

Lesson 1 Electrolysis

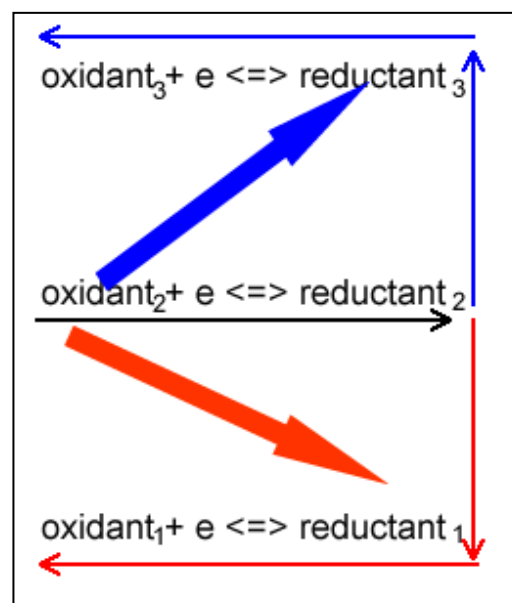
[Click here](#) for a detailed explanation of electrolysis

The table below summarises the differences between a galvanic cell and an electrolytic cell.

	Electrochemical (galvanic)	Electrolytic
Oxidation	Occurs at the anode	Occurs at the anode
Reduction	Occurs at the cathode	Occurs at the cathode
Polarity of the anode	Negative	Positive
Polarity of the cathode	Positive	Negative
Energy	Produced	Supplied
Electron flow	From -ve to +ve	From +ve to -ve
Salt bridge	Required	Not required
Direction of electron flow	Anode=>Cathode	Anode=>Cathode

- It is a non-spontaneous process where energy is supplied by an external source to drive the redox reaction.
- Reduction occurs at the cathode and oxidation occurs at the anode.
- Cathode has a negative polarity while the anode is positive.
- Electrodes can be inert or can take part in the oxidation or reduction reactions.
- Energy conversion is electrical into chemical.
- The strongest reductant will be oxidised at the (+) anode and the strongest oxidant will be reduced at the (-) cathode. Only when these have expired will the next strongest species, according to the electrochemical series react.
- An electrochemical series is required to predict reactions in an electrolytic cell and galvanic cells.
- When writing balanced half equations use the electrochemical series
 - write the half equation involving the oxidant as it appears on the electrochemical series.
 - reverse the half equation involving the reductant.
- In an electrolytic cell the reductant is located above the oxidant on the electrochemical series. In a galvanic cell the reductant is located below the oxidant on the electrochemical series.
- Note that in concentrated solutions a less stronger oxidant or reductant may react. For example, when concentrated NaCl solution (brine) is electrolysed it is the Cl⁻ ions that react at the anode rather than the H₂O, however, when dilute solutions of NaCl are used it is, the more stronger reductant, H₂O that reacts at the anode.

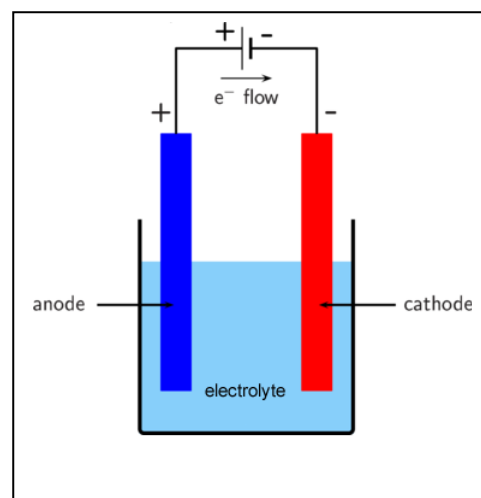
Au ⁺ (aq) + e ⁻ ⇌ Au(s)	+1.68
Cl ₂ (g) + 2e ⁻ ⇌ 2Cl ⁻ (aq)	+1.36
O ₂ (g) + 4H ⁺ (aq) + 4e ⁻ ⇌ 2H ₂ O(l)	+1.23
Br ₂ (l) + 2e ⁻ ⇌ 2Br ⁻ (aq)	+1.09
Ag ⁺ (aq) + e ⁻ ⇌ Ag(s)	+0.80
Fe ³⁺ (aq) + e ⁻ ⇌ Fe ²⁺ (aq)	+0.77
O ₂ (g) + 2H ⁺ (aq) + 2e ⁻ ⇌ H ₂ O ₂ (aq)	+0.68
I ₂ (s) + 2e ⁻ ⇌ 2I ⁻ (aq)	+0.54
O ₂ (g) + 2H ₂ O(l) + 4e ⁻ ⇌ 4OH ⁻ (aq)	+0.40
Cu ²⁺ (aq) + 2e ⁻ ⇌ Cu(s)	+0.34
Sn ⁴⁺ (aq) + 2e ⁻ ⇌ Sn ²⁺ (aq)	+0.15
S(s) + 2H ⁺ (aq) + 2e ⁻ ⇌ H ₂ S(g)	+0.14
2H ⁺ (aq) + 2e ⁻ ⇌ H ₂ (g)	0.00
2H ₂ O(l) + 2e ⁻ ⇌ H ₂ (g) + 2OH ⁻ (aq)	-0.83
Mn ²⁺ (aq) + 2e ⁻ ⇌ Mn(s)	-1.18
Al ³⁺ (aq) + 3e ⁻ ⇌ Al(s)	-1.66
Mg ²⁺ (aq) + 2e ⁻ ⇌ Mg(s)	-2.37
Na ⁺ (aq) + e ⁻ ⇌ Na(s)	-2.71



Example 1

A dilute sodium chloride solution undergoes electrolysis using inert electrodes as shown below.

- What is the possible reaction that occurs at the anode?
Since at the anode oxidation takes place we should look for the strongest reductant present. List all the reductants that are present in the solution. We have two, H₂O and Cl⁻ ions. Pick the strongest. In this case it is H₂O
 $2\text{H}_2\text{O} (l) \Rightarrow \text{O}_2(g) + 4\text{H}^+(aq) + 4e^-$
- What is the possible reaction that occurs at the cathode?
Now list all the oxidants present in the solution. We have H₂O and Na⁺ ions. Pick the strongest. In this case it is H₂O.
 $2e^- + 2\text{H}_2\text{O} (l) \Rightarrow \text{H}_2(g) + 2\text{OH}^-(aq)$



Example 2

Lithium metal is produced by the electrolysis of molten lithium chloride, LiCl.

- What are the products at the cathode and the anode?

At the cathode reduction takes place

List all the oxidants present

Li⁺ only hence

Li⁺(l) + e⁻ => Li(l)

Lithium metal and the cathode

At the anode oxidation takes place

List all the reductants present

Cl⁻ only hence

2Cl⁻(l) => Cl₂(g) + 2e⁻

Cl gas at the anode

- Why is a solution of lithium chloride not used?

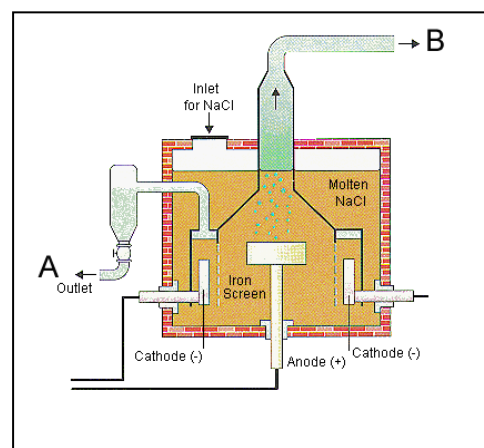
H₂O is a stronger oxidant than Li⁺ and a stronger reductant than Cl⁻, hence it would react to form an explosive mixture of oxygen and hydrogen gases.

$\text{Cl}_2(g) + 2e^- \rightleftharpoons 2\text{Cl}^-(aq)$	+1.36
$\text{O}_2(g) + 4\text{H}^+(aq) + 4e^- \rightleftharpoons 2\text{H}_2\text{O}(l)$	+1.23
$\text{Br}_2(l) + 2e^- \rightleftharpoons 2\text{Br}^-(aq)$	+1.09
$\text{Ag}^+(aq) + e^- \rightleftharpoons \text{Ag}(s)$	+0.80
$\text{Fe}^{3+}(aq) + e^- \rightleftharpoons \text{Fe}^{2+}(aq)$	+0.77
$\text{O}_2(g) + 2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{H}_2\text{O}_2(aq)$	+0.68
$\text{I}_2(s) + 2e^- \rightleftharpoons 2\text{I}^-(aq)$	+0.54
$\text{O}_2(g) + 2\text{H}_2\text{O}(l) + 4e^- \rightleftharpoons 4\text{OH}^-(aq)$	+0.40
$\text{Cu}^{2+}(aq) + 2e^- \rightleftharpoons \text{Cu}(s)$	+0.34
$\text{Sn}^{4+}(aq) + 2e^- \rightleftharpoons \text{Sn}^{2+}(aq)$	+0.15
$\text{S}(s) + 2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{H}_2\text{S}(g)$	+0.14
$2\text{H}^+(aq) + 2e^- \rightleftharpoons \text{H}_2(g)$	0.00
$2\text{H}_2\text{O}(l) + 2e^- \rightleftharpoons \text{H}_2(g) + 2\text{OH}^-(aq)$	-0.83
$\text{Mn}^{2+}(aq) + 2e^- \rightleftharpoons \text{Mn}(s)$	-1.18
$\text{Al}^{3+}(aq) + 3e^- \rightleftharpoons \text{Al}(s)$	-1.66
$\text{Mg}^{2+}(aq) + 2e^- \rightleftharpoons \text{Mg}(s)$	-2.37
$\text{Na}^+(aq) + e^- \rightleftharpoons \text{Na}(s)$	-2.71
$\text{Ca}^{2+}(aq) + 2e^- \rightleftharpoons \text{Ca}(s)$	-2.87
$\text{K}^+(aq) + e^- \rightleftharpoons \text{K}(s)$	-2.93
$\text{Li}^+(aq) + e^- \rightleftharpoons \text{Li}(s)$	-3.04

Example 3

An electrolytic cell known as the Downs Cell, pictured on the right, operates at high currents with molten NaCl.

- Write the equation for the reaction that occurs at the cathode.
Reduction occurs at the cathode and hence the strongest oxidant will react.
 $\text{Na}^+(l) + e^- \Rightarrow \text{Na}(l)$
- Identify substance "A". Na(l)



iii. Write the equation for the reaction that occurs at the anode. Oxidation occurs at the anode and hence the strongest reductant will react $2Cl^-(l) \Rightarrow Cl_2(g) + 2e$

iv. Identify substance "B". $Cl_2(g)$

v. Consider the electrolytic cell on the right, it has aqueous NaCl as the electrolyte.

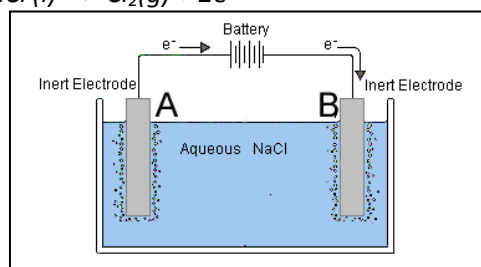
a) Label the anode and the cathode

Electrode "A" is the anode and electrode "B" is the cathode.

b) Give the balanced ionic equations for the reactions that occur at each electrode.

Electrode "A" – oxidation takes place hence the strongest reductant present (Cl^-) will react. $2Cl^-(aq) \Rightarrow Cl_2(g) + 2e$

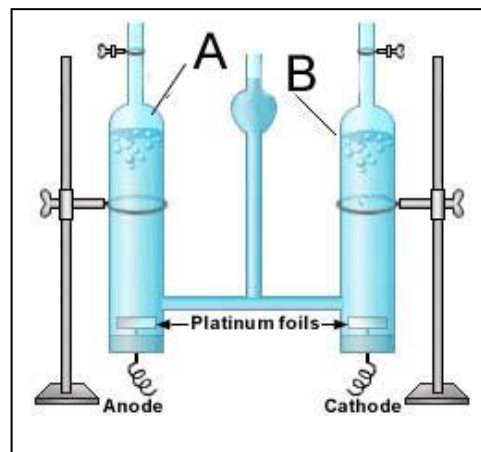
Electrode "B" - reduction takes place and hence the strongest oxidant present (H_2O) will react. $2H_2O(l) + 2e \Rightarrow H_2(g) + 2OH^-(aq)$



1) Electrolysis of water takes place with the apparatus shown on the right.

i. To what terminal of an external power source will the anode be connected to?

ii. Write the balanced ionic equations for the reactions taking place at electrodes "A" and "B".



iii. Aqueous $SnCl_4$ is added to the water. Explain, using the table below, how the products formed at each electrode change?

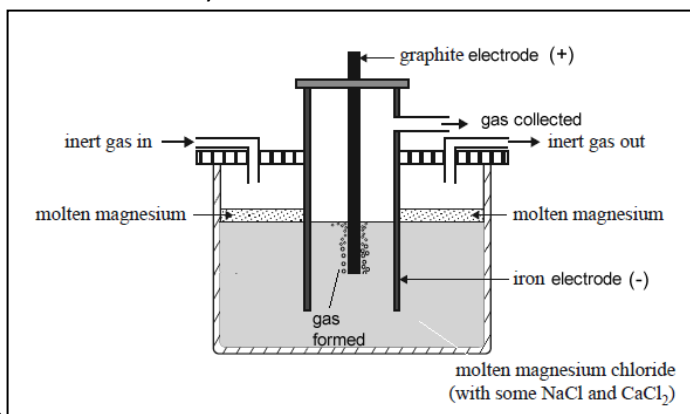
iv. Write the balanced equation to the overall reaction occurring in the electrolytic cell in iii. above.

$Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$	+1.36
$O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(l)$	+1.23
$Br_2(l) + 2e^- \rightleftharpoons 2Br^-(aq)$	+1.09
$Ag^+(aq) + e^- \rightleftharpoons Ag(s)$	+0.80
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$O_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons H_2O_2(aq)$	+0.68
$I_2(s) + 2e^- \rightleftharpoons 2I^-(aq)$	+0.54
$O_2(g) + 2H_2O(l) + 4e^- \rightleftharpoons 4OH^-(aq)$	+0.40
$Cu^{2+}(aq) + 2e^- \rightleftharpoons Cu(s)$	+0.34
$Sn^{4+}(aq) + 2e^- \rightleftharpoons Sn^{2+}(aq)$	+0.15
$S(s) + 2H^+(aq) + 2e^- \rightleftharpoons H_2S(g)$	+0.14
$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$	0.00
$2H_2O(l) + 2e^- \rightleftharpoons H_2(g) + 2OH^-(aq)$	-0.83
$Mn^{2+}(aq) + 2e^- \rightleftharpoons Mn(s)$	-1.18
$Al^{3+}(aq) + 3e^- \rightleftharpoons Al(s)$	-1.66
$Mg^{2+}(aq) + 2e^- \rightleftharpoons Mg(s)$	-2.37
$Na^+(aq) + e^- \rightleftharpoons Na(s)$	-2.71
$Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$	-2.87
$K^+(aq) + e^- \rightleftharpoons K(s)$	-2.93
$Li^+(aq) + e^- \rightleftharpoons Li(s)$	-3.04

- 2) Magnesium is one of the most abundant elements on Earth. It is used extensively in the production of magnesium-aluminium alloys. It is produced by the electrolysis of molten magnesium chloride. A schematic diagram of the electrolytic cell is shown below.

The design of this cell takes into account the following properties of both magnesium metal and magnesium chloride:

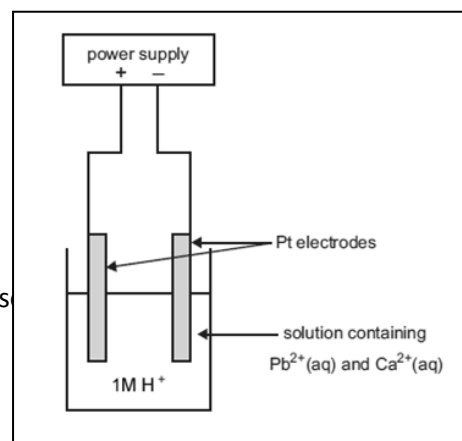
- Molten magnesium reacts vigorously with oxygen.
- At the temperature of molten magnesium chloride, magnesium is a liquid.
- Molten magnesium has a lower density than molten magnesium chloride and forms a separate layer on the surface.



- a) Label the following electrodes as the anode or cathode
- iron _____
- graphite _____
- b) Explain why an inert gas is used?
- c) Write a balanced half-equation for the reaction occurring at the
- anode
 - Cathode
- d) The melting point of a compound can often be lowered by the addition of small amounts of other compounds. In an industrial process, this will save energy. In this cell, NaCl and CaCl₂ are used to lower the melting point of MgCl₂, however, FeCl₂ cannot be used. Explain why NaCl and CaCl₂ can be used but FeCl₂ cannot.

- e) What difference would it make to the half-cell reactions if the graphite was replaced with iron? Write the half-equation for any different half-cell reaction. Justify your answer.

- 3) A mineral ore contains a mixture of compounds of lead and calcium, in approximately equal proportions. A chemist extracts the metal ions by roasting the ore in air and treating the product with acid. The solution that contains the Pb²⁺(aq) and Ca²⁺(aq) is then placed in an electrolytic cell as shown in the diagram on the right. Assume diffusion of ions in the electrolyte takes some time.



- a) When the current begins to flow in the cell, write equations for the half reaction that is likely to occur at the
- anode _____
 - cathode _____

- b) After some time has elapsed, a new half reaction occurs at one of the electrodes. Assume diffusion of ions in the electrolyte takes some time. Write the equation for this half reaction. _____

- c) If the chemist had used copper electrodes instead of platinum electrodes, how would this have affected the half reactions at each electrode the moment the power was turned on?