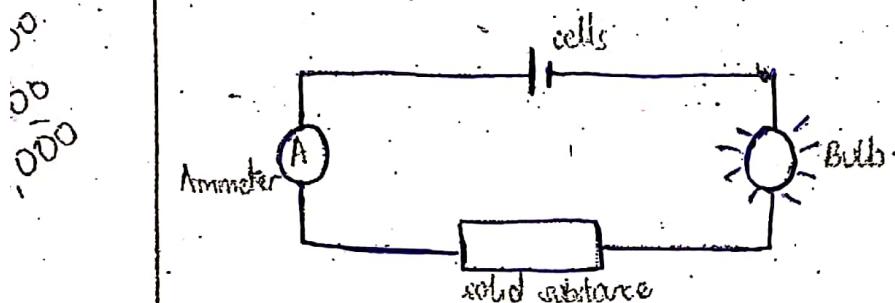


12/4/11

EFFECT OF ELECTRICITY ON SUBSTANCES (Electrolysis)

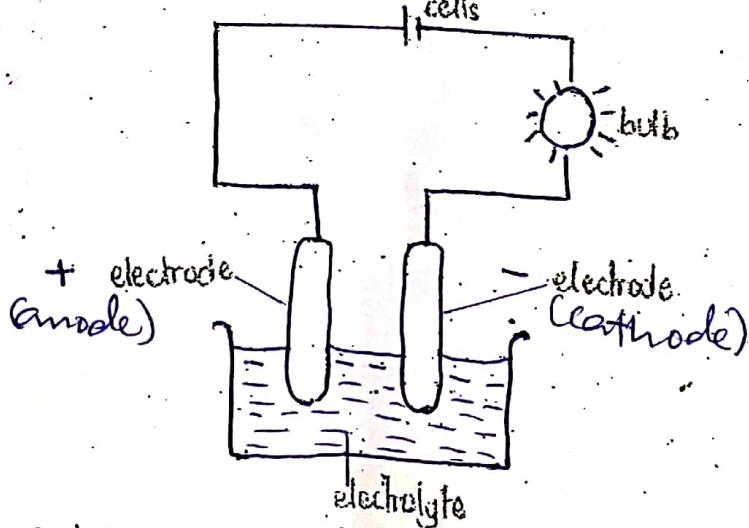
Electric current is the flow of electrons from one point to another through a solid/liquid.



Some solid substances allow current to pass through them, as result a bulb gives light. These solids are known as conductors. However, solids like wood, plastics, etc don't allow a flow of electric current & are therefore called non-conductors/insulators.

⇒ Conductors have free mobile electrons which move about within the solid transferring a stream of electrons i.e. current hence conduction of electricity.

② Solutions of ionic compounds and molten (liquid) ionic compounds that conduct electricity in a liquid state are known as electrolytes.



Electrolytes use a few mobile ions to transmit the electrons from one point to another. Electrolytes include aqueous solutions of copper sulphate, sodium chloride, copper(II) chloride, sulphuric acid, hydrochloric acid, etc. and molten salts of lead(II) bromide, zinc chloride, etc.

Liquids which don't conduct electricity are known as non-electrolytes e.g. carbon tetrachloride, benzene etc.

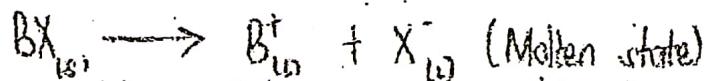
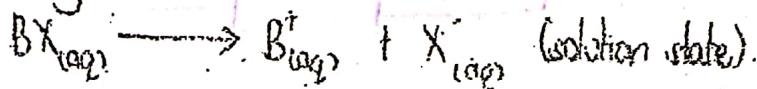
ELECTROLYTES

An electrolyte is a compound which conducts electricity in solution or molten states and is decomposed by it.

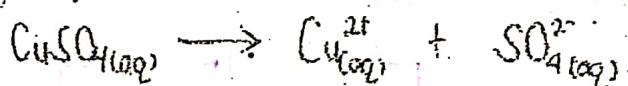
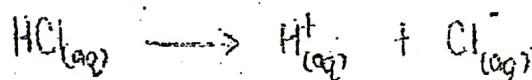
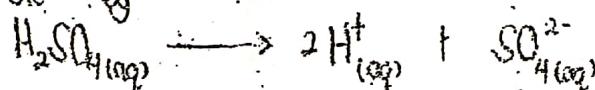
There are two types of electrolytes.

1. Strong electrolytes

These completely ionise in aqueous solutions and are good conductors of electricity i.e.

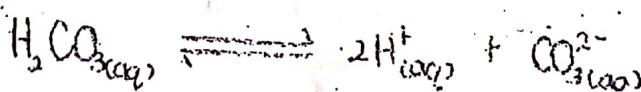
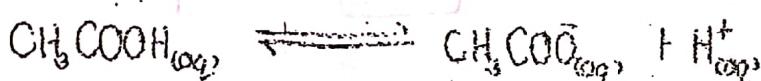
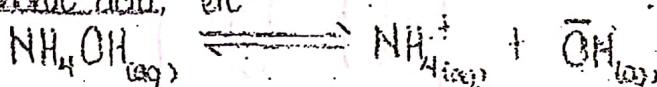


Strong electrolytes include sulphuric acid (dilute), dilute hydrochloric acid, dilute nitric acid, sodium hydroxide solution, copper(II) sulphate soln. etc. e.g.



2. Weak electrolytes

These partially ionise therefore they have fewer ions per unit volume to transmit the electric current. For e above reason, they aren't conductors. Weak electrolytes include aqueous ammonia, ethanol, carbonic acid, etc.



Definitions

1. Electrodes

These are 2 poles of metal/carbon at which the electric current enters/leaves the electrolyte.

Anode: This is the positive electrode at which electrons leave the electrolyte/enter external circuit.

OR Anode is an electrode at which oxidation reaction occurs.

Or Anode is an electrode where at which oxidation reaction only takes place / occurs.

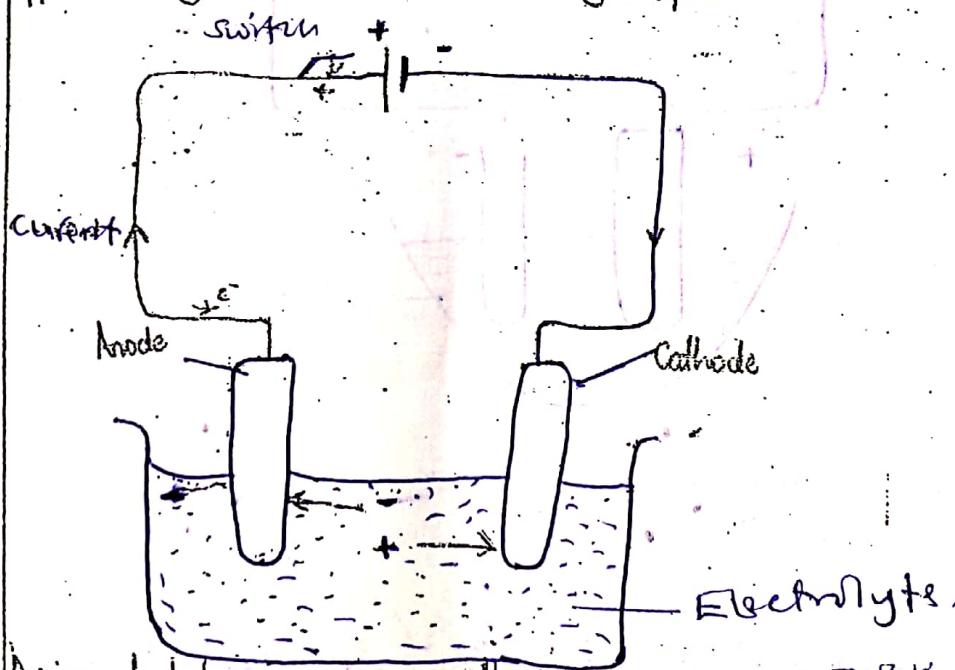
- Cathode: This is a negative electrode at which electrons leave a external circuit / enter a electrolyte. An electrode at which reduction reaction occurs.
- NOTE: Non-electrolytes don't ionise at all therefore they exist as molecules.

- 14/4/11 - ELECTROLYSIS

This is the decomposition of an electrolyte by passing electric current through it. It only occurs when a electrolyte is in molten/ solution states.

Ionic theory of electrolysis

1. Ionic substances contain negative and positive particles called ions.
2. In a solid state/concentrated liquid, the ions are strongly attracted to each other (aren't free to move) hence the electrolyte doesn't conduct.
3. On melting / dissolving the ionic compound in water, the ions are separated from each other. i.e. the ions become free and mobile hence the electrolyte conducts.
4. On applying an electric current, the ions move to the opposite ends of the electric field. Positively charged ions migrate to the negative electrode while negatively charged ions migrate to the positive electrode. (opposite charges attract while like charges repel)



During electrolysis, the ions are attracted to electrodes of opposite charges. Cations are attracted to cathode and anions to anode.

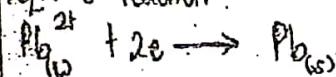
At the cathode

The lead(II) ions migrate to the cathode from where they gain electrons and are discharged.

Observation

A grey solid is deposited at the cathode.

Eqn of reaction:



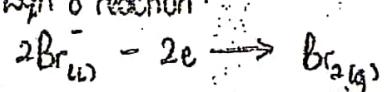
At the anode

The bromide ions migrate to the anode from where they are discharged by loss of electrons.

Observation:

A reddish brown gas is given off at the anode.

Eqn of reaction:

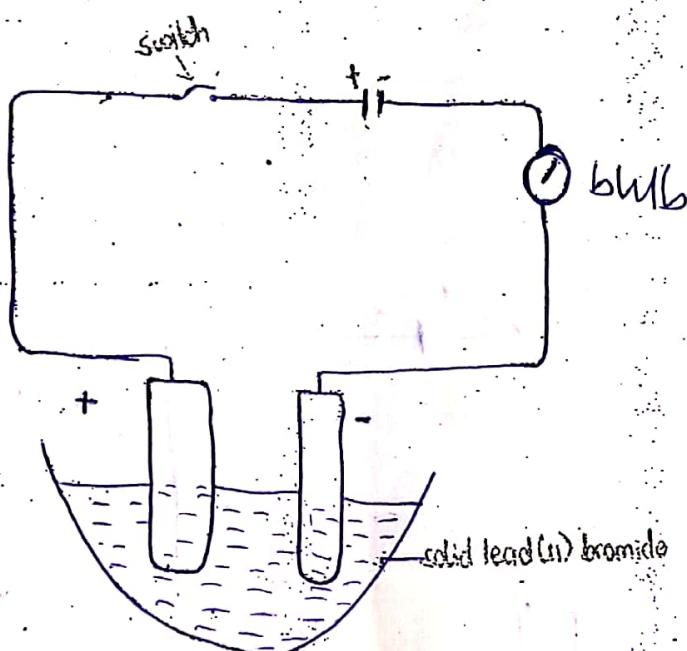


NOTE:

The bulb does not give light when solid lead(II) bromide is not molten because solid lead(II) bromide has no mobile ions but as soon as solid lead(II) bromide melts, the ions become free & are able to conduct electric current therefore the bulb gives light.

Questions

1. A circuit for electrolysis of lead(II) bromide was set up as shown below.



- a. State what was observed when,

i. Switch was turned on.

No observable change.

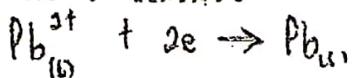
ii. Lead(II) bromide was melted at the switch turned on.

iii. When melted, a reddish brown gas was evolved at the anode.

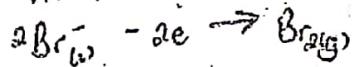
Bulb gave light lead solid " " " " "

- b. Explain your observations in a(i) & a(ii).
- In a(i), there is no observable change because solid lead(II) bromide has no mobile ions therefore cannot conduct electricity.
 - In a(ii), molten lead(II) bromide has mobile ions which conduct electricity. Therefore it bulb gives light. Also, lead(II) ions migrate to the cathode from where they are discharged to form lead (grey solid) & bromide ions migrate to the anode from where they are discharged as bromine gas.

At the cathode:



At the anode:



2. Molten lead(II) bromide was electrolysed b/w carbon electrodes.

- a. State what was observed at i.

- i. Anode

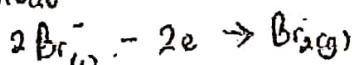
A reddish brown gas is given off.

- ii. Cathode

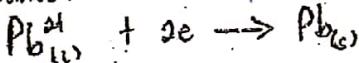
A grey solid is deposited.

- b. Write eqn for the reaction that took place at:

- i. anode



- ii. cathode



3. Molten lead(II) bromide was electrolysed b/w carbon electrodes.

- a. Explain why lead(II) bromide was electrolysed in the molten state and not solid state.

Molten lead(II) bromide has mobile ions which can conduct electric current while in solid lead(II) bromide, the ions aren't free to move.

- b. State what was observed at i.

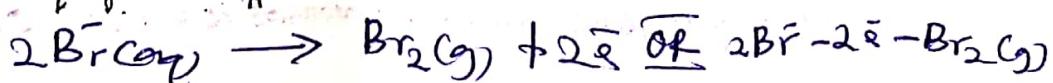
- i. Anode

A reddish brown gas is given off.

- ii. Cathode

A grey solid is deposited.

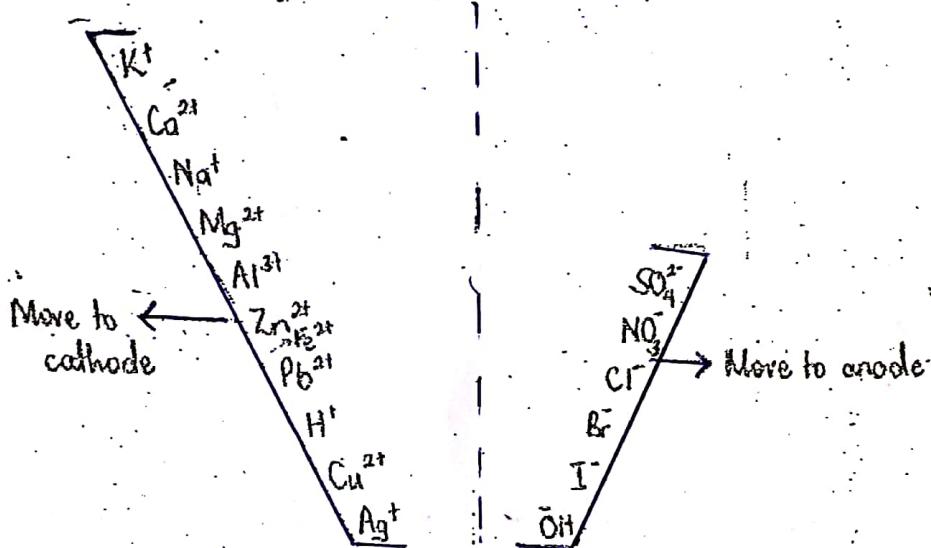
- c. Write eqn for the reaction that took place at the anode



SELECTIVE DISCHARGE OF IONS

When 2 or more ions with similar charges are present in a solution under similar conditions eg sodium ion & hydrogen ion / hydroxide ion & sulphate ion, one is preferentially discharged & selection of ion to be discharged depends on a number of factors which include:

1. Position of an ion in the electrochemical series.

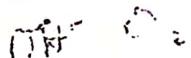
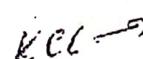
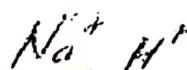


Given that all other factors are constant, an ion will be discharged from solution in preference to those above it in the electrochemical series. eg Sodium hydroxide solution contains sodium ions & hydrogen ions in water. but when these 2 ions migrate to the cathode, the hydrogen ions are discharged in preference to sodium ions b/c they are lower in the electrochemical series therefore hydrogen is evolved at the cathode.

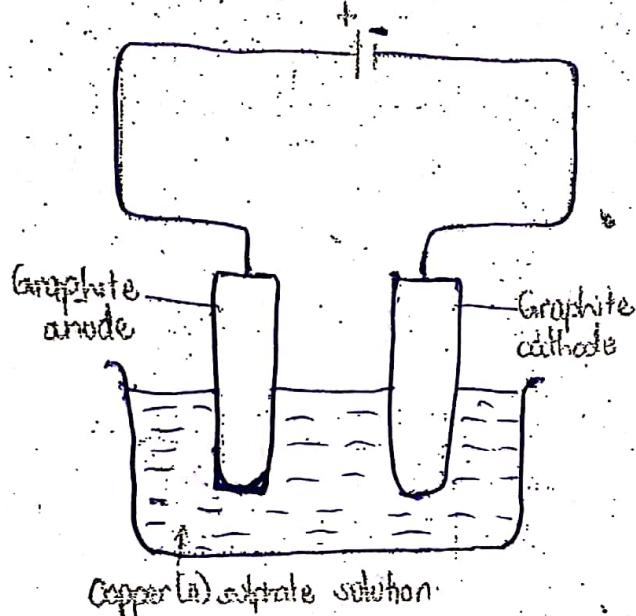
ELECTROLYSIS OF COPPER(II) SULPHATE SOLUTION

Procedure

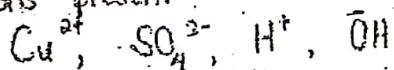
A known mass of copper(II)sulphate is dissolved in a known volume of water in a beaker. Graphite electrodes are then connected to 6 volts direct current supply, dipped in a beaker containing copper(II)sulphate solution. Electric current is then passed thru the electrolyte.



Experimental set up:



Ions present



At the cathode

Copper(II) ions & hydrogen ions migrate. The hydroxide ions & sulphate ions to the cathode but Cu^{2+} ions migrate to the anode but OH^- ions are discharged in preference to SO_4^{2-} . Hydrogen ions are discharged in preference to SO_4^{2-} because they are lower in ions b/w them & are lower in the electrochemical series.

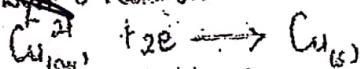
At the anode

OH^- ions are discharged in preference to SO_4^{2-} because they are lower in the electrochemical series.

Observation:

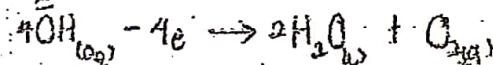
A reddish brown solid is deposited at the cathode.

Eqn. of reaction



pH at the cathode

Bubbles of a colourless gas are given off.
Eqn. of reaction



pH at the anode

Discharge of hydroxide ions upsets the ionic equilibrium of water therefore the water accumulation of hydrogen ions at the anode. In presence of hydrogen ions the hydroxide ions are discharged. Cathode is responsible for the acidity of the solution before the hydrogen ions migrate to the solution around the cathode i.e. pH less than 7. They do accumulate around the anode hence making the soln around the anode acidic i.e. pH less than 7.

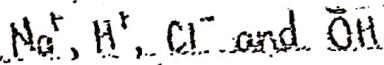
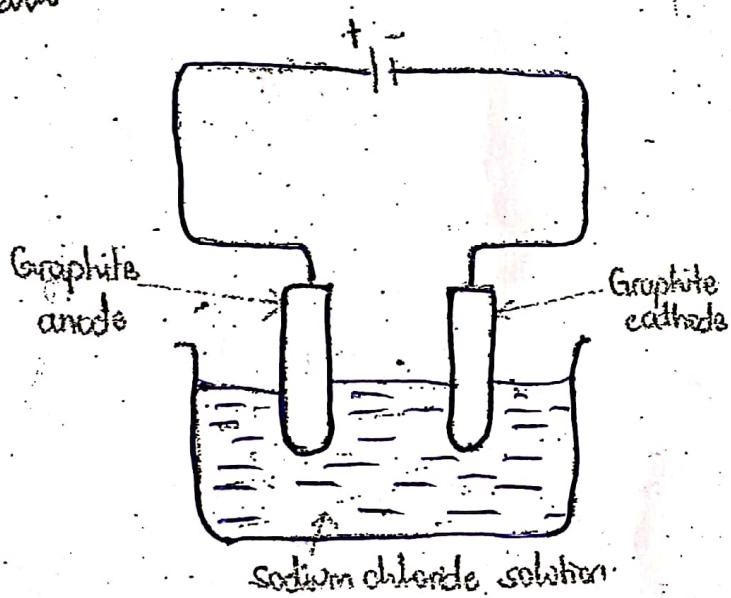
General observations:

1. The overall pH of the soln after electrolysis is less than 7 i.e. the soln becomes acidic.
2. The blue colour of copper(II) sulphate soln fades as copper is discharged i.e. the blue solution turns colourless.

ELECTROLYSIS OF DILUTE SODIUM CHLORIDE SOLUTION

Procedure:

A known mass of sodium chloride is dissolved in a known volume of water in a beaker. Graphite electrodes are then connected to a 6 Volts direct current power supply & dipped into a soln of a beaker. Experiment is set up as shown below:



At the cathode

The sodium ions and hydrogen ions migrate to the cathode but H^+ ions are discharged in preference to the Na^+ ions b/c they are lower in the electrochemical series.

Observation:

Bubbles of a colourless gas are given off.



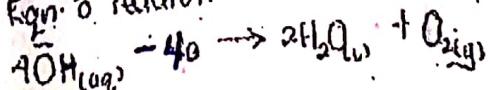
At the anode

Chloride ions & hydroxide ions migrate to the anode but OH^- ions are discharged in preference to the chloride ions b/c they are lower in the electrochemical series.

Observation:

Bubbles of a colourless gas are given off.

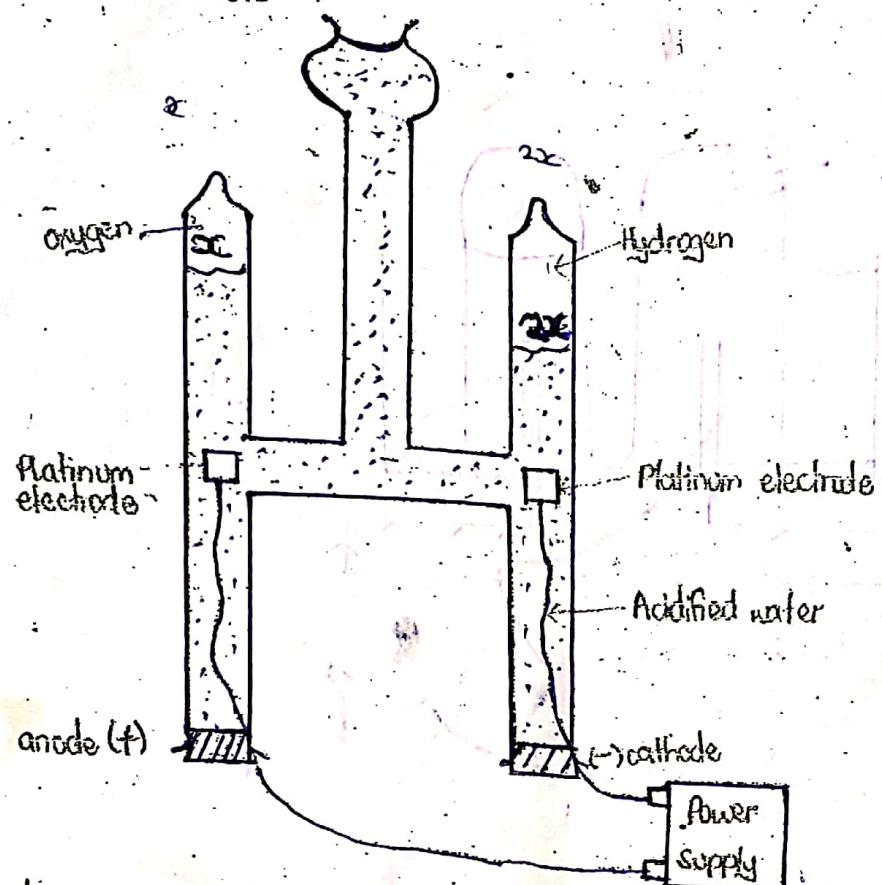
Eqn. of reaction:



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ELECTROLYSIS OF ACIDIFIED WATER

Hofmann's Voltmeter



Procedure

Fill the voltmeter with acidified water (acidified with sulphuric acid) and connect the electrolyte to a 6 volts direct current power supply. Pass an electric current through the electrolyte.

Ions present

Hydrogen ions H^+

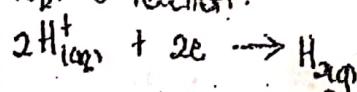
Hydroxide ions OH^-

Sulphate ions SO_4^{2-}

At the cathode

decomposition: bubbles of a colourless gas are given off.

Eqn of reaction:



At the anode

conservation: bubbles of a colourless gas are given off.

Eqn of reaction:

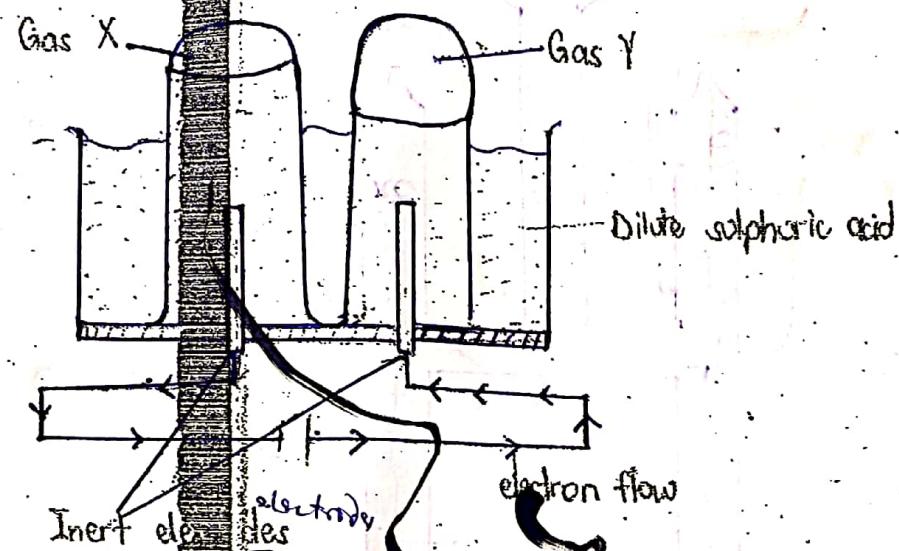


Note:

The volume of hydrogen produced is twice that of oxygen.
Overall eqn of reaction:

Question:

The diagram below shows an electrolytic cell in which electrolysis of dilute sulphuric acid occurs.

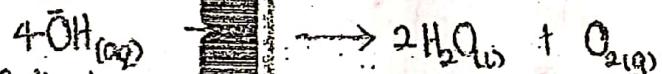


- a. Name the gases that are evolved during electrolysis.

X oxygen
Y hydrogen

- b. Write equations for the reaction that took place at the;

i. Anode



ii. Cathode



- c. Indicate the direction of electron flow in the circuit.

- d. State 2 industrial applications of electrolysis.

- Extraction of metals.
- Purification of metals.
- Prevention of rusting.

2. Concentration

The discharge

Therefore, the

Concentrated

negative ions

are discharged

the electrolyte.

An ion is promoted by its increase in concentration.

In a larger concentration is preferentially discharged.

Concentrated hydrochloric acid contains Cl^- & OH^- ions from water as

(HCl) since the chloride ions are in a higher concentration

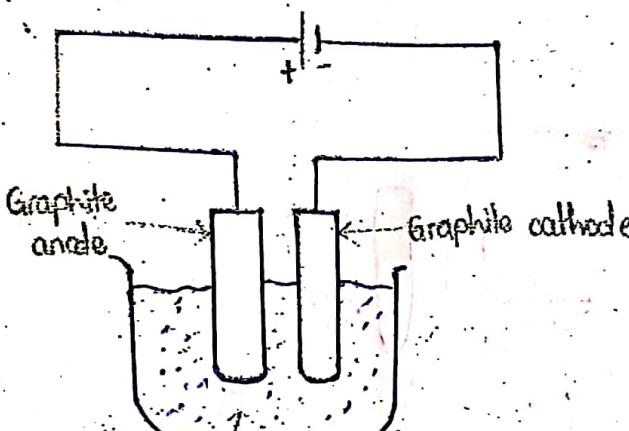
in preference to hydroxide ions.

In dilute hydrochloric acid, the hydroxide ions are in a larger concentration compared to that of the chloride ions; therefore the hydroxide ions are discharged in preference to chloride ions.

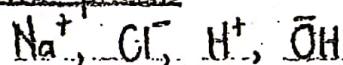
Electrolysis of concentrated sodium chloride soln.

Procedure

Prepare a conc soln of NaCl. Dip graphite electrodes into the solution and connect the electrodes to a 6 volts direct current power supply. Pass an electric current through the electrolyte.



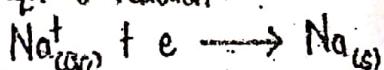
Ions present



At the cathode

The sodium ions and hydrogen ions migrate to the cathode but the Na^+ ions are discharged in preference to the H^+ because they are in a higher concentration.

Eqn of reaction

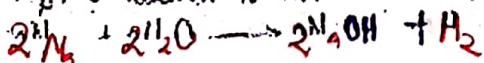


The sodium formed is very reactive. It reacts with H_2O to form hydrogen gas.

Observation

Bubbles of a colourless gas are given off around the cathode. There

Eqn of reaction to formation of H_2



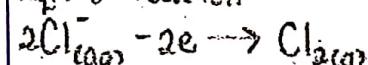
At the anode

The chloride ions and hydroxide ions migrate to the anode but the Cl^- ions are discharged to the preference of OH^- because they are in a higher concentration.

Observation

A greenish yellow gas is given off.

Eqn of reaction



at the anode

The discharge of chloride ions leaves hydroxide ions around the anode. There

the sdn at the anode is alkaline

hence the overall pH is greater than 7

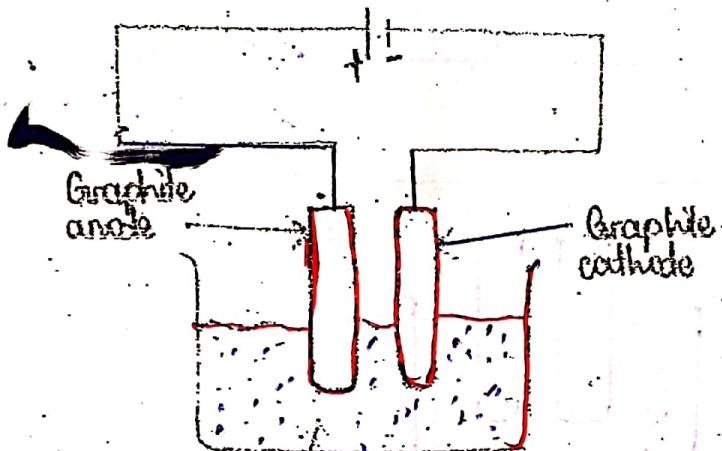
hence the overall pH is greater than 7

cathode is responsible for making the soln alkaline hence a pH greater than 7.

Electrolysis of concentrated copper(II) chloride soln:

Procedure

Prepare a concentrated solution of copper(II) chloride. Dip graphite electrodes into the solution and connect the electrolyte to a 6 volts direct current power supply. Pass an electric current through the electrolyte.



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Ions present:

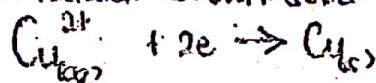
Copper(II) ions, chloride ions, hydrogen ions & hydroxide ions.

At the cathode

Copper(II) ions & hydrogens ions migrate to the cathode but the copper(II) ions are discharged in preference to hydrogens because they are in a higher concentration.

Observation

A reddish brown solid is deposited off.

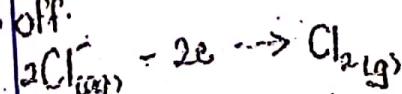


At the anode

The chloride ions & OH⁻ migrate to the anode but the Cl⁻ are discharged in preference to the OH⁻ because they are in a higher concentration.

Observation

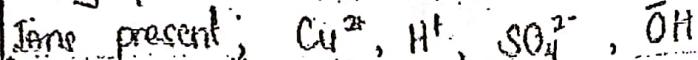
A greenish yellow gas is given



3. Nature of the electrode

(i) Electrolysis of copper(II) sulphate solution

a. Using platinum electrodes



At the anode

The OH^- & SO_4^{2-} migrate to the anode but the OH^- ions are discharged in preference becoz E° are lower in the electrochemical series.

Observation:

Bubbles of a colourless gas are given off.

Eqn of reaction:



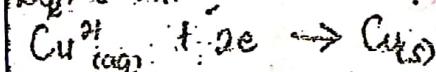
At the cathode

The Cu^{2+} & H^+ ions migrate to the cathode but the Cu^{2+} are discharged in preference bcoz E° are lower in the electrochemical series.

Observation:

A reddish brown solid is deposited.

Eqn of rxn.



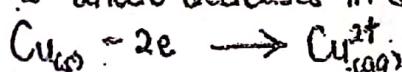
b. Using copper electrodes

At the anode

The SO_4^{2-} & OH^- ions migrate to the anode but none of them is discharged instead the copper anode dissolves into the solution (electrolyte) to form copper(II) ions. This is known as electrode ionisation.

Observation:

The anode decreases in size.

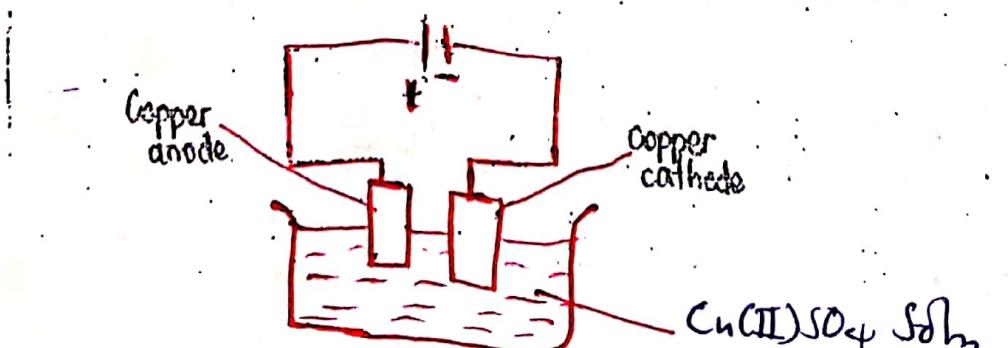
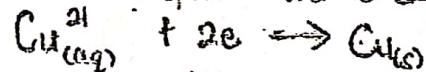


At the cathode

The Cu^{2+} & H^+ ions migrate to the cathode but the Cu^{2+} ions formed on dissolution of the anode are the ones that are discharged at the cathode.

Observation:

The cathode increases in size or a reddish brown solid is deposited.



NOTE:

1. The mass lost by e⁻ anode is equal to the mass gained by e⁻ cathode.
2. The blue colour of copper(II) sulphate solution is not discharged since copper(II) ions discharged are formed as a result of the dissolution of the anode.

(ii) Electrolysis of concentrated sodium chloride solution (Brine).

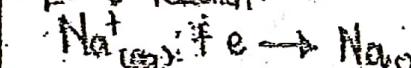
a. Using mercury cathode.

Ions present: Na^+ , Cl^- , OH^- , H^+ . Ions.

At the cathode.

Na^+ & H^+ ions migrate to the cathode but e⁻ Na^+ ions are discharged in preference to the H^+ ions b/c e⁻ are higher in the electrochemical series.

Eqn o reaction.



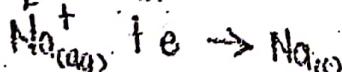
The sodium deposited reacts with e⁻ mercury cathode to form sodium amalgam.

b. Using platinum cathode.

At the cathode.

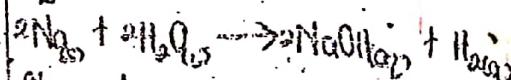
H^+ & Na^+ ions migrate to the cathode but the Na^+ ions are discharged in preference.

Eqn o rfn.



The $\text{Na}_{(\text{s})}$ formed immediately reacts with H_2O to form hydrogen gas.

Eqn o rfn.



Observation:

Bubbles of a colourless gas.

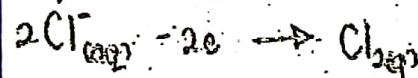
At the anode.

Cl^- & OH^- ions migrate to the anode but e⁻ Cl^- ions are discharged in preference to e⁻ OH^- due to their high concentration.

Observation:

A greenish yellow gas is given off.

Eqn o reaction.



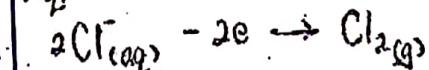
At the anode.

Cl^- & OH^- ions migrate to the anode but e⁻ Cl^- ions are discharged in preference b/c e⁻ are in a higher concentration.

Observation:

A greenish yellow gas is given off.

Eqn o rfn.



APPLICATIONS OF ELECTROLYSIS

1- Extraction of metals:

Metals that are on top on the reactivity series are extracted by electrolysis. These metals include, potassium, sodium, calcium, magnesium & aluminium. The metals can be obtained by electrolysis of their molten salts eg magnesium can be got from molten magnesium chloride, sodium from molten sodium chloride, etc. The solution/molten salts & ions are used as electrolytes, when current is switched on, the cations gain electrons at the cathode.

2- Anodising aluminium:

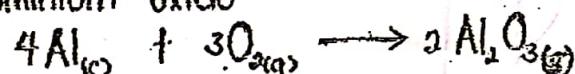
This is the process of coating objects made of aluminium with a very thin oxide layer to protect them from corrosion. This is carried out by electrolysis of dilute sulphuric acid using an aluminium object as the anode.

The OH^- & SO_4^{2-} ions migrate to the anode but the OH^- ions are discharged in preference because they are lower in the electrochemical series therefore oxygen gas is given off at the anode.

Equation of reaction;



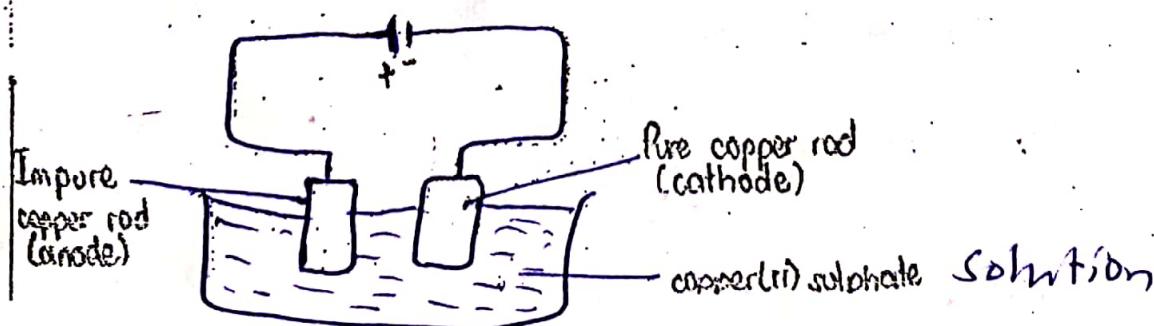
The oxygen gas then reacts with the surface of the aluminium object & coats it with a thin invisible but protective coating of aluminium oxide.



3- Purification of copper:

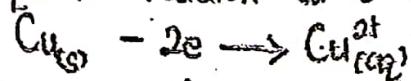
Copper can be purified by electrolysis of copper(II)sulphate solution using an impure copper rod as the anode & a pure copper rod as the cathode.

Experimental setup:



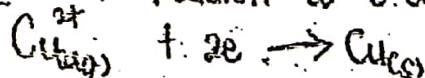
The anode dissolves into the electrolyte to form copper(II) ions & impurities which collect at the bottom of the cell.

Eqn for reaction at the anode:



The copper(II) ions migrate to the cathode arm where they gain electrons & are deposited as copper metal.

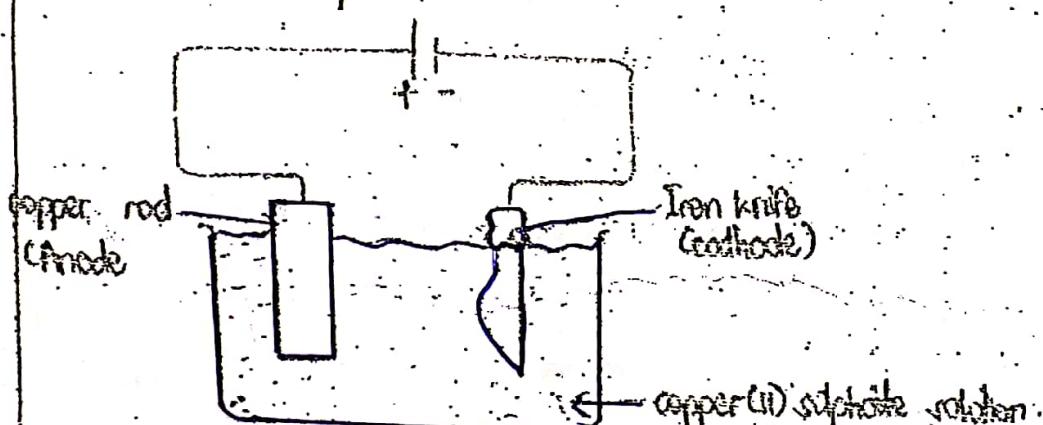
Eqn for reaction at the cathode:



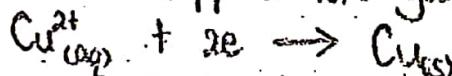
4. Electroplating metals (copper plating, galvanisation, etc.)

This is the coating of objects/metal with a layer of another metal by electrolysis. The object to be electroplated is used as the cathode if made a cathode will the metal to be used is made the anode eg. when copper plating an iron knife, an iron knife is used as the cathode while the anode is made of copper and copper(II) sulphate solution is used as the electrolyte.

Experimental setup:



Anode dissolves to form copper(II) ions which migrate to the cathode. At the cathode, the copper(II) ions gain electrons & are discharged.



Copper is deposited on the knife as a reddish brown coating.

5. Manufacture of chlorine (Roux's preparation of chlorine).

6. Manufacture of sodium hydroxide (See the extraction of sodium ahead).

Advantages of electropolating metals

1. To improve on their appearance
2. To protect them from corrosion/rusting
3. To improve on their tensile strength.

Questions

1. Copper(II) sulphate solution was electrolysed using carbon electrodes.

a. State what was observed at O_1 :

i. Anode

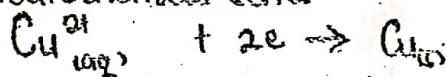
Bubbles of a colourless gas.

ii. Cathode

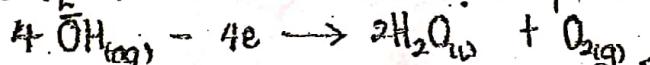
A reddish brown solid is deposited.

b. Explain your answer in a(ii).

The copper(II) ions and hydrogen ions migrate to the cathode but the copper(II) ions are discharged in preference because they are lower in the electrochemical series.



c. Write eqn for a reaction which took place at O_1 anode



Ans:

2000 Paper 2 (2)

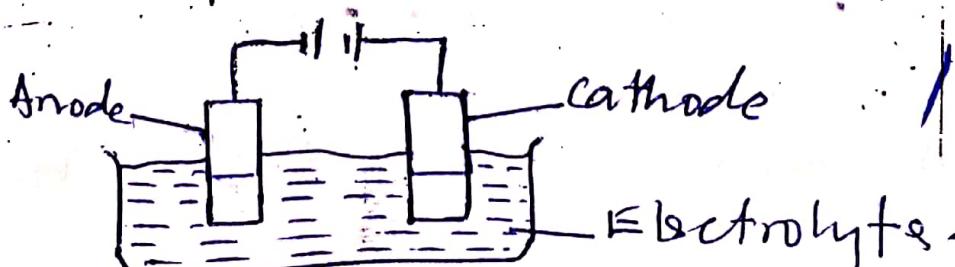
2002 Paper 2 (4)

1998 Paper 2 (5)

1997 Paper 2 (14)

2000 Paper 2 No. 2

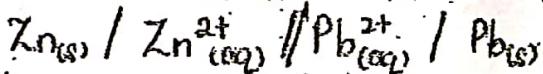
The diagram in figure 1 shows an arrangement of the apparatus used for the purification of copper.



- a) Name the substance used at:
- anode
Tin(II) copper rod
 - cathode
Pure copper rod
- b) Name the electrolyte
Copper(II) sulphate solution
- c) Write equation for the reaction that took place at:
- anode
Solution:
 $\text{Cu(s)} - 2e \rightarrow \text{Cu}^{2+}$
 - cathode
 $\text{Cu}^{2+} + 2e \rightarrow \text{Cu(s)}$

2001 Paper 2 No. 4

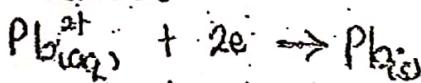
The cell convention for an electrochemical cell is shown below.



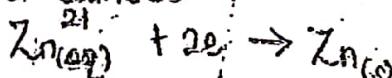
- (a) Name two substances that could be used as electrolytes.
Lead(II) nitrate solution

- (b) State which one of the electrodes is the anode.
 $\text{Pb}^{2+}_{(\text{aq})}$

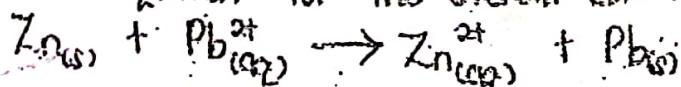
- (c) Write equation for the reaction at
- the anode



- ii) the cathode

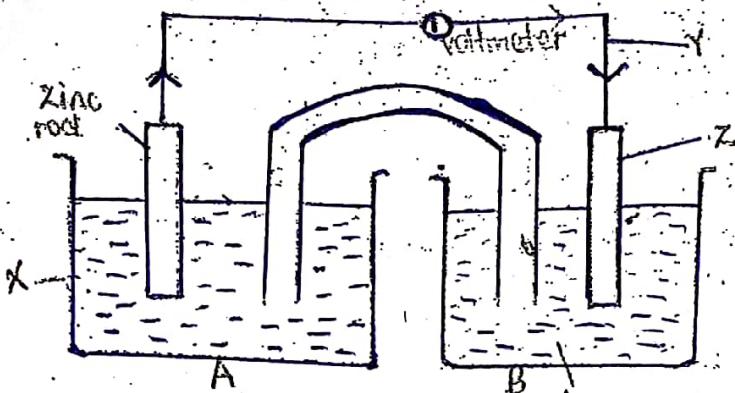


- d) Write equation for the overall cell reaction.

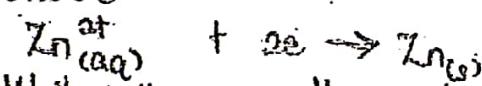
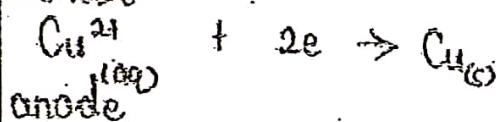


1998 Paper 2 No. 5

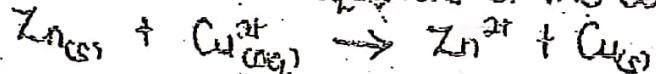
Figure 2 below shows a simple voltaic cell.



- a(i) Write equations for the reaction taking place at the cathode.



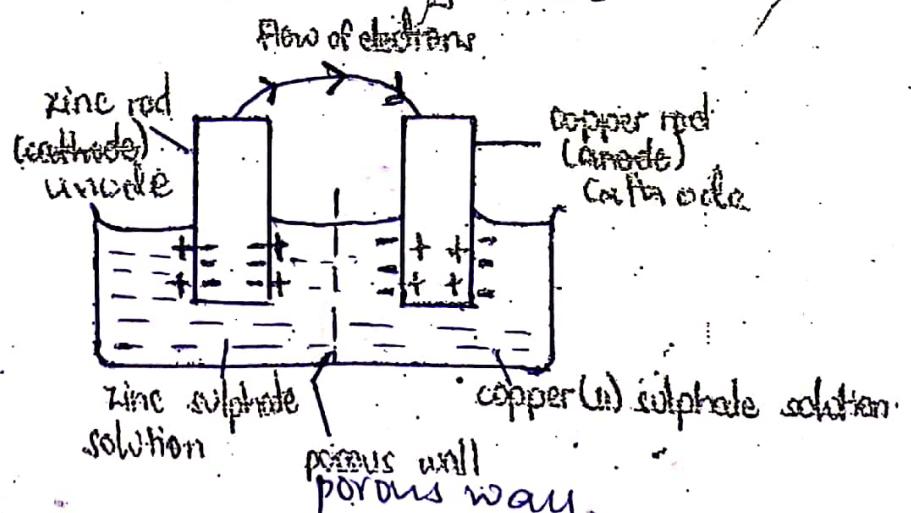
- b. Write the overall equations of the cell reaction.



- b. Draw an arrow on the diagram to show the direction of flow of electrons.

1997 Paper 2 No. 14:

- a. Draw a diagram of a Daniell cell consisting of a zinc rod dipped in zinc sulphate and a copper rod dipped in copper sulphate solution; the solutions separated by a porous wall; and the rods connected by a wire.

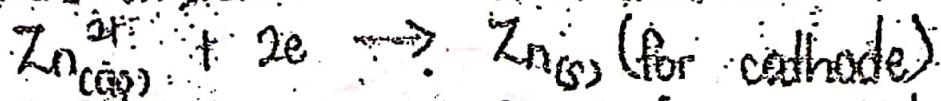


- b. Indicate

- the charges on each electrode
- the direction of electron movement in the wire.

Q. Write:

i) equations for reactions at each electrode



ii). an equation for the overall reaction.

