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Chemistry
Teach Yourself Series
Topic 5: Electrolysis (Unit 3)

A: Level 14, 474 Flinders Street Melbourne VIC 3000
T: 1300 134 518 **W:** tssm.com.au **E:** info@tssm.com.au

Contents

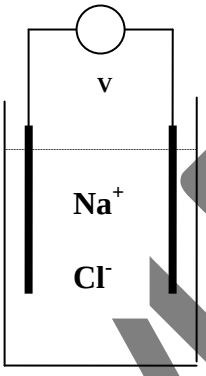
Electrolysis

What is electrolysis?

As it appears in Unit 3

Example 1
Molten NaCl solution

NaCl(l)



Electrodes are placed in a molten 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.

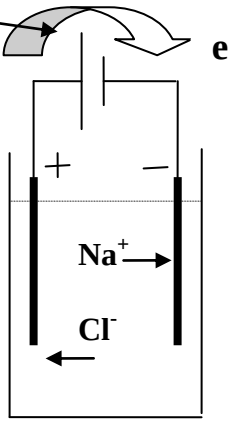
However, if the voltmeter is replaced by an **external power supply** a reaction **DOES** occur.

power supply

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.

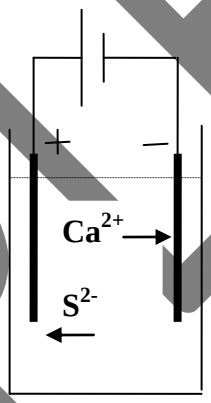
Electrolysis: Redox reactions that require an **external power supply**.

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.

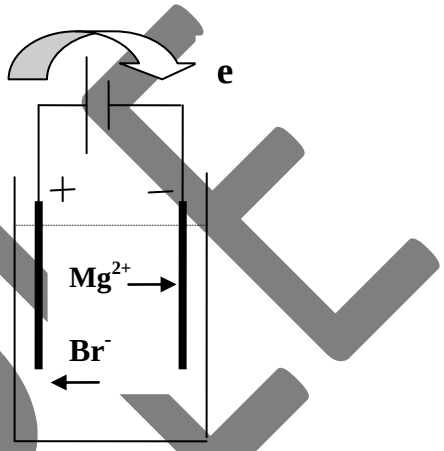
_____

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.

Solutions to review 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
$2Br^-(l) \rightarrow \underline{Br_2}(l) + 2e^-$
$K^+(l) + e^- \rightarrow K(l)$

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
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2\underline{H_2O(l)}$
$I_2(l) + 2e^- \rightarrow \underline{2I^-}(aq)$ ←
$\underline{Zn^{2+}}(aq) + 2e^- \rightarrow Zn(s)$ ← *the strongest oxidant reacts with the strongest reductant*
$\underline{2H_2O}(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

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.

Relevant half equations
$O_2(g) + 4H^+(aq) + 4e^- \rightarrow 2\underline{H_2O(l)}$ ←
$\underline{Cu^{2+}}(aq) + 2e^- \rightarrow Zn(s)$ ← *the strongest oxidant reacts with the strongest reductant*
$\underline{2H_2O}(l) + 2e^- \rightarrow H_2(g) + 2OH^-(aq)$

Reverse top equation
$2\underline{H_2O(l)} \rightarrow O_2(g) + 4H^+(aq) + 4e^-$
$Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

Overall
$2H_2O(l) + 2Cu^{2+}(aq) \rightarrow 2Cu(s) + O_2(g) + 4H^+(aq)$

Products: copper, oxygen gas and hydronium ions.