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Chemistry
Teach Yourself Series
Topic 5: Electrolysis

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Contents

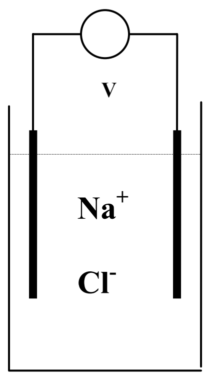
Electrolysis

What is electrolysis?

As it appears in Unit 4

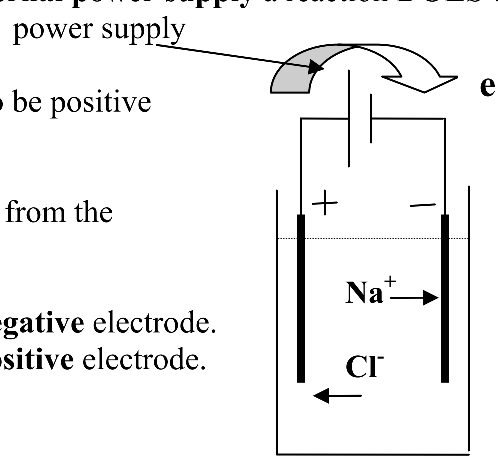
Example 1
Molten NaCl solution

NaCl(l)



Electrodes are placed in a NaCl solution. The electrodes are connected by a wire and a voltmeter. Time passes but **NO** reaction occurs. This is no surprise as sodium ions and chloride ions are relatively stable.
Point of this: Not all solutions and electrodes make galvanic cells.

However, if the voltmeter is replaced by an **external power supply** a reaction **DOES** occur.



The power supply causes one electrode to be positive and the other to be negative.

Due to the power supply, electrons travel from the positive to the negative electrode.

The sodium ions, **Na^+** are attracted to the **negative** electrode.
The chloride ions, **Cl^-** are attracted to the **positive** electrode.

Half equations

positive electrode $2Cl^- \rightarrow Cl_2 + 2e$
negative $Na^+ + e \rightarrow Na$

Overall equation: $2Na^+ + 2Cl^- \rightarrow 2Na + Cl_2$

Products sodium metal and chlorine gas

The power supply causes a reaction to occur that was not going to happen.
Why bother? Because the products, sodium and chlorine in this case, are very difficult to make any other way.

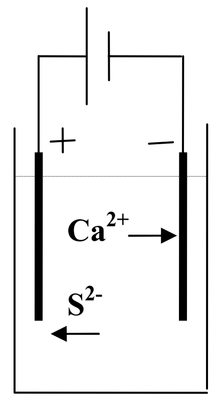
Electrolysis: Redox reactions that require an **external power supply**.

Purposes:
1. To obtain products that might be difficult to produce.
2. To electroplate metals onto surfaces.

Example 2

Electrolysis of CaS(l) molten solution

(Note: Example 1 and 2 refer to molten solutions.
A molten solution is formed when an ionic substance is heated until it melts. It contains no water)



Ca^{2+} ions move to the negative electrode and S^{2-} ions to the positive.

Half equations

$Ca^{2+}(l) + 2e \rightarrow Ca(l)$ reduction => cathode
$S^{2-}(l) \rightarrow S(l) + 2e$ oxidation => anode

$Ca^{2+}(l) + S^{2-}(l) \rightarrow Ca(l) + S(l)$ **Products**: calcium and sulfur

Galvanic cells compared to electrolytic cells	
Galvanic	**Electrolytic**
• spontaneous reaction • usually 2 separate half cells • portable source of energy • oxidation at anode; anode negative • reduction at cathode, cathode positive • electrons flow to positive electrode • salt bridge or membrane used • strongest oxidant reacts with strongest reductant	• non spontaneous reaction • external power supply • used to produce reactive elements • oxidation at anode, anode positive • reduction at cathode, cathode negative • electrons flow to negative electrode • only one compartment needed • strongest oxidant reacts with strongest reductant

Review Questions

1. A molten solution of magnesium bromide, $MgBr_2$ is electrolysed.
Draw this cell showing the
a. direction of electron flow
b. direction of ion movement
c. relevant half equations
d. overall equation

____

____

2. The cells covered so far have been molten solutions. Explain what a molten solution of copper (II) iodide is.

____

____

3. **Fact 1**: Sodium can react with chlorine to produce electrical energy in a galvanic cell.
Fact 2. Sodium ions will not react readily with chloride ions to produce electricity.

a. Use your knowledge of these two elements to explain the reactivities evident in Fact 1 and Fact 2.

____

b. Explain why both reactions are considered redox reactions.

____

c. Explain which reaction will suit a galvanic cell and which an electrolytic cell.

____

4. Fill in the blanks.
In electrolysis, an external ________ ________ is used. Electrons are pushed to the ________ electrode. When a reaction occurs, oxidation will be at the _______, which is the ________ electrode. If several reactions are possible, the _________ oxidant will react with the ___________ reductant.

Using the Electrochemical series

As it appears in Unit 4

The cells in examples 1 and 2 could have been analysed using the electrochemical series.

Example 1 NaCl(l)

Species present: Na^+, Cl^-
Relevant **half equations**
with species present **underlined**

$Cl_2(g) + 2e \rightarrow \underline{2Cl^-}(l)$

$\underline{Na^+}(l) + e \rightarrow Na(l)$

Example 2 CaS(l)

Species present Ca^{2+}, S^{2-}
Relevant **half equations**
with species present **underlined**

$S(l) + 2e \rightarrow \underline{S^{2-}}(l)$

$\underline{Ca^{2+}}(l) + 2e \rightarrow Ca(l)$

An electrolytic cell is possible if there is an **oxidant and a reductant**, and the **oxidant is placed lower down the table than the reductant**. Both of these cells meet this criteria.

Reactions occurring

$2Cl^-(l) \rightarrow Cl_2(g) + 2e$	oxidation => anode	$S^{2-}(l) \rightarrow S(l) + 2e$
$Na^+(l) + e \rightarrow Na(l)$	reduction =>cathode	$Ca^{2+}(l) + 2e \rightarrow Ca(l)$

Overall

$2Na^+(l) + 2Cl^-(l) \rightarrow 2Na(l) + Cl_2(g)$ $\qquad$ $Ca^{2+}(l) + S^{2-}(l) \rightarrow Ca(l) + S(l)$

Products: sodium and chlorine $\qquad$ calcium and sulfur

In general, for an electrolytic cell, there must be

$Cl_2 + 2e \rightarrow \underline{2Cl^-}$ ***a reductant***

*an **oxidant*** $\underline{Na^+} + e \rightarrow Na$

reductant must be higher on Table

Note: $Cl_2(g)$ and Na(l) will react spontaneously, hence they represent a galvanic cell, not an electrolytic cell. $Na^+(l)$ and $Cl^-(l)$ react in an electrolytic cell.

Review Questions

5. Use the electrochemical series, and the examples above, to fill in a template for the electrolysis of KBr(l).

Species present: ____

Relevant half equations with species present underlined

Reverse top half equation

Overall equation

6. Given the two half equations below from the electrochemical series

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

a. Identify two species that will react together spontaneously to form a galvanic cell.

____

b. Identify two species that an external power supply can cause to react in an electrolytic cell.

____

Aqueous solutions

As it appears in Unit 4

When a saltwater solution is electrolysed the products are very different from sodium and chlorine. Why? **Because water reacts instead**.

Example 1: Electrolysis of **NaCl(aq),** a salt water aqueous solution.
Species present: Na^+, Cl^- and H_2O

Relevant half equations

$Cl_2 + 2e \rightarrow 2Cl^-$
$O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l)$
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$
$Na^+ + e \rightarrow Na$

the strongest oxidant reacts with the strongest reductant

Reverse top half equation

$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$ oxidation: anode : +ve
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ reduction: cathode:-ve

Overall equation

$6H_2O(l) \rightarrow 2H_2(g) + O_2(g) + 4H^+(aq) + 4OH^-(aq)$
or more simply
$2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$

Products: hydrogen and oxygen gas (not sodium and chlorine)

Therefore, when **solutions are aqueous** the process is still the same:

- Find the relevant half equations
- The same two half equations for water should be used each time, the half equation at 1.23 V and the half equation at – 0.83 V.
- Identify the strongest oxidant and the strongest reductant.
- Reverse the reductant half equation

Example 2: Electrolysis of $NiBr_2(aq)$

Species present: Ni^{2+}, Br^- and H_2O

Relevant half equations

$O_2(g) + 4H^+(aq) + 4e \rightarrow 2\underline{H_2O(l)}$
$Br_2(l) + 2e \rightarrow \underline{2Br^-}(aq)$
$\underline{Ni^{2+}}(aq) + 2e \rightarrow Ni(s)$ *the strongest oxidant reacts with the strongest reductant*
$\underline{2H_2O}(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

Reverse top equation

$\underline{2Br^-}(aq) \rightarrow Br_2(l) + 2e$ oxidation: anode : +ve
$\underline{Ni^{2+}}(aq) + 2e \rightarrow Ni(s)$

Overall

$2Br^-(aq) + Ni^{2+}(aq) \rightarrow Ni(s) + Br_2(l)$

Products: nickel and bromine (water does not react this time)

Review Question

7. Use the format above to predict the products formed in the electrolysis of $ZnI_2(aq)$

Metals or not metals

As it appears in Unit 4

Electrolysis of $NiBr_2(aq)$ → nickel and bromine
Electrolysis of $NaCl(aq)$ → hydrogen and oxygen

} very different results. Why?

The water half equation at - 0.83 volts represents the dividing line between easy to produce metals and difficult to produce metals.

$O_2(g) + 4H^+(aq) + 4e \rightarrow 2\underline{H_2O(l)}$
$\underline{Ag^+}(aq) + e \rightarrow Ag(s)$
$\underline{Cu^{2+}}(aq) + 2e \rightarrow Cu(s)$
$\underline{Ni^{2+}}(aq) + 2e \rightarrow Ni(s)$ ◄ nickel ions will react with water
$\underline{2H_2O}(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$ -0.83 V
$\underline{Mg^{2+}}(aq) + 2e \rightarrow Mg(s)$ ◄ magnesium ions will not react with water, water will react with itself instead
$\underline{Li^+}(aq) + e \rightarrow Li(s)$

All metals placed below the water half equation must be produced through electrolysis of molten solutions

Reactive electrodes

If the electrodes are made from metals, there are further possible reactions but the process of lining up the half equations and picking the strongest oxidant and the strongest reductant is still the same.

Example
Electrolysis of $NiCl_2(aq)$ using a copper anode.
Species present: Ni^{2+}, Cl^-, H_2O and Cu(s)

Relevant half equations
$Cl_2 + 2e \rightarrow \underline{2Cl^-}$
$O_2(g) + 4H^+(aq) + 4e \rightarrow 2\underline{H_2O(l)}$
$Cu^{2+}(aq) + 2e \rightarrow \underline{Cu(s)}$
$\underline{Ni^{2+}}(aq) + 2e \rightarrow Ni(s)$
$\underline{2H_2O}(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$
$\underline{Na^+} + e \rightarrow Na$

This time the Ni^{2+} ions react with Cu metal
(the strongest oxidant with strongest reductant)

Reactions occurring
$Cu(s) \rightarrow Cu^{2+}(aq) + 2e$ oxidation: anode : +ve
$Ni^{2+}(aq) + 2e \rightarrow Ni(s)$ reduction :cathode:-ve

Overall equation

$Cu(s) + Ni^{2+}(aq) \rightarrow Cu^{2+}(aq) + Ni(s)$ **Products**: nickel metal and copper ions

Concentrated solutions involving chloride ions

The use of concentrated solutions can lead to unexpected products.
Example: Electrolysis of NaCl(c) where (c) stands for a **concentrated** solution

$Cl_2(g) + 2e \rightarrow \underline{2Cl^-}(aq)$	1.36 V	With dilute solutions, it is expected
$O_2(g) + 4H^+(aq) + 4e \rightarrow 2\underline{H_2O(l)}$	1.23 V	that water will react with itself.
$\underline{2H_2O}(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$	- 0.83 V	In this case however, the Cl^- ions react
$\underline{Na^+}(aq) + e \rightarrow Na(s)$	- 2.71 V	instead of the water.

Reasons for the change in reaction are

- the solution is **not 1 M**. E^0 values are derived for 1 M solutions
- Cl^- ions have a bigger negative charge than the dipoles on water, hence they can surround the positive electrode.

The same issue does not arise at the negative electrode because the voltage for sodium is very different from that of water.

Reactions occurring

$2Cl^-(aq) \rightarrow Cl_2(g) + 2e$

$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

Overall equation

$2H_2O(l) + 2Cl^-(aq) \rightarrow H_2(g) + Cl_2(g) + 2OH^-(aq)$

Products: hydrogen gas, chlorine gas and sodium hydroxide (caustic soda)
Note the products are very useful ones, all obtained from room temperature electrolysis of very inexpensive sea water.

Review Questions

8. Electrolysis is conducted on two different cells, a 0.1 M solution of NaCl and a 5.0 M solution of NaCl

Complete the table provided to show the products formed in each cell.

	anode reaction	cathode reaction
0.1 M NaCl		
5.0 M NaCl		

9. **a.** Name three metals that can be formed from electrolysis of aqueous solutions

____

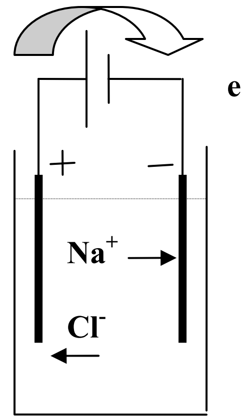
b. Name three metals that cannot be formed from electrolysis of aqueous solutions

____

Faraday's Laws

As it appears in Unit 4

The manufacturers of metals such as aluminium want to predict how much aluminium they are likely to produce in any given period. This can easily be done if the number of electrons flowing in the circuit, the electric current, is known.



Consider the NaCl cell shown. The half equation is

$Na^+ \quad + \quad e \quad \rightarrow \quad Na$

1 atom of sodium requires 1 electron
7 atoms of sodium requires 7 electrons
1200 atoms of sodium requires 1200 electrons
1 mole of sodium requires 1 mole of electrons

The charge on an electron is 1.60×10^{-19} Coulomb and the number in a mole is 6.02×10^{23}

Therefore the charge on **1 mole of electrons** = $1.6 \times 10^{-19} \times 6.023 \times 10^{23}$ = **96500 C**

1 faraday of charge = 96500 C mol^{-1}

Amount of charge is determined using **$Q = It$**

charge in coulomb — current in amp — time in sec

Example 1

Calculate the mass of sodium formed when a current of 5.00 amps runs for 3.00 hours

Procedure

It = Q → **n**(e) = $\frac{\mathbf{Q}}{\mathbf{96500}}$ → n(metal) from balanced equation → mass(metal) = **n x M**

$Q = I \times t = 5 \times 3 \times 60 \times 60 = 54000\ C$

$$n(\text{e}) = \frac{54000}{96500} = 0.560 mol$$

$n(\text{Na}) = n(\text{e}) = 0.560\ mol$

$m(\text{Na}) = 0.560 \times 23 = 12.9\ g$

Example 2

Calculate the current required to produce 1.00 kg of magnesium from an electrolytic cell in 100 minutes

Procedure is the reverse of above

n(metal) = $\frac{\mathbf{m}}{\mathbf{M}}$ → **n**(e) from balanced equation → **Q = n x 96500** → **I** = $\frac{\mathbf{Q}}{\mathbf{t}}$

$$n(\text{Mg}) = \frac{m}{M} = \frac{1000}{24.3} = 41.2\ mol$$

$n(\text{e}) = 2\text{x}\ n(\text{Mg})$ (as Mg^{2+}) $= 2 \times 41.2 = 82.4\ mol$

$Q = n(\text{e}) \times 96500 = 82.4 \times 96500 = 7.94 \times 10^6$

$$I = \frac{Q}{t} = \frac{7.94 \times 10^6}{6000} = 1330\ amps$$

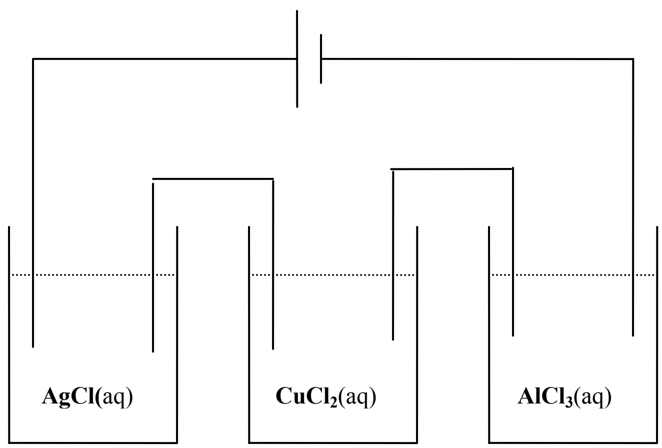
Review Questions

10. Calculate the mass of aluminium produced when a current of 4.20 amps runs through an $AlCl_3$ cell for 24.0 hours

11. Calculate the time required to produce 22.0 kg of calcium from a cell where the current is 12.0 amps

Complex question

10 mole of electrons is passed through the circuit below. The cells are all connected in series. Calculate the mass of each metal produced in each cell.



As the cells are connected in series, the same number of mole of electrons passes through each cell. The metals have different oxidation states, so the number of mole of metal obtained will differ.

$Ag^+(aq) + e \rightarrow Ag(s)$ $Cu^{2+}(aq) + 2e \rightarrow Cu(s)$ $2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

(note: water reacts instead of aluminium)

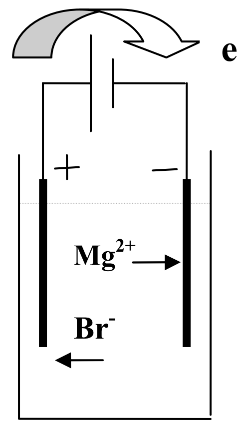
10 mol electrons therefore gives

10 mol of silver **5 mole** of copper and **no** aluminium

Points to note:

- The same number of mole of electrons passes through each electrode
- Reactive metals are not produced in aqueous solutions
- Metal ions are often chosen to reflect oxidation states of +1, +2 and +3

Solutions to questions



1. A molten solution of magnesium bromide, $MgBr_2$ is electrolysed.

   positive electrode $2Br^-(l) \rightarrow Br_2(l) + 2e$
   negative $Mg^{2+}(l) + 2e \rightarrow Mg(l)$

   overall
   $2Br^-(l) + Mg^{2+}(l) \rightarrow Br_2(l) + Mg(l)$

2. Copper (II) iodide crystals are heated in a crucible until they melt to form a thick liquid.

3. **Fact 1**: Sodium can react with chlorine to produce electrical energy in a galvanic cell.
   Fact 2. Sodium ions will not react readily with chloride ions to produce electricity.

   a. sodium atoms have one electron in the outer shell. They are reactive because they are trying to lose this electron. Chlorine atoms require one electron for their outer shell. It is an obvious arrangement for them to swap electrons with sodium. Once the ions are formed that have complete outer shells, it will be difficult to return to the elemental form.
   b. Both reactions involve the transfer of electrons

   c. Galvanic cell – reaction of sodium and chlorine
   Electrolytic cell – reaction of Na^+ and Cl^- ions

4. In electrolysis, an external power supply is used. Electrons are pushed to the negative electrode. When a reaction occurs, oxidation will be at the anode, which is the positive electrode. If several reactions are possible, the strongest oxidant will react with the weakest reductant.

5. **Species present**: K^+, Br^-

   Relevant half equations
   $Br_2(l) + 2e \rightarrow \underline{2Br^-(l)}$
   $\underline{K^+(l)} + e \rightarrow K(l)$

Reverse top half equation
$2Br^-(l) \rightarrow Br_2(l) + 2e$
$K^+(l) + e \rightarrow K(l)$

Overall equation
$2Br^-(l) + 2K^+(l) \rightarrow Br_2(l) + 2K(l)$

6. **a.** Ag^+, Cr(s)

b. Ag(s), $Cr^{3+}(aq)$

7. Use the format above to predict the products formed in the electrolysis of $ZnI_2(aq)$
Relevant half equations
$O_2(g) + 4H^+(aq) + 4e \rightarrow 2H_2O(l)$
$I_2(l) + 2e \rightarrow 2I^-(aq)$
$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$ *the strongest oxidant reacts with the strongest reductant*
$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

Reverse top equation
$2I^-(aq) \rightarrow I_2(l) + 2e$
$Zn^{2+}(aq) + 2e \rightarrow Zn(s)$

Overall
$2I^-(aq) + Zn^{2+}(aq) \rightarrow Zn(s) + I_2(l)$

Products: zinc and iodine (water does not react this time)

8.

	anode reaction	cathode reaction
0.2 M NaCl	$2H_2O(l) \rightarrow O_2(g) + 4H^+(aq) + 4e$	$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$
5.0 M NaCl	$2Cl^-(aq) \rightarrow Cl_2(g) + 2e$	$2H_2O(l) + 2e \rightarrow H_2(g) + 2OH^-(aq)$

9. **a.** silver, copper, lead, nickel etc

b. potassium, magnesium, sodium etc

10. $Q=It = 4.2x24x60x60 = 363000$ C

$$n(\text{e}) = \frac{363000}{96500} = 3.7mol \qquad n(\text{Al}) = 1/3\ n(\text{e}) = 1/3x3.7 = 1.25mol$$

$$mass(\text{Al}) = nxM = 1.25x26.9 = 33.7g$$

11.

$$n(\text{Ca}) = \frac{22000}{40} = 550mol$$

$$n(\text{e}) = n(\text{Ca})\ x\ 2 = 550x2 = 1100mol$$

$$Q = nx96500 = 1100x96500 = 1.06\ x\ 10^8\ C$$

$$\text{t}=\frac{Q}{i} = \frac{1.06 \text{ x } 10^8}{12} = 8.85x10^6\ sec$$