Cambridge GCSE Notes 5070 Chemistry

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1 Electrochemistry

1.1 Electrolysis

Electrolysis is the decomposition of an ionic compound, in molten or aqueous form, by passage of electric current.

A simple electrolytic cell consists of two electrodes, the cathode and anode, connected to either side of a battery and an electrolyte. The anode is positively charged whereas the cathode is negatively charged. The electrolyte is the aqueous or molten substance that undergoes decomposition through electrolysis.

In the external circuit consisting of wires connected to the batteries, electrons flow from the battery to the cathode, making the cathode negatively charged. Here electrons are lost to substances in the electrolyte which are oxidised. The anode, being positively charged, attracts the negative ions from the ionic compound, oxidising them, by taking their excess electrons electrons. Electrons are gained at the anode from negative ions, and are lost at the cathode to positive ions. The electrodes can be made of any conductive material, such as metals or graphite. Graphite electrodes are said to be inert as they do not take part in the reaction. Note that, oxidation occurs at anodes and reduction occurs at cathodes.

In case of the substance, lead (II) bromide, PbBr₂, the following happens during electrolysis with inert electrodes at either electrode:

at anode:
$$2\,\mathrm{Br}^- \longrightarrow \mathrm{Br}_2 + 2\,\mathrm{e}^-$$
 at cathode: $\mathrm{Pb}^{2+} + 2\,\mathrm{e}^- \longrightarrow \mathrm{Pb}$

It is observed that a silvery solid accumulates at the cathode, i.e. lead (II) and a red-brown gas is given off at anode. Note that, from here we can judge that for molten ionic compounds, the metal part of the compound will always form at the cathode, and the non metal will form at the anode.

During electrolysis of concentrated aqueous sodium chloride, using inert electrodes, the following reactions occur at the electrodes:

at anode:
$$2 \operatorname{Cl}^- \longrightarrow \operatorname{Cl}_2 + 2 \operatorname{e}^-$$

at cathode: $\operatorname{H}^+ + 2 \operatorname{e}^- \longrightarrow \operatorname{H}_2$

It is observed that a colourless gas is given off at cathode and a green gas is given off at the anode.

The reason why the metal, i.e., sodium is not discharged at the cathode is because it is not the least reactive amongst the cations present in the electrolyte. The ions present in the electrolyte are: H⁺, Na⁺, Cl⁻ and OH⁻. Of these, at the cathode the ion discharged is the least reactive of the cations, and at the anode the ion discharged is the ion that loses electrons more readily, and is hence easier to discharge. The reactivity series of cations and the prefential discharge rule of anions are given below:

$$Na^+ > Mg^{2+} > Al^{3+} > Zn^{2+} > H^+ > Cu^{2+} > Ag^{+[1]}$$

^[1] where the ion to the left of > is more reactive than the ion to the right.

$$SO_4^{2-} < NO_3^- < OH^- < Cl^- < Br^- < I^{-[2]}$$

During the electrolysis of dilute sulfuric acid, the ions in the electrolyte are: $\mathrm{H^+}$, $\mathrm{OH^-}$, $\mathrm{SO_4^{2-}}$. The only cation, $\mathrm{H^+}$ is released at the cathode and, by preferential rule, $\mathrm{OH^-}$ is the one which is oxidised at anode.

at cathode:
$$2 H^+ + 2 e^- \longrightarrow H_2$$

at anode: $4 OH^- \longrightarrow O_2 + 2 H_2 O + 4 e^-$

Colourless gases are given off at both electrodes, but the volume of oxygen produced is half that of hydrogen. This is a result of the fact that, the mole ratio of oxygen to hydrogen in the electrolyte is 1:2.

Consider the case of the electrolysis of aqueous copper (II) sulfate using inert electrodes. Uncharged copper (Cu) has a pinkish-orange colour, whereas copper ions, Cu^{2+} have a blue colour. The following happens at the electrodes in this electrolysis:

at cathode:
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$
 at anode: $OH^{-} \longrightarrow O_{2} + 2H_{2}O + 4e^{-}$

Notice that, the copper ions are reduced to copper, reducing the number of copper ions in electrolyte. It is observed that the blue colour of solution fades and a pinkish orange solid accumulates on the cathode.

An active electrode is that which takes part in the electrolytic process. Consider the case of the electrolysis of aqueous copper (II) sulfate with copper electrodes. It is seen that copper deposites on the cathode and copper is dissolved at the anode.

at cathode:
$$Cu^{2+} + 2e^{-} \longrightarrow Cu$$

at anode: $Cu \longrightarrow Cu^{2+} + 2e^{-}$

This property of active electrodes and metals comes in use during electroplating, which is a process of electrolysis in which a metal object is coated/plated with a layer of another metal.

To electroplate a metal object, we must place it as the cathode, and have the anode be the metal with which we want to plate the metal object. The electrolyte must be the solution of a salt with the metal to plate with.

1.2 Hydrogen-oxygen fuel cells

It is possible to use chemical reactions to produce electrical energy. Everyday batteries work in this way. A more efficient method would be using a fuel cell. A hydrogen oxygen fuel cell uses the following chemical reaction

$$2 H_2(g) + O_2(g) \longrightarrow 2 H_2O(l)$$

Here, the hydrogen is considered to be a non-polluting fuel.

As a fuel, hydrogen is more efficient than any other, and the only waste product formed is water. However, due to it being difficult to produce and unsafe to store, it has failed to gain precedence.

^[2] where the ion to the left of < is less likely to be discharged than that to the right.

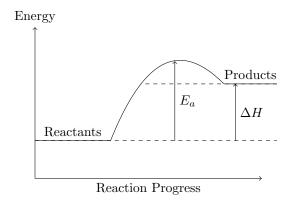
2 Chemical energetics

2.1 Exothermic and endothermic reactions

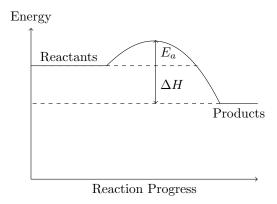
An exothermic reactions transfers thermal energy to the surroundings leading to an increase in the temperature of the surroundings. An endothermic reaction takes in thermal energy from the surroundings leadin gto a decrease in the temperature of the surroundings.

The transfer of energy during a reaction is caleed the enthalpy change, ΔH of the reaction. The value is negative for exothermic reactions and positive for endothermic reactions.

Activation energy, E_a is the minimum energy that colliding particles must have to react.



Endothermic Reaction



Exothermic Reaction

Above are reaction pathway diagrams, showing the energy of a reaction as it progresses. The energy of products is greater than that of the reactants in endothermic reactions and the opposite is true for exothermic reactions. The differences in energy and their correspondences are labelled.

Remember that M-EXO (making is exo) and B-ENDO (breaking is endo). Bond breaking is an endothermic process and bond making is an exothermic

process. When a reaction, overall, has bonds broken with more energy than bonds made, it is endothermic. The opposite is also applies.

Enthalpy change can be calculated as:

 $enthalpy = (energy\ needed\ to\ break\ bonds) \ \hbox{-}\ (energy\ needed\ to\ make\ bonds)$

$$\Delta H = E_b - E_f$$

where E_b is the energy needed to break bonds and E_f is that needed to form bonds.

3 Chemical reactions

3.1 Physical and chemical changes

In a physical change, the substances present remain chemically the same and no new substances are formed. Such changes are often easy to reverse.

Changes such as melting and boiling are endothermic as heat is taken in, changes such as condensing and freezing are exothermic as heat is given out.

Chemical changes are those where a new substances is formed. Most chemical changes happen through chemical reactions, almost all of which are exothermic, very few are endothermic.

3.2 Rate of reaction

A reaction progresses when effective collisions occur between reactants to form a molecule of a product. The rate of effective collisions is hence the rate of the reaction. This rate of effective collisions can be influenced. These effective collisions can only occur if the colliding particles have a minimum energy (E_a) .

Increasing the number of particles per unit volume means there are more particles per unit volume, when that is the case the particles are more likely to react.

Increasing the kinetic energy (KE) of particles by applying heat makes them move faster, meaning more particles are likely to collide more frequently and with energy greater that E_a .

A catalyst is that which increases the rate of a reaction, decreases the E_a and is unchanged at the end of the reaction.

Changing solution concentration changes particles per unit volume, refer above.

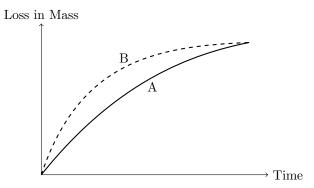
Changing gas pressure does the same, refer above.

Increasing surface area of solids means there are more exposed surfaces with which reactants can effectively collide, meaning effective collisions are more likely. The opposite is also true.

Increasing temperature increases KE of particles, refer above.

Addition of a catalyst, including enzymes, increases reaction rate and decreases E_a .

Investigating the rate of a reaction comes down to measuring the rate at which reactants are used up or the rate at which products are formed. The information can be represented in a graph:



In reaction B, the reactants were powdered, with increased surface area and hence the reaction had a faster rate than A with just solid reactants. Notice that they loss in mass is equal but the rate of loss of mass is the difference.

3.3 Reversible reactions and equilibrium

Most reactions are one-way, i.e., reactants react to form products and that's it. Some reactions, are reversible, in such reactions, reactants react to form products and those products also react to form reactants. Such reactions are shown with a "\Rightarrow":

$$N_2(g) + 3 H_2(g) \xrightarrow{\text{forward reaction}} 2 NH_3(g)$$

Changing the direction of a reversible reaction can depend on the conditions applied to it. Such is the case for hydrating and making anhydrous salts.

$$\begin{aligned} & \operatorname{CoCl}_2 \cdot 6 \operatorname{H}_2 \operatorname{O} \xrightarrow{\underbrace{\operatorname{heat}}} & \operatorname{CoCl}_2 + 6 \operatorname{H}_2 \operatorname{O} \\ & \operatorname{CuSO}_4 \cdot 6 \operatorname{H}_2 \operatorname{O} \xrightarrow{\underbrace{\operatorname{heat}}} & \operatorname{CuSO}_4 + 6 \operatorname{H}_2 \operatorname{O} \end{aligned}$$

Note that, $CuSO_4$ is white while the hydrated form $CuSO_4 \cdot H_2O$ is blue. Hydrated cobalt (II) chloride is pink whereas the anhydrous form is blue.

A closed system is that where no reactants or products can escape from the reacting system. In such a system, a reversible reaction is in equilibrium when the rate of forward reaction equals the rate of backward reaction and the concentrations of reactants and products are not changing. The reagents are reacting but the concentrations do not change.

The position of equilibrium tells us the rate of forward reaction compared to backward reactions. That means, if the position of equilibrium is to the right, the rate of forward reaction is greater than that of the backward reaction and vice versa.

Note that, when a change is made to the conditions of a system in dynamic equilibrium, the system moves so as to oppose that change.

Changing temperature affects the reaction depending on the enthalpy of the reaction. Changing the temperature will cause the equilibrium to shift in the direction that will reverse that change. Increasing the temperature in a reaction where the forward reaction is exothermic will shift equilibrium to left, as the system will oppose the change by increasing rate of endothermic reaction to lower temperature. The opposite is also true.

Changing pressure only affects reactions whose reagents are all gaseous. Increasing pressure moves equilibrium toward the side which has less gaseous moles. The opposite is also true.

Increasing concentration of reactants moves equilibrium to right and more products are formed and vice versa.

Using a catalyst does not affect equilibrium position, but the speed at which the system reaches equilibrium is affected by catalyst.

Below is the symbol equation for the Haber process.

$$N_2(g) + 3 H_2(g) = \frac{450 \, ^{\circ} \text{C}}{200 \, \text{atm}} 2 \, \text{NH}_3(g) \, \Delta H < 0$$

The nitrogen is gotten from fractional distillation of liquid air and hydrogen is gotten from cracking of crude oil. The above reaction requires an iron catalyst.

In the Contact process, sulfur dioxide is converted into sulfur trioxide.

$$2 SO_2(g) + O_2(g) = \frac{450 °C}{2 atm} 2 SO_3(g) \Delta H < 0$$

The Contact process requires a vanadium (V) oxide, V_2O_5 catalyst. Sulfur dioxide is gotten from burning or roasting sulfide ores:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$

and oxygen is gotten from air.

The conditions in the above industrial processes are such that to optimise economical costs and safety.

3.4 Redox

Roman numbers are used to indicate the oxidation number of an element in a compound (iron (II), vanadium (V), etc.).

A redox reaction is where reduction and oxidation occurs simultaneously.

The oxidation of a compound is its gain of oxygen, loss of electrons or increase in oxidation number.

The reduction of a compound is its loss of oxygen, gain of electrons or decrease in oxidation number.

Rules for identifying oxidation number:

- It is zero in uncombined states (B, Mg).
- It is the same as the charge on an ion (B^{+2}) .
- Sum of oxidation numbers in a compound is zero.

• Sum of oxidation numbers in an ion is equal to the charge in the ion.

Acidified potassium manganate(VII), KMnO₄, is an oxidising agent with a purple colour, which it loses when it is added to a reducing agent. Aqueous potassium iodide, KI, is a reducing agent which turns brown in presence of an oxidising agent.

An oxidising agent is that which oxidises another substance and is itself reduced. A reducing agent as a substance that reduces another substance and is itself oxidsed.

Using changes in oxidation numbers, oxidising and reducing agents can be identified.

4 Metals

4.1 Properties of metals

A metal is an element whose ion forms as a result of loss of electrons, i.e., elements whose ions are positively charged are called metals. They exist between groups two to three in the Periodic Table.

In comparison to non-metals, metals are more thermally and electrically conductive. They are more malleable, which means they can be beaten into many shapes. They are ductile as they can be wrought out into wires. They tend to have high melting and boiling points.

The reactions of metals depend entirely on the metals themselves, or rather, the reactivity of the metals, which follow:

$$\underbrace{K > Na > Ca > Mg > Al}_{high\ reactivity} > C > \underbrace{Zn > Fe > Pb}_{moderate\ reactivity} > H > \underbrace{Cu > Ag > Au}_{low\ reactivity}^{[3]}$$

Note the presence of the two non-metals: carbon and hydrogen. Though these are out of place, it is these non-metals whose displacement or otherwise determined the reactivity of the metals. That is, the metals more reactive than carbon are show high reactivity, those less reactive are moderate and low reactive. Those that are more reactive than hydrogen show moderate and high reactivity, while those are less reactive show low reactivity.

Metals with high and moderate reactivity react with dilute hydrochloric acid, displacing the hydrogen in HCl to give the corresponding metal chloride and hydrogen gas. So, lets consider the reaction of a metal Λ which is more reactive than hydrogen, with dilute hydrochloric acid:

$$2\Lambda(s) + 2HCl(aq) \longrightarrow 2\Lambda Cl(aq) + H_2(g)$$

Note that, if Λ is highly reactive, the above reaction is very strong and often infeasible.

Highly reactive metals, react with cold water directly, giving respective hydroxides and hydrogen. An example with Λ as the metal follows:

$$2\,\Lambda(s) + 2\,H_2O(l) \longrightarrow 2\,\Lambda OH(aq) + H_2(g)$$

Note that the ratio of OH to Λ will depend on the electronic charges on the metal itself.

Moderately reactive metals react with water in the gaseous form, i.e., steam. The metal itself must also be heated. Such a reaction always gives the metal oxide and hydrogen gas. In this case, magnesium and aluminium act as moderately reactive metals. Once again, with Λ representing such a metal:

$$\Lambda(s) + H_2O(g) \longrightarrow \Lambda O(s) + H_2(g)$$

^[3] where the metal to the left of > is more reactive than the ion to the right.

Metals with high and moderate reactivity both react with oxygen^[4]. The product is that metal's oxide:

$$2\Lambda(s) + O_2(g) \longrightarrow 2\Lambda O$$

Note that, iron only reacts in the above reaction as powder or wool. Iron also reacts with air and moisture forming a layer of rust, which is hydrated iron(III) oxide. Low reactive metals, such as copper and lead react very slowly to give an oxide layer, under heat.

4.2 Uses of metals

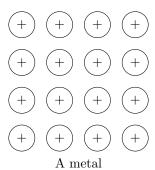
Aluminium is a metal that shows low reactivity as a result of its oxide layer, which forms due to its reaction with the air. It is a metal with very low density and hence is used in manufacturing aircraft. It is also used in overhead electrical cables as it is a good electrical conductor and low density. It is also used in food containers as it does not corrode easily as a result of the oxide layer.

Copper is also a good electrical conductor, it is also ductile and is hence used in smaller scale wiring.

4.3 Alloys and their properties

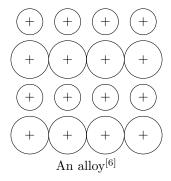
An alloy is a mixture of a metal with other elements. Brass is such a mixture consisting of copper and zinc. Stainless steel is a mixture of iron and other elements such as chromium, nickel and carbon.

The structure of a metal consists of layers of metal cations with a sea of delocalised electrons^[5]. These layers are arranged such that they can cascade and slide over each other, which is why metals are malleable and ductile. However, in alloys, the cations are differently sized due to the different atoms present. This stops the layers from sliding easily, making alloys stronger and harder than pure metals. A structure of a metal and an alloy follows:



^[4] Any reaction with oxygen is called burning.

^[5] A delocalised electron is that which is not bound to any atom and can move freely



4.4 Reactivity series

As shown at the beginning of the chapter, the order of reactivity of the metals is:

$$\underbrace{K > Na > Ca > Mg > Al}_{high\ reactivity} > C > \underbrace{Zn > Fe > Pb}_{moderate\ reactivity} > H > \underbrace{Cu > Ag > Au}_{low\ reactivity}$$

The reactivity of a metal is said to be the tendency of the metal to form a positive ion. The relative reactivity of each metal is seen in displacement reactions involving the metals, where the more reactive metal displaces the less reactive metal from its compound. An example follows, where Λ is a more reactive metal than Π .

$$\Lambda + \Pi SO_4 \longrightarrow \Pi + \Lambda SO_4$$

Note that, the less reactive metal is reduced and the more reactive metal is oxidised. The reactions of metals with water, hydrochloric acid and steam have all been discussed, some further observations are given below.

Potassium, sodium and calcium have very strong reactions with cold water, where the potassium and calcium are seen to skip over the water's surface while melting. Calcium reacts strongly. Magnesium, only reacts with cold water very slowly, but burns with a brilliant flame when steam is passed over heated magnesium.

Metals which are highly reactive have very violent reactions with dilute acid, so it is unsafe to add them directly.

Magnesium reacts strongly, disappearing into the acid while forming bubbles of gas. The result is a colourless solution.

Aluminium is slow to react in cold acid, but bubbles form on heating, causing the aluminium to disappear into the acid resulting in a colourless solution.

Zinc, disappears in cold acid, producing bubbles of gas and a colourless solution forms. Same is the case with iron, only a pale green solution is formed.

 $^{^{[6]}}$ These diagrams are far too bad to be acceptable answers to O-Level questions, please refer to prescribed book.

Copper silver and gold, i.e., metals with low reactivity have no reaction with acids at all.

Aluminium, when kept exposed to air, reacts with the surrounding oxygen in the air resulting in a layer of aluminium oxide around the sample of aluminium. This layer is unreactive, so aluminium is *apparently* unreactive.

Given a set of experimental observations, using the strength of reactions described and the knowledge from the reactivity series of metals, we can deduce the reactivity of given metals.

4.5 Corrosion of metals

Metals corrode under certain conditions as results of certain reactions.

Iron and steel corrode in presence of oxygen or water producing a layer of iron (III) oxide, called rust. Prevention of this comes down to many strategies, including barrier protection, where the metal is either coated by another or painted so as to prevent contact of water and oxygen with the metal. Barriers used to protect metals from corrosion can be painting, greasing or coating the metal with plastic.

Sacrificial protection consists of another more reactive metal being placed adjacent the metal to be protected. The moisture and air will then react with the more reactive metal in precedence to the relatively less reactive metal. In other words, the higher reactive metal loses electrons more readily, as a result, that metal is oxidised and the lower reactive metal is not corroded.

The two strategies can be combined in that zinc can be used to electroplate any metal, where since zinc is more reactive, it will be reduced in precedence to the metal being coated. The disadvantage to barrier protection is that when the coating comes off, that area will immediately be corroded. This method prevents that as even if the layer is scratched, the moisture will react with the zinc instead. This method is called galvanising.

4.6 Extraction of metals

Metals can be extracted easily depending on their reactivity.

Iron is found naturally in an ore called haematite, which is iron (III) oxide. Iron is extracted from iron (III) oxide in a blast furnace, by means of reduction by carbon monoxide.

Raw materials, iron ore, coke (carbon made from coal) and the mineral^[7] limestone. The furnace has blasts of hot air sent near the bottom, allowing a series of chemical reactions to occur resulting in the production of pure iron.

Firstly, the coke burns in the air blast and the furnace gets very hot from this exothermic reaction:

$$C + O_2 \longrightarrow CO_2$$

^[7] A naturally ocurring rock containing a particular compound

As carbon dioxide rises through the furnace it reacts with more carbon and is reduced to carbon monoxide:

$$CO_2 + C \longrightarrow 2CO$$

The most important reaction is the reduction of haematite by this carbon monoxide

$$Fe_2O_3 + 2CO \longrightarrow 2Fe + CO_2$$

This produced iron flows to the bottom of the furnace where it can be tapped off

Iron ore contains the impurity sand, which is silicon (IV) oxide, also called silica. Limestone, calcium carbonate is added to the blast furnace to rid the iron of this impurity. Firstly, the calcium carbonate decomposes in the heat of the furnace:

$$CaCO_3 \longrightarrow CaO + CO_2$$

Subsequently, this calcium oxide reacts with silica to form calcium silicate

$$SiO_2 + CaO \longrightarrow CaSiO_3$$

Aluminium is a metal that shows high reactivity, as a result reduction cannot be used for its extraction, rather, electrolysis is employed.

Cryolite is used as a solvent for aluminium as it reduces the melting point of the substance allowing the mixture to be liquid at lower temperatures which is economical. It also conducts electricity and as a result can be used in electrolysis.

The ore for aluminium is bauxite, which is simply aluminium oxide.

Bauxite, dissolved in cryolite is electrolysed using carbon electrodes. The cathode reactions are as follows:

$$\begin{array}{l} at\ cathode:\ Al^{3+}(l)+3\,e^- \longrightarrow Al(l)\\ at\ anode:\ 2\,O^{2-}(l) \longrightarrow O_2(g)+4\,e^- \end{array}$$

At the very high temperature of the electrolysis conditions, the oxygen being formed at the anode burns the carbon in the anode,

$$C(s) + O_2(g) \longrightarrow CO_2(g)$$

forming carbon dioxide and causing the anodes to corrode and be regularly replaced.