

CHAPTER NINE

ELECTROCHEMISTRY

Electrochemistry is the branch of chemistry that deals with chemical changes that are produced by passing electric current into a chemical system or the generation of electricity by spontaneous chemical reactions.

MODES OF CONDUCTION OF SUBSTANCES

The substances that allow electric current to flow through them are called conductors. Those that do not allow electric current to flow through them are called non-conductors or insulators. The conductors are classified into two type i.e. **metallic conductors** and **electrolytic conductors**.

1. Metallic conductors

Metals or alloys allow electric current to flow through them without undergoing any chemical change. The metals conduct electric current by use of **free mobile electrons (delocalised electrons)**. These include copper, silver, aluminium and others. This mode of conduction is called **electronic conduction**.

2. Electrolytic conductors

These include **aqueous solutions of electrolytes** or molten electrolytes. They are compounds and chemical changes occur when they conduct electricity. The electrolytes conduct electric current by use of **free mobile ions**. Examples include dilute hydrochloric acid, aqueous sodium chloride, molten lead(II) bromide and others. This mode of conduction is called **electrolytic conduction**.

ELECTROLYSIS

Electrolysis is the decomposition of a compound in its molten state or in solution by passage of an electric current through it.

or

The overall chemical change that occurs at the electrodes when an electric current passes through a fused electrolyte or its aqueous solution

The electrolyte, solvent or electrode may all be involved in the electrolytic reaction

The common terms used in electrolysis

1. Electrolytes

These are compounds which conduct electric current in solution or in molten state and are decomposed by it.

A non-electrolyte is a substance which does not conduct electric current in molten state or aqueous solution and cannot be decomposed by electric current. For example sucrose

Electrolytes can be salts, acids or bases.

Electrolytes can be classified as **strong** or **weak**.

(i) Strong electrolytes

These are electrolytes which almost completely ionise in solution. Their solutions do not contain unionized molecules.

They include most salts, strong acids and strong alkalis.

(ii) Weak electrolytes

These are electrolytes which partly ionise in solution. Their solutions contain ions in equilibrium with unionized molecules.

They include most organic acids and bases and ammonia.

Examples of strong and weak electrolytes

Strong electrolytes	Weak electrolytes
Sodium chloride	Ethanoic acid
Calcium chloride	Ammonia solution
Sodium hydroxide	Ethylamine
Hydrochloric acid	Carbonic acid

Electrolytes can as well be *ionic* or *covalent*.

(i) Ionic electrolytes

These electrolytes are made up of ions in the solid state but the ions are not free to move. For example sodium chloride, Na^+Cl^- .

When ionic electrolytes are heated, sufficient energy is absorbed to break the crystal lattice so that the ions are free to move within the molten electrolyte.

When ionic electrolytes are dissolved in water (or any other ionizing solvent), the crystal lattice is broken, the ions become free to move. The ions are hydrated (solvated, completely surrounded by water molecules)

(ii) Covalent electrolytes

These electrolytes do not contain ions so they conduct electricity in the liquid state as ionic electrolytes do. The covalent electrolytes that contain polar bonds such as $O-H$ or $H-halogen$ bonds. They react with water or any other ionizing solvent to form hydrated ions. These include all mineral acids.

2. Electrodes

These are conductors which carry electricity into and out of the cell. The electrodes include the *anode* and the *cathode*.

(i) Anode

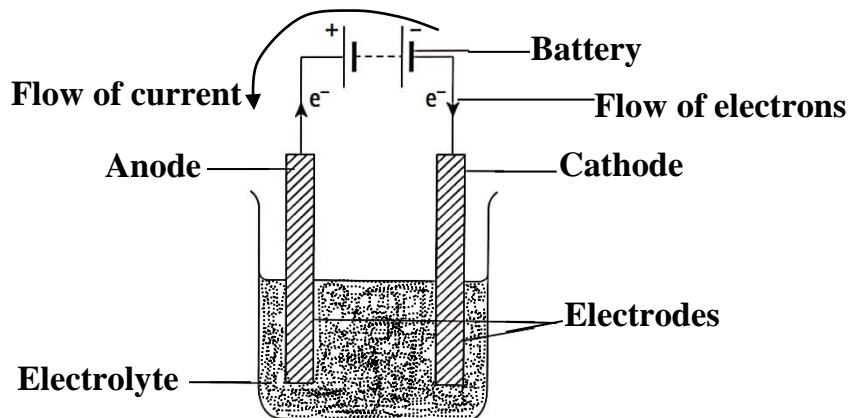
This is the electrode at which oxidation takes place

(ii) Cathode

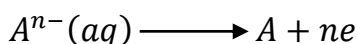
This is the electrode at which reduction takes place

Explaining the changes that take place during electrolysis

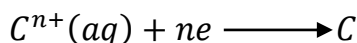
Electrolysis is generally carried out in an *electrolytic cell* as shown below.



The electrolytic cell is set up as shown above. The electrolyte contains both cations and anions. During electrolysis, the anions migrate to the anode and lose electrons (are oxidised) to form neutral elements or new molecules.



The cations migrate to the cathode and combine with the electrons there (are reduced) to form neutral elements or new molecules.





Principles of electrolysis (selective discharge of ions)

Under similar conditions, when two or more ions with a similar charge are present in a solution, i.e. H^+ and Na^+ or Cl^- and $\bar{O}H$, one ion is preferentially selected for discharge at each electrode and the selection of the ion depends on the following factors:

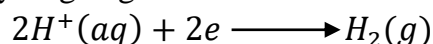
- (i) *Position of the ion in the electrochemical series*
- (ii) *Concentration of the ions in solution*
- (iii) *Nature of the electrode.*

(i) *Position of the ion in the electrochemical series*

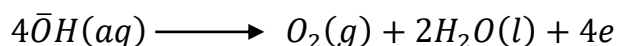
Cations (move to cathode)	Anions (move to anode)
K^+ Ca^{2+} Na^+ Mg^{2+} Al^{3+} Zn^{2+} Fe^{2+} Sn^{2+} Pb^{2+} H^+ Cu^{2+} Ag^+	F^- SO_4^{2-} NO_3^- Cl^- Br^- I^- $\bar{O}H$
Increasing ease of discharge at cathode 	 Increasing ease of discharge at anode

If all the other factors (stated above) are constant, any ion is discharged from solution in preference to the ions above it in the electrochemical series.

For example in electrolysis of sodium hydroxide solution, the solution contains the cations; H^+ from water and Na^+ . The hydrogen ion discharges in preference to the sodium ion at the cathode. Hydrogen gas is formed at the cathode.



During electrolysis of silver nitrate solution, the solution contains the anions; $\bar{O}H$ from water and NO_3^- . The hydroxide ion is discharged in preference to the nitrate ion at the anode. Oxygen gas is formed at the anode.

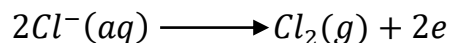


Note: The order of preferential discharge given in the table above only applies for discharge from aqueous solutions containing ions at comparable concentrations approximately 1M. Sometimes exceptions arise as a result of large differences in concentration.

(ii) *Concentration of the ions in solution*

An ion present at a lower concentration is more difficult to discharge than an ion present at a higher concentration.

The electrolysis of sodium chloride solution liberates chlorine at the anode during manufacture of chlorine. This is because although the solution contains the anions; $\bar{O}H$ and Cl^- . The chloride ion is discharged because it is present in a higher concentration than the hydroxide ion.



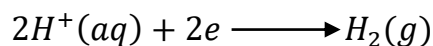
The electrolysis of concentrated hydrochloric acid liberates chlorine at the anode for the same reason as in the case above.

(iii) Nature of the electrode.

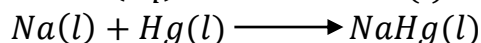
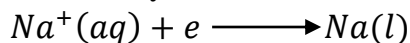
Inert electrodes like platinum may not affect the products of electrolysis. Some electrodes may affect the products of electrolysis. For example:

(a) Electrolysis of concentrated sodium chloride solution (saturated brine) using platinum cathode and mercury cathode.

When a platinum cathode is used, hydrogen ions are discharged in preference to sodium ions because hydrogen is lower than sodium in the electrochemical series. Hydrogen gas is therefore formed at the platinum cathode.

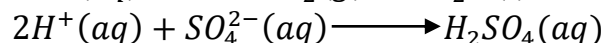
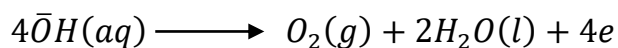


When a mercury cathode is used, sodium ions are discharged in preference to hydrogen ions because the discharge of sodium ion requires less energy than the discharge of hydrogen ions. Sodium amalgam is therefore formed at the mercury cathode by the reaction between sodium and the mercury cathode.



(b) Electrolysis of copper(II) sulphate solution using platinum anode and copper anode.

When a platinum anode is used, hydroxide ions are discharged in preference to sulphate ions because the hydroxide ion is lower than the sulphate ion in the electrochemical series. Oxygen gas is therefore formed at the platinum anode. The solution at the anode also becomes acidic due to the reaction between hydrogen ions and sulphate ions to form sulphuric acid.



When a copper anode is used, neither the hydroxide ions nor the sulphate ions are discharged but instead the copper anode dissolves in the solution to form copper(II) ions. The electrolysis is merely a transfer of copper from the anode to the cathode.



Laws of electrolysis

Micheal Faraday studied the quantitative relationships between the electricity passed through an electrolyte and the amount of material liberated or deposited at the electrodes.

1. Faraday's first law of electrolysis states that *the mass of the substance liberated at an electrode during electrolysis is directly proportional to the quantity of electricity passed through the electrolyte.*

$$m \propto Q \text{ but } Q = It$$
$$\text{Therefore } m \propto It$$
$$m = EIt$$

Where; m is the mass of substance consumed or produced at an electrode

Q is the quantity of charge passed in Coulombs

I is the current in amperes

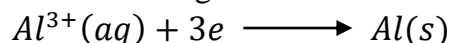
t is the time in **seconds** for which the current was passed.

E is a proportionality constant called the electro-chemical equivalent.

2. Faraday's second law of electrolysis states that ***the quantity of electricity required to liberate one mole of any element is proportional to the charge number of its ion.***

The charge number of an ion, represented by z is the number of positive or negative charges which the ion possesses. It can be positive or negative. For example for H^+ ; $z = 1$, for Al^{3+} ; $z = 3$, for Cl^- ; $z = -1$ and for O^{2-} ; $z = -2$.

The magnitude of the charge number(z) is usually equal to the number of moles electrons required for the ion to be discharged.



3 moles of electrons are required for discharge of 1 mole of Al^{3+}

3 Faraday are transferred for discharge of 1 mole of Al^{3+}

(3×96500) Coulombs are transferred for discharge of 27g of Al^{3+}

($3 \times 96500 \times 6.02 \times 10^{23}$) electrons are transferred for discharge of 27g of Al^{3+}

Note that 1 mole of electrons has a charge of 96500 Coulombs

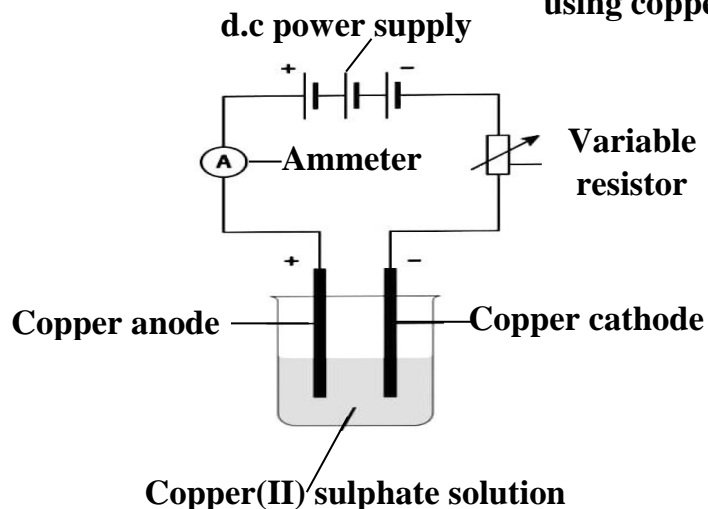
1 Faraday = 96500 Coulombs

Therefore 1 Faraday = 1 mole of electrons

Since 1 mole of electrons = 6.02×10^{23} electrons

Then 1 Faraday = 6.02×10^{23} electrons

Experiment to determine the Faraday constant by electrolysis of copper(II) sulphate using copper electrodes.



Arrange the apparatus as shown

The variable resistor is used to keep the current constant

Weigh the mass of the pure copper anode(x_1 g) and pure copper cathode(y_1 g) separately

Pass a constant electric current(I Amperes) for a measured time interval(t seconds)

Remove the cathode and anode and wash them with distilled water and then propanone and dry them.

The washed and dried cathode and anode again and their new masses (x_2 g) and (y_2 g) recorded respectively.

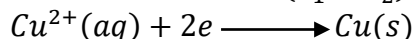
Treatment of results

Mass of copper removed from the anode = $(x_1 - x_2)g$

Quantity of charge passed, $Q = (It)$ Coulombs

$(x_1 - x_2)g$ of Cu are deposited by $(It)C$ of charge

63.5g of Cu are deposited by $\left(\frac{63.5 \times I \times t}{(x_1 - x_2)}\right) C$ of charge



1 mole of Cu is deposited by 2 moles of electrons

63.5g of Cu are deposited by 2 moles of electrons

Therefore 2 moles of electrons have a charge of $\left(\frac{63.5 \times I \times t}{(x_1 - x_2)}\right) C$

1 mole of electrons has a charge of $\left(\frac{63.5 \times I \times t}{(x_1 - x_2) \times 2}\right) C$

The value of $\left(\frac{63.5 \times I \times t}{(x_1 - x_2) \times 2}\right)$ is found to be

$\approx 96500C$ which is the Faraday's constant

Trial question;

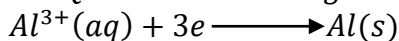
A student passed a constant electric current of 0.15A through a solution of silver nitrate using pure silver electrodes for exactly 45 minutes. The mass of the anode decreased by 0.45g. Use this data to calculate the charge on a mole of electrons. ($Ag = 108$)

Calculations of electrolysis

Examples

1. Calculate the quantity of charge required to deposit 40.5g of aluminium during electrolysis of a solution of aluminium ions.
($1F = 96500C$; $Al = 27$)

$$Q = ? \quad m = 40.5g$$



1 mole of Al is deposited by 3 moles of electrons

$(1 \times 27)g$ are deposited by $(3 \times 96500) C$ of charge

$$\begin{aligned} 40.5 g \text{ are deposited by } \left(\frac{3 \times 96500 \times 40.5}{27}\right) C \text{ of charge} \\ = 434250 \text{ Coulombs} \\ Q = 434250 C \end{aligned}$$

2. When current was passed through a solution of silver nitrate for 10 minutes, 0.54g of silver was deposited at the cathode. Calculate the current.

$$(1F = 96500C; Ag = 108)$$

$$I = ? \quad t = 10 \text{ minutes} \quad m = 0.54g$$

$$Ag^+(aq) + e \longrightarrow Ag(s)$$

1 mole of Ag is deposited by 1 mole of electrons
 $(1 \times 108)g$ are deposited by $(1 \times 96500) C$ of charge
 $0.54 g$ are deposited by $\left(\frac{96500 \times 0.54}{108}\right) C$ of charge
 $= 482.5 \text{ Coulombs}$

$$Q = 482.5C$$

$$Q = It$$

$$482.5 = I \times 10 \times 60$$

$$I = \frac{482.5}{600} = 0.804 A$$

3. Determine the time taken to deposit 1.0g of chromium when a current of 0.120A flows through a solution of chromium(III) sulphate.

$$(Faraday's \text{ constant} = 96500C; Cr = 52)$$

$$I = 0.120A \quad t = ? \quad m = 1.0g$$

$$Cr^{3+}(aq) + 3e \longrightarrow Cr(s)$$

1 mole of Cr is deposited by 3 moles of electrons
 $(1 \times 52)g$ are deposited by $(3 \times 96500) C$ of charge
 $1.0 g$ of Cr are deposited by $\left(\frac{3 \times 96500 \times 1.0}{52}\right) C$ of charge
 $= 5567.308 \text{ Coulombs}$

$$Q = 5567.308 C$$

$$Q = It$$

$$5567.308 = 0.120 \times t$$

$$t = \frac{5567.308}{0.120}$$

$$t = 46394 \text{ seconds}$$

4. Calculate the mass of lead deposited at the cathode during electrolysis when a current of 1.50A flows through molten lead(II) bromide for 20 minutes.

$$(Pb = 207)$$

$$I = 1.50A \quad t = 20 \text{ minutes} \quad m = ?$$

$$Q = It = 1.50 \times 20 \times 60$$

$$Q = 1800C$$

$$Pb^{2+}(aq) + 2e \longrightarrow Pb(s)$$

2 moles of electrons deposit 1 mole of Pb
 $(2 \times 96500) C$ of charge deposit $(1 \times 207)g$ of Pb
 $1800 C$ deposit $\left(\frac{1800 \times 207}{2 \times 96500}\right) g$ of Pb
 $= 1.931g$ of Pb

5. An electric current was passed through a solution of copper(II) sulphate electrolyzed using platinum electrodes for 1 hour.

(a) Calculate the strength of the current used to deposit 0.106g of copper.

(b) If the electrolytic cell above was in series with a silver nitrate cell. Calculate the mass of silver deposited on the cathode of the second cell.

(a)

$$I = ? \quad t = 1 \text{ hour} \quad m = 0.106g$$

$$Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$$

1 mole of Cu is deposited by 2 moles of electrons
 $(1 \times 63.4)g$ are deposited by $(2 \times 96500) C$ of charge
 $0.106 g$ are deposited by $\left(\frac{2 \times 96500 \times 0.106}{63.4}\right) C$ of charge
 $= 322.68 \text{ Coulombs}$

$$Q = 322.68 C$$

$$Q = It$$

$$322.68 = I \times 1 \times 60 \times 60$$

$$I = \frac{322.68}{3600} = 0.0896 A$$

<p>(b) $I = 0.0896A$ $t = 1 \text{ hour}$ $m = ?$ For cells in series, the quantity of charge is the same; $Q = 322.68C$</p>	$Ag^+(aq) + e \longrightarrow Ag(s)$ <p>1 mole of electrons deposit 1 mole of Ag $(1 \times 96500) C$ of charge deposit $(1 \times 108)g$ of Ag $322.68 C$ deposit $\left(\frac{322.68 \times 108}{96500}\right)g$ of Ag $= 0.361g$ of Ag</p>
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6. A current of 89.6mA was passed through an electrolytic cell containing dilute sulphuric acid electrolyzed between platinum electrodes for 1 hour. Calculate the total volume of gas measured at 15°C and 100kPa liberated.

<p>$I = 89.6 \times 10^{-3}A$ $t = 1 \text{ hour}$ $Q = It = 0.0896 \times 1 \times 60 \times 60$ $Q = 322.56C$ At cathode ; $2H^+(aq) + 2e \longrightarrow H_2(g)$ 2 moles of electrons liberate 1 mole of H_2 $(2 \times 96500) C$ of charge liberate 1 mole of H_2 $322.56 C$ liberate $\left(\frac{1 \times 322.56}{2 \times 96500}\right)$ moles of H_2 $= 0.001671$ moles of H_2</p>	<p>At anode ; $4\bar{O}H(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e$ 4 moles of electrons are released for 1 mole of \bar{O}_2 $(4 \times 96500) C$ of charge liberate 1 mole of O_2 $322.56 C$ liberate $\left(\frac{1 \times 322.56}{4 \times 96500}\right)$ moles of O_2 $= 0.000836$ moles of O_2 Total moles of gas produced $= (0.001671 + 0.000836) = 0.002507$ moles $pV = nRT$ $V = \frac{nRT}{p} = \frac{0.002507 \times 8.31 \times (15 + 273)}{100 \times 1000}$ $= 5.999 \times 10^{-5}m^3$</p>
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7. Calculate the volume of oxygen liberated at anode at s.t.p in the electrolysis of copper(II) sulphate solution when a current of 1500 milliamperes is passed for 10 minutes.

$$\begin{aligned}
 I &= 1500 \text{ mA} \quad t = 10 \text{ minutes} \\
 Q &= It = 1500 \times 10^{-3} \times 10 \times 60 \\
 Q &= 900C \\
 \text{At anode ; } 4\bar{O}H(aq) &\longrightarrow 2H_2O(l) + O_2(g) + 4e \\
 4 \text{ moles of electrons are released for 1 mole of } O_2 \\
 (4 \times 96500) C \text{ of charge liberate 1 mole of } O_2 \\
 900 C \text{ liberate } \left(\frac{1 \times 900}{4 \times 96500}\right) \text{ moles of } O_2 \\
 &= 0.002332 \text{ moles of } O_2 \\
 1 \text{ mole of } O_2 &\text{ occupies } 22.4 \text{ dm}^3 \text{ at s.t.p} \\
 0.002332 \text{ moles of } O_2 &\text{ occupy } (0.002332 \times 22.4) \text{ dm}^3 \\
 &= 0.0522 \text{ dm}^3
 \end{aligned}$$

8. (a) A current of 32.2A was passed through molten lead(II) bromide for 5 hours and the bromine liberated reacted with 94g of hydroxybenzene. Calculate the number of moles of ;
- bromine liberated
 - hydroxybenzene that reacted

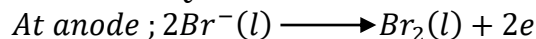
(b) State what is observed and write equation for the reaction that took place between bromine and hydroxybenzene in (a) above.

(a) (i)

$$I = 32.2A \quad t = 4 \text{ hours}$$

$$Q = It = 32.2 \times 5 \times 60 \times 60$$

$$Q = 579600 \text{ C}$$



2 moles of electrons are released for 1 mole of Br_2

$(2 \times 96500) \text{ C}$ of charge liberate 1 mole of Br_2

$$579600 \text{ C liberate } \left(\frac{1 \times 579600}{2 \times 96500} \right) \text{ moles of } \text{Br}_2$$

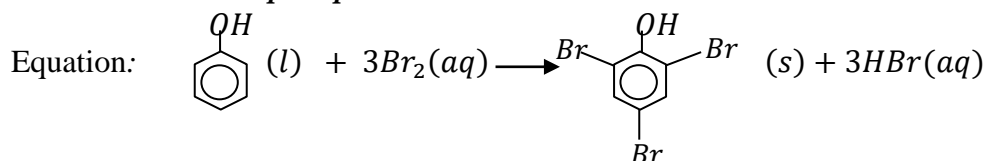
$$= 3 \text{ moles of } \text{Br}_2$$

(ii)

$$\text{Molar mass of } \text{C}_6\text{H}_5\text{OH} = 72 + 6 + 16 = 94g$$

$$\text{Moles of } \text{C}_6\text{H}_5\text{OH} = \frac{94.0}{94} = 1 \text{ mole}$$

(b) Observation: **White precipitate**



9. 20cm^3 of 0.05M aqueous phenylamine was mixed with 50cm^3 of 1M sodium bromide and electrolyzed at current of 0.2A . The first permanent bromine colour was observed after 48.25 minutes and then electrolysis was stopped. (*Faraday's constant* = 96500Cmol^{-1}).

(i) Calculate the moles of bromine that reacted with 1 mole of phenylamine

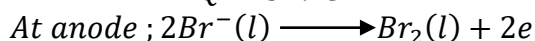
(ii) Hence write equation of the reaction between bromine and phenylamine. Name the product

(i)

$$I = 0.2A \quad t = 48.25 \text{ minutes}$$

$$Q = It = 0.2 \times 48.25 \times 60$$

$$Q = 579 \text{ C}$$



2 moles of electrons are released for 1 mole of Br_2

$(2 \times 96500) \text{ C}$ of charge liberate 1 mole of Br_2

$$579 \text{ C liberate } \left(\frac{1 \times 579}{2 \times 96500} \right) \text{ moles of } \text{Br}_2$$

$$= 0.003 \text{ moles of } \text{Br}_2$$

$$\text{Moles of } \text{C}_6\text{H}_5\text{NH}_2 = \left(\frac{20 \times 0.05}{1000} \right) = 0.001 \text{ moles}$$

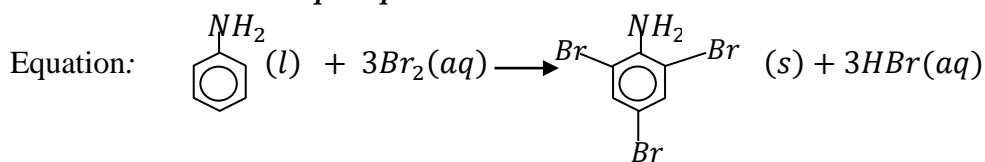
$0.001 \text{ moles of } \text{C}_6\text{H}_5\text{NH}_2$ react with $0.003 \text{ moles of } \text{Br}_2$

$$1 \text{ mole of } \text{C}_6\text{H}_5\text{NH}_2 \text{ reacts with } \left(\frac{1 \times 0.003}{0.001} \right) \text{ moles of } \text{Br}_2$$

$$= 3 \text{ moles of } \text{Br}_2$$

Hint: Electrolysis of sodium bromide yields bromine at the anode. The sodium bromide was such an excess such that enough bromine is liberated to react with all the phenylamine. The first bromine colour only appears if just enough bromine has been formed to react with all the phenylamine present.

(ii) Observation: **White precipitate**



10. A direct current of 0.45A was passed through a dilute solution of copper(II) sulphate using graphite electrodes for 5.96 hours.

(a) Write equation for the reaction at the:

(i) cathode

(ii) anode

(b) If 3.1767g of copper was deposited and 560cm³ of oxygen at stp were evolved, calculate the quantity of electricity required to produce 1 mole of each substance at their respective electrodes.

(a) (i) At cathode: $Cu^{2+}(aq) + 2e \longrightarrow Cu(s)$

(iii) At anode: $4OH(aq) \longrightarrow 2H_2O(l) + O_2(g) + 4e$

(b) $I = 0.45A$ $t = 5.96 \text{ hours}$

$$Q = It = 0.45 \times 5.96 \times 60 \times 60 = 9655.2 \text{ C}$$

$$\text{Moles of Cu deposited at cathode} = \frac{3.1767}{63.5} = 0.05 \text{ moles}$$

0.05 moles of Cu are deposited by 9655.2 coulombs

$$1 \text{ mole of Cu is deposited by } \left(\frac{1 \times 9655.2}{0.05} \right) \text{ coulombs}$$

$$= \mathbf{193,104 \text{ C}}$$

560 cm³ of O₂ are evolved by 9655.2 coulombs

$$22400 \text{ cm}^3 \text{ of O}_2 \text{ are evolved by } \left(\frac{22400 \times 9655.2}{560} \right) \text{ coulombs}$$

$$= \mathbf{386,208 \text{ C}}$$

$$\frac{193,104C}{193,104C} : \frac{386,208C}{193,104C}$$

$$\mathbf{1 : 2}$$

Questions

- 3 Faraday are needed to electroplate a given amount of metal using a current of 5.0A. How long will it take to electroplate the metal?
- Calculate the mass of copper deposited at the cathode when a current of 1.0A was passed through copper(II) sulphate solution for 10 minutes.
- Calculate the mass of silver deposited at the cathode during electrolysis when a current of 1.80A flows through an aqueous solution of silver nitrate for 45.0 minutes.

4. The same current was passed through molten sodium chloride and through molten cryolite containing aluminium oxide. If 4.60g of sodium were liberated in one cell. Calculate the mass of aluminium liberated in the other cell.
5. During the extraction of aluminium, a current of 0.2 ampere was passed for one hour through aluminium sulphate solution.
 - (a) Write an equation for the reaction that took place at each electrode
 - (b) Calculate the mass of aluminium produced
6. Calculate the mass of chlorine that can be produced by the electrolysis of molten sodium chloride with a current of 5.5 amperes for 25 minutes.
7. Calculate the mass of lead deposited when 0.2 moles of electrons are passed through lead(II) nitrate solution during electrolysis.
8. Calculate the volume of oxygen liberated at anode at s.t.p in the electrolysis of copper(II) sulphate solution when a current of 1500 milliamperes is passed for 10 minutes.
9. Calculate the volume of chlorine liberated at standard temperature and pressure by passing 0.2 moles of electrons during electrolysis sodium chloride solution.
10. Determine the mass of hydrogen liberated by passing 0.5 moles of electrons during electrolysis sodium chloride solution.
11. If a current is passed through a cell for 2 hours deposits 0.4818g of silver. Calculate the volume of oxygen that would be liberated in the same circuit where dilute sulphuric acid is electrolysed.
(1F = 96500C; 1 mole of gas occupies 22.4dm³ at stp)
12. Calculate the volume of oxygen produced at room temperature when a concentrated aqueous solution of sulphuric acid is electrolyzed for 30 minutes using a current of 0.50A. (1F = 96500C; 1 mole of gas occupies 24.0dm³ at room temperature)
13. During the electrolysis of a 1M copper(II) sulphate solution at 20°C, a current of 0.1A was passed for one hour through the electrolyte. The mass of the copper cathode increased by 0.118g. State how the change in mass would be affected if the experiment was repeated:
 - (a) at a current of 0.2A
 - (b) at 30°C
 - (c) with a 2M copper(II) sulphate solution
 - (d) for a time of 2 hours
14. (a) An aqueous solution of copper(II) sulphate was electrolyzed between copper electrodes.

Write equation for the reaction at the;

- (i) Cathode

- (ii) Anode
- (b) (i) Identify the species which carry the current through the solution and state their direction of flow.
- (ii) Explain the changes in the mass of each electrode and in the concentration of copper(II) sulphate near the anode.
- (iii) Calculate the change in mass of the anode if a current of 1.0A is maintained for one hour.
- (c) During the electrolysis of aqueous hydrogen chloride between silver electrodes, the anode mass increases and a white coating form on it. Explain this observation.

The applications of electrolysis in industry

The elements potassium, calcium, sodium, magnesium and aluminium being very reactive, are never found as free elements. They are extracted by electrolysis.

Potassium is extracted from fused potassium hydroxide. Sodium from molten sodium chloride, calcium from fused calcium chloride and aluminium from Bauxite.

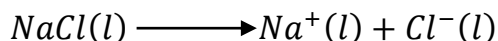
1. Extraction of sodium by electrolysis of molten sodium chloride in the Down's process. (The same process is used for manufacture of chlorine)

Sodium is extracted by *electrolysis of molten sodium chloride* in the *Down's cell*.

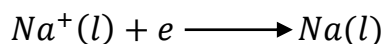
A *carbon anode* is used and an *iron cathode* and are separated from each other by an *iron gauze diaphragm*.

Calcium chloride is added to the electrolyte *to lower its melting point of sodium chloride from about 800°C to about 600°C*.

Sodium chloride is decomposed by electric current to form sodium ions and chloride ions.



Sodium ions are preferentially discharged at the cathode at the temperature used *forming sodium*.

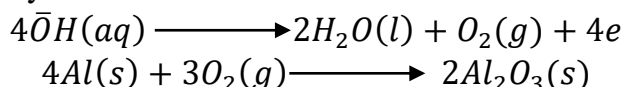


Chloride ions migrate to the anode and form chlorine gas which escapes from the cell.



2. Anodisation of aluminium

Aluminium is normally covered by a thin coating of aluminium oxide to protect it from corrosion and to make it resistant from chemical attack. The thickness of the oxide layer is increased by electrolyzing dilute sulphuric acid or chromic(VI) acid with the aluminium made the anode. The oxygen liberated at the anode reacts with the aluminium to form the protective layer of aluminium oxide.



3. Electroplating

This is the electrical coating of one metal with another metal to make it resistant to corrosion and improve its appearance. The metal to be electroplated is made the cathode and the electroplating metal made the anode. The electrolyte must contain a solution of ions of the electroplating metal.

4. Manufacture of sodium chlorate(I) and sodium chlorate(V) by electrolysis of concentrated sodium chloride solution.

A *cold concentrated solution of sodium chloride* is electrolyzed using *platinum electrodes placed close together*. The chlorine liberated at the anode combines with the hydroxyl ions left at the cathode to form sodium chlorate(I).



If the electrolysis is done using *a hot concentrated solution of sodium chloride at 80°C* The chlorine liberated at the anode combines with the hydroxyl ions left at the cathode to form sodium chlorate(V).



5. Extraction of aluminium by electrolysis of molten aluminium oxide

6. Manufacture of sodium hydroxide by electrolysis of concentrated sodium chloride solution (saturated brine) using a mercury cell (Castner-Kellner cell) or a diaphragm cell.

(The same process can as well be used for manufacture of chlorine)

7. Refining of copper

(Check for the details of 5, 6 and 7 in Demystifying Inorganic Chemistry by the same author)

CONDUCTIVITY OF SOLUTIONS OF ELECTROLYTES

When electric current flows through an electrolyte, there is resistance to the flow of current. The current that flows through a given solution under given conditions is inversely proportional to the reciprocal of resistance.

$$\text{Current flowing through an electrolytic solution} \propto \frac{1}{\text{Resistance of the solution}}$$

The common terms used

1. Conductance

Conductance is the reciprocal of resistance of an electrolytic solution.

$$\text{Conductance} = \frac{1}{R} \text{ where } R \text{ is Resistance}$$

The SI unit of conductance is the siemens (S) although it used to be measured in reciprocal ohms (Ω^{-1}). Therefore $1S = 1\Omega^{-1}$.

High resistance means low conductance and low resistance means high conductance.

2. Resistivity (ρ)

To compare resistances of different electrolytic solutions, the idea of resistivity is used.

Resistivity is the resistance of a solution placed between two parallel electrodes of cross-sectional area 1 m^2 and separated by a distance of 1 m apart.

Resistance(R) of an electrolytic solution is directly proportional to the length (l) between the electrodes;

$$R \propto l \dots \dots (i)$$

The resistance(R) of an electrolytic solution is also inversely proportional to the cross sectional area (A) of the electrodes;

$$R \propto \frac{1}{A} \dots \dots (ii)$$

Combining (i) and (ii);

$$R \propto \frac{l}{A}$$
$$R = \rho \frac{l}{A} \dots \dots (iii)$$

Where R is resistance

ρ is resistivity

l is length between the electrodes

A is the cross sectional area of the electrodes

From (iii) $R = \rho \frac{l}{A}$, then Resistivity, $\rho = \frac{RA}{l}$

Since R is measured in ohms (Ω), Area is measured in m^2 and length in metres(m), then the SI unit of resistivity is ohm metre(Ωm). But Ωcm can also be used.

3. Electrolytic conductivity (\mathcal{K})

It is also called *specific conductivity* or *specific conductance*.

To compare conductance of different electrolytes, electrolytic conductivity(\mathcal{K}) is used.

Electrolytic conductivity is defined as the conductivity of a solution of an electrolyte placed between two parallel electrodes of cross-sectional area 1 m^2 and separated by a distance of 1 m apart.

or

It is the reciprocal of resistivity.

$$\mathcal{K} = \frac{1}{\rho} = \frac{1}{RA/l} = \frac{l}{RA} = \frac{1}{R} \times \frac{l}{A}$$

The SI unit of electrolytic conductivity is siemen per metre(Sm^{-1}). But Scm^{-1} can also be used.

$$1\text{Sm}^{-1} = 1\Omega^{-1}\text{m}^{-1}$$
$$1\text{Scm}^{-1} = 1\Omega^{-1}\text{cm}^{-1}$$

4. Cell constant

From $R = \rho \frac{l}{A}$, the cell constant is the value of $\frac{l}{A}$. Its units are m^{-1} or can be cm^{-1} .
 l and A for any cell are constant.

Cell constant is therefore the distance between two parallel electrodes of a cell divided by the cross sectional area of one electrode.

Therefore, $R = \rho \frac{l}{A} = \text{resistivity} \times \text{Cell constant}$

Also $\mathcal{K} = \frac{1}{R} \times \frac{l}{A} = \text{conductance} \times \text{cell constant}$

$$\text{or } \mathcal{K} = \frac{l}{A} / R = \frac{\text{cell constant}}{\text{Resistance}}$$

5. Molar conductivity (Λ_c)

It is also called **molar conductance**.

Molar conductivity is the conductivity of a solution of containing 1 mole of an electrolyte placed between two parallel electrodes of cross-sectional area 1 m^2 and separated by a distance of 1 m apart.

OR

It is the electrolytic conductivity divided by concentration.

$$\Lambda_c = \frac{\mathcal{K}}{c}$$

since $\frac{1}{c} = \text{Dilution}(V)$, then $\Lambda_c = \mathcal{K} \times \frac{1}{c} = \mathcal{K} \times V$

The two above formulae show the relationship between electrolytic conductivity and molar conductivity.

The SI unit of molar conductivity is $\text{m}^2\text{mol}^{-1}$. But $\text{Scm}^2\text{mol}^{-1}$ can also be used.

$$1\text{Sm}^2\text{mol}^{-1} = 1\Omega^{-1}\text{m}^2\text{mol}^{-1}$$

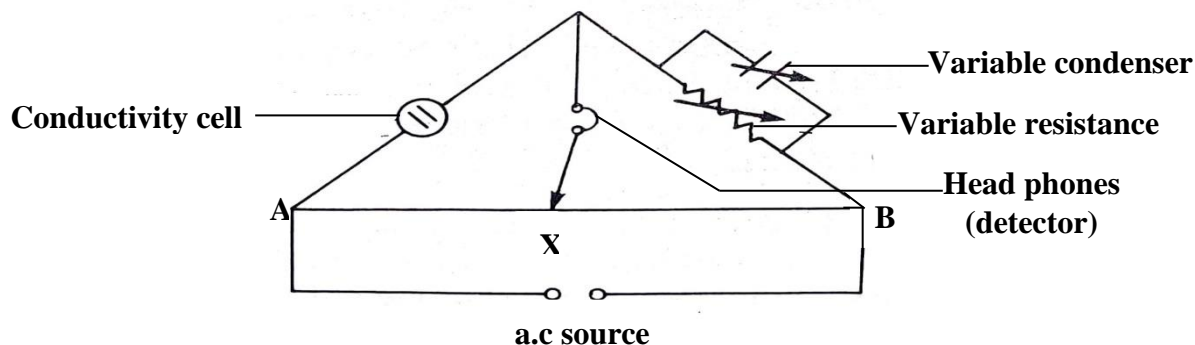
$$1\text{Scm}^2\text{mol}^{-1} = 1\Omega^{-1}\text{cm}^2\text{mol}^{-1}$$

The formula of molar conductivity used in calculations depends on the units of \mathcal{K} and c given. The formula used is intended to make units consistent.

If unit of \mathcal{K} is $\text{Scm}^2\text{mol}^{-1} (\Omega^{-1}\text{cm}^2\text{mol}^{-1})$ and that of c is mol dm^{-3} then; $\Lambda_c = \frac{1000\mathcal{K}}{c}$	If unit of \mathcal{K} is $\text{Sm}^2\text{mol}^{-1} (\Omega^{-1}\text{m}^2\text{mol}^{-1})$ and that of c is mol dm^{-3} then; $\Lambda_c = \frac{\mathcal{K}}{1000c}$	The expression $\Lambda_c = \frac{\mathcal{K}}{c}$ is only and only used if the units are consistent.
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Note: When the definitions are stated in terms of formulae, each term in the formula should be well defined.

Measurement of conductivity of solutions



A solution of the electrolyte of known concentration is prepared using conductivity water (demineralized water or water purified by ion exchange)

A known volume of the standard solution of the electrolyte is then pipetted and placed in a conductivity cell.

The conductivity cell and its solution is connected in a Wheatstone bridge circuit where it's made the unknown resistance.

A rapidly alternating current is applied from a small induction coil or a vacuum tube oscillator.

The variable resistance and the position X along wire AB are changed until no current passes through the head phones

At this balance point the buzzing sound in the head phones (used as detector) is a minimum.

The distances AX and XB at balance point are measured.

The area of the electrodes(A) in the conductivity cell and their distance of separation(l) is also measured.

Treatment of results

At the balance point ;

$$\frac{\text{Resistance of conductivity cell(solution)}}{\text{Resistance of variable resistance}} = \frac{AX}{XB}$$

The resistance of the solution is then calculated and used to find conductance from;

$$\text{Conductance} = \frac{1}{R} \text{ where } R \text{ is Resistance of solution}$$

$$\text{The electrolytic conductivity, } \mathcal{K} = \frac{1}{R} \times \frac{l}{A}$$

Calculations involving electrolytic conductance

Examples

1. (a) State what is meant by the term cell constant.
- (b) The resistivity of 0.02M potassium chloride solution is $361 \Omega cm$ and a conductivity cell having such a solution was found to have a resistance of 550Ω .
- (i) Calculate the cell constant
- (ii) if the same cell was filled with 0.1M zinc sulphate solution had a resistance of 72Ω . Calculate the conductivity of 0.1M zinc sulphate solution.

$$\begin{aligned}
 \text{(b) (i)} \quad \rho &= 361 \Omega cm \quad R = 550 \Omega \\
 \text{From } R &= \rho \frac{l}{A} \\
 R &= \rho \times \text{Cell constant} \\
 \text{Cell constant} &= \frac{R}{\rho} = \frac{550 \Omega}{361 \Omega cm} \\
 &= 1.5235 cm^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{(ii)} \quad R &= 72 \Omega \\
 \mathcal{K} &= \frac{1}{R} \times \frac{l}{A} = \frac{1}{R} \times \text{Cell constant} \\
 \mathcal{K} &= \frac{1}{72 \Omega} \times \text{Cell constant} \\
 &= \frac{1}{72 \Omega} \times 1.5235 cm^{-1} \\
 \mathcal{K} &= 0.02116 S cm^{-1}
 \end{aligned}$$

2. (a) A conductivity cell with electrodes $2 cm^2$ in area and $1 cm$ apart has a resistance of 7.25Ω when filled with 5 percent potassium chloride solution. Calculate the:
- (i) cell constant
- (ii) the conductivity of the potassium chloride solution.
- (b) If the same cell was filled with 0.02M potassium chloride with a resistivity of $361 \Omega cm$. Calculate the resistance.

$$\begin{aligned}
 \text{(a) (i)} \quad A &= 2 cm^2 \quad l = 1 cm \quad R = 7.25 \Omega \\
 \text{Cell constant} &= \frac{l}{A} = \frac{1}{2} = 0.5 cm^{-1} \\
 \text{(ii)} \quad \mathcal{K} &= \frac{1}{R} \times \frac{l}{A} = \frac{1}{R} \times \text{Cell constant} \\
 \mathcal{K} &= \frac{1}{7.25 \Omega} \times \text{Cell constant} \\
 &= \frac{1}{7.25 \Omega} \times 0.5 cm^{-1} \\
 \mathcal{K} &= 0.06897 S cm^{-1}
 \end{aligned}$$

$$\begin{aligned}
 \text{(b)} \quad \rho &= 361 \Omega cm \\
 R &= \rho \frac{l}{A} \\
 R &= \rho \times \text{Cell constant} \\
 R &= 361 \times 0.5 \\
 R &= 180.5 \Omega
 \end{aligned}$$

3. The resistance of a 0.01M sodium chloride solution in a conductivity cell was found to be 210Ω . The specific conductance of the solution is $4.5 \times 10^{-3} S cm^{-1}$. Determine the cell constant.

$$R = 210\Omega \quad \mathcal{K} = 4.5 \times 10^{-3} \text{ Scm}^{-1}$$

$$\mathcal{K} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{R} \times \text{Cell constant}$$

$$\mathcal{K} = \frac{\text{Cell constant}}{R}$$

$$\text{Cell constant} = \mathcal{K} \times R$$

$$= 4.5 \times 10^{-3} \times 210$$

$$\text{Cell constant} = 0.945 \text{ cm}^{-1}$$

4. A conductivity cell has electrodes of cross sectional area 4 cm^2 and 2 cm apart. The cell is filled with pure water of conductivity $8 \times 10^{-7} \text{ Scm}^{-1}$ and a potential difference of 10 V applied. Calculate the current that would flow through the cell.

$$A = 4 \text{ cm}^2 \quad l = 2 \text{ cm} \quad \mathcal{K} = 8 \times 10^{-7} \text{ Scm}^{-1}$$

$$V = 10 \text{ V}$$

$$\mathcal{K} = \frac{1}{R} \times \frac{l}{A}$$

$$8 \times 10^{-7} = \frac{1}{R} \times \frac{2}{4}$$

$$R = \frac{2}{4 \times 8 \times 10^{-7}} = 625000\Omega$$

$$V = IR$$

$$I = \frac{V}{R} = \frac{10}{625000} = 1.6 \times 10^{-5} \text{ A}$$

5. A 0.1 M solution of ethanoic acid when placed between two electrodes, each 2.5 cm^2 in area and separated by 0.8 cm has a resistance of 6956 ohms . Calculate the:

- (i) specific conductivity,
(ii) molar conductivity of the solution.

$$c = 0.1 \text{ mol dm}^{-3} \quad A = 2.5 \text{ cm}^2$$

$$l = 0.8 \text{ cm} \quad R = 6956\Omega$$

$$(i) \quad \mathcal{K} = \frac{1}{R} \times \frac{l}{A} = \frac{1}{6956} \times \frac{0.8}{2.5}$$

$$\mathcal{K} = 4.6 \times 10^{-5} \Omega^{-1} \text{ cm}^{-1}$$

$$(ii) \quad \Lambda_c = \frac{1000\mathcal{K}}{c} = \frac{1000 \times 4.6 \times 10^{-5}}{0.1}$$

$$\Lambda_c = 0.46 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

6. The molar conductivity of 0.1 M ethanoic acid solution is $4.6 \text{ Scm}^2 \text{ mol}^{-1}$. Calculate the:

- (i) electrolytic conductivity
(ii) resistivity.

$$(i) \quad \Lambda_c = 4.6 \text{ Scm}^2 \text{ mol}^{-1} \quad c = 0.1 \text{ mol dm}^{-3}$$

$$\mathcal{K} = ?$$

$$\Lambda_c = \frac{1000\mathcal{K}}{c} \quad \mathcal{K} = \frac{\Lambda_c \times c}{1000}$$

$$\mathcal{K} = \frac{4.6 \times 0.1}{1000} = 4.6 \times 10^{-4} \text{ Scm}^{-1}$$

$$(ii) \quad \mathcal{K} = \frac{1}{\rho}$$

$$\rho = \frac{1}{\mathcal{K}} = \frac{1}{4.6 \times 10^{-4} \text{ Scm}^{-1}}$$

$$\rho = 2173.91 \Omega \text{ cm}$$

7. The resistance of a conductivity cell of a conductivity cell when filled with 0.05 M solution of an electrolyte M_2N is 100Ω at 40°C . The same conductivity cell when filled with 0.01 M XY solution has a resistance of 50Ω . If the electrolytic conductivity of 0.05 M M_2N is 0.0001 Scm^{-1} . Calculate the:

- (i) electrolytic conductivity of 0.01 M XY solution
(ii) molar conductivity of 0.01 M XY solution

(i) For M_2N ;
 $c = 0.05 \text{ mol dm}^{-3}$ $R = 100 \Omega$
 $\mathcal{K} = 0.0001 \text{ S cm}^{-1}$
 $\mathcal{K} = \frac{1}{R} \times \text{cell constant}$
 $0.0001 = \frac{1}{100} \times \text{cell constant}$
 $\text{Cell constant} = 0.0001 \times 100$
Cell constant = 0.01 cm^{-1}

For XY ;
 $c = 0.01 \text{ mol dm}^{-3}$ $R = 50 \Omega$
 $\text{Cell constant} = 0.01 \text{ cm}^{-1}$
 $\mathcal{K} = \frac{1}{R} \times \text{cell constant}$
 $\mathcal{K} = \frac{1}{50} \times 0.01 = \mathbf{0.0002 \Omega^{-1} cm^{-1}}$
(ii) $\Lambda_c = \frac{1000\mathcal{K}}{c}$
 $\Lambda_c = \frac{1000 \times 0.0002}{0.01}$
 $\Lambda_c = \mathbf{20 \Omega^{-1} cm^2 mol^{-1}}$

8. Calculate the mass of ethanoic acid that must be dissolved in a litre of water to make a solution of molar conductivity $75.08 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ and electrolytic conductivity $0.027 \Omega^{-1} \text{ cm}^{-1}$.

$$\Lambda_c = 75.08 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\mathcal{K} = 0.027 \Omega^{-1} \text{ cm}^{-1}$$

$$\Lambda_c = \frac{1000\mathcal{K}}{c} \quad c = \frac{1000\mathcal{K}}{\Lambda_c}$$

$$c = \frac{1000 \times 0.027}{75.08} = \mathbf{0.3596 \text{ mol dm}^{-3}}$$

Molar mass of CH_3COOH
 $= 24 + 4 + 32$
 $= 60 \text{ g}$
Mass of CH_3COOH in one litre
 $= 60 \times 0.3596$
 $= \mathbf{21.576 \text{ g}}$

Questions

- A conductivity cell with electrodes 4 cm^2 in area and 1.5 cm apart has a resistance of 35.6Ω when filled with 2.085 percent barium chloride solution. Calculate the:
 - cell constant
 - the electrolytic conductivity of the barium chloride solution.
- A conductivity cell has electrodes of cross-sectional area of 5 cm^2 in area and 2 cm apart. Calculate the cell constant of the conductivity cell.
- A conductivity cell has electrodes of cross-sectional area of 10 cm^2 in area and 2 cm apart. Calculate the cell constant of the conductivity cell.
- The electrolytic conductivity of 2M potassium chloride solution of 0.3704 S cm^{-1} . The resistance of 2M potassium chloride solution in a conductivity cell is 1.5Ω . Calculate the cell constant of the conductivity cell.
- The conductivity of an aqueous solution of sodium chloride in a cell is $92 \text{ ohm}^{-1} \text{ cm}^{-1}$. The resistance offered by the cell is 247.8 ohm . Calculate the cell constant.
- The molar conductance of 2M potassium chloride solution is $185.2 \Omega^{-1} \text{ cm}^2$. Calculate the specific conductance of the solution.

7. A 0.05M sodium hydroxide solution offered a resistance of $31.6\ \Omega$ in a conductivity cell at 298K. If the cell constant of the cell is 0.367cm^{-1} . Calculate the molar conductivity of the sodium hydroxide solution.
8. (a) Define the terms;
- (i) conductivity
 - (ii) conductance
- (b) Using the same conductivity cell, the resistance of potassium chloride solution and 0.1M chloroethanoic acid solution were found to be 24.9 and 66.5 ohms respectively at 25°C. The conductivity of potassium chloride at 25°C is $0.01164\ \Omega^{-1}\text{cm}^{-1}$.
- (i) Calculate the cell constant
 - (ii) Calculate the conductivity of 0.1M chloroethanoic acid.

Factors affecting electrolytic conductivity of electrolytes

The factors affecting electrolytic conductivity include:

- (i) **Concentration**
- (ii) **Temperature**

(i) Concentration

For a strong electrolyte, as concentration increases, conductivity increases up to a maximum and then decreases.

Explanation;

As *concentration increases, the total number of conducting ions per unit volume solution increases*. This increases the conductivity. As *concentration increases further*, the total number ions in solution increases further since the electrolyte is completely ionized at all concentrations, *inter-ionic distance decreases, ionic interference increases and ionic mobility decreases*. This decreases the electrolytic conductivity.

For a weak electrolyte, as concentration increases, conductivity increases up to a maximum and then decreases.

Explanation;

As *concentration increases, the total number of conducting ions per unit volume solution increases*. This increases the conductivity. As *concentration increases further*, the total number unionized molecules of the electrolyte increases, *degree of dissociation decreases and the number of conducting ions per unit volume of solution decreases*. This decreases the electrolytic conductivity.

(ii) Temperature

For a strong electrolyte, conductivity increases with increase in temperature.

Explanation;

As temperature increases, the average kinetic energy of the conducting ions increases.

The viscosity of the water decreases and the ionic mobility increases.

For weak electrolytes, the effect of temperature depends on the enthalpy change which accompanies ionization.

For a weak electrolyte that ionizes exothermically, increase in temperature decreases the degree of dissociation according to Le Chatelier's principle. Hence *the number of conducting ions per unit volume of solution decreases*. This *decreases the electrolytic conductivity*.

For a weak electrolyte that ionizes endothermically, increase in temperature increases the degree of dissociation according to Le Chatelier's principle. Hence *the number of conducting ions per unit volume of solution increases*. This *increases the electrolytic conductivity*.

Factors affecting molar conductivity of electrolytes

The factors affecting molar conductivity include:

- (i) Temperature of the solution**
- (ii) Magnitude of the charge on the ions**
- (iii) Ionic radius**
- (iv) Viscosity of the solvent**
- (v) Concentration of the solution**

(i) Temperature of the solution

For a strong electrolyte, molar conductivity increases with increase in temperature.

Explanation;

As temperature increases, the average kinetic energy of the conducting ions increases.

The viscosity of the water decreases and the ionic mobility increases.

For weak electrolytes, the effect of temperature depends on the enthalpy change which accompanies ionization.

For a weak electrolyte that ionizes exothermically, increase in temperature decreases the degree of dissociation according to Le Chatelier's principle. Hence *the number of conducting ions per unit volume of solution decreases*. This *decreases the molar conductivity*.

For a weak electrolyte that ionizes endothermically, increase in temperature increases the degree of dissociation according to Le Chatelier's principle. Hence *the number of conducting ions per unit volume of solution increases*. This *increases the molar conductivity*.

Question

- (a) Distinguish between electrolytic conductivity and molar conductivity
(b) The molar conductivity of ethanoic acid containing 0.03mol dm^{-3} is 8.50 units at 18°C and 14.7 units at 100°C . Explain the difference in molar conductivities at the two temperatures.

(ii) **Magnitude of the charge on the ions**

Molar conductivity increases with increase in the magnitude of ionic charge. Ions with high charges are *more strongly attracted by the oppositely charged electrode* and *move faster*.

(iii) **Ionic radius**

Molar conductivity increases with increase in ionic radius. The *higher the ionic radius, the lower the charge density* and *the less hydrated the ion*. The less hydrated ions *move more faster than heavily hydrated ions* hence ions with smaller ionic radius are more conducting than ions with higher ionic radius.

Question; Explain why the:

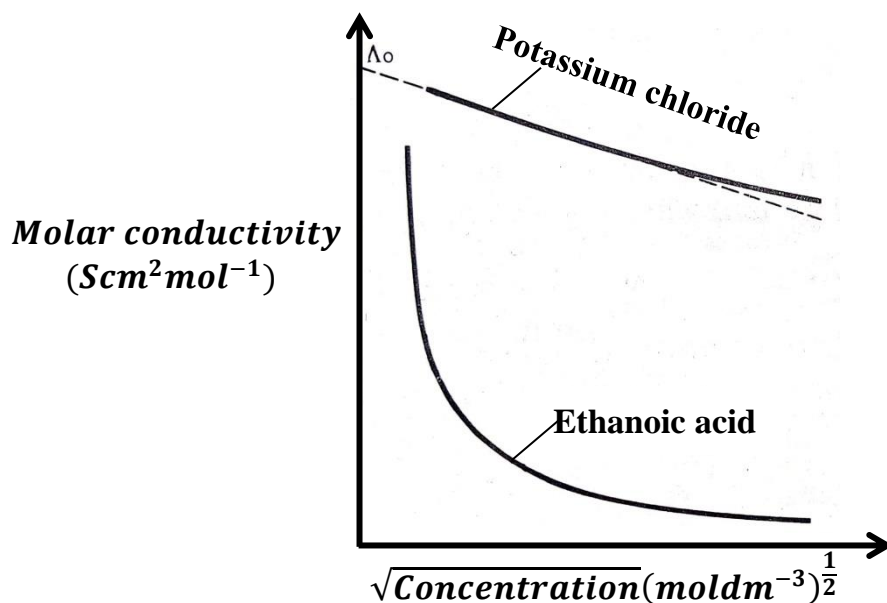
- (a) magnesium ion has a higher molar conductivity than the sodium ion
(b) sulphate ion has a higher molar conductivity than the chloride ion.
(c) the molar conductivity of the lithium ion is smaller than that of the sodium ion

(iv) **Viscosity of the solvent**

The *higher the viscosity of the solvent*, the *lower the ionic mobility* hence *the lower the molar conductivity*.

(v) **Concentration of the solution**

The sketches below show the variation of *molar conductivity* with the *square root of concentration* for both a *strong electrolyte* and a *weak electrolyte*.



Explanation of the shapes of the graphs

For potassium chloride, as concentration increases, molar conductivity decreases.

Potassium chloride is a *strong electrolyte*. As *concentration increases*, the *total number of conducting ions per unit volume increases*, *inter ionic distance decreases*, *ionic interference increases* and *ionic mobility decreases*.

At *zero concentration (infinite dilution)*, *molar conductivity reaches a maximum value* called *molar conductivity at infinite dilution* because *ionic interference is negligible*.

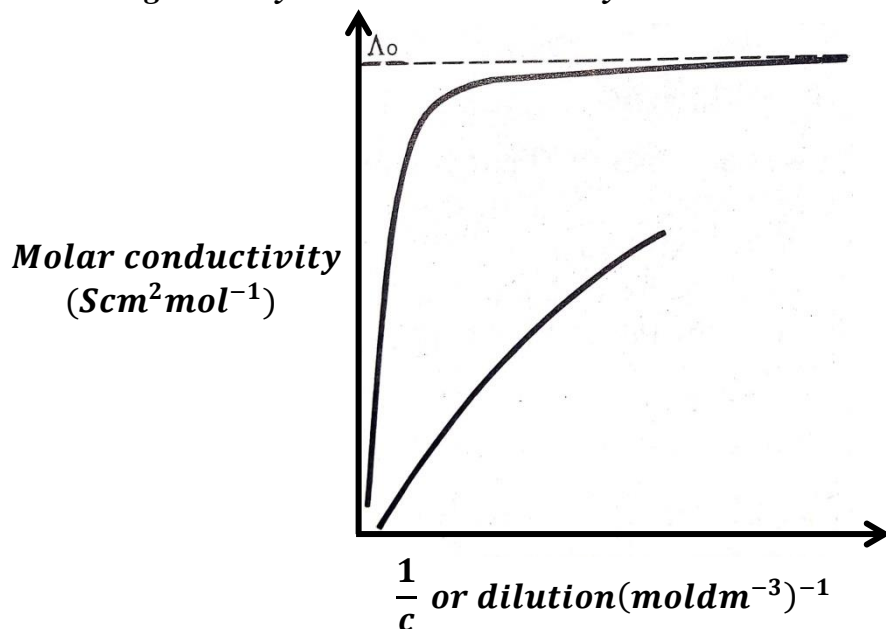
N.B Molar conductivity at infinite dilution is obtained from the graph by extrapolation.

For Ethanoic acid, as concentration increases, molar conductivity decreases.

Ethanoic acid is a *weak electrolyte*. As *concentration increases*, the *degree of dissociation decreases* and the *number of conducting ions per unit volume of solution decreases*.

Instead of concentration, reciprocal of concentration ($\frac{1}{c}$), also called dilution can be used.

The sketches below show the variation of *molar conductivity* with the *dilution* for both a *strong electrolyte* and a *weak electrolyte*.



Note that neither the graphs against concentration nor those against dilution begin from the origin. The graphs do not coincide anywhere too

Explanation of the shapes of the graphs

For potassium chloride, as dilution increases, molar conductivity increases to a maximum value at which it remains constant at infinite dilution.

Potassium chloride is a *strong electrolyte*. As dilution increases, inter-ionic distance increases, ionic interference decreases and ionic mobility increases.

At zero concentration(infinite dilution), the ionic interference is negligible.

N.B Molar conductivity at infinite dilution is obtained from the graph by extrapolation.

For Ethanoic acid, as dilution increases, molar conductivity increases.

Ethanoic acid is a *weak electrolyte*. As dilution increases, degree of dissociation increases and the number of conducting ions per unit volume of solution increases.

Questions

- The table below shows values of molar conductivity of ethanoic and potassium chloride at different concentrations.

Concentration(mol dm^{-3})	0.0001	0.001	0.01	0.1	1	2	3
$\Lambda_c, \text{CH}_3\text{COOH}(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$	107.0	41.0	14.3	4.6	1.32	0.80	0.54
$\Lambda_c, \text{KCl}(\Omega^{-1}\text{cm}^2\text{mol}^{-1})$	129.1	127.3	122.4	112.0	98.3	92.6	88.3
$(\text{Concentration})^{\frac{1}{2}}(\text{mol dm}^{-3})^{\frac{1}{2}}$							

- Complete the table above.
- On the same axes, plot graphs for molar conductivity against the square root of concentration.
- State and explain the shapes of the graphs in (b) above.

2. The table below shows values of molar conductivity of hydrochloric acid and ammonia solution at different concentrations at 18°C.

Concentration(mol dm^{-3})	0.001	0.01	0.1	1	3
$\Lambda_c, \text{HCl}(\text{S cm}^2 \text{mol}^{-1})$	377	370	351	301	215
$\Lambda_c, \text{NH}_3(\text{aq})(\text{S cm}^2 \text{mol}^{-1})$	28	9.6	3.3	0.89	0.36
Dilution(mol dm^{-3}) ⁻¹					

- (a) Complete the table above.
 (b) On the same axes, plot graphs for molar conductivity against dilution.
 (c) State and explain the shapes of the graphs in (b) above.
3. The table below shows values of molar conductivity of sodium chloride solution at different concentrations at 25°C.

Concentration(mol dm^{-3})	0.2	0.1	0.05	0.02	0.01	0.005	0.001
Molar conductivity of sodium chloride($\text{S m}^2 \text{mol}^{-1}$)	0.01015	0.0107	0.0111	0.0116	0.0118	0.0122	0.0124
Dilution(mol dm^{-3}) ⁻¹							
$\sqrt{\text{Concentration}}(\text{mol dm}^{-3})^{\frac{1}{2}}$							

- (a) Complete the table above.
 (b) On different axes, plot a graph for:
 (i) molar conductivity against dilution.
 (ii) molar conductivity against $\sqrt{\text{Concentration}}$
 (c) From each of the graphs determine the molar conductivity at infinite dilution of sodium chloride.
 (d) Explain the shape of each of the graphs in (b) above.
4. The table below shows values of molar conductivity of ethanoic acid solution at different concentrations at 18°C.

Concentration, $C(\text{mol dm}^{-3})$	0.001	0.01	0.1	1.0	3.0
$\Lambda_c, \text{CH}_3\text{COOH}(\Omega^{-1} \text{cm}^2 \text{mol}^{-1})$	41.00	14.30	4.60	1.32	0.54
$C^{\frac{1}{2}}(\text{mol}^{\frac{1}{2}} \text{dm}^{-\frac{3}{2}})$					
$\frac{1}{C}(\text{mol dm}^{-3})^{-1}$					

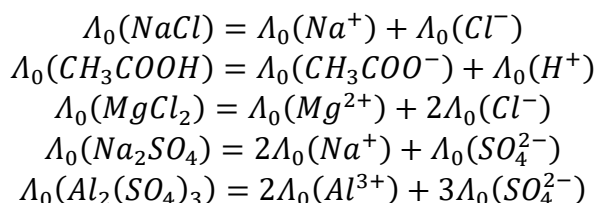
- (a) Complete the table above.
 (b) On different axes, plot a graph for:
 (i) molar conductivity against the square root of concentration.
 (ii) molar conductivity against dilution
 (c) Explain the shape of each of the graphs in (b) above.

5. (a) Define the term molar conductivity
- (b) On the same sketch, draw a graph to show variation of molar conductivity of aluminium sulphate and ethanoic acid.
- (c) Compare and explain the shape of your graph for:
- (i) ethanoic acid
- (ii) aluminium sulphate

Kohlrausch's law of independent migration of ions and its application

Kohlrausch Friedrich investigated the molar conductivity at infinite dilution of a large number of electrolytes and found that it was a sum of two quantities.

Kohlrausch's law states that the molar conductivity at infinite dilution of an electrolyte is equal to the sum of the molar conductivities at infinite dilution of the ions produced by the electrolyte.



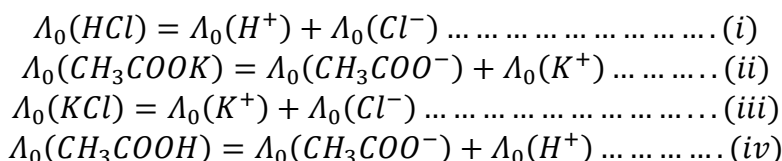
Applications of Kohlrausch's law

- (i) ***Indirect determination of molar conductivity at infinite dilution for weak electrolytes.***
- (ii) ***To determine solubility of sparingly soluble electrolytes***
- (iii) ***To determine solubility product of sparingly soluble electrolytes***
- (iv) ***To determine degree of dissociation and equilibrium constant of a weak electrolyte***

- (i) ***Indirect determination of molar conductivity at infinite dilution for weak electrolytes.***

The molar conductivity at infinite dilution of a weak electrolyte can be obtained if the molar conductivities of selected strong electrolytes are known.

For ethanoic acid, the molar conductivity at infinite dilution can be obtained from the molar conductivities at infinite dilution of hydrochloric acid, potassium ethanoate and potassium chloride.



Since equation (iv) can be obtained by adding (i) and (ii) and subtracting equation (iii);
Therefore;

$$\Lambda_0(\text{CH}_3\text{COOH}) = [\Lambda_0(\text{CH}_3\text{COO}^-) + \Lambda_0(\text{K}^+)] + [\Lambda_0(\text{H}^+) + \Lambda_0(\text{Cl}^-)] - [\Lambda_0(\text{K}^+) + \Lambda_0(\text{Cl}^-)]$$

$$\Lambda_0(\text{CH}_3\text{COOH}) = \Lambda_0(\text{CH}_3\text{COOK}) + \Lambda_0(\text{HCl}) - \Lambda_0(\text{KCl})$$

Examples

1. Given that the molar conductivities at infinite dilution of some electrolytes are as shown below;

Compound	$\Lambda_0(\text{Scm}^2\text{mol}^{-1})$
Sodium chloride	113
Ammonium chloride	134.1
Sodium hydroxide	225.2
Sodium methanoate	101.2
Hydrochloric acid	397.8

(a) Calculate the molar conductivity at infinite dilution of:

- (i) methanoic acid
- (ii) ammonia solution
- (iii) ammonium methanoate

(b) Explain the differences in your answers in a(i) and (iii) above

(i) $\Lambda_0(\text{HCOOH}) = \Lambda_0(\text{HCOONa}) + \Lambda_0(\text{HCl}) - \Lambda_0(\text{NaCl})$
 $\Lambda_0(\text{HCOOH}) = (101.2 + 397.8 - 113) = 386 \text{ Scm}^2\text{mol}^{-1}$

(ii) $\Lambda_0(\text{NH}_3(\text{aq})) = \Lambda_0(\text{NH}_4\text{Cl}) + \Lambda_0(\text{NaOH}) - \Lambda_0(\text{NaCl})$
 $\Lambda_0(\text{NH}_3(\text{aq})) = (134.1 + 225.2 - 113) = 246.3 \text{ Scm}^2\text{mol}^{-1}$

(iii) $\Lambda_0(\text{HCOONH}_4) = \Lambda_0(\text{HCOONa}) + \Lambda_0(\text{NH}_4\text{Cl}) - \Lambda_0(\text{NaCl})$
 $\Lambda_0(\text{HCOONH}_4) = (101.2 + 134.1 - 113) = 122.3 \text{ Scm}^2\text{mol}^{-1}$

(b) The molar conductivity at infinite dilution of methanoic acid is higher than that of ammonium methanoate because the hydrogen ion in methanoic acid has a higher molar conductivity than the ammonium ion in ammonium methanoate.

2. The molar conductivity at infinite dilution of the sulphate ion is $160 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. If the molar conductivity at infinite dilution of aluminium sulphate is $858 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, calculate the molar conductivity at infinite dilution of the aluminium ion.

$\Lambda_0(\text{Al}_2(\text{SO}_4)_3) = 2\Lambda_0(\text{Al}^{3+}) + 3\Lambda_0(\text{SO}_4^{2-})$ $858 = 2\Lambda_0(\text{Al}^{3+}) + 3(160)$	$2\Lambda_0(\text{Al}^{3+}) = 858 - 480$ $\Lambda_0(\text{Al}^{3+}) = \frac{378}{2} = 189 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$
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(i) Determining solubility and solubility product of sparingly soluble electrolytes

The solubility of a sparingly soluble salt can be determined from the molar conductivity of its saturated solution using the steps below:

The electrolytic conductivity of the saturated solution ($\mathcal{K}_{\text{solution}}$) is measured using a conductivity meter.

Using a known value of $\mathcal{K}_{\text{H}_2\text{O}}$, the electrolytic conductivity of the electrolyte is then obtained from the expression;

$$\mathcal{K}_{\text{electrolyte}} = \mathcal{K}_{\text{solution}} - \mathcal{K}_{\text{water}}$$

The molar conductivity at infinite dilution of the electrolyte (Λ_0) is obtained from the known values molar conductivity at infinite dilution of its constituent ions or from the known values molar conductivity at infinite dilution of selected electrolytes using Kohlrausch's law. Since the solution is very dilute then; $\Lambda_0 = \Lambda_c$.

The expression; $\Lambda_c = \frac{1000 \mathcal{K}_{\text{electrolyte}}}{C}$ or $\Lambda_c = \frac{\mathcal{K}_{\text{electrolyte}}}{1000 C}$ is then used to calculate the solubility, C in mol dm^{-3} depending on the units of \mathcal{K} .

The stoichiometry of reaction is then used to determine the solubility product, K_{sp} .

Experiment to determine solubility and solubility product of silver chloride

Excess solid silver chloride is added to a given volume of distilled water in a container.

The mixture is shaken for some time and left to settle at a given temperature to attain equilibrium.

The mixture is **filtered** to obtain **a saturated solution of silver chloride** as filtrate.

The electrolytic conductivity of the saturated solution, $\mathcal{K}_{\text{solution}} (\text{ohm}^{-1} \text{cm}^{-1})$ is measured using a conductivity meter.

The electrolytic conductivity of water, $\mathcal{K}_{\text{H}_2\text{O}} (\text{ohm}^{-1} \text{cm}^{-1})$ at the same temperature is obtained from books

Also the molar conductivities at infinite dilution (Λ_0) of silver ions and chloride ions are read from the tables.

Treatment of results

The electrolytic conductivity of silver chloride is then obtained by;

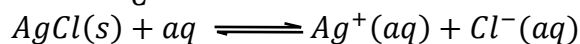
$$\mathcal{K}_{\text{AgCl}} = \mathcal{K}_{\text{solution}} - \mathcal{K}_{\text{H}_2\text{O}}$$

The molar conductivity of silver chloride at infinite dilution is obtained by the equation;

$$\Lambda_0(\text{AgCl}) = \Lambda_0(\text{Ag}^+) + \Lambda_0(\text{Cl}^-)$$

$\Lambda_0(\text{AgCl}) = \Lambda_c(\text{AgCl})$, where Λ_c is molar conductivity of silver chloride

$$\Lambda_c(\text{AgCl}) = \frac{1000 \mathcal{K}_{\text{AgCl}}}{C} \text{ where } C \text{ is solubility in } \text{mol dm}^{-3}$$



$$[\text{AgCl}] = C \text{ mol dm}^{-3}$$

$$\text{Since mole ratio of AgCl: Ag}^+ = 1:1$$

$$[AgCl] = [Ag^+] = [Cl^-] = C \text{ mol dm}^{-3}$$

$$K_{sp} = [Ag^+][Cl^-] = C^2$$

$$K_{sp} = C^2 \text{ mol}^2 \text{ dm}^{-6}$$

(Revisit the experiments on solubility product in the topic IONIC EQUILIBRIA for more experiments on solubility product)

Examples

1. The electrolytic conductivity of a saturated solution of silver chloride at 25°C is $3.1 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$. The molar conductivities at infinite dilution of silver and chloride ions are $6.2 \times 10^{-3} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ and $7.7 \times 10^{-3} \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$ respectively.

The electrolytic conductivity of pure water at 25°C is $1.6 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$

Calculate the:

(a) solubility of silver chloride at 25°C in grams per litre

(b) solubility product of silver chloride

(Ag = 108, Cl = 35.5)

$$(a) \mathcal{K}_{AgCl} = \mathcal{K}_{\text{solution}} - \mathcal{K}_{\text{water}}$$

$$\mathcal{K}_{AgCl} = (3.1 \times 10^{-4}) - (1.6 \times 10^{-4})$$

$$= 1.5 \times 10^{-4} \Omega^{-1} \text{ m}^{-1}$$

$$\Lambda_0(AgCl) = \Lambda_0(Ag^+) + \Lambda_0(Cl^-)$$

$$= (6.2 \times 10^{-3}) + (7.7 \times 10^{-3})$$

$$\Lambda_0(AgCl) = 0.0139 \Omega^{-1} \text{ m}^2 \text{ mol}^{-1}$$

$$\Lambda_0(AgCl) = \Lambda_c(AgCl)$$

$$\Lambda_c(AgCl) = \frac{\mathcal{K}_{AgCl}}{1000 C}$$

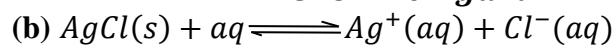
$$C = \frac{\mathcal{K}_{AgCl}}{1000 \Lambda_c(AgCl)} = \frac{1.5 \times 10^{-4}}{1000 \times 0.0139}$$

$$= 1.079 \times 10^{-5} \text{ mol dm}^{-3}$$

$$\text{Molar mass of AgCl} = 108 + 35.5 = 143.5 \text{ g}$$

$$\text{Solubility in g dm}^{-3} = (143.5 \times 1.079 \times 10^{-5})$$

$$= 1.548 \times 10^{-5} \text{ g dm}^{-3}$$



$$K_{sp} = [Ag^+][Cl^-] = (1.079 \times 10^{-5})^2$$

$$= 1.164 \times 10^{-10} \text{ mol}^2 \text{ dm}^{-6}$$

2. The electrolytic conductivity of a saturated solution of silver bromide at 25°C is $8.486 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. The electrolytic conductivity of pure water at 25°C is $7.5 \times 10^{-7} \Omega^{-1} \text{ cm}^{-1}$. Calculate the solubility product of silver bromide.

(The molar conductivities at infinite dilution of potassium bromide, silver nitrate and potassium nitrate at infinite dilution are 137.4, 133 and 131 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ respectively at 25°C)

$$\mathcal{K}_{AgBr} = \mathcal{K}_{\text{solution}} - \mathcal{K}_{\text{water}}$$

$$\mathcal{K}_{AgBr} = (8.486 \times 10^{-7}) - (7.5 \times 10^{-7})$$

$$= 9.86 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$$

$$\Lambda_0(AgBr) = \Lambda_0(AgNO_3) + \Lambda_0(KBr) - \Lambda_0(KNO_3)$$

$$= (133 + 137.4 - 131) \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

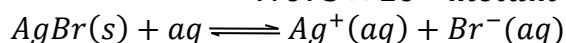
$$\Lambda_0(AgBr) = 139.4 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\Lambda_0(AgBr) = \Lambda_c(AgBr)$$

$$\Lambda_c(AgBr) = \frac{1000 \mathcal{K}_{AgBr}}{C}$$

$$C = \frac{1000 \mathcal{K}_{AgBr}}{\Lambda_c(AgBr)} = \frac{1000 \times 9.86 \times 10^{-8}}{139.4}$$

$$= 7.073 \times 10^{-7} \text{ mol dm}^{-3}$$



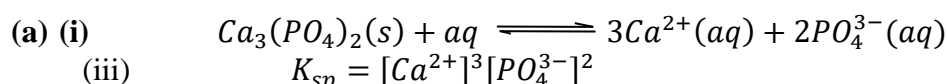
$$K_{sp} = [Ag^+][Br^-] = (7.073 \times 10^{-7})^2$$

$$= 5 \times 10^{-13} \text{ mol}^2 \text{ dm}^{-6}$$

3. (a) Calcium phosphate is sparingly soluble in water.

Write:

- (i) equation for the solubility of calcium phosphate in water
 - (ii) the expression for the solubility product of calcium phosphate
 - (b) The molar conductivities of calcium chloride, sodium phosphate and sodium chloride at infinite dilution at 25°C are 271.8, 390.3 and 126.5 $\Omega^{-1}cm^2mol^{-1}$ respectively. Calculate the:
 - (i) molar conductivity of calcium phosphate at infinite dilution at 25°C.
 - (ii) solubility product of calcium phosphate at 25°C.
- (Electrolytic conductivity of calcium phosphate is $1.31 \times 10^{-2} \Omega^{-1}cm^{-1}$)



(b) (i) $3CaCl_2(aq) + 2Na_3PO_4(aq) \longrightarrow Ca_3(PO_4)_2(s) + 6NaCl(aq)$
 $\Lambda_0(Ca_3(PO_4)_2) = 3\Lambda_0(Ca^{2+}) + 2\Lambda_0(PO_4^{3-})$
 $\Lambda_0(Ca_3(PO_4)_2) = 3\Lambda_0(CaCl_2) + 2\Lambda_0(Na_3PO_4) - 6\Lambda_0(NaCl)$
 $\Lambda_0(Ca_3(PO_4)_2) = [3(271.8) + 2(390.3) - 6(126.5)]\Omega^{-1}cm^2mol^{-1}$
 $\Lambda_0(Ca_3(PO_4)_2) = 837\Omega^{-1}cm^2mol^{-1}$

(ii) $\Lambda_0(Ca_3(PO_4)_2) = \Lambda_c(Ca_3(PO_4)_2)$
 $\mathcal{K}_{Ca_3(PO_4)_2} = 1.31 \times 10^{-2} \Omega^{-1}cm^{-1}$
 $\Lambda_c(Ca_3(PO_4)_2) = \frac{1000\mathcal{K}_{Ca_3(PO_4)_2}}{C}$
 $C = \frac{1000\mathcal{K}_{Ca_3(PO_4)_2}}{\Lambda_c(Ca_3(PO_4)_2)} = \frac{1000 \times 1.31 \times 10^{-2}}{837} = 0.01565 \text{ moldm}^{-3}$
 $[Ca^{2+}] = 3[Ca_3(PO_4)_2] = (3 \times 0.01565) = 0.04695M$
 $[PO_4^{3-}] = 2[Ca_3(PO_4)_2] = (2 \times 0.01565) = 0.0313M$
 $K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2 = (0.04695)^3 \times (0.0313)^2 (\text{moldm}^{-3})^5$
 $K_{sp} = 1.014 \times 10^{-7} \text{ mol}^5\text{dm}^{-15}$

(ii) Determining degree of dissociation and equilibrium constant of a weak electrolyte

The degree of dissociation(α) of a weak electrolyte can be obtained if the molar conductivity at a given concentration (Λ_c) and the molar conductivity at infinite dilution(Λ_o) are known.

$$\alpha = \frac{\Lambda_c}{\Lambda_o}$$

The acid dissociation constant, K_a of a weak acid can then be obtained from the expression;

$$K_a = \frac{c\alpha^2}{(1-\alpha)}$$

However, if α is small compared to 1, then $(1-\alpha)$ is approximately equal to one, so that;

$$K_a = c\alpha^2$$

The concentration of hydrogen ions is obtained from the expression $[H^+] = c\alpha$ and the pH can be calculated.

The base dissociation constant and hydrolysis constant for salts.

Examples

1. The electrolytic conductivity of a 0.16M ethanoic acid solution at 18°C is $0.0195 \Omega^{-1}m^{-1}$. The molar conductivity at infinite dilution of hydrogen ion and ethanoate ion are $3.15 \times 10^{-2} \Omega^{-1}m^2mol^{-1}$ and $0.35 \times 10^{-2} \Omega^{-1}m^2mol^{-1}$ respectively. Calculate the:

(i) degree of dissociation, α of ethanoic acid.

(ii) acid dissociation constant, K_a , at 25°C.

$$\begin{aligned} \text{(i)} \quad c &= 0.16M \quad \mathcal{K} = 0.0195 \Omega^{-1}m^{-1} \\ \Lambda_0(CH_3COOH) &= \Lambda_0(CH_3COO^-) + \Lambda_0(H^+) \\ \Lambda_0(CH_3COOH) &= (0.35 \times 10^{-2}) + (3.15 \times 10^{-2}) \\ &= 3.5 \times 10^{-2} \Omega^{-1}m^2mol^{-1} \\ \Lambda_c &= \frac{\mathcal{K}}{1000c} = \frac{0.0195}{1000 \times 0.16} = 1.22 \times 10^{-4} \Omega^{-1}m^2mol^{-1} \\ \alpha &= \frac{\Lambda_c}{\Lambda_0} = \frac{1.22 \times 10^{-4}}{3.5 \times 10^{-2}} = 3.486 \times 10^{-3} \end{aligned}$$

$$\begin{aligned} \text{(ii)} \quad &\text{Since } \alpha \text{ is very small compared to one, (0.3486\%)} \\ &K_a = c\alpha^2 \\ &= 0.16 \times (3.486 \times 10^{-3})^2 \\ &K_a = 1.944 \times 10^{-6} moldm^{-3} \end{aligned}$$

2. (a) (i) Define the term “molar conductivity at infinite dilution, Λ_0 ”.

(ii) State how you would expect the molar conductivity of sodium chloride solution to vary as the dilution of the solution is increased. Give a reason for your answer.

(b) The values of Λ_0 at 25°C for some electrolytes are as follows;

Electrolyte	$\Lambda_0(Sm^2mol^{-1})$
<i>HCOONa</i>	104.7
<i>NaCl</i>	126.5
<i>HCl</i>	426.2

- (i) Calculate Λ_0 at 25°C for methanoic acid.

- (ii) If the value of molar conductivity, Λ , for 0.01M methanoic acid is $50.5 \text{ Sm}^2\text{mol}^{-1}$ at 25°C . Calculate the acid dissociation constant, K_a , for methanoic acid.

(b) (i)

$$\begin{aligned}\Lambda_0(\text{HCOOH}) &= \Lambda_0(\text{HCOONa}) + \Lambda_0(\text{HCl}) - \Lambda_0(\text{NaCl}) \\ \Lambda_0(\text{HCOOH}) &= (104.7 + 426.2 - 126.5) \text{ Sm}^2\text{mol}^{-1} \\ &= 404.4 \text{ Sm}^2\text{mol}^{-1}\end{aligned}$$

$$\Lambda_c = 50.5 \text{ Sm}^2\text{mol}^{-1}, c = 0.16\text{M}$$

$$\alpha = \frac{\Lambda_c}{\Lambda_0} = \frac{50.5}{404.4} = 0.1249$$

(ii)

The value of α is not very small as compared to one (12.49%) so $K_a = c\alpha^2$ cannot be used in the calculation.

$$\begin{aligned}K_a &= \frac{c\alpha^2}{(1-\alpha)} = \frac{0.16 \times 0.1249^2}{(1-0.1249)} \\ K_a &= 2.852 \times 10^{-3} \text{ moldm}^{-3}\end{aligned}$$

3. The molar conductivity of a 0.093M solution of ethanoic acid at 25°C is $5.34 \times 10^{-4} \text{ Sm}^2\text{mol}^{-1}$. The molar conductivity at infinite dilution of hydrogen ion and ethanoate ion are $3.15 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$ and $0.4 \times 10^{-2} \text{ Sm}^2\text{mol}^{-1}$ respectively. Calculate the:

- (i) molar conductivity of ethanoic acid at infinite dilution.
(ii) degree of dissociation, α of ethanoic acid.
(iii) acid dissociation constant, K_a , at 25°C .
(iv) pH of the acid.

(i) $\begin{aligned}\Lambda_0(\text{CH}_3\text{COOH}) &= \Lambda_0(\text{CH}_3\text{COO}^-) + \Lambda_0(\text{H}^+) \\ \Lambda_0(\text{CH}_3\text{COOH}) &= (0.4 \times 10^{-2}) + (3.15 \times 10^{-2}) \\ &= 3.55 \times 10^{-2} \Omega^{-1}\text{m}^2\text{mol}^{-1}\end{aligned}$

(ii) $\begin{aligned}\Lambda_c &= 5.34 \times 10^{-4} \text{ Sm}^2\text{mol}^{-1} \\ \alpha &= \frac{\Lambda_c}{\Lambda_0} = \frac{5.34 \times 10^{-4}}{3.55 \times 10^{-2}} = 0.015\end{aligned}$

(iii) The value of α very small as compared to one (1.5%) so $K_a = c\alpha^2$ can be used in the calculation. $K_a = c\alpha^2$
 $K_a = 0.093 \times 0.015^2 = 2.093 \times 10^{-5} \text{ moldm}^{-3}$

(iv) $\begin{aligned}[\text{H}^+] &= c\alpha = (0.093 \times 0.015) \\ &= 1.395 \times 10^{-3} \text{ M} \\ \text{pH} &= -\log_{10}[\text{H}^+] \\ &= -\log_{10}(1.395 \times 10^{-3}) = 2.86\end{aligned}$

4. The conductivity of a 0.063M solution of 2-hydroxypropanoic acid was found to be $0.001138 \text{ Scm}^{-1}$. The molar conductivity of the acid at infinite dilution at 25°C is $388.5 \text{ Scm}^2\text{mol}^{-1}$. Calculate the pH of the solution and the acid dissociation constant.

$$\begin{aligned}c &= 0.063\text{M} \quad \mathcal{K} = 0.001138 \text{ Scm}^{-1} \\ \Lambda_0\left(\begin{array}{c} \text{CH}_3\text{CHCOOH} \\ | \\ \text{OH} \end{array}\right) &= 388.5 \text{ Scm}^2\text{mol}^{-1} \\ \Lambda_c &= \frac{1000\mathcal{K}}{c} = \frac{1000 \times 0.001138}{0.063} \\ &= 18.06 \text{ Scm}^2\text{mol}^{-1} \\ \alpha &= \frac{\Lambda_c}{\Lambda_0} = \frac{18.06}{388.5} = 0.0465\end{aligned}$$

$$\begin{aligned}[\text{H}^+] &= c\alpha = (0.063 \times 0.0465) = 2.93 \times 10^{-3} \\ \text{pH} &= -\log_{10}[\text{H}^+] = -\log_{10}(2.93 \times 10^{-3}) \\ &= 2.53 \\ K_a &= \frac{c\alpha^2}{(1-\alpha)} = \frac{0.063 \times 0.0465^2}{(1-0.0465)} \\ K_a &= 1.43 \times 10^{-4} \text{ moldm}^{-3}\end{aligned}$$

5. The molar conductivities at infinite dilution of the ammonium ion and the chloride ion are $73.5 \text{ Scm}^2\text{mol}^{-1}$ and $76.2 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively. The electrolytic conductivity of a 0.1M ammonium chloride is $1.288 \times 10^{-2} \text{ Scm}^{-1}$. Calculate the hydrolysis constant of ammonium chloride.

$$\begin{aligned} c &= 0.1\text{M} & \mathcal{K} &= 1.288 \times 10^{-2} \text{ Scm}^{-1} \\ \Lambda_0(\text{NH}_4\text{Cl}) &= \Lambda_0(\text{NH}_4^+) + \Lambda_0(\text{Cl}^-) \\ \Lambda_0(\text{NH}_4\text{Cl}) &= 73.5 + 76.2 \\ &= \mathbf{149.7 \text{ Scm}^2\text{mol}^{-1}} \\ \Lambda_c &= \frac{1000\mathcal{K}}{c} = \frac{1000 \times 1.288 \times 10^{-2}}{0.1} \\ &= \mathbf{128.8 \text{ Scm}^2\text{mol}^{-1}} \end{aligned}$$

$$\alpha = \frac{\Lambda_c}{\Lambda_0} = \frac{128.8}{149.7} = \mathbf{0.86}$$

The value of α is not very small as compared to one (86%) so $K_a = c\alpha^2$ cannot be used in the calculation.

$$\begin{aligned} K_h &= \frac{c\alpha^2}{(1-\alpha)} = \frac{0.1 \times 0.86^2}{(1-0.86)} \\ &= \mathbf{0.063 \text{ moldm}^{-3}} \end{aligned}$$

Questions

- Calculate the molar conductivity of water at infinite dilution at 25°C if at the same temperature, $\Lambda_0(\text{NaOH}) = 129.2 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$, $\Lambda_0(\text{HNO}_3) = 212.8 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and $\Lambda_0(\text{NaNO}_3) = 117.1 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$.
- Calculate the molar conductivity at infinite dilution of ethanoic acid from the following data.

Compound	$\Lambda_0(\text{Scm}^2\text{mol}^{-1})$
Hydrochloric acid	426
Sodium chloride	126
Sodium ethanoate	91

- The molar conductivity at infinite dilution of sodium ion and the carbonate ion respectively are 50.11 and $144 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ respectively. Calculate the molar conductance at infinite dilution of sodium carbonate.
- (a) State Kohlrausch's law of independent conductivity of ions.
(b) Some ionic conductivity at infinite dilution at 25°C are shown below:

Ion	Ionic conductivity ($\Omega^{-1}\text{cm}^2$)
OH^-	198.6
Cl^-	76.4
NH_4^+	73.6
Na^+	50.1

Calculate the molar conductivity at infinite dilution of:

- (i) Sodium hydroxide
 - (ii) Ammonium chloride
5. The electrolytic conductivity of a saturated solution of silver chloride at 18°C after deducting the electrolytic conductivity of water is $1.22 \times 10^{-4} Sm^{-1}$. The molar conductivities at infinite dilution of silver and chloride ions are 0.0054 and $0.00652 Sm^2mol^{-1}$ respectively at 18°C. Calculate the:
- (a) solubility of silver chloride at 18°C
 - (b) solubility product of silver chloride 18°C.
6. (a) Explain what is meant by solubility product
- (b) The electrolytic conductivity of a saturated solution of silver chloride in pure water at 25°C is $3.41 \times 10^{-6} ohm^{-1}cm^{-1}$ and the electrolytic conductivity of pure water is $1.6 \times 10^{-6} ohm^{-1}cm^{-1}$. The molar conductivities at infinite dilution of the following salts are given as:

Salt	$AgNO_3$	KNO_3	KCl
Molar conductivity($ohm^{-1}cm^2mol^{-1}$)	133.4	145.0	149.9

Calculate the solubility product of a saturated solution of silver chloride at 25°C.

7. (a) Define the following terms in relation to an aqueous solution of an electrolyte;
- (i) specific conductance
 - (ii) molar conductance
- (b) The electrolytic conductivity of an aqueous saturated solution of XCl at 25°C is $2.40 \times 10^{-3} ohm^{-1}cm^{-1}$. The molar conductivities at infinite dilution of XOH , sodium hydroxide and sodium chloride are 273, 248 and $126 ohm^{-1}cm^2mol^{-1}$ respectively. Calculate the:
- (i) molar conductivity at infinite dilution of XCl
 - (ii) the solubility of XCl in water at 25°C in $mol dm^{-3}$
8. The conductivity of dichloroethanoic acid at a dilution of $8 dm^3$ is $0.0238 Scm^{-1}$. The molar conductivity at infinite dilution for the acid is $385 Scm^2mol^{-1}$. Calculate the degree of ionization of the acid at a concentration of $0.125 mol dm^{-3}$.
9. The conductivity of a 0.01M ethanoic acid at is $1.43 \times 10^{-4} Scm^{-1}$. The molar conductivities of hydrogen ion and ethanoate ion at infinite dilution are $349.8 Scm^2mol^{-1}$ and $40.9 Scm^2mol^{-1}$ respectively. Calculate the acid dissociation constant, K_a , of ethanoic acid.
10. The electrolytic conductivity of a solution containing 6.66g of ethanoic acid per litre is $5.21 \times 10^{-2} Sm^{-1}$ at 25°C. The molar conductivity of the acid at infinite dilution at this temperature is $3.91 \times 10^{-2} Sm^2mol^{-1}$. Calculate the degree of dissociation of ethanoic acid.

11. (a) Write an equation for the:
- acid dissociation constant, K_a , for ethanoic acid
 - relationship between acid dissociation constant, K_a , and degree of ionisation of an acid.
- (b) The electrolytic conductivity of a $1.6 \times 10^{-2} M CH_3COOH$ at $20^\circ C$ is $1.96 \times 10^{-2} Sm^{-1}$ and its molar conductivity at infinite dilution is $3.5 \times 10^{-2} Sm^2mol^{-1}$. Calculate:
- the molar conductivity of the ethanoic acid at $20^\circ C$
 - the degree of ionisation of the acid at $20^\circ C$
 - the pH of the acid
- (c) Besides concentration, state one other factor that can affect the pH of the acid.
12. (a) State factors that can affect molar conductivity of an electrolyte.
- (b) The molar conductivities at infinite dilution at $25^\circ C$ for some electrolytes are given in the table below.

Electrolyte	$\Lambda_\infty (Sm^2mol^{-1})$ at $25^\circ C$
Sodium nitrate	122
Nitric acid	421
Sodium ethanoate	91

Calculate the molar conductivity at infinite dilution for ethanoic acid.

- (c) The molar conductivity of a $0.016M CH_3COOH$ aqueous solution at $25^\circ C$ is $13.0 Sm^2mol^{-1}$. Calculate the acid dissociation constant (K_a for ethanoic acid).
13. (a) Explain why hydrogen fluoride is a weaker acid than hydrogen chloride.
- (b) Molar conductivities at infinite dilution at $25^\circ C$ for some compounds are shown in the table below.

Compound	$\Lambda_o (ohm^{-1}m^2mol^{-1})$ at $25^\circ C$
Nitric acid	0.0421
Potassium nitrate	0.0145
Potassium fluoride	0.0129

The conductivity of a $0.1 moldm^{-3}$ aqueous solution of hydrogen fluoride is $3.15 \times 10^{-3} ohm^{-1} m^{-1}$. Calculate the:

- molar conductivity of solution
 - degree of ionization of hydrogen fluoride.
14. (a) Explain the molar conductivity of an electrolyte.
- (b) Sketch a graph to show the variation of conductivity of a strong electrolyte with dilution.
- (c) Briefly explain the shape of the graph in (b) above.

(d) The molar conductivities of nitric acid, potassium nitrate and potassium fluoride are 421 , 145 and $129 \Omega^{-1}cm^2mol^{-1}$ respectively at infinite dilution. Calculate the:

- (i) molar conductivity of hydrofluoric acid at infinite dilution
- (ii) dissociation constant of K_a , of $0.1M$ hydrofluoric acid solution.
(Electrolytic conductivity of hydrofluoric acid is $3.15 \times 10^{-5} \Omega^{-1}cm^{-1}$)

15. (a) Define the terms:

- (i) conductivity
- (ii) molar conductivity
- (iii) conductance

(b) The table below shows the molar conductivities of aqueous potassium hydroxide at given dilutions.

Dilution($mol^{-1}dm^3$)	100	25	11.11	6.25	4.0	2.8
Molar conductivity($ohm^{-1}cm^2mol^{-1}$)	239	228	224	215	210	201

- (i) Plot a graph of molar conductivity against dilution
 - (ii) Use the graph to determine molar conductivity of potassium hydroxide at infinite dilution.
 - (iii) Explain the shape of the graph
- (c) (i) Draw a sketch graph to show change in conductivity with volume of aqueous sodium hydroxide when $25cm^3$ of a $0.1M$ propanoic acid is titrated with $0.1M$ sodium hydroxide solution.
- (ii) Explain the shape of the graph.
- (d) The conductivity of a saturated solution of silver phosphate at $25^\circ C$ is $2.65 \times 10^{-6} ohm^{-1}cm^{-1}$ and that of pure water is $1.52 \times 10^{-6} ohm^{-1}cm^{-1}$. If the molar ionic conductivities of phosphate ions and silver ions are 240 and $62 ohm^{-1}cm^2mol^{-1}$ at infinite dilution at $25^\circ C$ respectively, calculate the:
- (i) solubility of silver phosphate at $25^\circ C$
 - (ii) solubility product of silver phosphate at $25^\circ C$ and give its units.

Application of conductance (conductivity measurements)

The applications of conductivity measurements include:

- (i) *To determine solubility of sparingly soluble salts*
- (ii) *To determine solubility product of sparingly soluble salts*
- (iii) *To determine degree of dissociation of weak electrolytes*
- (iv) *To determine the ionisation constant of a weak electrolyte*
- (v) *To determine ionic product of water*
- (vi) *To determine formulae of complexes*

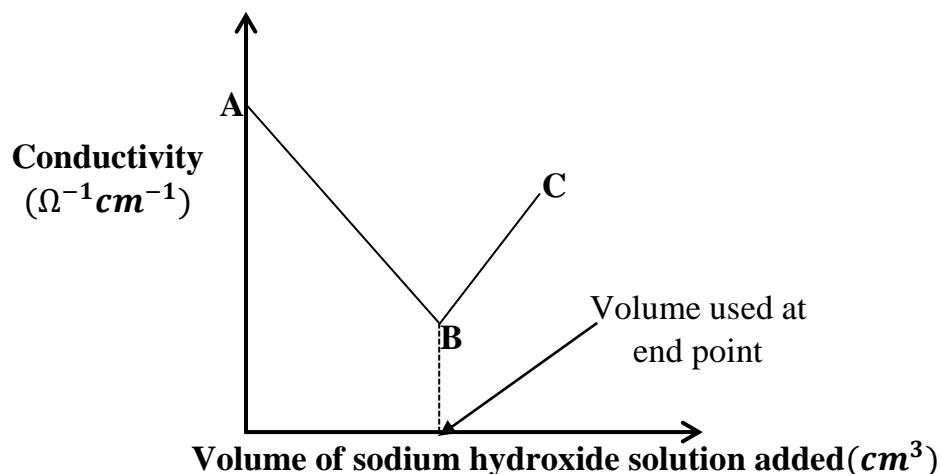
(vii) *Conductimetric titrations*

Conductimetric titrations

The conductivity of a solution changes during an acid-base titration. The change in conductivity of the solution can be measured. There is a sharp change in conductivity at the end point. Such a titration is called a conductimetric titration.

The different velocities of the ions are used to ascertain the end point of a titration.

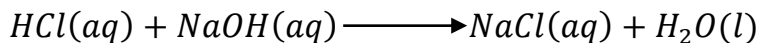
1. Titration of a strong base against a strong acid (sodium hydroxide solution against hydrochloric acid)



Explanation of shape of the graph

Initially, *conductivity is high at A* due to *very many fast moving and highly conducting hydrogen ions* from the *strong completely ionized hydrochloric acid*.

Conductivity *decreases along AB* as *sodium hydroxide solution is added* because the *fast moving highly conducting hydrogen ions are being neutralized* to form water and being *replaced by the slow moving less conducting sodium ions*.

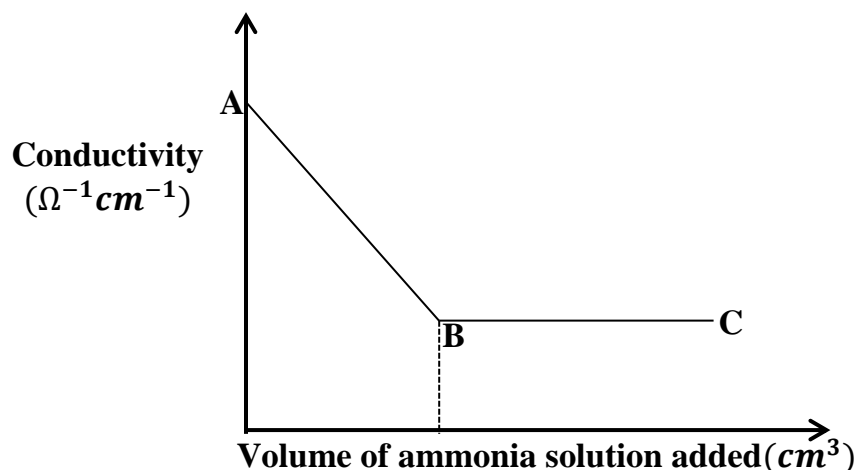


At B, the end point is reached. Conductivity is low and is due to *the sodium ions and chloride ions* from the sodium chloride salt formed.

Along BC, conductivity increases because the *concentration of sodium ions is being increased* and also the *fast moving hydroxyl ions are being added*.

Note: The volume at end point is usually obtained by extrapolation since the minimum point from plotted graphs is not usually as shown on the sketch above. The point where two extrapolated lines meet gives the end point.

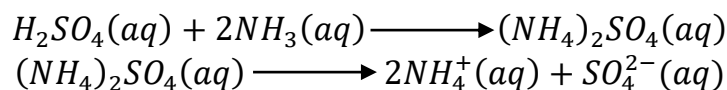
2. Titration of a weak base against a strong acid (ammonia solution against sulphuric acid or hydrochloric acid)



Explanation of shape of the graph

Initially, **conductivity is high at A** due to **very many fast moving and highly conducting hydrogen ions** from the **strong completely ionized sulphuric acid**.

Conductivity **decreases along AB** as **ammonia solution is added** because the **fast moving highly conducting hydrogen ions are being replaced by the slow moving less conducting ammonium ions**.

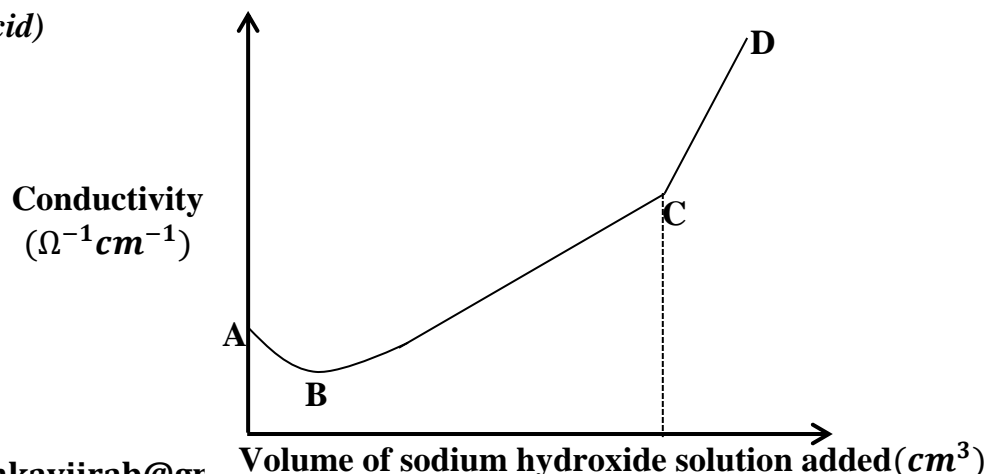


At B, the end point is reached. Conductivity is low and is due to **the ammonium ions and sulphate ions** from the ammonium sulphate salt formed.

Along BC, conductivity remains almost constant because the **ionization of the excess weak ammonia solution added is suppressed by the ammonium ions from the completely ionized ammonium sulphate salt formed**. This makes the **conductivity of hydroxyl ions negligible**.

Note: Using data obtained practically, when a graph is plotted, the conductivity may slightly increase along BC but the explanation still holds.

3. Titration of a strong base against a weak acid (sodium hydroxide solution against ethanoic acid)

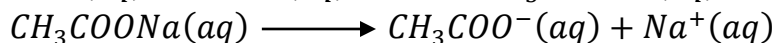
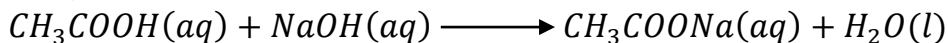


Explanation of shape of the graph

Initially, **conductivity is low at A** due to **very few fast moving, conducting hydrogen ions** from the **weak partially ionized ethanoic acid**.

Conductivity **slightly decreases along AB** as **sodium hydroxide solution is added** because the **few fast moving highly conducting hydrogen ions are being neutralized** to form water and being **replaced by the slow moving less conducting sodium ions**.

Also the **ethanoate ions from completely ionised sodium ethanoate salt formed suppress the ionisation of the weak ethanoic acid**.

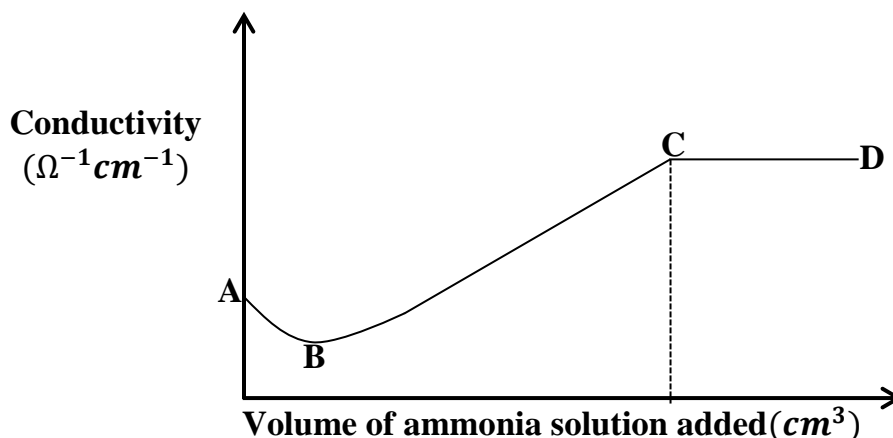


Conductivity **gradually increases along BC** due to **increase in number of conducting ethanoate ions and sodium ions from completely ionized sodium ethanoate formed**.

At **C**, the **end point is reached**. Conductivity is **only due to the sodium ethanoate salt formed**.

Along **CD**, conductivity **rapidly increases** because **excess fast moving hydroxyl ions are being added**.

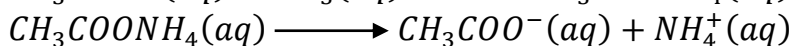
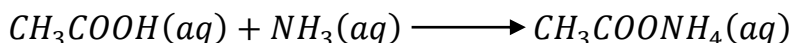
4. Titration of a weak base against a weak acid (ammonia solution against ethanoic acid)



Explanation of shape of the graph

Initially, **conductivity is low at A** due to **very few highly conducting hydrogen ions** from the **weak partially ionized ethanoic acid**.

Conductivity **slightly decreases along AB** as **ammonia solution is added** because the **ethanoate ions from ammonium ethanoate formed suppress the ionisation of the weak ethanoic acid**.



Conductivity gradually increases along BC due to increase in number of conducting ethanoate ions and ammonium ions from completely ionized ammonium ethanoate formed.

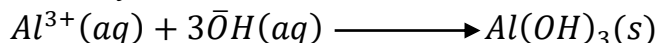
At C, the end point is reached. Conductivity is only due to the ammonium ethanoate salt formed.

Along CD, conductivity remains almost constant because the ionization of the excess weak ammonia solution added is suppressed by the ammonium ions from the completely ionized ammonium ethanoate salt formed.

However, conductimetric titration is not only confined to acids and bases. Copper(II) sulphate can be titrated with sodium hydroxide, sodium ethanoate with hydrochloric acid, etc.

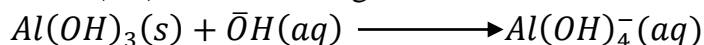
Explain why in the conductimetric titration of aluminium nitrate solution against sodium hydroxide solution, the conductivity of the mixture decreases to a minimum value, then increases gradually and finally increases rapidly with excess base.

Aluminium ions react with hydroxide ions to form insoluble aluminium hydroxide.



The reaction *reduces the concentration of aluminium ions in solution* and conductivity decreases to a minimum *on complete precipitation*.

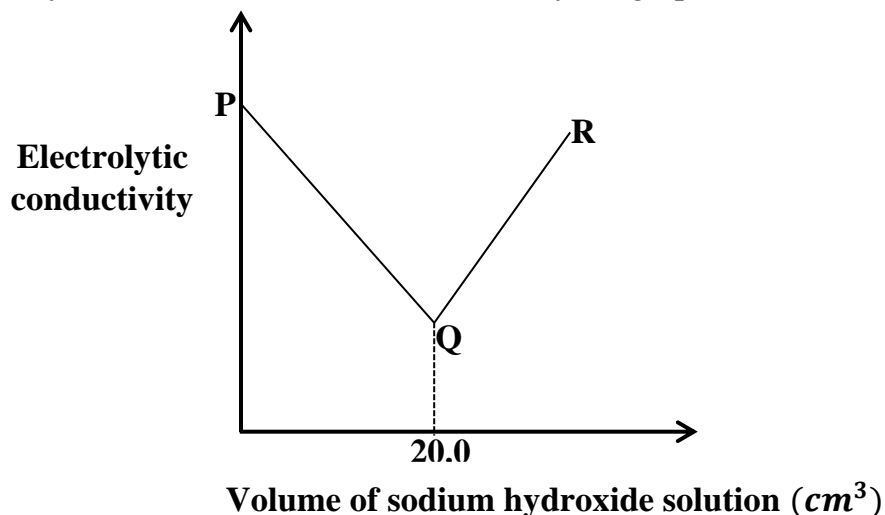
The *aluminium hydroxide reacts with more hydroxide ions* to form a *soluble complex of tetrahydroxoaluminate(III) ions* hence a gradual increase in conductivity.



The conductivity then increases rapidly due to *excess mobile highly conducting hydroxide ions*.

Questions

1. The conductivity of $25cm^3$ of copper(II) sulphate solution varies with the volume of 0.1M sodium hydroxide solution added as shown by the graph below;



- (a) Define the term electrolytic conductivity
(b) Give a reason why:
(i) conductivity is high at point P.
(ii) conductivity increases along QR
(c) Calculate the initial concentration of copper(II) sulphate solution
(d) (i) The electrolytic conductivity at P was $1.536 \times 10^{-2} \Omega^{-1} \text{cm}^{-1}$ at 25°C . Determine the molar conductivity of the copper(II) sulphate solution.
(ii) State and explain the effect of dilution on the answer in d(i) above.
2. The molarity of a sample of hydrochloric acid about 0.1M was determined accurately by measuring the conductivity of the solution as 1.0M sodium hydroxide solution was added to 50cm^3 of the acid. The results were as shown below:

Conductivity($\Omega^{-1}\text{cm}^{-1}$)	4.1	3.3	2.4	1.7	1.5	1.8	2.2	2.5
Volume of 1.0M sodium hydroxide(cm^3)	1	2	3	4	5	6	7	8

- (a) Plot a graph of conductivity against volume of 1.0M sodium hydroxide
(b) Determine from the graph, the volume of sodium hydroxide used to reach end point
(c) Calculate the molarity of hydrochloric acid
(d) Explain the shape of the graph
(e) (i) Distinguish between solubility and solubility product.
(ii) Describe an experiment to determine the solubility product of calcium phosphate in the laboratory.
3. The table below shows the conductivity of a solution of when a small volume of sodium hydroxide solution was added to 50cm^3 of 0.1M hydrochloric acid.

Volume of sodium hydroxide(cm^3)	0	1	2	3	4	5	6	7	8	9	10
Conductivity ($\Omega^{-1}\text{cm}^{-1}$)	3.90	3.35	2.80	2.27	1.72	1.11	0.62	0.76	1.19	1.62	2.0

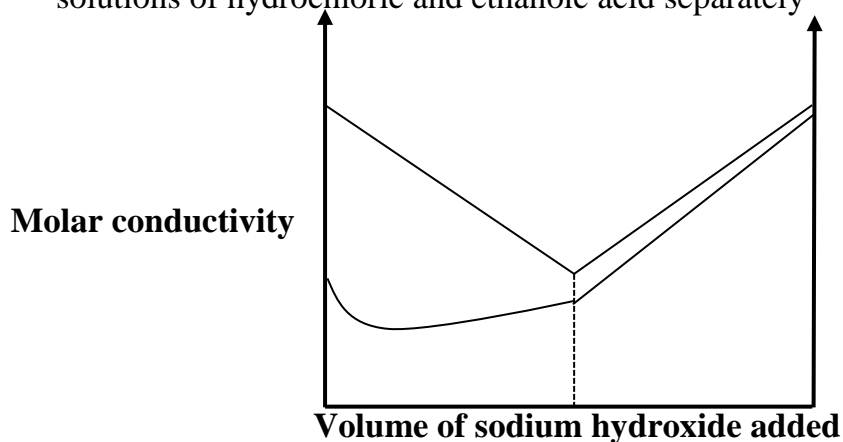
- (a) (i) Plot a graph of conductivity against volume of sodium hydroxide
(ii) Use your graph to determine the volume of sodium hydroxide used to neutralize the acid
(iii) Calculate the molarity of sodium hydroxide
(iv) Explain the shape of the graph
(b) State one other application of conductivity measurements.

4. (a) The ionic radii and ionic conductivities at infinite dilution of some ions are shown in the table below:

Ion	Ionic radius(nm)	Ionic conductivity($\Omega^{-1}cm^2$)
Li^+	0.060	38.7
Na^+	0.095	50.1
K^+	0.133	73.5

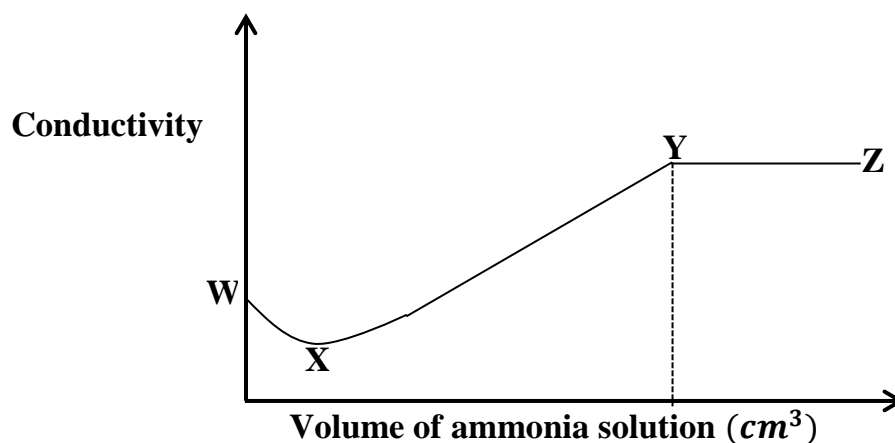
Explain the results in the table

- (b) The diagram below shows curves A and B obtained when aqueous sodium hydroxide was gradually added separately to equimolar solutions of hydrochloric and ethanoic acid separately



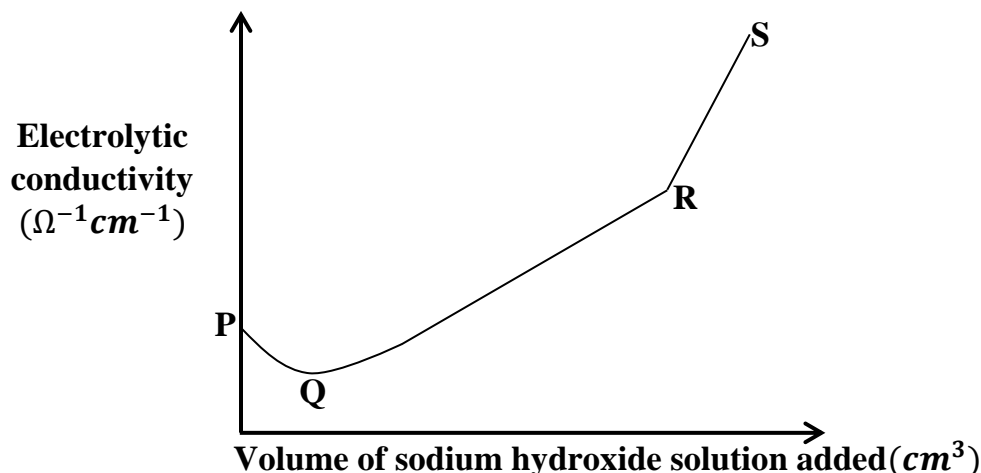
Explain the shape of the curves:

- Curve A
 - Curve B
5. (a) The conductimetric curve for titration of ethanoic acid and ammonia solution is given below:



Explain the shape of the graph.

- (b) The molar conductivities of nitric acid, sodium bromoethanoate and sodium nitrate are 421 , 89.3 and $121.3\Omega^{-1}cm^2mol^{-1}$ respectively at infinite dilution at $25^\circ C$. Calculate the:
- molar conductivity of bromoethanoic acid at infinite dilution
 - dissociation constant, K_a , of a $0.1M$ bromoethanoic acid solution. (Electrolytic conductivity of bromoethanoic acid is $4.38 \times 10^{-3}\Omega cm^{-1}$)
6. (a) The conductimetric curve for the titration of ethanoic acid and sodium hydroxide is given below.



Explain the shape of the curve PQRS

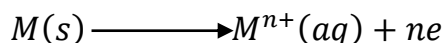
- (b) The molar conductivity of silver nitrate, potassium nitrate and potassium chloride are 134.0 , 143.2 and $140.8 S cm^2 mol^{-1}$ respectively at infinite dilution and $25^\circ C$. Calculate the:
- molar conductivity of silver chloride at infinite dilution at $25^\circ C$
 - solubility product, K_{sp} of silver chloride at $25^\circ C$.(The electrolytic conductivity of water and that of a saturated solution of silver chloride are 5.5×10^{-8} and $1.934 \times 10^{-6} S cm^{-1}$ respectively)
- (c) The molar conductivities of sodium bromoethanoate, hydrochloric acid and sodium chloride are 89 , 326 and $126\Omega^{-1}cm^2mol^{-1}$ respectively at infinite dilution at $25^\circ C$. Calculate the:
- degree of ionization of $0.1M$ bromoethanoic acid solution at $25^\circ C$. (The molar conductivity of $0.1M$ bromoethanoic acid solution is $43.7 \Omega^{-1}cm^2mol^{-1}$)
 - ionisation constant, K_a , of a $0.1M$ bromoethanoic acid solution at $25^\circ C$.
7. (a) Define the terms:
- electrolytic conductivity
 - molar conductivity

- (b) Draw a sketch graph to show how molar conductivity varies with concentration for:
- hydrochloric acid
 - ethanoic acid
- (c) Explain the shape of the curve in each case.
- (d) 25cm^3 of 0.1M ethanoic acid was titrated with sodium hydroxide solution.
- Draw a sketch graph to show how conductivity of the solution changes when sodium hydroxide is added to the acid
 - Explain the shape of the graph.

ELECTRODE POTENTIAL AND ELECTROCHEMICAL CELLS

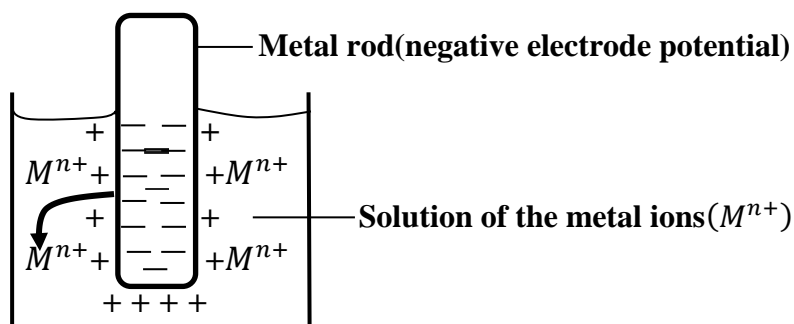
ELECTRODE POTENTIAL

A metal rod consists of metal ions and a cloud of delocalized valence electrons. If the metal is dipped in a solution of its ions, some of the cations dissolve leaving up an excess of electrons on the surface of the metal.

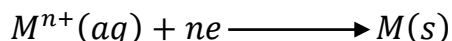


The metal will become negatively charged with respect to the solution surrounding it.

The tendency of the metal to lose ions to the surrounding solution is known as *electrolytic solution pressure*.

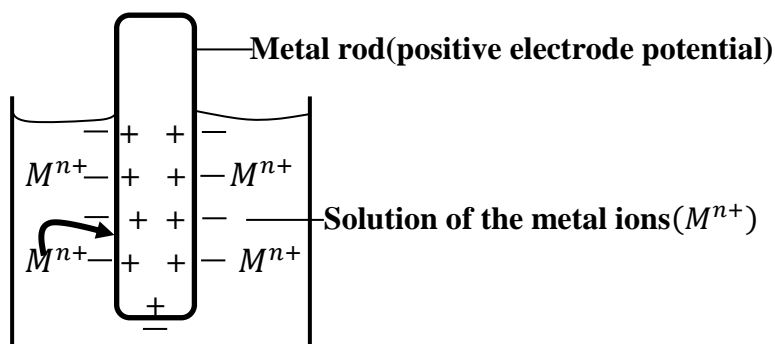


Alternatively, metal ions may take electrons from the strip of the metal and get discharged as metal atoms.



In this case, the metal becomes positively charged with respect to the solution surrounding it.

The tendency of the ions to deposit on the metal from a solution is called the *deposition pressure*.



The potential difference between the strip of the metal and the solution depends on the nature of the metal and on the concentration of the ions in equilibrium with the metal surface.

For a zinc rod dipped in a solution of zinc ions, the zinc has a **negative electrode potential** because it has a greater tendency to dissolve to form ions (greater electrolytic solution pressure) and a smaller tendency to be deposited as a metal (lower deposition pressure). The zinc rod is said to be a **negative electrode**.

For a copper rod dipped in a solution of copper(II) ions, the copper has a **positive electrode potential** because it has a greater tendency to be deposited as a metal (higher deposition pressure) and a smaller tendency to dissolve to form ions (lower electrolytic solution pressure). The copper rod is said to be a **positive electrode**.

An equilibrium is established when the rate at which electrons are gained is equal to the rate at which electrons are lost.



The position of equilibrium differs for different combinations of metals placed in solutions of their ions.

Electrode potential is the potential difference developed between a metal placed in contact with a solution of its ions.

Its symbol is **E** (measured in volts, V).

By IUPAC convention, the term electrode potential means reduction electrode potential.

Therefore in most of the work hereafter we shall deal with reduction potentials.

Electrochemical series

The electrochemical series is an arrangement of elements in increasing order of their electrode potential. Reduction potentials are used in the arrangement.

Reduction equation	Electrode potential, E^θ (V)
$Li^+(aq) + e \rightleftharpoons Li(s)$	-3.04
$K^+(aq) + e \rightleftharpoons K(s)$	-2.92
$Ca^{2+}(aq) + 2e \rightleftharpoons Ca(s)$	-2.87
$Na^+(aq) + e \rightleftharpoons Na(s)$	-2.71
$Mg^{2+}(aq) + 2e \rightleftharpoons Mg(s)$	-2.38
$Al^{3+}(aq) + 3e \rightleftharpoons Al(s)$	-1.66
$Mn^{2+}(aq) + 2e \rightleftharpoons Mn(s)$	-1.18
$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	-0.76
$Cr^{3+}(aq) + 3e \rightleftharpoons Cr(s)$	-0.51
$Fe^{2+}(aq) + 2e \rightleftharpoons Fe(s)$	-0.44
$Co^{2+}(aq) + 2e \rightleftharpoons Co(s)$	-0.28
$Ni^{2+}(aq) + 2e \rightleftharpoons Ni(s)$	-0.25
$Sn^{2+}(aq) + 2e \rightleftharpoons Sn(s)$	-0.14
$Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$	-0.13
$2H^+ + 2e \rightleftharpoons H_2(g)$	0.00
$Sn^{4+}(aq) + 2e \rightleftharpoons Sn^{2+}(aq)$	+0.15
$Cu^{2+}(aq) + e \rightleftharpoons Cu^+(aq)$	+0.15
$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	+0.34
$Cu^+(aq) + e \rightleftharpoons Cu(s)$	+0.52
$I_2(s) + 2e \rightleftharpoons 2I^-(aq)$	+0.54
$Fe^{3+}(aq) + e \rightleftharpoons Fe^{2+}(aq)$	+0.77
$Ag^+(aq) + e \rightleftharpoons Ag(s)$	+0.80
$Hg^{2+}(aq) + 2e \rightleftharpoons Hg(l)$	+0.85
$Br_2(l) + 2e \rightleftharpoons 2Br^-(aq)$	+1.07
$MnO_2(s) + 4H^+(aq) + 2e \rightleftharpoons Mn^{2+}(aq) + 2H_2O(l)$	+1.23
$Cr_2O_7^{2-}(aq) + 14H^+(aq) + 6e \rightleftharpoons 2Cr^{3+}(aq) + 7H_2O(l)$	+1.33
$Cl_2(g) + 2e \rightleftharpoons 2Cl^-(aq)$	+1.36
$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq)$ (in H_2SO_4)	+1.45
$MnO_4^-(aq) + 8H^+(aq) + 5e \rightleftharpoons Mn^{2+}(aq) + 4H_2O(l)$	+1.52
$Ce^{4+}(aq) + e \rightleftharpoons Ce^{3+}(aq)$ (in HNO_3)	+1.61
$MnO_4^-(aq) + 4H^+(aq) + 3e \rightleftharpoons MnO_2(s) + 2H_2O(l)$	+1.69
$H_2O_2(aq) + 2H^+(aq) + 2e \rightleftharpoons 2H_2O(l)$	+1.77
$F_2(g) + 2e \rightleftharpoons 2F^-(aq)$	+2.87

Note:

1. The elements with more negative values of electrode potential are highly electropositive metals i.e. Lithium, potassium, sodium and magnesium.
2. The elements with more positive values of electrode potential are strongly electronegative elements i.e. Bromine, chlorine and fluorine.
3. From the half-cell reactions, any reagent on the right is a reducing agent and any reagent on the left is an oxidizing agent.
4. Any species on the right for a reaction with a lower (more negative) electrode potential is a stronger reducing agent than a species with a higher (less negative or more positive) electrode potential. Lithium is the strongest reducing agent and the fluoride ion is the weakest reducing agent. On the other hand, fluorine, with a more positive electrode potential is the strongest oxidizing agent and the lithium ion is the weakest oxidizing agent.
5. The more positive (or less negative) the electrode potential, the easier it is to reduce the ions on the left. So the metal on the right is relatively unreactive and is a relatively poor reducing agent. For example: $Ag^+(aq) + e \rightleftharpoons Ag(s) \quad E^\theta = +0.80V$
6. The more negative (or less positive) the electrode potential, the more difficult it is to reduce the ions on the left. So the metal/ species on the right is relatively reactive and is a relatively good reducing agent. For example:
 $Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s) \quad E^\theta = -0.76V$
7. The Lithium electrode can as well be written as $Li^+(aq)/Li(s)$. The process is a reduction and the electrode potential is a reduction potential.

Question

The standard electrode potentials of some half-cell reactions are given below:

	$E^\theta (V)$
$Cu^{2+}(aq) + 2e \rightleftharpoons Cu(s)$	+0.34
$Co^{2+}(aq) + 2e \rightleftharpoons Co(s)$	-0.28
$Zn^{2+}(aq) + 2e \rightleftharpoons Zn(s)$	-0.76
$Ag^+(aq) + e \rightleftharpoons Ag(s)$	+0.80
$Pb^{2+}(aq) + 2e \rightleftharpoons Pb(s)$	-0.13

State which species is the:

- (a) strongest reducing agent
- (b) strongest oxidizing agent
- (c) most difficult to reduce
- (d) most reactive metal
- (e) easiest to reduce

Absolute and relative electrode potential

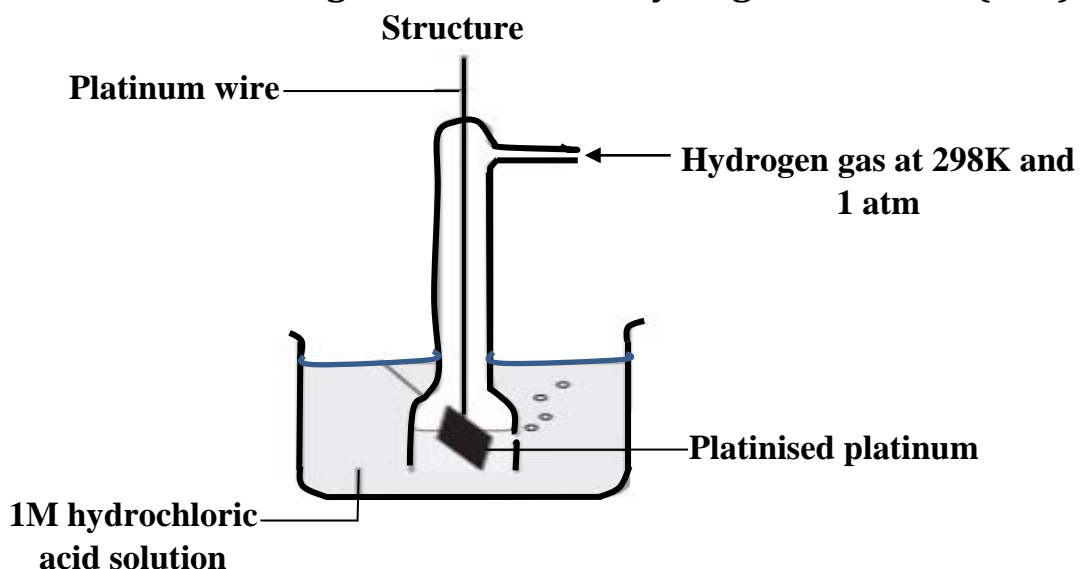
Absolute electrode potential is the potential difference developed between a metal surface and the solution with which it is in contact.

The relative electrode potential is the potential difference developed between a metal surface and the solution with which it is in contact relative to a reference electrode. The standard hydrogen electrode is the commonest reference electrode used.

Other reference electrodes include the saturated calomel electrode, the quinhydrone electrode, the silver/ silver chloride electrode and the glass electrode.

It is impossible to measure the absolute potential difference of a metal with respect to its solution because it is necessary to have a second electrode which also has its own potential difference with respect to its solution.

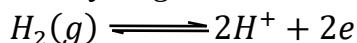
The structure and functioning of the Standard Hydrogen Electrode (SHE)



The standard hydrogen electrode consists *pure hydrogen gas continuously bubbled over the surface of a platinum foil coated with platinum black* at 298K and 1 atmosphere. The platinized platinum is dipped in *1M solution of hydrogen ions*.

Functioning

The *hydrogen is adsorbed on the platinum black* and *equilibrium is set up between the adsorbed layer of hydrogen and the hydrogen ions* in the solution.



The platinum black is inert hence does not take part in the reaction and is finely divided platinum *to catalyse the set up of this equilibrium*. There will be an *electrode potential between the adsorbed hydrogen and the solution* which is *arbitrary taken as 0.00V*.

This fixes a scale against which other standard electrode potentials are measured by combining the standard hydrogen electrode with other electrodes and measuring the emf of the cell formed.

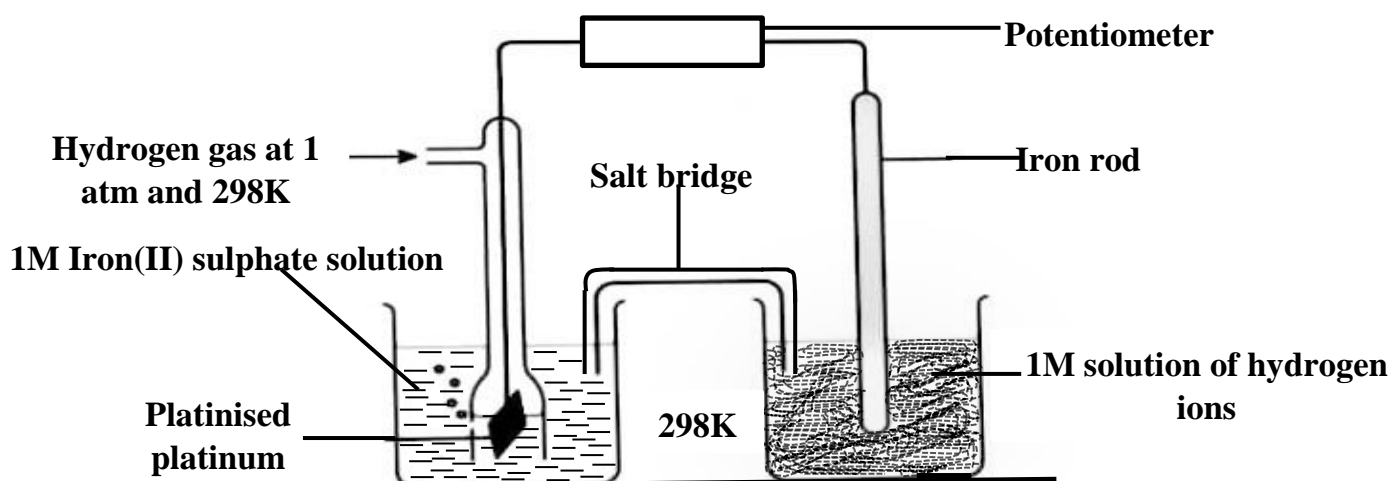
Standard electrode potential, E^θ (V)

When the standard hydrogen electrode is used in conjunction with a metal electrode placed in a solution containing 1M of the ions of the metal at 298K and 1 atmosphere, the electromotive force (emf) obtained is called the *standard electrode potential*.

Standard electrode potential is the potential difference or reduction potential established when a metal electrode is dipped in a 1 molar solution of its ions measured relative to the standard hydrogen electrode at 25 °C and 1 atmosphere.

Experiment to measure standard electrode potential of a metal

Considering an iron electrode;



An iron rod is dipped in a 1molar solution of iron(II) sulphate

The *iron half-cell* is connected externally by electric wires to a standard hydrogen electrode via a high resistance voltmeter or a potentiometer to measure the emf of the cell.

The iron half-cell is connected to the standard hydrogen electrode *internally by means of a salt bridge* to allow exchange of ions without mixing of the two solutions in the half-cells.

The temperature of the solution is maintained at 298K

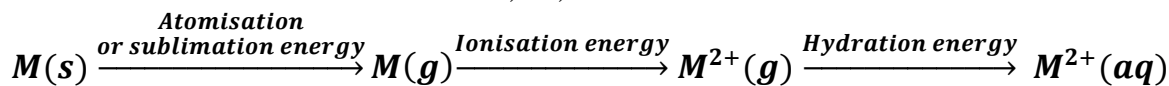
Since the standard hydrogen electrode has a standard electrode potential of 0.00V, the reading on the voltmeter/ potentiometer is the standard electrode potential of the iron electrode.

NOTE:

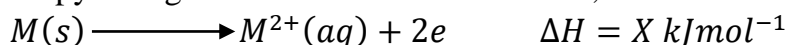
- (i) *The emf of the cell is measured without passing any current so that the composition of the chemicals in the cell is not changed.*
- (ii) *The salt bridge consists of a bent glass tube containing some inactive solution such as saturated potassium chloride or a folded filter paper saturated with potassium chloride.*
- (iii) *A standard hydrogen electrode is not easy to use because it is bulky, slow to reach equilibrium and susceptible to presence of impurities. It is also not easy to maintain a stream of hydrogen at 1 atmosphere.*
- (iv) *Electrode potentials of other metals are measured in the same way*
- (v) *A porous partition may be used instead of a salt bridge*

Factors affecting magnitude of electrode potential

When a metal rod is dipped or a gas is bubbled in/through a solution of its ions, it undergoes the energy changes. First, it's converted to free gaseous atoms. Electrons are then removed from the gaseous atoms to form gaseous ions. The gaseous ions then combine with water molecules to form hydrated ions. The energy changes involved are summarized below for a divalent metal, M ;



Therefore the enthalpy change associated with the reaction;



$$X = (\text{Enthalpy of atomisation} + \text{Ionisation enthalpy} + \text{Enthalpy of hydration})$$

Therefore the factors that affect the magnitude of electrode potential include;

- (i) *Atomization energy*
- (ii) *Ionization energy*
- (iii) *Hydration energy*
- (iv) *Concentration of the solution of the electrolyte*

Note that any endothermic process decreases the electrode potential (makes it less negative or more positive) and any exothermic process increases the electrode potential (makes it more negative or less positive).

(i) Atomization energy

Atomisation energy is endothermic. The higher the atomisation energy, the lower (more positive) the electrode potential. This is because it becomes difficult to convert an element into its gaseous atoms.

(ii) Ionization energy

Ionization energy is endothermic. The higher the ionization energy, the lower (more positive) the electrode potential. This is because it becomes difficult to form gaseous ions from gaseous atoms.

(iii) Hydration energy.

Hydration is an exothermic reaction. The higher the hydration energy the higher (more negative) the electrode potential. This is because more energy is given off when gaseous ions are completely surrounded by water molecules.

Variation of electrode potential in group II and period 3

1. The table below shows the standard electrode potential values of Group II elements.

Element	<i>Be</i>	<i>Mg</i>	<i>Ca</i>	<i>Sr</i>	<i>Ba</i>
Standard electrode potential(E^θ) (Volts) for M^{2+}/M	-1.70	-2.37	-2.87	-2.89	-2.90

(a) Name with reasons;

(i) the strongest reducing agent

(ii) the weakest reducing agent

(b) Explain the general trend in standard electrode potential of the elements

(c) explain why beryllium has an abnormally less negative value

(a) (i) Barium (but not Ba) Because it has the most negative standard electrode potential

(ii) Beryllium (but not Be) Because it has the least negative standard electrode potential

(b) Standard electrode potential generally becomes more negative from beryllium to barium because ionic radius increases, ionisation energy decreases, atomisation energy decreases and hydration energy also decreases. However, the decrease in ionisation energy and atomisation energy is more rapid than decrease in hydration energy.

(c) Beryllium has an abnormally less negative value because the beryllium ion has the smallest ionic radius, highest charge density and highest polarising power, thus attracting many water molecules, giving off highest amount of hydration energy that counterbalances its high positive ionization energy and its high atomisation energy.

2. The table below shows the standard electrode potential values of some of the elements in Period 3 of the Periodic Table.

Element	Na	Mg	Al	Cl
Standard electrode potential(E^θ) (V) for $M^{n+/-}(aq)/M(s/g)$	-2.71	-2.37	-1.66	+1.36

(a) State;

- (i) the factors that affect the magnitude of standard electrode potential
- (ii) with a reason, name the strongest reducing agent
sodium because it has the most negative standard electrode potential
- (iii) with a reason, name the strongest oxidizing agent
chlorine because it has a positive standard electrode potential

(a) Explain the trend in standard electrode potential of the metallic elements

Standard electrode potential becomes less negative(decreases) from sodium to aluminium because ionic radius decreases, ionization energy increases, atomization energy increases and hydration energy also increases. However, the increase in ionization energy and atomization energy is more rapid than increase in hydration energy.

3. Although standard electrode potentials of alkali metals and alkaline earth metals become more negative down the groups, the standard electrode potentials of Lithium and beryllium are most negative in the respective groups.

ELECTROCHEMICAL CELLS

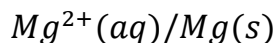
An electrochemical cell is a cell that converts chemical energy into electricity. Examples of electrochemical cells include a Daniel cell, dry cells, Lead-acid battery cell and fuel cells.

The cell consists two metal/ metal ion convention half cells.

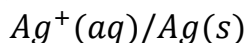
Metal/ metal ion convention cells (RHE and LHE)

When a metal rod is dipped in a 1 molar solution of its ions, the cell generated is called a **half cell**.

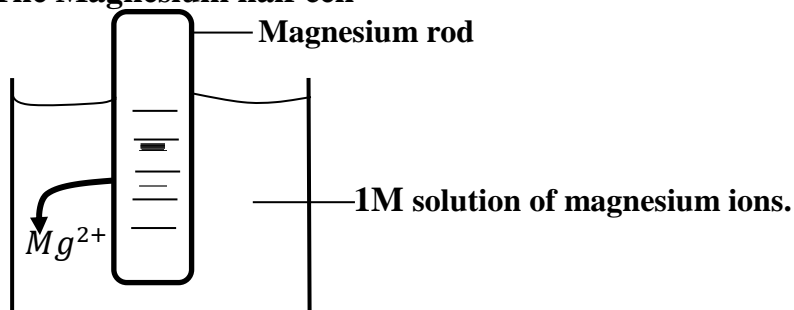
A magnesium half-cell is made by dipping a pure magnesium rod in a 1M solution of magnesium ions (for example a 1M magnesium sulphate solution) at 298K. The magnesium half-cell is represented as



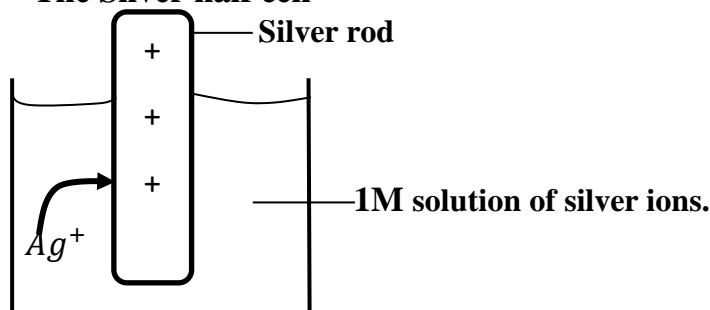
A silver half-cell is made by dipping a pure silver rod in a 1M solution of silver ions (for example a 1M silver nitrate solution) at 298K. The silver half-cell is represented as;



The Magnesium half cell



The Silver half cell



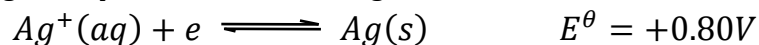
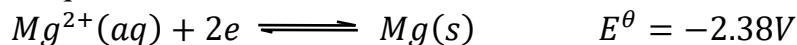
To construct an electrochemical cell, the two half cells above are made by dipping the metal rods in 1 molar solution of their ions in separate beakers.

The two half cells are then connected using electric wires to connect the metal rods via a high resistance voltmeter.

A salt bridge is used to *complete the internal circuit* and *allowing the movement of ions* between the two half-cells so that ionic balance is maintained.

How do you come up with the conventional arrangement of the cell?

The reduction equations and reduction potentials for the half-cells can be represented by the following half-equations:

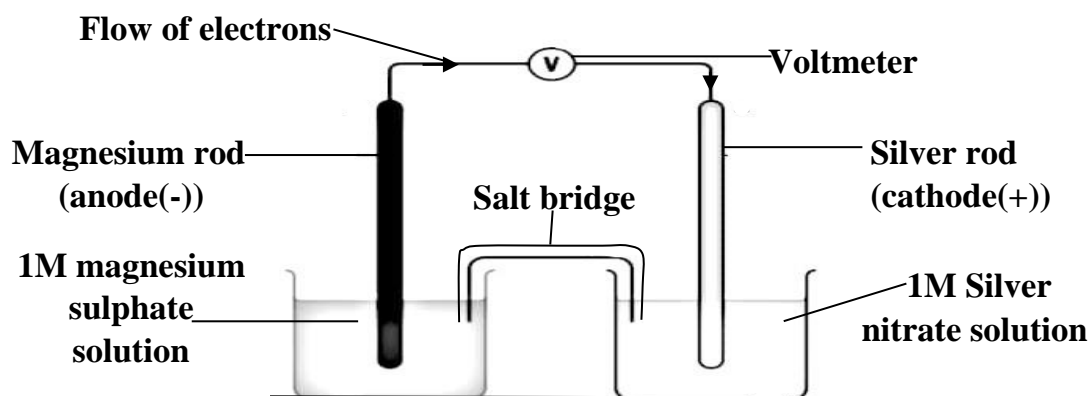


The relative values of these voltages show that Mg^{2+} ions are more difficult to reduce than Ag^{+} ions. So Ag^{+} ions will accept electrons from the $Mg^{2+}(aq)/Mg(s)$ half-cell and magnesium will lose electrons to the $Ag^{+}(aq)/Ag(s)$ half-cell.

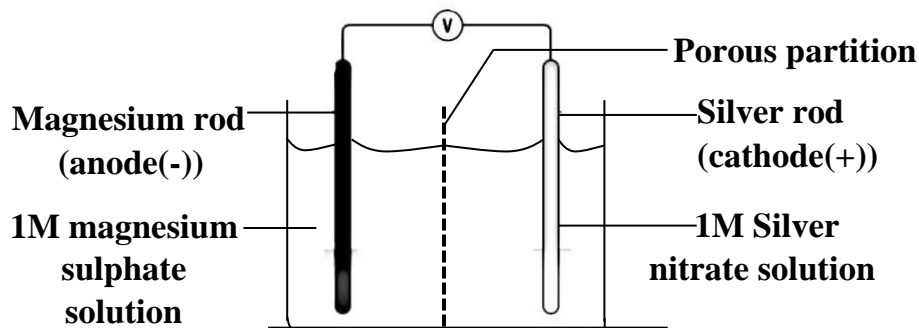
By convention, the electrode with a **negative standard electrode potential** constitutes the **Left Hand Electrode (LHE)**. This electrode is also called the **negative electrode** or the **anode**.

The electrode with a **positive standard electrode potential** constitutes the **Right Hand Electrode (RHE)**. This electrode is also called the **positive electrode** or the **cathode**.

The electrochemical cell can be drawn as shown below:



If a porous partition is used instead of a salt bridge, then the cell has the structure below:



Construction of a Daniel cell

A Daniel cell consists of a zinc half-cell made by dipping a pure zinc rod in a 1M solution of zinc ions and a copper half-cell made by dipping a pure copper rod in a 1M solution of copper(II) ions in separate beakers at 298K.

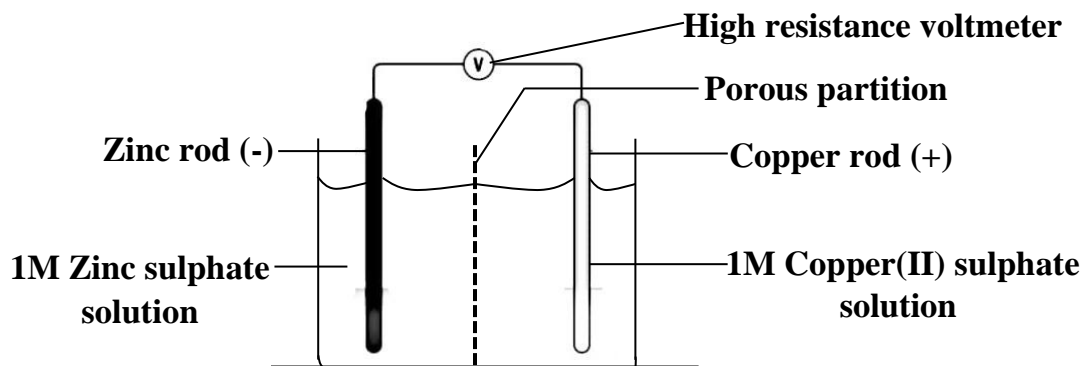
The two half cells are then connected using electric wires to connect the metal rods via a high resistance voltmeter.

A salt bridge is used to complete the internal circuit to allow the movement of ions between the two half-cells without the two solutions mixing.

The zinc electrode constitutes the Left Hand Electrode and the copper electrode constitutes the Right Hand Electrode.

Electrons move from zinc rod to copper rod. The sulphate ions move from the cathode to the anode to maintain the charge balance throughout the cell

The Structure of the Daniell cell:



The cell notation/cell convention

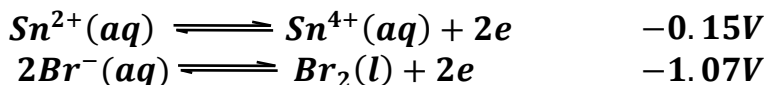
Symbolic representation used to represent an electrochemical cell is called the cell notation.

The following steps are followed to come up with a cell notation of any cell:

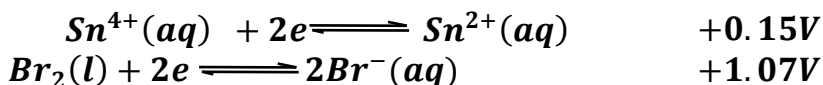
1. *Make sure the electrode potentials given are reduction potentials. i.e. The equations show reduction(electrons on left hand side). If instead oxidation potentials are given, reverse the reactions to make them reduction equations and also the sign of electrode potential. For example;*



The electrode potentials given above are reduction potentials and require no changes.



The electrode potentials given above are oxidation potentials and both equations and the values should be reversed to make them reduction reactions and potentials as shown below;



Recall:

OIL RIG – Oxidation is loss of electrons, Reduction is gain of electrons

LEORA says **GEROA**- loss of electrons is oxidation (Reducing agent). Gain of electrons is reduction (Oxidising agent)

In some cases, one electrode potential can be given as reduction and the other oxidation. In such a case, only one equation is reversed.

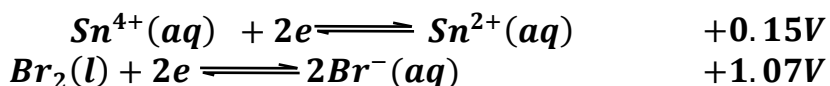
2. Identify the reaction that takes place at the anode (left hand electrode, negative electrode) and the cathode (right hand electrode, positive electrode). Use the table below to guide you.

Given two reduction potentials and equations;

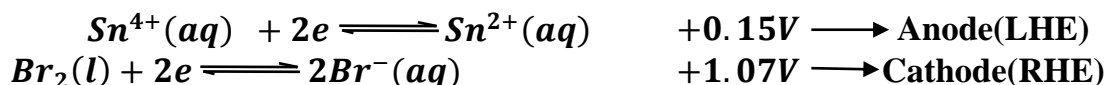
One reduction potential positive and one negative	Negative electrode potential	Represents reaction at anode(LHE)
	Positive electrode potential	Represents reaction at cathode(RHE)
Both reduction potentials positive	Less positive electrode potential	Represents reaction at anode(LHE)
	More positive electrode potential	Represents reaction at cathode(RHE)
Both reduction potentials negative	More negative electrode potential	Represents reaction at anode(LHE)
	Less negative electrode potential	Represents reaction at cathode(RHE)

3. After step 2, write down the equation at the anode (negative electrode) and equation at the cathode (positive electrode). Equation at the anode should be oxidation (gain of electrons) and that at the cathode should be reduction (loss of electrons)
RED CAT and AN OX- Reduction occurs at the cathode, Anode is for oxidation.

Consider the reactions;



Following step 2 shows that;



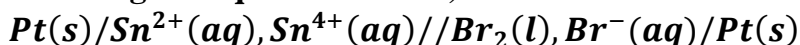
Equation at anode (oxidation reaction) is $\text{Sn}^{2+}(\text{aq}) \rightleftharpoons \text{Sn}^{4+}(\text{aq}) + 2\text{e}$

Equation at cathode (reduction reaction) is $\text{Br}_2(\text{l}) + 2\text{e} \rightleftharpoons 2\text{Br}^{-}(\text{aq})$

4. Write cell notation following the following guidelines;

- Use a vertical line (/) to separate different phases e.g. (aq) from (s), (s) from (l), (aq) from (g) or (s) from (g). However, (l) and (aq) are the same phase and cannot be separated by a line.
- Use a comma(,) to separate similar phases e.g (s) from (s) or (aq) from (l)
- Double vertical lines (/ /) show the salt bridge
- The anode is written on the left and the cathode on the right
- For half-cells that do not contain a solid metal electrode, platinum, Pt(s) is introduced as an inert electrode.

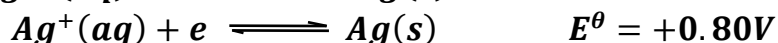
Using the equations above, the cell notation is:



The cell notation, if well written can guide you on how to draw a well labelled diagram of the electrochemical cell.

More examples

1. The standard electrode potentials of two half cells are given below.



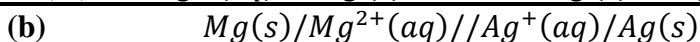
(a) Write ionic equation for the:

- (i) reaction at the cathode
- (ii) reaction at the anode
- (iii) overall equation for the reaction

(b) Write the cell notation for the cell made by combining the two half cells.

Hint: The negative electrode potential (−2.38V) shows the reaction that will take place at the anode, where oxidation (loss of electrons) should occur. The other reaction obviously should occur at the cathode and should be reduction (gain of electrons)

- (a) (i) At cathode $\text{Ag}^{+}(\text{aq}) + e \rightleftharpoons \text{Ag(s)}$
 (ii) At anode $\text{Mg(s)} \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2e$
 $(\text{Ag}^{+}(\text{aq}) + e \rightleftharpoons \text{Ag(s)}) \times 2$
 $\text{Mg(s)} \rightleftharpoons \text{Mg}^{2+}(\text{aq}) + 2e$
 (iii) $2\text{Ag}^{+}(\text{aq}) + \text{Mg(s)} \longrightarrow 2\text{Ag(s)} + \text{Mg}^{2+}(\text{aq})$



2. The Daniell cell has copper and zinc half cells as shown below:

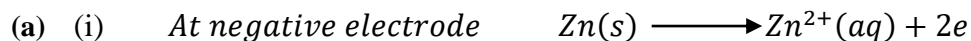


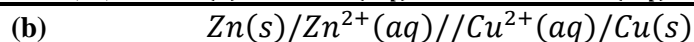
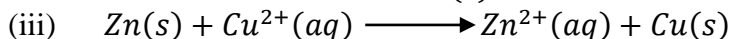
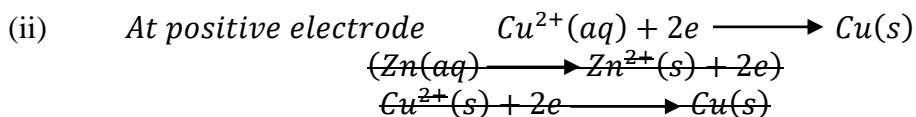
(a) Write ionic equation for the:

- (i) reaction at the negative electrode
- (ii) reaction at the positive electrode
- (iii) overall equation for the reaction

(b) Write the cell notation for the Daniell cell.

Hint: The negative electrode potential (−0.76V) shows the reaction that will take place at the negative electrode (anode), where oxidation (loss of electrons) should occur.





3. The electrode potentials of some half cells are given below.

	$E^\theta (V)$
$Sn(s)/Sn^{2+}(aq)$	+0.14
$Mn^{2+}(aq), MnO_4^-(aq), H^+(aq)/Pt$	-1.52

(a) Write ionic equation for the:

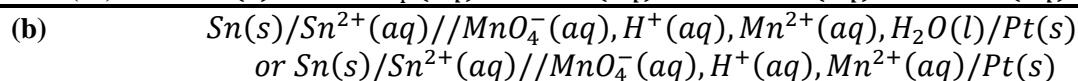
- reaction at the cathode
- reaction at the anode
- overall equation for the reaction

(b) Write the cell notation for the cell made by combining the two half cells.

Hint: The electrode potentials given are oxidation potentials as there is increase in oxidation state in each case. Standard reduction potentials should be obtained first reversing the equations and the symbols of the electrode potentials too.

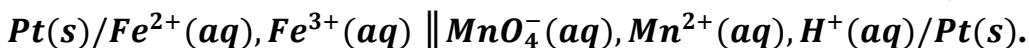
	$E^\theta (V)$
$Sn^{2+}(aq)/Sn(s)$	-0.14
$MnO_4^-(aq), H^+(aq), Mn^{2+}(aq)/Pt$	+1.52

- (a) (i) At anode $Sn(s) \longrightarrow Sn^{2+}(aq) + 2e$
 (ii) At cathode $MnO_4^-(aq) + 8H^+(aq) + 5e \longrightarrow Mn^{2+}(aq) + 4H_2O(l)$
 (iii) $5Sn(s) + 2MnO_4^-(aq) + 16H^+(aq) \longrightarrow 5Sn^{2+}(aq) + 2Mn^{2+}(aq) + 8H_2O(l)$



The platinum electrode Pt(s) is introduced as an inert electrode in the cathode half-cell because there is no solid metal electrode.

4. The convention of a cell is given below

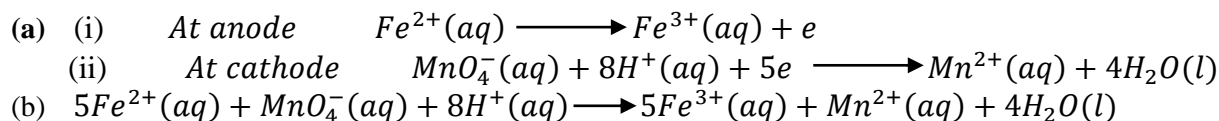


(a) Write equation for the half-cell reaction at the:

- anode
- cathode

(b) Write the overall equation for the cell reaction

Hint: When the cell notation is already given, well balanced half-cell equations are written directly from it.



Calculation of cell emf and prediction of spontaneity/feasibility of a reaction

The emf of a cell, E_{Cell}^θ is given by the expression;

$$E_{Cell}^\theta = E_{RHE} - E_{LHE}$$

or $E_{Cell}^\theta = E_{Cathode} - E_{Anode}$

The values substituted in the above expression **must be reduction potentials**.

The final answer should have a charge which should never be a superscript or subscript.

Wrong answers	Correct answers
-1.20, ⁻ 1.20V, ₋ 1.20V	-1.20V
+0.45, ⁺ 0.45V, ₊ 0.45V	+0.45V

- If the calculated value of emf is positive, the reaction is spontaneous/feasible
- If the calculated value of emf is negative, the reaction is not feasible

Examples

1. The standard electrode potential for some half cells are shown below:



- (a) What is meant by the term standard electrode potential
- (b) (i) Write the cell convention and the equation for the overall reaction that occurs when electrode potentials in (a) are combined.
 (ii) Calculate the overall electrode potential for the cell
 (iii) State whether the reaction in b(i) is feasible or not. Give a reason for your answer.

Hint: Electrode potentials are both positive. The less positive electrode potential (+0.54V) shows the reaction that will take place at the anode, where oxidation (loss of electrons) should occur. The other reaction obviously should occur at the cathode and should be reduction (gain of electrons)

- (b) (i) $Pt(s)/I^-(aq), I_2(aq)//Fe^{3+}(aq), Fe^{2+}(aq)/Pt(s)$
 Overall equation; $2I^-(aq) + 2Fe^{3+}(aq) \longrightarrow I_2(aq) + 2Fe^{2+}(aq)$
 (ii) $E_{Cell}^\theta = E_{RHE} - E_{LHE} = +0.76 - (+0.54) = +0.22V$
 (iii) The reaction is feasible, because the emf of the cell is positive.

2. The standard electrode potential for some half cells are shown below:

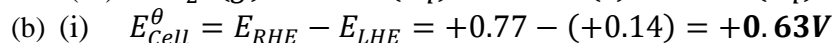
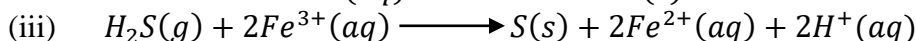
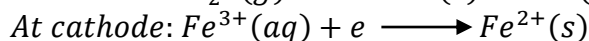
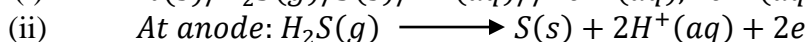
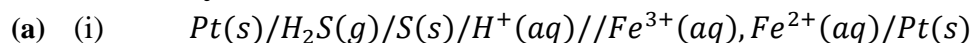


(a) Write the:

- (i) cell convention
- (ii) equation for the reaction that takes place at the anode and cathode
- (iii) equation for the overall cell reaction

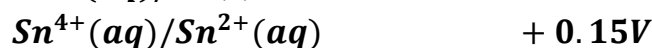
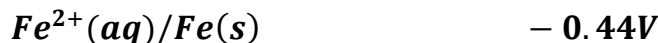
(b) (i) Calculate the emf of the cell.

- (ii) State whether the reaction in a(iii) is feasible or not. Give a reason for your answer.



(ii) The reaction is feasible because the emf of the cell is positive.

3. The standard electrode potential for some half cells are shown below:

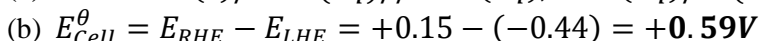
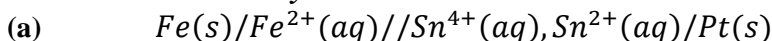


(a) Write the cell notation

(b) Calculate the emf for the cell

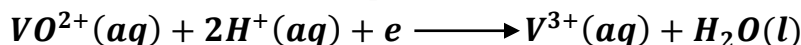
(c) State whether the cell reaction in (a) is feasible or not. Give a reason for your answer.

Hint: The negative electrode potential ($-0.44V$) shows the reaction that will take place at the anode. The other reaction obviously should occur at the cathode and should be reduction (gain of electrons)



(c) The reaction is feasible, because the emf of the cell is positive.

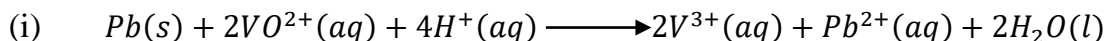
4. A galvanic cell consists of the following electrodes.



At $25^{\circ}C$, the emf of the cell was found to be $+0.76V$.

- (i) Write the overall cell equation
- (ii) Calculate the standard electrode potential for the $VO^{2+}(aq)/V^{3+}(aq)$ electrode.

Note; The reactions given are already reactions at the electrodes. However for calculations, the electrode potential at the LHE should be made a reduction one.



(ii)
$$\begin{aligned} E_{Cell}^{\theta} &= E_{RHE} - E_{LHE} \\ +0.76 &= E_{RHE} - (+0.13) \\ E_{RHE} &= +0.76 + 0.13 = +0.89V \end{aligned}$$

Gibb's free energy, ΔG , as a measure of spontaneity

The Gibb's free energy, ΔG^{θ} (in Joules) of a cell is given by the expression;

$$\Delta G^{\theta} = -nFE_{Cell}^{\theta}$$

where n is number of electrons taking part in the process

F is the Faraday's constant ($96500Cmol^{-1}$)

E_{Cell}^{θ} is the emf of the cell

- *The value of n is simply the number of electrons involved in writing the overall reaction.*
- *If the calculated value of ΔG^{θ} is negative, the reaction is spontaneous/ feasible*
- *If the calculated value of ΔG^{θ} is positive, the reaction is not feasible*
- *Gibb's free energy is also a measure of maximum useful work done by the cell.*

Examples

1. The electrode potentials of $S_2O_8^{2-}(aq)/SO_4^{2-}(aq)$ and $I_2(aq)/I^{-}(aq)$ are $+2.01V$ and $+0.54V$ respectively.

(a) Write an equation for the reaction that occurs at the:

- (i) anode
(ii) cathode

(b) Write the:

- (i) cell notation
(ii) overall cell reaction

(c) Calculate the :

- (i) emf of the cell generated from the cell reaction in c(ii) above.
(ii) Gibb's free energy for the cell (*Faraday's constant* = $96500C$)
(iii) State whether the above cell reaction is feasible or not. Give a reason for your answer.

- (a) (i) At anode: $2I^{-}(aq) \longrightarrow I_2(aq) + 2e$
(ii) At cathode: $S_2O_8^{2-}(aq) + 2e \longrightarrow 2SO_4^{2-}(aq)$
(b) (i) $Pt(s)/I^{-}(aq), I_2(aq) // S_2O_8^{2-}(aq), SO_4^{2-}(aq)/Pt(s)$
(ii) $2I^{-}(aq) + S_2O_8^{2-}(aq) \longrightarrow I_2(aq) + 2SO_4^{2-}(aq)$
(c) (i) $E_{Cell}^{\theta} = E_{RHE} - E_{LHE} = +2.01 - (+0.54) = +1.47V$
-

- (ii) $\Delta G^\theta = -nFE_{Cell}^\theta = -2 \times 96500 \times 1.47 = -283710J = -283.71kJ$
(iii) *The reaction is feasible because the value of Gibb's free energy of the cell is negative.*

2. The convention of a cell was set up as shown below
 $Pt(s)/Mn^{2+}(aq), MnO_4^-(aq), H^+(aq) // O_2(g) / H^+(aq), H_2O_2(aq) / Pt(s)$.

(a) Write equation for the half-cell reaction at the:

- (i) anode
(ii) cathode

(b) Write the overall equation for the cell reaction.

(c) The reduction potentials for the reactions in (a)(i) and (ii) above respectively are $+1.52V$ and $+0.68V$ respectively. Predict the spontaneity of the cell reaction.

- (a) (i) At anode: $Mn^{2+}(aq) + 4H_2O(l) \longrightarrow MnO_4^-(aq) + 8H^+(aq) + 5e^-$
(ii) At cathode: $O_2(g) + 2H^+(aq) + 2e^- \longrightarrow H_2O_2(aq)$
(b) $2Mn^{2+}(aq) + 8H_2O(l) + 5O_2(g) \longrightarrow 2MnO_4^-(aq) + 6H^+(aq) + 5H_2O_2(aq)$
(c) $E_{Cell}^\theta = E_{RHE} - E_{LHE} = +0.68 - (+1.52) = -0.84V$
 $\Delta G^\theta = -nFE_{Cell}^\theta = -10 \times 96500 \times -0.84 = 810600J = +810.6kJ$

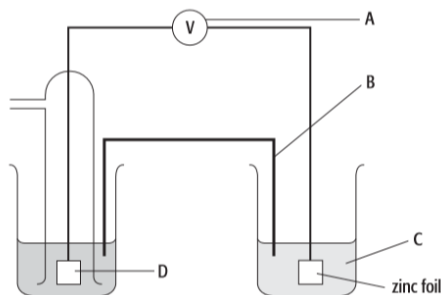
Since the emf of the cell is negative, giving a positive value of Gibb's free energy, the reaction is not spontaneous.

Applications of electrode potentials

- (i) Predicting feasibility of a reaction
(ii) Calculating emf of electrochemical cells
(iii) Determining equilibrium constant
(iv) Determining solubility of a sparingly soluble salt.

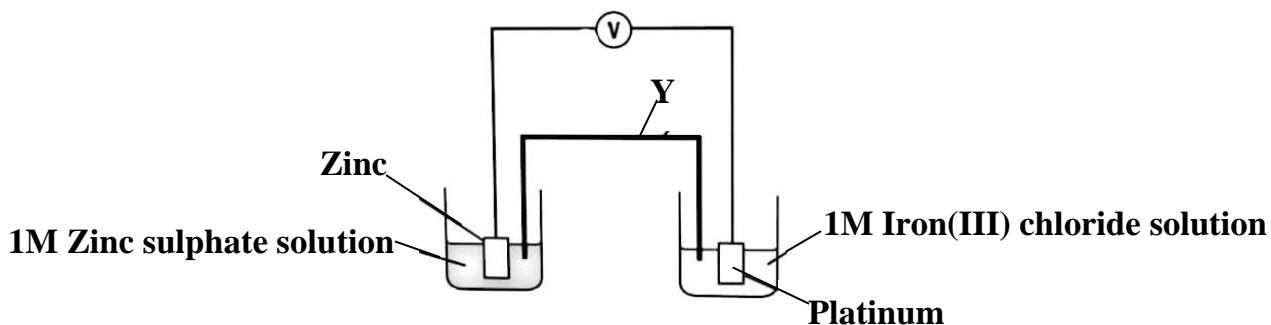
Questions

1. The diagram below shows an electrochemical cell designed to calculate the standard electrode potential of zinc.



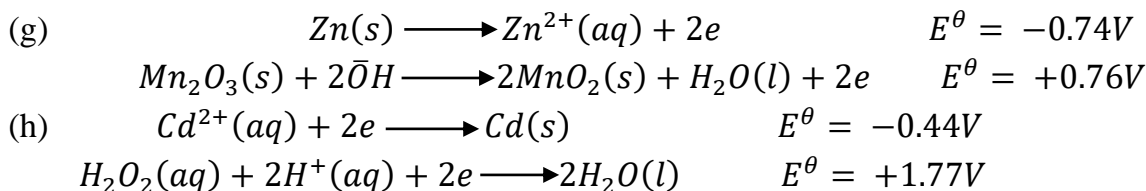
- (a) Name the apparatus labeled A and state a characteristic it should have
(b) (i) Name B and state its purpose.

- (ii) State how part B is prepared
 - (c) Identify C
 - (d) Name part D and explain its function.
 - (e) State three standard conditions for measuring of standard electrode potential.
2. The figure below shows a voltaic cell set up between two electrodes



- (a) (i) Define the term voltaic cell
 - (ii) Name Y and state its role in the above set up
 - (b) The reading on the voltmeter above was +1.53 volts.
 - (i) Write the equation for the redox reaction that takes place
 - (ii) State whether the reaction in b(i) is feasible . Give a reason for your answer.
 - (c) Calculate the electrode potential of the left hand electrode if the electrode potential of the right hand electrode is +0.77V
 - (d) Write the cell convention of the voltaic cell above.
3. Calculate the emf, write the cell notation, equation at each electrode and overall equation for each of the following cells

- | | | |
|-----|--|-----------------------------|
| (a) | $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ | $E^\theta = +0.34\text{V}$ |
| | $\text{Ag}^+(\text{aq})/\text{Ag}(\text{s})$ | $E^\theta = +0.80\text{V}$ |
| (b) | $\text{Cr}^{3+}(\text{aq})/\text{Cr}(\text{s})$ | $E^\theta = -0.744\text{V}$ |
| | $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ | $E^\theta = +0.34\text{V}$ |
| (c) | $\text{I}_2(\text{aq}) + 2e \longrightarrow 2\text{I}^-(\text{aq})$ | $E^\theta = +0.54\text{V}$ |
| | $\text{Br}_2(\text{l}) + 2e \longrightarrow 2\text{Br}^-(\text{aq})$ | $E^\theta = +1.08\text{V}$ |
| (d) | $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ | $E^\theta = +0.34\text{V}$ |
| | $\text{Fe}^{2+}(\text{aq})/\text{Fe}(\text{s})$ | $E^\theta = -0.44\text{V}$ |
| (e) | $\text{Al}^{3+}(\text{aq})/\text{Al}(\text{s})$ | $E^\theta = -1.66\text{V}$ |
| | $\text{Cu}^{2+}(\text{aq})/\text{Cu}(\text{s})$ | $E^\theta = +0.34\text{V}$ |
| (f) | $\text{Li}^+(\text{aq}) + e \rightleftharpoons \text{Li}(\text{s})$ | $E^\theta = -3.04\text{V}$ |
| | $\frac{1}{2}\text{I}_2(\text{s}) + e \rightleftharpoons \text{I}^-(\text{aq})$ | $E^\theta = +0.54\text{V}$ |



4. (a) State factors that can affect standard electrode potential of an element.

(b) The standard electrode potential for group II elements are given in the table below

Element	Be	Mg	Ca	Sr	Ba
Electrode potential	-1.85	-2.37	-2.87	-2.89	-2.91

(i) State and explain the trend in variation of standard electrode potential

(ii) Explain why the values of standard electrode potentials are negative

(c) Electrode potentials for some half cells are given below:

Half cell	$E^\theta(V)$
$Pt(s)/SO_4^{2-}(aq), SO_4^{2-}(aq)$	-0.90
$Cu^{2+}(aq)/Cu(s)$	+0.34

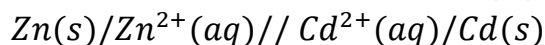
(i) Write the equations for the reactions that take place at anode and cathode

(ii) Write the overall cell reaction

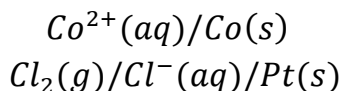
(iii) Calculate the emf of the cell

(d) State whether the reaction in c(iii) is feasible or not. Give a reason for your answer.

5. Calculate the standard electrode potential of the $Cd^{2+}(aq)/Cd(s)$ electrode if the electrode potential of the cell given below is $+0.36V$. $E^\theta_{Zn^{2+}(aq)/Zn(s)} = -0.76V$.



6. Two half cells are given below where combined:



(a) State which half-cell is suitable to make the:

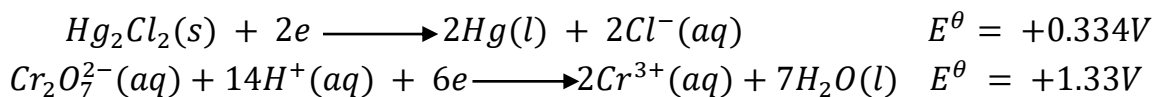
(i) negative electrode

(ii) positive electrode

(b) Write the equation for the cell reaction.

(c) If the emf of the cell is $1.63V$ and $E^\theta_{Cl_2(g)/Cl^-(aq)} = +1.36V$. Calculate the standard electrode potential for the cobalt half-cell.

7. Equations for some half-cell reactions are given below.

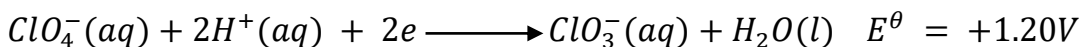
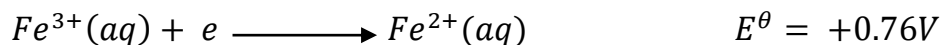


(a) Write the convention for the cell.

(b) Write equation for the overall reaction.

(c) Calculate the cell voltage.

8. Half equations for some cell reactions and the electrode potentials are given below:



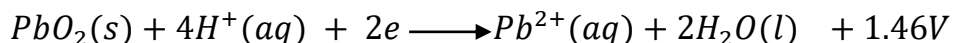
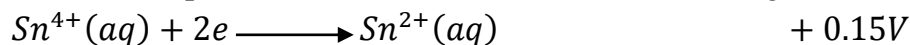
(a) Write:

- the cell notation of the cell formed when the half cells are combined.
- the overall cell reaction

(b) Calculate the emf of the cell

(c) Predict the feasibility of the reaction and give a reason for your answer.

9. The standard electrode potentials for some half cell reactions are given below:



(a) Write the overall equation for the cell reaction that occurs when the half cells are combined.

(b) (i) Calculate the Gibbs free energy for the cell reaction.

(Faraday's constant = 96500C)

(ii) State whether the cell reaction is feasible or not and give a reason for your answer.

10. (a) Explain what is meant by the terms

- standard electrode potential
- standard hydrogen electrode

(b) The standard electrode potentials for some half-cells are shown below.

Half cell	$E^\theta (V)$
$MnO_4^-(aq), H^+(aq)/Mn^{2+}(aq)$	+1.52
$I_2(aq)/I^-(aq)$	+0.54

State what is observed at the:

- positive electrode
- negative electrode

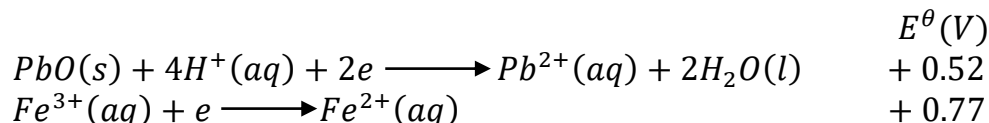
(c) Write:

- the cell convention for the combined cell
- the equation for the cell reaction that would take place if the half cells are combined.

(d) Calculate;

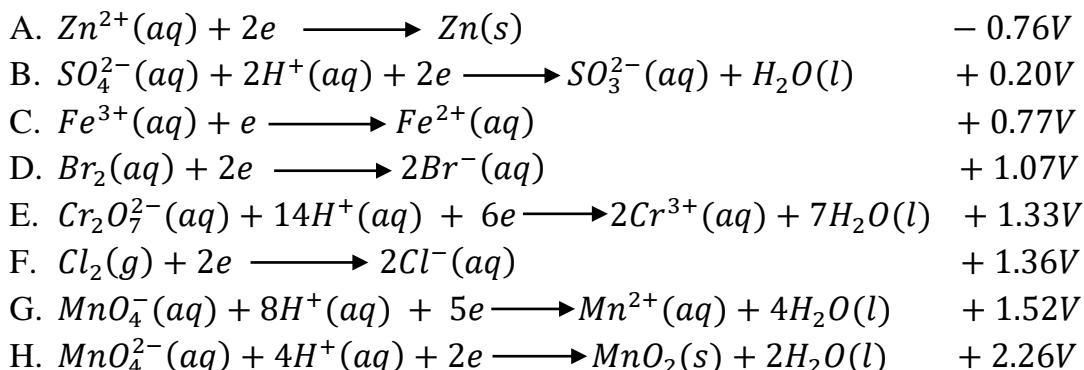
- the electrode potential for the cell
- the work done by the cell

11. The following half-cell reactions are given:



- (a) Write the cell notation for the cell formed by combining the two half cells.
 (b) State what will be observed and write equations for the reactions that take place at:
 (i) anode
 (ii) cathode
 (c) Calculate the emf of the cell.

12. The standard electrode potentials for some half cells, E^θ in volts are shown below:



- (a) State the species that is the most powerful oxidizing agent and give a reason for your answer.
 (b) State what would be observed and write equation for the reaction that would take place if the half cells:
 (i) A and E are connected
 (ii) B and G are connected
 (c) Calculate the emf of the cell in a(i)
 (d) Write the cell notation for the cell in (b)(ii) above
 (e) Explain why hydrochloric acid is not used to acidify titrants in volumetric analysis involving potassium manganate(VII) solution.
 (f) Write the cell convention when half cells C and D are combined.
13. (a)(i) Distinguish between **electrolytic conductivity** and **molar conductivity** of a solution.
 (ii) Write the equation to show the relationship between electrolytic conductivity and molar conductivity of a solution.
 (b) The table below gives the molar conductivity of a solution of ethanoic acid at 298K.

$[CH_3CO_2H](mol\,dm^{-3})$	0.001	0.01	0.1
Molar conductivity ($\Omega^{-1}cm^2mol^{-1}$)	50	16	5

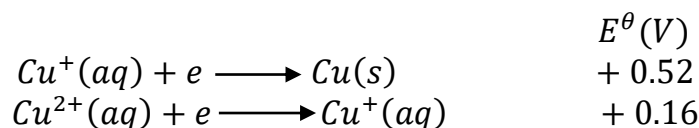
- (i) Give a reason for the decreasing values of molar conductivity of ethanoic acid with increase in concentration.
 (ii) Calculate the pH and ionization constant, K_a of 0.01M ethanoic acid.

(The molar conductivity of ethanoic acid at infinite dilution is $390\Omega^{-1}cm^2mol^{-1}$)

- (c) (i) Define the term **standard electrode potential**.
(ii) Discuss the factors that affect the value of standard electrode potential.
(iii) State **two** applications of standard electrode potential.
- (d) The standard electrode potentials of systems, $Pt(s)/H_2(g)/HCl(aq)$ and $CuSO_4(aq)/Cu(s)$ are $0.00 V$ and $+0.34 V$ respectively.
(i) Write equation for the overall cell reaction.
(ii) Calculate the maximum energy obtained from the cell.

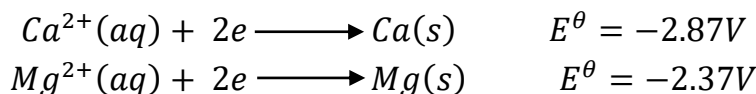
$$(1F = 96500C)$$

14. (a) State three factors which determine the magnitude of electrode potential of a metal
(b) The standard electrode potentials for the following reactions are given



Write;

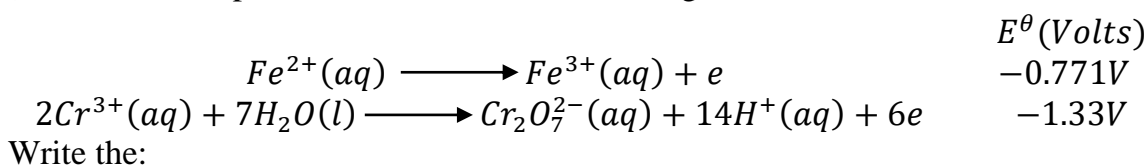
- (i) the cell notation for the cell formed when the two half cells are connected.
(ii) the equation for the overall cell reaction
- (c) (i) Calculate the emf of the cell.
(ii) What deduction do you make from your answer in (c)(i)?
- (d) When dilute sulphuric acid is added to copper(I) oxide, a brown solid and a pale blue solution were formed. Explain the observation.
15. The standard redox potentials of $Fe^{3+}(aq)/Fe^{2+}(aq)$ and $Sn^{4+}(aq)/Sn^{2+}(aq)$ are $+0.76 V$ and $+0.15V$ respectively.
(a) Write the cell convention for the combined cell
(b) Write an equation for the half-cell reaction at the:
(i) cathode
(ii) anode
(c) Write the overall cell reaction equation.
(d) State two conditions under which the electrode potentials above are measured
(e) Deduce if the overall reaction is feasible or not. Give a reason for your answer.
(f) State one application of electrode potentials
16. The standard electrode potentials for some systems are given below:



- (a) Write the convention for the cell
(b) Write the equation for the overall reaction

- (c) (i) Calculate the cell voltage
(ii) What conclusion can you draw from the emf value in c (i) above
17. The standard electrode potentials of lead and magnesium are given below:
- $$Pb^{2+}(aq) + 2e \longrightarrow Pb(s) \quad E^\theta = -0.13V$$
- $$Mg^{2+}(aq) + 2e \longrightarrow Mg(s) \quad E^\theta = -2.40V$$
- (a) Write the convention for the cell that can be formed
(b) Write the equation;
(i) for the reaction taking place at each electrode
(ii) for the overall reaction
(c) Calculate the emf of the cell
18. (a) (i) Define the term standard electrode potential.
(ii) Give reasons why it is not possible to measure standard electrode potential absolutely.
(iii) Explain the factors that affect the value of standard electrode potential.
(b) Describe:
(i) the structure of a standard hydrogen electrode.
(ii) how you would measure standard electrode potential of magnesium in a solution of its ions.
(c) The standard electrode potential of copper and zinc are given below.
- $$Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \quad E = +0.34V$$
- $$Zn^{2+}(aq) + 2e \longrightarrow Zn(s) \quad E = -0.76V$$
- Write the cell notation for a zinc-copper cell and calculate the emf of the cell.
(d) State two ways by which an electrolytic cell differs from an emf cell.
19. Given the following electrode potentials.
- $$Na^+(aq) + e \longrightarrow Na(s) \quad -2.71V$$
- $$Cu^{2+}(aq) + 2e \longrightarrow Cu(s) \quad +0.337V$$
- $$Zn^{2+}(aq) + 2e \longrightarrow Zn(s) \quad -0.763V$$
- $$Ag^+(aq) + e \longrightarrow Ag(s) \quad +0.799V$$
- (a) Arrange the electrodes in order of reducing power starting with the least reducing
(b) (i) Which two electrodes will form a cell of maximum emf ?
(ii) Write the cell notation for the cell you gave in b(i) above.
(iii) Write the overall cell reaction for the cell in b(i).
20. (a)(i) What is meant by the term “**standard electrode potential**”?
(ii) Write down the factors that affect the magnitude of standard electrode potential.
(b) (i) With the aid of a labeled diagram, describe how the standard electrode potential of a metal can be measured.

- (ii) State two applications of standard electrode potentials.
- (c) Some half equations and their standard electrode potentials are given below:
- $$\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e} \longrightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l}) \quad E^\theta = +1.33\text{V}$$
- $$\text{Cl}_2(\text{g}) + 2\text{e} \longrightarrow 2\text{Cl}^-(\text{aq}) \quad E^\theta = +1.36\text{V}$$
- $$\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e} \longrightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l}) \quad E^\theta = +1.52\text{V}$$
- (i) Name the species that is the strongest reducing agent. Give a reason for your answer.
- (ii) Write the cell notation of the cell made by combining half cells of dichromate(VI) and chlorine and calculate the emf of the cell. Draw a well labeled diagram for the cell arrangement.
- (iii) Calculate the energy given out by the cell in (c)(ii) above. Comment on your answer. (1 Faraday = 96500 coulombs)
- (iv) Using the standard electrode potentials given, explain why hydrochloric acid cannot be used to acidify aqueous manganate(VII) solutions.
21. Draw a well labeled diagram of a half cell consisting of;
- (a) a Cr^{3+}/Cr half-cell and a Cl_2/Cl^- half-cell.
- (b) a Mn^{2+}/Mn half-cell and a Pb^{2+}/Pb half-cell.
22. (a) The molar conductivity of a carboxylic acid, RCOOH at infinite dilution at 25°C is $390.7 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ and the acid dissociation constant, $K_a = 1.80 \times 10^{-5}\text{M}$.
- (i) Define the term molar conductivity
- (ii) Calculate the molar conductivity of a 0.01M solution of RCOOH .
- (b) The zinc/ silver oxide cell used in hearing aids and electric watches has the following electrode potentials.
- $$\text{Zn}(\text{s}) \longrightarrow \text{Zn}^{2+}(\text{aq}) + 2\text{e} \quad E^\theta = +0.76\text{V}$$
- $$\text{Ag}_2\text{O}(\text{s}) + \text{H}_2\text{O}(\text{l}) + 2\text{e} \longrightarrow 2\text{Ag}(\text{s}) + 2\text{OH}^- \quad E^\theta = +0.344\text{V}$$
- (i) Calculate the emf of the zinc/silver oxide cell
- (ii) Write the overall redox reaction that generates the emf calculate in b(i) above
- (iii) Draw a well labeled diagram to show the zinc/ silver oxide cell can be set up and the emf measured.
23. (a) State and discuss three factors that affect the value of standard electrode potential
- (b) Draw a well labeled diagram to show how the standard electrode potential of the zinc electrode can be determined.
- (c) The electrode potentials of some half cells are given below;



- (i) cell notation for the cell formed when the two half cells are combined.
- (ii) equation at the anode, cathode and overall cell reaction.
- (d) Calculate the emf of the cell in (c)(i)
- (e) (i) State Faraday's law of electrolysis.
- (ii) How long will it take 48 cm^3 of hydrogen at room temperature and pressure when acidified water is electrolyzed using a current of 0.25 A .

Assignment:

Batteries

- *Research, read and make notes about batteries (dry cells, mercury cell, Nickel-Cadmium cell and fuel cells)*
- *Uses of batteries*
- *Explain the functioning of a battery*
- *Explain the conversion of one form of energy to another*