

OCR (B) Chemistry A-level

Storyline 3: Elements from the Sea Detailed Notes

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Formulae, Equations and Amount of Substance

Atom Economy

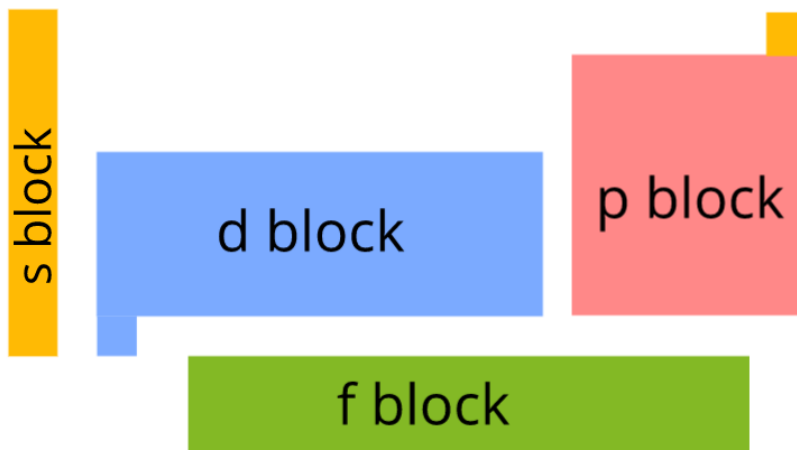
$$\% \text{ atom economy} = \frac{\text{Mr of desired product} \times 100}{\text{Mr of reactants}}$$

In industrial chemical processes, it is desirable to have a **high atom economy** for a reaction. This means there is **little or no waste product**, only the desired product. This means the process is more **economically viable** for industrial-scale manufacturing. It also helps to **preserve raw materials**.

Redox

Electrons are contained within **orbitals**. These orbitals correspond with **blocks** on the Periodic Table. Each element in the block has **outer electrons in that orbital**.

Example: The blocks of the periodic table



It is also possible to predict an element's ionic charge from its position in the **periodic table**:

- Group 1 metals lose an electron to **form 1+ ions**.
- Group 2 metals lose two electrons to **form 2+ ions**.
- Group 7 elements gain an electron to form a **1- ion**.
Group 7 elements are known as the **halogens** and their negative ions are known as **halide ions**.





Redox reactions

A redox reaction is a reaction in which **oxidation and reduction** take place. Oxidation is the loss of electrons, or increase in oxidation number. Reduction is the gain of electrons, or decrease in oxidation number.

This redox rule is remembered using the acronym **OILRIG** (**O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain).

Disproportionation is when a species is simultaneously reduced and oxidised to give two different products. For example:



Oxidation Numbers

Oxidation numbers are useful to show what is being oxidised and reduced in a redox reaction. Below are some rules to follow when assigning oxidation states:

- The oxidation number of an **element is zero** (this is still true when the element has a molecular structure like O_2 or a giant structure like carbon).
- In **neutral compounds**, the **sum of the oxidation states** of all the atoms is **0**.
- Oxidation numbers in a charged compound add up to the **total charge**.
- **More electronegative** elements in a substance have a **negative** oxidation state while **less electronegative** elements have a **positive** oxidation state.
- **Hydrogen** has an oxidation number of **+1**.
- **Oxygen** has an oxidation number of **-2**.
- **Halogens** have an oxidation number of **-1**.
- **Group I** metals have an oxidation number of **+1**.
- **Group II** metals have an oxidation number of **+2**.

However, there are some **exceptions** to these rules:

- **Oxygen** has an oxidation number of **-1** in **peroxides**.
- **Hydrogen** has an oxidation number of **-1** in **metal hydrides**.

These rules are summarised in the table below:

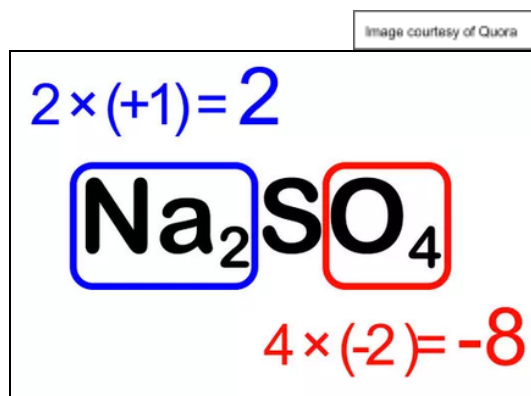




Element	Oxidation number
Group 1 metals	+1
Group 2 metals	+2
Oxygen	-2 (usually)
Hydrogen	+1 (usually)
Fluorine	-1
Hydrogen in metal hydride (HX)	-1
Oxygen with fluorine	+2
Oxygen in peroxides	-1

These rules can be used to work out the oxidation number of species or elements in a reaction.

Example:



This compound is neutral, so the oxidation numbers must total zero. Therefore, using the rules above, the oxidation number of sulfur can be found.

$$2 - 8 + x = 0$$

$$-6 + x = 0$$

$$x = 6$$

Roman numerals can be used to give the oxidation number of an element that has a **variable oxidation state**, depending on the compound it's in.





Example:

Copper(II) sulphate - this tells you the oxidation number of copper is +2

Iron(II) sulphate(VI) - this tells you the oxidation number of iron is +2 and the oxidation number of sulphur is +6

Oxidising and Reducing Agents

An oxidising agent **accepts electrons** from the species that is being oxidised. Therefore, it **gains electrons** and is **reduced**. This is seen as a **reduction** in oxidation number for the oxidising agent (gets less positive).

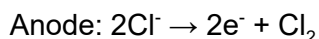
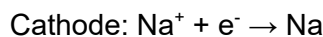
A reducing agent **donates electrons** to the species being reduced. Therefore, it **loses electrons** and is **oxidised**. This is seen as an **increase** in oxidation number for the reducing agent (gets more positive).

Electrolysis

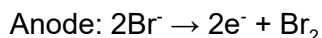
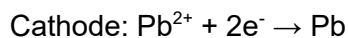
Electrolysis is the **decomposition of a molten or aqueous ionic compound** (an electrolyte) by passing an **electric current** through it. The solution must contain a cathode (negative electrode) and an anode (positive electrode).

When the electrolyte is molten, cations (positive ions) move to the cathode and gain electrons to form atoms. Anions move towards the anode and lose electrons to form atoms. Examples are shown below:

- Electrolysis of aqueous NaCl:

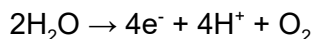


- Electrolysis of molten lead(II) bromide:

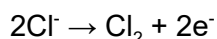


When using inert electrodes to electrolyse a solution, if the metal ions are **below hydrogen** in the **electrochemical series** (more positive E^\ominus), the metal atoms will be produced at the cathode. If the metal is above hydrogen in the electrochemical series, hydrogen gas will be produced at the cathode.

Generally, when a solution is electrolysed using **inert electrodes**, **oxygen** is produced at the anode:



However, if concentrated chlorine ions are present, **chlorine** will form:

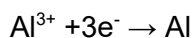




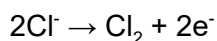
When electrolysing a solution with **non-inert electrodes**, the same reaction takes place at the cathode. At the anode, atoms in the anode lose electrons to form ions in the electrolyte. The net charge is a transfer of an element from the **anode to the cathode**.

Half Equations

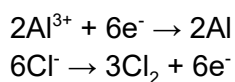
Half equations show the reactions occurring at each of the electrodes during electrolysis. When a substance gains electrons it is said to be **reduced**, this occurs at the negative electrode. For example:



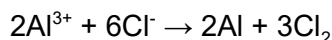
When a substance loses electrons it is said to be **oxidised**, this occurs at the positive electrode. For example:



To balance **half equations** the number of electrons in each equation must be the same so they can be combined and cancelled out. Using the two half equations above:



Now there are 6 electrons on either side they can be cancelled out to form a **full equation**.

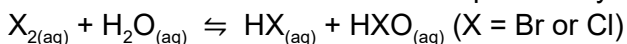


Halogen Extraction

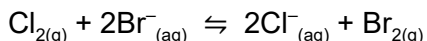
The halogens are in **group 7** of the periodic table (F, Cl, Br, etc.) and can be extracted from minerals in the sea. The extraction of bromine from the sea can be completed in 4 stages:

1) **Oxidation** of Br^{-} to Br_2

The water is first acidified using sulfuric acid to stop the halogens reacting with water, as this would lead to a loss of bromine product by the following reaction.



Then, excess chlorine is used to **displace** bromine by the following reaction.



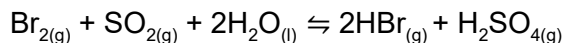
The **oxidation state** of chlorine changes from 0 to -1 (**reduction**), while the **oxidation state** of bromine changes from -1 to 0 (**oxidation**).

2) The bromine vapours are removed.

3) **Reduction** of Br_2 to HBr

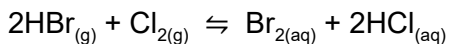
Sulfur dioxide, water and bromine vapours react to form hydrogen bromide - this is a much more **concentrated** solution than the bromine in seawater.





4) **Oxidation** of hydrogen bromide to bromine.

Steam and chlorine are used to oxidise the bromide ions to reform bromine.



The bromine is then dried using concentrated sulfuric acid.

Naming Ionic Compounds

Ionic compounds are named in a systematic way. This means each formula has a scientific name which is **unambiguous** and can only refer to one compound.

- An ionic compound is named first by its **cation and then its anion**.
- The charge/oxidation state of the cation (if it has multiple charges) is written using **Roman numerals** in parentheses next to the name of the ion.
- The net charge of the compound must be **zero**. The ratio of anions to cations in the molecular formula will therefore be such that there is no overall charge.

Example:

Iron(II) Sulfate, Fe has an oxidation state/charge +2, and sulfate has the formula SO_4^{2-} so a charge of 2-. Therefore, to give a compound with an overall charge of zero, the ions will be present in a 1:1 ratio. So the formula is FeSO_4 .

Inorganic Chemistry and the Periodic Table

Halogens

The Group 7 elements are **highly reactive nonmetals**. The halogens exist as **diatomic** molecules with single covalent bonds. In reactions, in order to achieve a full outer shell, the halogens gain an electron and form a **1- ion**.

Appearance

The colour and state of the halogens at room temperature and pressure are listed below:

Fluorine - pale yellow gas

Chlorine - pale green gas

Bromine - red/brown liquid

Iodine - dark grey solid which sublimes to a purple vapour

Volatility

The **volatility** of the halogens **decreases** down the group as the boiling point increases. This trend is highlighted by the physical state of the halogens at room temperature as you move down the group - fluorine (gaseous) to iodine (solid).





Solubility in Water

Fluorine reacts violently in water so its solubility is hard to measure. The solubility of the other halogens in water has no trend as they all dissolve sparingly in water at 25°C:

Halogen	Solubility/mol dm ⁻³	Colour in solution
Chlorine	0.091	Green
Bromine	0.21	Orange/Red
Iodine	0.0013	Brown

Solubility in Organic Solvents

Halogens are more soluble in organic solvents than water. This is because halogens are non-polar molecules, so are more soluble in non-polar solvents like hexane.

Reactivity

Halogens have s²p⁵ outer shell **electron configuration**. When halogen atoms react, they tend to gain an electron. As their atomic radius increases, this becomes harder as the positive attraction of the nucleus is weakened by additional **shielding**. Therefore, as you move down group 7 it becomes harder to attract an electron so **reactivity decreases**.

Oxidising Power of the Halogens

The halogens act as good **oxidising agents** as they accept electrons from the species being oxidised and are themselves reduced. This oxidising power **decreases down the group** as their ability to attract electrons decreases due to shielding and a greater atomic radius.

From this table, you can observe the halogen displacement **basic trend**:

'A halogen will displace a halide from a solution if the halide ion is below it in the periodic table.'

Halogen/ Halide	Cl ₂	Br ₂	I ₂
Cl ⁻	No reaction	No reaction	No reaction
Br ⁻	Cl ₂ + 2Br ⁻ → 2Cl ⁻ + Br ₂ Solution goes from colourless to orange .	No reaction	No reaction
I ⁻	Cl ₂ + 2I ⁻ → 2Cl ⁻ + I ₂ Solution goes from colourless to brown .	Br ₂ + 2I ⁻ → 2Br ⁻ + I ₂ Solution goes from orange to brown .	No reaction





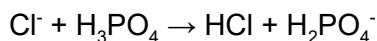
Characteristic Reactions of Halide Ions

When combined with acidified **silver nitrate**, halide ions react to form different **coloured precipitates**, depending on the ion present. The precipitates formed can be used to identify which halide is present in a solution. It may not always be clear to distinguish the colour of the precipitate so they can be tested further by observing how they react with **ammonia**.

Halide ion	Cl ⁻	Br ⁻	I ⁻
+ AgNO ₃	White precipitate (AgCl)	Cream precipitate (AgBr)	Yellow precipitate (AgI)
+ dilute NH ₃	Precipitate dissolves	No change	No change
+ conc. NH ₃	Precipitate dissolves	Precipitate dissolves	No change

Preparation of HCl, HBr and HI

HCl is prepared using **concentrated phosphoric acid** and a solid chloride like sodium chloride. The phosphoric acid donates a hydrogen ion to the chloride ion to make hydrogen chloride, which is a gas.



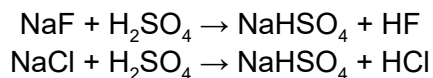
The method is used to make hydrogen bromide and hydrogen iodide.

Sulfuric acid can be used for making hydrogen chloride but not hydrogen bromide or iodide, this is because sulfuric acid is a good **oxidising agent** and would further oxidise hydrogen bromide and iodide to bromine and iodine. This only occurs with bromine and iodine and not chlorine as they are stronger **reducing agents**. The secondary reactions that occur with bromine and iodine can be seen below.

Reactions with Concentrated Sulfuric Acid

All halide ions react with **concentrated sulfuric acid** to produce a **hydrogen halide**. A secondary reaction then takes place, which differs depending on the halide present.

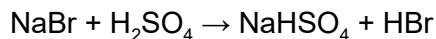
Reaction of **NaF** and **NaCl** with H₂SO₄



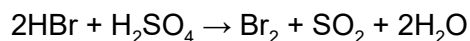
For both of these reactions, HF and HCl can be identified as **misty fumes**. HF and HCl are **not strong enough reducing agents** so no further reactions occur.

Reaction of **NaBr** with H₂SO₄

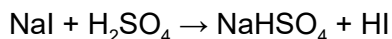




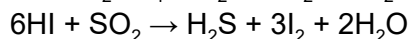
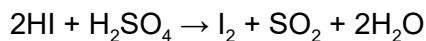
Misty fumes of HBr are produced. HBr is a strong enough **reducing agent** to react with H_2SO_4 . This second reaction produces the **choking gas SO_2** and **brown fumes of Br_2** in a **redox reaction**:



Reaction of **NaI** with H_2SO_4



Misty fumes of HI are produced. HI is a strong enough **reducing agent** to react with the H_2SO_4 . Similarly to the reaction above, **SO_2** is produced. Since HI is a **very strong reducing agent**, the SO_2 is further reduced to **H_2S** - which smells of **rotten eggs**.



The **greater** the reducing power of the halide, the **further** the reaction will proceed as the halide is powerful enough to reduce more species. These reactions, therefore, represent the trend in reducing power in halide ions. Clearly, **reducing power increases** down Group 7.

Thermal Stability of the Hydrides

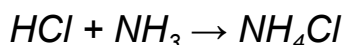
The **thermal stability** of a hydride is how easily a hydrogen halide is broken up into its constituent elements when heated.

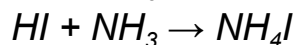
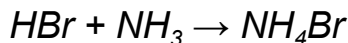
- **Hydrogen fluoride** and **hydrogen chloride** are **very thermally stable**. They will not split into hydrogen and the halogen if heated under laboratory conditions.
- **Hydrogen bromide** will **split** into hydrogen and bromine when **heated**.
- **Hydrogen iodide** will split into hydrogen and iodine **more easily than hydrogen bromide**.

These reactions show that **thermal stability of the hydrides decreases down Group 7**. This is because further down the group, the **covalent bonds are weaker** so they can be broken more easily upon heating. The bonds are weaker further down the group because the halogen atoms get larger. This means that the **bonding pair gets further away from the nucleus** so the attraction gets **weaker** and the bond is easier to break.

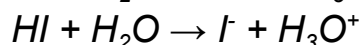
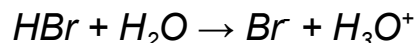
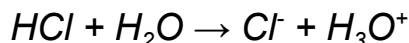
Reactions of Hydrogen Halides

Hydrogen halides react with ammonia gas to form **ammonium salts**. The hydrogen halides (hydrogen chloride, hydrogen bromide and hydrogen iodide) are strong acids in solution and react with ammonia in an **acid-base reaction** to form a salt.





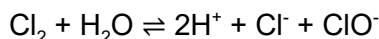
Hydrogen halides react with water to form **dilute acids**. In solution, these strong acids **dissociate** to release their halide ions and hydrogen ions. The hydrogen ions form a **hydroxonium ion (H_3O^+)** with water molecules in solution. The resulting solution is **acidic**.



Chlorine in Water Purification

Chlorine is used in water purification because it **kills bacteria**.

Chlorine reacts with water in a **disproportionation** reaction, producing chloride (Cl^-) and chlorate ions (ClO^-). The reaction produces HCl , so an **alkali** is usually added to the water to **reduce the acidity**.



Chlorate ions kill bacteria so treating water with chlorine or chlorate ions makes it safe to drink or swim in.

Chlorine treats water in different ways:

- **Kills dangerous microorganisms** that could cause diseases.
- Some chlorine persists in the water which **prevents reinfection** in the long term.
- Prevents the growth of **algae**.
- **Removes bad tastes** and smells.
- Removes **discolouration**.

Chlorine is **toxic** so there are **debates** about whether chlorine should be added to water. In addition to this, chlorine can react with organic matter in the water, forming potentially **cancer-causing** compounds. On balance, since only a small amount of chlorine is added, it is agreed that the **benefits outweigh the risks**.

Equilibria

Dynamic Equilibrium

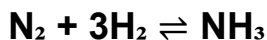
Reversible reactions are reactions in which the products of a reaction can react together to reform the original reactants. They are represented using a **double arrow**. In each reaction





system, one reaction direction will be **endothermic** and the opposite reaction direction will be **exothermic**.

Example:



Reversible reactions will eventually reach a state of **dynamic equilibrium**. Dynamic equilibrium exists in a closed system when the **rate** of the forward reaction is **equal** to the rate of the reverse reaction. At this point, the **concentrations** of the reactants and products remain **constant**.

Dynamic equilibrium can only occur in **closed systems** where no substances can get in or out.

Opposing Change (Le Chatelier's Principle)

This method is used to predict how an equilibrium mixture will change if the **reaction conditions are altered**. It states:

When a system is subject to a change in conditions, the position of equilibrium will shift to lessen the effect of that change.

It is a useful principle to consider in industrial manufacturing, since the reaction conditions can be altered to **maximise the yield** of a desired product.

Effect of Changing Temperature

If you **increase** the temperature, the position of equilibrium will shift to favour the **endothermic reaction** (+ve ΔH), because the excess heat needs to be removed from the system to lessen the effect of the initial increase. It will increase the yield of the products of the endothermic reaction.

Likewise, if you **decrease** the temperature, the position of equilibrium will shift to favour the **exothermic reaction** (-ve ΔH), because heat needs to be gained. It will increase the yield of the products of the exothermic reaction.

In exam questions, the **ΔH of the forward reaction will be given** so it is clear which direction is endothermic and which is exothermic.

Effect of Changing Pressure

Increasing pressure favours the side of the reaction with **fewer moles** of gas, as this helps to release the buildup in pressure. It will increase the yield of the products on the side of the equilibrium with the fewest moles of gas.

Likewise, **decreasing** pressure favours the side of the equilibrium with **more moles**, as pressure has been lost. The yield of the products on this side of the reaction will be increased.





Effect of Changing Concentration

Increasing the concentration of the reactants will favour the **forward** reaction that **produces the products** as more molecules are available to react. It will increase the yield of the products on the right-hand side of the reaction.

Likewise, **decreasing** the concentration of reactants will favour the **reverse** reaction that **reforms the reactants**.

Effect of Adding a Catalyst

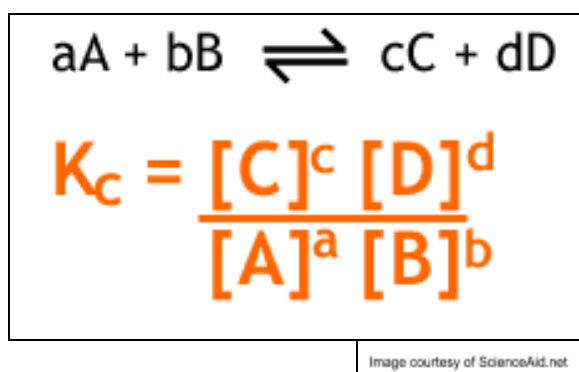
Catalysts do not affect the equilibrium position as they **increase the rate of the forward and backward reactions equally**. This means they allow equilibrium to be reached **faster** but have no effect on the position of equilibrium.

The Equilibrium Constant, (K_c)

For reversible reactions, there is an equilibrium constant, K_c , that indicates the **position of equilibrium** for a reaction at a certain temperature. K_c for a reaction always has the **same value** unless the reaction conditions are changed, which in turn changes the position of equilibrium and hence K_c .

In order to find the value of K_c , the **concentrations** of the reactants and products at equilibrium must be known. K_c is equal to the **concentration of the products divided by the concentration of the reactants**. Any variation in the number of moles **raises the concentration of that substance to a power** with the same value as the number of moles.

Example:

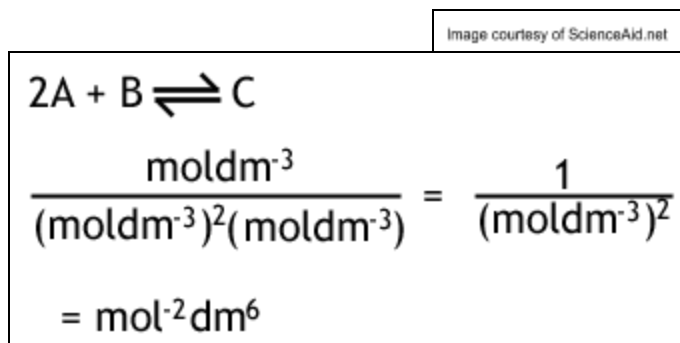


The equilibrium constant has **varying units** depending on the chemical reaction. The units can be found by **subbing the concentration units into the K_c expression**. Some of these then cancel to give the overall units of K_c for that reaction.





Example:



The value of K_c is **not affected by concentration change or use of a catalyst**, however, it is affected by changing the reaction **temperature**, as this changes the position of the equilibrium and therefore results in different concentrations of reactants and products.

Concentration changes and the addition of a **catalyst** affect the **rate** of the reaction (the kinetics) but not the **position** of the equilibrium. They only affect how fast the system reaches equilibrium, hence they have **no impact** on the equilibrium constant.

The **position of equilibrium** can be estimated by the **magnitude** of the value of **K_c** . A large value for K_c indicates that product formation is favourable and the position of equilibrium will be far to the right. A small value for K_c indicates the opposite.

