RWANDA TVET BOARD

RQF LEVEL 5

TRADE: ALL

MODULE CODE: GENIC501

TEACHER'S GUIDE

Module name: INTRODUCTION TO ANALYTICAL CHEMISTRY

RTB | RWANDA TVET BOARD

MODULE NAME:GENIC501 INTRODUCTION TO ANALYTICAL CHEMISTRY

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Acronyms

MS: Mass spectrometry
EMF: Electromagnetic Field
Ksp: solubility product constant
E^{o} Standard Electrode potential
e.m.f: electromotive force
°C: Celsius degree

Introduction

This module describes the knowledge, skills and attitudes required to explain the introduction to Analytical Chemistry. At the end of this module, learners will be able to describe qualitative and quantitative chemical analysis, describe solubility and describe the electrochemical cell reactions.

ELEMENTS OF COMPETENCE AND PERFORMANCE CRITERIA	
LEARNING UNIT	**PERFORMANCE CRITERIA**
1. Differentiate qualitative and quantitative chemical analysis	1.1 Explain clearly qualitative chemical analysis according to the analytical methods
	1.2 Explicate properly chemical quantitative analysis according to the analytical methods
	1.3 Discuss correctly the applications of qualitative and quantitative chemical analysis based on area of application
2. Discuss solubility	2.1 Identify properly the factors that affect solubility according to the nature of solution
	2.2 Explain correctly the solubility product based on the nature of salt
	2.3 Calculate accurately the solubility product according to the solubility equilibrium
3. Describe the electrochemical cell reactions	3.1Explain clearly the electrolysis according to Faraday's Law
	3.2 Illustrate properly the electrochemical cells according to redox half equations
	3.3 Determine accurately overall energy of electrochemical cell based on the half-cell reactions.

GENIC501: INTRODUCTION TO ANALYTICAL CHEMISTRY

Learning Units:

1. Differentiate qualitative and quantitative chemical analysis
2. Solubility and solubility product of sparingly soluble salts
3. Describe electrochemical cell reactions

Learning Unit 1: Differentiate qualitative and quantitative chemical analysis

STRUCTURE OF LEARNING UNIT

Learning outcomes:

1.1. Explain qualitative chemical analysis

1.2. Explicate quantitative analysis

1.3. Discuss the applications of qualitative and quantitative chemical analysis.

Learning outcome 1.1 Explain qualitative chemical analysis

Duration: 4hrs

Learning outcome 1.1 objectives:
By the end of the learning outcome, the trainees will be able to:

1. Explain clearly qualitative chemical analysis according to the analysis methods
2. Explicate properly Factors/criteria considered for qualitative analysis.
3. Differentiate correctly organic and inorganic qualitative analysis.

Resources

Equipment	**Tools**	**Materials**
✓ Video ✓ Projector ✓ Computer ✓ Books ✓ Internet	✓ Pens/Pencils ✓ Notebook ✓ Papers ✓ Marker ✓ White/ Chalk ✓ Boards ✓ Chalks	✓ Test-tube ✓ Beaker ✓ Conical flask ✓ Distiller ✓ Measuring cylinder ✓ Washing bottle ✓ Funnel ✓ Retort stand ✓ Burette ✓ Pipette ✓ Manufactured product having content label ✓ teabag

Advance preparation:

- Prepare all material needed and describe their brief uses
- Bring the product and share to the trainees then ask about what they are seeing on label

Introduction

Analytical chemistry: *is the science of obtaining, processing, and communicating information about the composition and structure of matter.* In other words, it is the art and science of determining what matter is and how much of it exists**.**

Analytical chemistry involves ***qualitative*** and ***quantitative*** **analysis** of matter.

1.1.1.Qualitative analysis of matter

It is a branch of chemistry that deals with the identification of elements or grouping of elements present in a **sample**. *It determines the presence or absence of a particular compound, but not the mass or concentration.*

Sample: is a portion of material selected from a larger quantity of material and used to determine what the large quantity looks like*.*

This involves **organic** and **inorganic** qualitative analysis

- **Inorganic qualitative analysis** is a method of analytical chemistry that seeks to find the elemental composition of inorganic compounds. It mainly focused on detecting ions in an aqueous solution. The solution treated with various reagents to test for reactions characteristic of certain ions, which may cause color change, solid forming, and other visible changes.
- **Organic qualitative analysis** involve detecting the presence of organic compounds, type of molecules, functional group, and chemical bonds.

The determination of species present in a given sample requires the uses of different method.

1.1.2 Qualitative methods of analysis

This involve typically measures changes in color, melting point, odor, reactivity, radioactivity, boiling point, bubble production, and precipitation. Methods include *flame test, distillation, extraction, precipitation, chromatography, and spectroscopy*

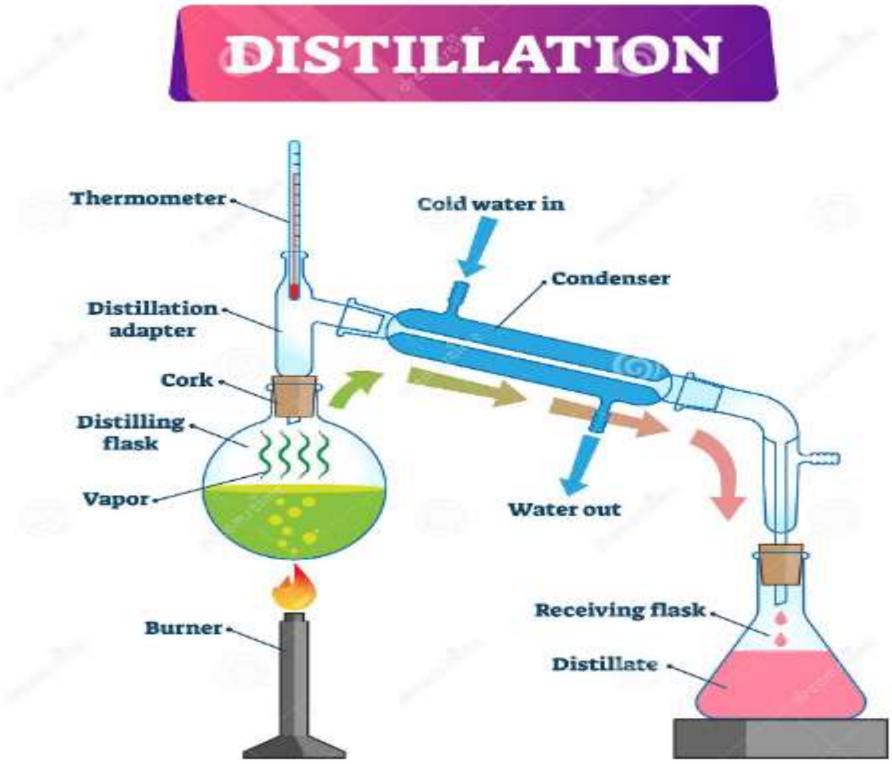
Flame tests

This is a method used to identify the presence of a relatively small number of metal ions in a compound. Not all metal ions give flame colors but most of them produce specific color used to differentiate them from others.

Origin of flame color: The colors observed during the flame test result from the **excitement** of the electrons caused by the increased temperature. The electrons "*jump*" from their ground state to a higher energy level. As they return to their ground state, they emit visible light. The color of the light connected to the location of the electrons and the affinity the outer-shell electrons have to the atomic nucleus.

Distillation*:*

This is the most commonly used method for the separation of homogeneous fluid mixtures. Separation exploits differences in boiling point, or volatility, between the components in the mixture. Repeated **vaporization** and **condensation** of the mixture allows virtually complete separation of most homogeneous fluid mixtures.



Extraction

Extraction is a common technique used in organic analysis to **isolate** a target compound. In the extraction process, a solute transferred from one phase to another to separate it from unreacted starting materials or impurities.

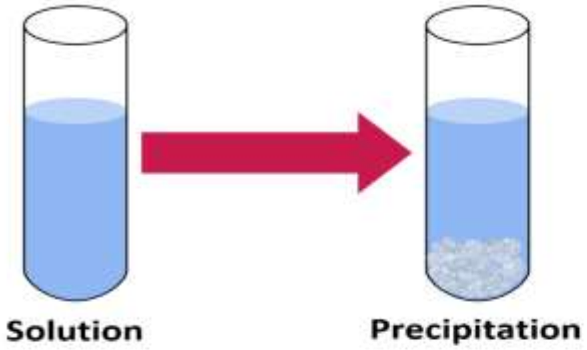
Making tea is a good example of extraction. Water placed in contact with tea bags and the "tea" extracted from the tealeaves into the water. This works because the "tea" is soluble in water but the leaves are not.

Precipitation

This is a method used through formation of a separable solid substance from a solution, either by converting the substance into an insoluble form or by changing the composition of the solvent to diminish the solubility.

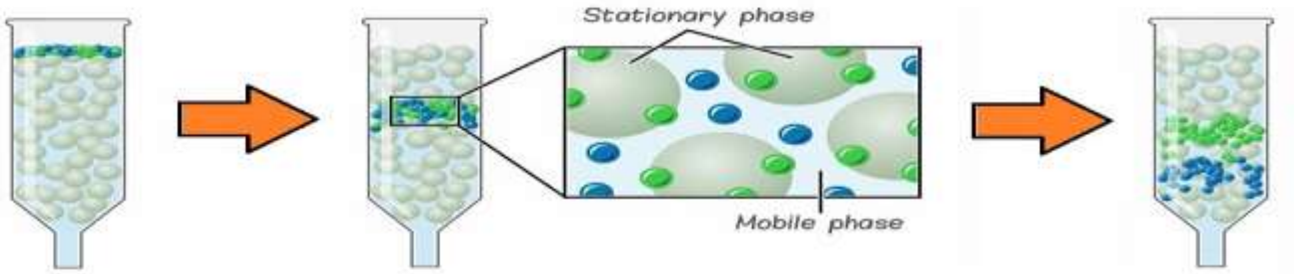
This method can be used to **detect the presence** or **remove** metal ions from aqueous solutions: for silver ions present in a solution of a soluble salt, such as silver nitrate, are precipitated by addition of chloride ions, provided,

For example, by a solution of sodium chloride; the chloride ions and the silver ions combine to form silver chloride, a compound that is not soluble in water



Chromatography

In chemical analysis, Chromatography is a laboratory technique for the separation of a mixture. The mixture is dissolved in a fluid called the **mobile phase**, which carries it through a system on which a material called the **stationary phase** is fixed. The mobile phase may be either a liquid or a gas, while the stationary phase is either a solid or a liquid.



Chromatography has numerous applications in **biological** and **chemical** fields. It is widely used in **biochemical** research for the separation and identification of chemical compounds of biological origin. In the petroleum industry, the technique employed to analyze complex mixtures of hydrocarbons.

Spectroscopy

This method show the presence of different **atoms** or **functiona**l **group** by the relationship that exists between the appearance of a spectrum and the structure, concentration and environment of the sample. The existence of any compounds goes with the pick formed after the absorption and emission of radiation. Spectrometric methods often used for pesticide analysis in formulations.

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **organic and inorganic qualitative analysis** within groups
- ✓ Let the trainees form a group of four or six and discuss on qualitative method of analysis and factor considered.

Practical learning Activity

- ✓ In-group of four trainees perform and explain the extraction of tea from tealeaves.

Points to Remember (Take home message)

- ✓ Analytical chemistry deals **with identification** of **composition** and **structure of matter**.
- ✓ The qualitative analysis determines the presence or absence of a particular atom or compound.
- ✓ The qualitative method of analysis measure the **change in;** color, odor, reactivity, radioactivity, precipitation, melting and boiling point.

1.1.1.Factors/criteria considered for qualitative analysis

There are numerous factors to consider while conducting qualitative analysis of any chemical but the crucial ones are **Color, Odor**, **melting and boiling point, solubility, radioactivity** and **reactivity**

Color:

The color of chemicals is a physical property of matter that in most cases comes from the excitation of electrons due to an absorption of energy performed by the chemical. Different chemical differentiated by their color. What the eye sees is not the color absorbed, but the complementary color from the removal of the absorbed wavelengths.

An odor:

An odor primarily originates from a compound volatilizing at ambient temperature and thus reaching the nose. However, the vapor pressure value is not sufficient to predict whether a compound is odorant or not. For example, humans, on the one hand, can smell NO_2 but not CO_2. Odorant molecules are not limited to carbon-containing compounds, as both organic and inorganic molecules may have a smell.

For example, ammonia (NH_3) is an inorganic compound that has a distinctive fishy scent; elemental chlorine gas (Cl_2) has an acrid smell. Hydrogen sulfide (H_2S) is another inorganic odorant with a rotten egg scent.

Odorant compounds that have the same functional group seem to have similar odors, as esters have a fruity and floral smell.

Melting point and Boiling Point:

The melting points is the temperature at which a solid change into a liquid. **The boiling point** of a substance is the temperature at which the vapor pressure of the liquid is equal to the surrounding atmospheric pressure thus facilitating transition of the material between gaseous and liquid phases. At its melting point, the disruptive vibrations of the particles of the solid overcome the attractive forces operating within the solid.so this could be factor to consider while conducting analytical analysis since different chemical have different boiling points

Solubility:

This is the ability of a solid, liquid, or gaseous chemical substance *(referred to as the solute)* to dissolve in solvent *(usually a liquid)* and form a solution. This can distinguish different chemicals since organic compounds are insoluble in water but soluble in organic solvents while inorganic compounds do the opposite.

Radioactivity/ reactivity:

Chemical substance differs in way of their reactivity. Some react with a substance that cannot react with others.

The radioactivity refers to natural process by which some atoms spontaneously disintegrate, emitting both particles and energy as they transform into different, more stable atoms. The ability to emit different radiation can distinguish different atoms.

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **how can color, odor, melting and boiling point can differentiate different chemical** within groups
- ✓ Let the trainees form a group of four or six and discuss on distinguishing chemical based on their reactivity or radioactivity.

Practical learning Activity

- ✓ Trainees in group of four perform the test of solubility of table salt(NaCl) vs limestone ($CaCO_3$).

Points to Remember (Take home message)

- ✓ The factor to consider for qualitative analysis are **Color, Odor**, **melting and boiling point, solubility, radioactivity** and **reactivity.**
- ✓ We can distinguish different based on the factors for qualitative analysis.

Learning out come 1.1: formative assessment

Written assessment

Q1. The following are the qualitative method of analysis except

a) Flame tests b) distillation c) titration d) Extraction e) Precipitation

Q2. Explain clearly how reactivity can be used to distinguish different substances.

Q3. Differentiate organic and inorganic qualitative alalysis.

Practical assessment

Take two beaker each filled with 100 ml and add 30 g of table salt and 40g of limestone and discuss the result obtained.

Learning outcome 1.2. Explicate quantitative analysis

Duration: 4 hrs

Learning outcome 1.2 objectives:

By the end of the learning outcome, the trainees will be able to:

1. Explicate properly chemical quantitative analysis according to the analysis methods

2. Describe clearly factors/criteria considered for quantitative analysis.

3. Differentiate unmistakeably physical and chemical quantitative analysis.

Resources

Equipment	**Tools**	**Materials**
✓ Video ✓ Projector ✓ Computer ✓ Books ✓ Internet	✓ Pens/Pencils ✓ Notebook ✓ Papers ✓ Marker ✓ White/ Chalk ✓ Boards ✓ Chalks	✓ Test-tube ✓ Beaker ✓ Conical flask ✓ Measuring cylinder ✓ Washing bottle ✓ Funnel ✓ Retort stand ✓ Burette ✓ Pipette ✓ Analytical balance ✓ Acid and base ✓ Table salt

Advance preparation:

- Prepare all material needed and describe their brief uses
- Weigh the NaCl sample and dissolve it into water

Quantitative chemical analysis is a branch of chemistry that deals with the determination of the amount (mass or volume) or percentage of one or more constituents of a sample.

Mass is a measure of the amount of matter in an object. Mass is usually measured in grams (g) or kilograms (kg).

Volume is the space occupied by different substances. We use it to determine the quantity of liquid or gas substances in a given sample.

1.2.1. Quantitative methods

A variety of methods employed for quantitative analyses, which fall into **chemical** or **physical**, depending upon which properties utilized.

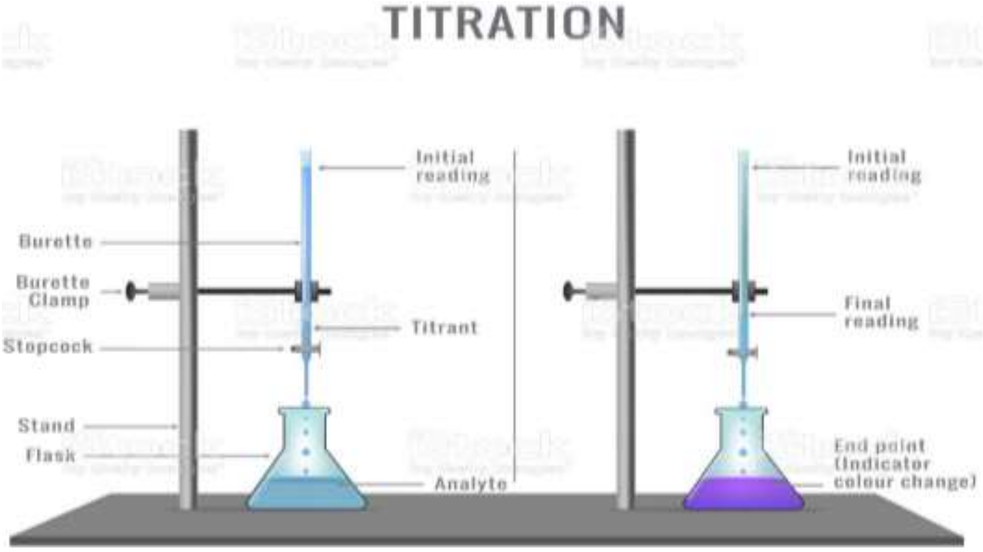
Chemical methods

Chemical methods depend upon such reactions as precipitation, neutralization, oxidation, or, in general, the formation of a new compound. The major types of strictly chemical methods known as **gravimetric analysis and volumetric, or titrimetric, analysis** and **combustion**.

a. Titration:

Titration (also known as titrimetric or volumetric analysis) is a common laboratory method of quantitative chemical analysis to determine the concentration of an identified **analyte** (analysed substance).

A reagent, termed the titrant is prepared as a standard solution of known concentration and volume. The titrant reacts with a solution of analyte (which may also be termed the titrand) to determine the analyte's concentration. The volume of titrant that reacted with the analyte is termed the titration volume.



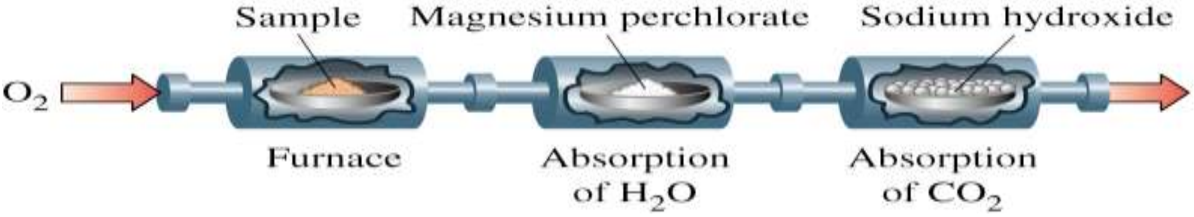
b. Gravimetric analysis,

Gravimetric analysis describes a set of methods used in analytical chemistry for the quantitative determination of an analyte (the ion being analysed) based on its mass. The principle of this type of analysis is that once an ion's mass has been determined as a unique compound, that known measurement can then be used to determine the same analyte's mass in a mixture, as long as the relative quantities of the other constituents are known.

The four main types of this method of analysis are *precipitation, volatilization, electro-analytical and miscellaneous physical method.*

c. Combustion:

This is a type of quantitative analysis used to determine the empirical formula of an unknown organic compound consisting of carbon, hydrogen and oxygen. The combustion analysis involves burning a sample of known mass in excess oxygen. It then passes through H_2O and CO_2 absorbers that collect the hydrogen (in the form of H_2O) and carbon (in the form of CO_2) that were in the original sample. Since we know the mass percent of hydrogen in water (2.01/18.01 or 11.2%) and the mass percent of carbon in carbon dioxide (12.01/44.01 or 27.3%) we can identify their masses from the water and carbon dioxide produced. Once those we know masses, the mass of the oxygen can be determined by subtracting the mass of the carbon and hydrogen from the original sample mass. This helps us determine the empirical formula.



Physical methods

This involves the measurement of some physical property such as **mass spectroscopy,** density, refractive index, absorption or polarization of light, electromotive force, magnetic susceptibility, and numerous others.

Mass spectrometry (MS) is an analytical technique used to measure the mass-to-charge ratio of ions. In a typical MS procedure, a sample, which may be solid, liquid, or gaseous, ionized, for example by bombarding it with a beam of electrons. The break some of the sample's molecules into positively charged fragments or simply become positively charged without fragmenting. The ions (fragments) separated according to their mass-to-charge ratio, for example by accelerating them and subjecting them to an electric or magnetic field: ions of the same mass-to-charge ratio will undergo the same amount of deflection. The ions detected by a mechanism capable of detecting charged particles, such as an electron multiplier. Spectra of signal intensity of detected ions as a function of the mass-to-charge ratio displayed as result. The atoms or molecules in the sample identified by correlating known masses (e.g. an entire molecule) to the identified masses or through a characteristic fragmentation pattern, Mass spectrometry is used in many different fields and is applied to pure samples as well as complex mixtures.

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **gravimetric analysis** within groups
- ✓ Let the trainees discuss in pair about the combustion as a method of quantitative analysis.

Practical learning Activity

- ✓ In-group of four trainees perform and explain acid base titration as leant in level 3.

Points to Remember (Take home message)

- ✓ The quantitative chemical analysis deals with determination of amount of substance present in a sample.
- ✓ The quantitative methods include chemical methods and physical methods
- ✓ Chemical method include gravimetric analysis, titration and combustion
- ✓ Physical methods involve the measurement of physical properties such as mass spectroscopy

1.2.1.Factors considered for quantitative analysis

Numerous factors could help to conduct quantitative analysis effectively. The most common factors include; *density, refractive index, absorption and polarization of light, electric and magnetic field.*

a) **Density** is a physical property that refer to mass-to volume ratio that measured for all substances, solids, liquids and gasses. For solids and liquids, density often reported using the units of g/cm^3. Densities of gasses, which are significantly lower than the densities of solids and liquids, are often given using units grams/liter (g/L)

$$d = \frac{mass}{volume}$$

b) **Refractive index:** is a ratio of the speed of light in a medium relative to its speed in a vacuum. This change in speed from one medium to another is what causes light rays to bend. This is because as light travels through another medium other than a vacuum, the atoms of that medium constantly absorb and reemit the particles of light, slowing down the speed light travels at.

c) **Absorption and light polarization:** different chemicals absorb different radiation at a given wavelength so they may be distinguished for their **absorption. The light polarization used** distinguish between enantiomers that had similar chemical and physical properties. One enantiomer will rotate polarized light in a clockwise direction, termed dextrorotatory or (+), and its mirror-image partner in a counter-clockwise manner, termed levorotatory or (–).

d) **Electric or magnetic fields**

An electromagnetic field (also EM field or EMF) is a classical (i.e. non-quantum) field produced by accelerating electric charges. The electromagnetic field propagates at the speed of light.

The field viewed as the combination of an electric field and a magnetic field. The electric field produced by stationary charges, and the magnetic field by moving charges (currents); these two are often described as the sources of the field.

Theoretical learning Activity

✓ Ask trainees to brainstorm about **on different between absorption of light and light polarization** within groups

Practical learning Activity

✓ Trainees in pair work out on the calculation of density of Bromine if 14.0 mL of a bromine sample has a mass of 43.7 grams.

Points to Remember (Take home message)

✓ The factor to consider in quantitative analysis include; density, refractive index, absorption and polarization of light, electric and magnetic field.

Learning out come 1.2 : formative assessment

Written assessment

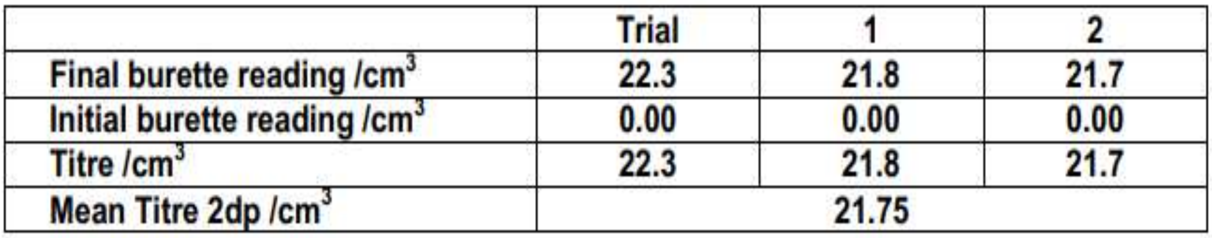
Q1. Answer by true or false

a) Volume of substance is equal to space it occupies
b) Chemical method of quantitative analysis depend on reactions
c) Titration involve the determining the empirical formula of substance.
d) Density is volume to mass ratio.

Q2. What volume of 0.75M HCl is required to neutralize 100ml of 0.01M Ca $(OH)_2$ solution

Practical assessment

In a titration, 0.01M sulphuric acid was added to 25cm3 of sodium hydroxide. Calculate the concentration of the sodium hydroxide given the following results:



	Trial	1	2
Final burette reading /cm^3	22.3	21.8	21.7
Initial burette reading /cm^3	0.00	0.00	0.00
Titre /cm^3	22.3	21.8	21.7
Mean Titre 2dp /cm^3	21.75		

Learning Outcome 1.3: Discuss the applications of qualitative and quantitative chemical analysis.

Duration: 2 hrs

Learning outcome 1.3 objectives:

By the end of the learning outcome, the trainees will be able to:

1. Discuss correctly the applications of qualitative and quantitative chemical analysis based on area of application.

Resources

Equipment	**Tools**	**Materials**
✓ Video ✓ Projector ✓ Computer ✓ Books ✓ Internet	✓ Pens/Pencils ✓ Notebook ✓ Papers ✓ Marker ✓ White/ Chalk ✓ Boards ✓ Chalks ✓ Pharmaceutical drug ✓ Processed food or drinks	✓ Test-tube ✓ Beaker ✓ Audio-visual

CONTENT

Qualitative and quantitative analysis have a wide use in determining the measure of chemical in unknown sample. Their found uses in food and pharmaceutical analysis, mining and petrochemical analysis and material characterization.

i. Pharmaceutical analysis

The qualitative and quantitative involves **raw material control** and **pharmaceutical finished products control**

This done through a series of process for identification, determination, quantification and purification of a substance, separation of the components of a solution or mixture, or determination of structure of chemical compounds.

ii. **Food analysis:** qualitative and quantitative analysis are widely found application in food science through; **Presence of contaminant control and Food production control.** This done through the study of the chemical composition of foods and the properties of their constituents helps to define their nutritional and commodity values. Furthermore, it allows for evaluation of the chemical modifications that the constituents of the food undergo following the treatments (Food Technology) to which they are subjected.

iii. **Mining analysis:** the qualitative and quantitative analysis are used in **radioactive control** and **control of content**

Radioactivity control on a mine operation is often necessary to determine the initial state of radiation. Some mining operations that involve radioactive materials (uranium sites, thorium, radon ...). On other hand, the **content control** used to identify the presence and quality of different chemical mines and impurities.

iv. **Petrochemical analysis:** the qualitative and quantitative analysis are widely used to determine the structure, composition and functional group present in petrochemical and their derivatives. Through this, we would be able to; **control petrol quality and control of petrochemical products components.**

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **the application of qualitative and quantitative analysis in mining and petrochemical analysis** within groups
- ✓ Let the trainees discuss in pair about the combustion as a method of quantitative analysis.

Practical learning Activity

- ✓ In-group of four trainees identify and explain the application of qualitative and quantitative analysis in pharmaceutical and food analysis.

Points to Remember (Take home message)

- ✓ Qualitative and quantitative analysis have a wide use in determining the measure of chemical in unknown sample.
- ✓ Their found uses in food and pharmaceutical analysis, mining and petrochemical analysis and material characterization.

Learning out come 1.3 : formative assessment

Written assessment

Q1. Describe the application of qualitative analysis in mining sector

Q2. In petrochemical industry the operator, determine the following information; the melting and boiling point, functional group, structure and types of bond. How does this be related to qualitative and quantitative analysis?

Practical assessment

Take among the following manufactured product and sort the information on label into qualitative and quantitative analysis.

a) Teabag b) yoghurt c) processed milk d) or any other available manufactured product

Learning Unit 2: Discuss solubility

STRUCTURE OF LEARNING UNIT

Learning outcomes:

- **2.1. Identify factors affecting solubility**
- **2.2. Explain solubility product**
- **2.3. Calculation of solubility product.**

Learning outcome 2.1 Identify factors affecting solubility

Duration: 4 hrs

Learning out come 2.1 Objectives:

By the end of the learning outcome, the trainees will be able to:

1. Identify properly the factors that affect solubility according to the nature of solution.

2. Explain clearly solubility and its rule.

3. Differentiate unmistakeably soluble and insoluble salts

Resources

Equipment	Tools	Materials

- ✓ Video
- ✓ Projector
- ✓ Computer
- ✓ Books
- ✓ Internet

- ✓ Pens/Pencils
- ✓ Notebook
- ✓ Papers
- ✓ Marker
- ✓ White/ Chalk
- ✓ Boards
- ✓ Chalks
- ✓

- ✓ Test-tube
- ✓ Beaker
- ✓ Bunsen burner
- ✓ Washing bottle
- ✓ Funnel
- ✓ Burette
- ✓ Pipette
- ✓ water
- ✓ Table salt
- ✓ Limestone
- ✓ Carbonated drinks

Advance preparation:

- ➢ Prepare all material needed and describe their brief uses
- ➢ Mix NaCl with a little amount of water and let trainees discover about solubility
- ➢ Mix limestone($CaCO_3$) with water and ask trainees to compare with what happen to the solution of salt and water
- ➢ Heat portion of NaCl and water solution with undissolved NaCl and show trainees then ask about the change occur.

2.1.1. Definition of solubility and molar solubility

In chemistry, **solubility** is ability of a substance (**solute)** to dissolve in solvent to form a solution. Insolubility is the opposite property, the inability of the solute to dissolve in solvent. ***A solution made by a solute dissolved in a solvent.***

Solubility is the maximum amount of a substance that will dissolve in a given amount of solvent at a specific temperature.

Solubility is most fundamentally expressed in molar (**mol** $\mathbf{l^{-1}}$ of solution) or molal (**mol** $\mathbf{kg^{-1}}$ of water) units. Certain substances are soluble in all proportions with a given solvent, such as organic solvent in water (i.e. ethanol). This property known as miscible.

Molar solubility expressed as the number of moles of a solute dissolved per litter of solution before the solution becomes saturated.

i. Soluble and insoluble salts

Soluble salts can dissolve in water at room temperature, whereas **insoluble salts** cannot dissolve in water at room temperature.

Sparingly soluble salts are those salts whose solubility is very low.

Most ionic salts are soluble in water while some are insoluble.

Specific examples of soluble salts include:

- All Nitrates,

- All Carbonates except calcium carbonate and silver carbonate

- All Chlorides except Lead Chloride.

- Sodium, Potassium, and Ammonium Sulphate are also soluble, the rest of the sulphate are insoluble. Soluble substances dissolve by forming free ions in solution; this forms a homogenous mixture.

ii. Solubility Rules

The following are the solubility rules for common ionic solids. If there two rules appear to contradict each other, the preceding rule takes precedence.

- ✓ **Salts containing Group I elements** (Li+, Na+, K+, Cs+, Rb+) **are soluble** . There are few exceptions to this rule. Salts containing the ammonium ion (NH4+) are also soluble.
- ✓ **Salts containing nitrate** ion (NO3-) are generally soluble.
- ✓ **Salts containing Cl -, Br -, or I - are generally soluble**. Important exceptions to this rule are halide salts of Ag^+, Pb^{2+}, and $(Hg_2)^{2+}$. Thus, AgCl, $PbBr_2$, and Hg_2Cl_2 are insoluble.
- ✓ **Most silver salts are insoluble**. $AgNO_3$ and $Ag(C_2H_3O_2)$ are common soluble salts of silver; virtually all others are insoluble.
- ✓ **Most sulfate salts are soluble**. Important exceptions to this rule include $CaSO_4$, $BaSO_4$, $PbSO_4$, Ag_2SO_4 and $SrSO_4$.
- ✓ **Most hydroxide salts** are only slightly soluble. Hydroxide salts of Group I elements are soluble. Hydroxide salts of Group II elements (Ca, Sr, and Ba) are slightly soluble. Hydroxide salts of transition metals and Al^{3+} are insoluble. Thus, $Fe(OH)_3$, $Al(OH)_3$, $Co(OH)_2$ are not soluble.
- ✓ **Most sulfides of transition** metals are insoluble, including CdS, FeS, ZnS, and Ag_2S. Arsenic, antimony, bismuth, and lead sulfides are also insoluble.
- ✓ **Carbonates are frequently insoluble**. Group II carbonates ($CaCO_3$, $SrCO_3$, and $BaCO_3$) are insoluble, as are $FeCO_3$ and $PbCO_3$.

- ✓ **Chromates are frequently insoluble**. Examples include PbCrO4 and BaCrO4.
- ✓ **Phosphates** such as $Ca_3(PO_4)_2$ and Ag_3PO_4 are frequently insoluble.
- ✓ **Fluorides** such as BaF_2, MgF_2, and PbF_2 are frequently insoluble.

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **soluble** and **insoluble salts** within groups
- ✓ Let the trainees form a group of four or six and discuss on solubility and rules involved.

Practical learning Activity

- ✓ In-group of four trainees mix NaCl with water and on other hand mix lime with water and link the result with solubility of salts.

Points to Remember (Take home message)

In chemistry, **solubility** is ability of a substance (**solute)** to dissolve in solvent to form a solution. *A solution made by a solute dissolved in a solvent.*

Soluble salts can dissolve in water at room temperature, whereas **insoluble salts** cannot dissolve in water at room temperature. **Sparingly soluble salts** are those salts whose solubility is very low.

2.1.2. Factors affecting solubility of salts

The factors affecting solubility of salts include; Temperature, pressure, polarity, molecular size of solute:

i. Temperature

Solubility ***increases with temperature***. It is the case for most of the solvents. The situation is though different for gases. With increase of the temperature, they became less soluble in each other and in water, but more soluble in organic solvents.

ii. Pressure

For majority of solid and liquid solutes, pressure does not affect solubility.

As for gasses, the **Henry's law** states that **solubility of gas is directly proportional to the pressure of this gas**. This is mathematically presented as **$p = kc$,** where **k** is a **temperature dependent constant** for a gas. A good proof of Henry's law observed when opening a bottle of carbonated drink. When we decrease the pressure in a bottle, the gas dissolved in the drink bubbles out of it.

iii. Polarity

In most cases, solutes dissolve in solvents that have a similar polarity. Chemists use a popular **aphorism** to describe this feature of solutes and solvents: ***"Like dissolves like".*** Non-polar solutes do not dissolve in polar solvents and the other

iv. Molecular size of solute

The larger the molecules of the solute are, the larger is their molecular weight and their size. **It is more difficult it is for solvent molecules to surround bigger molecules**. If all of the above-mentioned factors excluded, a general rule found that larger particles are generally less soluble. If the pressure and temperature are the same than out of two solutes of the same polarity, the one with smaller particles is usually more soluble.

Theoretical learning Activity

✓ Ask trainees to brainstorm about **how polarity and pressure affect solubility of salts** within groups

Practical learning Activity

✓ Trainees in group of four dissolves 40g of NaCl in 200ml of water then heat the solution

Points to Remember (Take home message)

The factor affecting solubility of salts are temperature, pressure, polarity and molecular size of solute

✓ *Solubility **increases with temperature***
✓ For majority of solid and liquid solutes, pressure does not affect solubility but as pressure increases the solubility of gases decreases.
✓ Solutes dissolve in solvents that have a similar polarity.

Learning out come 2.2: formative assessment

Written assessment

Complete the following passage with the correct term

At room temperature……………… dissolve in water while………..can’t be dissolved if the solubility of slightly soluble salt is low we can change different factor to enhance it among these include…………. Which is direct proportional to solubility of liquid and solid while………….. is indirectly proportional

Practical assessment

Take two beaker and fill 10ml in each then add 40g of table salt. Heat one of two beaker and explain the difference.

Learning outcome 2.2. Explain the solubility product

Duration: 6 hrs

Learning out come 2.2 objectives:

By the end of the learning outcome, the trainees will be able to:

1. Explain correctly the solubility product based on the nature of salt.
2. Describe clearly types of solutions according to their solubility
3. Dissociate properly a sparingly soluble salt and express its solubility product.

Resources

Equipment	Tools	Materials
✓ Video ✓ Projector ✓ Computer ✓ Books ✓ Internet	✓ Pens/Pencils ✓ Notebook ✓ Papers ✓ Marker ✓ White/ Chalk ✓ Boards ✓ Chalks ✓ Table salt	✓ Test-tube ✓ Beaker ✓ Conical flask ✓ Measuring cylinder ✓ Washing bottle ✓ Funnel ✓ Analytical balance

Advance preparation:

- Take two beaker each containing 100ml of water
- Add 30 g to the first beaker and 40 g of NaCl to the second and let trainees identify the different between saturated and unsaturated solution.

CONTENT

The solubility product is the equilibrium constant expressed in terms of concentrations of the ions produced from a sparingly soluble solid in contact with a saturated solution.

The equilibrium constant for the system is given the symbol **(Ksp)** where the **sp** added to **k** tell us that this equilibrium constant is a **solubility product**. Equilibrium is set up between the undissolved solid and the hydrated ions in solution. A precipitate will appear if the solubility product exceeded for the system containing silver chloride.

2.2.1. Types of solutions

Regarding to their solubility solution classified as; saturated, unsaturated and supersaturated.

✓ **Unsaturated solution**: A solution that contains less solute that can dissolve at a given temperature.

✓ **Saturated solution**: A solution that contains as much solute as can dissolve in the given solvent at a given temperature.

✓ **Super-saturated solution:** A solution that contains the maximum amount of solute at an elevated temperature.

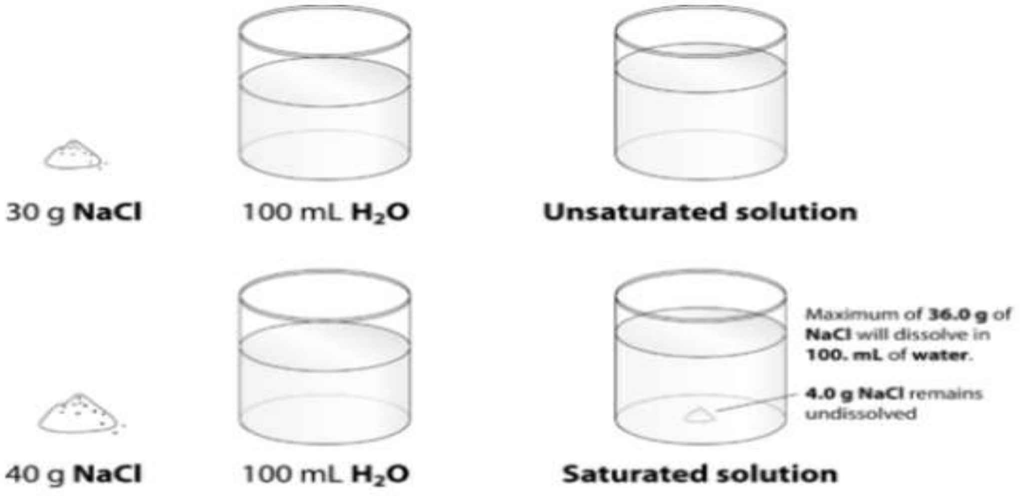


Figure 1. When 30.0 g of NaCl is added to 100 ml of water, it all dissolves, forming an unsaturated solution. When 40.0 g is added, 36.0 g dissolves and 4.0 g remains undissolved, forming a saturated solution. From the CK-12 Foundation – Christopher Auyeung.

2.2.2. Dissociation of sparingly soluble salts in water

A sparingly soluble solute is one, which slightly dissolves, in a given solvent. It partly dissociates into component ions.

The main examples of sparingly soluble salts include; **Barium sulphate, $BaSO_4$**; and Silver Chloride **AgCl.**

Both **barium sulphate** and **silver chloride** are precipitates formed because of mixing aqueous solution of silver nitrate and sodium chloride; the precipitated compound shown by the following equation

$$AgNO_3\ (aq) + NaCl\ (aq) \rightarrow AgCl\ (s) + NaNO_3\ (aq)$$

In addition, aqueous solution of barium nitrate and copper (II) sulphate.

$$Ba(NO_3)_2\ (aq) + CuSO_4\ (aq) \rightarrow BaSO_4\ (s) + Cu(NO_3)_2\ (aq)$$

The formation of a precipitate described by the equilibrium;

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

$$\text{And } Ba^{2+}\ (aq) + SO_4^{2-}\ (aq) \leftrightarrow BaSO_4\ (s)$$

Biological processes in our bodies also give a specific example of internal equilibrium system controlled by hormones, **example** *is Calcium phosphate $Ca_3(PO_4)_2$ is a constituent of bone that is an insoluble protein This substance is in equilibrium with its constituent ions in blood.* Its dissociation given by the equation below.

$$Ca_3(PO4)_2\ (s) \leftrightarrow 3Ca^{2+}\ (aq) + 2PO_4^{3-}\ (aq)$$

This equilibrium is well over to the left, so bones do not dissolve. When the balance goes wrong, a person may excrete dissolved bones in urine (Hyperparathyroidism).

Dissociation equation

Dissociation is the separation of ions that occurs when a solid ionic compound dissolves. It is important to be able to write dissociation equations. Simply undo the crisscross method that you learned when writing chemical formulas of ionic compounds. The subscripts for the ions in the chemical formulas become the coefficients of the respective ions on the product side of the equation. Shown below are dissociation equations for NaCl, $Ca(NO_3)_2$, and $(NH_4)_3PO_4$.

$$\mathbf{NaCl_{(s)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}}$$

$$\mathbf{Ca(NO_3)_{2(aq)} \longrightarrow Ca^{2+}_{(aq)} + 2NO_3^-{}_{(aq)}}$$

$$\mathbf{(NH_4)_3PO_{4(s)} \longrightarrow 3NH_4^+{}_{(aq)} + PO_4^{3-}{}_{(aq)}}$$

Expression of solubility product (Ksp)

The solubility product constant, **Ksp** , is the equilibrium constant for a solid substance dissolving in an aqueous solution. ***It represents the level at***

which a solute dissolves in solution. The more soluble a substance is, the higher the **Ksp** value it has.

Consider the general dissolution reaction below (in aqueous solutions):

$$aA(s) \rightleftharpoons cC(aq) + dD(aq)$$

To solve for the Ksp it is necessary to take the molarities or concentrations of the products (**cC** and **dD**) and multiply them. If there are coefficients in front of any of the products, it is necessary to raise the product to that coefficient **power** (and multiply the concentration by that coefficient). This shown below:

$$K_{sp} = [C]^c[D]^d$$

Note that the reactant, aA, is not included in the Ksp equation. Solids are not included when calculating equilibrium constant expressions, because their concentrations do not change the expression; any change in their concentrations are insignificant, and therefore omitted. Hence, Ksp represents the maximum extent that a solid that can dissolved in solution.

Examples of expression of Ksp for some compounds

(i) $AgCl_{(s)} \longleftrightarrow Ag^{+}_{(aq)} + Cl^{-}_{(aq)}$

Ksp of AgCl = $[Ag^{+}]\ [Cl^{-}]$

There is no denominator in the expression for the solubility product because the denominator is a pure solid and pure solids and liquids are never included in equilibrium constant expression.

A solubility product is generally a special example of a heterogeneous equilibrium constant. It involves more than one phase; that is solids in contact with liquids.

(ii) Solubility product for lead II sulphate ($PbSO_4$)

Suppose you made a saturated solution of lead (II) sulphate PbSO4 by shaking the solid with water until no more would dissolve. Lead (II) Sulphate is almost insoluble in water and a white solid observed suspended in the water; after sometime the solid will settle to the bottom.

Lead (II) Sulphate is an ionic compound and some Lead (II) ions (Pb2+) and Sulphate ions (SO4^{2-}) will break away from the lattice and go into solution; others, which had broken off previously, will return to attach themselves to the solid; this results into an equilibrium as follows.

$PbSO_{4(s)} \leftrightarrow Pb^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$ $\qquad$ $Ksp = [Pb^{2+}][SO_4^{2-}]$

(iii) Solubility product for lead II iodide (PbI_2)

$PbI_{2(s)} \leftrightarrow Pb^{2+}_{(aq)} + 2I^{-}_{(aq)}$

$Ksp = [Pb^{2+}][2I^{-}]^2$

iv) Solubility product for MgF_2

The relevant equilibrium is

$$MgF_{2(s)} \rightleftharpoons Mg^{2+}_{(aq)} + 2F^{-}_{(aq)}$$

Therefore, the associated equilibrium constant is

$$K_{sp} = [Mg^{2+}][F^{-}]^2$$

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **solubility product and its expression** within groups
- ✓ Let the trainees discuss in pair about the dissociation of sparingly soluble salt.

Practical learning Activity

- ✓ In-group of four trainees mix NaCl with 100ml water in three beaker according to the following ratios; first beaker add 30g, 40g and 60g in second and third beaker respectively and relate their findings with type of solution.
- ✓ In pair trainees workout the dissociation AgI,$CaSO_4$ and Ag_2CO_3

Points to Remember (Take home message)

- ✓ Regarding to their solubility solution fall into three classes; saturated, unsaturated and supersaturated.
- ✓ **Unsaturated solution** contains less solute that can dissolve while **saturated solution** contains, as much solute as can dissolve in the given solvent at a given temperature is a saturated solution. A solution that contains the maximum amount of solute at an elevated temperature is a **supersaturated**.
- ✓ Dissociation is the separation of ions that occurs when a solid ionic compound dissolves.

Learning out come 2.2 : formative assessment

Written assessment

Express the solubility product (Ksp) of the following sparingly soluble salts.

a) AgI(s) b) $CaSO_{4(s)}$ c) $Ag_2CO_{3(s)}$ d) Li_3PO_4

Practical assessment

Take three beaker and fill 10ml in each then add 30g, 40g and 60g of table salt in first, second and third beaker respectively. Heat the second and the third beaker at 45^0C and explain how types of solution having.

Learning Outcome 2.3: Calculation of solubility product

Duration: 5 hrs

Learning outcome 2.3 objectives:

By the end of the learning outcome, the trainees will be able to:

1. Explain clearly the relationship between solubility and solubility product.
2. Calculate correctly solubility product and solubility
3. Explicate properly the uses of solubility

Resources

Equipment	Tools	Materials
✓ Video ✓ Projector ✓ Computer ✓ Books ✓ Internet	✓ Pens/Pencils ✓ Notebook ✓ Papers ✓ Marker ✓ White/ Chalk ✓ Boards ✓ Chalks	✓ Test-tube ✓ Beaker ✓ Audio-visual

2.3.1. Relationship between solubility and solubility product

Solubility equilibrium refers to kind of equilibrium that exists in saturated solutions of sparingly soluble ionic salts. Solubility normally expressed in moldm^{-3} or (gdm^{-3}).

The term **solubility product** refers to the numerical value of the equilibrium constant for the equation that represents the substance dissolved in water.

i. Solubility (s) vs solubility product (Ksp)

The difference between solubility and solubility product is that *solubility describes the dissolution of a substance in a solvent* whereas the *solubility product describes the mathematical product of the dissolved ion concentrations raised to the power of their stoichiometric coefficients.*

ii. Formula of solubility and solubility product.

The solubility can be denoted by using**'s'** and solubility product is expressed by **Ksp**

The term solubility product constant suggests that Ksp related to the solubility of ionic solute .However, this does not remain that Ksp and molar solubility, molarity of solute in a saturated solution are equivalent .It means that one can determine Ksp, from molar solubility from Ksp.

Consider the following reaction:

$$A_mB_n\,(s) \rightleftharpoons mB^{n+}\,(aq) + nB^{m-}(aq)$$

The expression of solubility of product constant is given by

$$Ksp = [A^{n+}]^m[B^{m-}]^n = (mS)^m x (nS)^n$$

$$= m^m x n^n x S^{m+n}$$

$$\boxed{s = \sqrt[m+n]{\frac{Ksp}{m^m . n^n}}}$$

iii. Calculation of solubility(s) and solubility product (Ksp)

Calculations involving solubility product

In solubility equilibria calculations, usually expressed as grams of solute per litter of solution.

Molar solubility is the number of moles of solute per litter of solution.

Molar solubility, solubility and solubility product all refer to a saturated solution.

Worked examples:

1. The solubility of calcium carbonate $CaCO_3$, at 298K is 6.9×10^{-3} moldm^{-3}. Calculate the solubility product at this temperature.

Solution

$$CaCO_{3(s)} \leftrightarrow Ca^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

Key point

Every mole of calcium carbonate, which dissolves, gives 1 mole of calcium ions and 1 mole of carbonate ions; in solution; so 6.9×10^{-3} moles of calcium carbonate dissolves in 1dm^3 of solution, then there will be 6.9×10^{-3} moles of calcium carbonate ions and 6.9×10^{-3} moles of CO_3^{2-} ions in dm^3 of the solution.

$[Ca^{2+}]=6.9\times10^{-3}$ moldm^{-3}

$[CO_3^{2-}]=6.9\times10^{-3}$ moldm^{-3}

Ksp = $[Ca^{2+}][CO_3^{2-}]$ = (6.9×10^{-3} moldm$_3$)^2 **= 4.8×10-9mol^{2}dm^{-6}**

2. The solubility of calcium sulphate $CaSO_4$ at 298K is 0.67g/dm^3. Calculate the solubility product at this temperature. (O=16, S=32, Ca=40)

Solution:

$$CaSO_{4(s)} \leftrightarrow Ca^{2+}_{(aq)} + SO_4^{2-}{}_{(aq)}$$

Key point: number of moles = mass (g)/molar mass (gmol^{-1})

The concentration given in g/dm^3; Convert it to mol/dm^3

1 mole of $CaSO_4$ weighs: 40+32+ (16×4) =136g

0.67 corresponds to 0.67/136 = 4.93×10^{-3} mol/dm^3

The solubility of calcium sulphate is 4.93×10^{-3} mol/dm^3

Each mole of calcium sulphate that dissolves produce 1 mole of Ca^{2+} ions and 1 mole of **SO_4^{2-}** ions in solution.

$[Ca^{2+}]$ = 4.93×10^{-3} mol/dm^3

$[SO_4^{2-}]$ = 4.93×10^{-3} mol/dm^3

Ksp = $[Ca^{2+}][SO_4^{2-}]$ Ksp = $(4.93\times10^{-3})^2$ = **2.4×10^{-5} mol^{2}dm^{-6}**

3. The solubility of lead II chloride, PbCl2 is 0.016moldm3 at 298k. Calculate the solubility product at this temperature.

Solution

$PbCl_{2(s)} \longleftrightarrow Pb^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$

Key point

The ratio of the ions in the compound is **1:2;** each mole of **lead (II) chloride** produces**1mole** of **lead II**, and $[Pb^{2+}]$= 0.016 moldm^{-3}. However, each mole of lead (II) chloride produces **2 moles** of **chloride ions** in solution. **If 0.016 mol of lead (II) chloride dissolves, there will be twice this amount of chloride ions present.**

Then, $[Cl^-]$ = 0.016×2= **0.032 mol/dm^3**

Ksp = $[Pb^{2+}][Cl^-]^2$ = $0.016\times(0.032)^2$ = **1.6×10^{-5}mol^{3}dm^{-9}**

4. The solubility of calcium phosphate, $Ca_3(PO_4)_2$ is 7.7×10^{-4}g/dm^3 at 25^{0}c. Calculate the solubility product at this temperature. (O =16, P =31, Ca=40)

Solution

$Ca_3(PO_4)_{2(s)} \longleftrightarrow 3\ Ca^{2+}(aq) + 2PO_4^{3-}\ (aq)$

Key points:

i. Convert the concentration in **g/dm^3** to **mol/dm^3**

Number of moles = mass (g)/ molar mass (g)

1 mole of $Ca_3(PO_4)_2$ weighs **310g**.

Concentration in moldm^{-3} = $7.7\times10^{-4}/310$ = **2.48×10^{-6}mol/dm^3**

ii. Each **mole** of calcium phosphate that dissolves produces **3 moles** of calcium ions in solution and **2 moles** of phosphate ions.

$[Ca^{2+}]$= $3\times2.48\times10^{-6}$ = 7.44×10^{-6}mol/dm^3

$[PO_4^{3-}]$= $2\times2.48\times10^{-6}=4.96\times10^{-6}$ mol/dm^3

Ksp = $[Ca^{2+}]^3$ $[PO_4^{3-}]^2$ = $(7.44\times10^{-6})^3\times(4.96\times10-6)^2$ = 1.0×10^{-26}mol^{5}dm^{-15}.

Calculating solubility from solubility product

Examples

1. Calculate the solubility in mol/dm^3 of silver chloride, AgCl, at 298K if its solubility product is 1.8×10^{-10} mol^{2}dm^{-6}

Solution

$AgCl_{(s)} \longleftrightarrow Ag^+_{(aq)} + Cl^-_{(aq)}$

Key points

For every mole of silver chloride that dissolves, the solution will contain 1 mole of $Ag^+_{(aq)}$ and 1 mole of $Cl^-_{(aq)}$ so if **"s"** moles dissolved, the solution will contain **"s"** moles of each ion.

$[Ag^+]$= **s** moldm^{-3}

$[Cl^-]$= **s** moldm^{-3}

Ksp = $[Ag^+][Cl^-]$ hence **1.8×10^{-10} = s x s** and $S=\sqrt{1.8 \times 10^{-10}}$

2. Calculate the solubility in gdm-3 of chromium III hydroxide, $Cr(OH)_3$ at 25^{0}C if its solubility product is 1.0×10^{-33}mol^4 dm^{-12} (H=1, O=16,Cr=52)

Solution

$Cr(OH)_3$ (s) $\longleftrightarrow Cr^{3+}_{(aq)} + 3OH^-_{(aq)}$

Key points

Work out the solubility in moldm^{-3}

Number of moles = mass (g)/ molar mass (g)

1mole of $Cr(OH)_3$ produces **1 mole** of Cr^{3+}(aq) and **3 moles** of OH^- ions

$[Cr^{3+}]$= S moldm^{-3}

$[OH^-]$= 3S moldm^{-3}

Ksp = $[Cr^{3+}][OH^-]^3$ = 1.0×10^{-33}=**$S\times(3S)^3$**

S = $27S^4$= 1.0×10^{-33}

S= 2.47×10^{-9}moldm^{-3}

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **the relationship between solubility and solubility product** within groups
- ✓ Let the trainees express the solubility product of NaCl and $CaSO_4$ in pair.

Practical learning Activity

- ✓ In-group of four trainees calculate the molar solubility of $Sr_3(AsO_4)_2$ given its solubility product equal to 4.29×10^{-19}

Points to Remember (Take home message)

Consider the following reaction:

$$A_mB_n\,(s) \rightleftharpoons mB^{n+}\,(aq) + nB^{m-}(aq)$$

The expression of solubility of product constant is given by

$$Ksp = [A^{n+}]^m[B^{m-}]^n = (mS)^m x (nS)^n$$

$$= m^m x n^n x S^{m+n}$$

$$\boxed{s = \sqrt[m+n]{\frac{Ksp}{m^m . n^n}}}$$

2.3.2. Uses of solubility product

Some areas where solubility product is used:

i. Volumetric analysis:

The concentration of Chloride ions in a solution of soluble Chloride salt can be determined by titration with a standard solution of silver nitrate Potassium chromate is used as an indicator. A white precipitate of silver Chloride forms first due to lower solubility of silver Chloride, the end-point indicated by the formation of a red precipitate of silver chromate

This can be seen from the solubility product (Ksp) value of silver chloride and silver chromate. Ksp (Ag = 1.2×10^{-10} mol^2dm^{-6} Ksp (Ag_2CrO_4) = 2.4×10^{-12} mol^2dm^{-9} Low concertation of A^+ ions are needed to form a precipitate with chloride ions than chromate ions.

ii. Production of soap: saponification

Brine concentrated solution of sodium chloride (NaCI) is added to the mixture of fats and oils together with NaOH solution to precipitate out soap. Soap and sodium chloride are present in the form of ions.

Soap equilibrium: $C_{17}H_{35}COO^-Na^+_{(s)} \longleftrightarrow C_{17}H_{35}COO^-_{(aq)} + Na^+_{(aq)}$

When brine is introduced to the soap mixture, it introduces a common ion effect, which effects the equilibrium system in the backward direction. This is due to high concentration of sodium ions (Na^+) from sodium Chloride. As a result, the stearate ion ($C_{17}H_{35}COO^-$) combines with the excess sodium ions to form soap, which floats on top.

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **the use of solubility product in volumetric analysis** within group.

Practical learning Activity

- ✓ In-group of four trainees perform saponification and add brine to check common ion effect

Points to Remember (Take home message)

- ✓ The solubility product found use in volumetric analysis and production of soap

Learning outcome 2.3: formative assessment

Written assessment

Q1. Consider two compounds A and B where A has a solubility product of $3.3x10^{-3}$ while B has a solubility product of $4.4x10^{-7}$.Can we conclude that compound A has higher Molar solubility than B. Explain your answer?

Q2. Consider a compound with the formula L_3X_4 that dissolve to produce $L^{4+}$and X^{3-}ions in solution if the solubility product of this compound is $8.2x10^{-24}$. Calculate the molar solubility of the compound.

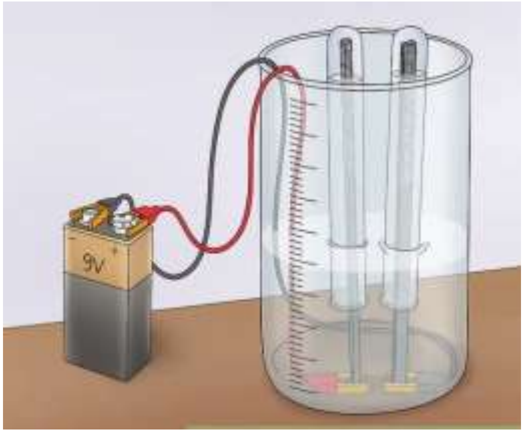
Practical assessment

Q1. Calculate the molar solubility of $Sr_3(AsO_4)_2$ given its solubility product equal 4.29×10^{-19}

Q2. Given the molar solubility of Ag_2CO_3 is equal to $1.27x10^{-4}$M. Calculate its solubility product.

Q3. The Ksp of $Mg(OH)_2$ is 1.8×10^{-11} Calculate the solubility of $Mg(OH)_2$ in pure water.

Learning Unit 3: Describe the electrochemical cell reactions



STRUCTURE OF LEARNING UNIT

Learning outcomes:

3.1. Explain electrolysis

3.2. Illustrate electrochemical cell.

3.3. Determine the electromotive force of the cell

Learning outcome 3.1 Explain electrolysis

Duration: 4 hrs

Learning outcome 3.1 objectives:
By the end of the learning outcome, the trainees will be able to:

1. Explain clearly the electrolysis according to Faraday's Law
2. Explicate correctly Components of electrolytic cells and working principles.
3. Describe properly the application of electrolysis.

Resources

Equipment	Tools	Materials

✓ Video ✓ Projector ✓ Computer ✓ Books ✓ Internet	✓ Pens/Pencils ✓ Notebook ✓ Papers ✓ Marker ✓ White/ Chalk ✓ Boards ✓ Chalks	✓ Test-tube ✓ Beaker ✓ Electrolyser ✓ Water ✓ salt

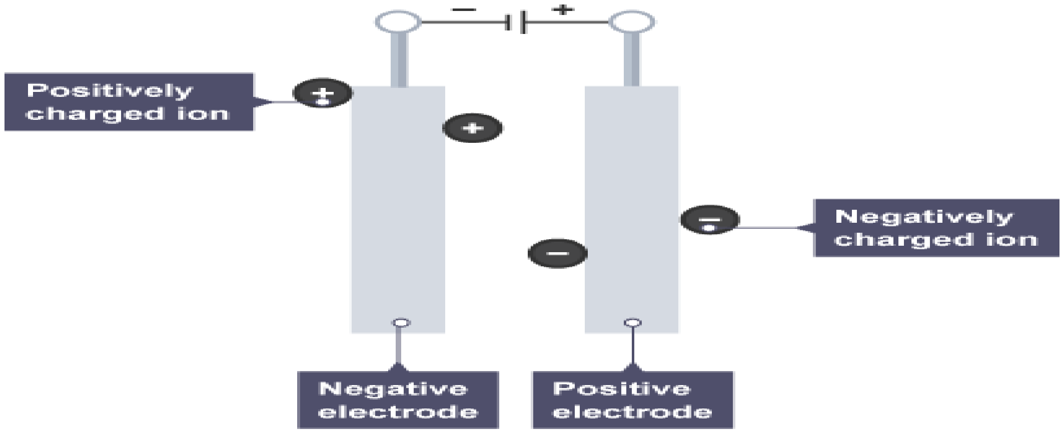
Advance preparation:

- Prepare all material needed and describe their brief uses
- Bring a set up for electrolysis and let trainees observe and explain their findings

CONTENT

Electrochemistry *is the study of chemical processes that cause electrons to move.* This movement of electrons called electricity, generated by movements of electrons from one element to another in a reaction known as an oxidation-reduction ("redox") reaction**.**

Electrolysis is the process by which ionic substances are decomposed (broken down) into simpler substances when an electric current passed through them.



This is what happens during electrolysis:

Electricity is the flow of electrons or ions. For electrolysis to work, the compound must contain ions. Covalent compounds cannot act as electrolytes because they contain neutral atoms.

3.1.1. Components of electrolytic cells

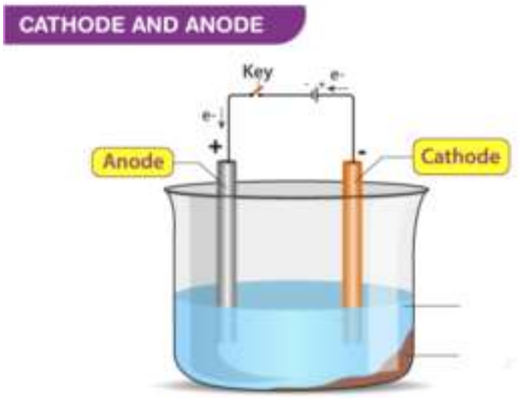
An electrolytic cell is an electrochemical cell that requires an external source of electrical energy (voltage applied between two electrodes) to drive a chemical reaction that would not otherwise occur.

There are two main components of electrolytic cells; **electrodes** and **electrolyte.**

1. **Electrodes:** are solids electric conductors that carry electric current into non-metallic solids, or liquids, or gases, or plasmas, or vacuums. Electrodes are typically good electric conductors, but they need not be metals. Electrode used in electrolysis are **anode** or **cathode**

The Anode is positive electrode that attract negative ion. It is a site for oxidation.

The Cathode is a negative electrode that attract positive ion. It is a site for reduction.



2. **The Electrolyte**: a substance that, in solution or when molten, ionizes and conducts electricity. When electric current passes through electrolyte ionize and its ion are transported toward cathode and anode of a cell.

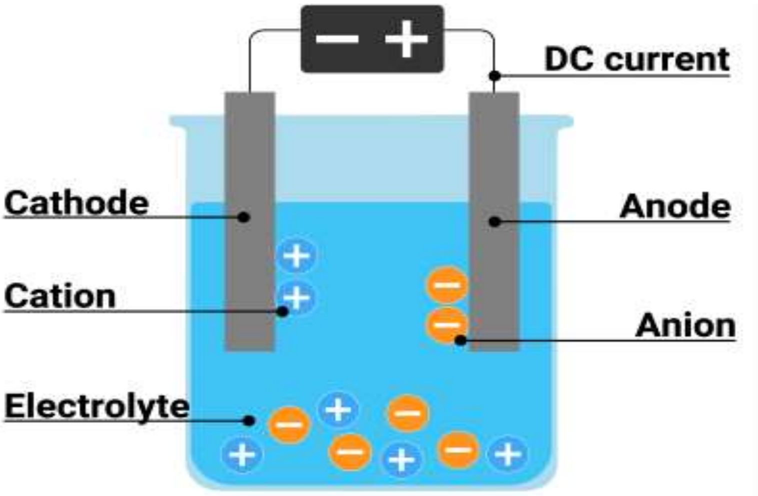
Electrolyte can either be strong or weak electrolyte depending on its level of ionization.

A strong electrolyte is a solution/solute that completely, or almost ***completely***, **ionizes or dissociates** in a solution. These ions are good conductors of electric current in the solution.

Strong electrolytes fall into three categories: **strong acids**, **strong bases**, and **salts.** (Salts also called ionic compounds)

A **weak electrolyte** is an electrolyte that does not completely dissociate in aqueous solution. *Weak electrolytes are only partially ionized.*

The weak electrolytes include weak acids and weak bases.



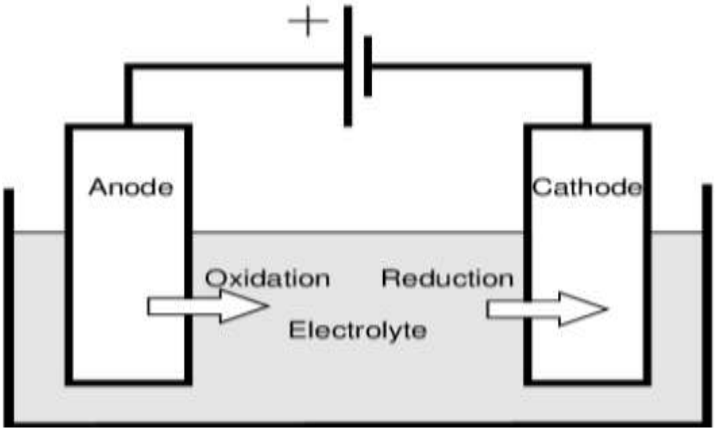
On passing current, **cations move to the cathode**, *take electrons from the cathode and discharge into the neutral atom.* The neutral atom, if solid, is deposited on the cathode and if gas, move upwards. **This is a reduction process** and the cation is, reduced at the cathode.

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.***

3.1.2. Electrolytic cell

An **electrolytic cell** is an electrochemical device that uses electrical energy to facilitate a non-spontaneous redox reaction. Electrolytic cells are electrochemical cells used for the electrolysis of certain compounds.

Diagram of electrochemical cell



Working Principle of an Electrolytic Cell

Electrochemical cells are devices based on the principle that when a chemical oxidation-reduction reaction occurs, electrons are transferred from one chemical species to another.

In the electrolytic cell, electrons in the form of an electric current are deliberately pumped through the chemicals in the section to force an electric current **oxidation-reduction** reaction to take place.

When an electric current passed into the circuit, the cathode becomes rich in electrons and develops a negative charge. The positively charged ion (**cations**) attracted towards the **negatively charged cathode**.

Simultaneously, the negatively charged ions attracted to the positively charged anode.

***(**To help you to remember, **Cathode** is the site of **reduction**, or, if you prefer, **CCC** = **C**athode **C**ollects **C**ations. **Anode** is the site of oxidation, or, **AAA** = **A**node **A**ttracts **A**nions.)*

Faraday's Law

The relationship between the mass of product formed at an electrode and the quantity of electricity passed through an electrolyte is given by Faraday's laws of electrolysis.

Michael Faraday (1791-1867) did the first work on electrolysis and formulated what known today as **Faraday's laws of electrolysis.**

These laws express the quantitative results of electrolysis. They assert that the amount (expressed in moles) of an element liberated during electrolysis depends upon:

1. The time of passing the steady current, **t**

2. The magnitude of the steady current passed, **I**

3. The charge of the ions

Faraday's first law

According to this law, "***The amount of substance liberated at an electrode is directly proportional to the quantity of electricity passed".***

Or $M \alpha Q$

Where **M** = amount of substance liberated in gram. **Q** = quantity of electricity passed in Coulomb. Since **Q = I.t**

Where **I** = Current in Ampere and **t** = time in seconds

Hence $M \alpha It \text{ or } M = Z x I x t = ZQ$

Where **Z** = proportionality constant, called **electrochemical equivalent**.

If **I = 1** ampere and **t = 1** second then **Z = M.** Therefore electrochemical equivalent defined as, *"The mass of substance (in grams) liberated at the electrode on passing current of **1** ampere for **1** second or on passing **1** coulomb of electricity is called electrochemical equivalent of the substance".*

$$Z = \frac{Atomic\ mass}{n\ x\ 96500} \quad [n = number\ of\ electrons\ exchanged]$$

1F = 96500 coulomb

So, 1 Faraday [96500 coulomb] of electricity will produce 1 gm equivalent of Ag, Cu and Al at cathode.

Faraday's second law

According to this law, ***"if same quantity of electricity is passed through different electrolytes, then the amount of substances liberated at the respective electrodes are in the ratio of their equivalent masses"***

Or

When the same quantity of electricity passes through solutions of different electrolytes, the amounts of the substances liberated at the electrodes are directly proportional to their chemical equivalents.

$$\frac{M1}{M2} = \frac{E1}{E2}$$

Suppose three cells containing HCI, $AgNO_3$ and $CuSO_4$ solutions are connected in series. If the same quantity of electricity is passed through these cells, then the amount of hydrogen, silver and copper deposited at the respective cathodes is in the ratio of their equivalent mass.

Hence, $$\frac{Amount\ of\ substance\ liberated}{Equivalent\ mass\ of\ the\ substance} = \frac{Mass\ of\ copper}{Equivalent\ mass\ of\ copper}$$

Equivalent mass.is the mass of a substance especially in grams that combines with or is chemically equivalent to eight grams of oxygen or one gram of hydrogen; the atomic or **molecular** Mass divided by the valence.

Example: Calculate the amount of electric charge in coulombs, which can deposit 5.2g of aluminium when a current passed through a solution of aluminium sulphate for some time.

Solution:

$Al^{3+} + 3e^- \longrightarrow Al_{(s)}$

3 moles of electrons are needed to deposit **1 mole** of aluminium (24g of aluminium)

1g of aluminium is deposited by $\frac{3}{24}$ moles of electrons 5.2g deposited by $\frac{3x\,5.2}{24}$moles of electrons

Number of coulombs required = $\frac{3x\,5.2}{24}x\mathbf{9500\ C}$ = 62725**C**

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **electrolysis** within groups
- ✓ Let the trainees form a group of four or six and discuss on faraday's laws of electrolysis

Practical learning Activity

- ✓ In-group of four trainees perform and explain the electrolysis of NaCl

Points to Remember (Take home message)

- ✓ Electrolysis is a process of decomposing, ionic compounds into their elements by passing a direct electric current through the compound in a fluid form.
- ✓ There are two main components of electrolytic cells; **electrodes** and **electrolyte** Cathode are negative while anode are positive electrodes.
- ✓ The amount of substance liberated at an electrode is directly proportional to the quantity of electricity passed

3.1.3.Applications of electrolysis

Electrolysis found a wide application in our daily life including; production of chemicals (Na, Cl_2, H_2,,,,), electroplating, electrometallurgy (metal extraction), Metal refining (Purification)

1. **Production of chemicals**

Many chemicals, such as **caustic soda, chlorine, potassium permanganate, ammonium per-sulphate, hydrogen and oxygen etc**. are produced by electrolysis on a large scale.

When an electric current is passed through the molten mixture of NaCl and $CaCl_2$, NaCl decomposes in to $\mathbf{Na^+}$ and **Cl** ion. $\mathbf{Na^+}$ ions migrate towards cathode while **Cl** ions towards the anode. The molten sodium collects in the cathode compartment where it rises to the top and is tapped off by a pipe. ***Chlorine is collected at the anode***.

These are manufactured by electrolysis of concentrated sodium chloride, called brine.

Hydrogen is also obtained as by products. In solution, sodium chloride ionizes:

$$\mathbf{NaCl_{(aq)} \longrightarrow Na^+_{(aq)} + Cl^-_{(aq)}}$$

In addition, water particularly ionizes as $\mathbf{H_2O \longrightarrow H^+ + OH^-}$

Using carbon electrodes, the products of electrolysis are chlorine at the anode and hydrogen at the cathode. Hydrogen is discharged in preference to sodium.

At the cathode: $\mathbf{2Na^+_{(aq)} + 2e^- \longrightarrow 2Na_{(s)}}$

At the anode: $\mathbf{2Cl^-_{(aq)} \longrightarrow Cl_2 + 2e^-}$

The sodium discharged at the mercury cathode forms a solution of sodium amalgam in mercury. The sodium amalgam is collected in a reservoir in which it reacts with water to form sodium hydroxide solution and hydrogen gas. Mercury is also recovered and returned to the electrolytic cell to pass through the process again.

$$\mathbf{2Na/Hg_{(l)} + 2H_2O_{(l)} \longrightarrow 2NaOH_{(aq)} + H_{2(g)}/Hg_{(l)}}$$

The sodium hydroxide produced is crystallized. It is used in:

- Manufacture of soap
- The paper industry-wood contains lignin, which is a nitrogenous compound, in addition to cellulose. Wood chips are converted into pulp by boiling the chips with sodium hydroxide solution to remove the lignin. The digested material is bleached with chlorine.

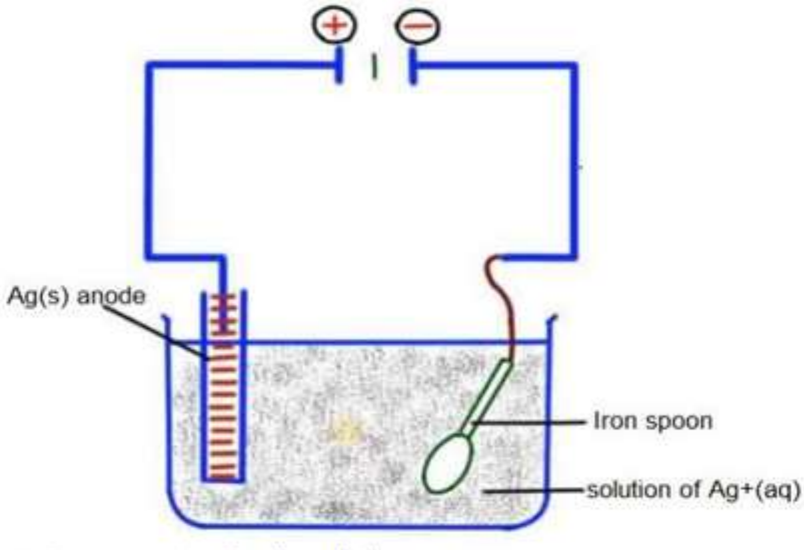
2. Electroplating

This is a process of coating a metal with another of interest mainly to prevent it from rusting, or/ and to improve its appearance, for example, in silver plating articles as cake dishes, made of base alloy, for example cupronickel, are made the cathode in plating bath of potassium (or sodium) dicyanoargentate(I), $KAg(CN)_2$ solution. This contains some silver ions, Ag^+. The anode is pure silver. When direct current passes, the following reactions occur.

- ✓ **At cathode**: $Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$ (silver deposits)
- ✓ At anode: $Ag_{(s)} \longrightarrow Ag^+_{(aq)} + e^-$ (silver dissolves)

In general;

- The metal being coated is made the cathode and the metal coating is the anode
- The solution used is made of the ions of a metal that is coating, so that the anode can dissolve. Anode is the pure plating metal.



set up for silver plating spoon

A good electroplating require steady electric current, appropriate concentration of electrolyte and temperature. The metal to electroplate must be clean.

3. Electrometallurgy (metal extraction)

Electrometallurgy' is the group of technologies used for extraction of metals from solutions, including molten salt solutions ('electrowinning'), or for the purification of metals by electrochemical dissolution into/deposition out of such solutions ('electro-refining').

Metals in group I and II of the periodic table cannot be reduced by chemical reducing agents; they are extracted from their fused halides by electrolysis. Sodium is obtained by electrolysis of molten sodium chloride in the Dawncell. Magnesium is obtained by electrolysis of $MgCl_2$, generated from dolomite and seawater.

Metal refining (Purification)

Metals such as **copper, zinc** and **aluminium** can be purified by electrolysis. The purification of metals is known as **refining**. The copper obtained after the reduction process is not very pure. It contains small amounts of impurities such as iron. This copper is called blister copper and is refined by an electrolytic method. It is cast into bars, which are used as anodes in acidified copper (II) sulphate solution.

The cathode is made of thin pure copper. During the electrolysis, Cu^{2+} ions are transferred from the anode to the cathode where they are discharged and copper is deposited.

At the anode: $Cu_{(s)} \longrightarrow Cu^{2+}{}_{(aq)} + 2e^-$ **impure copper**

At the cathode: $Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$ **pure copper**

The net effect is to dissolve the anode made of impure copper and thicken the cathode (pure copper) with more pure copper.

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **application of electrolysis in our daily life** within groups

Practical learning Activity

- ✓ Trainees in pair work out the redox reactions happening during purification of cupper.

Points to Remember (Take home message)

- ✓ Electrolysis found use in production of many chemicals such as chlorine.
- ✓ Electrolysis found use to coat a metal with another of interest to prevent rust or improve appearance.
- ✓ It is also used to extract metal of group I and II purification of some others.

Learning out come 3.1: formative assessment

Written assessment

Q1. Choose the correct answer from the options given below each of the following questions:

1) Which of the following substances is an electrolyte?

a) Mercury b) Copper c) Sodium sulphate d) Aluminium

2) Which of the following substances is a weak electrolyte?

a) Dilute hydrochloric acid b) Dilute sulphuric acid

c) A solution of potassium bromide. d) Carbonic acid

Q2. a) What is the difference between electrolytic extraction of a metal and electroplating?

b) What is the material for cathode and anode during electro refining of impure copper?

Practical assessment

When a constant current was passed through an aqueous solution of copper (II) nitrate for one hour the mass of the copper cathode increased by 15.24 g. Calculate the current in amperes which was used(F= 96500 Cu = 63.5)

Learning outcome 3.2. Illustrate electrochemical cell

Duration: 6 hrs

Learning outcome 3.2 objectives:

By the end of the learning outcome, the trainees will be able to:

1. Illustrate properly the electrochemical cells according to redox half equations methods

2. Demonstrate correctly the general representation of electrochemical cell.

3. Describe clearly types of batteries.

Resources

Equipment	Tools	Materials
✓ Video ✓ Projector ✓ Computer ✓ Books ✓ Internet	✓ Pens/Pencils ✓ Notebook ✓ Papers ✓ Marker ✓ White/ Chalk ✓ Boards ✓ Chalks	✓ Dry cell (radio battery cell) ✓ Lithium ion battery(phone battery ✓ Mercury cell (watch battery cell)

Advance preparation:

- Prepare all material needed and describe their brief uses
- Distribute different battery and then differentiate primary and secondary battery

3.2.1. Electrochemical cell

An electrochemical cell is a device, which is capable of either producing electrical energy from chemical reactions or causes chemical reactions to take place through the introduction of electrical energy.

There are two types of electrochemical cells: galvanic (voltaic) cells and **electrolytic** cells. A galvanic (voltaic) cell is a device used to convert chemical energy of a redox reaction into electrical energy.

Electrolytic cell is a type of chemical cell in which the flow of electric energy from an external source causes a redox reaction to occur.

A galvanic cell is named after Luigi Galvani, an Italian physicist (1780). It is also called Voltaic cell, after an Italian physicist, Alessandro Volta (1800). Both L. Galvani and A. Volta contributed greatly in the existence of this type of electrochemical cells.

Both types of cells contain **electrodes** where the oxidation and reduction reactions occur.

Oxidation occurs at the electrode called the **anode** and **reduction** occurs at the electrode called the **cathode**.

3.2.2. General representation of electrochemical cell

Oxidation-reduction (or redox) reactions take place in electrochemical cells. Spontaneous reactions occur in galvanic (voltaic) cells; non-spontaneous reactions occur in electrolytic cells.

The anode of an electrolytic cell is positive, since it attracts anions from the solution, whereas the cathode is negative and attracts positive ions. In a galvanic cell, the anode is negatively charged, since the spontaneous oxidation at the anode is the source of the cell's electrons or negative charge. The cathode of a galvanic cell is its positive terminal.

In both galvanic and electrolytic cells, oxidation takes place at the anode and electrons flow from the anode to the cathode.

Half-cells and Redox reactions in half-cells

The galvanic cell have two metal electrodes each immersed in a solution containing its own ions in separate container and these make half-cells.

For example when a strip of zinc metal is dipped in aqueous solution of zinc sulphate some zinc atoms are oxidised each Zn atom that is oxidised leaves behind $2e^-$ and enter the solution as Zn^{2+} ion

Oxidation $\mathbf{Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-}$

At the same time Zn^{2+} ion in solution gain $2e^-$ from zinc strip and deposit as Zn atom. They are reduced.

Reduction $\mathbf{Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}}$

Hence the overall reaction will be as follow $\mathbf{Zn^{2+}_{(aq)} + 2e^- \longleftrightarrow Zn_{(s)}}$

A simple electrochemical cell can be made by connecting together two half-cells with different electrode potentials.

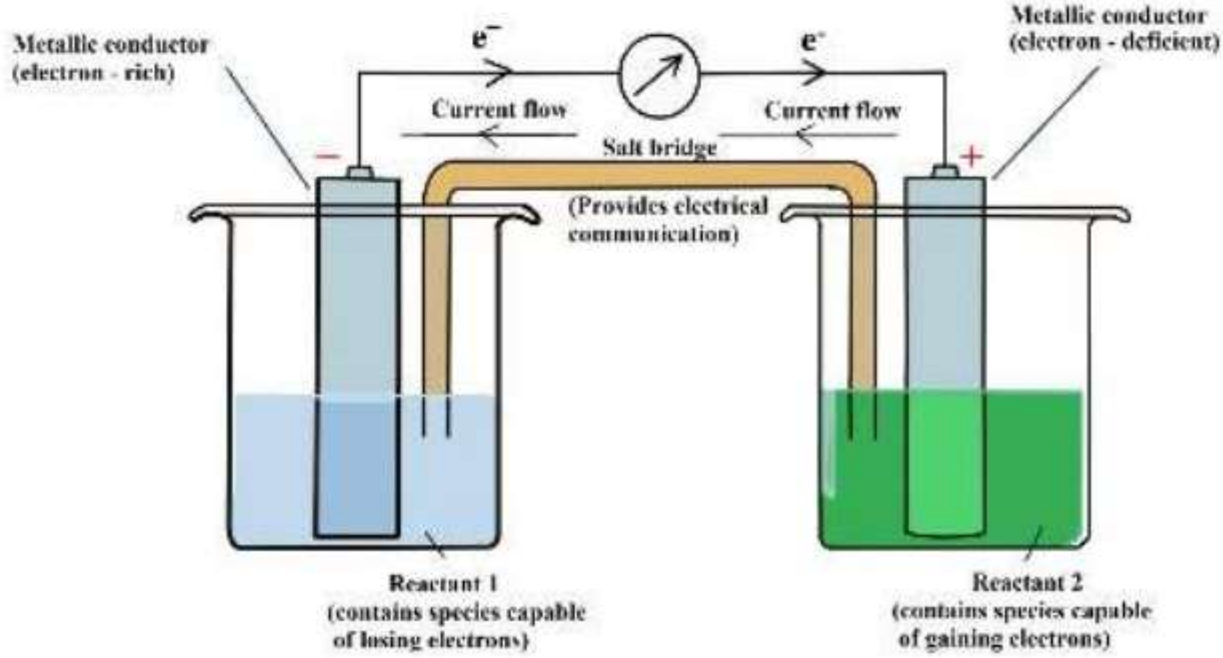


Figure A general cell constructed from its half-cells

- ✓ One half-cell releases electrons (**oxidation at the anode**).
- ✓ The other half-cell gains electrons (**reduction at the cathode**).

Note that, in the electrochemical cell, ***the electrons flow*** from the negative terminal (anode) to the positive terminal (cathode) and the ***current flows in the opposite direction*** i.e. from cathode to anode.

The salt bridge is usually an inverted U-tube filled with a concentrated solution of an inert electrolyte. The inert electrolyte is neither involved in any chemical change, nor does it react with the solutions in the two half-cells. Generally salts like KCl, KNO_3, Na_2SO_4 and NH_4NO_3 are used as the electrolytes.

The main function of salt bridge is to ***prevent the potential difference that arises between the two solutions when they are in contact with each other***. This potential difference is called the liquid junction potential.

- It completes the electrical circuit by connecting the electrolytes in the two half cells.
- It prevents the diffusion of solutions from one half-cell to the other.
- It maintains the electrical neutrality of the solutions in the two half cells.

Theoretical learning Activity

- ✓ Ask trainees to **differentiate galvanic cell from electrolytic cell** within groups.

Practical learning Activity

- ✓ In-group of four trainees workout and explain the half-cell redox reaction.

Points to Remember (Take home message)

- ✓ There are two types of electrochemical cells: galvanic (voltaic) cells and electrolytic cells.
- ✓ Spontaneous reactions occur in galvanic (voltaic) cells; non-spontaneous reactions occur in electrolytic cells
- ✓ A galvanic (voltaic) cell is a device used to convert chemical energy of a redox reaction into electrical energy
- ✓ Electrolytic cell dissociate ionic compound into cation and anion when electric current is supplied through it.
- ✓ Oxidation reaction occurs at the electrode called the anode and reduction occurs at the electrode called the cathode.

3.2.3. Types of batteries

In science and technology, a ***battery is a device that stores chemical energy and makes it available in an electrical form.*** Batteries are made of electrochemical devices such as one or more galvanic cells or fuel cells.

The importance of electrochemical cells or galvanic cells lies in their ability to provide us with a portable source of electrical energy.

Batteries have many uses including in:

- Torches
- Electrical appliances such as cellphones (long-life alkaline batteries)
- Digital cameras (lithium batteries)
- Hearing aids (silver-oxide batteries)
- Digital watches (mercury/silver-oxide batteries)
- Military applications (thermal batteries)

The galvanic cells can be broadly classified into two categories, namely; **primary cells** and **secondary cells.** Here we add also **fuel cells**.

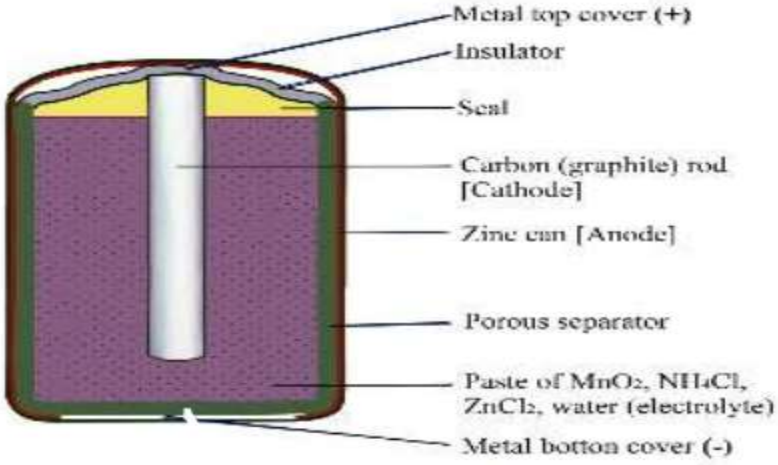
1. Primary cells

This type of cells becomes dead over a period of time and the chemical reaction stops. **They cannot be recharged or used again**. Some common examples are **dry cell, mercury cell**, etc.

a. DRY CELL

It is a compact form of Leclanché cell known after its inventor, a French chemist, G. Leclanché. In this cell, **anode consists of zinc container** while cathode is a **graphite rod** surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with the paste of NH_4Cl and $ZnCl_2$ (which is the electrolyte).

The arrangement is shown in the figure below.



Leclanché Dry Cell

The reactions taking place at the electrodes are given in their simplified form as follows:

- ***Cathode:*** $2\ MnO_2(s) + H_2(g) \rightarrow Mn_2O_3(s) + H_2O(l)$
  $2\ NH_4^+(aq) + 2e^- \rightarrow 2NH_3(g) + H_2(g)$
- ***Anode:*** $Zn(s) \rightarrow Zn^{2+}(aq) + 2e^-$

The zinc ions (Zn^{2+}) so produced combine with ammonia liberated in cathodic reaction to form diammine zinc (II) cation.

$$Zn^{2+}(aq) + 2NH_3(g) \rightarrow [Zn(NH_3)_2]^{2+}(aq)$$

Dry cells do not have long life as NH_4Cl, which is acidic, corrodes the zinc container even if the cell is not in use. The cell potential of dry cells lies in the range **1.25 V** to **1. 5 V.**

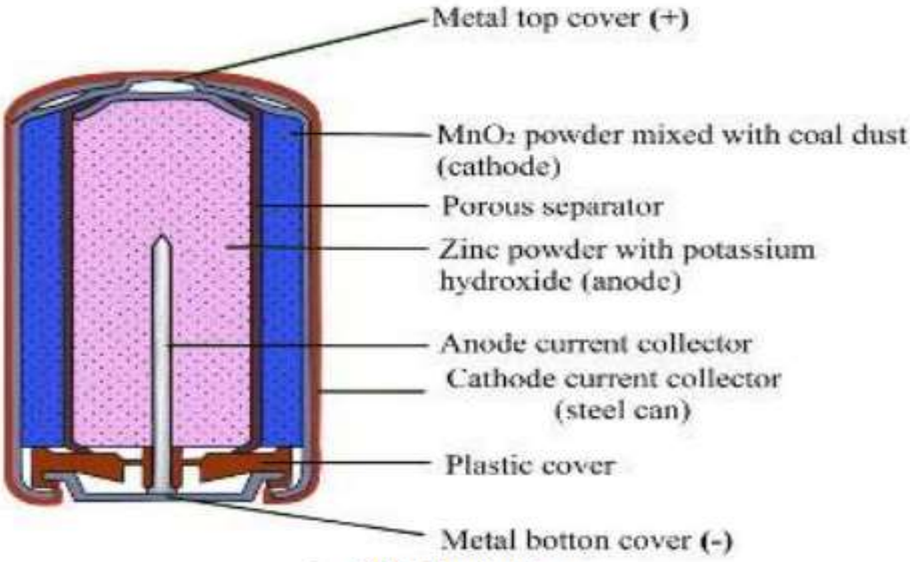
b. ALKALINE BATTERIES

Alkaline batteries were developed in the 1950s partly to address some of the performance issues with zinc–carbon dry cells. They are manufactured to be exact replacements for zinc-carbon dry cells. As their name suggests, these types of batteries **use alkaline electrolytes.**

They consist of Zn powder in the center of the pile as anode and MnO_2^+ graphite as cathode. Everything is contained in a steel housing. NH_4Cl is replaced by a solution of about 7 M of KOH, hence the term "alkaline".

The reactions are:

- **Anode:** $Zn(s) + 2OH^-(aq) \rightarrow Zn(OH)_2(s) + 2\ e^-$
- **Cathode:** $MnO_2\ (s) + 2H_2O(l) + 2\ e^- \rightarrow Mn(OH)_2(s) + 2OH^-(aq)$



Alikaline battery

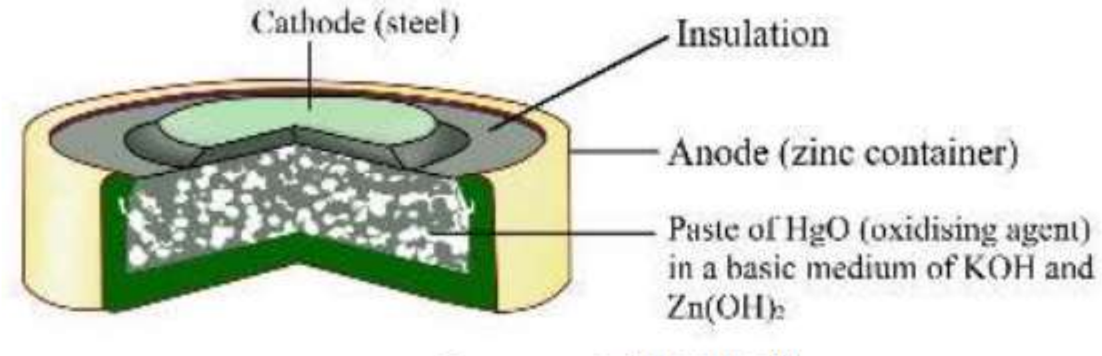
Alkaline cells last long than ordinary dry cell. They have a longer shelf life and can be kept in service longer. An alkaline cell has NaOH or KOH in place of NH4Cl as the electrolyte. It uses essentially the same reduction half-cell reaction as the ordinary dry cell, but in alkaline medium.

Alkaline cells develop a voltage of 1.5 V as Leclanché cells but have advantage over dry cell. Attempts to recharge an alkaline battery often lead to rupture of the battery and leakage of the potassium hydroxide electrolyte (this is because it is not rechargeable).

c. MERCURY CELL

Miniature cell (used in shape of button cell) finds a frequent use these days to supply energy for watches, video cameras, hearing aids and other compact devices. In mercury cell, the anode is zinc-mercury amalgam and the cathode is a paste of mercury (II) oxide and carbon.

Electrolyte is a moist paste of KOH-ZnO. The arrangement in its simple form is shown in figure below.



Mercury cell

This battery works on the same principle as the alkaline battery. The HgO or Ag_2O replaces the MnO_2.

The reactions are:

- **Anode:** Zn/Hg *(Amalgam)* $+ 2\ OH^- \rightarrow ZnO(s) + H_2O(l) + 2\ e^-$
- **Cathode:** $HgO(s) + H_2O(l) + 2\ e^- \rightarrow Hg(l) + 2\ OH^-$
- **Overall reaction:** Zn/Hg *(Amalgam)* $+ HgO \rightarrow ZnO(s) + Hg(l)$

This battery provides a potential difference of 1.35V. Its dimensions are very small and it lasts longer. It contains mercury, which is very toxic (it can be replaced by silver).

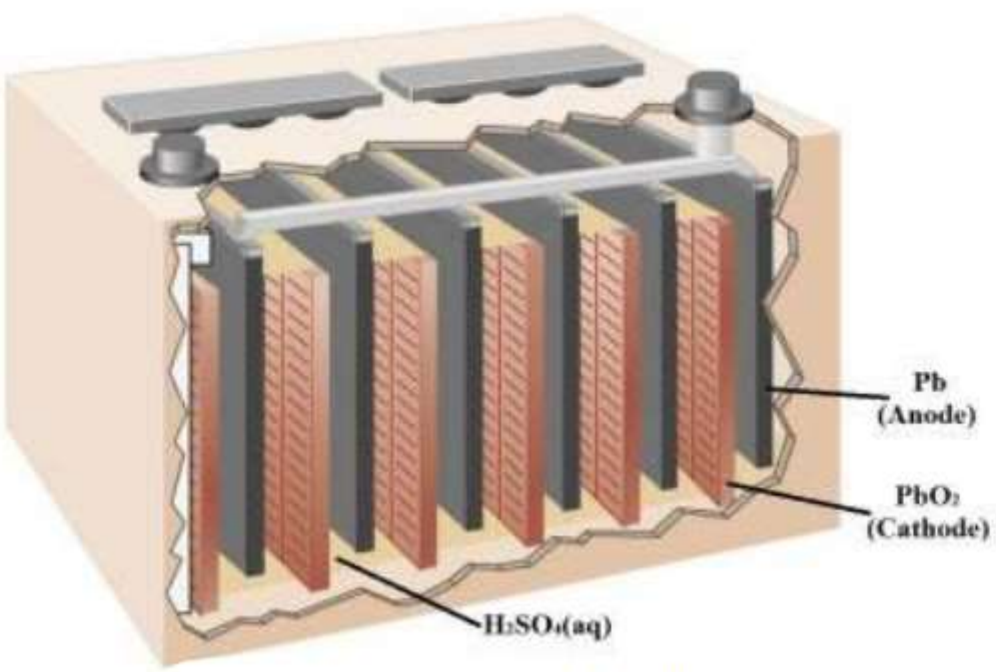
2. Secondary cells

This type of cells ***recharged by passing direct current through them and used repeatedly.*** These are the types of batteries found in devices such as smart phones, electronic tablets, and automobiles. Some examples are lead-storage battery, nickel-cadmium storage cell, etc.

a. LEAD-STORAGE BATTERY

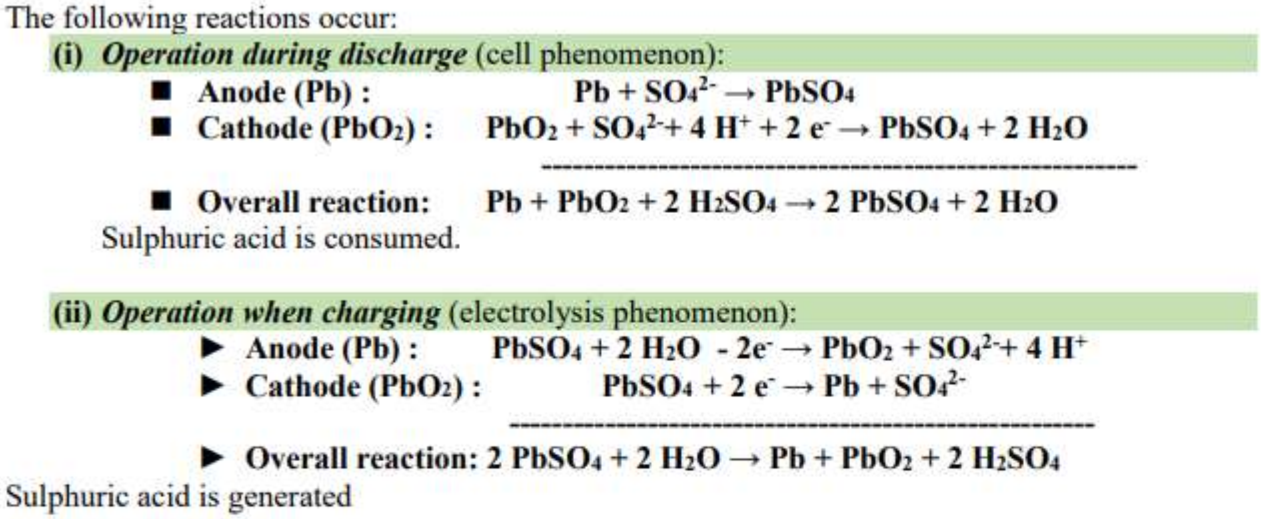
It is the most frequently used battery in automobiles. It consists of six voltaic cells connected in series. In each cell anode is made of spongy lead and cathode 'is a grid of lead packed with lead dioxide (PbO_2). The lead storage batteries are made of alternating lead electrodes on the one hand, and lead coated PbO_2 on the other. The electrolyte is the aqueous solution of 3M sulphuric acid (38% by mass).

These batteries provide a constant emf of about 12 V. Invented in 1859 by Gaston Planté, the lead-acid storage battery is still widely used in cars, trucks, and airplanes. The storage battery consists of a group of cells connected together in series. Each cell consists of a lead plate, a lead oxide plate, and an electrolytic solution of sulphuric acid.



Lead storage battery

When these types of batteries run down, they can be recharged by forcing current through the battery in the direction opposite the direction the current flows when the battery is fully charged.



The following reactions occur:

(i) *Operation during discharge* (cell phenomenon):

- **Anode (Pb) :** $Pb + SO_4^{2-} \rightarrow PbSO_4$
- **Cathode (PbO_2) :** $PbO_2 + SO_4^{2-} + 4\,H^+ + 2\,e^- \rightarrow PbSO_4 + 2\,H_2O$

- **Overall reaction:** $Pb + PbO_2 + 2\,H_2SO_4 \rightarrow 2\,PbSO_4 + 2\,H_2O$

Sulphuric acid is consumed.

(ii) *Operation when charging* (electrolysis phenomenon):

- **Anode (Pb) :** $PbSO_4 + 2\,H_2O\ - 2e^- \rightarrow PbO_2 + SO_4^{2-} + 4\,H^+$
- **Cathode (PbO_2) :** $PbSO_4 + 2\,e^- \rightarrow Pb + SO_4^{2-}$

- **Overall reaction:** $2\,PbSO_4 + 2\,H_2O \rightarrow Pb + PbO_2 + 2\,H_2SO_4$

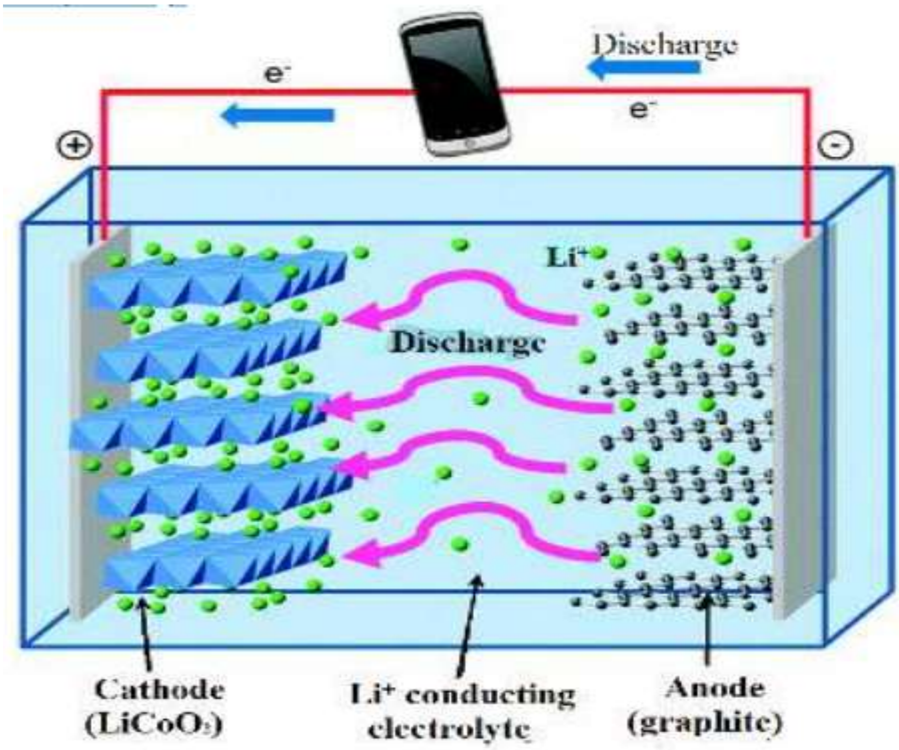
Sulphuric acid is generated

Note: When all of the **Pb** or **PbO_2** is converted to **$PbSO_4$**, the battery is depleted. But by the electric current, the reaction changes direction and the battery is charging.

Each cell produces 2 V, so six cells are connected in series to produce a 12-V car battery. Lead acid batteries are heavy and contain a caustic liquid electrolyte, but are often still the battery of choice because of their high current density. Since these batteries contain a significant amount of lead, they must always be disposed of properly.

b. LITHIUM ION BATTERIES

Lithium ion batteries are among the most popular rechargeable batteries and are used in many portable electronic devices. The most common lithium-ion cells have an anode of graphite carbon (C) and a cathode of lithium cobalt oxide ($LiCoO_2$). The electrolyte is lithium perchlorate ($LiClO_4$).



Lithium ion battery

DURING DISCHARGE

At the anode, lithium is oxidised. Lithium ions are released from the carbon, along with electrons: $\mathbf{LiC_6 \longrightarrow Li^+ + e^- + 6\ C}$

At the cathode, the lithium dioxide absorbs lithium-ions, and the electrode is reduced as it also receives the electrons from the circuit: $\mathbf{CoO_2 + Li^+ + e^- \longrightarrow LiCoO_2}$

The overall reaction is: $\mathbf{LiC_6 + CoO_2 \longrightarrow 6\ C + LiCoO_2}$

The structure of LiC_6 involves lithium inserted (intercalated) between the layers of graphite.

DURING RECHARGE

The opposite action occurs.

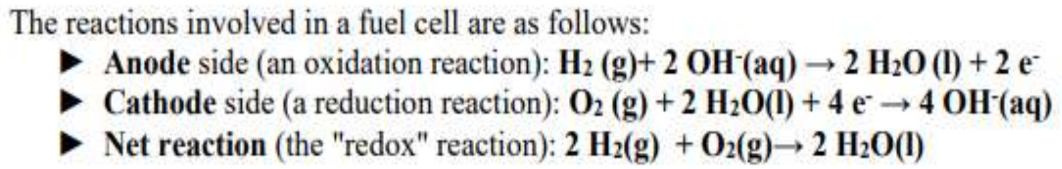
In a lithium ion battery, charge flows between the electrodes as the lithium ions move between the anode and cathode. The battery voltage is about **3.7 V.**

Lithium batteries are popular because they can provide a large amount current, are lighter than comparable batteries of other types, produce a nearly constant voltage as they discharge, and only slowly lose their charge when stored.

c. Fuel cells

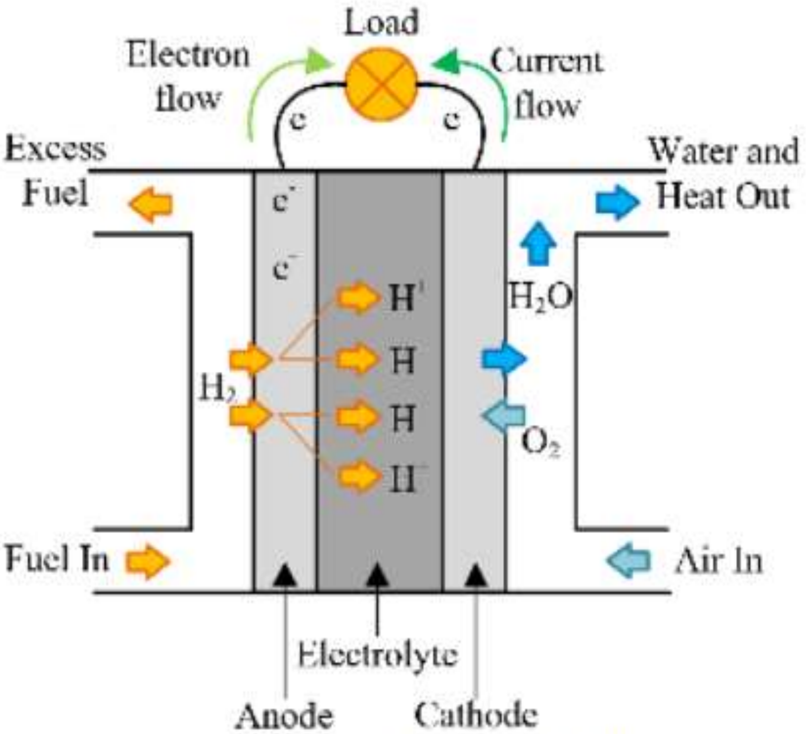
Fuel cells work like batteries but **they do not run down or need recharging**. They produce electricity and heat as long as fuel is supplied. A fuel cell consists of two electrodes: a negative electrode (or anode) and a positive electrode (or cathode) sandwiched around an electrolyte. **A fuel, such as hydrogen**, is fed to **the anode**, and air (**oxygen**) is fed to the **cathode**.

The anode is porous graphite coated with nickel, the cathode is porous graphite coated nickel and nickel (II) oxide and potassium hydroxide solution is used as electrolyte.



The reactions involved in a fuel cell are as follows:

- **Anode** side (an oxidation reaction): $H_2 (g) + 2 OH^-(aq) \rightarrow 2 H_2O (l) + 2 e^-$
- **Cathode** side (a reduction reaction): $O_2 (g) + 2 H_2O(l) + 4 e^- \rightarrow 4 OH^-(aq)$
- **Net reaction** (the "redox" reaction): $2 H_2(g) + O_2(g) \rightarrow 2 H_2O(l)$



Hydrogen fuel cell

In a **hydrogen fuel cell**, a catalyst at the anode separates hydrogen molecules into protons and electrons, which take different paths to the cathode. The electrons go through an external circuit, creating a flow of electricity. The protons migrate through the electrolyte to the cathode, where they unite with oxygen and the electrons to produce (drinking) water and heat. Platinum and platinum alloys (like Platinum-Ruthenium) are the most efficient catalysts for speeding up chemical reactions in hydrogen fuel cells.

The reaction in a single fuel cell typically produces only about 0.7 volts. Therefore, fuel cells are usually stacked or connected in some way to form a fuel cell system used in cars, generators, or other products that require power.

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **on types of battery** within groups

Practical learning Activity

- ✓ Trainees in pair identify and classify into primary or secondary among the battery cell shared.

Points to Remember (Take home message)

- ✓ Battery is a device that stores chemical energy and makes it available in an electrical form.
- ✓ The primary cell can't be recharged while secondary cell can be recharged
- ✓ Fuel cells work like batteries but they do not run down or need recharging.

Learning out come 3.2: formative assessment

Written assessment

Q1. Some cells, such as the nickel-cadmium cell used in calculators and electric shavers, can be recharged. Others, such as those used in watches and torches, cannot be recharged.

Are rechargeable cells primary or secondary cells?

Q2. State two differences and two similarities between an electrochemical cell and an electrolytic cell.

Q3. Which of these is a TRUE statement about galvanic cells?

a) Galvanic cells convert chemical energy to electrical energy using an oxidation-reduction reaction.

(b) Galvanic cells convert electrical energy to chemical energy using an oxidation-reduction reaction.

(c) Galvanic cells convert chemical energy to electrical energy using a decomposition reaction.

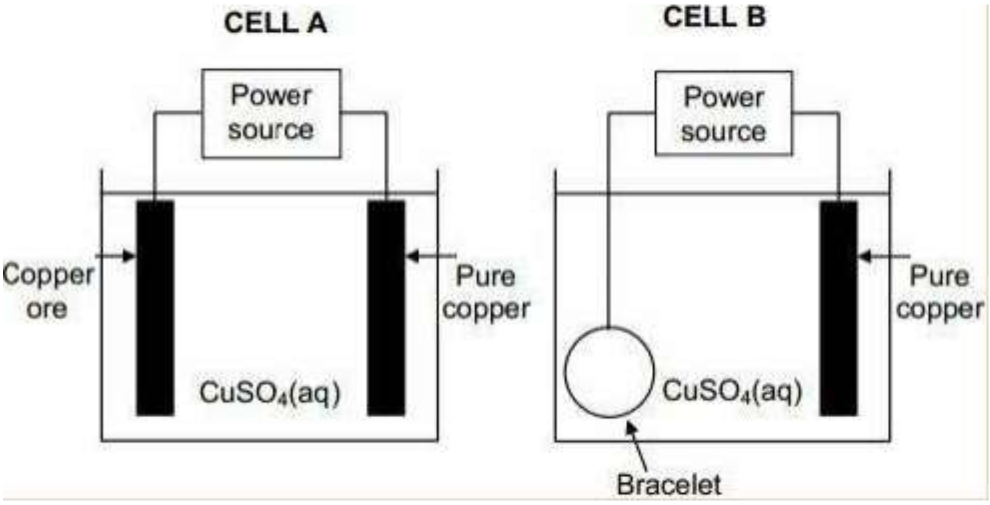
(d) Galvanic cells convert electrical energy to chemical energy using electrolysis.

Practical assessment

The simplified diagrams below represent two electrochemical cells, A and B, used in industry.

Cell A is used in the purification of copper ore containing silver and platinum impurities.

Cell B is used to electroplate a bracelet with a layer of copper.



a) Write down the name of the type of electrochemical cell of which the above two cells are examples.

b) Pure copper is used as one of the electrodes in each of the cells above. In which cell (A or B) is the pure copper the:

i) Cathode

ii) Anode

Learning Outcome 3.3: Determine the electromotive force of the cell

Duration: 5 hrs

Learning outcome 1.3 objectives:

By the end of the learning outcome, the trainees will be able to:

1. Discuss correctly the applications of qualitative and quantitative chemical analysis based on area of application.

Resources

Equipment	Tools	Materials
✓ Video ✓ Projector ✓ Computer ✓ Books ✓ Internet ✓ calculator	✓ Pens/Pencils ✓ Notebook ✓ Papers ✓ Marker ✓ White/ Chalk ✓ Boards ✓ Chalks ✓ calculator	✓ Test-tube ✓ Beaker ✓ Audio-visual

Advance preparation:

- Prepare all material needed and describe their brief uses
- Show the a video of redox reaction and electrode potential and ask trainees to they are seeing

CONTENT

3.3.1.Electrochemical cell reactions

Oxidation-reduction (or redox) reactions take place in electrochemical cells. Spontaneous reactions occur in galvanic (voltaic) cells; non-spontaneous reactions occur in electrolytic cells. Both types of cells contain electrodes where the oxidation and reduction reactions occur.

Oxidation reaction in electrochemical cell

- ✓ Increase of oxidation state
- ✓ Loss of electrons
- ✓ Happens at anode

Example of Cell Reaction: $Zn \longrightarrow Zn^{2+} + 2e^{-}$ **(Oxidation So anode)**

At the zinc rod, oxidation occurs. Therefore, it is the anode of the cell and negatively charged.

Reduction reaction in electrochemical cell

- ✓ Decrease of oxidation number
- ✓ Gain of electron
- ✓ Happens at cathode

Example of cell reaction: $Cu^{2+} + 2e^{-} \rightarrow Cu_{(s)}$

3.3.2.Standard electrode potential (SEP)

In electrochemistry, **standard electrode potential** is a measure of the reducing power of any element or compound.

When a metal electrode is dipped in a solution containing its metal ions, a potential difference is developed at the metal /solution interface. This potential difference is called the **electrode potential.**

For example, when a copper rod is dipped in a solution containing Cu^{2+} ions, the Cu^{2+} ions gain electrons from the copper rod leaving positive charge on the copper rod. As a result, a potential difference is set up between the copper rod and the solution and is called the electrode potential of copper.

In a **galvanic** cell, **the anode** has **a negative** potential and **cathode** has a **positive potential.** The potential of each individual half-cell cannot be measured. We can measure only the difference between the potential of the two half cells. While it is impossible to determine the electrical potential of a single electrode, we can assign an electrode the value of zero and then use it as a reference.

The electrode chosen as having the value of **"zero"** is called the Standard Hydrogen

Electrode (SHE). The SHE consists of **1 atm** of hydrogen gas bubbled through a **1 M** strong acid solution, usually at room temperature. Platinum or graphite, which is chemically inert, is used as the electrode.

Thus, electrode potential at standard conditions (temperature of **25°C,** pressure of **1 atm** and concentration of 1 M concentration for the electrolyte) is called the "standard electrode potential". It is denoted by the symbol $\mathbf{E^0}$ where the superscript **"0"** on the **E** denotes **standard conditions**.

Other standard electrode potentials can be determined using the SHE. The standard reduction (electrode) potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode. Here, the minus sign is necessary because oxidation is the reverse of reduction.

$$E^0_{cell} = E^0_{Cathode} - E^0_{Anode}$$

The diagram below shows how the standard potential, E^0 of copper can be determined.

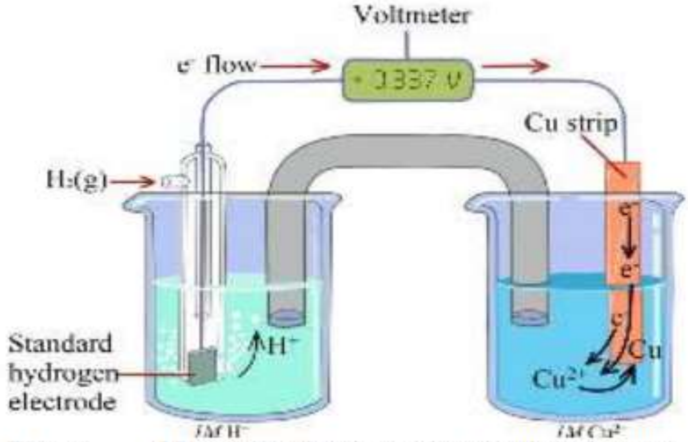


Figure *Measuring the electrode potential of copper*

The copper electrode contains Cu^{2+} ions in equilibrium with copper metal. The hydrogen electrode is linked via a salt bridge to the solution in which the copper electrode is immersed.

This permits charge transfer and potential measurement but not mass transfer of the acid solution in the electrode.

The oxidation and reduction at the electrodes leads to a standard electrode potential between the electrode and ions in solution. The standard electrode potential is expressed in Volts (V). Volt is the measure of electromotive force **(e.m.f.)** produced by a cell. Standard electrode potentials refer to redox potentials as well.

Standard Reduction Potentials in aqueous solution (at 25 °C).

				$E^0(V)$	
INCREASING STRENGTH OF OXIDISING AGENTS	$F_2(g)+2e^-$	$\longrightarrow$	$2F^-(aq)$	$+2.870$	INCREASING STRENGTH OF REDUCING AGENTS
	$H_2O_2(aq)+2H^+(aq)+2e^-$	$\longrightarrow$	$2H_2O(l)$	$+1.770$	
	$PbO_2(s)+SO_4^{2-}(aq)+4H^+(aq)+2e^-$	$\longrightarrow$	$PbSO_4(s)+2H_2O(l)$	$+1.685$	
	$MnO_4^-(aq)+8H^+(aq)+5e^-$	$\longrightarrow$	$Mn^{2+}(aq)+4H_2O(l)$	$+1.520$	
	$Au^{3+}(aq)+3e^-$	$\longrightarrow$	$Au(s)$	$+1.500$	
	$Cl_2(g)+2e^-$	$\longrightarrow$	$2Cl^-(aq)$	$+1.360$	
	$Cr_2O_7^{2-}(aq)+14H^+(aq)+6e^-$	$\longrightarrow$	$2Cr^{3+}(aq)+7H_2O(l)$	$+1.330$	
	$O_2(g)+4H^+(aq)+4e^-$	$\longrightarrow$	$2H_2O(l)$	$+1.229$	
	$Br_2(l)+2e^-$	$\longrightarrow$	$2Br^-(aq)$	$+1.066$	
	$NO_3^-(aq)+4H^+(aq)+3e^-$	$\longrightarrow$	$NO(g)+2H_2O(l)$	$+0.960$	
	$OCl^-(aq)+H_2O(l)+2e^-$	$\longrightarrow$	$Cl^-(aq)+2OH^-(aq)$	$+0.890$	
	$Hg^{2+}(aq)+2e^-$	$\longrightarrow$	$Hg(l)$	$+0.855$	
	$Ag^+(aq)+e^-$	$\longrightarrow$	$Ag(s)$	$+0.799$	
	$Fe^{3+}(aq)+e^-$	$\longrightarrow$	$Fe^{2+}(aq)$	$+0.771$	
	$I_2(s)+2e^-$	$\longrightarrow$	$2I^-(aq)$	$+0.535$	
	$Cu^+(aq)+e^-$	$\longrightarrow$	$Cu(s)$	$+0.521$	
	$O_2(g)+2H_2O(l)+4e^-$	$\longrightarrow$	$4OH^-(aq)$	$+0.400$	
	$Cu^{2+}(aq)+2e^-$	$\longrightarrow$	$Cu(s)$	$+0.337$	
	$Sn^{4+}(aq)+2e^-$	$\longrightarrow$	$Sn^{2+}(aq)$	$+0.150$	
	$2H^+(aq)+2e^-$	$\longrightarrow$	$H_2(g)$	0.000	
	$Pb^{2+}(aq)+2e^-$	$\longrightarrow$	$Pb(s)$	-0.126	
	$Sn^{2+}(aq)+2e^-$	$\longrightarrow$	$Sn(s)$	-0.140	
	$Ni^{2+}(aq)+2e^-$	$\longrightarrow$	$Ni(s)$	-0.250	
	$V^{3+}(aq)+2e^-$	$\longrightarrow$	$V^{2+}(aq)$	-0.255	
	$Co^{2+}(aq)+2e^-$	$\longrightarrow$	$Co(s)$	-0.280	
	$Tl^+(aq)+e^-$	$\longrightarrow$	$Tl(s)$	-0.340	
	$PbSO_4(s)+2e^-$	$\longrightarrow$	$Pb(s)+SO_4^{2-}(aq)$	-0.356	
	$Cd^{2+}(aq)+2e^-$	$\longrightarrow$	$Cd(s)$	-0.403	
	$Fe^{2+}(aq)+2e^-$	$\longrightarrow$	$Fe(s)$	-0.440	
	$Zn^{2+}(aq)+2e^-$	$\longrightarrow$	$Zn(s)$	-0.763	
	$2H_2O(l)+2e^-$	$\longrightarrow$	$H_2(g)+2OH^-(aq)$	-0.828	
	$Al^{3+}(aq)+3e^-$	$\longrightarrow$	$Al(s)$	-1.660	
	$Mg^{2+}(aq)+2e^-$	$\longrightarrow$	$Mg(s)$	-2.370	
	$Na^+(aq)+e^-$	$\longrightarrow$	$Na(s)$	-2.714	
	$K^+(aq)+e^-$	$\longrightarrow$	$K(s)$	-2.925	
	$Li^+(aq)+e^-$	$\longrightarrow$	$Li(s)$	-3.045	

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **standard electrode potential** within groups
- ✓ Let the trainees discuss in pair about **standard hydrogen potential**

Practical learning Activity

- ✓ In pair, trainees identify the oxidation and reduction reaction from the following reactions.

Points to Remember (Take home message)

The standard reduction (electrode) potential can be determined by subtracting the standard reduction potential for the reaction occurring at the anode from the standard reduction potential for the reaction occurring at the cathode.

$$E^{o}_{Cell} = E^{o}_{cathode} - E^{o}_{Anode}$$

- ✓ Oxidation reactions involve increasing in oxidation state, gaining oxygen and loss of electron.
- ✓ Reduction reactions involve decreasing in oxidation state, loss of oxygen and gaining electron.
- ✓ Standard electrode potential is a measure of the reducing power of any element or compound.
- ✓ In a galvanic cell, the anode has a negative potential and cathode has a positive potential.

CONTENT

3.3.3. Electrode potential and Calculations of electromotive force (emf)

To calculate the standard cell potential for a reaction:

- ✓ Write the oxidation and reduction half-reactions for the cell.
- ✓ Look up the reduction potential, E^0 reduction, for the reduction half-reaction in a table of reduction potentials

- ✓ Look up the reduction potential for the reverse of the oxidation half-reaction and reverse the sign to obtain the oxidation potential.
- ✓ For the oxidation half-reaction, $\mathbf{E^0_{oxidation} = —E^0_{reduction}}$.
- ✓ Add the potentials of the half-cells to get the overall standard cell potential.

$\mathbf{E^0_{cell} = E^0_{reduction} + E^0_{oxidation}}$

Example: Find the standard cell potential for an electrochemical cell with the following cell reaction. $Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

1) Write the half-reactions for each process.

$Zn_{(s)} \xrightarrow{\qquad\qquad} Zn^{2+}_{(aq)} + 2e^-$

$Cu^{2+}_{(aq)} + 2\ e^- \xrightarrow{\qquad\qquad} Cu_{(s)}$

2) Look up the standard potentials for the reduction half-reaction.

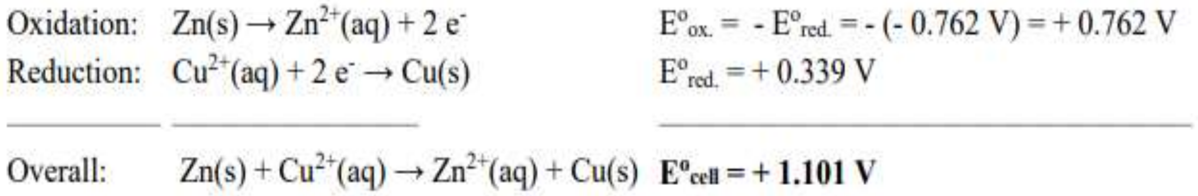
$\mathbf{E^o_{\ reduction}}$ **of** $\mathbf{Cu^{2+}}$ = + 0.339 V

3) Look up the standard reduction potential for the reverse of the oxidation reaction and change the sign.

$\mathbf{E^o_{reduction}}$ **of** $\mathbf{Zn^{2+}}$ = - 0.762 V

$E^o_{oxidation}$ of Zn = **—** (—0.762 V) = **+** 0.762 V

(4) Add the cell potentials together to get the overall standard cell potential.



Oxidation:	$Zn(s) \rightarrow Zn^{2+}(aq) + 2\ e^-$	$E^o_{ox.} = -\ E^o_{red.} = -\ (-\ 0.762\ V) = +\ 0.762\ V$
Reduction:	$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$	$E^o_{red.} = +\ 0.339\ V$
Overall:	$Zn(s) + Cu^{2+}(aq) \rightarrow Zn^{2+}(aq) + Cu(s)$	$E^o_{cell} = \mathbf{+\ 1.101\ V}$

How do we know which metal will become oxidized and which metal ion reduced?

By looking at a table of standard reduction potentials! One of the half-reactions must be reversed to yield an oxidation.

- ❖ Reverse the half-reaction that will yield the highest (positive) net emf for the cell.
- ❖ Remember that when one reverses a reaction, the sign of $\mathbf{E^0}$**(+ or –)** for that reaction is also reversed.
- ❖ **Worked Example**

Consider the following table of standard reduction potentials:

In aqueous solutions at 25 °C	
$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	**E° = 0.86 V**
$I_2(s) + 2e^- \longrightarrow 2\,I^-(aq)$	**E° = 0.54 V**
$2\,H^+(aq) + 2e^- \longrightarrow H_2(g)$	**E° = 0.00 V**
$Zr^{4+}(aq) + 4e^- \longrightarrow Zr(s)$	**E° = – 1.53 V**
$Rb^+(aq) + e^- \longrightarrow Rb(s)$	**E° = – 2.93 V**

The potential generated by a cell constructed from standard Zr and I2 electrodes may be calculated. From the table, we write a balanced reduction half-reaction for each electrode and copy down the reduction potentials:

$$I_2(s) + 2e^- \longrightarrow 2\,I^-(aq) \qquad \mathbf{E^0 = 0.54\ V}$$
$$Zr^{4+}(aq) + 4e^- \longrightarrow Zr(s) \qquad \mathbf{E^0 = -1.53\ V}$$

Reversing which reaction will yield most positive standard reduction potential? Let us try both.

Case 1: ***Reversing the iodine reduction:*** E° = - 0.54 V
Case 2: ***Reversing the zirconium reduction:*** E° = + 1.53 V

Thus, the highest positive potential is found by using the Zr oxidation half-reaction because: **+ 1.53 V > – 0.54 V**

Thus, the standard cell potential will be $\mathbf{E^o_{ox}\ (Zr) + E^o_{red}\ (I_2)}$

$$\mathbf{E^o_{cell} = (+\,0.54) + (+\,1.53)}$$
$$\mathbf{E^o_{cell} = +\,2.07\ V}$$

Even though we had to multiply the iodine reduction by a factor of 2 so that the electrons consumed would balance with those produced by the zirconium oxidation, we do NOT multiply the iodine reduction potential by this factor. In manipulating potentials, we should only change the signs of the values, not the magnitude.

- **A negative reduction** potential tells us that the zirconium ion is harder to reduce (is a worse oxidizing agent) than is the hydrogen ion; this also tells us that zirconium metal is a better reducing agent than is hydrogen gas.
    - A **positive reduction potential tells us that the iodide ion is easier to reduce** (is a better oxidizing agent) than is the hydrogen ion; this also tells us that iodine is a worse reducing agent than is hydrogen gas.

In general, the electrode with the more positive value of electrode potential is the cathode (the one which undergoes reduction) and the electrode with more negative value of electrode potential is the anode (easily oxidised)

Theoretical learning Activity

- ✓ Ask trainees to brainstorm about **how do we know the metal which will be oxidized or reduced** within groups

Practical learning Activity

- ✓ In pair, trainees calculate the standard cell potential for the following reactions.

Points to Remember (Take home message)

To calculate the standard cell potential for a reaction:

- ✓ Write the oxidation and reduction half-reactions for the cell.
- ✓ Look up the reduction potential, E^0 reduction, for the reduction half-reaction in a table of reduction potentials
- ✓ Look up the reduction potential for the reverse of the oxidation half-reaction and reverse the sign to obtain the oxidation potential.
- ✓ For the oxidation half-reaction, **E^0oxidation = —E^0reduction.**

Learning out come 3.3: formative assessment

Written assessment

Q1. Define standard electrode potential.

Q2. Is it possible to use another standard electrode than SHE? Justify your answer.

Q3. Answer by True or False.

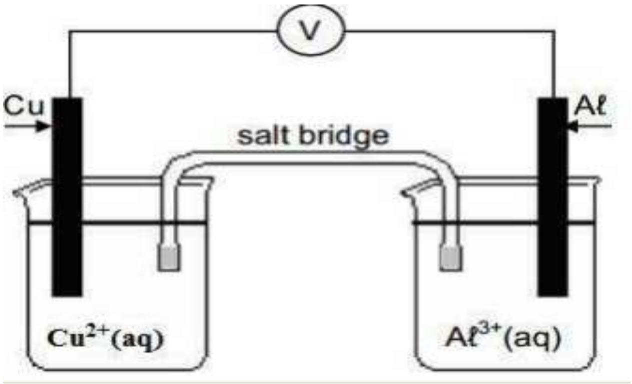
a) Hydrogen electrode which is the reference electrode can be used as Anode or Cathode.

b) If hydrogen electrode acts as cathode, hydrogen is oxidised.

c) With the aid of a diagram, explain how the standard electrode potential of zinc is measured.

Practical assessment

The electrochemical cell shown below functions at standard conditions.



i) Which electrode (Cu or Al) is the anode?

ii) Write down the cell notation for this cell.

iii) Calculate the emf of this cell.

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