Cambridge GCSE Notes
5070 Chemistry

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Contents

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, $PbBr_2$, the following happens during electrolysis with inert electrodes at either electrode:

$$\text{at anode: } 2\,Br^- \longrightarrow Br_2 + 2\,e^-$$
$$\text{at cathode: } Pb^{2+} + 2\,e^- \longrightarrow Pb$$
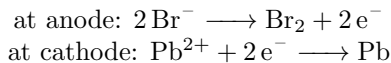
It is observed that a silvery solid accumulates at the cathode, i.e. lead (II) and a red-brown gas is given off at anode. Note that, from here we can judge that for molten ionic compounds, the metal part of the compound will always form at the cathode, and the non metal will form at the anode.

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

$$\text{at anode: } 2\,Cl^- \longrightarrow Cl_2 + 2\,e^-$$
$$\text{at cathode: } H^+ + 2\,e^- \longrightarrow H_2$$
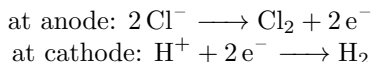
It is observed that a colourless gas is given off at cathode and a green gas is given off at the anode.
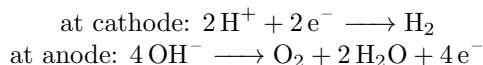
The reason why the metal, i.e., sodium is not discharged at the cathode is because it is not the least reactive amongst the cations present in the electrolyte. The ions present in the electrolyte are: H^+, Na^+, Cl^- and OH^-. Of these, at the cathode the ion discharged is the least reactive of the cations, 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:

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

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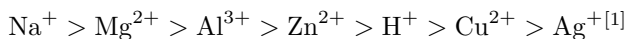
[1]where the ion to the left of > is more reactive than the ion to the right.

$$\mathrm{SO_4}^{2-} < \mathrm{NO_3}^{-} < \mathrm{OH}^{-} < \mathrm{Cl}^{-} < \mathrm{Br}^{-} < \mathrm{I}^{-\,[2]}$$
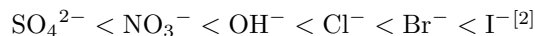
During the electrolysis of dilute sulfuric acid, the ions in the electrolyte are: $\mathrm{H^+}$, $\mathrm{OH^-}$, $\mathrm{SO_4}^{2-}$. The only cation, $\mathrm{H^+}$ is released at the cathode and, by preferential rule, $\mathrm{OH^-}$ is the one which is oxidised at anode.

$$\text{at cathode: } 2\,\mathrm{H^+} + 2\,\mathrm{e^-} \longrightarrow \mathrm{H_2}$$
$$\text{at anode: } 4\,\mathrm{OH^-} \longrightarrow \mathrm{O_2} + 2\,\mathrm{H_2O} + 4\,\mathrm{e^-}$$
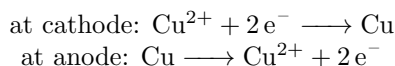
Colourless gases are given off at both electrodes, but the volume of oxygen produced is half that of hydrogen. This is a result of the fact that, the mole ratio of oxygen to hydrogen in the electrolyte is 1:2.

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, $\mathrm{Cu^{2+}}$ have a blue colour. The following happens at the electrodes in this electrolysis:

$$\text{at cathode: } \mathrm{Cu^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}$$
$$\text{at anode: } \mathrm{OH^-} \longrightarrow \mathrm{O_2} + 2\,\mathrm{H_2O} + 4\,\mathrm{e^-}$$
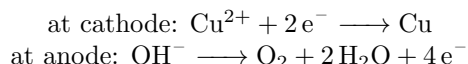
Notice that, the copper ions are reduced to copper, reducing the number of copper ions in electrolyte. It is observed that the blue colour of solution fades and a pinkish orange solid accumulates on the cathode.

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.

$$\text{at cathode: } \mathrm{Cu^{2+}} + 2\,\mathrm{e^-} \longrightarrow \mathrm{Cu}$$
$$\text{at anode: } \mathrm{Cu} \longrightarrow \mathrm{Cu^{2+}} + 2\,\mathrm{e^-}$$

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

$$2\,\mathrm{H_2(g)} + \mathrm{O_2(g)} \longrightarrow 2\,\mathrm{H_2O\,(l)}$$
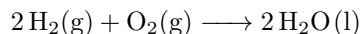
Here, the hydrogen is considered to be a non-polluting fuel.

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.

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

2 Chemical energetics
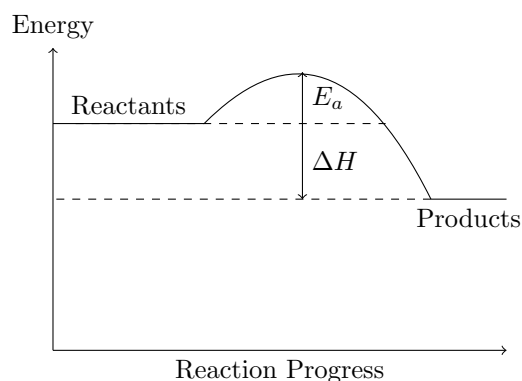
2.1 Exothermic and endothermic reactions

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.
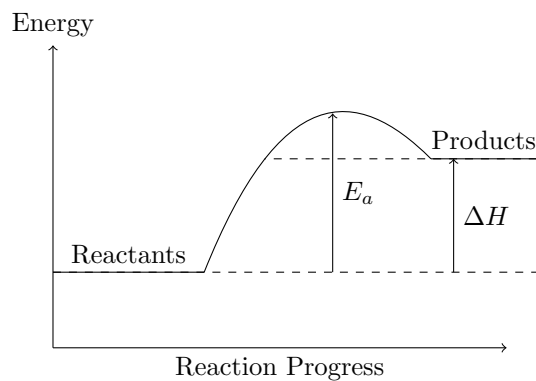
Endothermic Reaction

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) - (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.

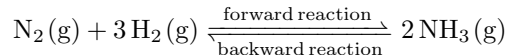Addition of a catalyst, including enzymes, increases reaction rate and decreases E_a.

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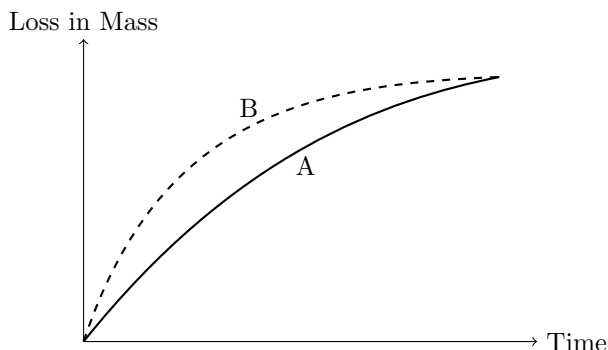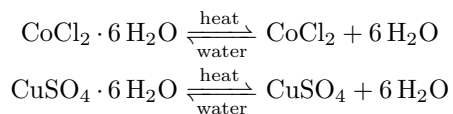
In reaction B, the reactants were powdered, with increased surface area and hence the reaction had a faster rate than A with just solid reactants. Notice that they loss in mass is equal but the rate of loss of mass is the difference.

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 "$\rightleftharpoons$":

$$\mathrm{N_2\,(g) + 3\,H_2\,(g) \underset{\text{backward reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} 2\,NH_3\,(g)}$$

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.

$$\mathrm{CoCl_2 \cdot 6\,H_2O \underset{\text{water}}{\overset{\text{heat}}{\rightleftharpoons}} CoCl_2 + 6\,H_2O}$$

$$\mathrm{CuSO_4 \cdot 6\,H_2O \underset{\text{water}}{\overset{\text{heat}}{\rightleftharpoons}} CuSO_4 + 6\,H_2O}$$

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.

$$N_2(g) + 3\,H_2(g) \xrightleftharpoons[200\,\text{atm}]{450\,^{\circ}\text{C}} 2\,NH_3(g) \ \Delta H < 0$$
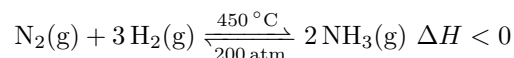
The nitrogen is gotten from fractional distillation of liquid air and hydrogen is gotten from cracking of crude oil. The above reaction requires an iron catalyst.

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

$$2\,SO_2(g) + O_2(g) \xrightleftharpoons[2\,\text{atm}]{450\,^{\circ}\text{C}} 2\,SO_3(g) \ \Delta H < 0$$
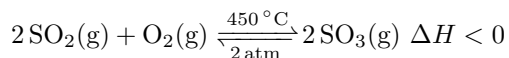
The Contact process requires a vanadium (V) oxide, V_2O_5 catalyst. Sulfur dioxide is gotten from burning or roasting sulfide ores:

$$S(s) + O_2(g) \longrightarrow SO_2(g)$$
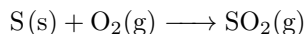
and oxygen is gotten from air.

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), $KMnO_4$, 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.