Electrolysis (A2)

Electrolysis is a process in which current is passed through an electrolyte of ionic compound either in solution or molten state. The electrolyte is then decomposed as solids or evolved as gases.

The conductors which connect the electrolyte with the applied voltage are called electrodes. The positive electrode is the anode, the negative electrode is the cathode.

During electrolysis,

At the cathode (− electrode):

- cations(+ve ions) travel to the cathode(−).
- reduction occurs at the cathode.
- cathode is connected to the −ve pole of the electricity supply.

At the anode (+ electrode):

- anions (−ve ions) travel to the anode (+).
- oxidation occurs at the anode.
- anode is connected to the +ve pole of the electricity supply.

Factors affecting selective discharge during electrolysis

1. Position of ions in the electrochemical series
2. Relative concentration of ions.
3. Nature of electrode.

Position of ions in the electrochemical series

a) At the cathode:

- In a mixture of cations, the cations of metal with the most positive $E^\ominus$ are discharged first.
- E.g., consider a mixture of $Zn^{2+}_{(aq)}$, $Cu^{2+}_{(aq)}$, $Pb^{2+}_{(aq)}$ and $Ag^{+}_{(aq)}$ ions.
- The order of metal/metal ions in the electrochemical series:

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $E^\ominus = -0.76V$ most negative

$Pb^{2+} + 2e^- \rightleftharpoons Pb$ $E^\ominus = -0.13V$ ↓

$Cu^{2+} + 2e^- \rightleftharpoons Cu$ $E^\ominus = +0.34V$

$Ag^{+} + e^- \rightleftharpoons Ag$ $E^\ominus = +0.80V$ most positive

- When the mixture is electrolyzed, the Ag^+ are discharged first (most positive $E^\ominus$). After all the Ag^+ have been discharged, the Cu^{2+} will be discharged, followed by the Pb^{2+} ions. Finally the Zn^{2+} ions will be discharged.

b) At the anode

- In a mixture of anions, the anion with the most negative $E^{\ominus}$ is discharged first. This anion is most easily oxidised.
- E.g., in a mixture of $Cl^-_{(aq)}$ and $I^-_{(aq)}$ ions the order of the ions in the redox series:

$$I_2 + 2e^- \rightleftharpoons 2I^- \quad E^{\ominus} = +0.54V$$ more negative

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E^{\ominus} = +1.36V$$ more positve

- When the mixture is electrolysed, the I^- ions are discharged first (more negative $E^{\ominus}$). After all the iodide ions have been discharged, the Cl^- ions will be discharged.

Relative concentration of ions

During electrolysis of dilute aqueous NaCl, concentration of Cl^- is low. Therefore OH^- ions get discharged at the anode and the O_2 gas produced.

$$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad E^{\ominus} = +1.36V$$ most positive

✓ $$O_2 + 2H_2O + 4e^- \rightleftharpoons 4OH^- \quad E^{\ominus} = +0.40V$$ most negative.

But during electrolysis of concentrated solution NaCl (brine), concentration of Cl^- ion is very high. Therefore Cl^- ions selectively get discharged at the anode and Cl_2 gas produced. Refer to Le Chatelier's principle, p.o.e. to direction of reducing $[Cl^-]$, Cl^- discharged to form Cl_2.

Nature of electrode

When dilute sulfuric acid is electrolyzed, using graphite electrodes, OH^- ions are discharged at the anode. The product at the anode is O_2 gas.

$$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-.$$

If the graphite electrodes are now replace with copper electrodes, the copper anode dissolves:

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

The solution gradually changes to blue colour due to the formation of $CuSO_4$.

Quantitative Electrolysis

During electrolysis of salts of metals low in the electrochemical series eg. silver, copper, gold, the cathode reactions are:

$$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$$

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

$$Au^{3+}_{(aq)} + 3e^{-} \longrightarrow Au_{(s)}$$

i.e.

1 mole of electrons discharge 1 mole Ag ions to give 1 mole Ag atoms
2 mole of electrons discharge 1 mole Cu ions to give 1 mole Cu atoms
3 mole of electrons discharge 1 mole Au ions to give 1 mole Au atoms

In General

$$\boxed{\begin{array}{c}\text{No. of moles of} \\ \text{element discharged}\end{array} = \frac{\text{No. of moles of electrons}}{\text{No. of charges on one ion of element}}}$$

The Faraday and Avogadro's constant

It is possible to measure the charge on an electron. Suppose we had 1 mole Ag ions and a current was passed which discharged all these ions to silver metal. Then the number of electrons that passes is L (Avogadro's constant). Let 'e' be the charge on one electron and F as the total charge required to discharge 1 mole of these ions.

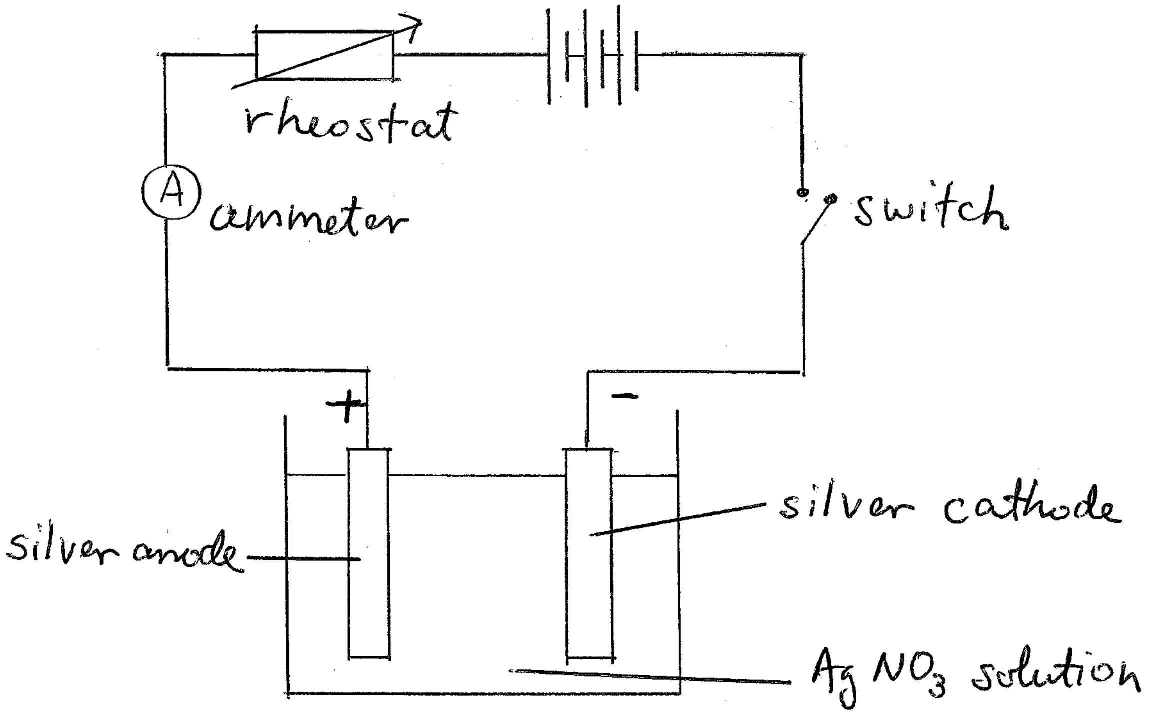
$$\boxed{F = Le}$$

Faraday constant, $F = 96500 \ \overset{\text{coulomb}}{\downarrow}\!\!\!\!\mathrm{C}\ \mathrm{mol}^{-1}$

Avogadro constant, $L = 6.02 \times 10^{23}\ \mathrm{mol}^{-1}$

charge on one electron, $e = 1.60 \times 10^{-19}$ coulombs

Finding Avogrado's constant by electrolysis



Set up the circult above. Ammeter records current used, rheostat used to maintain current at constant value. Cathode is weighed (record the mass). Close the switch and start stopwatch. Allow current to pass for a reasonable length of time. Open switch, stop the watch, record current used and time (in seconds). Remove cathode, rinse and dry then reweigh. The mass of silver deposited by a known charge (amps x seconds) is now known. If we know the charge one one electron, we can calculate the value for L.

From the readings of Ammeter and time recorded,

$Q = I \times t$

Q : quantity of charge produced, unit : coulomb, C

I : current (Ammeter reading), unit : ampere, A

t : time (stopwatch recordings), unit : second, s

It is found by experiment that 96500 coulombs of charge are required to discharge 1 mole of silver (108g); therefore 96500 coulombs must be the charge on one mole of electrons. The ratio 96500 C mol^{-1} is called the Faraday Constant.

Example.

A direct current of 10.0 mA flows for 4.00 hours through 3 cells in series. The cells contain solution of silver nitrate, copper(II) sulfate and gold(III) nitrate. Calculate the mass of deposited metal in each cell.

The quantity of charge, $Q = I \times t = 0.0100 \times 4.00 \times 60 \times 60$

$= 144 \text{ C}$

no mole of electron $= \frac{144}{96500}$ mole

No mole Ag deposited $= \frac{144}{96500}$ mole

mass Ag deposited $= \frac{144}{96500} \times 108 = 0.161g$

No mole Cu deposited $= \frac{144}{2 \times 96500}$ mole

mass Cu deposited $= \frac{144}{2 \times 96500} \times 63.5 = 0.0474g$

No mole Au deposited $= \frac{144}{3 \times 96500}$ mole

mass Au deposited $= \frac{144}{3 \times 96500} \times 197 = 0.0980g$

Exercise

A metal of Ar = 27 is deposited by electrolysis. If 0.176 g of the metal is deposited on the cathode when 0.15A flows for 3.5 hours, what is the charge on the cations of this metal?

Answers

The quantity of charge, $Q = I \times t = 0.15 \times 3.5 \times 60 \times 60$
$= 1{,}890\ C$

no mole of electron $= \frac{1890}{96500}$ mole

no mole of metal deposited $= \frac{0.176}{27}$ mole

Charge on the cation $= \frac{\text{no mole of electrons}}{\text{no mole of metal deposited}}$

$$= \frac{1890}{96500} \div \frac{0.176}{27}$$

$$= \frac{1890 \times 27}{96500 \times 0.176}$$

$$= 3$$

Example.

When a current of 7.66 amps is passed for 1 hour, it is found that 30.83 g silver are deposited.
Calculate Avogadro constant.

Answers.

The quantity of charge, $Q = I \times t = 7.66 \times 1 \times 60 \times 60$
$= 27{,}576 \text{ C}$

no mole of Ag deposited $= \frac{30.83}{108}$ mole

$$Ag^+ + e^- \longrightarrow Ag$$

1 mol electrons required to produce 1 mol Ag metal

charge of 1 mol of electrons, $F = \frac{Q}{n(Ag)}$

$$= \frac{27{,}576}{\left(\frac{30.83}{108}\right)} \text{ C}$$

charge of one electron, $e = 1.60 \times 10^{-19}$ C

$$F = L \times e$$

Avogrado's constant, $L = \frac{F}{e} = \frac{27576}{\left(\frac{30.83}{108}\right)} \div 1.60 \times 10^{-19}$

$$= \frac{27576 \times 108}{30.83 \times 1.60 \times 10^{-19}}$$

$$= \underline{6.04 \times 10^{23} \text{ mol}^{-1}}$$

Volume of gases formed during electrolysis

Solutions of salts high in electrochemical series evolve hydrogen gas at the cathode on electrolysis.

The cathode process is:

$H^+_{(aq)} + e^- \longrightarrow H_{(g)}$

followed by

$2H_{(g)} \longrightarrow H_{2(g)}$

2 moles of electrons are needed to evolve 1 mole of hydrogen molecules; i.e. 2g. of hydrogen (the molar mass) or 22.4 dm^3 at s.t.p. (the molar volume).

At the anode, concentrated solutions of halides evolve the halogen, and other salts evolve oxygen.

When chlorine is evolved, the anode process is:

$Cl^-_{(aq)} \longrightarrow Cl_{(g)} + e^-$

followed by.

$2Cl_{(g)} \longrightarrow Cl_{2(g)}$

2 moles of electrons are required for the evolution of 1 mole of chlorine molecules; i.e. 71.0g or 22.4dm^3 at s.t.p.

When oxygen is evolved, the anode process is the discharge of hydroxide ions, derived from the water in the solution:

$OH^-_{(aq)} \longrightarrow OH_{(aq)} + e^-$

followed by

$4OH_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)}$

4 moles of electrons are required for the evolution of 1 mole of oxygen molecules; i.e. 32.0g or 22.4 dm^3 at s.t.p.

Exercise.

Calculate the volumes of gases formed at the cathode and anode at s.t.p. when 0.0250A of current are passed for 4.00 hours through a solution of sulfuric acid.

Answers

The quantity of charge, $Q = I \times t = 0.0250 \times 4 \times 60 \times 60$
$= 360\ C$

no of mole of electron $= \frac{360}{96500} = 3.73 \times 10^{-3}$ mole

At cathode,

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

$n(H_2) = \frac{3.73 \times 10^{-3}}{2}$ mole

$V(H_2) = \frac{3.73 \times 10^{-3}}{2} \times 22.4$

$= \underline{4.18 \times 10^{-2}\ dm^3}$

At anode,

$4OH^-_{(aq)} \longrightarrow O_{2(g)} + 2H_2O_{(l)} + 4e^-$

$n(O_2) = \frac{3.73 \times 10^{-3}}{4}$ mole

$V(O_2) = \frac{3.73 \times 10^{-3}}{4} \times 22.4$

$= \underline{2.09 \times 10^{-2}\ dm^3}$