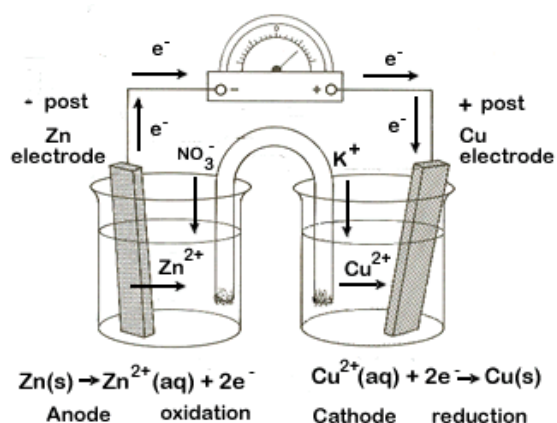
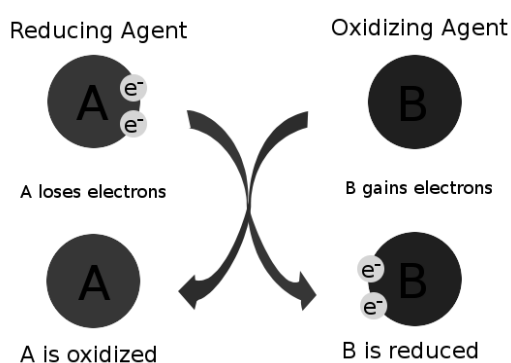


WASHINGTON LATIN PUBLIC CHARTER SCHOOL

HONORS CHEMISTRY 2019-20

UNIT 5B

CHEMICAL REACTIONS II – OXIDATION AND REDUCTION



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Key words: oxidation, reduction, oxidation number, oxidising agent, reducing agent, half-equation, redox reaction, disproportionation, alkali metal, displacement, reactivity series, anode, cathode, electrolyte, voltaic cell, galvanic cell, battery, electrolytic cell, electrochemical cell

Lesson 1 – What is oxidation, what is reduction and what are half-equations?

1) Oxidation and Reduction

a) Definitions of Oxidation and Reduction

- Oxidation and reduction are best defined in terms of electron transfer:
 - **Oxidation is the loss of electrons**; when a species loses electrons it is said to be oxidised
 - Eg A sodium atom (Na) can lose one electron to become a sodium ion (Na⁺)
This process can be represented as follows: $\text{Na} \rightarrow \text{Na}^+ + \text{e}^-$
 - Eg A magnesium atom (Mg) can lose two electrons to become a magnesium ion (Mg²⁺)
This process can be represented as follows: $\text{Mg} \rightarrow \text{Mg}^{2+} + \text{e}^-$
 - Eg Two iodide ions (I⁻) can each lose an electron to become an iodine molecule (I₂)
This process can be represented as follows: $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$
 - **Reduction is the gain of electrons**; when a species gains electrons it is said to be reduced
 - Eg Each Cl atom in Cl₂ can gain one electron to form two Cl⁻ ions
This process can be represented as follows: $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$
 - Eg Each O atom in O₂ can gain two electrons to become an oxide ion (O²⁻)
This process can be represented as follows: $\text{O}_2 + 4\text{e}^- \rightarrow 2\text{O}^{2-}$
 - Eg An Fe³⁺ ion can lose one electron to become a Fe²⁺ ion
This process can be represented as follows: $\text{Fe}^{3+} + \text{e}^- \rightarrow \text{Fe}^{2+}$
- Remember: LEO GER (loss of electrons is oxidation, gain of electrons is reduction) or OIL RIG (oxidation is loss, reduction is gain)
- Equations such as those shown above, which show the gain or loss of electrons by a species, are known as **half-reactions** or **half-equations**

b) Naming ionic compounds

- Most ionic compounds are named by stating the cation followed by the anion (eg NaCl - sodium chloride)
- Atoms in groups 1 only form +1 ions and atoms in group 2 only form +2 ions, so it is not necessary to specify the charge on the atom when naming these compounds

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- Some atoms, especially those in the d-block, form more than one stable cation and can therefore form different compounds with the same anion:

Eg Fe can form Fe^{2+} or Fe^{3+} ions, so can form FeCl_2 or FeCl_3

Eg Cu can form Cu^+ or Cu^{2+} ions, so can form Cu_2O or CuO

To distinguish between these different compounds by name, the charge on the cation must be specified; this is done by stating the charge in Roman numerals in parenthesis after the name of the cation:

Fe^{2+} is iron (II) so FeCl_2 is iron (II) chloride

Fe^{3+} is iron (III) so FeCl_3 is iron (III) chloride

Cu^+ is copper (I) so Cu_2O is copper (I) oxide

Cu^{2+} is copper (II) so CuO is copper (II) oxide

Other examples: PbO_2 is lead (IV) oxide (because it contains Pb^{4+} ions)

V_2O_5 is vanadium (V) oxide (because it contains V^{5+} ions)

Note: you do NOT need to state the charge when naming compounds of atoms in Group 1, Group 2 or aluminum, as these atoms only form one stable ion (MgO is magnesium oxide)

Lesson 2 – What are oxidation numbers?

c) Oxidation numbers

- The concepts of oxidation and reduction can be applied to non-ionic compounds using the concept of **oxidation numbers**
- The oxidation number of an atom is the charge that would exist on an individual atom if the bonding were completely ionic**
- In simple ions, the oxidation number of the atom is the same as the charge on the ion:
 - Na^+ , K^+ , H^+ all have an oxidation number of +1
 - Mg^{2+} , Ca^{2+} , Pb^{2+} all have an oxidation number of +2
 - Cl^- , Br^- , I^- all have an oxidation number of -1
 - O^{2-} , S^{2-} all have an oxidation number of -2
- In molecules and compounds, the sum of the oxidation numbers on the atoms is zero
 - In SO_3 ; oxidation number of S = +6, oxidation number of each O = -2 $(+6 + 3(-2) = 0)$
 - H_2O_2 ; oxidation number of each H = +1, oxidation number of each O = -1 $(2(+1) + 2(-1) = 0)$
 - SCl_2 ; oxidation number of S = +2, oxidation number of each Cl = -1 $(+2 + 2(-1) = 0)$
- In elements, the oxidation number of each atom is zero
 - In Cl_2 , S, Na and O_2 all atoms have an oxidation number of zero
- In polyatomic ions, the sum of the oxidation numbers on the atoms is equal to the overall charge on the ion.
 - In SO_4^{2-} ; oxidation number of S = +6, oxidation number of O = -2 $+6 + 4(-2) = -2$
 - In ClO^- ; oxidation number of Cl = +1, oxidation number of O = -2 $+1 + (-2) = -1$
 - In NH_4^+ ; oxidation number of N = -3, oxidation number of H = +1 $-3 + 4(1) = +1$

UNIT 5B – OXIDATION AND REDUCTION

- Many atoms, such as S, N and Cl, can exist in a variety of oxidation states and so it is not possible to assume that these atoms have a particular oxidation number in their compounds and ions; oxidation numbers can be predicted by following a number of basic rules:
 - All group I atoms always adopt the +1 oxidation state in their compounds (eg NaCl)
 - All group II atoms adopt the +2 oxidation state in their compounds (eg MgO)
 - Aluminum always adopts the +3 oxidation state in its compounds (eg Al₂O₃)
 - Fluorine always adopts the -1 oxidation state in its compounds (eg HF)
 - Hydrogen usually adopts the +1 oxidation state in its compounds and ions (eg HCl), but when it is bonded to a metal, silicon or boron it adopts the -1 oxidation state; these compounds are called **hydrides** (eg BH₃ – boron trihydride)
 - Oxygen usually adopts the -2 oxidation state in its compounds (eg H₂O, SO₄²⁻); in some cases, when bonded to a group I or group II metal or hydrogen, it can adopt the -1 oxidation state; these compounds are called **peroxides** (eg H₂O₂ – hydrogen peroxide); with fluorine, oxygen adopts an oxidation number of +2
 - The oxidation numbers of all other atoms in their compounds can vary

Example 1: What are the oxidation numbers of C and O in carbon monoxide, CO?

Solution: The oxidation number of O is -2, as C is not one of the exceptions to the oxidation number of O; therefore the oxidation number of C must be +2, because the overall charge on a molecule is zero **So ON of C = +2, ON of O = -2**

Example 2: What are the oxidation numbers of N and O in the nitrate ion, NO₃⁻?

Solution: The oxidation number of O is -2, as N is not one of the exceptions to the oxidation number of O; therefore the oxidation number of N must be +5, because the overall charge on the ion = -1 **So ON of N = +5, ON of O = -2**

- During oxidation and reduction, the oxidation numbers of atoms change:
 - If an atom is oxidized, its oxidation number increases (ie it becomes more +ve or less -ve)
 - If an atom is reduced, its oxidation number decreases (ie it becomes less +ve or more -ve)

| | | |
|------------------|-------------------|------------------------------|
| Oxidation | Loss of electrons | Increase in oxidation number |
| Reduction | Gain of electrons | Decrease in oxidation number |

Example: During a reaction, PbO₂ is converted into PbO. What has happened to the Pb in this reaction?

Answer: the ON of Pb in PbO₂ = +4; the ON of Pb in PbO = +2; so the Pb has been reduced

Example: During a reaction, CH₄ is converted into CO₂. What has happened to the C in this reaction?

Answer: the ON of C in CH₄ = -4; the ON of C in CO₂ = +4; so the C has been oxidised

- Oxidation and reduction processes involving polyatomic ions or molecules can also be expressed as half-equations, but they are more complex and often involve H⁺ and H₂O:
 - Eg The reduction of PbO₂ to Pb²⁺ can be written $\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$
 - Eg The oxidation of SO₃²⁻ to SO₄²⁻ can be written $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-$
- You will not be asked to derive these half-equations, but you will be expected to use them and to recognise them as oxidation or reduction

Lesson 3 – What are redox reactions, and what are oxidising and reducing agents?

2) Introduction to Redox reactions

- Half-equations consider gain and loss of electrons, but in fact electrons cannot be created or destroyed; they can only be transferred from species to species; the gain of electrons by one species necessarily involves loss of electrons by another; oxidation and reduction thus always occur simultaneously; an oxidation is always accompanied by a reduction and vice versa; any reaction consisting of the oxidation of one species and the reduction of another is known as a **redox** reaction
- A redox reaction can be described as a reaction which involves the **transfer of electrons from one species to another**

(i) Deriving equations for redox reactions

- A redox reaction can be derived by combining an oxidation half-equation with a reduction half-equation in such a way that the total number of electrons gained is equal to the total number of electrons lost; in some cases, H₂O and H⁺ may appear on both sides of the reaction, which must then be simplified

Eg $\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$ (reduction) and $2\text{I}^- \rightarrow \text{I}_2 + 2\text{e}^-$ (oxidation)

- the oxidation half-equation must be multiplied by 4 to equate the electrons: $8\text{I}^- \rightarrow 4\text{I}_2 + 8\text{e}^-$
- the two half-equations can then be added together:
- **$\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{I}^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O} + 4\text{I}_2$**

Eg $\text{PbO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O}$ (reduction) and $\text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^-$ (oxidation)

- the number of electrons is the same in both half-equations so multiplying one of them is not required
- adding the two half-equations together gives $\text{PbO}_2 + 4\text{H}^+ + \text{SO}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{Pb}^{2+} + 2\text{H}_2\text{O} + \text{SO}_4^{2-} + 2\text{H}^+$
- removing 2H⁺ and H₂O from both sides gives:
- **$\text{PbO}_2 + 2\text{H}^+ + \text{SO}_3^{2-} \rightarrow \text{Pb}^{2+} + \text{H}_2\text{O} + \text{SO}_4^{2-}$**

- A redox reaction can be derived by combining an oxidation half-equation with a reduction half-equation in such a way that the total number of electrons gained is equal to the total number of electrons lost; in some cases, H₂O and H⁺ may appear on both sides of the reaction, which must then be simplified

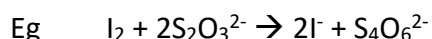
(ii) Oxidising agents and reducing agents

- The species which is reduced is accepting electrons from the other species and thus causing it to be oxidised; the reduced species is therefore an **oxidising agent**; an oxidising agent is an **electron acceptor**; it causes the oxidation number of the other species to increase
 - H₂SO₄, Al³⁺ and Cl₂ are all oxidising agents
- The species which is oxidised is donating electrons to another species and thus causing it to be reduced; it is therefore a **reducing agent**; a reducing agent is an electron donor; it causes the oxidation number of the other species to decrease

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- Na, O²⁻, I⁻ and S₂O₃²⁻ are all reducing agents

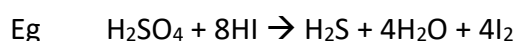
- A redox reaction can thus be described as a transfer of electrons from a reducing agent to an oxidising agent
- It is possible to identify what is oxidized and what is reduced (and hence the oxidizing agent and the reducing agent) in a chemical reaction by considering the changes in oxidation number of the different atoms:



The ON of I decreases from 0 to -1 (I₂ is reduced)

the ON of S increases from +2 to +2.5 (S₂O₃²⁻ is oxidized)

I₂ is the oxidizing agent; S₂O₃²⁻ is the reducing agent

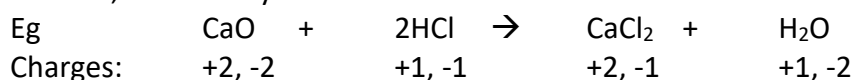


The ON of S decreases from +6 to -2 (H₂SO₄ is reduced)

the ON of I increases from -1 to 0 (HI is oxidized)

H₂SO₄ is the oxidizing agent, HI is the reducing agent

- Note - not all reactions are redox reactions; in acid-base reactions, it is H⁺ ions, not electrons, which are transferred, and usually the oxidation numbers on the atoms do not change:

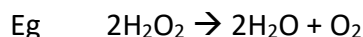


If the charges on the atoms do not change, the reaction is NOT a redox reaction

- Oxidizing agents are useful as disinfectants and in treating wounds, as the oxidation of microbes tends to kill them:
 - Swimming pools contain Cl₂, chlorox contains NaClO and I₂ is used to sterilize wounds
 - Cl₂, NaClO and I₂ are all oxidizing agents
- Reducing agents are often added to food to stop it going bad (due to oxidation); they are often referred to as “anti-oxidants”
 - Na₂SO₃ is a reducing agent; it is often added to wine (to prevent the alcohol from being oxidized into vinegar) and to some food (so they don't go bad as quickly)

(iii) **Disproportionation reactions**

- In some reactions, the same species is simultaneously both oxidized and reduced:

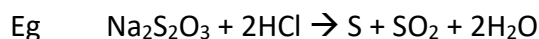


The oxidation number of O increases from -1 (in H_2O_2) to 0 (in O_2)

The oxidation number of O decreases from -1 (in H_2O_2) to -2 (in H_2O)

So H_2O_2 is oxidizing and reducing itself

H_2O_2 is the oxidizing agent and the reducing agent



The oxidation number of S increases from +2 (in $\text{Na}_2\text{S}_2\text{O}_3$) to +4 (in SO_2)

The oxidation number of S decreases from +2 (in $\text{Na}_2\text{S}_2\text{O}_3$) to 0 (in S)

So $\text{Na}_2\text{S}_2\text{O}_3$ is oxidizing and reducing itself

$\text{Na}_2\text{S}_2\text{O}_3$ is the oxidizing agent and the reducing agent

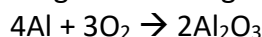
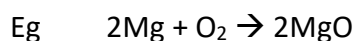
The simultaneous oxidation and reduction of the same species in a chemical equation is called **disproportionation**

Lesson 4 – How do metals react with acids?

3) Common Redox Reactions

(a) **Reaction of metals with non-metals**

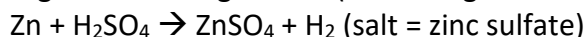
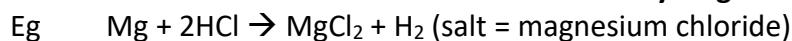
- Most metals react directly with oxygen to produce oxides:



- during these reactions, the metal is oxidised from 0 to its typical oxidation state:
eg $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$, or $\text{Al} \rightarrow \text{Al}^{3+} + 3\text{e}^-$
- the oxygen is reduced from 0 to -2 and is therefore acting as an oxidizing agent; this is where the name “oxidation” comes from
- the reaction of metals with oxygen to form oxides is an example of a redox reaction
- metals also react with other non-metals to produce binary compounds such as chlorides and sulphides; the metal is always oxidized (and so is the reducing agent) and the non-metal is always reduced (and so is the oxidizing agent)

(b) **Reaction of metals with acids**

- Most metals react with acids to make a **salt** and **hydrogen**



UNIT 5B – OXIDATION AND REDUCTION

- This reaction is an example of a **redox** reaction:
 - the metal is oxidised from 0 to +2 (in the above reactions): $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$ or $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
 - the H^+ ion in the acid is reduced from +1 to 0 (in hydrogen): $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
 - the overall equation can therefore be written: $\text{Mg} + 2\text{H}^+ \rightarrow \text{Mg}^{2+} + \text{H}_2$ or $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$
 - the metal is the reducing agent and the H^+ is the oxidizing agent
 - the chloride and sulfate ions are neither oxidized or reduced; they remain in solution, unchanged, and can be omitted from the equation; ions which are present in the reaction mixture but which do not take part in the reaction are called **spectator ions**
- The rate of reaction between metals and acids varies considerably, and many metals do not react with acids; it depends on the reactivity of the metal, which depends on the ability of the metal to give electrons to the H^+ ions; some metals lose their electrons much more easily than others; metals on the left of the Periodic Table contain the largest atoms with the weakest attraction to the nucleus; these electrons are easily lost and so these metals are the most reactive; the reactivity of metals **increases** down a group and **decreases** across a period
 - K is more reactive than Ca (fewer protons, so lower nuclear attraction, so electrons lost more easily)
 - Ca is more reactive than Mg (more shells, so more shielding, so electrons lost more easily)

(c) Reaction of metals with water

- Water also contains H^+ , ($\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$) although the H^+ ions are present in smaller concentrations than acids; some very reactive metals can react with the H^+ in water:
Eg $2\text{Na} + 2\text{H}_2\text{O} \rightarrow 2\text{NaOH} + \text{H}_2$
- In the above reaction, the Na is oxidised from 0 to +1 and the H is reduced from +1 to 0; the products are a metal hydroxide and hydrogen; if the hydroxide is soluble in water, the resulting solution will contain OH^- ions and will therefore be alkaline

Lesson 5 – What are displacement reactions?

(d) Metal displacement reactions

- A metal can displace another metal from any compound, provided that the other metal is less reactive (and therefore has a lower tendency to be oxidized):
Eg $\text{Zn} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{Cu}$
 - these reactions are known as **displacement reactions**
 - the more reactive metal (eg Zn) is oxidised from 0 to (in this case) +2 ($\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$)
 - the less reactive metal (eg Cu) is reduced from (in this case) +2 to 0 ($\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$)
 - the sulphate ion is not directly involved in the reaction (it is a **spectator ion**)
 - the equation can therefore also be written: $\text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu}$; this is called the **net ionic equation**; net ionic equations exclude spectator ions and are a good way of simplifying complex equations
 - the reverse reaction cannot happen, as copper is less reactive than zinc and so cannot displace zinc from its compounds: $\text{Cu} + \text{ZnSO}_4 \rightarrow$ (no reaction)

UNIT 5B – OXIDATION AND REDUCTION

- Reactions between metals and acids can also be described as displacement reactions; the metal is only able to displace hydrogen from acids if the metal is more reactive than hydrogen:
Eg $\text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2$; zinc is more reactive than hydrogen so can displace H from acids
(net ionic equation: $\text{Zn} + 2\text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2$)
 $\text{Cu} + 2\text{HCl} \rightarrow$ no reaction; copper is less reactive than hydrogen so cannot displace H from acids
- Many metals are found in nature (ie in their ores) as metallic oxides; during their extraction from their ores, they have to be converted from the metal oxide to the metal, this is often carried out by reacting them with a more reactive metal (or carbon or hydrogen)
Eg $\text{Fe}_2\text{O}_3 + 2\text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$ (extraction of iron from its ore)
 $\text{ZnO} + \text{C} \rightarrow \text{Zn} + \text{CO}$ (extraction of zinc from its ore)
 $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$ (extraction of copper from its ore)
 - in all of these reactions, the metal in the oxide is reduced from +2 or +3 to 0
 - the more reactive element is oxidised (H from 0 to +1, C from 0 to +2 or +4, Al from 0 to +3)
 - the reduction of metal oxides by more reactive metals (or carbon or hydrogen) is therefore an example of a redox reaction (or displacement reaction)
 - iron, copper and zinc are all extracted from their oxides commercially by reacting the oxides with carbon, because they are all less reactive than carbon
 - aluminium cannot be extracted from its oxide by reacting its oxide with carbon, because aluminium is more reactive than carbon

(e) Halogen displacement reactions

- All the Group 7 elements (**halogens**) are oxidising agents, as they can accept electrons and get reduced; they are most commonly found in the -1 oxidation state, as **halide** ions:
Eg $\text{Cl}_2 + 2\text{e}^- \rightarrow 2\text{Cl}^-$
- Fluorine is the strongest oxidising agent, followed by chlorine; iodine is a mild oxidising agent; the oxidizing power of the halogens decreases down a group; as the number of shells increases, the shielding increase and the attraction of the extra electron to the nucleus decreases; so iodine gets reduced less easily than bromine, which is reduced less easily than chlorine
- Halide ions are reducing agents; they can get oxidized back to halogens (from -1 to 0); this happens most easily with iodide ions (I^-) but is most difficult to achieve with chloride ions (Cl^-)
- The displacement reactions of halogens with halide ions provides a clear illustration of the trends in oxidizing properties of the halogens and the trends in reducing properties of the halide ions; the more reactive halogens (ie the strongest oxidising agents) will displace the more reactive halides (ie the strongest reducing agents) from solutions of their ions:
 - chlorine will displace bromide and iodide ions from solution:
 $\text{Cl}_2 + 2\text{NaBr} \rightarrow 2\text{NaCl} + \text{Br}_2$ (net ionic equation: $\text{Cl}_2 + 2\text{Br}^- \rightarrow 2\text{Cl}^- + \text{Br}_2$)
 - bromine will displace iodine from its compounds, but will not displace chlorine
 $\text{Br}_2 + 2\text{KI} \rightarrow 2\text{KBr} + \text{I}_2$ (net ionic equation: $\text{Br}_2 + 2\text{I}^- \rightarrow 2\text{Br}^- + \text{I}_2$)
 - iodine cannot displace either bromide or chloride ions from solution
 $\text{I}_2(\text{g}) + \text{MgBr}_2 \rightarrow$ no reaction

4) The Reactivity Series of Metals

- By analysing the results of metal displacement reactions, including the reactions of metals with acids, metals with water, and metals, carbon and hydrogen with metal compounds, it is possible to rank all metals (and some electropositive non-metals such as carbon and hydrogen) in order of reactivity; this is called the **reactivity series**
- The more reactive the metal, the greater its tendency to be oxidized, the more effective it is as a reducing agent, and the more difficult it is to extract from its compounds

| Metal | Notes |
|------------|---|
| potassium | very reactive – stored under oil – reacts violently with water |
| sodium | very reactive – stored under oil – reacts violently with water |
| calcium | reactive – must be kept in sealed container – reacts rapidly with water |
| magnesium | reacts rapidly with acids, very slowly with water |
| aluminium | very slow reactions with acids, water and air at room temperature* |
| (carbon) | can displace Zn and below from compounds but not Al or above |
| zinc | reacts steadily with acids |
| iron | rusts slowly in air and water |
| tin | reacts very slowly with acids |
| lead | reacts very slowly with acids |
| (hydrogen) | can displace Cu and below from compounds but not Pb or above |
| copper | no reaction with acids; very slow reaction with air and water |
| silver | no reactions with acids, air or water |
| gold | no reactions with acids, air or water |

- *Note the low apparent reactivity of aluminium, given its high position in the reactivity series; aluminium is a highly reactive metal, but quickly forms a layer of its oxide (Al_2O_3) on its surface; this oxide is very stable and unreactive, and sticks to the surface of the aluminium, significantly slowing down its reactions; for this reason, aluminium metal is relatively resistant to oxidation and is widely used in everyday materials

Lesson 6 – What are Galvanic cells?

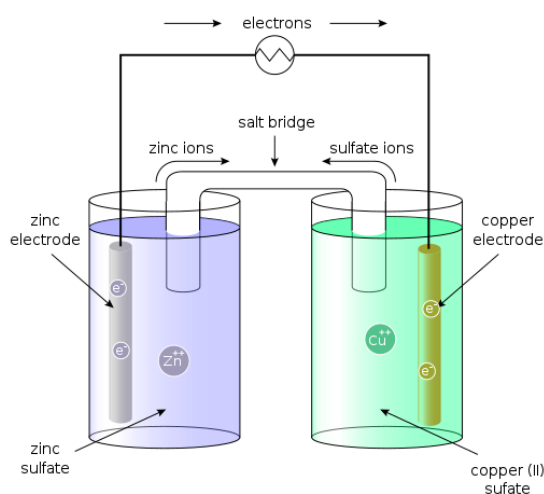
5) Galvanic Cells and Batteries

(a) Introduction to Galvanic cells

- A galvanic (or voltaic) cell is a device which uses a redox reaction to generate electricity
- The simplest example of a galvanic cell is a Daniell cell, which uses the reaction between zinc and copper sulfate to generate electricity
- Consider the reaction:

| | | | | | | |
|--------------------|---|------------------------|---|------------------------|---|-------|
| Zn | + | CuSO ₄ (aq) | → | ZnSO ₄ (aq) | + | Cu(s) |
| Oxidation numbers: | | | | | | |
| 0 | | 2 | | +2 | | 0 |

 - the Zn is oxidised to Zn²⁺: $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$
 - the Cu²⁺ is reduced to Cu: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 - the net ionic equation is: $\text{Zn} + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$
 - electrons move from the Zn to the Cu²⁺
 - the SO₄²⁻ (sulfate) ion is a spectator ion (it is present but does not take part in the reaction)
 - this reaction happens because Zn is more reactive than Cu, and hence more readily to be oxidised
- If CuSO₄ and Zn were mixed together, the electrons would move directly from the Zn to the Cu²⁺ when there was a collision between the two particles; the reaction is exothermic and so a significant amount of heat energy would be released (chemical potential energy → heat energy)
- It is possible, however, to create a device in which Zn and CuSO₄ are connected electrically, but not chemically; in this situation, the electrons cannot move directly from Zn to Cu²⁺ but can move indirectly between the two, via an electrical wire; this creates an electric current; the chemical reaction can still take place, but electrical energy is being produced instead of heat energy (chemical potential energy → electrical energy); this is an example of a galvanic (or voltaic) cell



UNIT 5B – OXIDATION AND REDUCTION

- A galvanic cell is always made up of two parts - a reduction (**cathodic**) compartment (half-cell) and an oxidation (**anodic**) compartment (half-cell)
 - each compartment consists of an electrical conductor dipped into the solution and connected to an electrical circuit; this conductor is called an **electrode** and is made of metal or graphite; the electrode in the reduction half-cell is called the **cathode** and the electrode in the oxidation half-cell is called the **anode**
 - each half-cell also consists of an aqueous solution containing ions; this solution is called the **electrolyte**
- The electrodes represent the external terminals of the cell; if you connect the two terminals to a circuit a current will flow, generating electrical power; electrons always flow from the anode (which is negatively charged) to the cathode (which is positively charged); the difference in charge between the electrodes is known as the **potential difference** or **emf** or **voltage of the cell**; a typical cell has an emf of 1 or 2 V
- In order to complete the internal circuit and stop charge building up in the solutions, the solutions must also be connected; this is done using a salt bridge or some kind of porous membrane or diaphragm; ions can move between the two solutions but do so very slowly
- This is a summary of what is going on in the Daniell cell:
 - the anode is made of Zn; Zn atoms lose electrons and move into the solution as Zn^{2+} ; the anode gets gradually smaller as a result; the electrons left behind give the anode a negative charge; the electrons move through the wire towards the anode
 - the cathode is made of Cu; as electrons arrive from the anode, the Cu^{2+} ions in the solution collect them, become Cu atoms and attach themselves to the cathode; the cathode gets gradually bigger as a result
 - the concentration of Zn^{2+} ions in the anodic half-cell gradually increases
 - the concentration of Cu^{2+} ions in the cathodic half-cell gradually decreases
 - the SO_4^{2-} ions move from the cathodic half-cell to the anodic half-cell via the salt bridge in order to balance out the charge in the solution
- Batteries are devices containing one more more cells linked together; the greater the voltage desired, the greater the number of cells which need to be linked up in a battery

(b) Important Examples of Galvanic Cells

- There are many important examples of Galvanic cells; they have a variety of uses and represent a significant area of current scientific research; three common examples are highlighted below:
- The **lead-acid Battery** was the first type of rechargeable cell to be invented
 - it is still used in cars and has several other applications, because it is able to withstand a high current flow for a short time; however it is very heavy which limits its wider use
 - the cathode is made of lead (IV) oxide; $\text{PbO}_2 + 2\text{H}^+ + \text{H}_2\text{SO}_4 + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$
 - the anode is made of lead; $\text{Pb} + \text{H}_2\text{SO}_4 \rightarrow \text{PbSO}_4 + 2\text{H}^+ + 2\text{e}^-$
 - the electrolyte in both compartments is H_2SO_4
 - when the cell is recharged, the reverse half-reactions take place at the two electrodes and so the overall reaction is also reversed

UNIT 5B – OXIDATION AND REDUCTION

- The **alkaline battery** is the most commonly used household battery, even though it is non-rechargeable
 - the cathode is made of MnO_2 ; $2\text{MnO}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{Mn}_2\text{O}_3 + 2\text{OH}^-$
 - the anode is made of Zn: $\text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$
 - the electrolyte in both compartments is KOH
- The **lithium-ion battery** is widely used in cellphones and other electronic devices; it is rechargeable and the electrolyte is a paste rather than a liquid
 - the cathode is made of CoO_2 ; $\text{CoO}_2 + \text{Li}^+ + \text{e}^- \rightarrow \text{LiCoO}_2$
 - the anode is made of Li $\rightarrow \text{Li}^+ + \text{e}^-$
 - the electrolyte is complex (and the above half-equations have also been simplified)

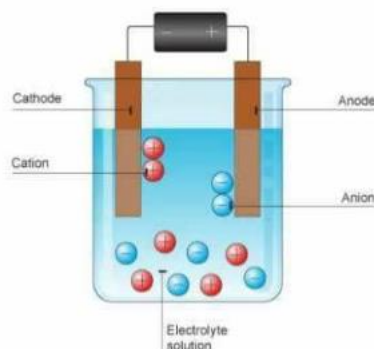
Lesson 7 – What is electrolysis?

6) Electrolysis

(a) Principles of Electrolysis

- Electrolysis is the use of an electric current to force a chemical reaction to take place which would not otherwise happen spontaneously
- If two electrodes are dipped into an electrolyte (ie any liquid containing ions) and a potential difference is applied across the electrodes, the anions in the solution will move towards the positively charged electrode (known as the anode) and the cations in the solution will move towards the negatively charged electrode (known as the cathode)
- Once the anions reach the anode, they are oxidised, usually to a non-metallic element (O^{2-} and OH^- ions are oxidised to O_2 , Cl^- ions are oxidised to Cl_2)
- Once the cations reach the cathode, they are reduced, usually to a metallic element or hydrogen (Cu^{2+} ions are reduced to Cu and H^+ ions are reduced to H_2)
- Electrolysis can be used to separate the components of any liquid provided it contains electrolytes; it is most commonly used to separate ionic compounds into their elements
- In most cases graphite electrodes are used, as they are cheap and relatively inert; if it is likely that graphite will cause a reaction of its own, platinum electrodes are used (these are more expensive)
- The apparatus in which electrolysis takes place is called an **electrolytic cell**; electrolytic cells are used to convert electrical energy into chemical energy; this is the opposite of a Galvanic cell, in which chemical energy is converted into electrical energy; an example of an electrolytic cell is shown below:

UNIT 5B – OXIDATION AND REDUCTION



(b) Electrolysis of molten binary ionic compounds

- Ionic compounds conduct electricity when molten as the ions are free to move:
 - almost all binary ionic compounds can be separated into their elements by electrolysis
 - for very reactive metals (such as sodium and potassium) and very reactive non-metals (such as fluorine) this is often the only way to make the pure element, as they are too reactive to be displaced chemically
 - the preparation of reactive elements by electrolysis of their molten compounds is very expensive, as lots of energy is needed (to first melt the compound and then electrolyse it)
- **eg molten sodium chloride** contains Na^+ and Cl^- ions
 - During electrolysis, the Na^+ ions move to the (iron) cathode where they are reduced, and the Cl^- ions move to the (graphite) anode where they are oxidised
 - Sodium is produced at the cathode: $\text{Na}^+ + \text{e}^- \rightarrow \text{Na}$
 - chlorine is produced at the anode: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - this is the reaction used in the industrial preparation of sodium
- **eg molten aluminium oxide** contains Al^{3+} and O^{2-} ions
 - During electrolysis, the Al^{3+} ions move to the graphite cathode where they are reduced, and the O^{2-} ions move to the graphite anode where they are oxidised
 - aluminium is produced at the cathode: $\text{Al}^{3+} + 3\text{e}^- \rightarrow \text{Al}$
 - oxygen is produced at the anode: $2\text{O}^{2-} \rightarrow \text{O}_2 + 4\text{e}^-$
 - the graphite anodes react with oxygen and so need to be regularly replaced
 - this is the reaction used in the industrial preparation of aluminium; it is an extremely important industrial process

(c) Electrolysis of aqueous ionic compounds

- Ionic compounds also conduct electricity when dissolved in water, as the ions are able to move; it is therefore possible to electrolyse aqueous solutions; this is much cheaper (and safer) as the ionic compound does not need to be heated to its melting point]
- Aqueous solutions, however, contain H^+ ions and OH^- ions due to the water present, as well as any ions which dissolve in water; this means that there is often a choice of cation to be reduced and a choice of anion to be oxidised

UNIT 5B – OXIDATION AND REDUCTION

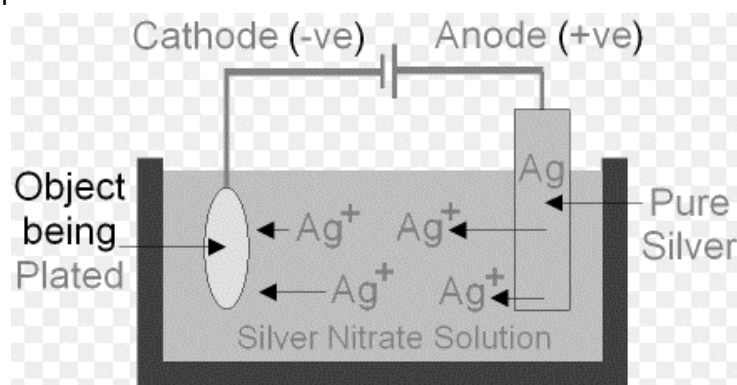
- When there is a choice of cation to be reduced, the cation which is easier to reduce will be reduced; this can generally be predicted from the reactivity series of metals; the less reactive the metal, the more easily the cation can be reduced:
 - most metals are above hydrogen in the reactivity series, so the hydrogen ions in water will be reduced
 - the half-equation for this is: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
 - so if aqueous solutions containing Zn^{2+} , Fe^{2+} , Pb^{2+} , Ca^{2+} etc are electrolysed, **hydrogen** will be produced at the cathode; the metal ion will remain in solution
 - copper and silver are below hydrogen in the reactivity series, so if solutions containing Cu^{2+} or Ag^+ ions are electrolysed, the **metal (copper or silver)** will be produced at the cathode and hydrogen ions will remain in solution
- When there is a choice of anion to be oxidised, the anion which is easier to oxidise will be oxidised; there is no simple way to predict this:
 - NO_3^- , SO_4^{2-} and CO_3^{2-} are much more difficult to oxidise than OH^- ions, so in aqueous solutions containing these ions, the OH^- ions will be oxidised
 - the half-equation for this is: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
 - so if aqueous solutions containing NO_3^- , SO_4^{2-} or CO_3^{2-} are electrolysed, **oxygen** will be produced at the anode
 - Br^- and I^- are easier to oxidise than OH^- ions, so in aqueous solutions containing these ions, the halogen (**bromine** or **iodine**) will be produced at the anode and the hydroxide ions will remain in solution
 - Cl^- and OH^- ions have a similar tendency to be oxidised, so if an aqueous solution containing Cl^- ions is electrolysed, the gas produced at the anode depends on the concentration of the Cl^- ions; in dilute solutions of Cl^- ions, OH^- ions are oxidised preferentially and oxygen is produced; in concentrated solutions of Cl^- ions, Cl^- ions are oxidised preferentially and **chlorine** is produced
- **Eg dilute aqueous sodium chloride** contains Na^+ and Cl^- ions, but it also contains water, which contains H^+ and OH^- ions
 - Hydrogen is less reactive than sodium, so H^+ ions in H_2O are reduced at the cathode:
$$2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$$
 - As the concentration of Cl^- ions is low, OH^- ions in H_2O are oxidised at the anode and oxygen gas is produced: $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
 - the overall reaction is: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$, the Na^+ and Cl^- ions remain in the solution, which becomes gradually more concentrated
- **Eg concentrated aqueous sodium chloride (brine)** contains the same ions as dilute aqueous sodium chloride but the concentration of Na^+ and Cl^- ions is much higher
 - H^+ ions in H_2O are still reduced at the cathode: $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
 - due to the high concentration of Cl^- ions, Cl^- ions and not OH^- ions are oxidised: $2\text{Cl}^- \rightarrow \text{Cl}_2 + 2\text{e}^-$
 - the overall reaction is: $2\text{NaCl} + 2\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{Cl}_2 + 2\text{NaOH}$, so the solution gradually turns into sodium hydroxide
 - the electrolysis of brine is used industrially to produce both sodium hydroxide and chlorine

UNIT 5B – OXIDATION AND REDUCTION

- **Eg dilute sulphuric acid** contains H^+ and SO_4^{2-} ions, but it also contains water, which contains H^+ and OH^- ions
 - H^+ is the only cation in the solution; it is reduced at the cathode: $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$
 - SO_4^{2-} ions are very difficult to oxidise, so OH^- ions in H_2O are oxidised at the anode:
 $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
 - the overall reaction is: $2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2$, so just as with dilute sodium chloride, this reaction is effectively the electrolysis of water; the sulphuric acid solution becomes gradually more concentrated
- **Eg copper sulphate solution** contains Cu^{2+} and SO_4^{2-} ions, but it also contains water, which contains H^+ and OH^- ions
 - copper is less reactive than hydrogen, so Cu^{2+} ions are reduced at the cathode: $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu}$
 - SO_4^{2-} ions are very difficult to oxidise, so OH^- ions in H_2O are oxidised at the anode:
 $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$
 - the overall reaction is: $2\text{CuSO}_4 + 2\text{H}_2\text{O} \rightarrow 2\text{Cu} + \text{O}_2 + 2\text{H}_2\text{SO}_4$, so the solution gradually turns into sulfuric acid

(d) Electroplating

- **Electroplating** is the use of electrolysis to cover the surface of one metal with a thin layer of another metal
 - it can be used either to protect or to decorate the metal
 - the metal to be plated is used as the cathode in an electrolytic cell
 - the electrolyte should contain the cations of a metal it is to be plated with
 - for example, to electroplate a copper vessel with a thin layer of silver, the vessel should be used as the cathode in the electrolytic cell and the electrolyte should be silver nitrate (AgNO_3); it is common for the anode also to be made of the metal you want to plate the metal with



- the Ag^+ ions move to the cathode and are reduced to Ag , covering the vessel with a thin layer of silver ($\text{Ag}^+ + \text{e}^- \rightarrow \text{Ag}$)
- electroplating with silver is commonly used to improve the appearance of cutlery, crockery and jewellery

UNIT 5B – OXIDATION AND REDUCTION

Summary – types of electrochemical cell

There are two types of electrochemical cell – galvanic cells and electrolytic cells

All cells involve redox reactions
Reduction always takes place at the cathode
Oxidation always takes place at the anode

| Type | galvanic | electrolytic |
|----------------------------|--|---|
| purpose | Use a chemical reaction to create a voltage | Use electricity to separate an ionic compound into its elements or to reverse a redox reaction in a galvanic cell |
| energy change | Chemical potential → electrical | Electrical → chemical potential |
| use | Batteries | Extracting reactive metals from their ores, charging batteries, electroplating |
| design | - electrodes immersed into two separate electrolytes which are connected only by a salt bridge - in simple cells, electrodes are made of the same metal as the cation in the solution they are in | - electrodes immersed into one electrolyte (except when charging batteries) - electrodes usually made of graphite |
| terminals | Cathode (reduction) is +ve Anode (oxidation) is -ve | Cathode (reduction) is -ve Anode (oxidation) is +ve |
| chemical reaction | - can be any redox reaction - the simplest cells involve metal displacement reactions; the more reactive metal is oxidised and the less reactive metal is reduced | - in molten binary electrolytes, the compound is separated into its elements - in aqueous solutions, either the ionic compound or water can be separated into its elements |
| ion movement | (simple cells only) - the metal atoms at the anode are oxidised and move into the anodic solution as cations - the metal cations in the cathodic solution are reduced and move onto the electrode - the anions move from the cathodic solution to the anodic solution via the salt bridge | - cations move to the cathode and are reduced - anions move to the anode and are oxidised |
| changes at the electrodes | (simple cells only) - anode gets smaller - cathode gets bigger | - either a metal or hydrogen is produced at the cathode - a non-metal is produced at the anode |
| changes to the electrolyte | (simple cells only) - anodic solution gets more concentrated - cathodic solution gets less concentrated | - if hydrogen and oxygen are both produced, the electrolyte doesn't change but will get more concentrated (water is electrolysed) - if hydrogen but not oxygen are produced, the electrolyte will become more alkaline (OH ⁻) - if oxygen but not hydrogen is produced, the electrolyte will become more acidic (H ⁺) - if neither hydrogen nor oxygen is produced, or you have a molten electrolyte, the electrolyte will get less concentrated |