Lesson 1 Electrolysis

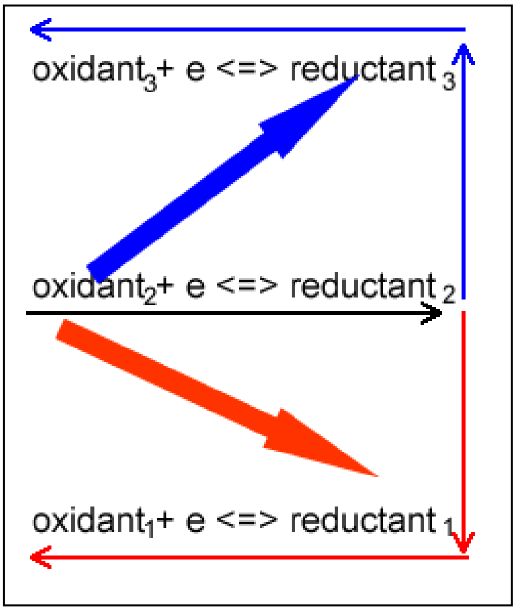
Click here for a detailed explanation of electrolysis

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 |

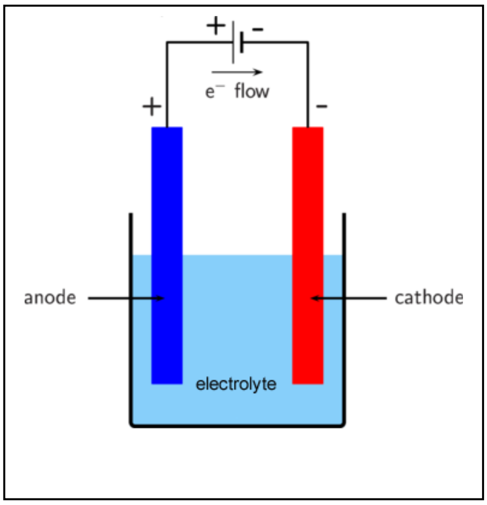
- It is a non-spontaneous process where energy is supplied by an external source to drive the redox reaction.
- Reduction occurs at the cathode and oxidation occurs at the anode.
- Cathode has a negative polarity while the anode is positive.
- Electrodes can be inert or can take part in the oxidation 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
  - i. write the half equation involving the oxidant as it appears on the electrochemical series.
  - ii. 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 $H_2O$, however, when dilute solutions of NaCl are used it is, the more stronger reductant, $H_2O$ that reacts at the anode.

| | |
|---|---|
| $Au^+(aq) + e^- \rightleftharpoons Au(s)$ | +1.68 |
| $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ | +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 |



Example 1

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




i. 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, $H_2O$ and $Cl^-$ ions.*

*Pick the strongest. In this case it is $H_2O$*

*$2H_2O\,(l) \Rightarrow O_2(g) + 4H^+(aq) + 4e$*

ii. What is the possible reaction that occurs at the cathode?

*Now list all the oxidants present in the solution*

*We have $H_2O$ and $Na^+$ ions.*

*Pick the strongest. In this case it is $H_2O$.*

*$2e + 2H_2O\,(l) \Rightarrow H_2(g) + 2OH^-\,(aq)$*

Example 2

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

| | |
|---|---|
| $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ | +1.36 |
| $O_2(g) + 4H^+(aq) + 4e^- \rightleftharpoons 2H_2O(1)$ | +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 |

i. What are the products at the cathode and the anode?

*At the cathode reduction takes place*

*List all the oxidants present*

*$Li^+$ only hence*

*$Li^+(l) + e \Rightarrow Li(l)$*

*Lithium metal and the cathode*

*At the anode oxidation takes place*

*List all the reductants present*

*$Cl^-$ only hence*

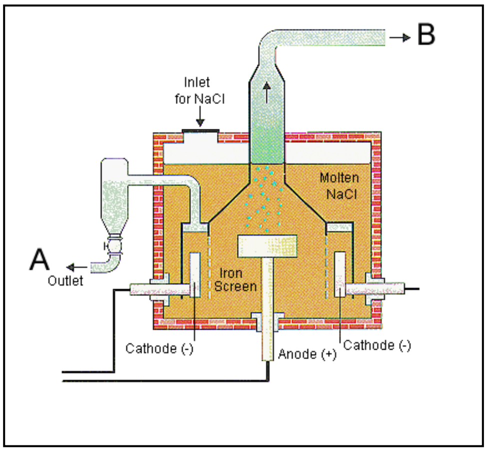
*$2Cl^-(l) \Rightarrow Cl_2(g) + 2e$*

*Cl gas at the anode*

ii. Why is a solution of lithium chloride not used?

*$H_2O$ 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.*

*Example 3*




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

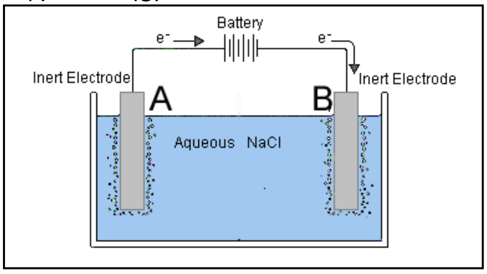
*i. Write the equation for the reaction that occurs at the cathode.*

*Reduction occurs at the cathode and hence the strongest oxidant will react.*

*$Na^+(l) + e \Rightarrow Na(l)$*

*ii. 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

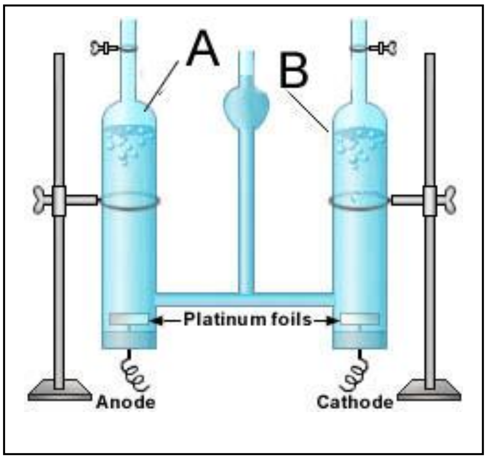
*Electrode "A" is the anode and electrode "B" is the cathode.*

b) Give the balanced ionic equation s 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 $SnCl_2$ is added to the water . Explain, using the table below, how the products formed at each electrode change?

| | |
|---|---|
| $Cl_2(g) + 2e^- \rightleftharpoons 2Cl^-(aq)$ | +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 |
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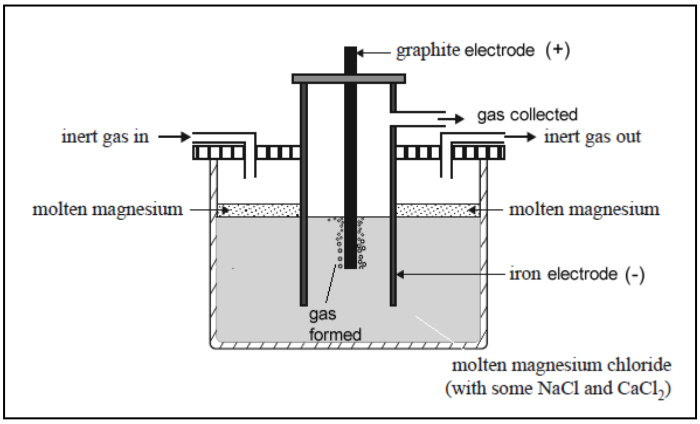
| $Ca^{2+}(aq) + 2e^- \rightleftharpoons Ca(s)$ | −2.87 |
| $K^+(aq) + e^- \rightleftharpoons K(s)$ | −2.93 |
| $Li^+(aq) + e^- \rightleftharpoons Li(s)$ | −3.04 |

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

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.

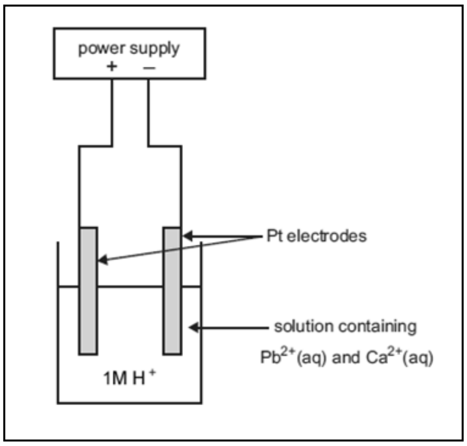
a) Label the following electrodes as the anode or cathode
   iron _______________
   graphite _______________

b) Explain why an inert gas is used?

*c)* Write a balanced half-equation for the reaction occurring at the
   i. anode
   ii. 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, $FeCl_2$ cannot be used. Explain why NaCl and $CaCl_2$ can be used but $FeCl_2$ 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 $Pb^{2+}(aq)$ and $Ca^{2+}(aq)$ is then placed in an electrolytic cell as shown in the diagram below.

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. 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? Indicate the new reactions and the electrodes each one takes place at.