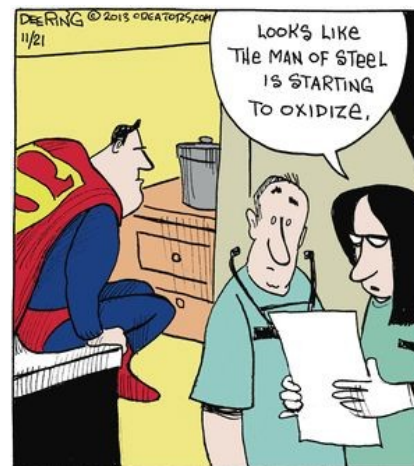# Oxidation and Reduction
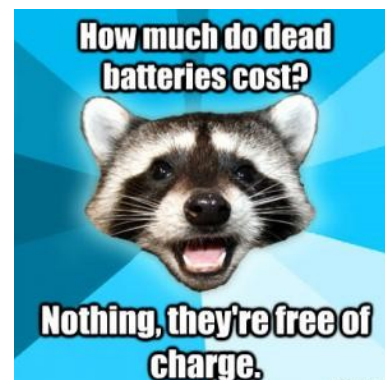

(Norwood n.d.)

(Varricchio n.d.)

(ServoCity 2015)

(Kappit n.d.)
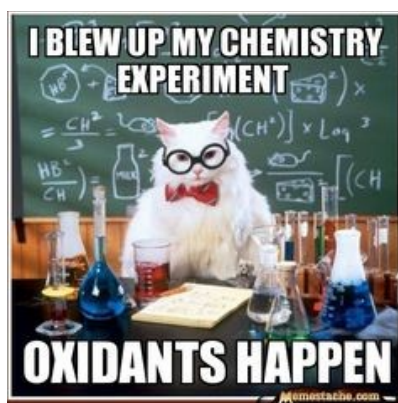
(Chemistry Cat n.d.)

WEEK	TOPIC	UNIT CONTENT	ASSESSMENT
11 – 14	Oxidation and Reduction	• the species being oxidised and reduced in a redox reaction can be identified using oxidation numbers • oxidation-reduction (redox) reactions involve the transfer of one or more electrons from one species to another • oxidation involves the loss of electrons from a chemical species, and reduction involves the gain of electrons by a chemical species; these processes can be represented using half-equations and redox equations (acidic conditions only) • a range of reactions involve the oxidation of one species and reduction of another species, including metal and halogen displacement reactions, and combustion in both limited and excess oxygen environments • the relative strength of oxidising and reducing agents can be determined by comparing standard electrode potentials, and can be used to predict reaction tendency • electrochemical cells, including galvanic and electrolytic cells, consist of oxidation and reduction half-reactions connected via an external circuit through which electrons move from the anode (oxidation reaction) to the cathode (reduction reaction) • galvanic cells produce an electric current from a spontaneous redox reaction • the electric potential difference of a cell under standard conditions can be calculated from standard electrode potentials; these values can be used to compare the voltages generated by cells constructed from different materials • electrochemical cells can be described in terms of the reactions occurring at the anode and cathode, the role of the electrolyte, salt bridge (galvanic cell), ion migration, and electron flow in the external circuit • corrosion of iron is an electrochemical process	

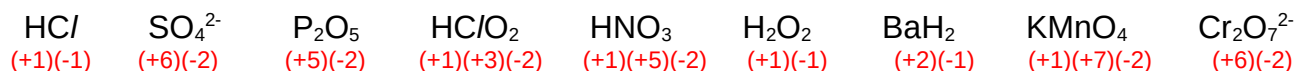|			
		that can be prevented by a range of techniques, including by exclusion of oxygen and/or water and through cathodic protection and sacrificial anodes	Extended Response 1
		• cell diagrams can be used to represent electrochemical cells	Practical 3
		• electrolytic cells use an external electrical potential difference to provide the energy to allow a non-spontaneous redox reaction to occur	Test 3
		• describe the use of electrolysis in electrolytic refining, including for purification of copper, and metal electroplating, including for silver	
		• spontaneous redox reactions can be used as a source of electrical energy, including primary cells (for example, the Leclanché cell), secondary cells (for example, the lead-acid accumulator) and fuel cells (for example, the hydrogen fuel cell). Fuel cells are a potential lower-emission alternative to the internal combustion engine and are already being used to power various modes of transport. Organisations, including the International Partnership for Hydrogen and Fuel Cells in the Economy, have been created to foster global cooperation on research and development, common codes and standards, and information sharing on infrastructure development.	

Redox Reactions

Reduction and oxidation (redox) reactions involve electron transfer. A species is oxidised when it loses one or more electrons and reduced when it gains one or more electrons (oil rig – **o**xidation **i**s **l**oss, **r**eduction **i**s **g**ain).

To help determine which atom or ion is oxidised and which is reduced, the concept of oxidation numbers has been developed. An atom's oxidation number can be described as 'the charge the atom would have if the bonds were purely ionic'. The following rules are used to help determine oxidation numbers.

i. Atoms in their elemental state have an oxidation number of zero e.g. Ag, H_2, Br_2, S_8, C, etc.
ii. Monatomic ions have an oxidation number equal to their charge e.g. Al^{3+}, S^{2-}, Na^+, N^{3-}, etc.
iii. Hydrogen has an oxidation number of +1 except in metal hydrides where it has an oxidation number of -1 e.g. NaH, CaH_2, etc.
iv. Oxygen has an oxidation number of -2 except in the case of F_2O where it has an oxidation number of +2 and in peroxides where it has an oxidation number of -1 e.g. H_2O_2, Na_2O_2, etc.
v. Group I and II elements have oxidation numbers of +1 and +2 respectively.
vi. The sum total of the oxidation numbers is equal to the charge on the compound or ion.

Examples: Determine the oxidation number of each of the atoms in the following species.

HCl	SO_4^{2-}	P_2O_5	$HClO_2$	HNO_3	H_2O_2	BaH_2	$KMnO_4$	$Cr_2O_7^{2-}$
(+1)(-1)	(+6)(-2)	(+5)(-2)	(+1)(+3)(-2)	(+1)(+5)(-2)	(+1)(-1)	(+2)(-1)	(+1)(+7)(-2)	(+6)(-2)

If an atom is oxidised, its oxidation number increases by the number of electrons it lost

e.g. Mg → Mg^{2+}
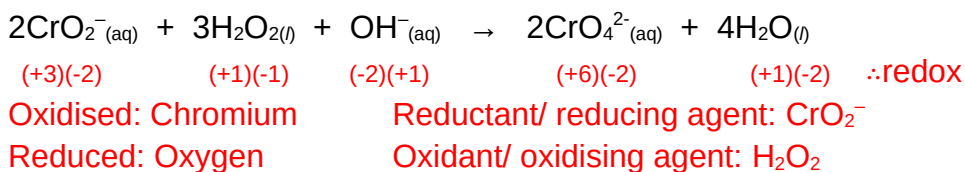oxidation number   (0)   (+2)   i.e. lost two electrons
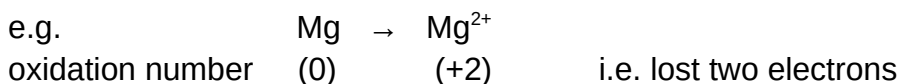
If an atom is reduced, its oxidation number decreases by the number of electrons it gained

e.g. N → N^{3-}
oxidation number   (0)   (-3)   i.e. gained three electrons
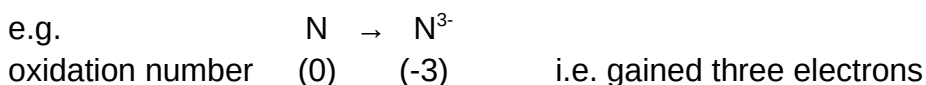
In a redox reaction, the species that is oxidised is called the reducing agent/reductant/reducer and the species that is reduced is called the oxidising agent/oxidant/oxidiser.

Whether a reaction is redox or not can be determined using oxidation numbers. In a redox reaction, the total loss of electrons must equal the total gain of electrons.

Examples: Determine whether each of the following reactions are redox or not. If it is a redox reaction, determine which species is oxidised and which species is reduced as well as which species is the oxidant and which is the reductant.

$$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$$
(0)　　　(+1)(-1)　　　(+2)(-1)　　　(0)　∴redox

Oxidised: Zinc　　　　　Reductant: Zn
Reduced: Hydrogen　　　Oxidant: HCl

$$2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \rightarrow Cr_2O_7^{2-}{}_{(aq)} + H_2O_{(l)}$$
(+6)(-2)　　　(+1)　　　(+6)(-2)　　　(+1)(-2)　∴not redox

$$2CrO_2^-{}_{(aq)} + 3H_2O_{2(l)} + OH^-{}_{(aq)} \rightarrow 2CrO_4^{2-}{}_{(aq)} + 4H_2O_{(l)}$$
(+3)(-2)　　　(+1)(-1)　　(-2)(+1)　　　(+6)(-2)　　　(+1)(-2)　∴redox

Oxidised: Chromium　　　Reductant/ reducing agent: CrO_2^-
Reduced: Oxygen　　　　　Oxidant/ oxidising agent: H_2O_2
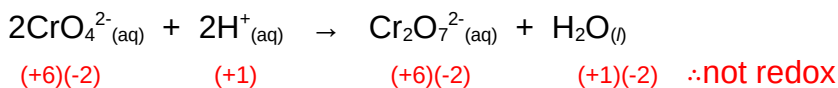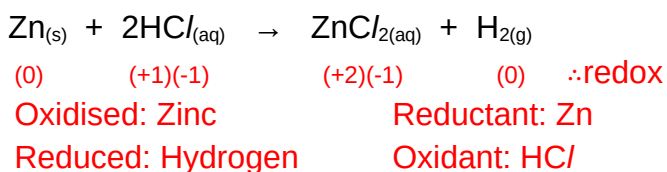
A disproportionation reaction involves one species that is both oxidised and reduced.

$$e.g. \ 2H_2O_{2(l)} \rightarrow O_{2(g)} + 2H_2O_{(l)}$$
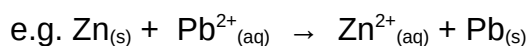(+1)(-1)　　　(0)　　　(+1)(-2)
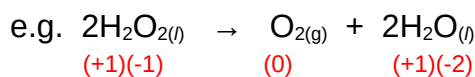
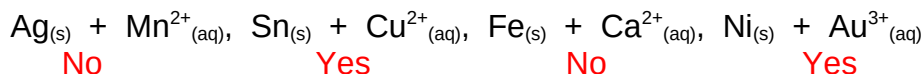A number of common reactions are also redox reactions. These include:

Metal-metal ion displacement
Electron transfer takes place from a metal element to the metal ion of a less reactive metal. Relative reactivity can be determined by using the table of standard reduction potentials in the data booklet.
If a solid metal is below the metallic ion, then it will displace the metallic ion.

$$e.g. \ Zn_{(s)} + Pb^{2+}{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + Pb_{(s)}$$

Example: Determine if the following metals will undergo displacement.

$$Ag_{(s)} + Mn^{2+}{}_{(aq)}, \ Sn_{(s)} + Cu^{2+}{}_{(aq)}, \ Fe_{(s)} + Ca^{2+}{}_{(aq)}, \ Ni_{(s)} + Au^{3+}{}_{(aq)}$$
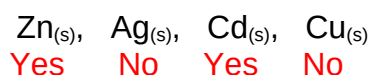No　　　　　　Yes　　　　　　No　　　　　　Yes

Metal-hydrogen ion displacement
Electron transfer takes place from a metal element to the hydrogen ion. Relative reactivity can be determined by using the table of standard reduction potentials in the data booklet.
If a solid metal is below the hydrogen ion ($2H^+{}_{(aq)} + 2e^- \rightleftharpoons H_{2(g)}$ (0.00 V)), then it will displace the hydrogen ion.
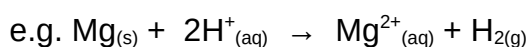
$$e.g. \ Mg_{(s)} + 2H^+{}_{(aq)} \rightarrow Mg^{2+}{}_{(aq)} + H_{2(g)}$$

Example: Determine if the following metals will undergo displacement with H^+.

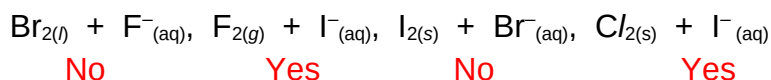$$Zn_{(s)}, \ Ag_{(s)}, \ Cd_{(s)}, \ Cu_{(s)}$$
Yes　　No　　Yes　　No

Halogen-halide ion displacement

Electron transfer takes place from a halide ion to a less reactive halogen. Relative reactivity can be determined by using the table of standard reduction potentials in the data booklet.

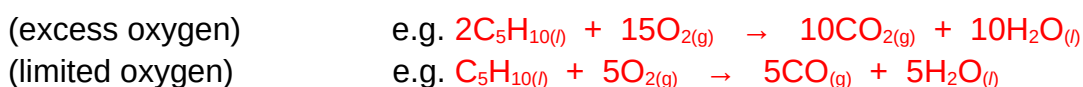If a halide ion is below the halogen, then it will displace the halogen.

$$e.g.\ Cl_{2(g)} + 2Br^-_{(aq)} \rightarrow 2Cl^-_{(aq)} + Br_{2(aq)}$$
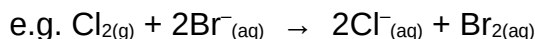
Example: Determine if the following halogens will undergo displacement.

$$Br_{2(l)} + F^-_{(aq)},\ F_{2(g)} + I^-_{(aq)},\ I_{2(s)} + Br^-_{(aq)},\ Cl_{2(s)} + I^-_{(aq)}$$
$$\text{No} \qquad\qquad \text{Yes} \qquad\qquad \text{No} \qquad\qquad \text{Yes}$$

Combustion

Electron transfer takes place from oxygen to carbon.

(excess oxygen) e.g. $2C_5H_{10(l)} + 15O_{2(g)} \rightarrow 10CO_{2(g)} + 10H_2O_{(l)}$

(limited oxygen) e.g. $C_5H_{10(l)} + 5O_{2(g)} \rightarrow 5CO_{(g)} + 5H_2O_{(l)}$

Corrosion

Corrosion is a redox process between a metal and oxygen. Some metals form a protective oxide layer (a passivating layer) preventing further oxidation (eg Al, Cr and Zn) whilst others flake and peel off, providing fresh metal to be oxidised (eg Fe).
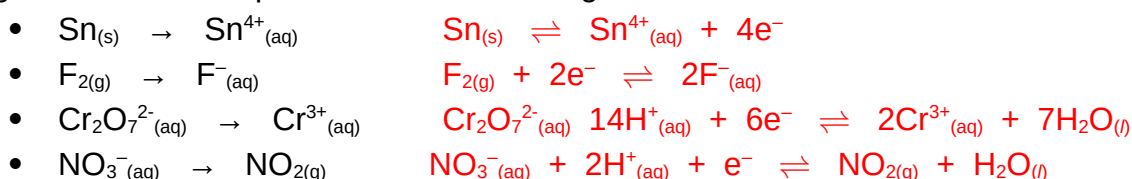
$$e.g.\ 4Al_{(s)} + 3O_{2(g)} \rightarrow 2Al_2O_{3(s)}$$
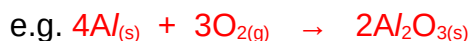
Complete Lucarelli Set 8 Oxidation Numbers and Redox Reactions (p66)

Half-Equations

Redox reactions involve both oxidation and reduction. It is possible to write the oxidation and reduction reactions separate in the form of half-equations. There are a number of rules that guide how to write correct half-equations.

i. Balance all atoms.
ii. Balance oxygen by adding water to the side that is deficient in oxygen.
iii. Balance hydrogen by adding hydrogen ions to the side that is deficient in hydrogen.
iv. Balance charges by adding electrons to one side.
v. Write in states.

E.g. Write the half-equations for the following reactions:

- $Sn_{(s)} \rightarrow Sn^{4+}_{(aq)}$ $Sn_{(s)} \rightleftharpoons Sn^{4+}_{(aq)} + 4e^-$
- $F_{2(g)} \rightarrow F^-_{(aq)}$ $F_{2(g)} + 2e^- \rightleftharpoons 2F^-_{(aq)}$
- $Cr_2O_7^{2-}{}_{(aq)} \rightarrow Cr^{3+}_{(aq)}$ $Cr_2O_7^{2-}{}_{(aq)}\ 14H^+_{(aq)} + 6e^- \rightleftharpoons 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$
- $NO_3^-{}_{(aq)} \rightarrow NO_{2(g)}$ $NO_3^-{}_{(aq)} + 2H^+_{(aq)} + e^- \rightleftharpoons NO_{2(g)} + H_2O_{(l)}$

When writing balanced, overall redox reactions, the steps to follow include:

i.   Determine which species is being oxidised and which is being reduced.
ii. For each half-equation, balance atoms (adding water and hydrogen ions if needed) and charges (by adding electrons).
iii. Multiply one or both half equations so that the number of electrons in each are equal.
iv. Add the two half-equations together cancelling out any common species.
v.   Write in states.

E.g. Write balanced, overall redox reactions for the following

- $Mg_{(s)} + H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$
  $Mg_{(s)} + 2H^+_{(aq)} \rightarrow Mg^{2+}_{(aq)} + H_{2(g)}$
- $Fe^{3+}_{(aq)} + H_2O_{2(l)} \rightarrow Fe^{2+}_{(aq)} + O_{2(g)}$
  $2Fe^{3+}_{(aq)} + H_2O_{2(l)} \rightarrow 2Fe^{2+}_{(aq)} + O_{2(g)} + 2H^+_{(aq)}$
- $MnO_4^-{}_{(aq)} + H_2C_2O_{4(aq)} \rightarrow Mn^{2+}_{(aq)} + CO_{2(g)}$
  $6H^+_{(aq)} + 2MnO_4^-{}_{(aq)} + 5H_2C_2O_{4(aq)} \rightarrow 2Mn^{2+}_{(aq)} + 10CO_{2(g)} + 8H_2O_{(l)}$
- $C_2H_5OH_{(l)} + Cr_2O_7^{2-}{}_{(aq)} + H^+_{(aq)} \rightarrow CH_3CHO_{(l)} + Cr^{3+}_{(aq)} + H_2O_{(l)}$
  $3C_2H_5OH_{(l)} + Cr_2O_7^{2-}{}_{(aq)} + 8H^+_{(aq)} \rightarrow 3CH_3CHO_{(l)} + 2Cr^{3+}_{(aq)} + 7H_2O_{(l)}$

Complete Lucarelli Set 9 Balancing Half-Equations and Redox Reactions (p68)

Electrochemistry

Electrochemical cells allow energy to transform between the forms of chemical potential energy and electrical energy. Galvanic cells use a redox reaction to produce a voltage (potential difference) that results in an electric current. It does this by preventing direct contact between the oxidant and reductant.
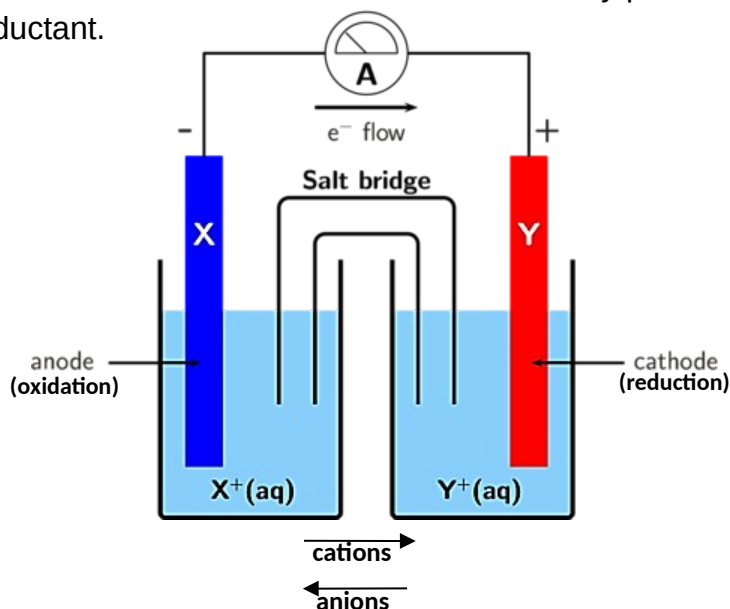

(Siyavula n.d.)

Components and terminology of electrochemical cells
- Electrodes – electrical conductors on which electron transfer occurs at the surface.
- Anode – electrode where oxidation occurs (an ox). It is denoted negative (–).
- Cathode – electrode where reduction occurs (red cat). It is denoted positive (+).

- Electrolyte – solution which contains ions that conduct charge.
- Salt bridge – contains a non-reactive electrolyte solution. It prevents direct contact of the oxidant and reductant and prevents charge building up in each half-cell. Anions flow from the salt bridge towards the anode and cations flow towards the cathode.
- Oxidation half-cell – half-cell where oxidation occurs. It contains the anode in an electrolyte.
- Reduction half-cell – half-cell where reduction occurs. It contains the cathode in an electrolyte.
- External circuit – a conductive path (usually wire) which allows electron flow to occur between cells.

The Daniell cell is a classic example of an electrochemical cell.
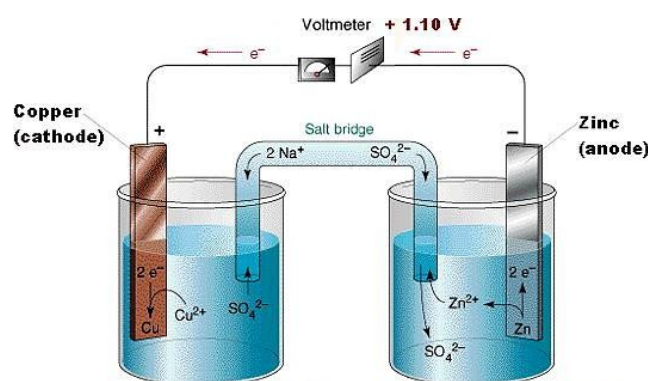
(Crujera and Perkin 2014)

Write the two half-equations and the overall redox equation for this electrochemical cell.

Reduction: $2e^- + Cu^{2+}_{(aq)} \rightarrow Cu_{(s)}$
Oxidation: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
Overall: $Cu^{2+}_{(aq)} + Zn_{(s)} \rightarrow Cu_{(s)} + Zn^{2+}_{(aq)}$
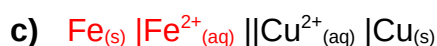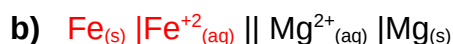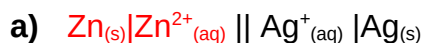
The table of standards reduction potentials is used to rank the strength of oxidising agents and can be used to calculate the voltage produced in an electrochemical cell. Reduction potentials are determined by measuring them against a reference cell which is the $H^+_{(aq)} | H_{2(g)}$ half-cell (which is arbitrarily given a standard reduction potential (E°) of 0.00 V). When operating at standard conditions (i.e. 25 °C, 1.0 mol L^{-1} and 100.0 kPa) the cell produces a voltage known as the standard cell potential (E°$_{cell}$).
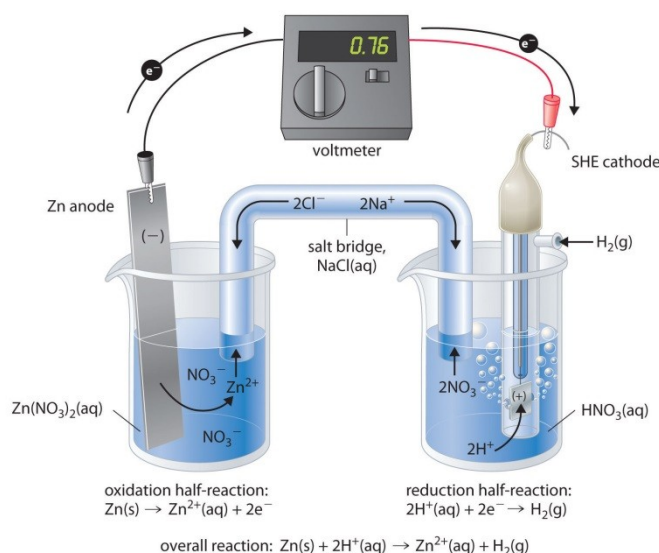
The standard reduction potentials table is a list of half-cells ranked in order of increasing ability to lose electrons. This means that the most powerful oxidising agents are on the top left of the table and the most powerful reducing agents are on the bottom right of the table. As such, the species which displays the more positive E^o value will be reduced (the oxidant).

Example: Predict which cell is the anode compartment in each of the following:

a) $Zn_{(s)}|Zn^{2+}_{(aq)}$ || $Ag^+_{(aq)}$ $|Ag_{(s)}$

b) $Fe_{(s)}$ $|Fe^{+2}_{(aq)}$ || $Mg^{2+}_{(aq)}$ $|Mg_{(s)}$

c) $Fe_{(s)}$ $|Fe^{2+}_{(aq)}$ $||Cu^{2+}_{(aq)}$ $|Cu_{(s)}$

Example Use the electrochemical series to decide the following:

a) Is chlorine a powerful oxidiser or a poor oxidiser? Powerful

b) Is the sodium ion a powerful or poor oxidant? Poor

c) Which is the more powerful oxidiser – iodine or chlorine? Cl_2

d) Which is the more powerful oxidising agent – iron (III) or hydrogen ions? Fe^{3+}

e) Which is the more powerful reductant – magnesium or gold? Mg

f) Which is the more powerful reducer – chloride ions or iodide? I^-

The $E°_{cell}$ or voltage or E.M.F. of an electrochemical cell is a measure of the difference in the standard potentials of each half-cell. A positive $E°_{cell}$ indicates that a reaction will occur spontaneously. A negative $E°_{cell}$ indicates that a reaction will not occur without external assistance. When determining $E°_{cell}$ it is important to remember that the values given in the standard reduction potentials table are for reduction half-equations. Once the oxidation half-equation has been identified, the sign of its $E°$ value must be reversed. This means the $E°_{cell}$ can be calculated using the formula:

$$E°_{cell} = E°_{reduction} + E°_{oxidation}$$

Electrochemical cells can be represented in the following notation: $Zn_{(s)}|Zn^{2+}_{(aq)}$ || $Ag^+_{(aq)}$ $|Ag_{(s)}$ or, if inert electrodes are used $Pt_{(s)}$ $|ClO_3^-_{(aq)}, ClO_4^-_{(aq)}$ || $MnO_4^-_{(aq)}, Mn^{2+}_{(aq)}$ $|Pt_{(s)}$ where | = phase boundary, || = salt bridge.

Redox reactions are not limited to those between metals and metal ions. As such, some half-cells require inert electrodes (most often graphite or platinum).
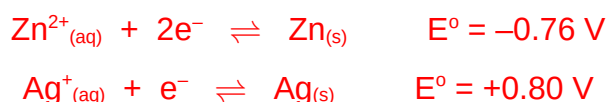
The type of electrode that can be used for particular half-cells include:

- Reactions involving metals and metal ions – the metal is the electrode (eg Mg and Mg^{2+}).

- Reactions involving metals ions in different oxidation states – an inert electrode is used (eg Cr^{3+} and Cr^{6+}).
- Reactions involving a dissolved non-metal and its ions – an inert electrode is used (eg Br_2 and Br^-).
- Reactions involving a gaseous non-metal and its ions – an inert electrode is used (eg Cl_2 and Cl^-).

Example: Find the overall reaction and the $E°_{cell}$ for the cell: $Zn_{(s)} |Zn^{2+}_{(aq)} || Ag^+_{(aq)} |Ag_{(s)}$

Step One: Write the half-cell equations and their E° from the standard reduction potentials table.

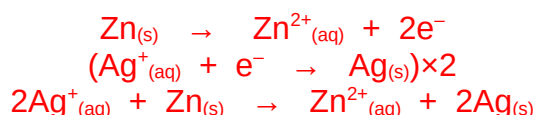$$Zn^{2+}_{(aq)} + 2e^- \rightleftharpoons Zn_{(s)} \qquad E° = –0.76 \text{ V}$$
$$Ag^+_{(aq)} + e^- \rightleftharpoons Ag_{(s)} \qquad E° = +0.80 \text{ V}$$

Step Two: Determine the reduction half-equation which has the more positive E°.

$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)} \qquad E° = +0.80 \text{ V}$$

Step Three: The $E°_{cell}$ of the can be calculated by performing $E°_{reduction} + E°_{oxidation}$ (remember you must reverse the sign on the oxidation half-equation).

$$E_{cell}° = +0.80 + (+0.76) \qquad = +1.56 \text{ V}$$

Step Four: Reverse the direction of the oxidation half-equation and rewrite the full redox equation (remember to balance the electrons).

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$
$$(Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)})\times 2$$
$$2Ag^+_{(aq)} + Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

(NB: Although E° values are additive, we do not multiply them if the half-equation needs to be multiplied in order to write the overall redox equation).

Example: For the galvanic cell shown below determine the following:
a)   The oxidising agent and reducing agent
b)   The anode and cathode
c)   The overall redox reaction
d)   The $E_{cell}°$
e)   The direction of flow of electrons, anions and cations
f)   A suitable salt bridge
g)   The changes you would expect to observe at the anode and cathode

(Lawson n.d.)
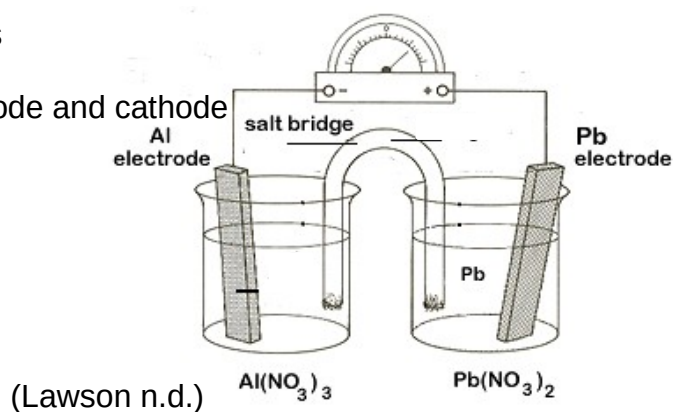
a) The oxidising agent ($Pb^{2+}_{(aq)}$) and reducing agent ($Al_{(s)}$)
b) The anode ($Al_{(s)}$)and cathode ($Pb_{(s)}$)
c) The overall redox reaction ($2Al_{(s)} + 3Pb^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Pb_{(s)}$)
d) The E_{cell}^o (= –0.13 + (+1.68) = +1.55 V)
e) The direction of flow of electrons (from anode to cathode), anions (towards anode) and cations (towards cathode)
f) A suitable salt bridge ($NaCl$, KCl, KNO_3, etc.)
g) The changes you would expect to observe at the anode (silver electrode begins to disintegrate) and cathode (grey solid begins to form on surface of electrode)

Complete Lucarelli Set 10 Understanding Galvanic Cells (p75)

The Corrosion of Iron

Corrosion of iron requires both oxygen and water.

Oxidation (anode): $Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$
Reduction (cathode): $O_{2(g)} + 2H_2O_{(l)} + 4 e^- \rightarrow 4OH^-_{(aq)}$
Precipitation: $Fe^{2+}_{(aq)} + OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$
Further oxidation of the iron (II) hydroxide then occurs. $Fe(OH)_{2(s)} + OH^-_{(aq)} \rightarrow Fe(OH)_{3(s)}$
This may then partially dehydrate to form rust, $Fe_2O_3.xH_2O$.
$2Fe(OH)_{3(s)} \rightarrow Fe_2O_3.H_2O_{(s)} + 2H_2O_{(l)}$
Overall, the equation is given by: $4Fe_{(s)} + 3O_{2(g)} + 2xH_2O_{(l)} \rightarrow 2Fe_2O_3.xH_2O_{(s)}$
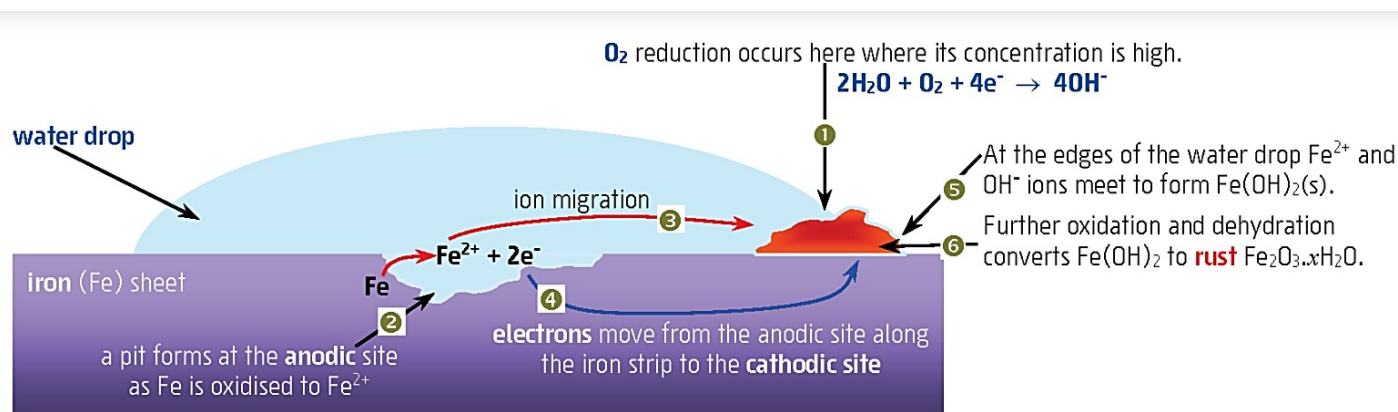
(Lucarelli 2020)

The water acts an electrolyte and salt bridge. Oxygen reduction occurs at the point where oxygen is at its greatest concentration and iron oxidation occurs where oxygen concentration is lowest (i.e. in two separate sites). The Fe^{2+} ions then migrate to the cathode to react with OH^- ions. The process of rusting can be affected by the following factors:

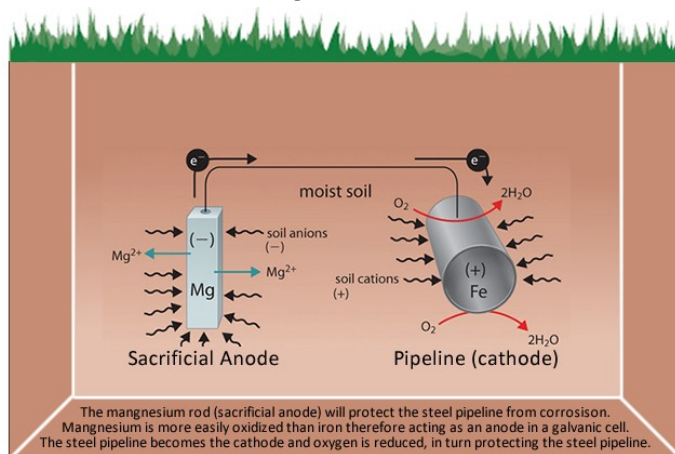- Presence of oxygen: this is the oxidising agent. The greater the concentration of oxygen, the greater the rate of corrosion.
- Presence of water: increases the flow of ions between anodic and cathodic sites which increases the rate of corrosion.
- pH: the lower the pH, the greater the rate of corrosion as the reduction potential of water increases (i.e. its reduction becomes more favourable).
- Presence of electrolytes: improves the efficiency of water as the salt bridge and increases the rate of corrosion.

- Presence of less or more reactive metals: if iron is in contact with a less reactive metal (i.e. more positive reduction potential), the rate of corrosion increases (more sites now available for iron to oxidise). If iron is in contact with a more reactive metal (i.e. less positive reduction potential), the rate of corrosion decreases.
- Temperature: increased temperature increases the rate of corrosion.

Prevention of Rusting

A number of methods can be used to prevent or minimise the rusting process.

- Inert, non-metallic coating: prevents contact with oxygen and water eg painting, plastic, oil, etc.
- Inert, metallic coating: prevents contact with oxygen and water eg Cu, Sn, Pb, etc. This can be problematic if the metallic barrier is damaged as it makes the point of contact with iron more anodic and so the iron will corrode faster.
- Galvanising: coating with the more reactive metal, zinc. Zinc oxidises more readily and forms a protective layer over the iron ($ZnCO_3.Zn(OH)_2$).
- Cathodic protection using a sacrificial anode: a more reactive metal is placed in contact with the iron. The more reactive metal oxidises and must be replaced periodically. The iron now becomes the site for reduction and so O_2 is reduced at this site. A very damp or wet environment is needed to act as a salt bridge.

The mangnesium rod (sacrificial anode) will protect the steel pipeline from corrosison. Magnesium is more easily oxidized than iron therefore acting as an anode in a galvanic cell. The steel pipeline becomes the cathode and oxygen is reduced, in turn protecting the steel pipeline.

(OTDS UK Ltd 2021)

- Cathodic protection using a DC current: the iron is connected to the negative terminal of a low voltage DC current. The excess of electrons prevents oxidation. The positive terminal of the power supply is attached to a piece of scrap metal or an inert material (eg Pt (which causes oxidation of H_2O) that is oxidised over time. As is the case in the use of a sacrificial anode, a very damp or wet environment is needed to act as a salt bridge.

(Marinethai.net 2016)
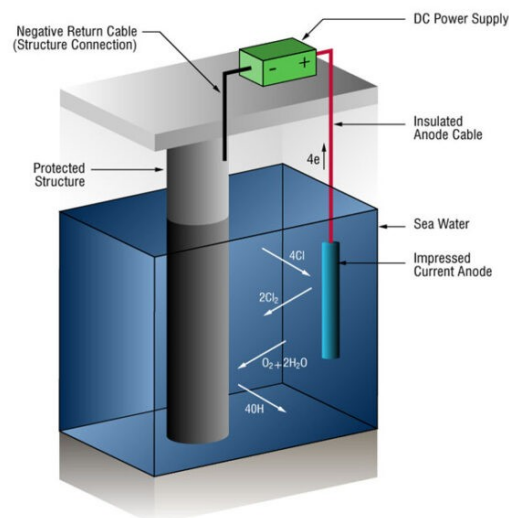
Complete Lucarelli Set 12 Electrochemistry in Action Questions 19 – 22 (p96)

Electrolytic Cells

Electrolysis occurs in an electrolytic cell and is essentially the reverse process to that which occurs in a galvanic cell (i.e. an electric current is applied to the cell in order to make a redox reaction occur).

Components and terminology of electrolytic cells
- Anode – electrode where oxidation occurs. It is attached to the positive terminal of the power supply and is denoted positive (+).
- Cathode – electrode where reduction occurs. It is denoted negative (–).
- Power supply – supplies the electrical energy which causes the redox reaction to occur. It pushes electrons to the cathode and draws them from the anode.
- Electrolyte – molten salt or aqueous solution in which the electrodes are immersed. Anions are attracted to the anode, cations to the cathode.
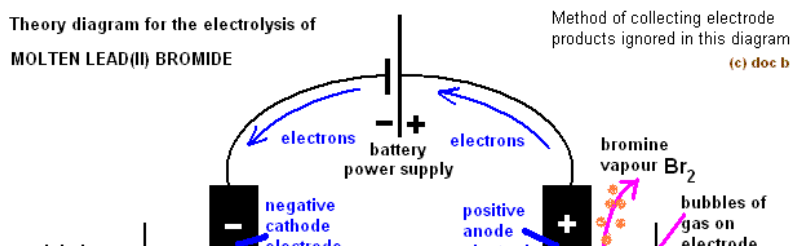

(Bodner Group n.d.)
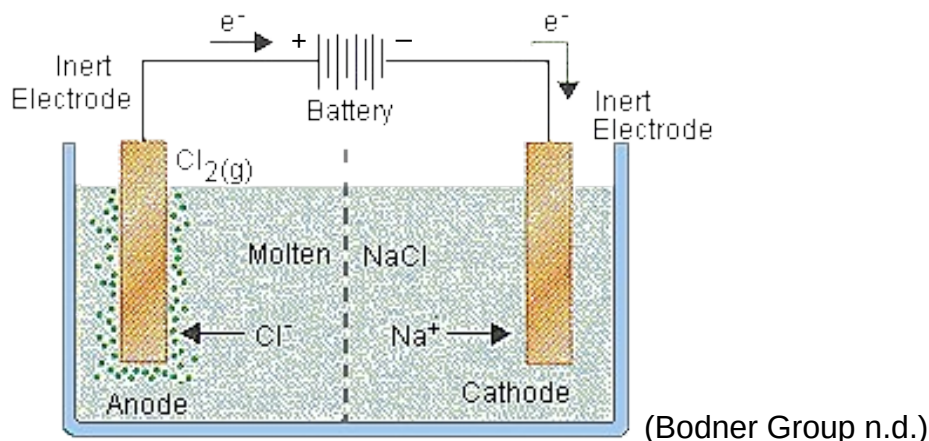
Electrolysis of a Molten Salt
Inert electrodes are placed in a molten salt and a voltage is applied. The voltage causes one electrode (cathode) to become negatively charged and the cations are attracted to this electrode where they are reduced. Simultaneously, the voltage causes the other electrode (anode) to become positively charged and the anions are attracted to this electrode where they are oxidised. In a molten salt, the ions are converted to their elemental forms.
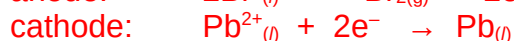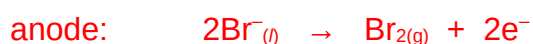
Example: An electrolytic cell contains two inert electrodes placed in molten lead (II) bromide.
a) Draw a labelled diagram showing this cell.
b) Draw the electron flow on your diagram.
c) Label the anode and cathode. Write the half-equations that occur at each electrode.
d) Show the direction of ion migration.
e) Write the overall, balanced redox reaction.
f) Describe any observations you would note at each electrode.
g) Calculate the minimum voltage needing to be applied to cause the redox reaction to occur.

anode:　　　$2Br^-_{(l)}$ → $Br_{2(g)}$ + $2e^-$
cathode:　　$Pb^{2+}_{(l)}$ + $2e^-$ → $Pb_{(l)}$
overall:　　　$Pb^{2+}_{(l)}$ + $2Br^-_{(l)}$ → $Br_{2(g)}$ + $Pb_{(l)}$
observations: colourless molten liquid produces a red liquid at the anode and a grey solid is formed on the cathode.
$E°_{cell} = E°_{reduction} + E°_{oxidation}$ = -0.13+(-1.08) = -1.21 V
i.e. 1.21 V needs to be applied
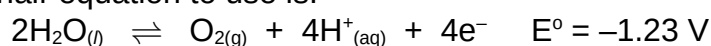
Electrolysis of an Aqueous Solution
Electrodes (which may be inert or otherwise) are placed in an aqueous solution containing a dissolved salt and a voltage is applied. The voltage causes one electrode (cathode) to become negatively charged and the cations are attracted to this electrode where they are reduced. Simultaneously, the voltage causes the other electrode (anode) to become positively charged and the anions are attracted to this electrode where they are oxidised. Depending on what is present in the cell, the aqueous salt, electrode(s) or water may be oxidised or reduced.

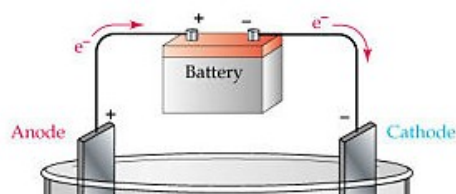If water is reduced, the half-equation to use is:
$$H_2O_{(l)} + 2e^- \rightleftharpoons H_{2(g)} + 2OH^-_{(aq)} \quad E° = –0.83 \text{ V}$$
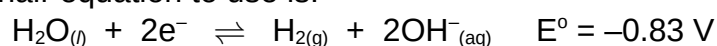
If water is oxidised, the half-equation to use is:
$$2H_2O_{(l)} \rightleftharpoons O_{2(g)} + 4H^+_{(aq)} + 4e^- \quad E° = –1.23 \text{ V}$$
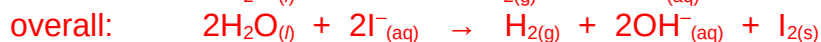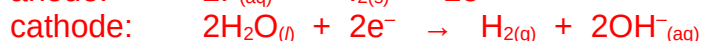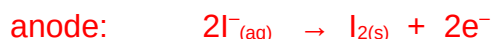
When determining which species is undergoing reduction and which is undergoing oxidation, it is necessary to write all possible reduction and oxidation half-equations that could take place and then choose the most positive reduction and oxidation options.

Example: An electrolytic cell contains inert electrodes placed in an aqueous solution of manganese (II) iodide.
a)　　Draw a labelled diagram showing this cell.
b)　　Draw the electron flow on your diagram.
c)　　Label the anode and cathode. Write the half-equations that occur at each electrode.
d)　　Show the direction of ion migration.
e)　　Write the overall, balanced redox reaction.
f)　　Describe any observations you would note at each electrode.
g)　　If tin electrodes were used instead of inert electrodes would this have made a difference? If so, write the new balanced, redox equation and observations.

anode: $\quad 2I^-_{(aq)} \rightarrow I_{2(s)} + 2e^-$
cathode: $\quad 2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$
overall: $\quad 2H_2O_{(l)} + 2I^-_{(aq)} \rightarrow H_{2(g)} + 2OH^-_{(aq)} + I_{2(s)}$
observations: pale pink solution produces colourless odourless gas on the cathode and a purple solid on the anode (a pale pink solid may also form in the cell).

If tin electrodes were used:
anode: $\quad Sn_{(s)} \rightarrow Sn^{2+}_{(aq)} + 2e^-$
cathode: $\quad 2H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2OH^-_{(aq)}$
overall: $\quad 2H_2O_{(l)} + Sn_{(s)} \rightarrow H_{2(g)} + 2OH^-_{(aq)} + Sn^{2+}_{(aq)}$
observations: pale pink solution produces colourless odourless gas on the cathode and anode begins to disintegrate (a white solid may also form in the cell).

Complete Lucarelli Set 11 Electrolysis (p80)

Applications of Electrochemical Cells

- **Electrolysis of Molten NaCl – The Downs Cell.**
Sodium is made commercially available through the electrolysis of molten sodium chloride.
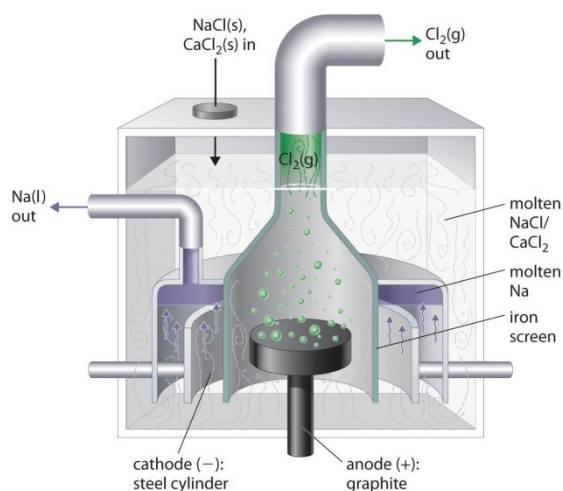
(Larsen n.d.)

The melting point of NaC*l* (approximately 800ºC) is reduced (to approximately 600ºC) by adding CaC*l*$_2$ to the mixture. The anode is graphite and the cathode is iron. The half reactions occurring are:

anode: $2Cl^-_{(l)} \rightarrow Cl_{2(g)} + 2e^-$
cathode: $Na^+_{(l)} + e^- \rightarrow Na_{(l)}$
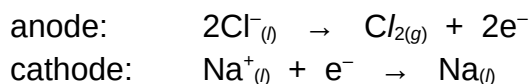
The chlorine is piped off as a gas and the molten sodium (which rises to the top of the molten salt due to a lesser density) is tapped off in the absence of air. The chlorine gas and molten sodium must not be allowed to come into contact as they are reactive enough to reform the molten NaCl.

This process of commercially producing metals from their molten salts is referred to as electrowinning. Calculate the minimum voltage required in this cell.

Minimum voltage required:

$E°_{cell} = E°_{red} + E°_{ox}$
$= -2.71 + (-1.36)$
$= -4.07$ V

Therefore a minimum voltage of + 4.07 must be applied in the cell.

- **Electroplating**

Electroplating involves the process of electrolysing in order to place a thin film of metal on an object. In this case, the metal to be used as the coating is the anode and the cathode is the object to be coated.

Example: Silver plating a spoon.

(Larsen n.d.)

anode: $Ag_{(s)} \rightarrow Ag^+_{(aq)} +$
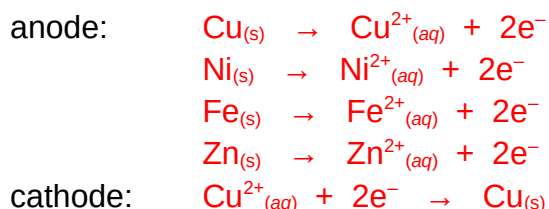cathode: $Ag^+_{(aq)} + e^- \rightarrow A$
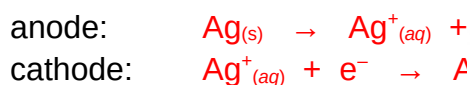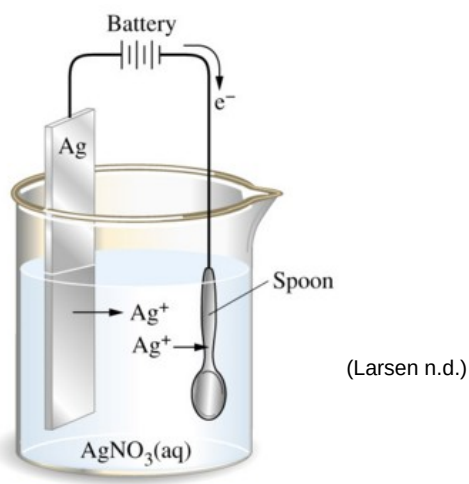
- **Electrorefining**

Electrorefining involves purifying a metal where the impure metal anode is itself oxidised.

In the example of electrorefining copper, the anode is made up of the impure (blister) copper metal (impurities often include Zn, Fe, Ni, Au, Ag and Pt) and the cathode is made of pure copper. The electrolyte in this case is a copper (II) sulphate solution.
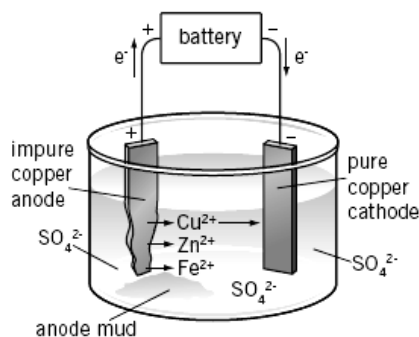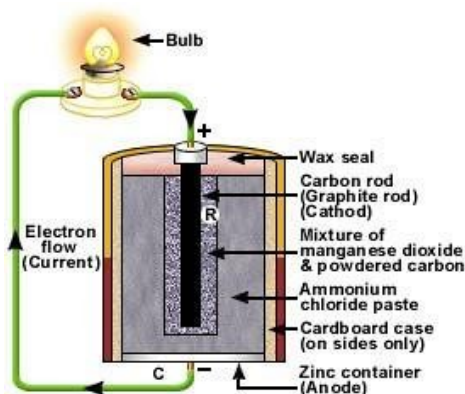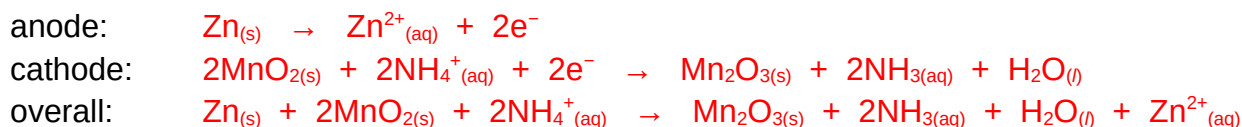
The impure copper is oxidised at the anode (along with Zn, Fe, and Ni) whilst the other metals fall to the bottom as an anode slime. As the voltage is carefully controlled, only the copper (II) ions are then reduced and deposited at the cathode.

anode: $Cu_{(s)} \rightarrow Cu^{2+}_{(aq)} + 2e^-$
$Ni_{(s)} \rightarrow Ni^{2+}_{(aq)} + 2e^-$
$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$
$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
cathode: $Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

- **Primary Cells**

These are non-rechargeable cells typically used as disposable batteries.

The dry or Leclanché cell is the most common type of primary cell. It produces a voltage of 1.48 V. It consists of a zinc anode (the casing) and a graphite rod cathode surrounded by powdered manganese dioxide (MnO_2). The electrolyte is a moist paste of ammonium chloride and zinc chloride. The half reactions are complex but may be represented as:

anode: $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$
cathode: $2MnO_{2(s)} + 2NH_4^+{}_{(aq)} + 2e^- \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)}$
overall: $Zn_{(s)} + 2MnO_{2(s)} + 2NH_4^+{}_{(aq)} \rightarrow Mn_2O_{3(s)} + 2NH_{3(aq)} + H_2O_{(l)} + Zn^{2+}_{(aq)}$
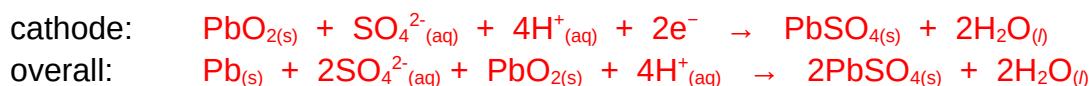

(tymkrs 2011)

This battery cannot be recharged because the zinc ions are removed from the anode and eventually the ammonium chloride produces an acidic environment that corrodes the zinc casing.

- **Secondary Cells**

These are rechargeable cells typically used as batteries.
The lead-acid accumulator battery is a secondary cell. It is made up of six cells connected in series, producing a voltage of around 12 V. It produces a much larger current than a dry cell. The cathode is a grid of lead alloy packed with lead (IV) oxide powder. The anode is a grid of lead alloy packed with spongy lead and the electrolyte is a solution of 35 % v/v sulfuric acid.

anode: $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

cathode: $PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+{}_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

overall: $Pb_{(s)} + 2SO_4^{2-}{}_{(aq)} + PbO_{2(s)} + 4H^+{}_{(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$
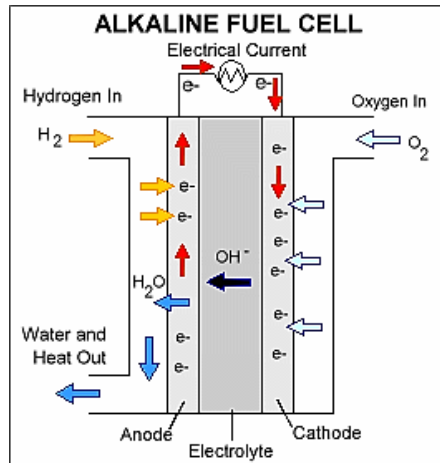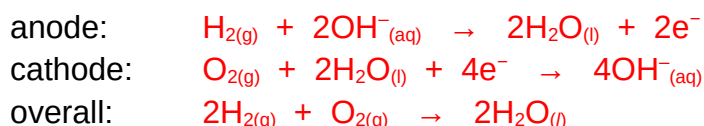
The lead sulphate produced coats the electrodes. To charge the battery the car's alternator provides an electric current which causes the reverse reaction to take place.

$$2PbSO_{4(s)} + 2H_2O_{(l)} \rightarrow Pb_{(s)} + PbO_{2(s)} + 4H^+{}_{(aq)} + 2SO_4^{2-}{}_{(aq)}$$

(Nave n.d.)
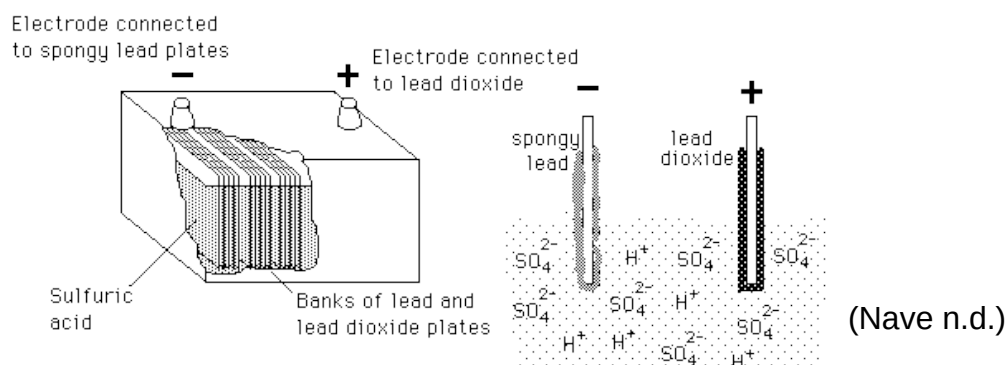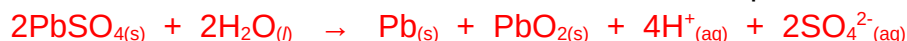
- **Fuel Cells**

These cells do not store the oxidising or reducing agent and are touted as being one of the more "environmentally friendly" way of the future in terms of energy production.

In the alkaline hydrogen fuel cell, gaseous hydrogen and oxygen are continuously fed into the cell producing only water as the waste product.

anode: $H_{2(g)} + 2OH^-{}_{(aq)} \rightarrow 2H_2O_{(l)} + 2e^-$

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

overall: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

(Konrad 2013)

Complete Lucarelli Set 12: Electrochemistry in Action (p92)

Bibliography

Norwood n.d.: , (Norwood n.d.),

Varricchio n.d.: , (Varricchio n.d.),

ServoCity 2015: , (ServoCity 2015),

Kappit n.d.: , (Kappit n.d.),

Chemistry Cat n.d.: , (Chemistry Cat n.d.),

Siyavula n.d.: , (Siyavula n.d.),

Crujera and Perkin 2014: , (Crujera and Perkin 2014),

Schmitz 2012: , (Schmitz 2012),

Lawson n.d.: , (Lawson n.d.),

Lucarelli 2020: , (Lucarelli 2020),

OTDS UK Ltd 2021: , (OTDS UK Ltd 2021),

Marinethai.net 2016: , (Marinethai.net 2016),

Bodner Group n.d.: , (Bodner Group n.d.),

Brown 2000: , (Brown 2000),

askllTians.com 2006: , (askllTians.com 2006),

Larsen n.d.: , (Larsen n.d.),

Lewis and Lewis 2012: , (Lewis and Lewis 2012),

tymkrs 2011: , (tymkrs 2011),

Nave n.d.: , (Nave n.d.),

Konrad 2013: , (Konrad 2013),