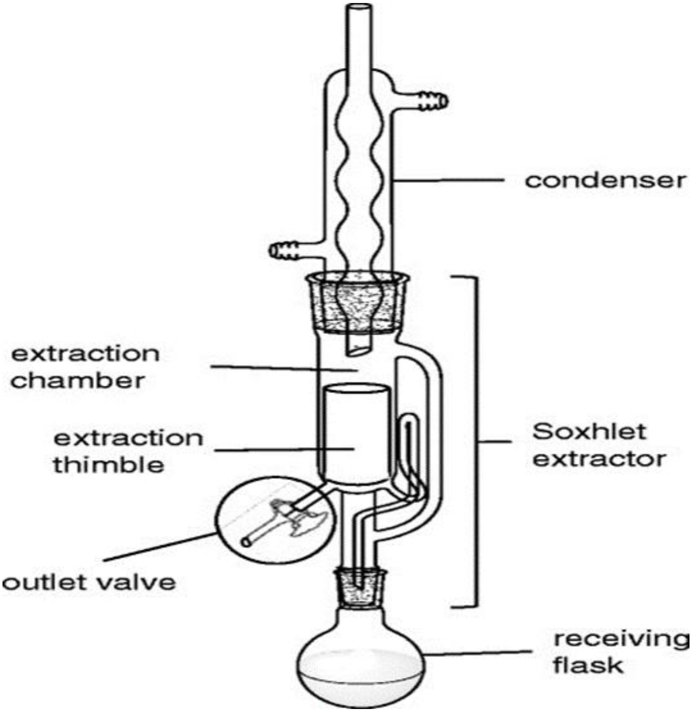
This cycle may be allowed to repeat many times, over hours or days. During each cycle, a portion of the non-volatile compound dissolves in the solvent.

After many cycles the desired compound is concentrated in the distillation flask.

After extraction the solvent is removed, typically by means of a rotary evaporator, yielding the extracted compound.

The non-soluble portion of the extracted solid remains in the thimble, and is usually discarded

b. ***Draw a labelled diagram of Soxhlet extraction apparatus***



6. ***a. Explain how fruit juice can be extracted using soxhlet extractor.***

The Soxhlet extractor is used for liquid-solid extractions when the compound to be extracted has limited solubility in the chosen solvent and the impurities are insoluble.

During the extraction, solvent vapour will flow up the distillation path, into the main chamber and up into the condenser where it will condense and drip down. The solvent will fill the main chamber, dissolving some of the desired compound from the solid sample. Once the chamber is almost full, it is emptied by the siphon, returning the solvent to the round bottom flask to begin the process again. Each time the extraction is repeated, more of the desired compound is dissolved, leaving the insoluble impurities in the thimble.

Unlike a traditional extraction method, a small amount of solvent is reused to perform an extraction many times. This means that much less solvent is *used in a Soxhlet extraction, making it more time and cost effective. Also, the Soxhlet extractor can run continuously without any further operation, making it an excellent choice for extracting compounds over hours or even days.*

The Soxhlet extractor is used whenever exhaustive extractions are needed, particularly in the oil and food industries. It is also widely used for extracting bioactive compounds from natural resources which is crucial in environmental analysis of soils and wastes. The Soxhlet extractor will run continuously once set up correctly

b. How to use a soxhlet extractor

✓*Load the sample material containing the desired compound into the thimble (the fruit sample in this case)*

✓*Place the thimble into the main chamber of the Soxhlet extractor*

✓*Add the chosen solvent to a round bottom flask and place onto a heating mantle*

✓*Attach the Soxhlet extractor above the round bottom flask*

✓*Attach a reflux condenser above the extractor, with cold water entering at the bottom and exiting above*

✓*Now the apparatus is set up, heat the solvent to reflux and leave to extract for the required amount of time*

c. State one disadvantage of Soxhlet extraction

Because of its small size, it only allow small scale laboratory extraction of samples but cannot be used in large scale industrial processing

*7. **Define chromatography** It is technique for rapid and efficient separation of components of a mixture and purification of compounds. It is based on differential migration of the various components of a mixture through a stationary phase under the influence of a moving phase.*

Explain the basis (principle) of chromatographic process ?

It is based on the differential migration of the individual components of a mixture through a – stationary phase under the influence of a moving phase.

*8. **Explain the following terms as used in chromatography***

- ✓ *Eluent: The mobile phase is used to perform a separation.*
- ✓ *Elution" The process of passing mobile phase through the column to transport solutes down a column called*
- ✓ *Solvent: A the term sometimes referring to the liquid stationary phase in partition chromatography.*
- ✓ *Absorption: The process of retention in which the solute partitions into a liquid-like coating.*

- ✓ *Adsorbent: Packing used in adsorption chromatography. Silica gel and alumina are the most frequently used adsorbents in high-performance liquid chromatography (HPLC)*
- ✓ *Analyst: The compound of interest to be analyzed by injection into and elution from an HPLC Column*
- ✓ *Asymmetry: Factor describing the shape of a chromatographic peak. The chromatographic theory assumes a Gaussian shape and that peaks are symmetrical. A quantitative measure is the peak asymmetry factor, which is the ratio of the distance from the peak apex to the backside of the chromatography curve over the distance from the peak apex to the front side of the chromatography curve at 10 % of the peak height.*
- ✓ *Buffer: A solution that maintains constant PH by resisting changes in PH from dilution o addition or small amounts of acids and bases.*
- ✓ *Chromatography: Chromatography is a physical method of separation in which the components to be separated are distributed between two phases, one of which is stationary (Stationary Phase) while the other (The mobile phase) moves in a definite direction.*
- ✓ *Chromatogram: A plot of detector signal output or sample concentration versus time or elution volume during the chromatographic process.*
- ✓ *Adsorbate*
- ✓ *Resolution*
- ✓ *Location*
- ✓ *Development*

9. define solvent

A solvent's molecules pull apart the solute's molecules, and eventually the solute's molecules become evenly distributed throughout the solvent. This homogeneous mixture cannot be separated physically.

That means heat or another chemical process must be applied to the solution in order to separate the solvent from the solute.

Popular solvents include water and organic compounds like benzene, tetrachloroethylene and turpentine.

10 Explain solvent extraction

Solvent extraction is a process in which compounds are separated based on their relative solubilities. Solvent extraction is the act of removing something or separating it.

This must be done through force and this process occurs over the course of two different immiscible phases.

This treatment method involves using a solvent - a fluid that has the ability to dissolve another substance. Solvent extraction does not destroy a *compound. It instead separates it, a process that can provide several valuable benefits depending on the industry in which the process is used.*

Immiscible liquids (liquids that do not dissolve in one another) form layers when put together. This is because each liquid differs in polarity, or orientations. The order of the phases, whether a particular liquid is on top or on the bottom, is determined by its density.

For example, if you use ether and water during the extraction process, water has a higher density than ether. Therefore, water will be the bottom phase.

Your method for extraction may vary depending on your equipment, but in its most simplistic form, extractions often use some kind of separatory funnel. The liquid mixture that is to be separated is first added to the funnel. When the two extraction solvents are then added to the funnel, they should separate into two phases.

After forcibly shaking the funnel and allowing it to stand for several minutes, the two layers can be collected. In the end, the target molecule for extraction will be located in one of the solvents.

10.Define the term partition coefficient

A partition coefficient is the ratio of the concentration of a substance in one medium or phase (C1) to the concentration in a second phase (C2) when the two concentrations are at equilibrium; that is, partition coefficient = (C1/C2)equil. The units of C1 and C2 may be different.

*11..**Briefly describe the technique of partition extraction***

This method is often called "extraction." Extraction means drawing a compound out of a mixture using a solvent. Solvent partitioning is more specific. It means compounds have a "choice" of two solvents that they can dissolve in. Some compounds dissolve in one solvent. Some compounds dissolve in the other solvent. That way the compounds in the mixture become separated into two groups.

Solvent partitioning depends on solubility. It depends on the solubility in two different solvents, though. It depends on an equilibrium: does the compound dissolve more in solvent A, or solvent B?

Solvent partitioning requires two solvents that are not miscible in each other. Usually one of the solvents is water. The other solvent is a liquid that does not dissolve very well in water, such as diethyl ether (this is the most common type of ether, and it is often called simply "ether"). If you look closely at a mixture of ether and water, you will see two layers because the two compounds do not dissolve very well in each other.

It's important that the two solvents are immiscible, because then it is easy to separate them from each other. The top liquid can be drawn off with a pipet, *or the bottom layer can be drained out via a stopcock. The compounds that dissolved in the ether have thus been separated from the water-soluble compounds. Because ether evaporates very easily, the compounds that dissolved in the ether can also be separated from the ether (see "distillation"). As a result, purer compounds can be obtained.*

The formula for the partition coefficient is,

$$Kd = \frac{Cs}{Cm}$$

Where,

In the stationary phase, the concentration of the solute is C_s,

In the mobile phase, the concentration of the solute is C_m.

12..The concentration of solute in the mobile phase is 5.00M and 7.00M in the stationary phase. Calculate the partition coefficient K_d ***between water and hexane.***

Given

$C_s = 7.00M$

$C_m = 5.00M$

Apply the numerics in the corresponding formula given below

$$Kd = \frac{Cs}{Cm}$$

$$Kd = \frac{7.00}{5.00}$$

$$Kd = 1.4$$

Using an illustrate , explain the multistage of solvent extraction.

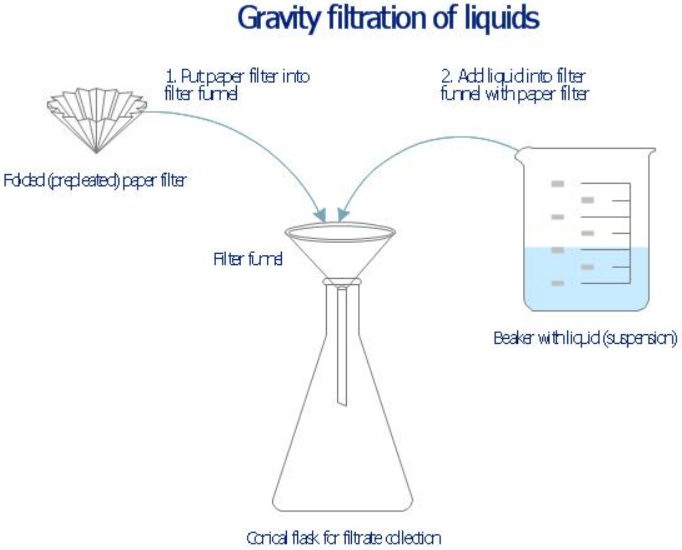
Multistage Liquid Liquid Extraction (LLE) is a process where extraction steps are repeated in order to increase the recovery of a product. This process is required when, due to a small partition coefficient, the recovery in a single extraction step is insufficient.

13. Draw a labeled diagram of gravity filtration techniques

"Filter paper is a semi-permeable paper barrier placed perpendicular to a liquid or air flow. It is used to separate fine solids from liquids or air."

Filtration is commonly the mechanical or physical operation which is used for the separation of solids from fluids (liquids or gases) by interposing a *medium through which only the fluid can pass. The fluid that pass through is called a filtrate. Oversize solids in the fluid are retained, but the separation is not complete; solids will be contaminated with some fluid and filtrate will contain fine particles (depending on the pore size and filter thickness)."*

1. Put folded filter paper cone into glass filter funnel inserted into neck of conical (Erlenmeyer) flask.
2. Add liquid suspension from the glass beaker with a spout into the funnel with paper filter.
3. Collect filtrate in the conical flask and solid on the paper filter in the funnel.



14. ***Explain the type of solvents are generally employed in chromatography ?***
Generally solvents having low viscosities are employed in chromatography. This is due to the fact that the rate of flow of a solvent varies inversely as its viscosity.

15. ***Give four chromatographic techniques.***
Paper chromatography, column chromatography, thin layer chromatography, gas chromatography.

16.Explain the mobile and stationary phases in paper chromatography

Water absorbed on cellulose constituting the paper serves as the stationary phase and organic solvent as moving phase.

17. Explain the term developing in chromatography

During chromatography, if the components to be separated are colourless, then these separated components on chromatogram are not visible. Their presence is detected by development, which involves spraying a suitable reagent (called developing reagent) on the chromatogram, or placing the chromatogram in iodine chamber, when various components become visible. This process is called developing of chromatogram.

18. Explain how does the liquid rise through the filter paper

By means of capillary action.

19. Explain the term R_f value

R_f (retention factor) of a substance is defined as the ratio of the distance moved up by the solute from the point of its application to the distance moved up by the solvent from the same point.

20.State factors that the R_f value of a compound depend

- ✓ *Nature of the compound.*
- ✓ *Nature of the solvent.*
- ✓ *Temperature.*

21.Give the biochemical uses of chromatography.

It helps in the separation of amino acids, proteins, peptides, nucleic acids, etc.

22. Define the term loading (or spotting)

The application of the mixture as a spot on the original line on the filter paper strip or addition of mixture to the column, is called loading (or spotting).

23. State essential characteristics of the substance used as a developer

1. *It should be volatile.*
2. *It should impart colour to the different spots.*
3. *It should not react with various compounds which are being separated.*

24. What are the main differences between high performance liquid chromatography and gas chromatography?

o *In HPLC the mobile phase is a liquid whereas in Gas Chromatography the mobile phase or carrier is a gas.*

o *HPLC is useful for analysis of samples which are liable to decompose at higher temperatures. GC involves high temperatures so compounds are stable at such temperatures.*

o Gas Chromatography is applied for analysis of volatile compounds whereas non volatile compounds can be easily analyzed on HPLC

o Gas Chromatography cannot be used for analysis of high molecular weight molecules whereas HPLC has applications for separation and identification of very high molecular weight compounds

o HPLC requires higher operating pressures than GC because liquids require higher pressures than gases for transport through the system

o HPLC columns are short and wide in comparison to GC columns

*25. **What Is The Basic Principle Of Paper Chromatography?***

Paper chromatography is a form of liquid chromatography where the components of a mixture of organic compounds get separated as unique spots by unidirectional flow of the developing liquid mobile phase solvent mixture over the filter paper to which a spot of the sample is applied. The distance travelled by each component is specific under the given set of operational conditions.

*26. **Why The Developing Solvent Mixture Is Prepared Fresh Before Use?***

The developing liquid phase comprises of a pure solvent but more often it is a mixture of two or more solvents in specified proportions. In case solvents are mixed and stored for long periods there could be loss of volatile component which will alter the mixing proportions.

27.Why Is It Necessary To Cover The Developing Chamber During The Paper Development?

During the chromatogram development chamber is covered.This is essential as the environment inside the chamber should remain saturated with the solvent vapour. Development times can vary from about an hour to several hours and a saturated environment prevents losses due to evaporation.

28.What Are The Common Techniques Used For Detecting Colourless Spots?

It is easy to distinguish coloured spots visually but for colourless compounds alternate techniques need to be adopted which can be specific or non-specific.

o A common non-specific method is suspension of developed chromatogram in iodine vapour. Most organic compounds show up as brown spots.

o The sheet is viewed in a UV Viewing cabinet under 366 nm and 254 nm wavelength lamp illumination. On observation the spots need to be carefully marked with a pencil for Rf calculations.

- *Under specific methods amines and amino acids are observed by spraying heated paper on development with 0.2% hydrazine. Deep blue or purple spots begin to appear.*
- *Alkaloids – Dragendroff's reagent spray results in orange or orange yellow spots.*
- *Aldehydes&Ketones – 2,4-DNPH spray in methanol and sulphuric acid results in orange or yellow spots.*

29. ***Why should the samples have reasonable solubility which is neither too high or too low in the developing solvent mixture?***

The samples should have a medium solubility in the developing solvent mixture.Too high a solubility will lead to transfer of the component alongwith the solvent front and on the other hand if the solubility is too low the component will not be carried by the solvent mixture and will remain close to the initial applied spot. In either case the resolution of the mixture components will be low. Thus reasonably good resolution can be obtained for medium solubility of compounds in the solvent mixture.

30. ***What Information You Get From The Retardation Factor Value?***

Retardation factor Rf is a measure of the separation of a particular component. It is expressed as

Rf = distance moved by the component spot/ distance moved by solvent front

Rf is a unit less quantity and lies between 0and 1.A value of 0 indicates no separation has taken place and 1 represents that the component has moved entire length alongwith the solvent front. In case two spots have same value of Rf it indicates that they are not resolved. At least a difference of 0.05 is necessary to discern the separation between two spots.

31. ***Explain Various Paper Chromatography Techniques?***

Paper chromatography separations are classified in accordance with the direction of flow of mobile phase along the filter paper.

- *Ascending paper chromatography – the carrier liquid moves from bottom upwards.*
- *Descending paper chromatography – the carrier liquid trough is on top and mobile phase moves downward on the filter paper.*
- *Ascending – descending paper chromatography – The paper is rolled downward over the rod at the top. On reaching the top in ascending mode it starts downward movement in the next phase.*

32. ***State the Essential Criteria For Selection Of Suitable Solvents For Paper Chromatography?***

    ✓ *Solvents are selected on the basis of solubility of the sample components. In general it is advisable to keep in mind:*

- ✓ *Solvents are not toxic or carcinogenic.*
- ✓ *Solvent constituents of mixture should not react with any of the sample constituents.*
- ✓ *Solvents selected should not interfere in detection of separated spots.*
- ✓ *Solvents should not be highly volatile as loss of components can result in change of mixture composition.*

33. *Give the advantages of paper chromatography over the other Advanced Instrumental Techniques?*

Chromatographic technique of analysis has seen an impressive growth over time. Such advances have increased laboratory throughputs lowered limits of detection and has made forays into new areas of applications. Paper chromatography has retained its ground till date and is popular in laboratories across the world. Some of the reasons for this are:

- ✓ *Low cost of analysis and freedom from maintenance.*
- ✓ *Separated spots are visible for coloured compounds and colourless compounds can be viewed by using alternate techniques.*
- ✓ *Minimum operation and training requirements.Solvent consumption is much less as compared to more sophisticated techniques.*
- ✓ *Paper chromatography serves as a good demonstration of basic concepts of separation for school and undergraduate students.*

34. *Give the Limitations Of Paper Chromatography Technique?*

Paper chromatography has some limitations such as:

- ✓ *Semi-quantitative in nature.*
- ✓ *Overlapping of spots of components having close Rf values.*
- ✓ *Higher concentration of components often leads to streaking instead of well-defined spots.*
- ✓ *Errors in Rf calculations can result from uneven flow of solvent front. This can be caused by running out of solvent at the bottom of the chamber, uneven cutting of the filter paper or unevenness of the bottom of the development chamber.*
- ✓ *Improper sample spotting, spotting below the marked line resulting in dipping into the solvent or accidental dipping of spot into solvent while inserting the paper into the solvent chamber.*

35. *Explain the separation principle in size exclusion chromatography?*

In size exclusion chromatography the separation does not involve chemical interactions between eluting molecules and stationary phase. The separation takes place on the basis of molecular size with larger molecules eluting first and small molecules in the end. Small molecules are retained longer in the pores of the stationary phase therefore they get eluted last.

36. ***Explain why it is necessary to degass the mobile phase?***

Mobile phases entrap air from the atmosphere and this trapped air gets released as small bubbles under high pressures encountered during the HPLC analysis. Such bubbles can lead to noise in detector response or hinder flow of mobile phase through columns. In order to overcome such problems degassing of mobile phase becomes essential.

37. ***What is the basis (principle) of chromatographic process?***

It is based on the differential migration of the individual components of a mixture through a — stationary phase under the influence of a moving phase.

38. ***State the type of solvents are generally employed in chromatography?***

Generally solvents having low viscosities are employed in chromatography. This is due to the fact that the rate of flow of a solvent varies inversely as its viscosity.

39. ***What Are The Moving And Stationary Phases In Paper Chromatography?***

Water absorbed on cellulose constituting the paper serves as the stationary phase and organic solvent as moving phase.

40. ***What Is Meant By The Term R_f Value?***

R_f (retention factor) of a substance is defined as the ratio of the distance moved up by the solute from the point of its application to the distance moved up by the solvent from the same point.

41. ***What are the advantages of chromatography over other techniques?***

- ✓ *It can be used for a mixture containing any number of components.*
- ✓ *Very small quantities of the substances can be effectively detected and separated from a mixture.*

42. ***Describe how a thin layer chromatography is prepared for laboratory work***

The experiment is conducted on a sheet of aluminium foil, plastic, or glass which is coated with a thin layer of adsorbent material.

The stationary phase that is applied to the plate, which is usually used is aluminium oxide, cellulose, or silica gel. is made to dry and stabilize on a clean glass slide .

To apply sample spots, thin marks are made at the bottom of the plate with the help of a pencil.

Apply sample solutions to the marked spots.

Pour the mobile phase into the TLC chamber and to maintain equal humidity, place a moistened filter paper in the mobile phase.

Place the plate in the TLC chamber and close it with a lid. It is kept in such a way that the sample faces the mobile phase.

Immerse the plate for development. Remember to keep the sample spots well above the level of the mobile phase. Do not immerse it in the solvent.

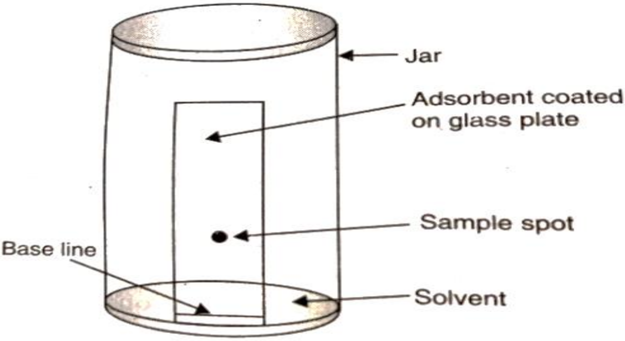
Wait till the development of spots. Once the spots are developed, take out the plates and dry them. The sample spots can be observed under a UV light chamber.

44.Explain four qualities of solvents suitable for solvent extraction

1. *The solvent should be able to dissolve at least one component to a large extent than the rest of the components in the mixture.*
2. *The solvent should not be miscible with the liquid to be extracted but not with the other components of the mixture or react with the solute.*
3. *The reaction taking place should be stable and irreversible. Reversible reactions can bring back the dissolved components in their previous form and the extraction will not be completed successfully.*
4. *The boiling point of the solvent should be low enough (well below the melting point of the solute) such that it can be Evaporated easily after collection.*
5. *The compound formed after the reaction should be easily separated from the extracted compound so that it can be reused.*
6. *The density of the compound should be different from the required component to help the separation readily.*
7. *. It should have a favorable temperature coefficient*
8. *.It should be inexpensive and cost-effective.*
9. *The solvent should not be toxic or corrosive as it can harm the extraction instruments.*

45. Thin Layer Chromatography

Here a sheet of alumina is taken (0.2 mm thick) over which a small spot of the mixture is placed and it is kept in a suitable solvent. The solvent rises due to capillary action and the constituents also rise with the solvent depending on their differential adsorption, and thereby, they are separated.



45.Outline Column Chromatography

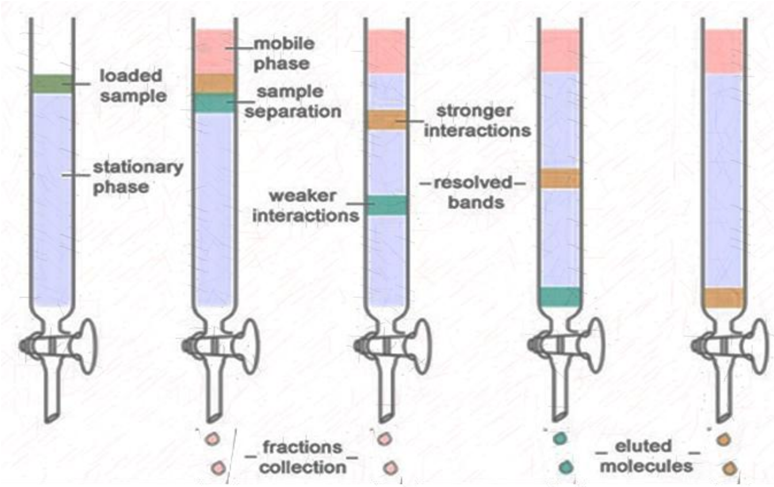
Column chromatography is technique in which the substances to be isolated are presented onto a column loaded with an adsorbent (stationary phase), go through the column at various rates that rely upon the affinity of every substance for the adsorbent and the solvent or solvent mixture, and are typically gathered in solution as they pass from the column at various time. The two most common examples of stationary phases for column chromatography are silica gel and alumina while organic solvents are regarded as the most common mobile phases.

46.Column Chromatography principle

The main principle involved in column chromatography is the adsorption of the solutes of the solution with the help of a stationary phase and afterward separates the mixture into independent components. At the point when the mobile phase together with the mixture that requires to be isolated is brought in from the top of the column, the movement of the individual components of the mixture is at various rates. The components with lower adsorption and affinity to the stationary phase head out quicker when contrasted with the greater adsorption and affinity with the stationary phase. The components that move rapidly are taken out first through the components that move slowly are eluted out last. The adsorption of solute molecules to the column happens reversibly. The pace of the movement of the components is communicated as:

R_f *= the distance traveled by solute/ the distance traveled by the solvent*

Where R_f *is called retardation factor*



47. explain the Column Chromatography components

Components of a typical chromatographic system using a gas or liquid mobile phase include:

- ***Stationary phase –*** *Generally it is a solid material having a good adsorption property and should be suitable for the analytes to be separate. It should not cause any hindrance in the flow of the mobile phase.*
- ***Mobile phase and delivery system –*** *This phase is made up of solvents that complement the stationary phase.*

The mobile phase acts as a solvent, a developing agent (promotes separation of components in the sample to form bands), and an eluting agent (to remove the components from the column that are separated during the experiment).

- ***Column –***

For liquid chromatography: *2-50cm long and 4mm internal diameter, fabricated with stainless steel*

For gas chromatography: *1-3m long and 2-4mm internal diameter, fabricated either with glass or stainless steel*

A column's material and its dimension are very crucial to support the stationary phase and promote effective separations.

- ***Injector system –*** *Responsible for delivering test samples to the column's top in a reproducible pattern.*
- ***Detector and Chart Recorder –*** *This gives a continuous record of the presence of the analytes in the eluate as they come out from the column. Detection relies on the measurement of a physical parameter (like visible or UV*

adsorption).

On the chart recorder, each separated analyte is represented by a peak.

A collector at the bottom is placed at the bottom end of the column set up to collect the separated analytes.

48. Outline the procedure for preparing Column chromatography

The steps included in the column chromatography are:

1. ***Preparation of the column***

- *Mostly the column is comprised of a glass tube with an appropriate stationary phase*
- *The bottom end of the column is packed with a glass wool/cotton wool or an asbestos pad after which the stationary phase is packed.*
- *After packing the column, a paper disc is placed on the top to avoid the disturbance of the stationary phase during the introduction of the sample or mobile phase.*

The disturbance in the stationary phase (adsorbent layer) leads to the irregular bands of separation.

Two types of preparing the column, known as packing techniques namely:

1. ***Dry packing technique –*** *The amount of absorbent needed is added as a fine dry powder in the column and the solvent flows freely through the column until equilibrium is achieved.*

2. ***Wet packing technique –*** *The slurry of adsorbent is prepared along with the mobile phase and is poured into the column.*

It is regarded as the ideal technique for packaging.

The column should be properly washed and completely dried before in-use.

49.. Explain three criteria by chromatography techniques can be classified .

Chromatography is a laboratory technique which is frequently employed for the separation of mixtures. In this technique, the mixture that must be separated is first dissolved into a fluid (commonly referred to as the mobile phase). This fluid carries the mixture through a different structure (commonly referred to as the stationary phase). The fluid carries different components of the mixture at different speeds. Therefore, the components of the mixture are separated in the stationary phase of the chromatography setup. The following is the criteria by which chromatographic techniques can be classified.

(a) Classification of Chromatography based on the Chromatographic Bed Shape

- ***Column Chromatography:*** *In this type of chromatography, the stationary phase of the setup is placed inside a tube. Then, the particles of the stationary phase (which is in the solid state) are made to fill the inside with the tube. An unrestricted, open path is then prepared for the mobile phase (somewhere along the middle of the tube).*

- ***Planar Chromatography:*** *In this type of chromatography, the stationary phase of the apparatus usually has a planar shape. Different subcategories of planar chromatography include paper chromatography (where the stationary phase is a special type of paper) and thin layer chromatography (usually abbreviated as TLC).*

(b) Classification of Chromatography based on the Physical State of the Mobile Phase

- ***Gas Chromatography:*** *In this type of chromatography, the mobile phase is a substance that exists in the gaseous state. It can be noted that gas chromatography is also known as gas-liquid chromatography, and is often abbreviated to GLC. This type of chromatography almost always involves the use of a packed column.*

- ***Liquid Chromatography:*** *This type of chromatography involves the use of a mobile phase that exists in the liquid state. Liquid chromatography, often abbreviated to LC, can be carried out either on a plane or in a column. It can be noted that there exist many subcategories under liquid chromatography such as high-performance liquid chromatography and reversed phase liquid chromatography.*

(c) Classification of Chromatography based on the Mechanism of the Separation

- ***Ion Exchange Chromatography:*** *This type of chromatography is also known as ion chromatography. Ion exchange chromatography involves the separation of the components of the mixture via an ion exchange mechanism. Differently charged components of the mixture are separated with the help of different ions in this separation technique.*

- ***Size Exclusion Chromatography:*** *This type of chromatography involves the separation of different components of the mixture based on their sizes. In size exclusion chromatography, components of the mixture are filtered based on their hydrodynamic volume or hydrodynamic diameters. It can be* *noted that size exclusion chromatography is also known as gel permeation chromatography or gel filtration chromatography.*

- ***Expanded Bed Adsorption Chromatography:*** *This type of chromatography is commonly used for biochemical separation processes. It is a specialized technique which is used for the capturing of proteins from the mixture sample.*

50. Explain Types of Column chromatography

- ✓ ***Adsorption column chromatography –*** *Technique of separation in which compounds to be separated (solute) is retained or adsorbed on the surface of the adsorbent (stationary phase).*
- ✓ ***Partition column chromatography –*** *It is based on the variance in partition coefficient of the individual components of the mixture, where the stationary phase and the mobile phase both are in the liquid state.*
- ✓ ***Gel column chromatography –*** *Here, the separation is carried out through a column packed with gel and possesses a porous stationary phase. It is also referred to as* ***size exclusion chromatography***
- ✓ ***Ion exchange column chromatography –*** *The basis relies on the charge of the molecules. The separation is done when molecules get attracted to the oppositely charged stationary phase.*

51. Describe techniques used in purification of substances after separation

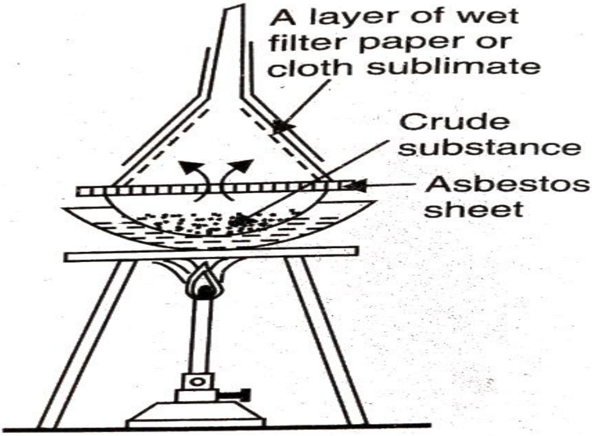
The purification of organic compounds is necessary, though complex, step after its extraction from a natural source or synthesis in the laboratory. The method of purification of the organic compound depends mainly on the nature of the compound and the impurities present.

One easy method to check the purity of an organic compound is to either melt or boil it as organic compounds tend to have sharp melting and boiling points.

Purification means the removal of unwanted impurities present in an organic compound. The general ***methods of purification*** *are:*

a. Sublimation

Some solids can directly pass to the vapour state without going through the liquid phase. The purification technique which exploits this property is called sublimation. It is helpful in separating sublimable compounds from non-sublimable ones.



Methods of Purification – Sublimation

The substance is heated in a china dish above which an inverted funnel is kept to collect the sublimable compounds. The funnel is kept cool so as to hasten the process. Vapours of the substance solidify on the funnel.

b. Crystallisation

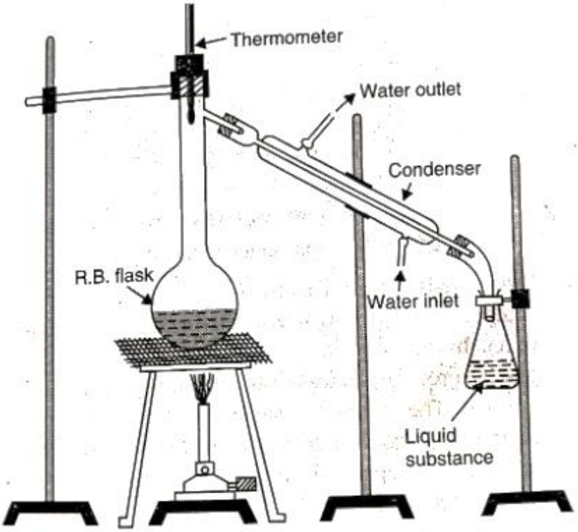
The principle here is that the compound and the impurities have different solubilities in a solvent. A solvent is chosen where the compound to be purified is sparingly soluble, that is, it is sparingly soluble at lower temperature and soluble at a higher temperature. The solution is heated to get a saturated solution, and on cooling, the crystals of the compounds are removed via filtration.

For example, crystals of benzoic acid can be crystallised with water. Benzoic acid is sparingly soluble in cold water and soluble in hot water.

If the mixture contains impurities that have the same solubility as of the compound to be purified, repeated crystallisation is performed.

c. Distillation

The underlying principle behind distillation is that the mixture of liquids can be separated by the difference in their boiling points. The boiling point is defined as that temperature at which the vapour pressure of the liquid is equal to the atmospheric pressure. This method separates volatile liquids from non-volatile liquids. The setup is given below.



(The vapours of the substance formed are condensed and the liquid is collected in a conical flask.)

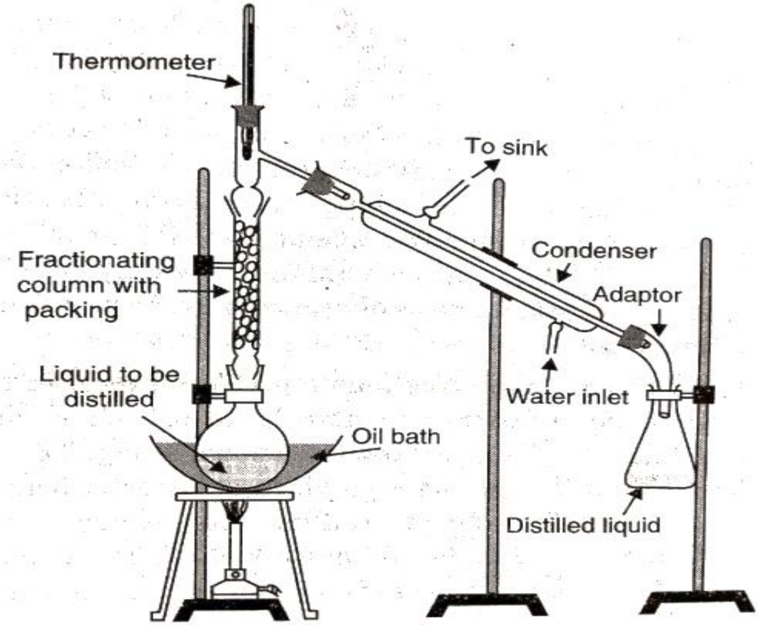
Purification of Liquids – Distillation

The mixture is taken in the round bottom flask and boiled. The more volatile or the component with lower boiling point evaporates faster and is collected in a separate container. A condenser is used to hasten the process of condensation.

For example, a mixture of chloroform and aniline can be separated by distillation. The boiling point of chloroform is 60°C and that of aniline is 189°C. Therefore distillation can be used to separate a mixture of chloroform and aniline.

Fractional Distillation

This method is employed when the difference between the boiling points of the liquids isn't much. Since the vapours of such liquids might condense together, a fractionating column is fixed to the mouth of the RB.



(The vapours of lower boiling fraction reach the tap of the column first followed by the vapours of higher boiling fractions.)

Explain the principle of fractional distillation

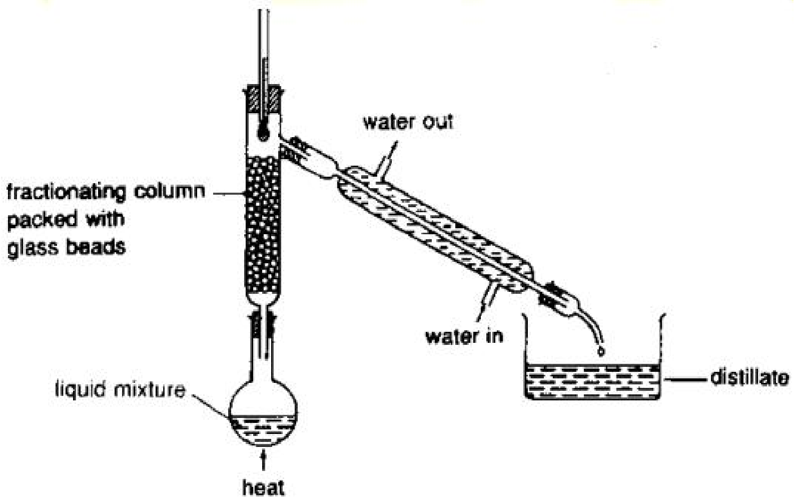
Fractional distillation is used to separate miscible liquids with different but very close boiling point. This method is more efficient than simple distillation.

Fractionating column is used to separate constituents whose volatility is nearly similar or differs by 77°F (25°C, at 1 atmosphere pressure) and which cannot be separated by simple distillation.

A fractionating column is introduced between the distillation flask and the condenser. A simple fractionating column is a tube packed with glass beads. The beads provide surface for the vapors to cool and condense repeatedly.

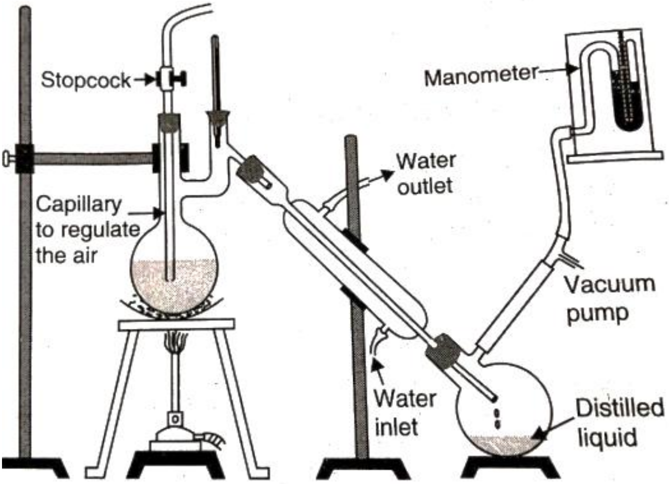
The upper portion of the column, which is closer to the condenser, is cooler than the lower portion and hence, only gases with the same temperature as the upper portion are allowed to pass on to the condenser. On the other hand, the gases with higher boiling points will condense and flow back to the bottom into the distillation flask, and is heated into a gas again. At the

end, liquid with the lowest boiling point will be the first to boil and hence the first to be distilled out and collected.
When vapors of a mixture are passed through the fractionating column, because of the repeated condensation and evaporation, the vapors of the liquid with the lower boiling point first pass out of the fractionating column, condense and are collected in the receiver flask. The other liquid, with a slightly higher boiling point, can be collected in similar fashion in another receiver flask.



It is a more effective and easier to use process, compared to simple distillation method. It is, however, relatively expensive than any other types of distillation.

Vacuum Distillation
Since the boiling point is dependent on the atmospheric pressure, the liquids will boil at a temperature lesser than their boiling points if they were distilled in an atmosphere having lower pressure. This is achieved by using a vacuum pump. Since the atmospheric pressure is reduced, the liquids also boil faster and hence the whole process of distillation is made fast.



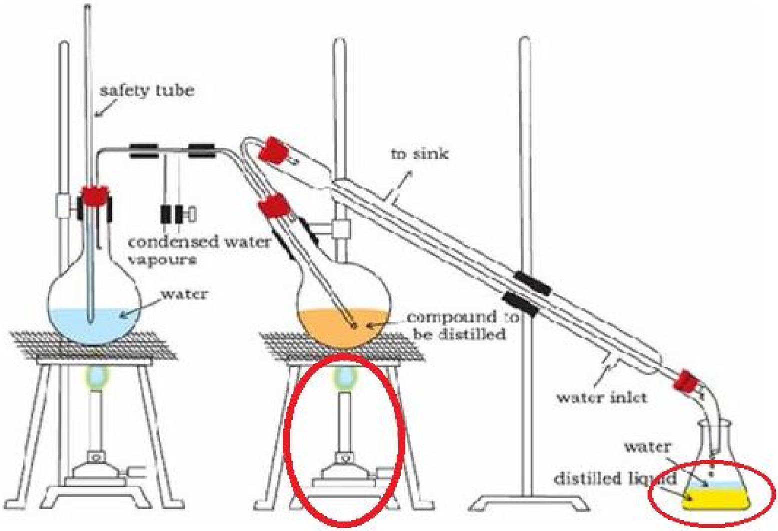
(A liquid boils at a temperature below its vapour pressure by reducing the pressure.)

Process of Vacuum Distillation

Steam Distillation

In this variant, steam is passed into the flask containing the liquids to be separated. The principle here is that the liquids will boil faster because of aqueous tension (vapour pressure of water) helps in equalising the atmospheric pressure.

Total pressure = Aqueous tension + vapour pressure of liquid components



Purification of Liquids by Steam Distillation

In the absence of aqueous tension, the process of boiling would have been continued until it equalises the atmospheric pressure. Now with the addition of steam, that process is expedited

52.Explain the basic principles involved in steam distillation

Steam distillation is used for the purification of mixtures in which the components are heat sensitive; for example, organic compounds.

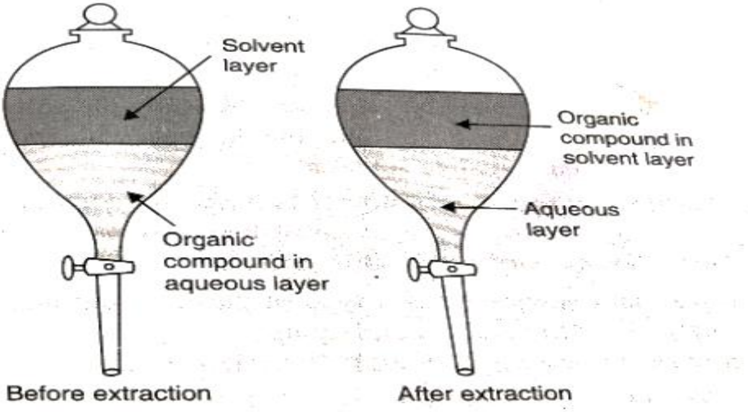
In this process, steam is introduced to the apparatus and the temperature of the compounds are depressed, by vaporizing them at lower temperature. This way, the heat sensitive compounds are separated before decomposition. The vapors are collected and condensed in the same way as other distillation types. The resultant liquid consists of two part, water and compound, which is then purified by using simple distillation..

The process requires some initial training and skill to operate the equipment. It also requires periodic maintenance. Steam distillation is widely used for large-scale separation of essential oils, fats, waxes, and perfumes.

d. Differential Extraction

This method is used for immiscible liquids, that is, liquids that do not mix together. For example, oil and water are immiscible.

The immiscible liquids are taken in a separating funnel and left undisturbed. After a while, they separate out according to their specific gravities, with the heavier liquid at the bottom. Then they are later collected.



(Extraction of compound takes place based on difference in solubility.)

Substances can also be separated according to their preferential solubilities in the liquid. For example, if phenol is to be extracted, it can be preferentially extracted using NaOH solution as one of the liquids used.

*53.**Outline the procedure used to obtain dry crystals from a hot solution by recrystallyzation techniques :***

1. The crude impure solid is dissolved in hot solvent. If some solid remains undissolved after adding solvent, it is likely to be an impurity and should be removed by filtrering the hot solution.

***Typical problems:** Adding too much solvent so that the product does not crystallize later. Filtering the hot solution too slowly so that the solvent cools and the solid starts crystallizing in the funnel and/or on the sides of glassware.*

2. The solution is allowed to stand without being disturbed. The temperature is allowed to gradually drop, leading to growth of large crystals. The flask should not be placed on a surface (it will shock-cool the solution), but either placed in an insulated jar, or clamped.

***Typical problems:** Crystals do not form at all (too much solvent), precipitate forms instead of crystals (temperature has dropped too quickly, or an oil forms).*

3. The solution is allowed to stand until crystallization is complete.

Typical problems: *Crystallization can be a slow process, and impatience can lead to low recovery.*

4. The solution is placed in an ice-water bath to lower the temperature even further, and allow more crystals to form. At this point, most crystals should already have formed.

5. The crystals are filtered and air-dried.

54.Explain how to determine if a recrystallization process success.

Simple visual inspection is a good start: The crystals should have shiny surfaces and catch the light. They should appear uniform, and you should have crystals of similar structure and size. A melting point analysis should also show a narrower and elevated melting point range compared to the crude material.

Like any purification technique, recrystallization has some limitations. First of all the compound you crystallize should be a solid at standard conditions. Greases, waxes and oils cannot be crystallized at standard conditions. Secondly, the crude material should be mostly pure. There is not any minimum purity standard for any crude material, because the success of any recrystallization depends on the identities of the other constituents and their respective solubilities, but in general the crude material should contain about 80% of the desired compound.

The crude material is transferred to a suitable crystallization vessel. The crude material is dissolved in a solvent, and gently heated.

The solution is allowed to gently and slowly cool down. Notice the crystals growing in the solution. The solution is cooled to room temperature, leading to the formation of large crystals.

55.Describe how ethanol can be obtained a mixture of ethanol and water

Fractional distillation is a method for separating a liquid from a mixture of two or more liquids. For example, liquid ethanol can be separated from a mixture of ethanol and water by fractional distillation. This method works because the liquids in the mixture have different boiling points. When the mixture is heated, one liquid evaporates before the other.

A water and ethanol mixture is heated in a flask. Vapour forms in the air above the mixture in the flask.

One way to check the purity of the separated liquids is to measure their boiling points. For example, pure ethanol boils at 78°C and pure water boils at 100°C.

56.Discuss four heating techniques used in laboratory

a) Bunsen Burners

Bunsen burners are generally used to rapidly heat high-boiling liquids with low flammability (such as water). Bunsen Burners can reach temperatures of approximately 1500oC and can easily ignite most organic compounds. If an apparatus is improperly set up, or if there is a small gap that allows organic vapors to escape from an apparatus, these vapors can ignite with a burner. Therefore, it is generally recommended to use other heat sources to warm flammable organic liquids. Bunsen burners should never be used with highly flammable solvents such as diethyl ether.

b) Hotplates

Hotplates are perhaps the most versatile heat source in the laboratory and can be used to heat beakers, Erlenmeyer flasks, and various hot baths (water, sand, and oil baths).

Hotplates work by passing electricity through a heating element covered by a ceramic top. The hotplate surface can reach temperatures up to 350oC, which is hot enough to ignite many low-boiling solvents. Diethyl ether, pentane, hexane, low-boiling petroleum ether, and acetone should therefore never be heated in an open vessel with a hotplate.

Caution should be used when heating any flammable organic liquid in an open vessel on a hotplate, as organic vapors may spill out of containers and ignite upon contact with the heating element, which may be hotter than the ceramic surface.

c) A steam bath

A steam bath is a relatively safe way to heat flammable organic liquids. They are designed to heat beakers, Erlenmeyer flasks, and round-bottomed flasks...

d) Water baths.

e) Water bath are most commonly used to heat solutions to 100oC (boiling baths). Hot plate may be used in heating. They may also be used to heat to lower temperatures, although it can be difficult to maintain a constant temperature. Water baths can be covered with aluminum foil to prevent excessive evaporation, or to prevent excess moisture from entering open vessels. Cold water baths can also be used to cool apparatus in a quick manner

f) Sand baths.

Sand baths can be used to heat solutions to a wide variety of temperatures, from moderate to high temperatures (> 250oC). A vessel containing the substance to be heated should be buried in a sand bath as much as possible as the surface is often much cooler than the sand below. A metal spatula *can be used to pile the sand up to at least the height of liquid inside the flask. Sand takes a long time to heat up, and a long time to cool down. To save time, a sand bath may be preheated while an apparatus is assembled as long as it is preheated a distance away from volatile organic liquids.*

If the sand overheats and causes a liquid to boil uncontrollably, the flask can be partially lifted out of the sand, or the sand moved with a metal spatula away from contact with the liquid. Sand will remain warm even after turning off the hotplate, and therefore flasks have to be lifted out of the sand bath in order to cool.

g) Oil baths

Oil baths are much like water baths, but use silicone or mineral oils is used in order to enable temperatures hotter than the boiling point of water. Silicone oil baths can be heated to 250oC, while mineral oil baths can be heated to 300oC. Mineral oil is composed of mixtures of long-chain alkanes, and so is combustible. Direct contact with open flames should therefore be avoided.

h)Heating mantles

i) Heating mantles are a relatively safe way to heat flammable organic liquids in a round bottomed flask. The mantles are cup-shaped and designed for different sizes of round bottomed flask .If a mantle does not fit a round bottomed flask perfectly, sand can be added to ensure good thermal contact. Heating mantles take some time to warm up and also take some time to cool down. The mantle will remain warm even after turning off, and therefore flasks have to be removed from the mantle in order to cool.

*57.**Explain factors that govern the type of solvent used in soxhlet extraction***

✓ *The thermal stability of the extracted material determines the boiling range of solvent to be used.*

✓ *The polarity of the extracted material determines the polarity of the solvent.*

✓ *Some plant materials decomposes at 70 -100o C and thus solvents of relatively low B. P. must be used.*

58. Describe any four differences between batch extraction and continous extraction

***Batch extraction** is the simplest and most commonly used method, consists of extracting the solute from one immiscible layer in to other by shaking the two layers until equilibrium is attained, after which the layers are allowed to settle before sampling.*

This is commonly used on the small scale in chemical laboratories.

The most commonly employed apparatus for performing a batch extraction is a separatory funnel.

The batch extractions may also be used with advantage when the distribution ratio is large.

b) Continuous extraction

continuous extraction, makes use of a continuous flow of immiscible solvent through the solution or a continuous countercurrent flow of both phases.

Continuous extractions are particularly applicable when the distribution ratio is relatively small.

Continuous extraction device operates on the same general principle, which consist of distilling the extracting solvent from a boiler flask and condensing it and passing it continuously through the solution being extracted.

The extracting liquid separates out and flows back into the receiving flask, where it is again evaporated and recycled while the extracted solute remains in the receiving flask. When the solvent cannot easily be distilled, a continuous supply of fresh solvent may be added from a reservoir.

CHAPTER EIGHT

ACIDS, BASES BUFFERS AND PH ANALYSIS

1. List two properties of an acid and bases

An acid is basically a molecule which can donate an H+ ion and can remain energetically favourable after a loss of H+.

An acid is a substance that donates protons (in the Brønsted-Lowry definition) or accepts a pair of valence electrons to form a bond (in the Lewis definition).. :

✓ *Aqueous solutions of acids are electrolytes, meaning that they conduct electrical current. Some acids are strong electrolytes because they ionize completely in water, yielding a great many ions. Other acids are weak electrolytes that exist primarily in a non-ionized form when dissolved in water.*

✓ *Acids have a sour taste. Lemons, vinegar, and sour candies all contain acids.*

✓ *Acids change the color of certain acid-base indicates. Two common indicators are litmus and phenolphthalein. Blue litmus turns red in the presence of an acid, while phenolphthalein turns colorless.*

✓ *Acids react with active metals to yield hydrogen gas. Recall that an activity series is a list of metals in descending order of reactivity. Metals that are above hydrogen in the activity series will replace the hydrogen from an acid in a single-replacement reaction, as shown below:*

○ $Zn(s)+H2SO4(aq) \rightarrow ZnSO4(aq)+H2(g)$

Acids react with bases to produce a salt compound and water. When equal moles of an acid and a base are combined, the acid is neutralized by the base. The products of this reaction are an ionic compound, which is labeled as a salt, and water.

Examples: Sulfuric acid [H2SO4], Hydrochloric acid [HCl], Acetic acid [CH3COOH].

Bases, on the other hand, are characterized by a bitter taste and a slippery texture. A base that can be dissolved in water is referred to as an alkali. When these substances chemically react with acids, they yield salts. Bases are known to turn red litmus blue. A base is a substance that can accept protons or donate a pair of valence electrons to form a bond

✓ *Bases have properties that mostly contrast with those of acids.*

✓ *Aqueous solutions of bases are also electrolytes. Bases can be either strong or weak, just as acids can.*

✓ Bases often have a bitter taste and are found in foods less frequently than acids. Many bases, like soaps, are slippery to the touch.

✓ Bases also change the color of indicators. Litmus turns blue in the presence of a base while phenolphthalein turns pink.

✓ Bases do not react with metals in the way that acids do.

✓ Bases react with acids to produce a salt and water.

✓ Examples: Sodium hydroxide [NaOH], milk of magnesia [Mg(OH)2], calcium hydroxide [Ca(OH)2].

*2. **Distinguish between ;***

i. a strong and a weak acid and bases

A strong acid or alkali is one that is nearly or completely ionised in water. Examples are: hydrochloric acid, nitric acid and sulphuric acid. Sodium and potassium hydroxide are examples of strong bases.

A weak acid or alkali, on the other hand, is only partially ionised in water. Ethanoic, citric and carbonic acids are all weak acids. The ethanoic acid molecule and the ions reach a dynamic equilibrium with the equilibrium normally well to the left, so there is little H+ present.

1. Concentrated and dilute acid and bases

The concentration of an acid or alkali is a measure of how much acid or alkali is dissolved in a known volume of liquid, e.g. water. The molarity of a solution is a measure of concentration: the number of moles dissolved in 1000cm3 of water. Concentration of solutions is usually expressed in moles per litre of solution. (A litre is the same as 1dm3 or 1000cm3.). This way of stating concentration is sometimes called 'molarity'.

In a concentrated acid or alkali there is a relatively large amount of solute dissolved, compared with a dilute acid or alkali. However, this does not tell us what the concentration of H+ ions is in the acid or OH- ions is in the alkali. This depends on the strength of the acid or alkali. Strength refers to the degree of ionisation in water.

3. Define PH

pH is a measure of hydrogen ion concentration, a measure of the acidity or alkalinity of a solution.

Its is determined as $\mathbf{pH = -log[H^+]}$ *Where log is the base-10 logarithm and* $[H^+]$ *stands for the hydrogen ion concentration in units of moles per liter solution. The pH scale usually ranges from 0 to 14. Aqueous solutions at 25°C with a pH less than 7 are acidic, while those with a pH greater than 7 are basic or alkaline. A pH level of 7.0 at 25°C is defined as "neutral" because the concentration of* H_3O^+ *equals the concentration of* OH^- *in pure water. Very strong acids might have a negative pH, while very strong bases might have a pH greater than 14.*

4. *HCl is a strong acid and is completely dissociated in its solutions according to the process:*

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

From this process it is clear that one mole of HCl would give one mole of H^+ ions. Therefore, the concentration of H^+ ions would be equal to that of HCl i.e. 0.001 molar or 1.0×10^{-3} mol L^{-1}.

Thus, $[H^+] = 1 \times 10^{-3}$ mol L^{-1}

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

$$= -(-3 \times \log 10) = -(3 \times 1) = 3$$

Thus, pH = 3

5. *What would be the pH of an aqueous solution of sulphuric acid which is 5×10^{-5} mol L^{-1} in concentration.*

Sulphuric acid dissociates in water as:

$H_2SO_4(aq) \rightarrow 2H^+(aq) + SO_4^{2-}(aq)$

Each mole of sulphuric acid gives two mole of H^+ ions in the solution. One litre of 5×10^{-5} mol L^{-1} solution contains 5×10^{-5} moles of H_2SO_4 which would give $2 \times 5 \times 10^{-5} = 10 \times 10^{-5}$ or 1.0×10^{-4} moles of H^+ ion in one litre solution.

Therefore,

$$[H^+] = 1.0 \times 10^{-4} \text{ mol } L^{-1}$$

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

$$=-(-4\times1)=4$$

6. *Calculate the pH of 1×10^{-4} molar solution of NaOH.*

NaOH is a strong base and dissociate in its solution as:

$NaOH(aq) \rightarrow Na^+(aq) + OH^-(aq)$

One mole of NaOH would give one mole of OH^- ions. Therefore,

$$[OH^-] = 1 \times 10^{-4} \text{ mol } L^{-1}$$

$$pOH = -\log[OH^-] = -\log \times 10^{-4} = -(-4)$$

$$= 4$$

Since $pH + pOH = 14$

$$pH = 14 - pOH = 14 - 4$$

$$= 10$$

a. Calculate the PH of 0.1 M NaOH solution

0.1M. NaOH is a strong base, so this will produce 0.1mol/L of OH ions in solution. This will produce a pH of 13.

$$pOH = -\log [1\times10^{-1}]$$

$$=-\log1+(-\log10^{-1})$$

$$= 0 + (-(-1)) \log 10$$

$$= 0 + 1 \text{ x } 1$$

$$=1$$

Now we know that,

$pH + pOH = 14$

$pH + 1 = 14$

$pH = 14 - 1$

$pH = 13$

7. Calculate the pH of a solution in which the concentration of hydrogen ions is 1.0×10^{-8} mol L^{-1}.

Here, although the solution is extremely dilute, the concentration given is not of acid or base but that of H^+ ions. Hence, the pH can be calculated from the relation:

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

given $[H^+] = 1.0 \times 10^{-8}$ mol L^{-1}

$pH = -\log 10^{-8} = -(-8 \times \log 10)$

$= -(-8 \times 1) = 8$

Consider the mixture is made from a monobasic weak acid **HA** *and an alkali metal salt* $\boldsymbol{M^+A^-}$

e.g. $A = CH_3COO$, $M = K$ *or* Na

it is reasonable to assume for simple approximate calculations that ..

$\boldsymbol{[A^-_{(aq)}] = [salt_{(aq)}]}$ *since salt fully ionised and* M^+ *is a spectator ion, and*

$\boldsymbol{[HA_{(aq)}]_{equilib.}, = [HA_{(aq)}]_{initial}}$ *since little of the weak acid is ionised.*

Therefore the weak acid K_a *expression is ...*

$$\text{(i) } \boldsymbol{K_a} = \frac{[H^+_{(aq)}]\,[A^-_{(aq)}]}{[HA_{(aq)}]} \text{ mol dm}^{-3}$$

becomes

$$\text{(ii) } \boldsymbol{K_a} = \frac{[H^+_{(aq)}]\,[salt_{(aq)}]}{[acid_{(aq)}]} \text{ mol dm}^{-3}$$

therefore: $\boldsymbol{[H^+_{(aq)}] = \frac{K_a\,[acid_{(aq)}]}{[salt_{(aq)}]}}$ mol dm^{-3} ,

and taking $-\log_{10}$ *of both sides gives*

(iii) $\boldsymbol{pH_{buffer} = -\log_{10}\left(K_a \times \frac{[acid_{(aq)}]}{[salt_{(aq)}]}\right)}$

or (iv) $\boldsymbol{pH_{buffer} = pK_a + -\log_{10}\left(\frac{[acid_{(aq)}]}{[salt_{(aq)}]}\right)}$

or (v) $pH_{buffer} = pK_a + \log_{10}\left(\frac{[salt(aq)]}{[acid(aq)]}\right)$

which is how the equation is usually quoted, sometimes called the Henderson Equation.

Note: For a given conjugate pair (HA and A^-), the pH of the buffer is determined by the acid/salt ratio, though the more concentrated the buffer, the greater its capacity to neutralise larger amounts of added/formed in a reaction medium.

Another point is how to choose which weak acid is best for a desired buffer?

The useful range of a buffer is ***decided by the weak acid's K_a and the ratio of the salt and weak acid concentrations****.*

The buffer will be most useful when the ratio [salt]/[acid] is equal to one i.e. when both active ingredients are at their maximum concentrations at no expense to the other – by the principles of related chemical equilibrium, if you increase one concentration you would decrease the other.

Therefore the ***maximum buffer capacity is when [salt] = [acid]***

Now **$K_a = [H^+_{(aq)}]$** *when [salt] = [acid] in equation (i) or (ii) above*

therefore taking $-\log_{10}$ of both sides gives ...

$pK_a = pH$ *when [salt] = [acid], because $\log_{10}(1) = 0$ in equations (iv) or (v) and this simple mathematical argument gives the necessary guidance ...*

So for example, supposing you wanted a buffer to cover a ***pH range of 4.5 to 6.0****,and your choice of weak acid pK_a's was 2.8, 4.2,* ***5.5*** *and 6.5,*

you ***would choose the weak acid with a pK_a of 5.5*** *because its pK_a is well* ***in the desired pH range****.*

You would then formulate it with its sodium (or potassium) salt – note that sodium ion and potassium ion salts are usually used because they have virtually no acidic or basic character to complicate matters e.g. the hydrated ions $Na^+_{(aq)}$ and $K^+_{(aq)}$ do not donate protons in the way, for example, the hexa–aqua ions of aluminium can ...

$[Al(H_2O)_6]^{2+}_{(aq)} + H_2O_{(l)} \rightleftharpoons [Al(H_2O)_5(OH)]^+_{(aq)} + H_3O^+_{(aq)}$

because the polarising power of the central metal ions, Na^+ or K^+ is too small to effect this process.

8. Describe how you would prepare a phosphate buffer with a pH of about 7.40

For a buffer to function correctly , the concentration of the acid component must be roughly equal to the conjugate base component.

When the desired pH is close to the pKa of the acid , i.e. when pH=pKa

$$\log \frac{(\text{conjugate base})}{(\text{acid})} = 0$$

$$\frac{(\text{conjugate base})}{(\text{acid})} = 1$$

Because phosphoric acid is a trprotic acid , it undergoes three stages of ionization i.e. ;

$H_3PO_4H^+ \rightleftharpoons +H_2PO_4^-$ $Ka=7.5X10^{-3}$ $Pka=2.12$

H_2POH^+ ⇌ $+HPO_4^{-2}$ $Ka=6.2X10^{-8}Pka=7.21$

$HPO_4^{-2}\ H^+$ ⇌ $+PO_4^{-3}$ $KA=4.8X10^{-13}$ $Pka=12.32$

Therefore the most suitable of the three buffer system is $HPO_4^{-2}/H_2PO_4^-$ because the pKa of the acid is close to the desired pH

$$pH = pka + \log\frac{(conjugate\ base)}{(acid}$$

$$7.40 = 7.21 + \log\frac{(HPO_4^{-2})}{(H_2PO_4^-)}$$

$$\log\frac{(HPO_4-^{2})}{H_2PO_4-} = 0.19$$

Taking the antilog we obtain

$$\frac{(HPO_4^{-2})}{(H_2PO_4^-)} = 10^{0.19}$$

$$=1.5$$

Thus one way to prepare a buffer solution with a pH of 7.40 is to dissolve Disodium hydrogen phosphate(Na2HPO4) and Sodium dihydrogen phosphate (NaH2PO4) in a mole ratio of 1 .5:1.0 in water

9. ***A buffer solution was prepared which had a concentration of 0.20 mol dm^{-3} in ethanoic acid and 0.10 mol dm^{-3} in sodium ethanoate. If the K_a for ethanoic acid is 1.74 x 10^{-5} mol dm^{-3}, calculate the theoretical hydrogen ion concentration and pH of the buffer solution.***

$K_a = [H^+_{(aq)}]\ [salt_{(aq)}]/[acid_{(aq)}]$

$1.74 \times 10^{-5} = [H^+_{(aq)}] \times 0.10 / 0.20$

$\mathbf{[H^+_{(aq)}]} = 1.74 \times 10^{-5} \times 0.20/0.10$

$= 3.48 \times 10^{-5}$ mol dm^{-3}

$\mathbf{pH} = -\log(3.48 \times 10^{-5})$

$\mathbf{= 4.46}$

10. ***In what ratio should a 0.30 mol dm^{-3} of ethanoic acid be mixed with a 0.30 mol dm^{-3} solution of sodium ethanoate to give a buffer solution of pH 5.6?***

K_a for ethanoic acid is 1.74 x 10^{-5} mol dm^{-3}

$[H^+_{(aq)}] = 10^{-pH} = 10^{-5.6} = 2.51 \times 10^{-6}$ mol dm^{-3}

$K_a = [H^+_{(aq)}]\ [salt_{(aq)}]/[acid_{(aq)}]$

$\mathbf{[salt]/[acid] = K_a/[H^+_{(aq)}]} = 1.74 \times 10^{-5}/2.51 \times 10^{-6}$

= 6.93 *Therefore volume ratio is* ***6.93 : 1*** *for* ***salt : acid****, e.g. 6.93 cm^3 of 0.30M sodium ethanoate is mixed with 1.0 cm^3 of 0.30 M ethanoic acid to give a buffer solution of pH 5.6.*

Note that the pH is determined by the ratio of concentrations, but the buffering capacity of the solution can be increased by increasing the concentrations of both components in the same molar concentration ratio.

11. **What is the pH of a buffer solution made from dissolving 2.0g of benzoic acid and 5.0g of sodium benzoate in 250 cm^3 of water?**

$K_{a\ benzoic\ acid} = 6.3 \times 10^{-5}$ mol dm^{-3}, A_r's: H = 1, C = 12, O = 16, Na = 23

Molecular masses: $M_r(C_6H_5COOH) = 122$,

$M_r(C_6H_5COO^-Na^+) = 144$,

250 cm^3 = 0.25dm^3

moles acid C_6H_5COOH = 2.0/122 = 0.0164 mol, molarity = 0.0656 mol dm^{-3}

moles salt $C_6H_5COO^-Na^+$ = 5.0/144 = 0.0347 mol, molarity = 0.139 mol dm^{-3}

$[H^+_{(aq)}] = K_a [acid_{(aq)}]/[salt_{(aq)}]$

$[H^+_{(aq)}] = 6.3 \times 10^{-5} \times 0.0656 / 0.139 = 2.97 \times 10^{-5}$ mol dm^{-3}

pH = $-\log[H^+_{(aq)}] = -\log(2.97 \times 10^{-5}) =$ **4.53**

$K_{a\ propanoic\ acid} = 1.3 \times 10^{-5}$ mol dm^{-3}, total volume of buffer = 150 cm^3

molarities in the mixture:

[salt] = 0.40 x 100/150 = 0.267 mol dm^{-3}

[acid] = 0.20 x 50/150 = 0.0667 mol dm^{-3}

$[H^+_{(aq)}] = K_a [acid_{(aq)}]/[salt_{(aq)}]$

$[H^+_{(aq)}] = 1.3 \times 10^{-5} \times 0.0667 / 0.267$

$= 3.24 \times 10^{-6}$ mol dm^{-3}

pH = $-\log[H^+_{(aq)}]$

$= -\log(3.24 \times 10^{-6})$

= **5.48**

Using the Henderson equation

$pH_{buffer} = pK_a + \log_{10}([salt_{(aq)}] / [acid_{(aq)}])$

12. **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} mol dm^{-3}**

Now because the volumes are not equal, the real concentrations in the mixture must be worked out.

The total volume is 150 cm^3, therefore the dilutions are given by

[acid] = 0.1 x 100/150 = 0.06667

[salt] = 0.4 x 50/150 = 0.1333

Substituting in the Henderson Equation gives

$pH_{buffer} = -\log_{10}(1.74 \times 10^{-5}) + \log_{10}(0.1333/0.0667)$

$pH_{buffer} = -\log_{10}(1.74 \times 10^{-5}) + \log_{10}(2)$

$pH_{buffer} = 4.76 + 0.3010$

$\mathbf{pH_{buffer} = 5.06}$

CHAPTER NINE

MOLES AND MOLAR CONCENTRATIONS

1. Define the following terms

*a. **Normality:** A concentration unit (N); defined as the number of equivalents of solute per liter of solution (e.g., 1 M H2SO4= 2 N H2SO4)*

*b. **Molarity** : The molarity of a solution is defined as the number of moles of solute per one liter of solution. Note that the unit of volume for molarity is liters, not milliliters or some other unit.*

Also, note that one liter of solution contains both the solute and the solvent. Molarity, therefore, is a ratio between moles of solute and liters of solution. To prepare laboratory solutions, usually a given volume and molarity are required. To determine molarity, the formula weight or molar mass of the solute is needed.

c. ppm

Parts per million (PPM) is a unit of measurement used when expressing a very dilute concentration level of pollutants in the air, water and other fluids. For example, 1 PPM of ink in water means that in a million mass units of water there would be one mass unit of ink. Thus, PPM refers to one item in a million of anything of the same size. PPM is commonly used in measuring air, water and body fluids pollution. PPM is the mass ratio between a component and a solution. Mathematically, 1 PPM can be expressed as following:

1 PPM = 1 mg/kg
1 PPM = 1 mg/ltr
1 PPM = 0.0001 %

d. Mass-volume percent solutions

Are also very common. These solutions are indicated by w/v% and are defined as the grams of solute per 100 milliliters of solution.

Example: 1 g of phenolphthalein in 100 mL of 95% ethyl alcohol is a 1 w/v% solution

*e. **Decinormal Solution***

The solution that contains 1/10th gram equivalent of solute in one liter of its solution is called decinormal solution.

2 Define the following terms

Normality ? How It Is Related To Molarity?

The number of gram equivalent of solute present in in 1 litre of the solution is called normality. It is represented by N.

Normality=Number of gram equivalent of solute/volume of solution in litre

✓ ***It is related to molarity as:***

Normality (N) = Molarity × Basicity of acid
also, Normality (N) = Molarity × Acidity of base

c. Normality Equation

The equation which is used to determine the strength of unknown solution is called normality equation.

Volume of acid × Normality of acid = Volume of Base × Normality of base

3. If 5.00g of sodium chloride is dissolved in exactly 250 cm^3 of water in a calibrated volumetric flask,

(a) What is the concentration in g/dm^3?

Volume = 250/1000 = 0.25 dm^3
Concentration = mass / volume
= 5/0.25
= ***20 g/dm^3***

b. What is the molarity of the solution?

$A_r(Na) = 23$, $A_r(Cl) = 35.5$,
so $M_r(NaCl) = 23 + 35.5 = 58.5$
mole NaCl = 5.0/58.5 = 0.08547
volume = 250/1000 = 0.25 dm^3
molarity = mol of solute / volume of solvent
Molarity *= 0.08547/0.25*
= ***0.342 mol/dm^3***

c.Calculate the molar concentration of sulfuric acid from the following data. S.G=1.46

%H2SO4= 78%
RMM=98

Mass of solution = 1,000 mL x 1.46 g/mL = 1,460 g

$$\text{Mass \%} = \frac{78}{100} \times 1460$$

=1138g

Molar mass of Sulfuric acid = 98 g/mol

$$= \frac{\text{mass x mass \%}}{\text{MM}\mathbf{HCl}}$$

$$= \frac{1138g}{98} \qquad = \quad 11.62M$$

Determine molarity of 37.2% hydrochloric acid (density 1.19 g/mL)

Mass of solution = 1,000 mL x 1.19 g/mL = 1,190

Mass % = 37.2 % = 0.372

Molar mass of hydrochloric acid = 36.4 g/mol

$$= \frac{\text{mass x mass \%}}{MM\mathbf{HCl}}$$

$$= \frac{1,190\text{ g x }0.372}{36.4\text{ g/mol}}$$

= 12.1 moles

Molarity = moles/liters

= 12.1

moles/1 liter = 12.1 M

Calculate the the pH of $1\times10^{-4}M$ H_2 SO_4 solution?

Sulphuric acid is a dibasic acid and hence gives two H+ atoms in it's solution. Since, it is a strong acid it dissociates completely as:

$H2\ SO4 \rightleftharpoons 2H^{+}+SO4^{2-}$

$[H+] = 2 X 0.0001M$

Ph $= -\log(2 X 0.0001)$

=3.70

4. 5.95g of potassium bromide was dissolved in 400cm^3 of water.

(a) Calculate its molarity. *[A_r's: K = 39, Br = 80]*

moles = mass / formula mass, (KBr = 39 + 80 = 119)

mol KBr = 5.95/119 = 0.050 mol

400 cm^3 = 400/1000 = 0.400 dm^3

molarity = moles of solute / volume of solution

molarity of KBr solution** = 0.050/0.400 = **0.125 mol/dm^3

○ ***(b) What is the concentration in grams per dm^3?***

Concentration = mass / volume, the volume = 400 / 1000 = 0.4 dm^3

*Concentration = 5.95 / 0.4 = **14.9 g/dm^3***

5. What mass of sodium hydroxide (NaOH) is needed to make up 500 cm^3 (0.500 dm^3) of a 0.500 mol dm^{-3} (0.5M) solution? *[A_r's: Na = 23, O = 16, H = 1]*

1 mole of NaOH = 23 + 16 + 1 = 40g

*molarity = moles / volume, so **mol needed = molarity x volume in dm^3***

500 cm^3 = 500/1000 = 0.50 dm^3

mol NaOH needed = 0.500 x 0.500 = 0.250 mol NaOH

therefore mass = mol x formula mass
= 0.25 x 40 = ***10g NaOH required***

6. ***How many moles of H_2SO_4 are there in 250 cm^3 of a 0.800 mol dm^{-3} (0.8M) sulphuric acid solution? What mass of acid is in this solution?***

[A_r's: H = 1, S = 32, O = 16]

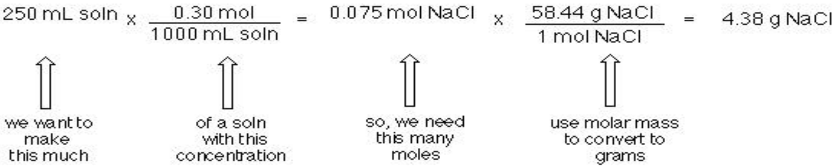
(a) *molarity = moles / volume in dm^3, rearranging equation for the sulfuric acid*
mol H_2SO_4 = molarity H_2SO_4 x volume of H_2SO_4 in dm^3
mol H_2SO_4 = 0.800 x 250/1000 = ***0.200 mol*** *H_2SO_4*
(b) *mass = moles x formula mass*
formula mass of H_2SO_4 = 2 + 32 + (4x16) = 98
0.2 mol H_2SO_4 x 98 = ***19.6g of H_2SO_4***

7. ***A solution of calcium sulphate ($CaSO_4$) contained 0.500g dissolved in 2.00 dm^3 of water. Calculate the concentration in (a) g/dm^3, (b) g/cm^3 and (c) mol/dm^3.***

(a) concentration *= 0.500/2.00* ***= 0.250 g/dm^3,***
then since 1dm^3 = 1000 cm^3
(b) concentration *= 0.250/1000* ***= 0.00025 g/cm^3***
(or from 0.500/2000)
(c) *At. masses: Ca = 40, S = 32, O = 64,*
formula mass $CaSO_4$ = 40 + 32 + (4 x 16) = 136
moles $CaSO_4$ = 0.5 / 136 = 0.00368 mol in 2.00 dm^3 of water
concentration $CaSO_4$ *= 0.00368 / 2*

8. Describe how to prepare 250 mL of a 0.30 M NaCl solution.

A 0.30 M NaCl solution means that there is 0.30 mol NaCl in every liter of solution.
For example:
To make the solution we need to calculate the amount of NaCl to dissolve to make 250 mL of solution.
Start with 250 mL



$$250\text{ mL soln} \times \frac{0.30\text{ mol}}{1000\text{ mL soln}} = 0.075\text{ mol NaCl} \times \frac{58.44\text{ g NaCl}}{1\text{ mol NaCl}} = 4.38\text{ g NaCl}$$

b. Distinguish between a working solution and stock solution

A stock solution is a large volume of common reagent, such as hydrochloric acid or sodium hydroxide, at a standardized concentration. This term is commonly used in analytical chemistry for procedures such as titrations, where it is important that exact concentrations of solutions are used.

Working solutions are any dilutions that are made using the stock, generally into aqueous solution.

8. Explain the limitation of using tap water in preparing potassium permanagenage standard solution

Any kind of chemical or biochemical experiment demands use of deionized or distilled water for preparing all solutions. Dionized water is highly prefered becouse it is almost completely free of all disolved ions unlike distilled water which may still be having some dissolved ions . Tap water is not used to prepare standard solutions for titration because of the impurities it contains which could interfere with the results. If you were titating with an acid, the results would be on the high side and if you were titrating with alkaline they would tend to be on the low side because of the minerals likely to be in the tap water.

9.Outline the procedure for standardizing potassium thocyanate solution using 0.1M silver nitrate solution

Potassium thiocyanate solution has to be standardized, as it is not possible to prepare and dry KSCN pure enough so that it can be used as a standard substance for solution preparation. The easiest method if the standardization require standardized solution of silver nitrate. As KSCN solution is used for back titration of the excess of $AgNO_3$*, when we need to standardzie KSCN solution we usually have standardized silver nitrate solution ready.*

Reaction taking place is

$$AgNO_3 + KSCN \rightarrow AgSCN\downarrow + KNO_3$$

Procedure to follow:

- *Pipette 25 mL aliquot of about 0.1M* $AgNO_3$ *solution into 250mL erlenmayer flask.*
- *Add 50 mL of distilled water.*
- *Add 1 mL of 10%* $FeNH_4(SO_4)_2$ *solution.*
- *Titrate with potassium thiocyanate till the first visible color change.*

10.Explain why iodine solution is prepared using potassium iodide solution

Molecular iodine is only slightly soluble in water. Adding potassium iodide to iodine in water rapidly converts the molecular iodine (I2) to the much more soluble triiodide ion (I3-).

An equimolar solution of iodine and potassium iodide is called Lugol's solution. The iodine in Lugol's solution is mostly in the form of triiodide ion, in equilibrium with molecular iodine. In short, potassium iodide is used to be able to attain much higher concentrations of iodine in aqueous solution without having to use organic solvents

CHAPTER TEN

TITRIMETRIC ANALYSIS

1. ***Define the following terms***

c. ***Volumetric analysis***

Volumetric analysis refers to quantitative chemical analysis carried out by determining the volume of a solution of accurately known concentration which is required to react quantitatively with a measured volume of a solution of the substance to be determined.

d. ***Titrand:*** *the substance being titrated*

e. ***Titrant:*** *the reagent of known concentration*

f. ***Titre:*** *The volume used of the substance titrated*

g. ***Titration:*** *The process of adding the standard solution until the reaction is just complete*

h. ***Indicator:*** *Indicator is a chemical substance which changes colour at the end point.*

i. ***End Point:****The stage during titration at which the reaction is just complete is known as the end point of titration*

j. ***Equivalent point;*** *The point at which this occurs is called the equivalence point or the theoretical (or stoichiometric) end point*

2. ***Explain the differences between***

a. ***End point and equivalence point?***

End point is the point which indicates the completion of reaction by changing its color. It is indicated by the indicator. While equivalence point is the theoretical point at which the equivalent amount of titrand and titrant are added together. It is a theoretical point.

b. ***Equivalence & endpoint in titrations?***

The point at which the reaction b/w titrant & titrate is just complete is called equivalence point or theoretical point.

The point at which a clear visual change is observed after the reaction b/w titranta and titrate is practically complete is end point.

Thus there exists a very small difference b/w the end point & equivalence point.

3. Explain the term

a. Equivalent weight of an Acid?

Equivalent weight of an acid is defined as the number of parts by mass of an acid that is neutralised completely by one equivalent weight of base. ***Equivalent weight of an acid = molecular weight / basicity***

b.Equivalent weight of a Base?

Equivalent weight of a base is defined as the number of parts by mass of a base that is required to neutralise completely one equivalent weight of an acid. ***Equivalent weight of a base = molecular weight / acidity***

EX: *Equivalent weight of NaOH =40/1=40*

2. ***Which indicator is used in the titration of sodium carbonate against hydrochloric acid and what is the colour change at the end point?***

Methyl orange. The colour change is yellow to pinkish red

3. ***List any two advantages of volumetric over gravimetric analysis***

Volumetric analysis require simpler apparatus, and are, generally, quickly performed; tedious and difficult separations can often be avoided.

4. State conditions necessary for analysis of a sample by volumetric analysis

✓ *. There must be a simple reaction which can be expressed by a chemical equation; the substance to be determined should react completely with the reagent in stoichiometric or equivalent proportions.*

✓ *The reaction should be relatively fast. (Most ionic reactions satisfy this condition.) In some cases the addition of a catalyst may be necessary to increase the speed of a reaction.*

✓ *There must be an alteration in some physical or chemical property of the solution at the equivalence point.*

✓ *An indicator should be available which, by a change in physical properties (colour or formation of a precipitate), should sharply define the end point of the reaction. If no visible indicator is available, the detection of the equivalence point can often be achieved by following the course of the titration by measuring*

5. State four advantages of titrimetric as a method of analysis

✓ *Volumetric analysis require simpler apparatus,*

✓ *Is generally quickly performed;*

✓ *Tedious and difficult separations can often be avoided.*

✓ *Require less skills*

6. ***Define a standard solution***

A standard solution is a solution containing a precisely known concentration of an element or a substance. A known mass of solute is dissolved to make a specific volume. It is prepared using a standard substance, such as a primary standard. Standard solutions are used to determine the concentrations of other substances, such as solutions in titration.

The concentrations of standard solutions are normally expressed in units of moles per litre (mol/L, often abbreviated to M for molarity), moles per cubic decimetre (mol/dm3), kilomoles per cubic metre (kmol/m3) or in terms related to those used in particular titrations (such as titres A simple standard is obtained by the dilution of a single element or a substance in a soluble solvent with which it reacts. A primary standard is a reagent that is extremely pure, stable, has no waters of hydration, and has high molecular weight. Some primary standards of titration of acids include sodium carbonate.

7. ***Distinguish between a primary and a secondary standard solution***

A primary standard is a highly purified compound that serves as a reference material in titrations and in other analytical methods.

The accuracy of a method critically depends on the properties of the primary standard.

10 ***The criteria for a solution to be primary standard solution are as follows:***

- a. *It should be available in pure and dry state.*
- b. *Its composition should not be changed on storage. i.e., It should not be toxic, volatile, hygroscopic and deliquescent.*
- c. *It should be highly soluble in water without any change in its composition.*
- d. *It should have higher molecular and equivalent weight*
- e. *Modest cost or relatively affordable .*
- f. *Should have reasonable solubility in the titration medium.*
- g. *Reasonably large molar mass so that the relative error associated with weighing the standard is minimized.*

Very few compounds meet or even approach these criteria, and only a limited number of primary-standard substances are available commercially. As a consequence, less pure compounds must sometimes be used in place of a primary standard. The purity of such a secondary standard must be established by careful analysis.

A secondary standard is a compound whose purity has been determined by chemical analysis. The secondary standard serves as the working standard material for titrations and for many other analyses.

8. ***Give examples of primary standard solution :***
   Sodium carbonate (Na_2CO_3), Potassium dichromate ($K_2Cr_2O_7$), oxalic acid $(COOH)_2.2H_2O$, Mohr's salt etc.

9. ***Explain the importance of primary and standard solutions***

A primary standard is an ultrapure compound that serves as the reference material for a titration or for another type of quantitative analysis.

Standard Solutions play a central role in the determination of the concentration of an analyte species. Just like a primary standard ,the standard solution is a reference guide to discover the molarity of unknown species.

Titration methods can be used to acquire the concentration of a standard solution. These involve using equipment such as a burette.

By comparing the absorbance of the sample solution at a specific wavelength to a series of standard solutions at differing known as concentrations of the analyse species, the concentration of the sample solution can be found via Beer's Law. Any form of spectroscopy can be used in this way so long as the analyte species has substantial absorbance in the spectra.

Therefore, we must consider the desirable properties for such solutions, how they are prepared, and how their concentrations are expressed.

The ideal standard solution for a titrimetric method will:

1. *Re sufficiently stable so that it is necessary to determine its concentration only once;*
2. *React rapidly with the analyte so that the time required between additions of reagent is minimized;*
3. *React more or less completely with the analyte so that satisfactory end points are realized;*
4. *Undergo a selective reaction with the analyte that can be described by a balanced equation.*

Few reagents completely meet these ideals. The accuracy of a titration can be no better than the accuracy of the concentration of the standard solution used.

10. ***Explain the methods used to establish the concentration of standard solutions***

Two basic methods are used to establish the concentration of such solutions. The first is the direct method in which a carefully determined mass of a *primary standard is dissolved in a suitable solvent and diluted to a known volume in a volumetric flask.*

The second is by standardization in which the titrant to be standardized is used to titrate

(1) a known mass of a primary standard,

(2) a known mass of a secondary standard, or

(3) a measured volume of another standard solution.

A titrant that is standardized is sometimes referred to as a secondary standard solution. The concentration of a secondary-standard solution is subject to a larger uncertainty than is the concentration of a primary-standard solution. If there is a choice, then, solutions are best prepared by the direct method.

Many reagents, however, lack the properties required for a primary standard and, therefore, require standardization

13.Outline the various types of titration

There are many types of titration when considering goals and procedures. However, the most common types of titration in quantitative chemical analysis are redox titration and acid-base titration.

Titrations can be classified as:

1. *Acid-base Titrations*
2. *Redox Titrations.*
3. *Precipitation Titrations.*
4. *Complexometric Titrations*

a. Acid-Base Titration

The strength of an acid can be determined using a standard solution of a base. This process is called acidimetry. In the same way, the strength of a base can be found with the help of a standard solution of an acid, which is known as alkalimetry. Both titrations involve in the neutralization reaction of an alkali.

Acid- base titration is a quantitative analysis method to determine an acid's or bases' concentration by precisely neutralizing them with a standard solution of either acid or base of known concentration. It is monitored with the help of a pH indicator to know the development of the acid-base reaction.

$HA+BOH \rightarrow BA+H_2O$

Acid + Alkali→Salt + Water

Or $H^+ + A^- + B^+ + OH^- \rightarrow B^+ + A^- + H_2O$

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

The acid-base titration is based on the reaction that neutralization is between a base or an acidic and analyte. In this type, a reagent is mixed with the sample solution until it reaches the required pH level. This type of titration majorly depends on the track change in pH or a pH meter.

b. Redox Titrations

The redox titration is also known as an oxidation-reduction reaction. In this type of titration, the chemical reaction takes place with a transfer of electrons in the reacting ions of aqueous solutions. The titrations are named after the reagent that is used in are as follows;

- *Permanganate Titrations*
- *Dichromate Titrations*
- *Iodimetric and Iodometric Titrations*

Permanganate Titrations

In this titration, the potassium permanganate is used as an oxidizing agent. It is maintained with the use of dilute sulphuric acid. Here is the equation.

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

Or

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Further, the solution remains colourless before the endpoint. The potassium permanganate is used to estimate oxalic acid, ferrous salts, hydrogen peroxide, oxalates and more. While the solution of potassium permanganate is always standardized before it is used.

Dichromate Titrations

These are titrations in which, potassium dichromate is used as an oxidising agent in acidic medium. The medium is maintained acidic by the use of dilute sulphuric acid. The potential equation is:

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

Or

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2\,Cr^{3+} + 7H_2O$$

The solution of potassium dichromate can be directly used for titrations. It is mainly used for the estimation of ferrous salts and iodides.

Iodimetric and Iodometric Titrations

The reduction of free iodine to iodide ions and
oxidation of iodide ions to free occurs in these titrations.

$l_2 + 2e^- \rightarrow 2I^-$ *……………. (reduction)*

$2I^- \rightarrow I_2 + 2e^-$ *……………. (oxidation)*

The solution is used as an indicator. Free iodine is used in the iodometric titration, while in the iodometric titration an oxidation agent is used to react to liberate free iodine.

c. Precipitation Titrations

The titration is based on the insoluble precipitate formation when the two reacting substances are brought into contact are called precipitation titration. For instance, when the solution of silver nitrate is used to a solution of ammonium thiocyanate or sodium chloride, it reacts and forms a white precipitate of silver thiocyanate or silver chloride.

$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$

$AgNO_3 + NH_4CNS \rightarrow AgCNS + NH_4NO_3$

d. Complexometric Titrations

The complexometric titration is where an undissociated complex is formed at an equivalence point. It is greater than the precipitation titrations, and there will be no error due to co-precipitations.

$Hg^{2+} + 2SCN^{-} \rightarrow Hg(SCN)_2$

$Ag^{+} + 2CN^{-} \rightarrow [Ag(CN)_2]^{-}$

Ethylenediaminetetraacetic acid (EDTA) is an important reagent that forms complexes with metals.

13. Explain Acid-base reaction

*An **acid-base reaction** is one in which a hydrogen ion, H^+, is transferred from one chemical species to another. Such reactions are of central importance to numerous natural and technological processes, ranging from the chemical transformations that take place within cells and the lakes and oceans, to the industrial-scale production of fertilizers, pharmaceuticals, and other substances essential to society. The subject of acid-base chemistry, therefore, is worthy of thorough discussion.*

*The reaction between an acid and a base is called an acid-base reaction or a **neutralization reaction**. Although acids and bases have their own unique chemistries, the acid and base cancel each other's chemistry to produce a rather innocuous substance—water. In fact, the **general acid-base reaction** is*

acid + base ⟶ water + salt

*where the term **salt** is used to define any ionic compound (soluble or insoluble) that is formed from a reaction between an acid and a base. In chemistry, the word salt refers to more than just table salt. For example, the balanced chemical equation for the reaction between HCl(aq) and KOH(aq) is*

$HCl(aq) + KOH(aq) \longrightarrow H_2O(\ell) + KCl(aq)$

where the salt is KCl. By counting the number of atoms of each element, we find that only one water molecule is formed as a product. However, in the *reaction between* $HCl(aq)$ *and* $Mg(OH)_2(aq)$*, additional molecules of* HCl *and* H_2O *are required to balance the chemical equation:*

$2\ HCl(aq) + Mg(OH)_2(aq) \longrightarrow 2\ H_2O(\ell) + MgCl_2(aq)$

Here, the salt is $MgCl_2$*. This is one of several reactions that take place when a type of antacid—a base—is used to treat stomach acid. There are acid-base reactions that do not follow the "general acid-base" equation given above. For example, , the balanced chemical equation for the reaction between* $HCl(aq)$ *and* $NH_3(aq)$ *is*

$HCl(aq) + NH_3(aq) \longrightarrow NH_4Cl(aq)$

Neutralization reactions are one type of chemical reaction that proceeds even if one reactant is not in the aqueous phase. For example, the chemical reaction between $HCl(aq)$ *and* $Fe(OH)_3(s)$ *still proceeds according to the equation*

$3\ HCl(aq) + Fe(OH)_3(s) \longrightarrow 3\ H_2O(\ell) + FeCl_3(aq)$

Even though $Fe(OH)_3$ *is not soluble. When one realizes that* $Fe(OH)_3(s)$ *is a component of rust, this explains why some cleaning solutions for rust stains contain acids—the neutralization reaction produces products that are soluble and wash away. Washing with acids like HCl is one way to remove rust and rust stains, but HCl must be used with caution!*

Complete and net ionic reactions for neutralization reactions will depend on whether the reactants and products are soluble, even if the acid and base react. For example, in the reaction of $HCl(aq)$ *and* $NaOH(aq)$*,*

$$HCl(aq) + NaOH(aq) \longrightarrow H_2O(\ell) + NaCl(aq)$$

the complete ionic reaction is

$H^+(aq) + Cl^-(aq) + Na^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell) + Na^+(aq) + Cl^-(aq)$

The $Na^+(aq)$ *and* $Cl^-(aq)$ *ions are spectator ions, so we can remove them to have*

$H^+(aq) + OH^-(aq) \longrightarrow H_2O(\ell)$

as the net ionic equation. If we wanted to write this in terms of the hydronium ion, $H_3O^+(aq)$*, we would write it as*

$H_3O^+(aq) + OH^-(aq) \longrightarrow 2H_2O(\ell)$

With the exception of the introduction of an extra water molecule, these two net ionic equations are equivalent.

However, for the reaction between $HCl(aq)$ *and* $Cr(OH)_2(s)$*, because chromium(II) hydroxide is insoluble, we cannot separate it into ions for the complete ionic equation:*

$2\ H^+(aq) + 2\ Cl^-(aq) + Cr(OH)_2(s) \longrightarrow 2\ H_2O(\ell) + Cr^{2+}(aq) + 2\ Cl^-(aq)$

The chloride ions are the only spectator ions here, so the net ionic equation is

$2\ H^+(aq) + Cr(OH)_2(s) \longrightarrow 2\ H_2O(\ell) + Cr^{2+}(aq)$

14.Outline the basic steps in back titration

A back titration, also called an indirect titration, is a titration method where the concentration of an analyte is determined by reacting it with a known amount of excess reagent.

Back titration allows the user to find the concentration of a reactant of unknown concentration by reacting it with an excess volume of another reactant of known concentration.

The resulting mixture is then titrated back with another, second reagent. The second titration's result shows how much of the excess reagent was used in the first titration, thus allowing the original analyte's concentration to be calculated.

Back titrations can be used for many reasons, including: when the sample is not soluble in water, when the sample contains impurities that interfere with forward titration, or when the end-point is more easily identified than in forward titration.

A back titration is used when the molar concentration of an excess reactant is known, but the need exists to determine the strength or concentration of an analyte.

Back titration is typically applied in acid-base titrations:

1. *When the acid or (more commonly) base is an insoluble salt (e.g., calcium carbonate)*
2. *Back titrations are applied, more generally, when the endpoint is easier to see than with a normal titration, (e.g., weak acid and weak base titration) or reactions which applies to some precipitation reactions.*

13. Write the neutralization reactions between each acid and base.

a) $HNO_3(aq)$ **and** $Ba(OH)_2(aq)$

b)$H_3PO_4(aq)$ **and** $Ca(OH)_{2(aq)}$

First, we will write the chemical equation with the formulas of the reactants and the expected products; then we will balance the equation.

a) The expected products are water and barium nitrate, so the initial chemical reaction is

$HNO_3(aq) + Ba(OH)_2(aq) \longrightarrow H_2O(\ell) + Ba(NO_3)_2(aq)$

To balance the equation, we need to realize that there will be two H_2O *molecules, so two* HNO_3 *molecules are required:*

$2HNO_3(aq) + Ba(OH)_2(aq) \longrightarrow 2H_2O(\ell) + Ba(NO_3)_2(aq)$

This chemical equation is now balanced.

b) The expected products are water and calcium phosphate, so the initial chemical equation is

$H_3PO_4(aq) + Ca(OH)_2(aq) \longrightarrow H_2O(\ell) + Ca_3(PO_4)_2(s)$

According to the solubility rules, $Ca_3(PO_4)_2$ *is insoluble, so it has an (s) phase label. To balance this equation, we need two phosphate ions and three calcium ions; we end up with six water molecules to balance the equation:*

$2\ H_3PO_4(aq) + 3\ Ca(OH)_2(aq) \longrightarrow 6\ H_2O(\ell) + Ca_3(PO_4)_2(s)$

This chemical equation is now balanced.

Write balanced chemical equations for the acid-base reactions described here:

*a) the **weak acid** hydrogen hypochlorite reacts with water*

b) a solution of barium hydroxide is neutralized with a solution of nitric acid

The two reactants are provided, HOCl and H_2O*. Since the substance is reported to be an acid, its reaction with water will involve the transfer of* H^+ *from HOCl to* H_2O *to generate hydronium ions,* H_3O^+ *and hypochlorite ions,* OCl^-*.*

$HOCl(aq)+H2O(l)\rightleftharpoons OCl-(aq)+H3O+(aq)$

A double-arrow is appropriate in this equation because it indicates the HOCl is a weak acid that has not reacted completely.

The two reactants are provided, $Ba(OH)_2$ *and* HNO_3*. Since this is a neutralization reaction, the two products will be water and a salt composed of the cation of the ionic hydroxide (*Ba^{2+}*) and the anion generated when the acid transfers its hydrogen ion (*NO^{3-}*).*

$Ba(OH)2(aq)+2HNO3(aq)\longrightarrow Ba(NO3)2(aq)+2H2O(l)$

Write the net ionic equation representing the neutralization of any strong acid with an ionic hydroxide. *Hint: Consider the ions produced when a strong acid is dissolved in water.*

$H3O+(aq)+OH-(aq)\longrightarrow 2H2O(l)$

14.Oxalic acid, $H_2C_2O_4(s)$***, and*** $Ca(OH)_2(s)$ ***react very slowly. What is the net ionic equation between these two substances if the salt formed is insoluble? The anion in oxalic acid is the oxalate ion,*** $C_2O_4^{2-}$***.***

The products of the neutralization reaction will be water and calcium oxalate:

$$H_2C_2O_4(s) + Ca(OH)_2(s) \longrightarrow 2\ H_2O(\ell) + CaC_2O_4(s)$$

Because nothing is dissolved, there are no substances to separate into ions, so the net ionic equation is the equation of the three solids and one liquid.

What is the net ionic equation between $HNO_3(aq)$ and $Ti(OH)_4(s)$?

$4\ H^+(aq) + Ti(OH)_4(s) \longrightarrow 4\ H_2O(\ell) + Ti^{4+}(aq)$

14. ***A solution of sodium hydroxide contained 0.250 mol dm^{-3}. Using phenolphthalein indicator, titration of 25.0 cm^3 of this solution required 22.5 cm^3 of a hydrochloric acid solution for complete neutralisation.***

(a) write the equation for the titration reaction. $NaOH_{(aq)} + HCl_{(aq)} \Longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

(b) what apparatus would you use to measure out (i) the sodium hydroxide solution? (ii) the hydrochloric acid solution?

(i) pipette (ii) burette

(c) ***what would you rinse your apparatus out with before doing the titration ?***

everything with distilled water, then pipette with a little of the NaOH(aq) and the burette with a little of the HCl(aq)

(d) what is the indicator colour change at the end-point?

pink to colourless*, the first drop of excess acid removes the pink alkaline colour of phenolphthalein*

(e) calculate the moles of sodium hydroxide neutralised.

moles sodium hydroxide neutralised: 0.250 x 25.0/1000

= 0.00625 mol NaOH

(remember: moles = molarity x volume in dm^3 and its two rearrangements and 1 dm^3 = 1000 cm^3)

(f) calculate the moles of hydrochloric acid neutralised.

moles HCl = moles NaOH (equation) ***= 0.00625 mol HCl*** *(in 22.5 cm^3)*

(g) calculate the concentration of the hydrochloric acid in mol/dm^3 (molarity).

concentration hydrochloric acid *= 0.00625 x 1000 ÷ 22.5*

= 0.278 mol dm^{-3} (3sf)

(scaling up to 1 dm^3 = 1000 cm^3 to get the molarity)

Another way to work it out is 22.5 cm^3 = 22.5 ÷ 1000 = 0.0225 dm^3

Therefore molarity = 0.00625 ÷ 0.0225 = ***0.278 mol dm^{-3}***

15. A 25 ml solution of 0.5 M NaOH is titrated until neutralized into a 50 ml sample of HCl. What was the concentration of the HCl?

Step 1: Determine [OH-]

Every mole of NaOH will have one mole of OH-. Therefore [OH-] = 0.5 M.

Step 2: Determine the number of moles of OH-

Molarity = number of moles/volume

Number of moles = Molarity x Volume

Number of moles OH- = (0.5 M)(0.025 L)

Number of moles OH- = 0.0125 mol

Step 3: Determine the number of moles of H+
When the base neutralizes the acid, the number of moles of H+ = the number of moles of OH-. Therefore, the number of moles of H+ = 0.0125 moles.
Step 4: Determine the concentration of HCl
Every mole of HCl will produce one mole of H+; therefore, the number of moles of HCl = number of moles of H+.
Molarity = number of moles/volume
Molarity of HCl = (0.0125 mol)/(0.05 L)
Molarity of HCl = 0.25 M
Answer
The concentration of the HCl is 0.25 M.

Another Solution Method

The above steps can be reduced to one equation:
MacidVacid = MbaseVbase
Where
Macid = concentration of the acid
Vacid = volume of the acid
Mbase = concentration of the base
Vbase = volume of the base

This equation works for acid/base reactions where the mole ratio between acid and base is 1:1. If the ratio were different, as in Ca(OH)2 and HCl, the ratio would be 1 mole acid to 2 moles base. The equation would now be:

Macid Vacid = 2Mbase Vbase

For the example problem, the ratio is 1:1:
Macid Vacid = Mbase Vbase
Macid(50 ml)= (0.5 M)(25 ml)

$$Macid = \frac{12.5\ MmL}{50\ ml}$$

Macid = 0.25 M

16. In an experiment an unknown mass of anhydrous sodium carbonate was dissolved in water and the solution made up to $250cm^3$. $25cm^3$ of this solution neutralized $20cm^3$ of 0.25M nitric acid. (Na = 23.0 C =
$Na_2CO_{3(aq)} + 2HNO_{3(aq)} \rightarrow 2NaNO_{3(aq)} + CO_{2(g)} + H_2O_{(l)}$
Calculate:

a. Moles of Nitric acid used

Na2CO3(aq) + 2HNO3(aq) → 2NaNO3(aq) + CO2(g) + H2O(l)
Mole ration 1 : 2

Moles of HNO_3 in $20cm^3 = {}^{20}/_{1000}$ x 0.25
= 0.005 moles

b. *Moles of sodium carbonate in 25cm of the solution*
Moles of Na_2CO_3 in $25cm^3$ = ½ of 0.005 moles
= 0.0025

c. *Mass of unknown sodium carbonate used*
If $25cm^3$ = 0.0025 moles
in $250cm^3$ = ?

$$\frac{250 \times 0.0025}{25}$$

= 0.025 moles
RFM of Na_2CO_3 = 106
1 mole of Na_2CO_3 = 106g
0.025 moles = ?

$$\frac{0.025 \times 106}{1}$$

= 2.65g of Na_2CO_3

17. ***A solution made from pure barium hydroxide contained 2.74 g in exactly 100 cm^3 of water. Using phenolphthalein indicator, titration of 20.0 cm^3 of this solution required 18.7 cm^3 of a hydrochloric acid solution for complete neutralisation. [atomic masses: Ba = 137, O = 16, H = 1)***

(a) write the equation for the titration reaction.

$$Ba(OH)_{2(aq)} + 2HCl_{(aq)} ==> BaCl_{2(aq)} + 2H_2O_{(l)}$$

(b) Calculate the molarity of the barium hydroxide solution.

formula mass of $Ba(OH)_2$ = 171, moles = 2.74 ÷ 171 = 0.016 mol in 100 cm^3, (scaling up x 10)
therefore 0.16 mol in 1000 cm^3, so ***molarity of $Ba(OH)_2$ = 0.16 mol dm^{-3}***

(c) calculate the moles of barium hydroxide neutralised.

moles $Ba(OH)_2$ used in titration = 0.16 x 20/1000 ***= 0.0032 mol***

(d) calculate the moles of hydrochloric acid neutralised.

moles HCl titrated = 2 x moles of $Ba(OH)_2$ used (2 : 1 in equation) 2 x .0032
= 2 x 0.0032 = ***0.0064 mol HCl in 18.7 cm^3 of the acid solution****, 18.7 cm^3 = 0.0187 dm^3*

(e) calculate the molarity of the hydrochloric acid.

therefore ***molarity of $HCl_{(aq)}$*** *= 0.0064/0.0187* ***= 0.342 mol dm^{-3}***

18. 4.90g of pure sulphuric acid was dissolved in water, the resulting total volume was 200 cm^3. 20.7 cm^3 of this solution was found on titration, to completely neutralise 10.0 cm^3 of a sodium hydroxide solution. [atomic masses: S = 32, O = 16, H = 1)

(d) Write the equation for the titration reaction.

$2NaOH_{(aq)} + H_2SO_{4(aq)} ==> Na_2SO_{4(aq)} + 2H_2O_{(l)}$

(b) calculate the molarity of the sulphuric acid solution.

moles H_2SO_4 = 4.90 ÷ 98 = 0.050 mol in 200cm^3

scaling up to get molarity of the sulphuric acid solution, 0.050 x 1000 ÷ 200 = ***0.25 mol dm^{-3}***

(c) calculate the moles of sulphuric acid neutralised.

moles of sulphuric acid neutralised = 0.250 x 20.7/1000 = 0.005175 mol

(d) calculate the moles of sodium hydroxide neutralised.

moles of sodium hydroxide neutralised = 2 x 0.005175

= 0.01035 mol *(2 : 1 in equation)*

(e) calculate the concentration of the sodium hydroxide in mol dm^{-3} (molarity).

concentration of the sodium hydroxide = 0.01035 x 1000 ÷ 10 = 1.035 mol dm-3 (molarity 1.04, 3sf)

19. 100 cm^3 of a magnesium hydroxide solution required 4.5 cm^3 of sulphuric acid (of concentration 0.100 mol dm^{-3}) for complete neutralisation.

[atomic masses: Mg = 24.3, O = 16, H = 1)

(a) Give the equation for the neutralisation reaction.

$Mg(OH)_{2(aq)} + H_2SO_{4(aq)} ==> MgSO_{4(aq)} + 2H_2O_{(l)}$

(b) Calculate the moles of sulphuric acid neutralised.

moles of sulphuric acid neutralised = 0.100 x 4.5/1000

= 0.00045 mol

(c) Calculate the moles of magnesium hydroxide neutralised.

moles of magnesium hydroxide neutralised also

= 0.00045 *(1:1 in equation) in 100 cm^3*

(d) Calculate the concentration of the magnesium hydroxide in mol dm^{-3} (molarity).

concentration of the magnesium hydroxide

= 0.00045 x 1000 ÷ 100 ***= 0.0045 mol dm***

(scaling up to 1000cm^3 = 1dm^3, to get molarity)

(e) calculate the concentration of the magnesium hydroxide in g cm^{-3}.

molar mass of Mg(OH)$_2$ = ***58.3***

so concentration of the magnesium hydroxide

= 0.0045 x 58.3 = ***0.26 g dm^{-3}*** *(= g per 1000 cm^3),*

20. 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 2.00 mol dm^{-3} (in excess). The excess acid required 19.7 cm^3 of sodium hydroxide (0.200 mol dm^{-3}) for neutralisation using phenolphthalein indicator and the end-point is the first permanent pink colour. This 2nd titration is called a 'back-titration', and is used to determine the unreacted acid. [atomic masses: Mg = 24.3, O = 16)

(a) *(i)* ***Why do you have to use excess acid and employ a back titration?***

The magnesium oxide is ***insoluble*** *in water and so cannot be titrated directly by a volumetric analysis method. By dissolving in* ***excess*** *acid you are sure to get all the MgO into solution, and then determine the excess acid, from which you can derive the amount of MgO that dissolved.*

*(ii****) Write equations for the two neutralisation reactions.***

$MgO_{(s)} + 2HCl_{(aq)} \Longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$

$NaOH_{(aq)} + HCl_{(aq)} \Longrightarrow NaCl_{(aq)} + H_2O_{(l)}$

(b) Calculate the moles of hydrochloric acid added to the magnesium oxide.

moles of hydrochloric acid added to the magnesium oxide = 2 x 100/1000 = ***0.20 mol HCl***

(c) Calculate the moles of excess hydrochloric acid titrated.

moles of excess hydrochloric acid titrated

= 19.7 ÷ 1000 x 0.200 = ***0.00394 mol HCl***

{mole ratio NaOH : HCl is 1 : 1 from equation (ii)}

(d) Calculate the moles of hydrochloric acid reacting with the magnesium oxide.

mole MgO reacted *= 0.196 ÷ 2*

= 0.098 *{1: 2 in equation (i)}*

the formula mass of MgO = 40.3

therefore mass of MgO reacting with acid

= 0.098 x 40.3 = ***3.95 g***

(e) Calculate the moles and mass of magnesium oxide that reacted with the initial hydrochloric acid.

molar mass of $\underline{Mg(OH)_2}$ = $\underline{\mathbf{58.3}}$

so concentration of the magnesium hydroxide

= 0.0045 x 58.3 **= *0.26 g dm***$^{-3}$ *(= g per 1000 cm*^{3}*),*

so concentration = 0.26 ÷ 1000 ***= 0.00026 g cm***$^{-3}$

(f) *hence the % purity of the magnesium oxide.*

% purity *= 3.95 ÷ 4.06 x 100*

= 97.3% MgO

21. 2.00 dm^{3} of concentrated hydrochloric acid (10.0 M) was spilt onto a laboratory floor. It can be neutralised with limestone powder. [atomic masses: Ca = 40, C = 12, O = 16)

(a) give the equation for the reaction between limestone and hydrochloric acid.

$$CaCO_{3(s)} + 2HCl_{(aq)} ==> CaCl_{2(aq)} + H_2O_{(l)} + CO_{2(g)}$$

(b) how many moles of hydrochloric acid was spilt?

moles of hydrochloric acid was spilt

= 2.00 x 10.0 ***= 20 mol HCl***

(c) how many moles of calcium carbonate will neutralise the acid?

moles of calcium carbonate to neutralise the acid

= 20 ÷ 2 ***= 10.0 mol*** $\mathbf{CaCO_3}$ *(1:2 in equation)*

(d) what minimum mass of limestone powder is needed to neutralise the acid?

formula mass of $CaCO_3$ *= 100,*

so mass of limestone powder needed to neutralise the acid

= 100 x 10 = 1000g $CaCO_3$

(e) If 1000 dm^{3} *of sulphuric acid, of concentration 2.00 mol dm*$^{-3}$*, leaked from a tank,*

calculate the minimum mass of magnesium oxide required to neutralise it.

the neutralisation reaction is $\mathbf{MgO + H_2SO_4 ==> MgSO_4 + H_2O}$***,***

moles H_2SO_4 *= 1000 x 2 = 2000 mol acid,*

2000 mol MgO needed *(1:1 in equation),*

mass MgO needed = 2000 x 40.3 ***= 80600 g*** *or* ***80.6 kg***

b. A 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 1.00 mol dm***$^{-3}$ ***aqueous***

sodium hydroxide required 20.0 cm^3 of the diluted sulphuric acid for neutralisation.

(a) Give the equation for the full neutralisation of sulphuric acid by sodium hydroxide.

$2NaOH_{(aq)} + H_2SO_{4(aq)} ==> Na_2SO_{4(aq)} + 2H_2O_{(l)}$

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

moles of sodium hydroxide used in the titration

= 25.0 x 1/1000 = ***0.025 mol NaOH***

(c) Calculate the concentration of the diluted acid.

mol H_2SO_4 *= mol NaOH ÷ 2 = 0.0125 mol in 20.0 cm*^{3}*,*

so scaling up to 1000 cm^3 *to get molarity of diluted acid*

= 0.0125 x 1000 ÷ 20 = ***0.625 mol dm***$^{-3}$

(or molarity = 0.0125 mol/0.02 dm^3 *= 0.625 mol dm*$^{-3}$*)*

(e) Calculate the concentration of the original concentrated sulphuric acid solution.

scaling up from 50 to 1000 cm^3*, gives the concentration of the original concentrated sulphuric acid solution,*

= 0.625 x 1000 ÷ 50 = ***12.5 mol dm***$^{-3}$

23. A sample of sodium hydrogencarbonate was tested for purity using the following method. 0.400g of the solid was dissolved in 100 cm^3 of water and titrated with 0.200 mol dm^{-3} hydrochloric acid using methyl orange indicator. 23.75 cm^3 of acid was required for complete neutralisation. [Ar's: Na = 23, H = 1, C = 12, O = 16]

(a) Write the equation for the titration reaction. ***(a)*** $NaHCO_{3(s)} + HCl_{(aq)} ==> NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

(b) Calculate the moles of acid used in the titration and the moles of sodium hydrogencarbonate titrated.

mol = molarity x volume in dm^3*, mol acid*

= 0.200 x 23.75/1000

= 4.75 x 10^{-3} *mol HCl*

from equation HCl:$NaHCO_3$ *is 1:1 by ratio*

so mol HCl = ***mol*** $NaHCO_3$ ***= 4.75 x 10***$^{-3}$

(c) Calculate the mass of sodium hydrogen carbonate titrated and hence the purity of the sample.

mass = mol x formula mass, f. mass $NaHCO_3$ ***= 23 + 1 + 12 + (3 x 16) = 84***

mass $NaHCO_3$ *= 4.75 x 10*$^{-3}$ *x 84*

= 0.399 g

***% purity of $NaHCO_3$** = 0.399 x 100/0.40*

= 99.75% (99.8%, 3sf)

(d) If 0.400g of another group 1 hydrogen carbonate in its pure state, was titrated with the same acid and it took 20.00 cm3 to neutralise it, calculate ...

(i) moles of acid needed for neutralisation and moles of hydrogen carbonate titrated)

mol = molarity x volume in dm^3, mol acid

= 0.200 x 20.00/1000

= 4.00×10^{-3} mol HCl

from equation above HCl : $MHCO_3$ is 1 : 1 by ratio

*so mol HCl **= mol $MHCO_3$***

= 4.00×10^{-3}

(ii) the formula mass of the hydrogencarbonate

to get to the relative formula mass

*moles = mass / M_r, **M_r = mass / mol***

*= 0.400 / 4.00×10^{-3} **= 100***

(iii) by working out the atomic mass of M, suggest the identity of M in the group 1 hydrogencarbonate formula $MHCO_3$

for $MHCO_3$, $M_r(HCO_3) = 1 + 12 + 48 = 61$,

***A_r (M)** = 100 - 61 = **39**,*

which, from the periodic table relative atomic mass values, corresponds to potassium

*So the formula of the group 1 hydrogencarbonate titrated was **$KHCO_3$***

***a)(i) Write out the equation, complete with state symbols for the reaction between hydrochloric acid and sodium carbonate.** $Na_2CO_{3(aq)} + 2HCl_{(aq)} \Longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$*

Atomic masses: O = 16, H = 1, Na = 23, C = 12, Ca = 40, P = 31.09

(ii) A pipetted 25.0 cm^3 aliquot of a solution of sodium carbonate is to be titrated with an approximately 1.0 mol dm^{-3} hydrochloric acid to be standardised.

20.0 cm^3 of 1.0 mol dm^{-3} hydrochloric acid contains 1.0 x 20.0/1000 = 0.02 mol HCl

From the equation, 0.020 mol HCl reacts with 0.010 mol Na_2CO_3, $M_r(Na_2CO_3) = 106$

therefore mass Na_2CO_3 titrated = 0.01 x 106 = 1.06 g per aliquot,

since 250 cm^3 is $^1/_{10}$th of the aliquot,

10 x 1.06 = 10.6 g of Na_2CO_3 would be used to make up the solution.

***Molarity of $Na_2CO_{3(aq)}$** = (10.6 g/106 g mol^{-1})/0.25 dm^3*

= 0.40 mol dm^{-3}

24. What mass of dried anhydrous sodium carbonate must be dissolved in 250 cm^3 of deionised water, so that a 25.0 cm^3 aliquot of the carbonate solution will give a 20.0 cm^3 titration with the hydrochloric acid?

a. What is the molarity of the sodium carbonate solution, assuming 100% purity.

(b)*(i) The simplified molecular structure of 2-ethanoylhydroxybenzoic acid ('Aspirin') is* $CH_3COOC_6H_4COOH$.

Give the equation of its reaction with sodium hydroxide.

$\mathbf{CH_3COOC_6H_4COOH + NaOH \Longrightarrow CH_3COOC_6H_4COO^-Na^+ + H_2O}$

(ii) A sample of aspirin was to be analysed for purity by titrating it with standardised 0.100 mol dm^{-3} sodium hydroxide using phenolphthalein indicator. Assuming 100% purity and access to a 4 decimal place electronic balance, calculate the mass of Aspirin that should be weighed out to give a titration of 23.0 cm^3 of the alkali.

23.0 cm^3 of 0.100 mol dm^{-3} NaOH contains 0.100 x 23.0/1000 = 0.0023 mol NaOH

From the equation, mol Aspirin = mol NaOH, $M_r(CH_3COOC_6H_4COOH) = 180$

so need Aspirin mass of 0.0023 x 180 ***= 0.414 g***

(iii) ***The main contaminant is likely to be unreacted 2-hydroxybenzoic acid. Why is this likely to be an impurity? and how will this affect the % purity you calculate i.e. why and how will the % purity be in error?***

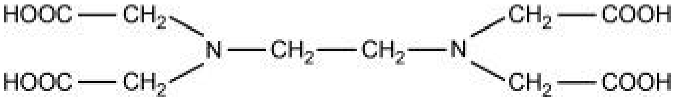
The last stage in the synthesis of 2-ethanoylhydroxybenzoic acid ('Aspirin') is made by esterifying 2-hydroxybenzoic acid with ethanoic anhydride.

$M_r(HOC_6H_4COOH) = 138$*, is 42 units less than aspirin. In terms of this particular impurity the %* ***aspirin will be overestimated*** *for the following reason. The 2-hydroxybenzoic acid will also be titrated with the aspirin, and, with its smaller molecular mass, it will need more alkali to neutralise than aspirin per equivalent mass of material. This can result in >100% purity!!!!*

c. Outline complexiometric titration

Complexometric titrations are used mainly to determine metal ions by use of complex-forming reactions. Although many complexing agents (cyanide, thiocyanate, fluoride, 1,2-diaminoethane, etc.) can be used for this purpose, in practice the titrants are almost always compounds having the iminodiacetic acid functional groups.

The most widely applied are ethylenediaminetetraacetic acid, H_4Y *and the dihydrate of the sodium salt,* $Na_2H_2Y \cdot 2H_2O$ *(better soluble in water).*



Ethylenediaminetetraacetic acid, H4Y

d. Explain the properties of EDTA that makes it suitable for complexiometric titration

EDTA fulfills most of the conditions for a good complexometric titrant. i. It forms sufficiently stable complexes with most metal ions (except the alkali metals which form too weak complexes), all the complexes have exact 1:1 stoichiometry (regardless of the charge of the cation)

1. the reaction with most metal ions (except Cr^{3+}) is rapid,

2. the complexes are water soluble and colorless (unless the metal ion itself is colored).

The reaction between a typical metal ion and EDTA (H_4Y) can be written as:

$$Men^{+}+H4Y\rightleftarrows MeY4^{-}n^{-}+4H^{+}$$

that is, as a competition between the metal ion and hydrogen ions for binding with Y^{2-}. The stability of binding of Me^{n+} with Y^{2-} is measured by its stability constant K_{MeY}, which is the equilibrium constant for the reaction:

$$Men^{+}+Y4^{-}\rightleftarrows MeY4^{-}n^{-}$$

$$KMeY=MeY4^{-}n^{-}Men+Y4^{-}$$

Generally metals forming weaker complexes require less acidic (i.e., higher pH) conditions for complex formation. Metals forming stronger complexes can be titrated at lower pH values, at which the weaker complexing metals do not react, thus selective titration of Fe^{3+} or Bi^{3+} can be carried out in the presence of Mg^{2+} and Ca^{2+} or Pb^{2+}, respectively at pH 1–2. The reaction of metal ions with EDTA generates H^{+}. Thus, to prevent a pH change during the titration, the solution must be adequately buffered.

1. **State properties of Eriochrome Black T(EBT) that makes it suitable indicator in Ethylenediamine tetra acetic acid (EDTA) titration.**

Eriochrome Black T is a complexometric indicator that is used in complexometric titrations, e.g. in the water hardness determination process. It is an azo dye. In its deprotonated form, Eriochrome Black T is blue. It turns or changes colour from blue to pink in the process when it forms a complex with calcium, magnesium, or other metal ions.

The dye–metal ion complex is less stable than the EDTA–metal ion complex.

Eriochrome black T is used as an indicator for complexometric titrations because it forms a complex with calcium, magnesium and other metal ions in its protonated form. When titrated with EDTA, the metal ions complexed with eriochrome black T reacts with the EDTA forming a blue solution.

100. Outline the process of preparing 0.1M Silver nitrate solution given deionized water , clean and dry volumetric flask (1000ml) and silver nitrate crystals

e. Pure calcium carbonate can be used to make a standard calcium ion solution to practice a complexometric titration of calcium ions with EDTA or determine the molarity of the EDTA reagent.

(i) Give a simple equation to show the chelation reaction between hydrated calcium ions and the EDTA anion at pH10 and what sort of reaction is it?

It is a ligand substitution/replacement reaction.

$[Ca(H_2O)_6]^{2+}_{(aq)} + EDTA^{4-}_{(aq)} \Longrightarrow [CaEDTA]^{2-}_{(aq)} + 6H_2O_{(l)}$

more simply $Ca^{2+}_{(aq)} + EDTA^{4-}_{(aq)} \Longrightarrow [CaEDTA]^{2-}_{(aq)}$

or $[Ca(H_2O)_6]^{2+}_{(aq)} + H_2EDTA^{2-}_{(aq)} \Longrightarrow [CaEDTA]^{2-}_{(aq)} + 2H^+_{(aq)} + 6H_2O_{(l)}$

more simply $Ca^{2+}_{(aq)} + H_2EDTA^{2-}_{(aq)} \Longrightarrow [CaEDTA]^{2-}_{(aq)} + 2H^+_{(aq)}$

(ii) ***To make a standard calcium ion solution 0.250 g of A.R. calcium carbonate was dissolved in a little dilute hydrochloric acid and made up to 250 cm³ in a calibrated volumetric flask. Calculate the molarity of the calcium ion in this solution***.

$M_r(CaCO_3) = 100$, *mol* $CaCO_3$ = *mol* Ca^{2+} *in solution*

= 0.250/100 ***= 0.00250 mol***

since 250 cm³ = 0.25 dm³, ***molarity*** Ca^{2+} *= 0.0025/0.25*

= 0.010 mol dm⁻³

f. Approximately 1.0g of the solid disodium dihydrate salt of EDTA was dissolved in 250 cm³ of water in a volumetric flask. 25.0 cm³ of this was pipetted into a conical flask and ~1 cm³ of a conc. ammonia/ammonium chloride pH10 buffer was added. After adding a few drops of Eriochrome Black T indicator, the EDTA solution was titrated with the standard calcium ion solution (from part ii) until the reddish tinge turns to blue at the endpoint. If 25.7 cm³ of the EDTA solution was required to reach the equivalence point, what was the molarity of the EDTA?

mole $CaCO_3$ *= mol* Ca^{2+} *= mol EDTA used in titration.*

Therefore from c(ii) mol Ca^{2+} *= mol EDTA*

= 0.01 x 25.0/1000

= 0.00025 mol in 25.70 cm³ (0.0257 dm³) EDTA solution,

so ***molarity EDTA*** *= 0.00025/0.0257*

= 0.00973 mol dm^{-3} *(3 sf)*

g. In human teeth, approximately 96% of the outer enamel and 70% of the inner dentine are composed of the apatite mineral, calcium hydroxy phosphate. If the simplest empirical formula is $Ca_5(PO_4)_3OH$
calculate the % calcium in the apatite mineral.

M_r(apatite) = (5 x 40) + 3 x (31 + 4 x 16) + (16 + 1) = 502
% Ca in apatite *= 200 x 100/502*
= 39.8%

h. A dried 1.40g human tooth was dissolved in a small quantity of hot conc. nitric acid. A drop of methyl orange indicator was added followed by drops of 6M sodium hydroxide until the indicator turned orange to neutralise the solution. The solution was then made up to 250 cm^3 in a volumetric flask. 10.0 cm^3 of this solution was pipetted into a conical flask and ~1 cm^3 of a conc. ammonia/ammonium chloride pH10 buffer was added.

This solution was then titrated with 0.0200 mol dm^{-3} EDTA using Eriochrome Black T indicator. The indicator turned blue after 22.5 cm^3 of EDTA was added. Calculate the average % by mass of calcium throughout the tooth.

In the titration mol Ca^{2+} = mol EDTA,
therefore mol Ca^{2+} = 22.5 x 0.0200/1000 = 0.00045,
since $^{10}/_{250}$ of the original solution was used in the titration,
the total mol of calcium in the tooth solution = 0.00045 x 250/10
= 0.01125 mol Ca
total mass of Ca in tooth = 0.01125 x 40
= 0.45 g
% by mass Ca in the tooth *= 0.45 x 100/1.40*
= 32.1 %

i. 25.0 cm^3 of seawater was diluted to 250 cm^3 in a graduated volumetric flask.

A 25.0 cm^3 aliquot of the diluted seawater was pipetted into a conical flask and a few drops of potassium chromate(VI) indicator solution was added.

On titration with 0.100 mol dm^{-3} silver nitrate solution, 13.8 cm^3 was required to precipitate all the chloride ion.

[Atomic masses: Na = 23, Cl = 35.5]

(a) ***Give the ionic equation for the reaction of silver nitrate and chloride ion.***

$Ag^+_{(aq)}$ + $Cl^-_{(aq)}$ ==> $AgCl_{(s)}$ *(sodium ions and nitrate ions etc. are spectator ions)*

(b) Calculate the moles of chloride ion in the titrated 25.0 cm^3 aliquot.
from equation: moles silver nitrate ($AgNO_3$) = moles chloride ion (Cl)
moles = molarity $AgNO_3$ x volume of $AgNO_3$ in dm^3
= 0.100 x 13.8/1000
= 1.38 x 10^{-3} mol Cl^- *(in 25.0 cm^3 aliquot)*
(c) Calculate the molarity of chloride ion in the diluted seawater.
moles in 1 dm^3 of diluted seawater = 1.38 x 10^{-3} x 1000/25
= 0.0552 (scaling up to 1000 cm^3)
So molarity of chloride in diluted seawater is 0.0552 mol dm^{-3}
(d) Calculate the molarity of chloride ion in the original seawater.
Now in the titration 25.0 cm^3 of the 250 cm^3 was used,
so the molarity of chloride ion in the original seawater must be scaled up accordingly.
molarity of chloride ion in seawater *= 0.0552 x 250/25.0*
= 0.552 mol dm^{-3}
(e) Assuming that for every chloride ion there is a sodium ion, what is the theoretical concentration of sodium chloride salt in g dm^{-3} in seawater?
M_r(NaCl) = 23 + 35.5 = 58.5
concentration of NaCl in g dm^{-3} *= molarity x formula mass*
= 0.552 x 58.5 = ***32.3 g dm^{-3}***
33. 0.12 g of rock salt was dissolved in water and titrated with 0.100 mol dm^{-3} silver nitrate until the first permanent brown precipitate of silver chromate is seen.
19.7 cm^3 was required to titrate all the chloride ion.
[Atomic masses: Na = 23, Cl = 35.5]
(a) How many moles of chloride ion was titrated?
moles = molarity $AgNO_3$ x volume in dm^3
= 0.100 x 19.7/1000
= 1.97 x 10^{-3} mol Cl^- ion
[$AgNO_3$:NaCl or Ag^+ : Cl^- is 1 : 1,
mass NaCl = 23 + 35.5 = 58.5
(b) What mass of sodium chloride was titrated?
mass = mol x formula mass = 1.97 x 10^{-3} x 58.5
= 0.1152 g NaCl
(c) *What was the % purity of the rock salt in terms of sodium chloride?*
% purity *= 0.1152 x 100/0.12*
= 96.0 % in terms of NaCl *(3sf)*

j. 5.00g of a solid mixture of anhydrous calcium chloride($CaCl_2$) and sodium nitrate ($NaNO_3$) was dissolved in 250 cm^3 of deionised water in a graduated volumetric flask. A 25.0 cm^3 aliquot of the solution

was pipetted into a conical flask and a few drops of potassium chromate(VI) indicator solution was added.

On titration with 0.1 mol dm^{-3} silver nitrate solution, until the first permanent brown precipitate of silver chromate was formed, 21.2 cm^{3} was required to precipitate all the chloride ion. [Atomic masses: Ca = 40, Cl = 35.5]

(a) Calculate the moles of chloride ion titrated.

mole Cl^- = moles Ag^+ [=$AgNO_3$, see Q10(a)/(b)]

mole Cl^- = molarity $AgNO_3$ x vol $AgNO_3$

= 0.100 x 21.2/1000

= 2.12 x 10^{-3} mol Cl^-

(b) Calculate the equivalent moles of calcium chloride titrated.

Since calcium chloride is $CaCl_2$, mol $CaCl_2$ = mole Cl^-/2

= 2.12 x 10^{-3}/2

= 1.06 x 10^{-3} mol $CaCl_2$

(d) Calculate the equivalent mass of calcium chloride titrated.

$M_r(CaCl_2)$ = 40 + (2 x 35.5) = 111

***<u>mass</u>** = mol x f. mass*

= 1.06 x 10^{-3} x 111

= 0.1177 g $CaCl_2$

(d) Calculate the total mass of calcium chloride in the original 5.0 g of the mixture. Since $^{1}/_{10}$th of original solution titrated, original mass of $CaCl_2$ in mixture

= 10 x 0.1177 g

***= 1.177g $CaCl_2$** (1.78g 3sf)*

(e) The % of calcium chloride and sodium nitrate in the original mixture.

Therefore % = 1.177 x 100/5.0

***= 23.5% $CaCl_2$** (3 sf)*

*and **% $NaNO_3$** = 100 - 23.5*

***= 76.5%** (3 sf)*

34. A bulk solution of hydrochloric acid was standardised 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 250 cm^{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

24.65 cm^3 of a hydrochloric acid solution, of unknown molarity, to completely neutralise it. [atomic masses: Na = 23, C = 12, O = 16]

(a) Calculate the molarity of the prepared sodium carbonate solution.

moles = mass/f. mass, f. mass Na_2CO_3 = 106, mol Na_2CO_3 = 13.25/106 = 0.125

molarity = mol/vol. in dm^3, 250 cm^3 = 0.250 dm^3,

***molarity Na_2CO_3** = 0.125/0.250*

= 0.50 mol dm^{-3}

(b) Write out the equation between sodium carbonate and hydrochloric acid, including state symbols.

$Na_2CO_{3(aq)} + 2HCl_{(aq)} \Longrightarrow 2NaCl_{(aq)} + H_2O_{(l)} + CO_{2(g)}$

(c) How many moles of sodium carbonate were titrated?

mol = molarity x volume

*mol Na_2CO_3 titrated = 0.5 x 25.0/1000 = **0.0125 mol Na_2CO_3** (in the 25 cm^3 aliquot pipetted)*

(e) How many moles of hydrochloric acid were used in the titration?

from equation, mole ratio Na_2CO_3:HCl is 1:2,

so mol HCl = 2 x mol Na_2CO_3 = 2 x 0.0125

***= 0.025 mol HCl** (in the 24.65 cm^3 titre)*

(e) What is the molarity of the hydrochloric acid?

molarity = mol/vol. in dm^3,

dm^3 = cm^3/1000, 24.65/1000 = 0.02465 dm^3

*therefore **molarity HCl** = 0.025/0.02465*

***= 1.014 mol dm^{-3}** (1.01 3sf)*

36. Describe a procedure that can used to determine the molecular mass of an organic acid by titration with standardised sodium hydroxide solution. Indicate any points of the procedure that help obtain an accurate result and explain your choice of indicator.

An appropriate quantity of the acid is weighed out, preferably on a 4 sf electronic balance. It can be weighed into a conical flask by difference i.e. weight acid added to flask = (weight of boat + acid) - (weight of boat). The acid is dissolved in water, or aqueous-ethanol if not very soluble in water. The solution is titrated with standard sodium hydroxide solution using phenolphthalein indicator until the first permanent pink.

The burette should be rinsed with the sodium hydroxide solution first. During the titration the flask should be rinsed around the inside to ensure all the acid and alkali react, and drop-wise addition close to the end-point to get it to the nearest drop - the first permanent pink colour.

37. 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 0.100 mol dm^{-3} sodium hydroxide solution.

It took 20.5 cm^3 of the alkali to obtain the first permanent pink. [at. masses: C = 12, H = 1 and O = 16]

The pK_{ind} for phenolphthalein is 9.3, and its effective pH range is 8.3 to 10.0. The pH of a solution of the sodium salt of the acid (from strong base + weak acid) is in this region and so the equivalence point can be detected with this indicator.

(b) How many moles of sodium hydroxide were used in the titration? moles = molarity x volume in dm^3 (dm^3 = cm^3/1000)

***mol NaOH** = 0.100 x 20.5/1000*

= 0.00205 mol

(c) How many moles of the organic acid were titrated? and explain your reasoning.

*mol NaOH = **mol RCOOH***

= 0.00205

because 1:1 mole ratio for a monobasic acid: RCOOH + Na^+OH^- ==> $RCOO^-Na^+$ + H_2O

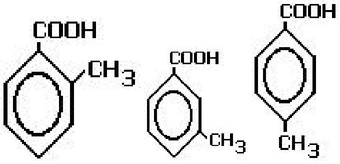
*(e) Calculate the molecular mass of the acid. moles = mass (g)/M_r, so **M_r** = mass/mol = 0.279/0.00205*

<u>= 136.1</u>

*(e) **Suggest possible structures of the acid with your reasoning.***

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)



2-, 3- or 4-methylbenzoic acid.

38. 0.103g of a dibasic/diprotic non-aromatic carboxylic acid required 19.85 cm^3 of a standardised sodium hydroxide solution for complete

neutralisation. If the concentration of the alkali was 0.0995 mol dm^{-3}. [at. masses: C = 12, H = 1 and O = 16]

Calculate ...

(a) moles of sodium hydroxide used in the titration, moles = molarity x volume in dm^3 (dm^3 = cm^3/1000)

***mol NaOH** = 0.0995 x 19.85/1000*

= 0.001975 mol

(b) Moles of dibasic/diprotic acid titrated giving your reasoning, The titration reaction for complete neutralisation is:

$R(COOH)_2 + 2Na^+OH^- ==> R(COO^-Na^+)_2 + 2H_2O$

*this 1 : 2 reaction mole ratio means that **mol dibasic acid** = mol NaOH/2 = 0.001975/2 **= 0.0009875***

(b) the molecular mass of the acid, moles = mass (g)/M_r,

*so M_r = mass/mol = 0.103/0.0009875 **= 104.3 (approx. 104 3sf)***

(d) a possible structure of the acid.

*Since a dibasic acid, and 2 x COOH = 2 x 45 = 90 mass units, the remaining 14 units could be CH_2, and so the structure is likely to be **$HOOC-CH_2-COOH$, propanedioic acid (malonic acid), M_r = 144***

339. 0.236g of benzoic acid required 19.25 cm^3 of 0.100mol dm^{-3} sodium hydroxide for complete neutralisation.

Calculate ...

(a) moles of sodium hydroxide used in titration,

mol NaOH = 0.100 x 19.25/1000

= 0.001925

(b) Moles and mass of benzoic acid titrated [at. masses: C = 12, H = 1 and O = 16]

mol NaOH = mol acid = 0.001925, mol ratio 1:1,

$C_6H_5COOH + Na^+OH^- ==> C_6H_5COO^-Na^+ + H_2O$

M_r (C_6H_5COOH) =122, mol = mass (g)/M_r or mass = mol x M_r

*so **mass acid** = 0.001925 x 122*

= 0.2349 g

(c) % purity of benzoic acid from this assay titration.

*% purity = actual mass of acid titrated x 100 / mass of original sample **% purity** = 0.2349 x 100/0.236 **= 99.5% (3 sf)***

40. Sodium hydroxide solution can be standardised. 0.250 g of very pure benzoic acid (C_6H_5COOH) was titrated with a solution of sodium hydroxide of unknown molarity. If 22.5 cm^3 of the alkali was required for neutralisation, Calculate ...

(a) moles of acid titrated [at. masses: C = 12, H = 1 and O = 16],

M_r (C_6H_5COOH) =122, mol acid = mass (g)/M_r

= 0.250/122

= 0.002049 mol

(b) mol alkali used in titration,

mol alkali = ***0.002049 mol****, since mol acid, 1:1 mole ratio in reaction (see Q17(b)).*

(c) the molarity of the alkali.

Since 0.002049 mol NaOH in 22.5 cm^3, so scaling up

molarity NaOH *= 0.002049 x 1000/22.5*

= 0.0911 mol dm^{-3} *(3 sf)*

41. The solubility of calcium hydroxide in water can be measured reasonably accurately to 3sf by titrating the saturated solution with standard hydrochloric acid.

(a) If the standard hydrochloric acid is made by diluting '2M' bench acid, what volume of the '2M' acid is required to make up 250 or 500 cm^3 of approximately 0.1 mol dm^{-3} hydrochloric acid and how might you do it?

The ratio of 2M/0.1M is 20, so need to do 20 fold dilution.

So 25.0 cm^3 of 2M diluted to 500 cm^3 gives an approximately 0.1 mol dm^{-3} solution. You can do this with a measuring cylinder and beaker.

In practice you could make up 12.5 cm^3 of the 2M acid up to 250 cm^3. You could do this with a burette and a 250 cm^3 standard volumetric flask, but standardisation of the acid is still required.

(c) Why must the 2M acid be diluted and why must the diluted acid be standardised?

The solubility of calcium hydroxide is low, so it would give a very inaccurate tiny titration value with relatively concentrated acid. For any accurate work e.g. to 3sf, standardisation of reagents is required.

In the calculation below assume the molarity of the standardised hydrochloric acid is 0.1005 mol dm^{-3}.

At 25°C, a few grams of solid calcium hydroxide was shaken with about 400 cm^3 of deionised water, and then filtered. 50.0 cm^3 samples of the 'limewater' gave an average titration of 15.22 cm^3 of 0.1005 mol dm^{-3} hydrochloric acid using phenolphthalein indicator. If the acid is in the burette, how would you measure out the calcium hydroxide solution? and why is phenolphthalein indicator used?

1 x 50.0 cm^3 pipette or 2 x 25.0 cm^3 pipette would be the most convenient (or accurate burette?). Phenolphthalein is used for strong base-strong acid titrations.

(d) Give the equation for calcium hydroxide reacting with hydrochloric acid.

$Ca(OH)_{2(aq)} + 2HCl_{(aq)} ==> CaCl_{2(aq)} + 2H_2O_{(l)}$

(e) What is the reacting mole ratio of $Ca(OH)_2$: HCl and hence calculate the moles of them involved in the titration.

from equation, ***mole ratio $Ca(OH)_2$: HCl is 1:2***

and since moles solute = molarity x volume in dm^3

mol HCl used in titration = 0.1005 x 15.22/1000

= 0.001530 mol HCl

therefore ***mol $Ca(OH)_2$*** *= 0.001558/2*

= 0.000765 mol $Ca(OH)_2$

(f) Calculate the molarity of the solution in terms of mol $Ca(OH)_2$ dm^{-3}.

Mr[$Ca(OH)_2$] =74, so solubility in g dm^{-3}

= 0.153 x 74

= 1.13 g dm^{-3} (3 sf)

(g) What is the approximate solubility of calcium hydroxide in g $Ca(OH)_2$ per 100g water?

Since density of water is ~1.0 g cm^{-3}, the ***solubility of $Ca(OH)_2$ is about 0.113 g/100 cm^3 H_2O***

CHAPTER ELEVEN

REDOX REACTIONS

Redox reaction

Redox reactions are reactions where both oxidation and reduction are taking place.

Oxidation is the loss of electrons by a reactant.

When a metal element is reacting to form a compound then it is being oxidised.

For example:

$$Mg(s)+O_2(g)\rightarrow MgO(s)$$

The metal atoms are losing electrons to form an ion. They are being oxidised.

$$Mg(s)\rightarrow Mg_2+(aq)+2e-$$

This is known as an ion-electron equation.

Reduction is the opposite of oxidation. It is the gain of electrons.

Compounds reacting that result in metal elements being formed are examples of reduction reactions.

For example:

$$Cu^{2+}(aq)+2e-\rightarrow Cu(s)$$

The metal ions are gaining electrons to form atoms of the element. They are being reduced.

Redox reactions takes place in the same reaction and at the same time and they result into displacement of one species by another

For example, if magnesium was added to copper sulphate solution, the magnesium metal would be oxidised, while the copper ions were being reduced.

$$Cu(s)\rightarrow Cu^{2+}(aq)+2e- \text{ oxidation reaction}$$

$$2Ag+(aq)+2e-\rightarrow 2Ag(s) \text{ reduction reaction}$$

$$Cu(s)+2Ag+(aq)\rightarrow Cu_2+(aq)+2Ag(s) \text{ redox reaction}$$

The superscript along with the sign is, called 'oxidation state' of the atom.

The oxidation number

The oxidation number of an atom is the charge it appears to have when you count the electrons according to some arbitrary rules.

By definition, the ***oxidation number*** *of an atom is the charge that atom would have if the compound was composed of ions.*

It is often useful to follow chemical reactions by looking at changes in the oxidation numbers of the atoms in each compound during the reaction.

Oxidation numbers also play an important role in the systematic nomenclature of chemical compounds.

1. The oxidation number of an atom is zero in a neutral substance that contains atoms of only one element. Thus, the atoms in O_2, O_3, P_4, S_8, and aluminum metal all have an oxidation number of 0.

2. The oxidation number of simple ions is equal to the charge on the ion. The oxidation number of sodium in the Na^+ ion is +1, for example, and the oxidation number of chlorine in the Cl^- ion is -1.

3. The oxidation number of hydrogen is +1 when it is combined with a nonmetal as in CH_4, NH_3, H_2O, and HCl.

4. The oxidation number of hydrogen is -1 when it is combined with a metal as in. LiH, NaH, CaH_2, and $LiAlH_4$.

5. The metals in Group IA form compounds (such as Li_3N and Na_2S) in which the metal atom has an oxidation number of +1.

6. The elements in Group IIA form compounds (such as Mg_3N_2 and $CaCO_3$) in which the metal atom has a +2 oxidation number.

7. Oxygen usually has an oxidation number of -2. Exceptions include molecules and polyatomic ions that contain O-O bonds, such as O_2, O_3, H_2O_2, and the O_2^{2-} ion.

8. The elements in Group VIIA often form compounds (such as AlF_3, HCl, and $ZnBr_2$) in which the nonmetal has a -1 oxidation number.

9. The sum of the oxidation numbers in a neutral compound is zero.

$H_2O: 2(+1) + (-2) = 0$

10. The sum of the oxidation numbers in a polyatomic ion is equal to the charge on the ion. The oxidation number of the sulfur atom in the SO_4^{2-} ion must be +6, for example, because the sum of the oxidation numbers of the atoms in this ion must equal -2.

$SO_4^{2-}: (+6) + 4(-2) = -2$

11. Elements toward the bottom left corner of the periodic table are more likely to have positive oxidation numbers than those toward the upper right corner of the table. Sulfur has a positive oxidation number in SO_2, for example, because it is below oxygen in the periodic table.

$SO_2: (+4) + 2(-2) = 0$

In redox reactions:

In redox reactions, atoms or ions either loss or gain electrons and have different oxidation states, before and after the reaction.

- *Oxidation number can be positive or zero or negative*
- *Oxidation number has to be an integer as the number of electrons can only be an integer.*

- *Oxidation number cannot be fractional*
- *The oxidation number is the same as the oxidation state.*

Balancing Redox Reactions

Oxidation-Reduction or "redox" reactions occur when elements in a chemical reaction gain or lose electrons, causing an increase or decrease in oxidation numbers. The Half Equation Method is used to balance these reactions.

In a redox reaction, one or more element becomes oxidized, and one or more element becomes reduced. Oxidation is the loss of electrons whereas reduction is the gain of electrons. An easy way to remember this is to think of the charges: an element's charge is reduced if it gains electrons (an acronym to remember the difference is LEO = Lose Electron Oxidation & GER = Gain Electron Reduction). Redox reactions usually occur in one of two environments: acidic or basic. In order to balance redox equations, understanding oxidation states is necessary.

Some points to remember when balancing redox reactions

- *The equation is separated into two half-equations, one for oxidation, and one for reduction.*
- *The equation is balanced by adjusting coefficients and adding* H_2O, H^+, *and* e^- *in this order:*

1. *Balance the atoms in the equation, apart from O and H.*
2. *To balance the Oxygen atoms, add the appropriate number of water* (H_2O) *molecules to the other side.*
3. *To balance the Hydrogen atoms (including those added in step 2), add* H^+ *ions.*
4. *Add up the charges on each side. They must be made equal by adding enough electrons* (e^-) *to the more positive side.*

- *The* e^- *on each side must be made equal; if they are not equal, they must be multiplied by appropriate integers to be made the same.*
- *The half-equations are added together, cancelling out the electrons to form one balanced equation. Cancel out as much as possible.*

These reactions can take place in either acidic or basic solutions.

- *(If the equation is being balanced in a basic solution, the appropriate number of* OH^- *must be added to turn the remaining* H^+ *into water molecules)*
- *The equation can now be checked to make sure it is balanced.*

a. In Acidic Aqueous Solution

Balance this reaction

$$MnO^-_4+I^-\longrightarrow I_2+Mn2^+$$

Solution

Steps to balance:

Step 1: Separate the half-reactions that undergo oxidation and reduction.

Oxidation:

$I^{-} \longrightarrow I_2$

This is the oxidation half because the oxidation state changes from -1 on the left side to 0 on the right side. This indicates a gain in electrons.

Reduction:

$MnO^{-}{}_4 \longrightarrow Mn^{2+}$

This is the reduction half because the oxidation state changes from +7 on the left side to +2 on the right side. This indicates a reduction in electrons.

Step 2: In order to balance this half reaction we must start by balancing all atoms other than any Hydrogen or Oxygen atoms.

***Oxidation**:*

$2I^{-} \longrightarrow I_2$

In order to balance the oxidation half of the reaction you must first add a 2 in front of the II on the left hand side so there is an equal number of atoms on both sides.

***Reduction**:*

$MnO^{-}{}_4 \longrightarrow Mn^{2+}$

For the reduction half of the reaction, you can notice that all atoms other than Hydrogen and Oxygen are already balanced because there is one manganese atom on both sides of the half reaction.

Step 3: Balance Oxygen atoms by adding H_2O to the side of the equation that needs Oxygen. Once you have completed this step add H+ to the side of the equation that lacks H atoms necessary to be balanced.

Oxidation:

$2I^{-} \longrightarrow I^{2}$

Because there are no Oxygen or Hydrogen atoms in this half of the reaction, it is not required to perform any kind of balancing.

***Reduction**:*

$MnO^{-4} \longrightarrow Mn^{2+} + 4H_2O$

The first step in balancing this reaction using step 3 is to add4 H_2O atoms in order to balance the Oxygen atoms with the 4 on the other side of MnO_4^-

***Reduction**:*

$MnO^{-}{}_4 + 8H^{+} \longrightarrow Mn^{2+} + 4H_2O$

Now that the Oxygen atoms have been balanced you can see that there are 8 H atoms on the right hand side of the equation and none on the left.

Therefore, you must add 8 H^+ atoms to the left hand side of the equation to make it balanced.

Step 4: Now that the two half reactions have been balanced correctly one must balance the charges in each half reaction so that both the reduction and oxidation halves of the reaction consume the same number of electrons.

***Oxidation**:*

$$2I^- \longrightarrow I_2+2e^-$$

Because of the fact that there are two I's on the left hand side of the equation which a charge of -1 we can state that the left hand side has an overall charge of -2. The I on the left side of the equation has an overall charge of 0. Therefore to balance the charges of this reaction we must add 2 electrons to the right side of the equation so that both sides of the equation have equal charges of -2.

***Reduction**:*

$$5e^-+8H^++MnO^-_4 \longrightarrow Mn^{2+}+4H_2O$$

Looking at the left hand side of the equation you can notice that there are 8 Hydrogen atoms with a +1 charge. There is also a MnO^-_4 ion that has a charge of -1. When we add these two charges up we can calculate that the left hand side of the equation has an overall charge of +7. The right hand side has an Mn atom with a charge of +2 and then 4 water molecules that have charges of 0. Therefore, the overall charge of the right side is +2. We must add 5 electrons to the left side of the equation to make sure that both sides of the equation have equal charges of +2.

Step 5: Multiply both sides of both reactions by the least common multiple that will allow the half-reactions to have the same number of electrons and cancel each other out.

***Oxidation**:*

$$10I^- \rightarrow 5I_2+10e^-$$

We multiply this half reaction by 5 to come up with the following result above.

Reduction: $10e-+16H^++2MnO^-_4 \rightarrow 2Mn^{2+}+8H_2O$

We multiply the reduction half of the reaction by 2 and arrive at the answer above.

By multiplying the oxidation half by 5 and the reduction half by 2 we are able to observe that both half-reactions have 10 electrons and are therefore are able to cancel each other out.

Step 6: Add the two half reactions in order to obtain the overall equation by canceling out the electrons and any H_2O and H^+ ions that exist on both sides of the equation.

***Overall**:*

$$10I^-+16H^++2MnO^-_4\longrightarrow 5I_2+2Mn^{2+}+8H_2O$$

In this problem, there is not anything that exists on both halves of the equation that can be cancelled out other than the electrons. Finally, double check your work to make sure that the mass and charge are both balanced. To double check this equation you can notice that everything is balanced because both sides of the equation have an overall charge of +4.

a. In Basic Aqueous Solutions

The balancing procedure in basic solution differs slightly because OH^- ions must be used instead of H^+ ions when balancing hydrogen atoms. To give the previous reaction under basic conditions, sixteen OH^- ions can be added to both sides. on the left the OH^- and the H^+ ions will react to form water, which will cancel out with some of the H^2Oon the right.

$$10I^-(aq)+2MnO^-_4(aq)+16H^+(aq)+16OH^-(aq)\longrightarrow 5I_2(s)+2Mn^{2+}(aq)+8H_2O(l)+16OH^-(aq)$$

On the left side the OH- and the H+ ions will react to form water, which will cancel out with some of the H2O on the right:

$$10I^-(aq)+2MnO^-_4(aq)+16H_2O(l)\longrightarrow 5I_2(s)+2Mn^{2+}(aq)+8H_2O(l)+16OH^-(aq)$$

Eight water molecules can be canceled, leaving eight on the reactant side:

$$10I^{-(}aq)+2MnO^-_4(aq)+8H_2O(l)\longrightarrow 5I_2(s)+2Mn^{2+}(aq)+16OH^-(aq)$$

This is the balanced reaction in basic solution.

Balance the following in an acidic solution.

$$SO_3^{2-}(aq)+MnO^-_4(aq)\rightarrow SO_2-4(aq)+Mn^{2+}(aq)$$

Solution

To balance a redox reaction, first take an equation and separate into two half reaction equations specifically oxidation and reduction, and balance them.

Step 1: Split into two half reaction equations: Oxidation and Reduction

- *Oxidation:*

$$SO_3^{2-}(aq)\longrightarrow SO_4^{2-}(aq)$$

[oxidation because oxidation state of sulfur increase from +4 to +6]

- *Reduction:*

$$MnO^+4(aq)\longrightarrow Mn^{2+}(aq)$$

[Reduction because oxidation state of Mn decreases from +7 to +2]

Step 2: Balance each of the half equations in this order:

- *Atoms other than H and O*
- *O atoms by adding H_2Omolecules with proper coefficients*
- *H atoms by adding H^+ with proper coefficients*

The S and Mn atoms are already balanced,
Balancing O atoms
Oxidation:$SO3^{2-}\ (aq)+H_2O(l)\rightarrow SO_4^{2-}\ (aq)$
Reduction:$MnO_4(^{-}aq\rightarrow Mn^{2+}(aq)+4H_2O(l)$
Then balance out H atoms on each side
Oxidation:$SO^{2-}3(aq)+H_2O(l)\rightarrow SO_4^{2-}\ (aq)+2H^{+}(aq)$
Reduction:$MnO4^{-}\ (aq)+8H^{+}\rightarrow Mn^{2+}(aq)+4H_2O(l)$
Step 3: Balance the charges of the half reactions by adding electrons
Oxidation:$SO_3^{2-}\ (aq)+H_2O(l)\rightarrow SO_4^{2-}\ (aq)+2H^{+}(aq)+2e-$
Reduction:$MnO4^{-}\ (aq)+8H^{+}+5e-\rightarrow Mn^{2+}(aq)+4H_2O(l)$
Step 4: Obtain the overall redox equation by combining the half reaction, but multiply entire equation by number of electrons in oxidation with reduction equation, and number of electrons in reduction with oxidation equation.
Oxidation:$5\times[SO_3^{2-}\ (aq)+H_2O(l)\rightarrow SO_4^{2-}\ (aq)+2H^{+}(aq)+2e-]$
Reduction:$2\times[MnO_4^{-}\ (aq)+8H^{+}+5e-\rightarrow Mn^{2+}(aq)+4H_2O(l)]$
Overall Reaction:
Oxidation:$5SO_3^{2-}\ (aq)+5H_2O(l)\rightarrow 5SO_4^{2-}\ (aq)+10H^{+}(aq)+10e-$
$\underline{\text{Reduction:}2MnO_4^{-}\ (aq)+16H^{+}+10e-\rightarrow 2Mn^{2+}(aq)+8H_2O(l)}$
total:$5SO_3^{2-}\ (aq)+5H_2O(l)+2MnO4^{-}\ (aq)+16H^{+}+10e-\rightarrow 5SO_4^{2-}\ (aq)+10H^{+}(aq)+2Mn^{2+}(aq)+8H_2O(l)+10e-$
Step 5: Simplify and cancel out similar terms on both sides
To get
$5SO_3^{2-}(aq)+2MnO4^{-}(aq)+6H^{+}\rightarrow 5SO_4^{2-}(aq)+2Mn^{2+}(aq)+3H^{2}O(l)$

Balance this reaction in both acidic and basic aqueous solutions

$MnO4^{-}(aq)+SO_3^{2-}\ (aq)\longrightarrow MnO2\ (s)\ +SO_4^{2-}\ (aq)$

Solution

First, they are separated into the half-equations:

$MnO_4^{-}\ (aq)\longrightarrow MnO2(s)$

This is the reduction half-reaction because oxygen is LOST)
and

$SO_3^{2-}\ (aq)\longrightarrow SO_4^{2-}\ (aq))$

(the oxidation, because oxygen is GAINED)
Now, to balance the oxygen atoms, we must add two water molecules to the right side of the first equation, and one water molecule to the left side of the second equation:

$MnO_4^{-}\ (aq)\longrightarrow MnO_2(s)+2H_2O(l)$
$H2O(l)+SO_3^{2-}\ (aq)\longrightarrow SO_4^{2-}\ (aq)$

To balance the hydrogen atoms (those the original equation as well as those added in the last step), we must add four H^+ ions to the left side of the first equation, and two H^+ ions to the right side of the second equation.

$$4H^{+}+MnO_4^{-}\ (aq)\longrightarrow MnO_2(s)+2H_2O(l)$$

$$H_2O(l)+SO_3^{2-}\ (aq)\longrightarrow SO_4^{2-}\ (aq)+2H^{+}$$

Now we must balance the charges. In the first equation, the charge is +3 on the left and 0 on the right, so we must add three electrons to the left side to make the charges the same. In the second equation, the charge is -2 on the left and 0 on the right, so we must add two electrons to the right.

$$3e-+4H^{+}+MnO_4^{-}\ (aq)\longrightarrow MnO_2(s)+2H_2O(l)$$

$$H_2O(l)+SO_3^{2-}\ (aq)-\longrightarrow SO_4^{2-}\ (aq)+2H^{+}+2e-$$

Now we must make the electrons equal each other, so we multiply each equation by the appropriate number to get the common multiple (in this case, by 2 for the first equation, and by 3 for the second).

$$2(3e-+4H^{+}+MnO_4^{-}\ (aq)\longrightarrow MnO_2(s)+2H_2O(l))$$

$$3(H_2O(l)+SO_3^{2-}\ (aq)\longrightarrow SO_4^{2-}\ (aq)+2H^{+}+2e-)$$

With the result:

$$6e-+8H^{+}+2MnO_4^{-}(aq)\longrightarrow 2MnO_2(s)+4H_2O(l)$$

$$3H_2O(l)+3SO_3^{2-}\ (aq)\longrightarrow 3SO_4^{2-}\ (aq)+6H^{+}+6e-$$

Now we cancel and add the equations together. We can cancel the $6e^{-}$ because they are on both sides. We can get rid of the $6H^+$ on both sides as well, turning the $8H^+$ in the first equation to 2H+. The same method gets rid of the 3H2O(l) on the bottom, leaving us with just one H2O(l) on the top. In the end, the overall reaction should have no electrons remaining. Now we can write one balanced equation:

$$2MnO_4^{-}\ (aq)+2H^{+}+3SO_3^{2-}\ (aq)\longrightarrow H2O(l)+2MnO_2(s)+3SO_4^{2-}\ (aq)$$

The equation is now balanced in an <u>acidic environment</u>.

To balance in a basic environment add OH− to each side to neutralize the H+ into water molecules:

$$2MnO_4^{-}\ (aq)+2H_2O+3SO_3^{2-}\ (aq)\longrightarrow H_2O(l)+2MnO_2(s)+3SO_4^{2-}\ (aq)+2OH-$$

and then cancel the water molecules

$$2MnO_4^{-}(aq)+H_2O+3SO_3^{2-}(aq)\longrightarrow +2MnO_2(s)+3SO_4^{2-}\ (aq)+2OH-$$

The equation is now balanced in a <u>basic environment</u>.

Balance this reaction in acidic solution

$$Fe(OH)^{3+}OCl-\longrightarrow FeO_4^{2-}+Cl^{-}$$

Solution

Step 1:

- *Reduction:*

$OCl^- \longrightarrow Cl^-$

- *Oxidation:*

$Fe(OH)_3 \longrightarrow FeO_4{}^{2-}$

Steps 2 and 3:

- *Reduction:*

$2H^+ + OCl^- + 2e- \longrightarrow Cl^- + H_2O$

- *Oxidation:*

$Fe(OH)_3 + H_2O \longrightarrow FeO_4^{2-} + 3e- + 5H^+$

Overall Equation:

$3\times[2H^+ + OCl^- + 2e- \longrightarrow Cl^- + H_2O]$

$6H^+ + 3OCl^- + 6e- \longrightarrow 3Cl^- + 3H_2O$

and

$2\times[Fe(OH)_3{}^+H_2O \longrightarrow FeO4^{2-} + 3e^- + 5H^+] \longrightarrow 2FeO_4{}^{-2} + 6e- + 10H^+$

Adding these together results

$6H^+ + 3OCl^- + 2e- + 2Fe(OH)_3 + 2H_2O \longrightarrow 3Cl^- + 3H_2O + 2FeO_4^{2-} + 6e- + 10H+$

Step 5:

Simplify:

$3OCl^- + 2Fe(OH)_3 \rightarrow 3Cl_- + H_2O + 2FeO_4^{2-} + 4H^+$

Balance this equation in acidic aqueous solution

$VO_4^{3-} + Fe^{2+} \longrightarrow VO^{2+} + Fe^{3+}$

Step 1:

- *Oxidation:*

$Fe^{2+} \longrightarrow Fe^{3+}$

- *Reduction:*

$VO_4^{3-} \longrightarrow VO^{2+}$

Step 2/3:

- *Oxidation:*

$Fe^{2+} \longrightarrow Fe^{3+} + e-$

Reduction:

$6H^+ + VO_4^{3-} + e- \longrightarrow VO^{2+} + 3H_2O$

Step 4:

Overall Reaction:

$Fe^{2+} \longrightarrow Fe^{3+} + e-$

$6H^+ + VO_4^{3-} + e- \longrightarrow VO^{2+} + 3H_2O$

$$Fe^{2+}+6H^{+}+VO_4^{3-}+e-\rightarrow Fe^{3+}+e-+VO^{2+}+3H_2O$$

Step 5:

Simplify:

$$Fe^{2+}+6H^{+}+VO_4^{3-}\rightarrow Fe^{3+}+VO^{2+}+3H_2O$$

1. ***calculate the Oxidation number of Manganese in permanganate ion*** MnO_4^-

Charge on the permanganate ion is -1

Oxidation state of permanganate ion =Oxidation state of manganese + 4 oxidation state of oxygen = -1.

Oxidation state of oxygen = -2

Oxidation states → $x + (4*-2) = -1: x = +7$

Atoms in the species → Mn 4O

Oxidation state of manganese = +7

2. Work out the oxidation numbers of the following metal ion in a complex.

i) $Ni(CO)_4$.

The total charge of the complex is zero. CO is a neutral molecule.

Oxidation states → $x + (4*0) = 0: x = 0$

Atoms in the species → Ni 4 CO

Nickel is also in zero oxidation state.

ii) $[CoCl_2(NH_3)_4]Cl$.

The complex can be written in the ionic forms as $[CoCl_2(NH_3)_4]^+Cl^-$.

Metal is in a cationic complex with a unitary positive charge. Ammonia is a neutral ligand and chlorine has a unit negative charge.

Oxidation number of $[CoCl_2(NH_3)_4]^+$

= Oxidation number of (Co + 2Cl + 4×0) = +1.

Oxidation states → $x + (2*-1) + 4*0 = +1: x = +3$

Atoms in the species → Co 2Cl 4 NH_3

Oxidation number of cobalt in the complex = +3

3. Calculate the oxidation numbers in Cl_2O, Cl_2O_5 ***and*** Cl_2O_7.

i) Cl_2O:

Cl_2O *is neutral and so, net charge=0.*

Net oxidation state of $Cl_2O = 2x$

Oxidation state of chlorine + 1x

Oxidation state of oxygen = -2.

Oxidation states → $2x + (-2) = 0$:

$2x= 2$

$x = +1$

$Cl= 1$

ii) Cl_2O_5:

Cl_2O_5 is neutral and so, net charge=0
Oxidation state of chlorine + 5 x oxidation state of oxygen = 0.
∵ Oxidation state of oxygen = -2.
Oxidation states → $2x + (5 X -2) = 0$:
$2x = 10$
$x = +5$
Oxidation state of chlorine in Cl_2O_5 = +5

iii) Cl_2O_7:

Cl_2O_7 is neutral and so, net charge=0
Oxidation state of Cl_2O_7 = 2 X Oxidation state of chlorine + 7 X oxidation state of oxygen = 0.
∵ Oxidation state of oxygen = -2.
Oxidation states → $2x + (7X-2) = 0$:
$2x= 14$
$x = +7$
Oxidation state of chlorine in Cl_2O = +7

Note: Except the atoms/molecules/ions mentioned, as having a constant oxidation state, oxidation state of other atoms/molecule and ions will vary depending on the molecule they are present.

In the given examples, the oxidation state of chlorine is not constant, but variable (+1, +5 and +7)

6.Calculate the Oxidation state of chromium in dichromate anion.

Dichromate ion is $Cr_2O_7^{2-}$.
Charge on the ion is -2.
Oxidation state of dichromate ion
= 2 X (Oxidation state of chromium)+ 7 X (oxidation state of oxygen) = -2.
Oxidation state of oxygen = -2.
Oxidation states → $2x + (7X-2) = -2$:
$2x= -2+14$
$2x= 12$
$x = +6$
Oxidation state of chromium= 12 / 2 = 6

8. Calculate the oxidation state of Chlorine in Cl_2O_4

i) The average oxidation state of chlorine
Cl_2O_4 is neutral and so, net charge = 0
Oxidation state of Cl_2O_4 = 2 x(Oxidation state of chlorine) + 4 x (oxidation state of oxygen) = 0.

∵ Oxidation states → $2x + (4X-2) = 0$:

$2x = 8$

$x = +4$

Oxidation state of chlorine in Cl_2O_5 = +4

11. Given the following two half–reactions:

(i) $MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \Longrightarrow Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$

and (ii) $Fe^{3+}{}_{(aq)} + e^- \Longrightarrow Fe^{2+}{}_{(aq)}$

(a) Construct the fully balanced redox ionic equation for the manganate(VII) ion oxidising the iron(II) ion:

$MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5Fe^{2+}{}_{(aq)} \Longrightarrow Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + 4H_2O_{(l)}$

*(b) **24.3** cm^3 of **0.0200** mol dm^{-3} $KMnO_4$ reacted with **20.0** cm^3 of an iron(II) solution acidified with dilute sulfuric acid.*

(i) Calculate the molarity of the iron(II) ion.

mol MnO_4^- = 0.0200 x 24.3 / 1000

= 0.000486

therefore mol Fe^{2+} = 5 x 0.000486 (1 : 5 in equation)

= 0.00243 in 20 cm^3

*so scaling up to 1 dm^3, the **molarity of Fe^{2+}***

= 0.00243 x 1000 / 20

*= **0.122 mol dm^{-3}**.*

(ii) How do recognise the end–point in the titration?

*The end point is the **first faint permanent pink** due to a trace excess of $KMnO_4$.*

12. Calculate the percentage of iron in a sample of steel wire if 1.51 g of the wire was dissolved in excess of dilute sulfuric acid and the solution made up to 250 cm^3 in a standard graduated flask. A 25.0 cm^3 aliquot of this solution was pipetted into a conical flask and needed 25.45 cm^3 of O.0200 mol dm^{-3} $KMnO_4$ for complete oxidation.

mol MnO_4^- = 0.0200 x 25.45 / 1000 = 0.000509

mol Fe = 5 x 0.000509 = 0.002545,

mass Fe = 0.002545 x 55.9 = 0.1423 g

total Fe in wire = 0.1423 x 10 = 1.423 g (only $^1/_{10}$th of the made up solution used in titration)

*so **<u>% Fe</u>** = 1.423 x 100 / 1.51*

*= **<u>94.2 %</u>***

(a) Suggest reasons why the presence of dil. sulfuric acid is essential for an accurate titration and why dil. hydrochloric and nitric acids are unsuitable to be used in this context.

The titrations are done with (i) dilute sulfuric acid present to prevent side reactions e.g. MnO_2 formation (brown colouration or black precipitate).
(ii) Nitric acid is an oxidising agent and would oxidise iron(II) ions to iron(III) ions,
and (iii) chloride ions are oxidised to chlorine by manganate(VII) ions (see half-cell potential data in Q3c),
therefore, using either acid (ii) or (iii) would give a false titration result.

7. ***The analysis of a soluble iron(II) salt to obtain the percentage of iron in it.8.25g of an iron(II) salt was dissolved in 250 cm^3 of pure water. 25.0 cm^3 aliquots were pipetted from this stock solution and titrated with 0.0200 mol dm^{-3} potassium manganate(VII) solution.***

The titration values obtained were 23.95 cm^3, 23.80 cm^3 and 23.85 cm^3.

(i) What titration value should be used in the calculation and why?
***23.87 cm^3**, i.e. the **average titration value**, which is statistically more accurate than an individual titration result.*
(ii) molarity = mol / volume in dm^3
BUT, remember, 1 dm^3 = 1000 cm^3,
burettes and pipettes work in cm^3 and molarity works in dm^3,
a bit of pain I know, but live with it and go with the flow!
therefore mol = molarity x vol in cm^3 / 1000
mol MnO_4^-** = 0.0200 x 23.87/1000 = **4.774×10^{-4}
From the balanced redox equation, 1 mol MnO_4^- oxidises 5 mol of iron(II) ions
mol Fe^{2+}** = 5 x 4.774 x 10^{-4} = **2.387×10^{-3}
(ii) Calculate the moles of manganate(VII) used in the titration.
You can assume mass of Fe = mass of Fe^{2+} ion, (2 electrons don't weigh much!)
mol = mass/atomic mass, so mass = mol x atomic mass
mass Fe** = 2.387 x 10^{-3} x 55.8 = **0.1332 g
*(iii) calculate the moles of iron(II) ion titrated **Total mass of iron** in original sample = 10 x 0.1332 = **1.332 g** (scaling up by factor of 250/25)*
(iv) Calculate the mass of iron(II) titrated
You can assume mass of Fe = mass of Fe^{2+} ion, (2 electrons don't weigh much!)
mol = mass/atomic mass, so mass = mol x atomic mass
mass Fe** = 2.387 x 10^{-3} x 55.8 = **0.1332 g
(v) Calculate the total mass of iron in the original sample of the iron(II) salt.
***Total mass of iron** in original sample*
*= 10 x 0.1332 = **1.332 g***
(vi) calculate the % iron in the salt.

% iron in the original salt *= 1.332 x 100 / 8.25 =* ***16.1%*** *(1dp, 3sf)*

8. Given the following two half–reactions

1. ***Given***
2. ***(i)*** $S_4O_6^{2-}{}_{(aq)} + 2e^- ==> 2S_2O_3^{2-}{}_{(aq)}$

    and

    (ii) $I_{2(aq)} + 2e^- ==> 2I^-{}_{(aq)}$

construct the full ionic redox equation for the reaction of the thiosulfate ion $S_2O_3^{2-}$ ***and iodine*** I_2***.***

(i) $I_2(aq) + 2e^- ==> 2I^-(aq)$ *(iodine reduced by thiosulfate ion, reduction is electron gain)*

(ii) $2S_2O_3^{2-}(aq) ==> S_4O_6^{2-}(aq) + 2e^-$ *(thiosulfate ion oxidised by iodine, oxidation is electron loss)*

(Note that you needed to reverse the half-cell equation as given in question to arrive at the full ionic redox equation)

(i) + (ii) gives: $2S_2O_3^{2-}(aq) + I_2(aq) ==> S_4O_6^{2-}(aq) + 2I^-(aq)$

(b) what mass of iodine reacts with ***23.5*** *cm³ of* ***0.0120*** *mol dm⁻³ sodium thiosulfate solution.*

mol $S_2O_3^{2-} = 0.0120 \times 23.5 / 1000$

= 0.000282, mole iodine as I_2

= mol $S_2O_3^{2-} / 2$ *(1 : 2 in equation)*

= 0.000141,

$A_r(I) = 126.9$*, so* $M_r(I_2)$

= 2 x 126.9

= 253.8

therefore: ***mass of iodine*** *= 0.000141 x 126.9 x 2 =* ***0.0358 g***

9. ***25.0*** *cm³ of a solution of iodine in potassium iodide solution required* ***26.5*** *cm³ of* ***0.0950*** *mol dm⁻³ sodium thiosulfate solution to titrate the iodine.*

What is the molarity of the iodine solution and the mass of iodine per dm³?

mol $S_2O_3^{2-} = 0.095 \times 26.5 / 1000$

= 0.002518,

mol of iodine = mole 'thio' / 2

= 0.002518 / 2

= 0.001259 in 25.0 cm³,

scaling up to 1 dm³ gives 0.001259 x 1000 /25

= ***0.0504 mol dm⁻³ of molecular iodine*** I_2*.*

mass concentration of I_2 *= 0.0504 x 2 x 126.9*

= ***12.8 g dm⁻³ of iodine***

13. 2.83 g of a sample of haematite iron ore [iron (III) oxide, Fe_2O_3] were dissolved in concentrated hydrochloric acid and the solution diluted to 250 cm^3.

25.0 cm^3 of this solution was reduced with tin(II) chloride (which is oxidised to Sn^{4+} in the process) to form a solution of iron(II) ions. This solution of iron(II) ions required 26.4 cm^3 of a 0.0200 mol dm^{-3} potassium dichromate(VI) solution for complete oxidation back to iron(III) ions.

(a) given the half–cell reactions

(i) $Sn^{4+}_{(aq)} + 2e^- \Longrightarrow Sn^{2+}_{(aq)}$

And

(ii) $Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6e^- \Longrightarrow 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

deduce the fully balanced redox equations for the reactions

(i) the reduction of iron(III) ions by tin(II) ions $Sn^{2+}_{(aq)} + 2Fe^{3+}_{(aq)} \Longrightarrow Sn^{4+}_{(aq)} + 2Fe^{2+}_{(aq)}$

(ii) the oxidation of iron(II) ions by the dichromate(VI) ion

$Cr_2O_7^{2-}{}_{(aq)} + 14H^+_{(aq)} + 6Fe^{2+}_{(aq)} \Longrightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$

(b) Calculate the percentage of iron(III) oxide in the ore.

for a 25.0 cm^3 aliquot titrated

mol $Cr_2O_7^{2-}$ = 0.0200 x 26.4 / 1000

= 0.000528,

mol Fe^{2+} titrated = 6 x $Cr_2O_7^{2-}$ = 0.003168

(from 1 mol $Cr_2O_7^{2-}$: 6 mol Fe^{2+} in the redox equation),

mol Fe_2O_3 = mol Fe^{2+} / 2 = mol Fe^{3+} / 2

= 0.003168 / 2

= 0.001584

(moles Fe^{2+} or Fe^{3+} halved, because of 2 moles of Fe^{3+} in in one mole of Fe_2O_3)

$M_r(Fe_2O_3)$ = 159.8 (Fe = 55.9, 0 = 16.0)

so mass of Fe_2O_3 = 0.001584 x 159.8 = 0.2531 g.

Total mass of Fe_2O_3 = 0.2531 x 10 = 2.531 g

Remember only $^1/_{10}$th titrated, so need to scale up by 10 to account for all the iron oxide in the original sample.

*Therefore **% Fe_2O_3** = 2.531 x 100 / 2.83 = **89.4%***

Note that that overall the ratio of mol $Cr_2O_7^{2-}$: mol Fe_2O_3 is 3 : 1.

Now its ok to solve this problem using the 3 : 1 ratio if you are very confident to use short cuts in this type of calculation. However, I think from a teaching and learning point of view, I prefer to show the full logic of each step in the calculation, particularly when dealing with mole ratios and this is what I've tried to do on this page!

(c) Suggest why potassium manganate(VII) isn't used for this titration? (though it was ok in Q1)

Potassium manganate(VII) isn't used for this titration because it is strong enough to oxidise chloride ions (from the hydrochloric acid) to form chlorine, giving a completely false titration.

14. An approximately 0.02 mol dm^{-3} potassium manganite (VII) solution was standardized against precisely 0.100 mol dm^{-3} iron(II) ammonium sulfate solution. 25.0 cm^3 of the solution of the iron(II) salt were oxidized by 24.15 cm^3 of the manganate(VII) solution.

What is the molarity of the potassium manganate(VII) solution ?

mol Fe^{2+} = 0.100 x 25.0 / 1000 = 0.0025,

mol MnO_4^- = mol Fe^{2+} / 5 (from equation 1 : 5)

= 0.0005 in 24.15 cm^3,

*scaling up to 1 dm^3, **molarity of MnO_4^-** = 0.0005 x 1000 / 24.15 = **0.0207 mol dm^{-3}**.*

15. 10.0 g of iron(II) ammonium sulfate crystals were made up to 250 cm^3 of acidified aqueous solution. 25.0 cm^3 of this solution required 21.25 cm^3 of 0.0200 mol dm^{-3} potassium dichromate(VI) for oxidation.

Calculate x in the formula $FeSO_4.(NH_4)_2SO_4.xH_2O$

mol $Cr_2O_7^{2-}$ = 0.0200 x 21.25 / 1000 = 0.000425,

mol of Fe salt = mol Fe^{2+} titrated = 6 x $Cr_2O_7^{2-}$

= 6 x 0.000425 = 0.00255,

BUT only $^1/_{10}$th of Fe^{2+} salt used in titration,

*so 1 g of $FeSO_4.(NH_4)_2S0_4$.**x**H_2O is equal to 0.00255 mol.*

Scaling up to 1 mol gives a molar mass for the salt in g mol^{-1} of 1 x 1 /0.00255 = 392.2.

*So the formula mass for $FeSO_4.(NH_4)_2S0_4$.**x**H_2O is 392.2.*

Now the formula mass of $FeSO_4.(NH_4)_2S0_4$ = 284.1,

this leaves 392.2 – 284.1

= 108.1 mass units.

*$M_r(H_2O)$ = 18, so 108.1 / 18 = 6.005 mol of water, so **x = 6 in the salt formula,** $FeSO_4.(NH_4)_2S0_4$.**6**H_2O.*

16. Given the half–reaction $C_2O_4^{2-}{}_{(aq)} - 2e^- ==> 2CO_{2(g)}$

or $H_2C_2O_{4(aq)} - 2e^- ==> 2CO_{2(g)} + 2H^+{}_{(aq)}$

(a) write out the balanced redox equation for manganate(VII) ions oxidising the ethanedioate ion (or ethanedioic acid).

$2MnO_4^-{}_{(aq)} + 16H^+{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} ==> 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(g)}$

*or **$2MnO_4^-{}_{(aq)} + 6H^+{}_{(aq)} + 5H_2C_2O_{4(aq)} ==> 2Mn^{2+}{}_{(aq)} + 8H_2O_{(l)} + 10CO_{2(g)}$***

*(b) **1**.520 g of ethanedioic acid crystals, $H_2C_2O_4.2H_2O$, was made up to 250.0 cm^3 of aqueous solution and 25.00 cm^3 of this solution needed 24.55 cm^3 of a potassium manganate(VII) solution for oxidation.*
Calculate the molarity of the manganate(VII) solution and its concentration in g dm^{-3}.
$M_r(H_2C_2O_4.2H_2O) = 126.0$
total mol $H_2C_2O_4.2H_2O$ (or $C_2O_4^{2-}$) = 1.52 / 126
= 0.0120635
but mol of $C_2O_4^{2-}$ in titration = 0.0120635/10
= 0.00120635 ($^1/_{10}$th used, 25 of 250 cm^3),
mol MnO_4^- = mol of $C_2O_4^{2-}$ / 2.5 (2:5 or 1:2.5 ratio),
mol MnO_4^- = 0.00120634 / 2.5
= 0.00048254 (in 24.55 cm^3),
*scaling up to 1 dm^3 the **molarity of MnO_4^-***
= 0.00048254 x 1000 / 24.55
= 0.0196554
*= **0.01966 mol dm^{-3}** (5dp, 4sf) OR **0.0197 mol dm^{-3}** (4dp, 3sf)*
*$M_r(KMnO_4)$ = 158.0, so in terms of mass **concentration***
= 0.01965523 x 158 = 3.10555
*= **3.106 g dm^{-3}** (3dp, 4sf) OR **3.11 g dm^{-3}** (2dp, 3sf)*
[NOTE: The titration volume, mass and formula masses are quoted to four significant figures (4sf), so it might be considered legitimate to quote the answer to four significant figures]

17. ***A standardization of potassium manganate(VII) solution yielded the following data: 0.150 g of potassium tetraoxalate dihydrate, $KHC_2O_4.H_2C_2O_4.2H_2O$ needed 23.20 cm^3 of the manganate(VII) solution.***

What is the molarity of the manganate(VII) solution?
mol $KHC_2O_4.H_2C_2O_4.2H_2O$ (M_r = 254.2)
= 0.150 / 254.2
= 0.000590087
ratio of tetroxalate to manganate(VII) is 2:2.5 or 1:1.25 (note equiv of 2 $C_2O_4^{2-}$ in salt),
so mol MnO_4^- in titration = 0.000590087 / 1.25
= 0.000472069 in 23.2 cm^3,
*scaling up to 1 dm^3 gives for **[MnO_4^-]***
= 0.000472069 x 1000 / 23.2
= 0.02034781

= ***0.02034 mol dm^{-3}*** *(5dp, 4sf) OR* ***0.0203 mol dm^{-3}*** *(4dp, 3sf)*

[NOTE: Quoting the concentration to 4dp, 3sf is more appropriate here because the mass is only quoted to 3sf and the titration is only likely to be accurate to the nearest 0.05 cm^3]

18. Given the half–cell equation $O_{2(g)} + 2H^+_{(aq)} + 2e^- ==> H_2O_{2(aq)}$

(a) construct the fully balanced redox ionic equation for the oxidation of hydrogen peroxide by potassium manganate(VII)) $2MnO_4^-{}_{(aq)} + 6H^+_{(aq)} + 5H_2O_{2(aq)} ==> 2Mn^{2+}_{(aq)} + 8H_2O_{(l)} + 5O_{2(g)}$

(b) ***50.0 cm^3 of solution of hydrogen peroxide were diluted to 1.00 dm^3 with water. 25.0 cm^3 of this solution, when acidified with dilute sulfuric acid, reacted with 20.25 cm^3 of 0.0200 mol dm^{-3} KMnO$_4$. What is the concentration of the original hydrogen peroxide solution in mol dm^{-3}?***

in titration mol MnO_4^- = 0.0200 x 20.25 / 1000 = 0.000405,

MnO_4^-:H_2O_2 ratio is 2:5 or 1:2.5, so mol H_2O_2 in titration = 0.000405 x 2.5 = 0.0010125,

scaling up for total mol H_2O_2 in diluted solution (of 1 dm^3 or 1000 cm^3) = 0.0010125 x 1000 / 25.0 = 0.0405 mol,

but in the original 50 cm^3 solution,

therefore scaling up to 1 dm^3, the ***original molarity of H_2O_2*** *is*

0.0405 x 1000 / 50 = ***0.810 mol dm^{-3}****.*

19. 13.2 g of iron(III) alum were dissolved in water and reduced to an iron(II) ion solution by zinc and dilute sulfuric acid. The mixture was filtered and the filtrate and washings made up to 500 cm^3 in a standard volumetric flask. If 20.0 cm^3 of this solution required 26.5 cm^3 of 0.0100 mol dm^{-3} KMnO$_4$ for oxidation.

(a) give the ionic equation for the reduction of iron(III) ions by zinc metal.

$Zn_{(s)} + 2Fe^{3+}_{(aq)} ==> Zn^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$

(b) Calculate the percentage by mass of iron in iron alum.

You need to know the redox equation to get the mole ratio involved in this titration

$MnO_4^-{}_{(aq)} + 8H^+_{(aq)} + 5Fe^{2+}_{(aq)} ==> Mn^{2+}_{(aq)} + 5Fe^{3+}_{(aq)} + 4H_2O_{(l)}$

Changes in oxidation state: Mn from +7 to +2 and Fe from +2 to +3

Therefore, on electron/oxidation state change, 1 mole of MnO_4^- can oxidise 5 moles of Fe^{2+}

Therefore:

mol MnO_4^- in titration = 0.0100 x 26.5 / 1000 = 0.000265, mol Fe (Fe^{2+}) = mol MnO_4^- x 5 = 0.001325 in 20.0 cm^3 of the alum solution, scaling up gives total mol Fe = 0.001325 x 500 / 20 = 0.033125, total mass Fe in the 13.2 g of alum = 0.033125 x 55.9 = 1.852, so **% Fe =** 1.852 x 100 / 13.2 = **14.0%**

20. **Calculate the concentration in mol dm^{-3} and g dm^{-3}, of a sodium ethanedioate ($Na_2C_2O_4$) solution, 5.00 cm^3 of which were oxidized in acid solution by 24.50 cm^3 of a potassium manganate(VII) solution containing 0.05 mol dm^{-3}**.

mol MnO_4^- in titration = 0.05 x 24.5 / 1000 = 0.001225,

ratio MnO_4^-:$Na_2C_2O_4$ is 2:5 or 1:2.5,

so mol $Na_2C_2O_4$ titrated

= 0.001225 x 2.5 = 0.003063 in 5 cm^3,

scaling up to 1 dm^3, **molarity $Na_2C_2O_4$** = 0.003063 x 1000 / 5 = **0.613 mol dm^{-3}**

$M_r(Na_2C_2O_4)$ = 134, so **concentration** = 0.613 x 134 = **82.1 g dm^{-3}**

21. Calculate x in the formula $FeSO_4.xH_2O$ from the following data: 12.18 g of iron(II) sulfate crystals were made up to 500 cm^3 acidified with sulfuric acid.

25.0 cm^3 of this solution required 43.85 cm^3 of 0.0100 mol dm^{-3} $KMnO_4$ for complete oxidation.

mol $KMnO_4$ = 0.0100 x 43.85 / 1000

= 0.0004385, mol Fe (Fe^{2+}) = mol $KMnO_4$ x 5,mol Fe = 0.0004385 x 5

= 0.0021925, so mol $FeSO_4.\mathbf{x}H_2O$ is also 0.0021925,

in the titration $^1/_{20}$th of the salt was used ($^{25}/_{500}$), so $^1/_{20}$th of 12.18 g = 0.0021925 mol of the salt = 0.609 g,

scaling up the mass of 1 mole of the salt is 0.609 x 1 / 0.0021925

= 277.8,

so formula mass of $FeSO_4.\mathbf{x}H_2O$ is 277.8, now the formula mass of $FeSO_4$ is 152.0,

so the formula mass of $\mathbf{x}H_2O$ = 277.8 – 152.0 = 125.8,

$M_r(H_2O)$ = 18, so x = 125.8 / 18 = 6.989,

so **x = 7** and the formula of the salt is **$FeSO_4.7H_2O$**, i.e. seven molecules of water of crystallisation.

22. Given the half–reaction

$NO_3^-{}_{(aq)} + 2H^+_{(aq)} + 2e^-$ ==> $NO_2^-{}_{(aq)} + H_2O_{(l)}$

(a) give the ionic equation for potassium manganate(VII) oxidising nitrate(III) to nitrate(V)

$2MnO_4^-{}_{(aq)} + 6H^+_{(aq)} + 5NO_2^-{}_{(aq)}$ ==> $Mn^{2+}_{(aq)} + 5NO_3^-{}_{(aq)} + 3H_2O_{(l)}$

(b) ***24.2*** *cm^3 of sodium nitrate(III) [sodium nitrite] solution, added from a burette, were needed to discharge the colour of* ***25.0*** *cm^3 of an acidified* ***0.0250*** *mol dm^{-3} $KMnO_4$ solution.*

What was the concentration of the nitrate(III) solution in grammes of anhydrous salt per dm^3?

mol $KMnO_4$ in titration = 0.0250 x 25 / 1000

= 0.000625,

mol ratio $MnO_4^-:NO_2^-$ is 2:5 or 1:2.5, so mol NO_2^- in titration

= 0.000625 x 2.5

= 0.0015625 in 24.2 cm^3,

scaling up to 1 dm^3 gives a ***molar concentration of $NaNO_2$*** *of 0.0015625 x 1000 / 24.2*

= 0.0646 mol dm^{-3}

$M_r(NaNO_2)$ = 69, so in terms of mass ***concentration***

= 0.0646 x 69

= 4.46 g dm^{-3}

23. 2.68 g of iron(II) ethanedioate, FeC_2O_4, were made up to 500 cm^3 of acidified aqueous solution. 25.0 cm^3 of this solution reacted completely with 28.0 cm^3 of 0.0200 mol dm^{-3} potassium manganate(VII) solution.

Calculate the mole ratio of $KMnO_4$ to FeC_2O_4 taking part in this reaction.

Give the full redox ionic equation for the reaction. *$M_r(FeC_2O_4)$ = 143.9,*

mol FeC_2O_4 in original solution

= 2.68 / 143.9 = 0.01862,

scaling down the mol FeC_2O_4 in the titration

= 0.01862 x 25 / 500 = 0.000931,

mol $KMnO_4$ in titration = 0.0200 x 28.0 / 1000

= 0.00056,

so ratio $KMnO_4:FeC_2O_4$ is 0.00056:0.000931 = giving the 'not so easy to spot' ***3:5 the reacting mole ratio****.*

FeC_2O_4 is made up of a Fe^{2+} ion and a $C_2O_4^{2-}$ ion, and the full redox equation is:

$3MnO_4^-{}_{(aq)} + 5FeC_2O_{4(aq)} + 24H^+{}_{(aq)} \Longrightarrow 3Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + 12H_2O_{(l)} + 10CO_{2(g)}$

or $3MnO_4^-{}_{(aq)} + 5Fe^{2+}{}_{(aq)} + 5C_2O_4^{2-}{}_{(aq)} + 24H^+{}_{(aq)} \Longrightarrow 3Mn^{2+}{}_{(aq)} + 5Fe^{3+}{}_{(aq)} + 12H_2O_{(l)} + 10CO_{2(g)}$

24. Given the half–cell reaction $IO_3^-{}_{(aq)} + 6H^+{}_{(aq)} + 5e^- \Longrightarrow {}^1/_2I_{2(aq)} + 3H_2O_{(l)}$ (see also Q2)

(a) Deduce the redox equation for iodate(V) ions oxidising iodide ions.

$IO_3^-{}_{(aq)} + 5I^-{}_{(aq)} + 6H^+{}_{(aq)} \Longrightarrow 3I_{2(aq)} + 3H_2O_{(l)}$

*(b) What volume of **0.0120** mol dm^{-3} iodate(V) solution reacts with **20.0** cm^3 of **0.100** mol dm^{-3} iodide solution?*

mol I^- titrated = 0.100 x 20.0 / 1000 = 0.002, mole ratio $IO_3^-:I^-$ is 1:5,

so mole IO_3^- reacted = 0.002 / 5 = 0.0004,

so 0.0004 = 0.012 x (volume IO_3^- required) / 1000,

volume IO_3^- required** = 0.0004 x 1000 / 0.012 = **33.3 cm^3

*(c) **25.0** cm^3 of the potassium iodate(V) solution were added to about 15 cm^3 of a 15% solution of potassium iodide (ensures excess iodide ion). On acidification, the liberated iodine needed **24.1** cm^3 of **0.0500** mol dm^{-3} sodium thiosulfate solution to titrate it.*

(i) Calculate the concentration of potassium iodate(V) in g dm^{-3}

mole $S_2O_3^{2-}$ ('thio') = 0.0500 x 24.1 / 1000
= 0.001205,

$I_2:S_2O_3^{2-}$ ratio is 1:2 in the titration reaction, so mol I_2
= mole $S_2O_3^{2-}$ / 2
= 0.001205 / 2
= 0.0006025,

now the $IO_3^-:I_2$ reaction ratio is 1:3,

so mol IO_3^- reacting to give iodine = mole I_2 formed / 3
= 0.0006025 / 3 = 0.000201 in 25 cm^3,

so scaling up to 1 dm^3 the molarity of the KIO_3 (IO_3^-)
= 0.000201 x 1000 / 25
= 0.00804 mol dm^{-3},

$M_r(KIO_3)$ = 214.0, so in terms of mass, concentration
= 0.00804 x 214
= 1.72 g dm^{-3}.

A quicker approach if confident! – ratios from all equations involved are: $2S_2O_3^{2-}$: I_2 : $^1/_3IO_3^-$, means that the overall mole iodate(V) = mole thiosulphate / 6, so you can 'jump' from line '1' to the last 'few' lines. However in exams these days all the stages (i.e. , to , !) are often 'broken down' for you and it might be best you work through the problem thoroughly and methodically.

***(iii)** What indicator is used for this titration and what is the colour change at the end–point?*

***Starch indicator** is used for the titration, when the last of the iodine reacts with the thiosulphate, the blue colour from the starch–iodine 'complex' is discharged and the solution becomes colourless.*

25. ***Calculate the molarities of iron(II) and iron(III) ions in a mixed solution from the following data.***

(i) ***25.0*** *cm^3 of the original mixture was acidified with dilute sulfuric acid and required* ***22.5 cm^3*** *of* ***0.0200*** *mol dm^{-3} $KMnO_4$ for complete oxidation.*

mol $KMnO_4$ = 0.0200 x 22.5 / 1000

= 0.00045,

mol Fe^{2+} = mol $KMnO_4$ x 5

= 0.00225 in 25 cm^3,

scaling up to 1 dm^3, ***molarity of the original Fe^{2+}***

= 0.00225 x 1000 / 25.0

= 0.090 mol dm^{-3}

(ii) a further ***25.0*** *cm^3 of the original iron(II)/iron(III) mixture was reduced with zinc and acid and it then required* ***37.6*** *cm^3 of the $KMnO_4$ for complete oxidation.*

The 2nd titration gives the total concentration of Fe^{2+} + Fe^{3+} because any Fe^{3+} has been reduced to Fe^{2+},

mol $KMnO_4$ = 0.0200 x 37.6 / 1000

= 0.000752,

total mol Fe^{2+} titrated = mol $KMnO_4$ x 5

= 0.00376 in 25 cm^3,

scaling up to 1 dm^3, total molarity of Fe^{2+} + Fe^{3+} in original solution = 0.00376 x 1000 / 25.0

= 0.150 mol dm^{-3},

so using the result from (a) the ***Fe^{3+} concentration***

= 'Fe' total – Fe^{2+}

= 0.150 – 0.090

= 0.060 mol dm^{-3}

26. A piece of rusted iron was analysed to find out how much of the iron had been oxidised to rust [hydrated iron(III) oxide]. A small sample of the iron was dissolved in excess dilute sulfuric acid to give 250 cm^3 of solution. The solution contains Fe^{2+} ions from the unrusted iron dissolving in the acid, and, Fe^{3+} ions from the rusted iron.

(a) ***25.0*** *cm^3 of this solution required* ***16.9*** *cm^3 of* ***0.0200*** *mol dm^{-3} $KMnO_4$ for complete oxidation of the Fe^{2+} ions.*

Calculate the moles of Fe^{2+} ions in the sample titrated.

mol Fe^{2+} *= 5 x MnO_4^-*

= 5 x 0.0200 x 16.9 / 1000

= 0.00169 mol

= unreacted iron (which dissolved in the acid to form Fe^{2+}).

(c) *To a second* ***25.00*** *cm^3 of the rusted iron solution an oxidising agent was added to convert all the Fe^{2+} ions present to Fe^{3+} ions. The Fe^{3+} ions were titrated with a solution of $EDTA^{4-}{}_{(aq)}$ ions and* ***17.6*** *cm^3 of* ***0.100*** *mol dm^{-3} EDTA were required.*

mol Fe^{3+} *= $EDTA^{4-}$ = 0.100 x 17.6 / 1000* ***= 0.00176 mol =*** *total mol iron in the sample titrated.*

Assuming 1 mole of EDTA reacts with 1 mole of Fe^{3+} ions, calculate the moles of Fe^{3+} ions in the sample.

(d) From your calculations in (a) and (b) calculate the ratio of rusted iron to unrusted iron and hence the percentage of iron that had rusted.

calculation (a) gives the relative moles of unreacted iron Fe, as it dissolved to form the titratable Fe^{2+}.

Calculation (b) gives the total of unreacted Fe + the rust i.e. Fe^{3+}, because any Fe^{2+} formed from Fe has been oxidised to Fe^{3+}.

So from the original mixture (in terms of the 25 cm^3 sample), mol unreacted Fe = 0.00169,

mol of reacted iron = 0.00176 – 0.00169 = 0.00007.

Therefore the % rusted iron = 0.00007 x 100 / 0.00176 = ***3.98 % rusted iron****.*

25. ***25.0 cm^3 of an iodine solution was titrated with 0.100 mol dm^{-3} sodium thiosulfate solution and the iodine reacted with 17.6 cm^3 of the thiosulfate solution.***

(a) give the reaction equation.

$I_{2(aq)} + 2S_2O_3^{2-}{}_{(aq)} \Longrightarrow S_4O_6^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$

or $I_{2(aq)} + 2Na_2S_2O_{3(aq)} \Longrightarrow Na_2S_4O_{6(aq)} + 2NaI_{(aq)}$

(b) *what indicator is used? and describe the end–point in the titration.*

Starch indicator *is used, starch gives a blue/black colour with iodine, this colour disappears when the last of the iodine is titrated, so a* ***blue to colourless*** *sharp end–point is observed.*

(c) calculate the concentration of the iodine solution in mol dm^{-3} and g dm^{-3}.

mole 'thio' = 0.100 x 17.6/1000

= 0.00176,

mol I_2 = 0.00176 ÷ 2

= 0.00088 in 25 cm^3,

scaling up gives 0.00088 x 1000 ÷ 25

= ***0.0352 mol dm^{-3}*** *for molarity of iodine,*

formula mass I_2 = 2 x 127

= 254,

so ***concentration***

= 0.0352 x 254 ***= 8.94 g dm^{-}***

41. 1.01g of an impure sample of potassium dichromate (VI), $K_2Cr_2O_7$, was dissolved in dil. sulfuric acid and made up to 250 cm^3 in a calibrated volumetric flask. A 25.0 cm^3 aliquot of this solution pipetted into a conical flask and excess potassium iodide solution and starch indicator were added. The liberated iodine was titrated with 0.100 mol dm^{-3} sodium thiosulfate and the starch turned colourless after 20.0 cm^3 was added.

(a) Using the half–equations from Q3(a)(ii) and Q2(a)(ii), construct the full balanced equation for the reaction between the dichromate(VI) ion and the iodide ion.

$Cr_2O_7^{2-}{}_{(aq)} + 14H^+{}_{(aq)} + 6I^-{}_{(aq)} ==> 2Cr^{3+}{}_{(aq)} + 3I_{2(aq)} + 7H_2O_{(l)}$

(b) Using the half–equations from Q2(a) construct the balanced redox equation for the reaction between the thiosulfate ion and iodine.

$2S_2O_3^{2-}{}_{(aq)} + I_{2(aq)} ==> S_4O_6^{2-}{}_{(aq)} + 2I^-{}_{(aq)}$

(c) Calculate the moles of sodium thiosulfate used in the titration and hence the number of moles of iodine titrated.

mol 'thio' *= 20.0 x 0.100/1000*
= ***0.002****,*

therefore from equation

mol iodine *= mol 'thio'/2*
= ***0.001***

(d) Calculate the moles of dichromate(VI) ion that reacted to give the iodine titrated in the titration.

From equation (a) ***<u>mol dichromate(VI)</u>*** *reacting*
= mol iodine liberated/3
= ***0.000333*** *(3sf)*

(e) Calculate the formula mass of potassium dichromate(VI) and the mass of it in the 25.0 cm^3 aliquot titrated.

$M_r(K_2Cr_2O_7)$ = 294.2

mass $K_2Cr_2O_7$ titrated *= 0.000333 x 294.2*
= ***<u>0.0980 g</u>*** *(3 sf)*

(f) Calculate the total mass of potassium dichromate(VI) in the original sample and hence its % purity.

Since the aliquot of 25.0 cm^3 is 1/10th of the total solution in the flask, the ***total mass*** *of the* ***$K_2Cr_2O_7$ in original sample*** *dissolved in the flask solution = 10 x 0.0980g*
= ***0.98g***

and the ***% purity*** *of the* ***$K_2Cr_2O_7$*** *= 0.98 x 100/1.01*
= 97.0 % *(3 sf)*

42. This question involves titrating ethanedioic acid (oxalic acid), $H_2C_2O_4$ or $(COOH)_2$ (i) with standard sodium hydroxide solution and then with potassium manganate(VII) solution (potassium permanganate, $KMnO_4$).

The titration data is as follows:

10 cm^3 of a $H_2C_2O_4$ solution required 8.50 cm^3 of a 0.20 mol dm^{-3} (0.20M) solution of sodium hydroxide for complete neutralisation using phenolphthalein indicator (first permanent pink end-point).

10 cm^3 of the same $H_2C_2O_4$ solution required 8.20 cm^3 of a $KMnO_4$ solution for complete oxidation to carbon dioxide and water in the presence of dilute sulfuric acid to further acidify the ethanedioic acid solution (first permanent pink end-point).

(a) Write an equation for the neutralisation reaction of ethanedioic acid with sodium hydroxide.

$H_2C_2O_4 + 2NaOH \text{ ===> } Na_2C_2O_4 + 2H_2O$

or: $(COOH)_2 + 2NaOH \text{ ===> } (COONa)_2 + 2H_2O$

(b) Calculate the moles of $H_2C_2O_4$ in the solution and the molarity of the ethanedioic acid solution.

moles used in the NaOH in titration = 0.20 x 8.5/1000

= 0.0017 mol NaOH

from the equation mol $H_2C_2O_4$ = mol NaOH/2

therefore mol $H_2C_2O_4$ = 0.0017/2

*= **0.00085** in 10 cm^3 of the acid solution.*

volume of $H_2C_2O_4$ solution = 10/1000

g= 0.01 dm^3

therefore molarity of $H_2C_2O_4$ = 0.00085/0.01

*= **0.085 mol dm^{-3}** (0.085M)*

(c) Given the following half-reactions:

(i) $MnO_4^-{}_{(aq)} + 8H^+{}_{(aq)} + 5e^- \text{ ===> } Mn^{2+}{}_{(aq)} + 4H_2O_{(l)}$ involves the gain of 5 electrons,

(ii) $H_2C_2O_{4(aq)} - 2e^- \text{ ===> } 2CO_{2(g)} + 2H^+{}_{(aq)}$

involves the loss of 2 electrons, so to balance the electron gain and loss you need to add together 2 x (i) plus 5 x

CHAPTER TWELVE

ELECTROLYSIS

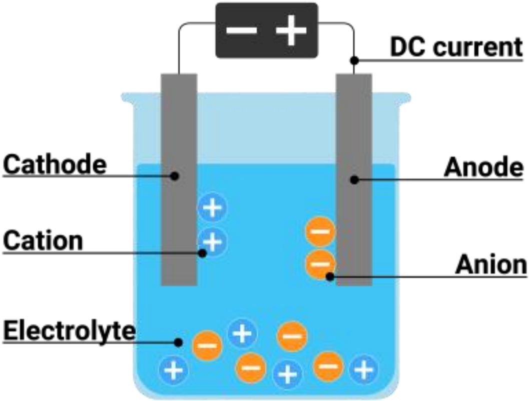
Define electrolysis

Electrolysis is defined as a process of decomposing ionic compounds into their elements by passing a direct electric current through the compound in a fluid form. The cations are reduced at cathode and anions are oxidized at the anode.

Describe the components of electrolysis

The main components that are required for conducting electrolysis are an electrolyte, electrodes, and some form of external power source is also needed. Additionally, a partition such as an ion-exchange membrane or a salt bridge is also used but this is optional. These are used mainly to keep the products from diffusing near the opposite electrode.

An acidified or salt-containing water can be decomposed by passing electric current to their original elements hydrogen and oxygen. Molten sodium chloride can be decomposed to sodium and chlorine atoms.



Electrolysis is usually done in a vessel named 'electrolytic cell' containing two electrodes (cathode and anode) connected to a direct current source and an electrolyte which is an ionic compound undergoing decomposition, in either molten form or in a dissolves state in a suitable solvent. Generally, electrodes that are made from metal, graphite and semiconductor materials *are used. However, the choice of a suitable electrode is done based on chemical reactivity between the electrode and electrolyte as well as the manufacturing cost.*

Describe the Electrolytic Process

In the process of electrolysis, there is an interchange of ions and atoms due to the addition or removal of electrons from the external circuit. Basically, on passing current, cations move to the cathode, take electrons from the cathode (given by the supply source-battery), and is discharged into the neutral atom. The neutral atom, if solid, is deposited on the cathode and if gas, move upwards. This is a reduction process and the cation is, reduced at the cathode.

At the same time anions, give up their extra electrons to the anode and is oxidized to neutral atoms at the anode. Electrons released by the anions travel across the electrical circuit and reach the cathode completing the circuit. Electrolysis involves a simultaneous oxidation reaction at anode and a reduction reaction at the cathode.

For example, when electric current, is, passed through molten sodium chloride, the sodium ion is attracted by the cathode, from which, it takes an electrode and becomes a sodium atom.

Chloride ion reaches the anode, gives its electron, and become chlorine atom to form chlorine molecule.

Na^+*(in electrolyte) +* e^-*(from cathode)* $\rightarrow$ *Na …. At Cathode*

Cl^-*(from electrolyte)* $\rightarrow e^- + Cl \rightarrow Cl_2$ *…. At Anode*

Electrolysis process, while useful to get elemental forms from compounds directly, it can also be used indirectly in the metallurgy of alkali and alkaline earth metals, purification of metals, deposition of metals, preparation of compounds etc.

Explain Cell Potential or Voltage

The minimum potential needed for the electrolysis process depends on their ability of the individual ions to absorb or release electrons. It is also sometimes described as decomposition potential or decomposition voltage which is the minimum voltage (difference in electrode potential) between anode and cathode of an electrolytic cell that enables electrolysis to occur.

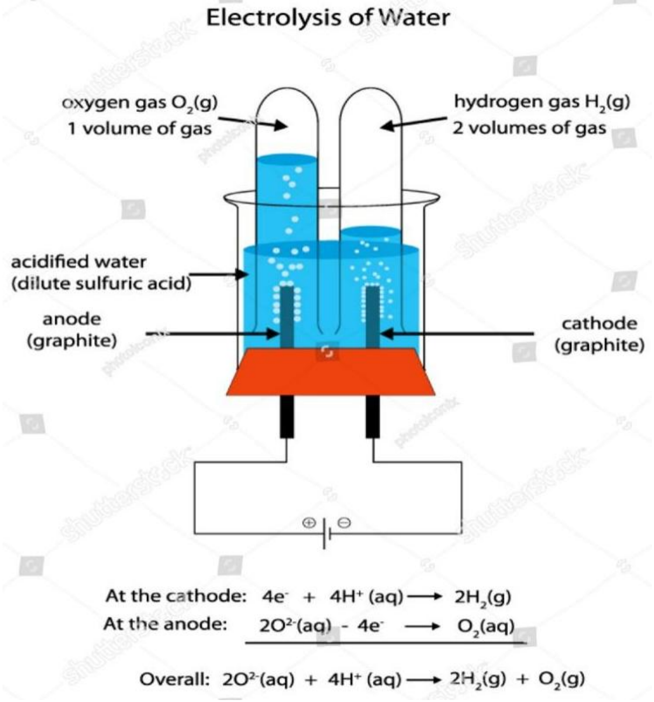
The voltage at which electrolysis is thermodynamically preferred is the difference of the electrode potentials as calculated using the Nernst equation. Applying additional voltage, referred to as overpotential, can increase the rate of reaction and is often needed above the thermodynamic value. It is especially necessary for electrolysis reactions involving gases, such as oxygen, hydrogen or chlorine.

This ability is, measured as an electrode potential of the ions present in the electrolytic cell. The cell potential is the sum of the potential required for the reduction and oxidation reaction. The potential involved in various redox reactions is available in literature as standard reduction potential.

Reaction with positive redox cell potentials only will be feasible as per thermodynamic Gibbs free energy (or standard potential). Generally, the electrolysis is thermodynamically controlled.

In electrolysis, a potential equal to or slightly more than that, is, applied externally. The ions, which are stable and not reacting, are made to undergo reaction in the presence of externally applied potential. External potential hence makes an unfavourable reaction to take place. In electrolysis, chemical bonds connecting atoms are either made or broken and so, electrolysis involves the conversion of electrical energy into chemical energy.

Draw a labeled diagram of apparatus used for the electrolysis of dilute sulphuric acid



b. ***Explain the Product of Electrolysis***

Electrolysis of only two ions (cation and anion) present in a single electrolyte is direct. Electrolysis will produce products present in the compound. When more than one cation and anions are present, each ion will compete for reduction and oxidations. Reactions with more positive redox potentials will be, reduced or oxidized, in preference, to others.

So, in spite of multiple redox couples present, only one can be reduced or oxidized. Sometimes the ions that are reduced or oxidized may depend on their relative amount. In other words, the redox reaction and electrolysis may become kinetically controlled. In such cases, the product of analysis may differ on the relative concentration of the various ions present in the electrolyte.

For example, electrolysis of aqueous sodium chloride may give different products-

1. *Hydrogen and chlorine,*
2. *Hydrogen and oxygen and*
3. *Hydrogen, oxygen and chlorine.*

State factors affecting Electrolysis

The factors that may affect the electrolysis are;

i) The nature of the electrode
ii) Nature and state of the electrolyte
iii) Nature and electrode potential of ions present in the electrolyte and
iv) Overvoltage at the electrodes.

List any two industrial application of electrolysis

There are many industrial applications of electrolysis. The most common applications are as follows:

✓ *Extraction of metals*
✓ *Purification of metals*
✓ *Electroplating of metals*

Explain faraday's first law of electrolysis

Faradays first electrolysis Law states that the quantity of reaction taking place in terms of mass of ions formed or discharged from an electrolyte is proportional to the amount of electric current passed. Since electric current (ampere) is the number of coulombs (Q) flowing in one second,

Mass of the ions formed or reacted (m) $\propto$ *electric current* α *Q, or*

$$m \propto Q$$

or

$$\boldsymbol{m = CQ}$$

Where, C is a proportionality constant, called the chemical equivalent of the element.

For a flow of, 1 Coulomb of charges for one second, m = C
The proportionality constant is equal to the mass of the substance involved in the reaction. Z is the electrochemical equivalent mass of one coulomb charge.
One coulomb of charge corresponds to a mass of one equivalent.

i) Electric current and Charge (Q)

Electric current is measured in ampere and it is the charges flowing per unit time (seconds).

$$I = \frac{Q}{t}$$

Quantity of Charges flowing (Q) = It = ampere × seconds

$$m = CIt$$

ii) Number of electrons–Charge Q of electrons – Faraday - Equivalent mass of substances

But the charges are associated with electrons. Every electron carries a charge of 1.6×10^{-19} coulombs.
Charges carried by one equivalent/ mole number of electrons (Q)

$= 6.02 \times 10^{23} \times (1.6 \times 10^{-19})$ *coulombs*
= 96485 coulombs

$\approx 96500C = 1$ *Faraday* $= 1F$

One equivalent (or mole or Avogadro's) of electrons $\propto$ 96485 coulombs ≈ 96500C = 1 Faraday = 1F

iii) Mass of substance undergoing electrolysis

Faraday Law says, $\boldsymbol{m = C \times Q}$ ***or*** $\boldsymbol{m = C\,I\,t}$.

When one coulomb corresponds to one electrochemical equivalent mass (C) of the substance, one equivalent (or mole) of electrons flowing per second, will correspond to 96485 Equivalents mass.
This, ***96485 electrochemical equivalents***

$= C \times 96485$

=Equivalent weight of substance in gram*.*

So,
Electrochemical equivalent of a substance = C

$$= \frac{\text{Equivalent weight of substance in gram}}{96485} = \frac{E}{96485}$$

Equivalent weight of a substance is, related to its molecular weight.

$$\text{Equivalent mass of a substance} = \frac{\text{Molecular weight of the substance}}{\text{Valency or charge}}$$

For every, one mole of electrons or charges (1Faraday) or 96485 ampere sec, passing through an electrolyte, one equivalent mass of the electrolyte is reacted, discharged/deposited etc.

One Avogadro's number of electrons = Charge of 1 Faraday
= 96485 coulombs = 96485 ampere sec
= 1equivalent mass (reacted / deposited / neutralized)

Mass of the substance (gm) = Equivalent weight (gm) × $\dfrac{\text{Coulombs}}{96485}$

Equivalent weight (gm) × $\dfrac{\text{ampere, sec}}{96485\ \text{ampere,sec}}$

$$\text{Or, } \mathbf{m} = \frac{EQ}{96485} = \frac{EIt}{96485}$$

For example, on passing electric current through a copper sulphate electrolyte solution, copper ions gets discharged and deposit on the anode.

$Cu^{2+} + 2e^{-} \rightarrow Cu$

Each copper ion needs two electrons for its reduction reaction to copper atom. More the electrons passing through the copper sulphate, solution more will be the copper ions being, deposited on the anode. Hence there is a direct relationship between the mass of material being, reduced and the numbers of electrons flowing into the electrolyte.

Here, one copper ion needs 2 electrons; so, One mole of copper ions needs 2 moles of electrons.

m = 2 × equivalent weight of copper

When 0.1M MnO_4^{2-} ***is oxidized to*** MnO_4^{-}***, the quantity of electricity required is***

a) 96500C
b) 2 × 96500C
c) 9650C
d) 96.50C

$MnO_4^{2-} \rightarrow MnO_4^{-} + e^{-}$

1mole of MnO_4^{2-} *lose 1 mole of electrons or 96500C*

$\because$ *0.1 mole of* MnO_4^{2-} *lose 0.1mole of electrons or 9650C*

Answer is (c)

How much electricity in terms of Faraday is required to produce

(i) 20.0 g of Ca from molten $CaCl_2$*?*

(ii) 40.0 g of Al from molten Al_2O_3*?*

i) $Ca^{2+} + 2\,e^{-} \rightarrow Ca$

One mole of Calcium ions gains two moles of electrons or 2 Faraday charge to produce one mole of calcium.

Molecular weight of Calcium is 40.

So, 20 gm of calcium shall need one Faraday of electricity.

ii) $Al^{3++} + 3\,e^{-} \rightarrow Al$

One mole of Aluminum ions gains two moles of electrons or 3 Faraday charge to produce one mole of aluminim.

Molecular weight of Aluminum is 27.

So, 40 gm of Aluminum ion shall need $\frac{40\times3}{27}$ *Faraday of electricity*

$= 4.44F$

A solution of Ni(NO3)2 is electrolyzed between platinum electrodes using a current of 5 amperes for 20 minutes. Calculate the weight of nickel reduced on the cathode.

Mass of nickel deposited = $\frac{E\,I\,t}{96500}$

Equivalent eight of nickel = Atomic weight/2 =58.7/2

Mass = $\frac{58.7\times5\times20\times60}{2\times96500} = 1.83gm$

The anodic half- cell of lead-acid battery is recharged using electricity of 0.05 Faraday. The amount of

PbSO4 electrolyzed in g during the process is ; (molar mass of PbSO4 = 303g/mole)

a) 22.8
b) 15.2
c) 7.6
d) 11.4

In lead sulphate, lead is in 2^{+} *state.*

One mole (303) of lead sulphate, shall need 2 Faraday electricity.

So, 0.05 Faraday will electrolyze $\frac{303\times0.05}{2}$ *g of lead sulphate*

= 7.6g So the answer is (c)

A cell, Ag | Ag+ || Cu2+ | Cu, initially contains 1 M Ag+ and 1 M Cu2+ ions. What will be the increase in potential of the cell after passing an electric current of 9.65amperes for one hour?

On passing electric current into the cell, the following reaction takes place.

$– Cu \rightarrow Cu^{2+} + 2^{e–}$; $Ag^{+} + e^{-} \rightarrow Ag$

i) Change in the concentration of copper and silver ions

Mass deposited= $\frac{EIt}{96500}$

Mass of copper ions additionally formed

$= \frac{63.54\times9.65\times60\times60}{2\times96500}$

= 11.43g

= 0.18M

Concentration of copper half-cell = 1-0.18 = 0.82M

Mass of silver ions lost $= \frac{108\times9.65\times60\times60}{96500}$

= 38.9g

= 0.36M

Concentration of silver half-cell = 1-0.36 = 0.64M

1. ***Calculate the amount of charge transferred when a 5 A current is used for 2 minutes during electrolysis.***

2 minutes = 2 × 60 = 120 s

Charge = current × time

Charge = 5 × 120 = 600 C

Sodium and chlorine are produced during the electrolysis of molten sodium chloride:

$$Na^+ + e^- \rightarrow Na$$

$$2Cl^- \rightarrow Cl_2 + 2e^-$$

9,650 coulombs of charge pass. Calculate the amount of sodium and chlorine produced. Remember that 1 F (faraday) = 96,500 C.

Number of moles of electrons = 9,650 ÷ 96,500

= 0.1 mol

1 mol of electrons are needed to produce 1 mol of sodium - so 0.1 mol of sodium is produced.

2 mol of electrons are needed to produce 1 mol of chlorine - so 0.05 mol (0.1 ÷ 2) of chlorine is produced.

2. ***Bromine is produced during the electrolysis of molten lead(II) bromide:***

$$2Br^- \rightarrow Br_2 + 2e^-$$

A +current of 13.4 A was used for 0.5 hours. Calculate the mass of bromine produced.

1 F = 96,500 C. Ar of Br_2 *= 160.*

Remember: charge = current × time

Charge = 13.4 × 1,800

= 24,120 C

Remember: One faraday represents one mole of electrons. It is equal to 96,500 coulombs.

Number of moles of electrons = 24,120 ÷ 96,500

= 0.25 mol

Amount of bromine produced = 0.25 ÷ 2
= 0.125 mol
Mass of bromine produced = Ar × mol = 0.125 × 160
= 20 g

3. ***During electrolysis of molten sodium chloride, 0.125 mol of chlorine gas was produced. Calculate the volume of chlorine at RTP.***
   Volume = amount of gas × molar volume

Volume of chlorine = 0.125 × 24

= 3 dm3 (or 3,000 cm3)

CHAPTER THIRTEEN

GRAVIMETRIC ANALYSIS

a. Define the term gravimetric analysis

Gravimetric methods are quantitative methods through which the amount of an analyte (the ion being analyzed) can be determined through the measurement of mass.

Gravimetric analyses depend on comparing the masses of two compounds containing the analyte.

The principle behind gravimetric analysis is that the mass of an ion in a pure compound can be determined and then used to find the mass percent of the same ion in a known quantity of an impure compound.

Since weight can be measured with greater accuracy than almost any other fundamental property, gravimetric analysis is potentially one of the most accurate classes of analytical methods .

b. State any two ideal conditions for gravimetric analysis

In order for the analysis to be accurate, certain conditions must be met:

1. *The ion being analyzed must be completely precipitated.*
2. *The precipitate must be a pure compound.*
3. *The precipitate must be easily filtered.*

3. Describe the significance of washing the precipitate in a gravimetric analysis

washing of the precipitate is aimed at removing impurities and other soluble salts adsorped on the surface of the already formed precipitates. Such impuritities would result into contamination due to post precipitation.

4. ***Define and explain causes for peptization***

peptization *is a process that may occurs during washing impurities. Each particle of the precipitate has two layer, the outer layer and inner layer. In primary layer certain ions are adsorbed and in the inner layer other ions of opposite charge are adsorbed . This situation makes the precipitate settle down . If the outer layer ions are removed then all the particles will have the same charge so the particles will be dissonant . This is called peptization .*

Peptization results in the loss of part of the precipitate because the colloidal form may pass through on filtration.

5. ***Describe the methods used to minimize peptization of precipitates in gravimetry***

In case of colloidal precipitates we should not use water as a washing solution since peptization would occur. In such situations dilute volatile electrolyte such as nitric acid, ammonium nitrate, or dilute acetic acid may be used.

Usually, it is a good practice to check for the presence of precipitating agent in the filtrate of the final washing solution. The presence of precipitating agent means that extra washing is required. Filtration should be done in appropriate sized Gooch or ignition ashless filter paper.

After the solution has been filtered, it should be tested to make sure that the analyte has been completely precipitated. This is easily done by adding a few drops of the precipitating reagent to the filtrate ; if a precipitate is observed, the precipitation is incomplete.

6. ***Explain the importance of drying and igniting the precipitate***

The purpose of drying (heating at about 120-150 oC in an oven) is to remove the remaining moisture while the purpose of ignition in a muffle furnace at temperatures ranging from 600-1200°C is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined . The precipitate is converted to a more chemically stable form. For instance, calcium ion might be precipitated using oxalate ion, to produce calcium oxalate (CaC_2O_4) which is hydrophil , therefore it is better to be heated to convert it into $CaCO_3$ or CaO . The $CaCO_3$ formula is preferred to reduce weighing errors.

7. ***Distinguish between co-precipitated and post precipited impurities***

Co precipitates and post precipites are terms used to reffer impurities that form on the forming precipitatesas a result of salts and ions that are otherwise soluble in water remain attach or get occluded withiin or on the surface the already forming crystal.

Occlusions form when interfering ions become trapped within the growing precipitate. An occlusion usually increases a precipitate's mass. Surface adsorbates occurs after a completely formed precipitate continue to attract contaminating ions from the solutions on to its external surface.

Inclusions, occlusions, and surface adsorbates are examples of Co-precipitates and post-precipitates.

Occlusions can be minimized by maintaining the precipitate in equilibrium with its supernatant solution (mother liquor) for an extended time. This process is called a digestion. During digestion ensures that the occlusion is reexposed to the supernatant solution.

We can minimize surface adsorption by decreasing the precipitate's available surface area and can be removed by washing the precipitate.
Co-precipitation relates to the inclusion and occlusion of foreign substances that occur during the process of crystal growth from the primary particles whereas Post precipitation is concerned with adsorption that form on the surface of the particles exposed to the solution. Appreciable errors may also be introduced by precipitations and post-precipitation.

. Post-precipitation differs from Co-precipitation in several respects:

(a) The contamination increases with the time that the precipitate is left in contact with the mother liquor in post-precipitation, but usually decreases in Co-precipitation.

(b) With post-precipitation, contamination increases the faster the solution is agitated by either mechanical or thermal means. The reverse is usually true with Co-precipitation.

(c) The magnitude of contamination by post-precipitation may be much greater than in Co-precipitation.

8. State two types of precipitating agents

Some of the most common substances used as the precipitating agents are hydroxide, sulfate, oxalate and carbonate

9. Explain properties of precipitating agents

Ideally, a gravimetric precipitating agent should react specifically or at least selectively with the analyte. Specific reagents, which are rare, react only with a single chemical species.

Ideal precipitating agents should be free of contaminants and easily filterable; produce a precipitate that is sufficiently insoluble that it will not dissolve during washing; the precipitate needs to be chemically stable; the precipitate needs to be of known composition after drying or even calcination

In addition to specificity and selectivity, the ideal precipitating reagent would react with the analyte to give a product that is

1. *easily filtered and washed free of contaminants*
2. *of sufficiently low solubility that no significant loss of the analyte occurs during filtration and washing*
3. *unreactive with constituents of the atmosphere*
4. *of known chemical composition after it is dried or, if necessary, ignited*

10. Explain how particles sizes influences filtrability of precipitate

Precipitates consisting of large particles are generally desirable for gravimetric work because these particles are easy to filter and wash free of impurities. In addition, precipitates of this type are usually purer than are precipitates made up of fine particles.

11. State four factors that affect size of precipitates

a) Precipitation should be carried out in dilute solution, due regard being paid to the solubility of the precipitate,

b) the time required for filtration, and the subsequent operations to be carried out with the filtrate. This will minimise the errors due to CO-precipitation.

c) The reagents should be mixed slowly and with constant stirring. This will keep the degree of supersaturation small and will assist the growth of large crystals.

d) A slight excess of the reagent is al1 that is generally required; in exceptional cases a large excess rnay be necessary. In some instances the order of mixing the reagents rnay be important.

e) Precipitation rnay be effected under conditions which increase the solubility of the precipitate, thus further reducing the degree of supersaturation .

f) Precipitation is effected in hot solutions, provided the solubility and the stability of the precipitate permit. Either one or both of the solutions should be heated to just below the boiling point or other more favourable temperature.

At the higher temperature:

a) The solubility is increased with a consequent reduction in the degree of supersaturation,

b) Coagulation is assisted and sol formation decreased,

c) The velocity of crystallisation is increased, thus leading to better-formed crystals.

12. Explain how precipitates can be recovered *There are several methods used to recover a precipitate:*

- ✓ ***Filtration**: In filtration, the solution containing the precipitate is poured over a filter. Ideally, the precipitate remains on the filter, while the liquid passes through it. The container may be rinsed and poured onto the filter to aid recovery. There is always some loss of the precipitate which may be caused by dissolution into the liquid, passing through the filter, or adhesion to the filter medium.*

- ✓ ***Centrifugation**: In centrifugation, the solution is rapidly rotated. For the technique to work, the solid precipitate must be denser than the liquid. The compacted precipitate, called the pellet, may be obtained by pouring off the liquid. There is typically less loss with centriguation than with filtration. Centrifugation works well with small sample sizes.*
- ✓ ***Decantation**: In decantation, the liquid layer is poured or suctioned away from the precipitate. In some cases, an additional solvent is added to separate the solution from the precipitate. Decantation may be used with the entire solution or following centrifugation*

*16. **Explain the influence of relative supersaturation (RSS)on the crystal size in a precipitation reaction** Experimental evidence indicates that the particle size of a precipitate varies inversely with the average relative supersaturation during the time when the reagent is being introduced. Thus, when (Q-S)/S is large, the precipitate tends to be colloidal, and when (Q-S)/S is small, a crystalline solid is more likely.*

10. Give the properties of an ideal gravimetric precipitating agent

- ✓ *the precipitate must be of low solubility,*
- ✓ *of high purity, the precipitate must be free from impurities.*
- ✓ *of known composition if its mass is to accurately reflect the analyte's mass.*
- ✓ *the precipitate must be easy to separate from the reaction mixture.*
- ✓ *The precipitate must be convertible into a pure substance of definite chemical composition; this may be effected either by ignition or by a simple chemical operation, such as evaporation, with a suitable liquid.*

11. State four advantages of colorimetry over other classical methods of analysis such as titrimetric and gravimetry

- ✓ *It is fast, economical, and has a simple operation of a spectrometer.*
- ✓ *It is a quite fast and convenient method to that of the gravimetric or volumetric processes,*
- ✓ *they are easily optimized for automation.*
- ✓ *To handle the Colorimeter, it does not require an experienced person.*

12. Give four conditions required for production of pure filterable precipitate

- ✓ *The precipitate must be so insoluble that no appreciable loss occurs when it is collected by filtration. In practice this usually means that the quantity remaining in solution does not exceed the minimum detectable by the ordinary analytical balance, viz. 0.1 mg.*
- ✓ *The physical nature of the precipitate must be such that it can be readily separated from the solution by filtration, and can be washed free of soluble*

impurities. These conditions require that the particles are of such size that they do not pass through the filtering medium, and that the particle size is unaffected (or, at least, not diminished) by the washing process.

- ✓ *Crystalline precipitates should be digested for as long as practical, preferably overnight, except in those cases where post-precipitation rnay occur. As a rule, digestion on the steam bath is desirable. This process decreases the effect of CO-precipitation and gives more readily filterable precipitates. Digestion has little effect upon amorphous or gelatinous precipitates.*
- ✓ *The precipitate should be washed with the appropriate dilute solution of an electrolyte. Pure water rnay tend to cause peptisation.*
- ✓ *If the precipitate is still appreciably contaminated as a result of co-precipitation or other causes, the error rnay often be reduced by dissolving it in a suitable solvent and then re-precipitating it. The amount of foreign substance present in the second precipitation will be mall, and consequently the amount of the entrainment by the precipitate will also be small.*

13. Why is it essential to wash the precipitate with water before estimating it quantitatively?

Most of the impurities are water soluble and make hydrogen bonds with most of the elements present in the precipitate. They can be easily removed by washing the precipitate with water before estimating it quantitatively.

14. State Qualities of a good precipitate

- ✓ *Precipitates ought to be easy to wash free of contaminants without loss of the precipitate either in solution or through the filter.*
- ✓ *The particle size of the precipitate ought to be large enough not to escape through the filter pores.*
- ✓ *That the precipitate has a low solubility is paramount.*
- ✓ *The precipitate ought not to react with the atmosphere*
- ✓ *it must have a known composition which remains stable after ignition.*

15. List any four desirable properties of a drying agent

- ✓ *Should be be free of contaminants and easily filterable*
- ✓ *Should produce a precipitate that is sufficiently insoluble that It will not dissolve during washing;*
- ✓ *The precipitate needs to be chemically stable;*
- ✓ *The precipitate needs to be of known composition after drying or even calcination.*

16. State four qualities of filter papers that determine their choice in gravimetric analysis

Filtration should be done in appropriate sized Gooch or ignition ashless filter paper.

17. Describe the steps involved in gravimetric analysis

a. Preparation of the Solution:

This may involve several steps including adjustment of the pH of the solution in order for the precipitate to occur quantitatively and get a precipitate of desired properties, removing interferences etc.

b. Precipitation:

This involves the addition of a precipitating agent solution to the sample solution. Upon addition of the first drops of the precipitating agent, supersaturation occurs, then nucleation starts to occur where every few molecules of precipitate aggregate together forming a nucleus which will eventually grow to give a precipitate with large particles .

c. . Digestion of the Precipitate:

In this step, the precipitate is left hot (below boiling) for 30 min to 1 hour in order for the particles to be digested. Digestion involves dissolution of small particles and reprecipitation on larger ones resulting in particle growth and better precipitate characteristics.

This process is called Ostwald ripening. An important advantage of digestion is observed for colloidal precipitates where large amounts of adsorbed ions cover the huge area of the precipitate. Digestion forces the small colloidal particles to agglomerate which decreases their surface area and thus adsorption. . Concentration of interfering species may be reduced by digestion.

d. Washing and Filtering

Immidiately after precipitates form, they require to be washed in order to remove any adsorbed impurities and and water soluble salts that may still be attachning on the surfaces of the crystles formed . it also help to reduce chaances of post precipitation

b) 5- Drying and Ignition:

The purpose of drying (heating at about 120-150 oC in an oven) is to remove the remaining moisture while the purpose of ignition in a muffle furnace at temperatures ranging from 600-1200 oC is to get a material with exactly known chemical structure so that the amount of analyte can be accurately determined . The precipitate is converted to a more chemically stable form.

c) Weighing the precipitate :

The precipitate cannot be weighed with the necessary accuracy in place on the filter paper; nor can the precipitate be completely removed from the filter paper in order to weigh it. The precipitate can be carefully heated in a crucible until the filter paper has burned away; this leaves only the precipitate. (As the name suggests, "ashless" paper is used so that the precipitate is not contaminated with ash.) . If you use Gooch crucible then after the precipitate is allowed to cool (preferably in a desicator to keep it from absorbing moisture), it is weighed (in the crucible). The mass of the crucible is subtracted from the combined mass, giving the mass of the precipitated analyte. Since the composition of the precipitate is known, it is simple to calculate the mass of analyte in the original sample

18. Distinguish between colloidal and crystaline precipitate

Colloidal precipitates	***Crystalline precipitates***
Are solid masses formed in colloidal suspension	*Are solid masses formed in crystalline suspension*
Not formed easily	*Formed easily*
The effect of gravity is less. These particles do not easily settle down	*The effect of gravity is considerably higher. These particles settle down spontaneously*
Cannot be filtered easily	*Can be easily filtered*

19. What is precipitation gravimetry?

Precipitation gravimetry is an analytical technique that uses a precipitation reaction to separate ions from a solution. The chemical that is added to cause the precipitation is called the precipitant or precipitating agent.

20. What is the importance of ignition process in gravimetric analysis ?

Ignition is the process of burning or incineration of substances so as to convert them into another oxidized form of known purity or to a desired compound or to completely remove the water

21. Which are the two major sources of errors in gravimetric analysis?

This are errors due to

(i) Co-precipitation- the carrying down by a precipitate of substances normally soluble under the conditions employed. This impurity occurs either by adsorption, occlusion or entrapment.

(ii) Post precipitation - It is the precipitation that occurs as a layer upon the already formed precipitate. It is a surface based contamination/impurity that occurs due to high primary adsorption and supersaturated solution

22. Describe four types of gravimetric analysis

There are four fundamental types of gravimetric analysis: physical gravimetry, thermogravimetry, precipitative gravimetric analysis, and electrodeposition. These differ in the preparation of the sample before weighing of the analyte.

Physical gravimetry is the most common type used in environmental engineering. It involves the physical separation and classification of matter in environmental samples based on volatility and particle size (e.g., total suspended solids).

With thermogravimetry, samples are heated and changes in sample mass are recorded. Volatile solids analysis is an important example of this type of gravimetric analysis.

precipitative gravimetry relies on the chemical precipitation of an analyte. Its most important application in the environmental field is with the analysis of sulfite.

Electrogravimetry involves the electrochemical reduction of metal ions at a cathode, and simultaneous deposition of the ions on the cathode.

23. The aluminum (FW 26.98 g/mole) in a 1.200g sample of impure ammonium aluminum sulfate was precipitated with aqueous ammonia as the hydrous $Al_2O_3 \cdot xH_2O$. The precipitate was filtered and ignited at 1000°C to give anhydrous Al_2O_3 (FW 101.96 g/mole) which weighed 0.1798g. Calculate the percentage of aluminum in the sample.

Al → Al_2O_3 One mole of Al_2O_3 yields two moles of Al
Moles of Al_2O_3 = (0.1798 g) (1 mole/ 101.96 g)
= $1.763x10^{-3}$ moles
Moles of Al = ($1.763x10^{-3}$ moles Al_2O_3)(2 moles Al/1 mole Al_2O_3)
= $3.526x10^{-3}$
Weight of Al = ($3.526x10^{-3}$ moles Al)(26.98 g/mole)
= $9.513x10^{-2}$ g
Percentage of Al in sample = ($9.513x10^{-2}$ g/1.200 g)x100
= 7.928%

24. A heterogeneous mixture of the 20 common amino acids was analyzed by gravimetric analysis. Adding 15% v/v of ethanol to the solution followed by slow titration of the samples pH down to 5.5 results in the selective precipitation of L-alanine (FW 89.09 g/mole) and L-glycine (FW 75.07 g/mole). The properly filtered and dried precipitate weighed 1.6259 g. Chromatographic analysis of standard 0.1000 g samples of

L-alanine and L-glycine gave peak areas of 126.8 and 373.1, respectively. A similar chromatographic analysis using 0.5884 g of the 1.6259 g precipitate gave peak areas of 499.9 for L-alanine and 724.5 for L-glycine. What was the weight of L-alanine in the original heterogeneous mixture?

Set weight of L-alanine = x and weight of L-glycine = y in sub-sample, then 0.5884 + y →

$$\frac{A_X}{[X]} = F\left(\frac{A_S}{[S]}\right) = \frac{126.8}{0.1000} = F\,\frac{373.1}{0.1000} \Rightarrow F = 0.3399$$

= x y = 0.5884-x

Calculate response factor for L-alanine relative to L-glycine:

Then

$$\frac{A_X}{[X]} = F\left(\frac{A_S}{[S]}\right) = \frac{499.9}{x} = (0.3399)\frac{724.5}{y}$$

Substitute y = 0.5884-x:

$$\frac{499.9}{x} = (0.3399)\frac{724.5}{(0.5884 - x)} \Rightarrow 1 = \frac{0.4926\,x}{(0.5884 - x)} \Rightarrow 0.5884 - x = 0.4926\,x \Rightarrow$$

$$0.5884 = 1.4926\,x \Rightarrow x = 0.3942\ g$$

Find total amount of L-alanine in precipitate, which is equal to amount in original mixture:

(1.6259 0.5884 g) (0.3942 g) = 1.0893 g

25. ***Six iron tablets containing $FeSO_4 \cdot 7H_2O$ were dissolved in 100-ml of 0.1M HNO_3 with gentle heating. All of the Fe^{2+} is converted to Fe^{3+} by the strong oxidizing conditions. After the solution had cooled to room temperature 2.5-ml of 35wt% NH_4OH was added. The precipitate Fe_2O_3-xH_2O that was filtered weighed 0.345g. Thermogravimetric analysis of the crude product showed a 10.5% weight loss below 150 C. How many waters of hydration were in the precipitate? (i.e. Solve for x in Fe_2O_3-xH_2O.)***

moles of H_2O =Mass(wt%/100)/FW-H_2O*
=0.345.105/18.01*
=0.00201 mol H_2O

moles of Fe_2O_3=mass((1-wt%)/100)/FW-Fe_2O_3 =.345*.895/159.69*
=0.001933 mol Fe_2O_3 mol Fe_2O_3/ molH_2O
=0.962 x

=1 Fe_2O_3 X 1H_2O

How much iron was in each of the tablets? Report the average mg-Fe per tablet.

from above: analysis gave 0.001933 mol Fe2O3

Mass of Fe =.001933 mol Fe_2O_3 X 2mol-Fe/mol-Fe_2O_3 X 55.845g/mol-Fe

=0.2159 g Fe

*mg Fe/ Tablet =0.2159 g-Fe/6-tablets*1000mg/g*

=35.98 or 36.0 mg-Fe/tablet

26. **To precipitate 10 moles of Ag+ as Ag_2S , how many moles of the precipitating agent S^{2-} do you need to obtain complete precipitation**?

Solution : According to the following precipitation reaction : $2Ag^+ + S^{2-} \rightarrow Ag_2S$ The equivalent amount of S^{2-} = 5 moles .

50% of the equivalent amount = 2.5 moles

So the total amount of S^{2-} needed for complete precipitation of Ag^+

= 5 + 2.5 = 7.5 moles

27. **To determine the amount of magnetite, Fe_3O_4, in an impure ore, a 1.5419- g sample is dissolved in concentrated HCl, giving a mixture of Fe^{2+} and Fe3+. After adding HNO3 to oxidize Fe^{2+} to Fe^{3+} and diluting with water, Fe^{3+} is precipitated as Fe(OH)3 by adding NH_3. Filtering, rinsing, and igniting the precipitate provides 0.8525 g of pure Fe_2O_3. Calculate the %w/w Fe_3O_4 in the sample.6mks**

A conservation of mass requires that all the iron from the ore is found in the Fe_2O_3. We know there are 2 moles of Fe per mole of Fe_2O_3 (FW= 159.69 g/mol) and 3 moles of Fe per mole of Fe_3O_4 (FW= 231.54 g/mol); thus

$$0.8525g\ Fe_2O_3 \times \frac{2\ mol\ Fe}{159.69g\ Fe_2O_3} \times \frac{231.54g\ Fe_3O_4}{3mol\ Fe} = 0.82405g\ Fe_3O_4$$

the w/w S Fe_3O_4 in the sample , therefore is

$$\frac{0\ 82405\ Fe_3O_4}{1.\ 5419\ sample} \times 100 = 53.44\%\ w/w\ Fe_3O_4$$

30. ***Certain barium halide exists as the hydrated salt $BaX_2.2H_2O$, where X is the halogen. The barium content of the salt can be determined by gravimetric methods. A sample of the halide (0.2650 g) was dissolved in water (200 $cm^{3)}$ and excess sulfuric acid added. The mixture was then heated and held at boiling for 45 minutes. The precipitate (barium sulfate) was filtered off, washed and dried. Mass of precipitate obtained = 0.2533 g. Determine the identity of X.***

The precipitate is barium sulfate. The first stage is to determine the number of moles of barium sulfate produced, this will, in turn give us the number of moles of barium in the original sample.
Relative Molecular Mass of barium sulfate
= 137.34 (Ba) + 32.06 (S) + (4 x 16.00) (4 x O)
= 233.40
Number of moles
= mass / RMM
= 0.2533 / 233.40
= 1.09×10^{-3}
This is the number of moles of barium present in the precipitate and, therefore, the number of moles of barium in the original sample. Given the formula of the halide, (i.e. it contains one barium per formula unit), this must also be the number of moles of the halide. From this information we can deduce the relative molecular mass of the original halide salt:
RMM = mass / number of moles
= $0.2650 / 1.09 \times 10^{-3}$
The relative atomic mass of 2 X will be given by the RMM of the whole salt - that of the remaining components;
So RAM of 2 X = 244.18 - 173.37 = 70.81
2 X = 70.81, so X = 35.41.
= 244.18

The relative atomic mass of 2 X will be given by the RMM of the whole salt - that of the remaining components;
So RAM of 2 X = 244.18 - 173.37 = 70.81
2 X = 70.81, so X = 35.41.

The RAM of chlorine is 35.45 which is in good agreement with the result obtained and hence the halide salt is hydrated barium chloride and X = Chlorine

In gravimetric analysis, we may also be interested in determining the percentage composition by weight of the analyte in the sample.

$$\% \text{ analyte} = \frac{\text{Weight of analyte (g)}}{\text{Weight of sample (g)}} \times 100$$

Weight of the analyte (g) = weight of the precipitate (g) X GF

We can rewrite a general formula for calculating the percentage composition of the analyte as:

31.Calculate the gravimetric factor for

(a) Phosphorous in Ag_3PO_4 precipitate

Molecular weight(mw) for Ag_3PO_4 = 419

Molecular weight for P= 31

R= Mole ration of P in Ag_3PO_4 = 1

$$GF = \frac{\text{mw of analyte (g/mole)}}{\text{mw of precipitate(g/mole}} \times R = \frac{\text{g analyte}}{\text{g precipitate}}$$

$$= \frac{31}{419} \times 1 = 0.074$$

(b) Aluminium in Aluminium sulphite (Al_2S_3) precipitate

Molecular weight(mw) for Al_2S_3 = 150

Molecular weight for Al= 27

R= Mole ration of Al in Al_2S_3= 2

$$GF = \frac{\text{mw of analyte (g/mole)}}{\text{mw of precipitate(g/mole}} \times R = \frac{\text{g analyte}}{\text{g precipitate}}$$

$$= \frac{27}{150} \times 2 = 0.54$$

31. A 0.5962 g sample of iron ore is dissolved in perchloric acid ($HClO_4$). All iron present is oxidized to Fe^{3+}. The solution is filtered to remove solid matrix materials and made basic with addition of ammonium hydroxide. The iron precipitates as the $Fe(OH)_3 .xH_2O$ gel. The precipitate is collected in a cistern crucible and ignited to produce Fe2O3. What is the wt. % of iron in the sample if the analysis produced 0.3210 g Fe_2O_3?

Solution *: The overall reaction is :*

$$2\,Fe^{3+} + 3\,OH^- \rightarrow Fe_2O_3 + 3/2\,H_2$$

From this we derive the gravimetric factor relating weight of final material to the weight of iron analyte :

$$GF = \frac{\text{mw of analyte (g/mole)}}{\text{mw of precipitate(g/mole}} \times R$$

Molecular weight(mw) for Fe2O3 = 159.69

Molecular weight for Fe = 55.85

R= Mole ration of Fe in Fe2O3= 2

$$= \frac{55.85}{159.69} \times 2 = 0.6696$$

Weight of iron (Fe) = weight of the precipitate (g) X GF

= 0.3210 X 0.6995

= 0.2245

$$\%\ \text{weight of Fe in the ore} = \frac{0.2245}{0.} \times 100 = 37.66$$

CHAPTER FOURTEEN

CALORIMETRIC ANALYSIS

i. Define Calorimetry

Calorimetry is the field of science that deals with the measurement of the state of a body with respect to the thermal aspects in order to examine its physical and chemical changes. The changes could be physical such as melting, evaporation or could also be chemical such as burning, acid-base neutralization etc. Calorimetry is applied extensively in the fields of thermochemistry in calculating the enthalpy, stability, heat capacity etc.

2.State the principle of calorimetry

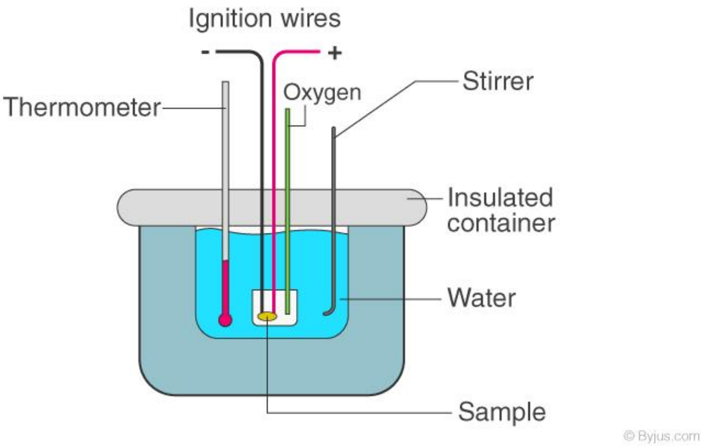
The principle of calorimetry (or principle of mixtures) states that for an insulated system, heat energy lost by the hot body is equal to the heat energy gained by the cold body.

$$m1c1(t1-t)=m2c2(t-t2\quad)$$

Note: Heat transfer occurs until both the bodies attain the same temperature(t).

b. Describe a calorimeter

A calorimeter is a device used for heat measurements necessary for calorimetry. It mainly consists of a metallic vessel made of materials which are good conductors of electricity such as copper and aluminium etc. There is also a facility for stirring the contents of the vessel. This metallic vessel with a stirrer is kept in an insulating jacket to prevent heat loss to the environment. There is just one opening through which a thermometer can be inserted to measure the change in thermal properties inside. Let us discuss how exactly heat measurements are made. In the previous article, we discussed the specific heat capacity of substances.



Such measurements can be made easily with this. Say in a calorimeter a fixed amount of fuel is burned. The vessel is filled with water, and the fuel is burned, leading to the heating of water. Heat loss by the fuel is equal to the heat gained by the water. This is why it is important to insulate the calorimeter from the environment; to improve the accuracy of the experiment. This change in heat can be measured through the thermometer. Through such a measurement we can find out both the heat capacity of water and also the energy stored inside a fuel.

c. Define the term enthalpy

- *Enthalpy is the heat energy that is being absorbed or evolved during the progression of a chemical reaction. The enthalpy is given the symbol H. H indicates the amount of energy. The change of enthalpy is given as ΔH, and the symbol Δ indicates the change of enthalpy. The heat of formation and heat of reaction are two forms of enthalpies.*

d. Explain the following terms

a. Heat capacity

Heat capacity is an intrinsic physical property of a substance that measures the amount of heat required to change that substance's temperature by a given amount. In the International System of Units (SI), heat capacity is expressed in units of joules per kelvin (J·K−1). Heat capacity is an extensive property, meaning that it is dependent upon the size/mass of the sample. For instance, a sample containing twice the amount of substance as another sample would require twice the amount of heat energy (Q) to achieve the same change in temperature (ΔT) as that required to change the temperature of the first sample.

b. ***Specific Heat Capacities*** *The* ***specific heat capacity****, often simply called specific heat, is the heat capacity per unit mass of a pure substance. This is designated* c_P *and* c_V *and its units are given in Jg·K.*

c. Molar heat capacity

The ***molar heat capacity*** *is the heat capacity per mole of a pure substance. Molar heat capacity is often designated CP, to denote heat capacity under constant pressure conditions, as well as CV, to denote heat capacity under constant volume conditions. Units of molar heat capacity are JK·mol.*

d. ***Thermochemical Equation*** *is a balanced stoichiometric chemical equation that includes the enthalpy change, ΔH. In variable form, a thermochemical equation would look like this:*

$A + B \rightarrow C$

$\Delta H = (\pm)\ \#$

Where {A, B, C} are the usual agents of a chemical equation with coefficients and "(±) #" is a positive or negative numerical value, usually with units of kJ.

6.State Hess's law of constant heat summation

Hess's Law of Constant Heat Summation (or just Hess's Law) states that regardless of the multiple stages or steps of a reaction, the total enthalpy change for the reaction is the sum of all changes. This law is a manifestation that enthalpy is a state function

28. Explain

a. Heat of formation

The heat of formation is the change of enthalpy when one mole of a compound is formed from its constituent elements. This is called standard heat of formation when it is given for the formation of substances at their standard states. However, there is no defined standard temperature. Hence, the heat of formation is given for a constant pressure. The symbol for the standard heat of formation is $\Delta H_f°$*. It can be calculated using the following equation.*

$$\boxed{\Delta H°_{\text{reaction}} = \Sigma\Delta H°_{f\,(\text{product})} - \Sigma\Delta H°_{f\,(\text{reactants})}}$$

According to this equation, the standard heat of formation is equal to the difference between the sum of the standard enthalpies of formation of the product and the standard enthalpies of formation of reactants.

(e) Heat of Reaction

The heat of reaction is the net amount of energy that should be added or released during a chemical reaction. In other words, it is the change in enthalpy in a chemical reaction that occurs at a constant pressure. The heat is either added or released in order to keep all the reactants at a constant temperature. It is measured per mole of a substance. The heat of reaction is given as below. When this is defined for the standard state, it is known as standard enthalpy of reaction. The standard state is the pure substance at 1 bar pressure and at a relevant temperature.

$$\boxed{\Delta H^\circ_{\text{reaction}} = \Sigma\Delta H^\circ_{\text{(product)}} - \Sigma\Delta H^\circ_{\text{(reactants)}}}$$

If the value of the heat of reaction is a positive value, it indicates that the reaction is endothermic (in which the heat is absorbed from outside). But if the value of the heat of reaction is a negative value, it indicates that the reaction is exothermic (in which heat is given off).

29. Distinguish between heat of formation and heat of reaction

The main difference between heat of formation and heat of reaction is that heat of formation is the amount of energy either absorbed or released during the formation of a compound whereas heat of reaction is the amount of energy either absorbed or released during any chemical reaction.

30. State and explain Hess law

Hess's law is useful for determining the overall change in enthalpy especially in a reaction which involves two or more parts.. It states that the enthalpy change for a reaction or process is independent of the route through which it occurs. This means that if reaction transforms a substance into another, it doesn't matter if the reaction occurs in one step (reactants become products immediately) or whether it goes through many steps (reactants become intermediaries and then become products), the resulting enthalpy change is the same in both cases.

Hess' law states that the change in enthalpy of the reaction is the sum of the changes in enthalpy of both parts. In this case, the combustion of one mole of carbon has $\Delta H = -394$ *kJ/mol (this happens six times in the reaction), the change in enthalpy for the combustion of one mole of hydrogen gas is* $\Delta H = -286$ *kJ/mol (this happens three times) and the carbon dioxide and water* *intermediaries become benzene with an enthalpy change of* $\Delta H = +3{,}267$ *kJ/mol.*

Take the sum of these changes to find the total enthalpy change, remembering to multiply each by the number of moles needed in the first stage of the reaction:

$$\Delta H_{total} = 6\times(-394) + 3\times(-286) + 3{,}267$$
$$= 3{,}267 - 2{,}364 - 858$$
$$= 45 \text{ kJ/mol}$$

The enthalpy change is negative because the reaction releases heat to the surroundings, resulting in an increase in temperature of the water.

31. A 50g sample of a metal was heated to *95oC* ***then quickly transferred to an insulated container containing 50g of*** *H2O* ***at*** *25oC****. The final temperature of the*** *H2O* ***was*** *30oC****. What can be concluded ?***

The specific heat of the water is greater than that of the metal. This is because when the heated metal is placed in the container of the cooler water there will be a transfer of thermal energy from the metal to the water. This transfer will occur towards an equilibrium of thermal energy in the water and in the metal. Thus we can conclude that the amount of thermal energy lost by the metal will equal the amount of thermal energy gained by the water. However we notice that the water increases by only $5^{o}C$ *and the metal decreases by* $65^{o}C$*. This is becasue of the difference of the specific heats of these substances. The specific heat capacity of a substance is the heat required to increase the temperature of 1g of a substance by* $1^{o}C$*. The metal can be conluded to have a smaller specific heat than the water because the same amount of energy transfer led to a much larger change in termperature for the metal as compared to the water.*

32. How much energy is needed to raise the temperature of five grams of ice from $-10^{o}C$ ***to*** $35^{o}C$***?*** *This question involves the total energy needed for three different processes: the temperature raise from −10oC to 0oC, the melting of the ice, and the temperature raise from 0oC to 35oC. For the first and third transitions we will use the equation* $q=mC\Delta T$*. For the melting of ice, we will use the equation* $q=m\Delta Hfusion$*.*

1. $q=miceCice\Delta T=(5g)(0.5cal/g{\circ}C)(10{\circ}C)=25cal$
2. $q=m\Delta Hfusion=(5g)(80cal/g)=400cal$
3. $q=mwaterCwater\Delta T=(5g)(1.0cal/g{\circ}C)(35{\circ}C)=175cal$

Finally, we will need to sum the energy required for each step to find the total energy.

25cal+400cal+175cal=600cal

33. A 20g sample of iron at a temperature of 120°C is placed into a container of water. There are 300 milliliters of water in the container at a temperature of 30°C.

$Ciron=0.444Jg^\circ C \quad Cwater=4.184Jg^\circ C \quad \rho water=1gmL$

How much heat does it take to heat 100g ice at 0C to boiling point?

You need heat for the phase change, using the enthalpy of fusion (100g X 334 J/g = 33400 J). Add to this the heat to get to boiling point using the specific heat of water

= 100g X 100C X 4.2 J

= 42000 J).

= 33400 J + 42000J

= 75400 J

Totalling = (75.4 kJ)

What is the final temperature of the water?

There are two things to note before solving for the final temperature.

1. The density of water allows us to say that 300 milliliters of water is the same thing as 300 grams of water.

$300ml x 1g1mL=300g$

2. Since the heat from the iron is being transferred to the water, we can say that the heat transfer is equal between both compounds. Since the heat is conserved in the system, we can set the two equations equal to one another.

$q=mC\Delta T$

$qi=qw \rightarrow miCi\Delta T=mwCw\Delta T$

$miCi(T_{initial}-T_{final})=mwCw(T_{final}-T_{initial})$

Notice how the change in temperature for iron has been flipped in order to avoid a negative number.

$(20g)(0.444J/g^\circ C)(120^\circ C-T_f)=(300g)(4.184J/g^\circ C)(T_f-30^\circ C)$

$T_f=30.63\,^\circ C$

Because water has a much higher heat capacity compared to iron, the temperature of the water is not changed significantly.

34. Calculate ΔH for the following reaction:

$CH_{4\,(g)} + O_2\,(g) \rightleftharpoons CO_{2\,(g)} + H_2O\,(l)$

Compound	ΔH
$CH_4\,(g)$	-74.8 kJ/mol
$H_2O\,(l)$	-285.8 kJ/mol
$CO_2\,(g)$	-393.5 kJ/mol

$\Delta H = \Sigma\,\Delta Hf\ products - \Sigma\,\Delta Hf\ reactants$

$\Delta Hf\ O_2$ or any element is 0
First step is to balance the equation:
$CH_{4\,(g)} + O_2\,(g) \rightleftharpoons CO_{2\,(g)} + 2H_2O\,(l)$
$\Delta H = \Sigma\,\Delta Hf$ *products* - $\Sigma\,\Delta Hf$ *reactants*
$= [-393.5\ kJ/mol + 2(-285.8)\ kJ/mol] - (-74.8\ kJ/mol)$
$= -890.3\ kJ/mol$

35. ***What mass of carbon monoxide must be burned to produce 175 kJ of heat under standard state conditions?***

Given that:

$$CH_4\ (g) \longrightarrow C\ (s) + 2\ H_2\ (g)\ \Delta H_r = 74.8\ kJmol^1$$

What is the ΔHf of CH_4 (g)?

$-74.8\ kJ\ mol^{-1}$

The required reaction is the reverse of formation, so as we are going in the opposite direction, it requires the opposite sign.

36. ***A metal weighing 4.82 g was heated to 115.0 °C and put into 35 mL of water of temperature 28.7 °C. The metal and water were allowed to come to an equilibrium temperature, determined to be 34.5 °C. Assuming no heat was lost to the environment, calculate the specific heat of the metal. Consider the specific heat capacity of water as 4.186 joule/gram °C.***

First, let us calculate the heat absorbed by the water and use the value obtained to calculate the specific heat of the metal.
The formula to find the heat absorbed by the water is given as
$q=mc\Delta t$
Substituting the values in the equation, we get
$q_{absorbed}=(4.186J/g\cdot{}^{o}C) \times 35g \times (5.8\ {}^{o}C)$
$= 850J$
Now, using this formula let us calculate the specific heat of the metal as follows:
$850J=s\times 4.82g\times 80.5\,{}^{o}C$
$s=2.19J/G\cdot{}^{o}C$
The specific heat of the metal is $2.19J/G\cdot{}^{o}C$
The molar heat capacity of water, C_P, is 75.2 Jmol·K.

37. ***How much heat is required to raise the temperature of 36 grams of water from 300 to 310 K?***

We are given the molar heat capacity of water, so we need to convert the given mass of water to moles:

$$36\ \text{grams} \times \frac{1\ \text{mol}\ H_2O}{18\ g} = 2.0\ \text{mol}\ H_2O$$

Now we can plug our values into the formula that relates heat and heat capacity:

$$q = nC_P\Delta T$$
$$q = (2.0\text{mol})(75.2\text{Jmol}\cdot\text{K})(10\text{K})$$
$$q = 1504\ J$$

38. ***A solution was made by dissolving a spatula of potassium nitrate into 50 cm3 of water. The temperature changed from 20.4°C to 18.7°C. Calculate the enthalpy change for this reaction***.

To calculate the enthalpy change (ΔH) we must know the values for c, m and ΔT. The specific heat capacity (c) is a constant, with a value of 4.18. Since 50 cm^3 *of water have been used, the mass of water (m) is 0.05 kg.*
From the question we can see that the temperature has decreased by 1.7 °C. This means that the reaction is endothermic (so ΔH will be positive).

$$\Delta H = cm\Delta T$$
$$= 4.18 \times 0.05 \times 1.7 \quad = 0.3553\ kJ$$

In an experiment on the specific heat of a metal a 0.20 kg block of the metal at 150oC is dropped in a copper calorimeter (of water equivalent 0.025 kg) containing 150cm3 of water at 27oC. The final temperature is 40oC. Compute the specific heat of the metal. If heat losses to the surroundings are not negligible, is your answer greater or smaller than the actual value for specific heat of the metal ?

Mass of the metal, m = 0.20 kg = 200 g
Initial temperature of the metal, T1 = 150 ^oC
Final temperature of the metal, T2 = 40 ^oC
Calorimeter has water equivalent of mass, m = 0.025 kg = 25 g
Volume of water, V = 150 cm3
Mass (M) of water at temperature T = 27oC:
$150\times1=150g$
Fall in the temperature of the metal:
$\Delta T_m = T_1 - T_2 = 150-40 = 110^oC$
Specific heat of water, $C_w = 4.186 J/g/K$
Specific heat of the metal =C
*Heat lost by the metal, =mCT .... **(i)***
Rise in the temperature of the water and calorimeter system:
$T_1 - T = 40-27 = 13^oC$
Heat gained by the water and calorimeter system:
$= m_1\ C_w\ T = (M+m)C_wT \ldots(ii)$
Heat lost by the metal = Heat gained by the water and colorimeter system
$mC\Delta T_m = (M+m)C_w\ T_w$

$200 \times C \times 110 = (150+25) \times 4.186 \times 13$

$C = (175 \times 4.186 \times 13)/(110 \times 200)$

$= 0.43 Jg^{-}1k^{-1}$

If some heat is lost to the surroundings, then the value of C will be smaller than the actual value.

39. A 360-g piece of rebar (a steel rod used for reinforcing concrete) is dropped into 425 mL of water at 24.0 °C. The final temperature of the water was measured as 42.7 °C. Calculate the initial temperature of the piece of rebar. Assume the specific heat of steel is approximately the same as that for iron and that all heat transfer occurs between the rebar and the water (there is no heat exchange with the surroundings).

Solution

The temperature of the water increases from 24.0 °C to 42.7 °C, so the water absorbs heat. That heat came from the piece of rebar, which initially was at a higher temperature. Assuming that all heat transfer was between the rebar and the water, with no heat "lost" to the surroundings, then heat given off by rebar = −heat taken in by water, or:

$q_{rebar} = -q_{water}$

Since we know how heat is related to other measurable quantities, we have:

$(c \times m \times \Delta T)_{rebar} = -(c \times m \times \Delta T)_{water}$

Letting f = final and i = initial, in expanded form, this becomes:

$C_{rebar} \times m_{rebar} \times (T_{f,rebar} - T_{i,rebar}) = -c_{water} \times m_{water} \times (T_{f,water} - T_{i,water})$

The density of water is 1.0 g/mL, so 425 mL of water = 425 g. Noting that the final temperature of both the rebar and water is 42.7 °C, substituting known values yields:

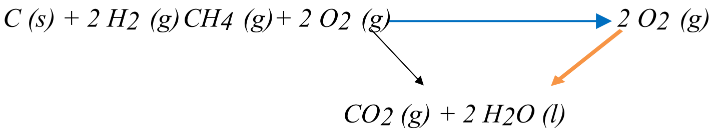
$(0.449 J/g°C)(360 g)(42.7°C - T_{i,rebar}) = (4.184 J/g°C)(425 g)(42.7°C - 24.0°C)$

$T_{i,rebar} = (4.184 J/g°C)(425 g(42.7°C - 24.0°C) = 42.7°C\ (0.449 J/g°C)(360 g)$

Solving this gives $T_{i,rebar} = 248$ °C, so the initial temperature of the rebar was 248 °C.

40. Calculate the ΔH_f of methane (CH_4 (g)), using the following ΔH_C data: CH_4 (g) = –882 kJ mol^{-1}; C (s) = –394 kJ mol^{-1}; H_2 (g) = –286 kJ mol^{-1}

Step I; Construct a Hess's Law cycle:



We want ΔHf which is the reaction going across the top (blue arrow). To get there we go down the black arrow and back up the orange arrow. We travel in the direction of the black arrow, but in the opposite direction for the orange arrow.

So, we get:

$$C\,(s) + 2\,H_2\ (g) + 2\,O_2\ (g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

$$-\,CH_4\ (g) + 2\,O_2\ (g) \longrightarrow CO_2\,(g) + 2\,H_2O\,(l)$$

$$= (-394 + 2 \times (-286)) - (-882)\ kJ\ mol^{-1}$$

$$= -84\ kJ\ mol^{-1}$$

41.Explain why instant cold packs used by athletes in managing muscular injuries contain ammonium nitrate and water.

Cold pack is a Popular and effective in treatments to ease pain and swelling from minor injuries, cold packs come in many different varieties. Some are sacks of gel that turn into ice packs in your freezer; others are packets designed to turn cold instantly with a simple squeeze, no refrigeration or freezing required. You can also make your own cold pack by wrapping some

Anyone who has ever sprained or twisted an ankle or pulled a muscle knows that cold is your friend. Bruises, insect bites, and repetitive strain injuries such as tendinitis, also respond well to treatment with cold packs. Cold therapy can help people with muscle spasms, whiplash, and various forms of arthritis as well.

Cold packs are very effective at reducing swelling and numbing pain. An injury swells because fluid leaks from blood vessels; cold causes vessels to constrict, reducing their tendency to ooze. The less fluid that leaks from blood vessels, the less swelling results. Cold also eases inflammation and muscle spasms, two common sources of pain. cold pack has a plastic bag containing water. Inside this bag is a smaller bag

containing ammonium nitrate. The outer bag is squeezed so that the inner bag bursts. The pack is shaken and quickly gets

very cold as the ammonium nitrate dissolves in the water according to the endothermic reaction. $NH_4NO_3(s) \rightarrow NH_4^{+}\ (aq) + NO^{-3(}aq)$

The ammonium nitrate produces lower mean minimum temperatures, and reaches them more quickly, demonstrating it is a more effective chemical for use in relieving pain.

The sooner you apply an ice pack to a sprain or strain, the sooner it can do its job reducing pain and swelling. For chronic problems such as low back pain or muscle spasms, ice whenever the symptoms start up.

A general rule of thumb is to ice an injury over a period of 24 to 72 hours. Apply cold packs for periods of up to 20 minutes every two to four hours. When your skin starts to feel numb, it's time to give your body a break from a cold pack.However ,prolonged, direct contact with cold can damage skin and nerves so always be sure to wrap your cold pack in a towel. Distinguish between exothermic and endothermic reaction

CHAPTER FIFTEEN

COLORIMETRY

a. Define colorimetry

Colorimetry is one of most widely used method for determining the concentration of biochemical compounds is which makes use of the property that when white light passes through a colored solution, some wavelengths are absorbed more than others. A colorimeter is the instrument designed to determine the concentration of a solution by analyzing its color intensity.

b. Explain the principle of colorimetry

Many compounds are not themselves colored but can be made to absorb light in the visible region by reaction with suitable reagents. These reactions are fairly specific and, in most cases, very sensitive. So that quantities of material in the region of mol/L concentrations can be measured.

The depth of the color is proportional to the concentration of the compound being measured, while the amount of light is proportional to the intensity of the color and hence the concentration.

The earliest colorimeters relied on the human eye to match the color of a solution with that of one of a series of colored discs. The results obtained were too subjective and not particularly accurate.

Different chemical substances absorb varying frequencies of the visible spectrum. Colorimeters rely on the principle that the absorbance of a substance is proportional to its concentration, i.e., a more concentrated solution gives a higher absorbance reading.

A quantitative reading for the concentration of a substance can be found by making up a series of solutions of known concentration of the chemical understudy, and plotting a graph of absorbance against concentration. By reading off the absorbance of the specimen substance on the graph, a value for its concentration is found.

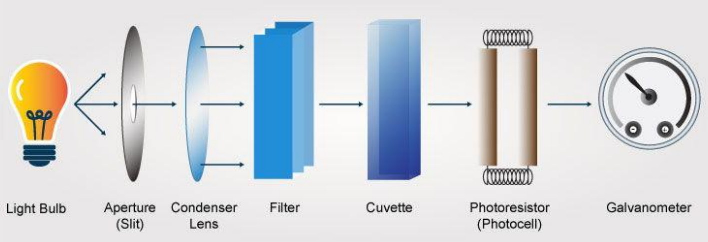
A colorimeter is generally any tool that characterizes color samples to provide an objective measure of color characteristics.

In chemistry, the colorimeter is an apparatus that allows the absorbance of a solution at a particular frequency (color) of visual light to be determined. Colorimeters hence make it possible to determine the concentration of a known solute since it is proportional to the absorbance.

c. Describe the components of a colorimeter

The essential parts of a colorimeter are:

- ✓ *a **light source**, which is usually an ordinary filament lamp;*
- ✓ *a **lens** with an **aperture** that can be adjusted;*
- ✓ *a set of **filters** in different colors;*
- ✓ *a **cuvette** that holds the working solution;*
- ✓ *a **detector** (usually - photoresistor or photocell), which measures the light that has passed through the solution;*
- ✓ *a **meter** to display the output from the detector.*



***Filter** in the colorimeter is used to select the color of light which the solute absorbs the most to maximize the accuracy of the experiment. Note that the color of the absorbed light is the 'opposite' of the color of the specimen, so a blue filter would be appropriate for an orange substance. Sensors measure the amount of light that has passed through the solution, compared to the amount entering, and a display reads the amount absorbed.*

***Cuvettes**. Solutions to be measured are put into a small square test tube-like vessel called a cuvette, which is available in various grades and made of plastic or glass. Note that all samples must be put only into a cuvette and never directly into the colorimeter itself or damage will certainly result - the colorimeter labeling makes this very clear for the benefit of new users. Each cuvette varies slightly optically, so when the procedure involves changing the concentration of a solution best practice is to use the same cuvette for the complete experiment. Most cuvettes have only two optical faces, which are very clear, the other two usually being duller or sometimes embossed to make them easier to grip.*

d. How does a colorimeter work?

1. White light from a tungsten lamp passes through a slit, then a condenser lens, to give a parallel beam which falls on the solution under investigation contained in an absorption cell or cuvette. The cell is made of glass with the sides facing the beam cut parallel to each other.

2. Beyond the absorption cell is the filter, which is selected to allow maximum transmission of the color absorbed. If a blue solution is under examination, then red is absorbed and a red filter is selected. NOTE: The color of the filter is complementary to the solution.

3. The light then falls onto a photocell, which generates an electrical current in direct proportion to the intensity of light falling on it.

4. This small electrical signal is increased by the amplifier, which passes to a galvanometer of digital readout to give absorbance reading directly.

5. Discribe how to operate a colorimeter

- ✓ *Switch on the instrument at least 5 minutes before use to allow it to stabilize.*
- ✓ *Select the most appropriate filter for the analysis and insert it in the light path (Griffin) or dial it in with the selector (Jenway).*
- ✓ *Place the reagent blank solution (or water) in the cuvette and zero the instrument (either using the ëset zeroí control or the ëcalibrateí switch. Make sure the clear faces of the cuvette are in the light path .*
- ✓ *Place the sample in the colorimeter and read the absorbance of the solution. If the absorbance is "over range" (usually > 2.0) then the sample must be diluted to yield a value within the limits of the instrument.*
- ✓ *At intervals, recheck the reagent blank to ensure that there is no drift in the zero value.*

6. Distinguish between visual colorimetry and photoelectric colorimetry

The filters are used to isolate a part of the visible light spectrum that is absorbed maximally by the sample. Different colourimeters use different sets of filters but typical wavelengths passed are red filter: 630-750nm, green filter: 510-570nm and blue filter: 360-480nm. Although you will normally be told which filter to use you should consider and understand the reason for this choice.

7. a . State Beer -Lambert's Law

Beer-Lambert Law (also known as Beer's Law) states that there is a linear relationship between the absorbance and the concentration of a sample.

b.State three causes for deviation from Beer -Lambert's Law

Beer-Lambert law only holds true in the following scenarios;

1. *The light passing through the sample must be monochromatic (of a single wavelength.*
2. *The solution must be homogeneous. If not, at high concentrations, the molecules may aggregate and this would lead to incorrect readings.*

3. The solution must not have a molecule that emits fluorescence when excited. If it does, then this can lead to erroneous readings.

4. The temperature of the solution must not change, as the molar extinction coefficient depends on it.

8.. Name two types of filters used in colorimeter

The filters are used to isolate a part of the visible light spectrum that is absorbed maximally by the sample.

Different colourimeters use different sets of filters but typical wavelengths passed are red filter: 630-750nm, green filter: 510-570nm and blue filter: 360-480nm.

9. State any three causes of deviation to Beer-Lamberts

These deviations are due to:

- ✓ *chemical reasons arising when the absorbing compound, dissociates, associates, or reacts with a solvent to produce a product having a different absorption spectrum,*
- ✓ *the presence of stray radiation, and*
- ✓ *the polychromatic radiation.*

CHAPTER SIXTEEN

FLAME PHOTOMETRY

1. Explain why alkali metals are analyzed by flame photometry

Flame photometry is usually useful for analysis of elements , which are easily, excited aseptically the alkali and alkaline earth metals ie Na, K, Ca, Ba, Li.. This elements are easily excited to higher energy levels at flame temperature.

2. Explain the origin of color in flames of alkali metals

The origin of color in flame of alkali metals are : When an element eg Na or K or Ca,is in its atomic state and is placed in a flame , its atoms increases in energy (i.e. they become excited) and hence move to the next higher energy level .These acquired energy makes these atoms to become less stable and they would then attempt to fall back or come back to their original energy level by losing or emitting these same amount of energy , These amount of energy is emitted in form of light . The light emitted is specific in wavelength for each element

*2. **Outline the principle on which flame photometry is based***

The basis of flame photometric working is that, the species of alkali metals (Group 1) and alkaline earth metals (Group II) metals are dissociated due to the thermal energy provided by the flame source.

Due to this thermal excitation, some of the atoms are excited to a higher energy level where they are not stable. When sample interacts with light, absorption process occurs.

Ground state electrons of the sample atom tend to move to the excited states with the energy of absorbed light. This process can also be called excitation. Apart from light, heat can cause excitation. Since excited state is unstable, electrons want to return back to the ground state. When an excited electron returns back to its ground state, a radiation is emitted that is equal to the energy difference between excited and ground states.

The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques. The subsequent loss of energy will result in the movement of excited atoms to the low energy ground state with emission of some radiations, which can be visualized in the visible region of the spectrum.

The absorbance of light due to the electrons excitation can be measured by using the direct absorption techniques while the emitting radiation intensity is measured using the emission techniques. The wavelength of emitted light is specific for specific elements.

When an element eg Na or K or Ca,is in its atomic state and is placed in a flame , its atoms increases in energy (i.e. they become excited) and hence move to the next higher energy level .these acquired energy makes these atoms to become less stable and they would then attempt to fall back or come back to their original energy level by losing or emitting these same amount of energy ,these amount of energy is emitted in form of light . The light emitted is specific in wavelength for each element e.g.

$Na+$ emits 589nm

$k+$ emits 404 and 767nm

The intensity of light emitted is proportional to the concentration of atoms present in the solution. The emitted wavelength is normally a measure from which the elements can be determined

3. ***State and explain components of a flame photometer***

1. Source of flame:

A burner that provides flame and can be maintained in a constant form and at a constant temperature.

***2. Nebuliser and mixing chamber**:*

Helps to transport the homogeneous solution of the substance into the flame at a steady rate.

***3. Optical system (optical filter)**:*

The optical system comprises three parts: convex mirror, lens and filter. The convex mirror helps to transmit light emitted from the atoms and focus the emissions to the lens. The convex lens help to focus the light on a point called slit. The reflections from the mirror pass through the slit and reach the filters. This will isolate the wavelength to be measured from that of any other extraneous emissions. Hence it acts as interference type color filters.

***4. Photo detector**:*

Detect the emitted light and measure the intensity of radiation emitted by the flame. That is, the emitted radiation is converted to an electrical signal with the help of photo detector. The produced electrical signals are directly proportional to the intensity of light.

4. ***List the steps followed when analyzing a sample for a given component using a flame photometer***

✓ *Both the standard stock solution and sample solution are prepared in fresh distilled water.*

✓ *The flame of the photometer is calibrated by adjusting the air and gas. Then the flame is allowed to stabilize for about 5 min.*

✓ *Now the instrument is switched on and the lids of the filter chamber are opened to insert appropriate colour filters.*

✓ *The readings of the galvanometer are adjusted to zero by spraying distilled water into the flame.*

✓ *The sensitivity is adjusted by spraying the most concentrated standard working solution into the flame. Now the full scale deflection of the galvanometer is recorded.*

✓ *Again distilled water is sprayed into the flame to attain constant readings of galvanometer. Then the galvanometer is readjusted to zero.*

✓ *Now each of the standard working solutions is sprayed into the flame for three times and the readings of galvanometer are recorded. After each spray, the apparatus must be thoroughly washed.*

✓ *Finally sample solution is sprayed into the flame for three times and the readings of galvanometer are recorded. After each spray, the apparatus must be thoroughly washed.*

✓ *Calculate the mean of the galvanometer reading.*

✓ *Plot the graph of concentration against the galvanometer reading to find out the concentration of the element in the sample.*

✓ *Flame Photometer graph, flame photometer readings, galvanometer readings, sample concentration*

5. *Outline the process involved in flame photometry*

In this technique, first aerosols are formed from sample solution by a jet of compressed gas. This process is called nebulization. Then the flow of the gas carries the aerosols into a flame where atomization takes place. A tomization is the conversion of sample aerosols into an atomic vapor by flame. When a sample is atomized, a substantial fraction of the metallic constituents are reduced to gaseous atoms and also depending on the temperature of the flame a certain fraction of these atoms are ionized. Then, electrons of the formed atoms are excited to upper state. Light is emitted at characteristic wavelengths for each metal as the electron returns to the ground state.

5. Summerize flame photometry process

1. The solvent is first evaporated leaving fine divided solid particles.

2. This solid particles move towards the flame, where the gaseous atoms and ions are produced.

3 The ions absorb the energy from the flame and excited to high energy levels.

4. When the atoms return to the ground state radiation of the characteristic element is emitted.

5. The intensity of emitted light is related to the concentration of the element.

6.Describe the process taking place in the flame during flame photometry

The various processes in the flame are discussed below:

- *a) Desolvation: The metal particles in the flame are dehydrated by the flame and hence the solvent is evaporated.*
- *b) Vapourisation: The metal particles in the sample are dehydrated. This also led to the evaporation of the solvent.*
- *c) Atomization: Reduction of metal ions in the solvent to metal atoms by the flame heat.*
- *d) Excitation: The electrostatic force of attraction between the electrons and nucleus of the atom helps them to absorb a particular amount of energy. The atoms then jump to the exited energy state.*
- *e) Emission process: Since the higher energy state is unstable the atoms jump back to the stable low energy state with the emission of energy in the form of radiation of characteristic wavelength, which is measured by the photo detector.*

7.State any three fuels and gases used in flame photometry

Fuels

- *a) Natural Gas*
- *b) Hydrogen*
- *c) Acetylene*

Gases : Air, Oxygen or nitrous oxide (N_2O) as oxidant

8.Explain self absorption as used in flame photography

Self absorption occurs when the radiation emitted from one atom is just the right energy to be absorbed by another atom . The effect is that several atoms may be involved but the detector may see only one or few atoms in the final process. These results in a lower reading than that actually present

9. State and explain the advantages and disadvantages of flame photometry

Advantages

- ✓ *Simple quantitative analytical test based on the flame analysis.*
- ✓ *Inexpensive.*
- ✓ *The determination of elements such as alkali and alkaline earth metals is performed easily with most reliable and convenient methods.*
- ✓ *Quite quick, convenient, and selective and sensitive to even parts per million (ppm) to parts per billion (ppb) range.*

Disadvantages:

Moreover the flame photometer has a wide range of applications in the analytical chemistry, it possess many disadvantages which are explained below:

- ✓ *The concentration of the metal ion in the solution cannot be measured accurately..*
- ✓ *A standard solution with known molarities is required for determining the concentration of the ions which will corresponds to the emission spectra.*
- ✓ *It is difficult to obtain the accurate results of ions with higher concentration.*
- ✓ *The information about the molecular structure of the compound present in the sample solution cannot be determined.*
- ✓ *The elements such as carbon, hydrogen and halides cannot be detected due to its non radiating nature.*

10.State and explain the application of flame photometry

Flame photometry can be applied in the following various fields

- ✓ *In analysis that are difficult or impossible to perform using other techniques or where speed is important than accuracy*
- ✓ *For analysis of alkali metals*
- ✓ *In biomedical research*
- ✓ *In clinical chemistry - Na+ and K+ ions in body fluids, muscles and heart can be determined by diluting the blood serum and aspiration into the flame.*
- ✓ *In sample chemistry- in the Analysis of soft drinks, fruit juices and alcoholic beverages can also be analyzed by using flame photometry*
- ✓ *In water and sewage treatment*
- ✓ *In agriculture – The fertilizer requirement of the soil is analyzed by flame test analysis of the soil. it also help to determine the availability of alkali and alkaline earth metals which are critical for soil cultivation*

CHAPTER SEVENTEEN

PROXIMATE ANALYSIS

i. *Define proximate analysis*

Proximate analysis refers to the quantitative analysis of macromolecules in food. A combination of different techniques, such as extraction, Kjeldahl, NIR are used to determine protein, fat, moisture, ash and carbohydrates levels.

ii. *Explain the importance of proximate analysis*

In the food industry, Proximate analysis" is of key commercial concern as food-manufacturing companies need to ensure that their products meet the appropriate laws and legal declaration requirements as well as the safety aspects of the end products when released to the end consumer

In the fuel or energy industry, proximate analysis of a fuel provides the percentage of the material that burns in a gaseous state (volatile matter), in the solid state (fixed carbon), and the percentage of inorganic waste material (ash), and is therefore of fundamental importance for biomass energy use and environmental pollution

iii. *Give four components of biological materials used in proximate analysis*

Water (moisture), ash, crude fat (ether extract), crude protein , Carbohydrates and crude fibre.

4. *Explain the following terms*

a. ***Total carbohydrate*** *content of foods has, for many years, been calculated by difference, rather than analysed directly. Under this approach, the other constituents in the food (protein, fat, water, alcohol, ash) are determined individually, summed and subtracted from the total weight of the food. This is referred to as total carbohydrate by difference and is calculated by the following formula:*

100 - (weight in grams [protein + fat + water + ash + alcohol] in 100 g of food)

It should be clear that carbohydrate estimated in this fashion includes fibre, as well as some components that are not strictly speaking carbohydrate, e.g.

organic acids.. Total carbohydrate can also be calculated from the sum of the weights of individual carbohydrates and fibre after each has been directly analysed.

b. ***Available carbohydrate*** *represents that fraction of carbohydrate that can be digested by human enzymes, is absorbed and enters into intermediary metabolism. (It does not include dietary fibre, which can be a source of energy only after fermentation - see the following subsections.) Available carbohydrate can be arrived at in two different ways: it can be estimated by difference, or analysed directly.*

(f) To calculate available carbohydrate by difference, the amount of dietary fibre is analysed and subtracted from total carbohydrate, thus:

100 - (weight in grams [protein + fat + water + ash + alcohol + dietary fibre] in 100 g of food)

This yields the estimated weight of available carbohydrate, but gives no indication of the composition of the various saccharides comprising available carbohydrate. Alternatively, available carbohydrate can be derived by summing the analysed weights of individual available carbohydrates. In either case, available carbohydrate can be expressed as the weight of the carbohydrate or as monosaccharide equivalents.

k. ***Dietary fibre*** *is a physiological and nutritional concept relating to those carbohydrate components of foods that are not digested in the small intestine. Dietary fibre passes undigested from the small intestine into the colon, where it may be fermented by bacteria (the microflora), the end result being variable quantities of short-chain fatty acids and several gases such as carbon dioxide, hydrogen and methane. Short-chain fatty acids are an important direct source of energy for the colonic mucosa; they are also absorbed and enter into intermediary metabolism*

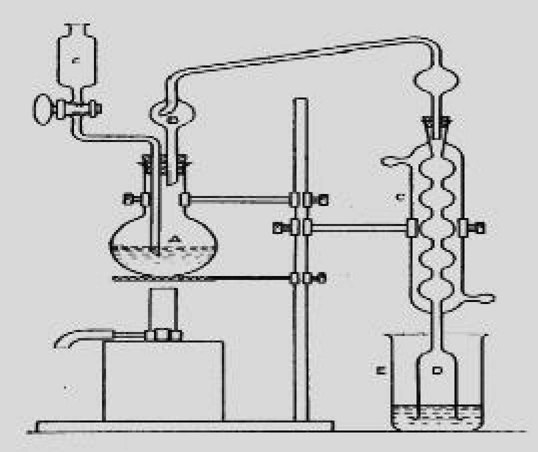
5. Describe the kjeldahl procedure for the determination of protein content in a food sample

Kjeldahl Method is a widely accepted method for the determination of protein in food products. The method follows three steps:

Digestion *– Decomposition of organic matter by heating in the presence of concentrated sulphuric acid, the end product is ammonium sulphate solution.*

Distillation *– Ammonium sulphate is converted into gaseous ammonia by addition of an excess base, followed by boiling and condensation of the ammonia in a receiving solution (acid).*

Titration *– Quantification of the unreacted acid in the collecting vessel. The rate of digestion and the completeness of the breakdown of nitrogenous compounds to ammonium sulphate mainly depend upon the heat input, amount of boiling point elevator of acid (alkali sulphate), addition of catalyst (mercury, copper sulphate, titanium dioxide), oxidant (hydrogen peroxide), reflux rate of sulphuric acid and length of digestion. Ammonia is liberated from the acid digestion mixture by distillation in the presence of alkali (50% NaOH). A total recovery of ammonia from the digest can be obtained within 5 to 20 min by direct distillation and about 10 min by steam distillation.*



Kjeldahl Nitrogen distillation assembly

2.