Chemistry Notes 2014

By: Bhaskar Harish Sai (01/4P)

Additions to Year 3 Stuff – Chemical Energetics

This is some stuff you guys might want to take note of because it appeared in some of the exercises and mock papers.

Exothermic Reactions

Combustion of Fuels: $C(s) + O_2(g) \rightarrow CO_2(g)$

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

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

Respiration: $C_6H_{12}O_6(s) + 6O_2(g) \rightarrow 6CO_2(g) + 6H_2O(g)$

Dissolving sodium hydroxide in water Neutralisation Displacement reaction (e.g. fireworks/firecrackers)

Haber Process: $3H_2(g) + N_2(g) \rightarrow 2NH_3(g)$

Dissolution of ammonium salts (such as ammonium nitrate and ammonium chloride) in water

Endothermic Reactions

Photosynthesis: $6CO_2(g) + 6H_2O(g) \rightarrow C_6H_{12}O_6(s) + 6O_2(g)$

Photodecomposition of silver halides: $2AgBr(s) \rightarrow 2Ag(s) + Br_2(l)$

Thermal decomposition of limestone: $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

Citric acid + sodium bicarbonate (hydrogen carbonate)

Ammonium chloride + barium hydroxide

Periodic Table

Trends in Group I

As one goes down the group, there are 3 noticeable trends.

1. Density increases
    - Relative atomic number increases down the group → increase in mass surpasses increase in volume → density increases
2. Melting point decreases – Caesium melts at only 29 °C vs Lithium, at 181 °C
    - The number of shells increases → distance between valence electrons and nucleus increases → attractive forces between delocalised "sea" of electrons, which is comprised of the valence electrons, and the nuclei of the atoms decreases → lower melting point
3. Reactivity increases – Caesium has a very violent reaction with water, compared with Lithium
    - Group I metals form cations – hence, to form ions, atoms must lose an electron
    - Down the group, number of shells increases → distance between valence electrons and nucleus increases → Attractive forces between valence electrons and nucleus decreases
    - The more easily removed the valence electron, the more reactive the element → Hence, reactivity increases down the group

Trends in Group VII

As one goes down the group, there are 3 noticeable trends.

1. Colour becomes darker
2. Melting and boiling point increases
    - Electron size increases → Probability of setting up temporary dipoles and the number of temporary dipoles set up increases → Weak intermolecular forces (Van der Waals forces) increases → Melting and boiling point increases
3. Reactivity decreases – When reacting with aluminium, fluorine produces an explosion with a blinding flash while chlorine only burns when the aluminium has been heated
    - Group VII metals form anions – hence, to form ions, atoms must gain an electron
    - Down the group, number of shells increases → distance between valence electrons and nucleus increases → Attractive forces between valence electrons and nucleus decreases
    - The harder it is to "accept" and electron, the less reactive the element → Hence, reactivity decreases down the group
4. A halogen higher up the group can displace a less reactive halogen from its salt solution
    - A more reactive halogen can displace a less reactive halogen from its salt solution

Trends amongst transition metals

All transition metals share common traits. They all generally:

1. Have high melting and boiling points
2. Have high density

3. Show variable oxidation states in their compounds
4. Form ionic compounds
5. Are usually used as catalysts in many biological and industrial reactions

Alkali metals versus Transition metals

While both alkali metals and transition metal are metals (metallic bonding), they display different characteristics.

However, they are alike as they are both:

1. Shiny
2. Malleable and ductile
3. Good conductors of electricity

They are different, however, as can be seen from the table below.

	Alkali metals	**Transition metals**
Electronic Structure	Outermost orbital is s orbital (only 1 electron)	Outermost orbital is d orbital (up to 10 electrons)
Atomic Radius	Larger	Smaller
Melting/Boiling Point	Low	High
Density	Low	High
Hardness	Soft, can be cut with a razor blade	High

They also have similar and differing chemical properties.

Both alkali metals and transtition metals:

1. React with acids to form salts and hydrogen gas.
2. React with non-metals to form ionic compounds.
3. Burn in oxygen gas to form basic (or amphoteric, for ZAP – Zinc, Aluminium and Lead) oxides.

However, they have differing chemical properties.

	Alkali metals	**Transition metals**
Oxidation states	Only one oxidation state when forming compounds, e.g.: Na only has an oxidation state of +1 when forming compounds	Have variable oxidation states when forming compounds, e.g.: Iron (Fe) can both iron (II) oxide, in which its oxidation state is +2, and iron (III) oxide, 3in which its oxidation state is +
Colour of compounds	White solids/colourless solutions	Variable colours, e.g.: Copper compounds generally form blue solutions, while iron compounds are generally insoluble and are green (if iron (II) compound) or red (if iron (III) compound)
Solubility of compounds	All soluble	Not all soluble (copper vs. iron)

Catalytic properties	None	Catalyse many reactions

Trends across Periods and Groups

Before we dive into the actual trends, we must understand what nuclear charge is and what shielding electrons are.

Definitions

Nuclear charge: Sum of all the protons in the nucleus of the atoms

Shielding electrons: Electrons that are not in the valence shell of the atom.

They shield the valence electrons from the attractive force of the nuclear charge. Across a period, shielding electrons do not differ because only the number of electrons in the valence shell differs. Down a group, the number of shielding electrons increases because the number of shells increases.

Trend of the size of atomic radii

While the size of an atom is difficult to describe because atoms do not actually have definite outer boundaries, scientists have attempted to overcome this by describing the radius of the atom through estimates made from measurements.

In metals, this is done by measuring the distance between 2 nuclei in the solid state and dividing this distance by 2. Such measurements can be made with X-ray diffraction.

For non-metallic elements that exist in pure form as molecules, such as chlorine, measurements can be made of the distance between nuclei of 2 atoms covalently bonded. Half of this distance is usually referred to as the covalent radius.

Generally, down a group, atomic radius increases, because the number of shells increases.

Across a period, the atomic radius decreases. The nuclear charge increases across a group, as well as the number of valence electrons, while at the same time, the number of shielding electrons remain the same. Hence, the attractive force between the valence electrons and the nucleus increases. The "amount of shielding" (do not use this in your exams this is just for understanding) remaining the same due to the same number of shielding electrons also helps with this increase in attractive force. Hence, valence electrons are increasingly pulled in towards the nucleus, so the atoms decrease in size across a period.

Trend of Ionization Energies

Ionization energy decreases generally down a group. As the number of shells increase down a group, the valence electrons get increasingly further away from the nucleus. Hence, the force of attraction between the valence electrons and the nucleus decreases, resulting in a decrease in ionization energy.

*The number of shielding electrons also increases because the number of shells increases, so there is basically an extra shell to shield the valence electrons. This also decreases the ionization energies.

Ionization energy increases across a Period. As mentioned before, the atomic size gets smaller, meaning that the valence electrons are closer to the nucleus, which increases attractive forces between the nucleus and the valence electrons. Hence, ionization energy will go up. (Side point, main point below)

Moreover, the nuclear charge and the number of valence electrons increase across a Period. However, the number of shielding electrons is constant. Hence, the attractive force between the valence electrons and the nucleus increases. This means that ionization energies will go up.

Trend of melting and boiling points

For metals, the melting point generally decreases down a group.

The number of shells increases → distance between valence electrons and nucleus increases → attractive forces between delocalised "sea" of electrons, which is comprised of the valence electrons, and the nuclei of the atoms decreases → less energy needed to overcome these forces → lower melting point

For non-metals, the melting and boiling points generally increase down a group.

Electron size increases → Probability of setting up temporary dipoles increases → Weak intermolecular forces (Van der Waals forces) increases → more energy required to overcome these forces → Melting and boiling point increases

Metals vs. Non-metals

This table essentially sums up all that you need to know about this.

Metals	Non-metals
• Usually solids at room temperature (except for mercury)	• Often gases (except carbon, sulfur and silicon)
• High melting and boiling points (except for Group I metals)	• Low melting and boiling points (except carbon and silicon) – weak IMF
• Good conductors of heat and electricity	• Poor conductors of electricity and heat (except graphite)
• Often shiny, ductile and malleable, and possess great tensile strength	• Normally dull and soft
• Oxides are usually basic or amphoteric	• Oxides are usually neutral of acidic
• Usually form cations	• Usually form anions

Qualitative Analysis

-JUST REMEMBER THE TABLE-

Equilibria

Many chemical reactions can proceed in two directions – forward and backward. They are called reversible reactions.

A reversible reaction is represented by a double arrow ($\rightleftharpoons$)

The reaction from left to right is called the forward reaction.

The reaction from right to left is the backward reaction or reverse reaction.

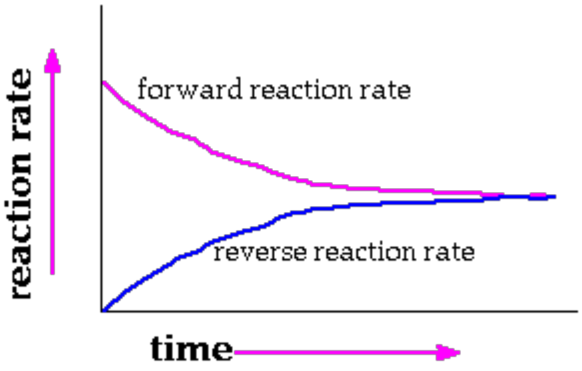
Reversible reactions tend not to go into completion. As such, a mixture of both the reactants and the products is obtained no matter how long the reaction goes on. When the concentration of the reactants and products are constant, we say that they are at equilibrium.

Dynamic Equilibrium

Consider a situation in which the following reaction takes place.

$$A + B \rightleftharpoons C + D$$

Only A and B are added in equal proportions to start the reaction, which means that A and B are at the maximum concentration. This also means that the rate of reaction is at its fastest. As A and B react with one another, the reaction rate of A and B, which is called the forward reaction, falls, as time goes on.



At the same time, the concentrations of C and D increase as time goes on. This means that over time, the backward reaction rate increases because the frequency of collisions between their particles increases as concentration increases.

As shown above, eventually, the rate of both the forward and backward reactions will become equal. A and B will be reacting to form C and D at the same rate as C and D reacting to form A and B.

As fast as something is being removed by the forward reaction, it is being replaced again by the backward reaction, and vice versa. This is the position of dynamic equilibrium.

Definition

Dynamic Equilibrium: Reversible reactions attain a state of equilibrium when the rate of the forward reaction is the same as that of the backward reaction. The reaction does not stop when equilibrium is attained, which is why it is described as being dynamic.

Notes

a) Equilibrium only exists if substances do not escape or enter a reaction container, i.e. in a closed system.
b) When equilibrium is reached, this does not necessarily imply that the equilibrium mixture consists of 50% reactants and 50% products. In fact, this is rarely the case. However, the concentrations of reactants and products do remain constant.

Le Chatelier's Principle

Le Chatelier's principle states that:

> If a system at equilibrium is subjected to a small change, the equilibrium's response is to counteract the change so as to minimize the effect of the change.

Reversible reactions obey this principle, and so can be manipulated to increase the yield of product(s).

This can be done using 3 methods: changing concentration, changing temperature and changing pressure.

Changing Concentration

When the concentration of a reactant is increased, the response of the system is to counteract the change by decreasing the concentration of the reactant. Hence, the system responds by favouring the forward reaction as compared to the backward reaction, by shifting the position of equilibrium to the right. This will result in an increased yield of the product.

The converse is also true. (Concentration decreased → response – increase concentration → favours backward reaction → position of equilibrium shifted to the left → decreased yield)

Changing Pressure

The effect of increasing or decreasing pressure has different effects depending on the equation of the reactions.

Generally, if the number of mol of the reactants needed is greater than that of the products yielded, such as in the equation $A + 2B \rightleftharpoons C + D$, the following effects are observed:

When the pressure is increased, the response of the system is to counteract the change by decreasing the pressure. Hence, the system responds by favouring the forward reaction as compared to the backward reaction, by shifting the position of equilibrium to the right. This will result in an increased yield of the product.

The converse is also true. (Pressure decreased → response – increase pressure → favours backward reaction → position of equilibrium shifted to the left → decreased yield)

However, if the number of mol of the reactants needed is smaller than that of the products yielded, such as in the equation $A + B \rightleftharpoons 2C + D$, the following effects are observed:

When the pressure is increased, the response of the system is to counteract the change by decreasing the pressure. Hence, the system responds by favouring the backward reaction as compared to the forward reaction, by shifting the position of equilibrium to the left. This will result in a decreased yield of the product.

The converse is also true. (Pressure decreased → response – increase pressure → favours forward reaction → position of equilibrium shifted to the right → increased yield)

Changing Temperature

The effects of increasing and decreasing temperature also differ according to the different reactions and their enthalpy changes.

Typically, for an exothermic reaction, the following happens:

When the temperature is increased, the response of the system is to counteract the change by decreasing the temperature. Hence, the system responds by favouring the backward reaction as compared to the forward reaction, by shifting the position of equilibrium to the left. This will result in a decreased yield of the product.

The converse is also true. (Temperature decreased → response – increase temperature → favours forward reaction → position of equilibrium shifted to the right → increased yield)

For an endothermic reaction, this happens instead:

When the temperature is increased, the response of the system is to counteract the change by decreasing the temperature. Hence, the system responds by favouring the forward reaction as compared to the backward reaction, by shifting the position of equilibrium to the right. This will result in an increased yield of the product.

The converse is also true. (Temperature decreased → response – decrease temperature → favours backward reaction → position of equilibrium shifted to the left → decreased yield)

These explanations should be sufficient to garner the marks in any question.

Metals Reactivity Series and Corrosion

Reactivity

Definition

The reactivity of a metal is defined by the ease in which a metal atom loses its electrons.

The reactivity of a metal can be partly explained by the size of the atoms. As atoms become larger, the outer shell electrons become further away from the nucleus. The attractive force exerted by the positive nucleus is less on the valence electrons; hence the outer electrons of larger atoms are lost more readily, making them more reactive. For example, potassium contains one additional shell when compared to sodium. Hence, potassium atoms form potassium ions more readily than sodium ions because the attractive force exerted on the valence shell electron by the potassium nucleus is less than that by the sodium nucleus. Hence, potassium loses its valence electrons more readily than sodium. This also occurs in group II with magnesium and calcium, and is why calcium is more reactive than magnesium.

Hence, the chemical activity of a metal is related to its position in the Periodic Table. The reactivity of the metals tend to increase down a group and decrease across a period from left to right. This is a general guideline that may not apply in all circumstances is a useful tool. (Parallel with ionization energy and atomic radius – similar explanation of nuclear charge and shielding electrons)

*Note: This is unlikely to be tested

Reactivity Series of Metals

Metal	Reaction with O_2 on heating	Reaction with cold water	Reaction with steam	Reaction with dilute strong acid*	Strength as reducing agents	Reactions with other aqueous cations	Reactions with Cl_2 on heating
K	Form oxides in limited O_2, but peroxides in excess	Displace H_2 from cold water with decreasing reactivity. Corresponding hydroxide formed	Displace H_2 from steam with decreasing vigour. The corresponding oxide is formed.	Displace H_2 from dilute strong acids with decreasing vigour	Decreasing strength as reducing agents (electrons are donated less readily by the metals)	A more reactive metal will displace a less reactive metal (lower in the reactivity series) from the solution of the metal ion of the less reactive metal.	All metals react with Cl_2 on heating to form the corresponding chloride with decreasing vigour.
Na							
Ca	Burning with decreasing vigour to form oxides						
Mg							
Al		Do not displace H_2 from cold water					
Zn							
Fe							
Sn							
Pb	Do not burn, but only form a surface layer of oxide		Do not displace H_2 from steam				
Cu				Do not displace H_2 from strong			

Ag Au	Do not burn or oxidise on surface			acid			

*Dilute strong acid refers to HCl or H_2SO_4. Using dilute HNO_3 **may** produce NO or NO_2 instead.

Thermal Stability of Metal Compounds

Metal	Action of heat on metal oxides	Action of heat on metal hydroxides	Action of heat on metal carbonates	Action of heat on metal nitrates
K Na	Stable to heating	Stable to heating	Stable to heating	Decomposes to the metal nitrite and oxygen
Ca Mg Al Zn Fe Sn Pb Cu	C H	Decomposes to the metal oxide and steam	Decomposes to the metal oxide and carbon dioxide	Decomposes to the **metal** oxide, nitrogen dioxide and oxygen
Ag Au	Decomposes to the metal and oxygen	Hydroxides do not exist	Decomposes to the metal, carbon dioxide and oxygen	Decomposes to the **metal**, nitrogen dioxide and oxygen

*Note: Assessments will focus only on the thermal decomposition of metal carbonates and metal nitrates only.

The Electric Cell

An electric cell is essentially made up of 2 electrodes immersed in an electrolyte.

Conditions

The 2 electrodes must be 2 metals of different reactivities.

An electrolyte contains free, mobile ions. The electrolyte could be aqueous or molten.

What happens?

When a wire connects the 2 electrodes, electrons flow from the more reactive metal through the wire of the external circuit to the less reactive metal. Basically, electricity is produced (which is why it is a cell).

Why?

A potential difference is set up between the 2 electrodes.

The more reactive metal loses electrons, thus oxidation occurs.

$$M \rightarrow M^+ + e^-$$

Electrons move from M through the wire to the other electrode. Hence, the more reactive metal is called the negative electrode.

The M^+ ions produced due to the oxidation of M will enter the electrolyte.

The less reactive metal receives the electrons and passes them to the electrolyte. The cation in the electrolyte, Y^+, accepts the electrons to undergo reduction.

$$Y^+ + e^- \rightarrow Y$$

Thus, the less reactive metal is called the positive electrode.

As the reaction progresses, the more reactive metal, which is the negative electrode, becomes smaller and smaller because more and more of it oxidises and enters the electrode.

Meanwhile, a substance is produced at the less reactive metal, which is the positive electrode. The product depends both on the metal M and the identity of the cation, Y^+ present in the electrolyte.

Usually, H_2 gas is produced from H^+ ions, unless Cu^{2+} ions are in the electrolyte.

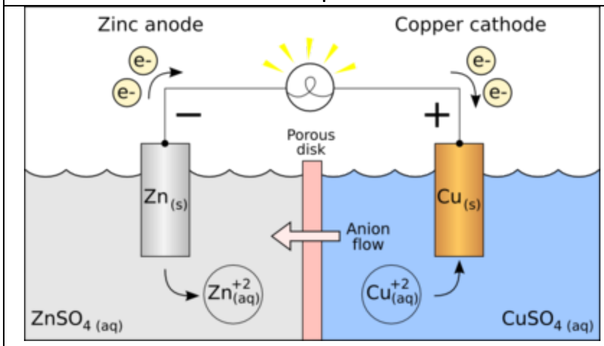
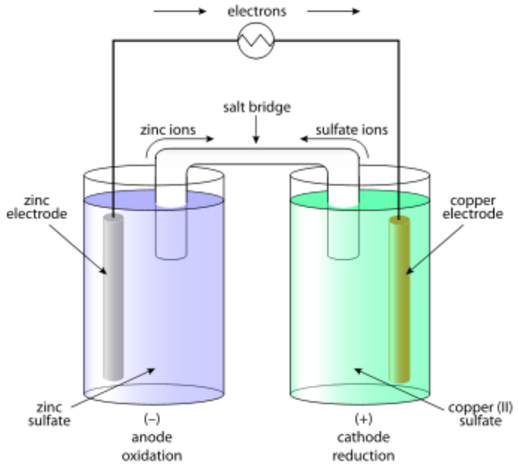
The overall cell equation is this:

$$M + Y^+ \rightarrow M^+ + Y$$

The further apart the two metal electrodes are in the reactivity/electrochemical series, the greater the voltage of the electric cell.

Galvanic Cell

A galvanic cell is a special type of electrochemical cell. It comprises two different half-cells connected either via a salt bridge or a porous membrane.

Galvanic Cell with a porous membrane	Galvanic Cell with a salt bridge
	

Basically, the oxidation and reduction occurs in different electrolytes and on different electrodes, to produce electricity. It is similar to the electrical cell discussed above, in that redox reactions occur to produce electricity.

The equation at the cathode for reduction is:

$$Cu^{2+}\,(aq) + 2e^- \rightarrow Cu\,(s)$$

The equation at the anode for oxidation is:

$$Zn\ (s) \rightarrow Zn^{2+}\ (aq) + 2e^{-}$$

Hence, the overall equation is:

$$Zn\ (s) + Cu^{2+}\ (aq) \rightarrow Zn^{2+}\ (aq) + Cu\ (s)$$

Salt Bridge/Porous Membrane

The significance of the salt bridge or the porous membrane is that it maintains electrical neutrality within the circuit by allowing ions to move across the membrane or the salt bridge. This balances the charges within the electrolyte on each half-cell and ensures that the overall charge of the electrolyte remains neutral.

Corrosion of Metals

Definition

Corrosion: The gradual destruction of any metal due to reaction with water, air or other chemicals

A fine example is iron, which reacts with dissolved oxygen to form iron (III) oxide.

When iron is in contact with water containing dissolved oxygen, a redox reaction takes place.

The iron atoms lose electrons to form iron (II) ions:

$Fe\ (s) \rightarrow Fe^{2+}\ (aq) + 2e^{-}$

The electrons are then transferred to oxygen and water molecules to form hydroxide ion:

$\frac{1}{2}O_2 + H_2O + 2e^{-} \rightarrow 2OH^{-}\ (aq)$

In the presence of oxygen, the iron (II) ions are oxidised to iron (III) ions. These ions react with OH^{-} ions to form $Fe(OH)_3$. This eventually changes into hydrated iron (III) oxide, which is rust.

Speeding up Rusting

Rusting is faster when the water contains other dissolved ionic substances.

Rusting is also faster when less reactive metals are in contact with it. As iron is higher up in the reactivity series, it loses electrons to the less reactive metal. Hence, when the iron loses electrons to both oxygen and the less reactive metal, it rusts more quickly.

Prevention of Corrosion (rusting specifically)

There are methods through which we can prevent the corrosion of metals.

1. Application of protective layer – Paint, Oil/Grease. This prevents the metal from coming into contact with oxygen, preventing it from losing electrons to oxygen.
2. Sacrificial Corrosion – E.g.: Galvanising. A more reactive metal comes into contact with the metal needed to be protected (e.g.: magnesium in contact with iron). What happens is that because magnesium loses electrons more easily than iron as it is higher up in the reactivity

series, it gets oxidised first and forms ions first. Hence, iron remains as iron metal and is not oxidised.

3. Layer of metal oxide – e.g.: Aluminium. Aluminium reacts with oxygen to produce a thin but non-porous/impervious layer of Al_2O_3. This oxide layer prevents further corrosion of the metal by disallowing oxygen and water from penetrating into the metal underneath. This does not happen with some other metals, especially iron, because they form porous layers of oxides that do allow oxygen and water to penetrate into the metal.
4. Anodizing. The oxide layer can be made thicker using an electrolysis process called "anodizing" that protects it better from corrosion.

Electrolysis

Definitions

Electrolysis: The process of chemical decomposition of a compound by passing a direct current through a solution of the compound d or the molten compound.

Electrolyte: A compound in solution or a molten compound which conducts electricity and is decomposed by it in the process.

Electrodes: Conductors by which an electric current enters or leaves the electrolyte.

Cathode: The negative electrode (although the cathode is the positive electrode in electric cell… Confusing rite? JUST REMEMBER). It is connected to the negative terminal of the battery (hence electrons enter the electrolyte here) and reduction occurs here.

Anode: The positive electrode. It is connected to the positive terminal of the battery (hence electrons leave the electrolyte here) and oxidation occurs here.

Battery: You know what a battery is, but in this case, a battery's purpose must be explained. In electrolysis, the battery is required to drive the flow of electrons in the electrolytic setup, and acts like a "pump" to push the electrons in one direction.

What happens?

During electrolysis, cations of the electrolyte migrate to the cathode (negative electrode) while anions migrate to the anodes (positive electrode). However, usually only one compound is oxidised or reduced at each electrode.

Factors affecting electrolysis

There are 3 factors affecting electrolysis, and they are:

1. Ease of cation in gaining electron(s)/anion in losing electron(s)
2. Concentration of ions in electrolyte
3. Nature of electrode

Gaining or losing electrons

One can use the electrochemical series to decide how easily a cation gains an electron or loses an electron.

Cations	Increasing Preferential Discharge	Anions	Increasing Preferential Discharge
K^+	↓	F^-	↓
Ca^{2+}		SO_4^{2-}	
Na^+		NO_3^-	
Mg^+			
Al^{3+}			
Zn^{2+}			
Fe^{2+}			
Sn^{2+}			
Pb^{2+}			
H^+		Cl^-	
Cu^{2+}		Br^-	
Ag^+		I^-	
Au^+		OH^-	

For example, when Na^+ and H^+ are in an electrolyte, during electrolysis, H^+ ions gain electrons more readily than Na^+ ions, thus H^+ ions are preferentially discharged/reduced.

When SO_4^{2-} and OH^- are in an electrolyte, during electrolysis, OH^- ions lose electrons more readily than SO_4^{2-} ions, thus OH^- ions are preferentially discharged/oxidised.

Note: Mentioning the gain or loss of electrons more readily gives the mark, and not the "preferentially discharged" bit.

Also notice that the electrochemical series resembles the reactivity series, except it goes downward instead of upward and this involves ions, not metals in their atomic state.

Concentration Effect of the ions in the solution

Experiments have shown that increasing the concentration of an ion in a solution tends to promote its discharge from the solution. Hence, if the two ions are very close enough to one another on the electrochemical series, and if the concentration difference is big enough, the order of discharge as indicated by the electrochemical series can be reversed by the concentration effect.

However, usually concentration is only secondary to the positions of the ions on the series, and this reversing can only occur if the ions are close enough in position on the series.

For example, although OH^- is lower on the electrochemical series, if the concentration of Cl^-, Br^-, or I^- is high enough and the OH^- concentration is low enough, the concentration effect may reverse the order of discharge as dictated by the electrochemical series.

Nature of electrodes

Electrodes which take no part in the electrolytic reaction are called inert electrodes. Usually, platinum and carbon (graphite) usually behave as inert electrodes. (However, platinum is attacked by liberated chlorine while carbon is attacked by liberated oxygen)

Some electrodes can influence ionic discharge due to their participation in the redox process or their strong affinity for certain ions. These electrodes are called 'active electrodes'.

For example, with copper electrodes and aq copper (II) sulfate solution as an electrolyte, no product will be collected at the anode, and instead the copper anode will dissolve. This is because instead of OH^- ions being discharged, Cu metal is instead oxidised to Cu^{2+} ions and loses electrons in the following equation:

$Cu\ (s) \rightarrow Cu^{2+}\ (aq) + 2e^-$

Another example is relevant. With mercury electrodes and aq NaCl solution as an electrolyte, instead of hydrogen gas, sodium metal will be produced at the cathode. This is because mercury tends to associate with sodium to produce sodium amalgam and so the discharge of Na^+ requires less energy than that of H^+. The equation for this is shown below:

$Na^+\ (aq) + e^- \rightarrow Na\ (s)$

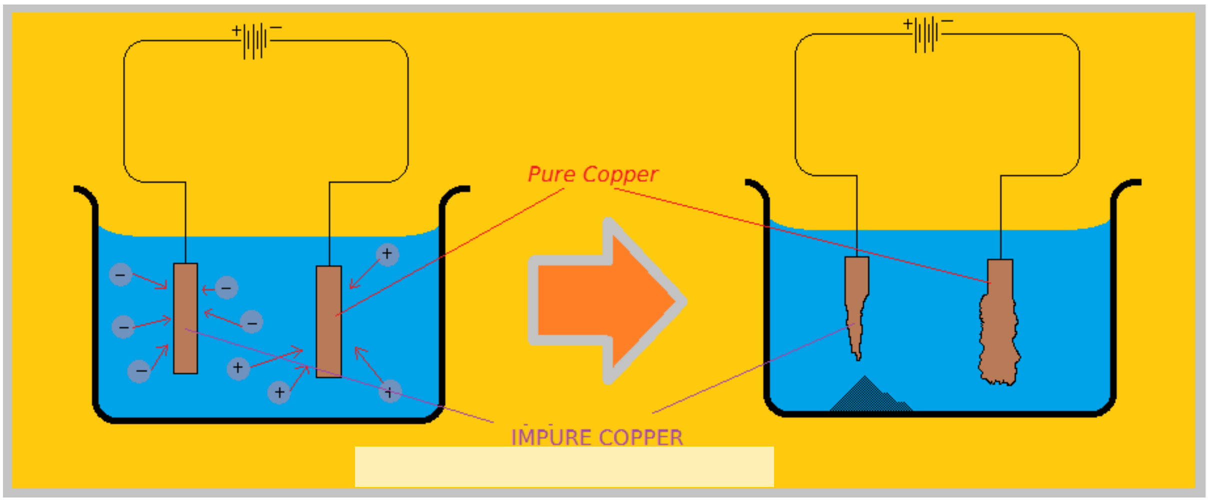
Applications

There are generally 4 applications of electrolysis. They are:

1. Purification/Refining of metals
2. Electroplating
3. Extraction of elements: Both metals (such as aluminium) and non-metals (such as chlorine)
4. Anodizing

Purification/Refining of Metals

A piece of metal can be purified by electrolysis.



The diagram here clearly illustrates this.

Note that the electrolyte is $CuSO_4$ solution, and the anode is on the left while the cathode is on the right of each set up.

During electrolysis, the copper atoms of the anode are oxidised, thus losing electrons and forming Cu^{2+} ions. These copper two ions migrate to the cathode, and then get reduced to form copper atoms again, thus resulting in copper being deposited on the cathode.

Reaction at anode: $Cu (s) \rightarrow Cu^{2+} (aq) + 2e^-$

Reaction at cathode: $Cu^{2+} (aq) + 2e^- \rightarrow Cu(s)$

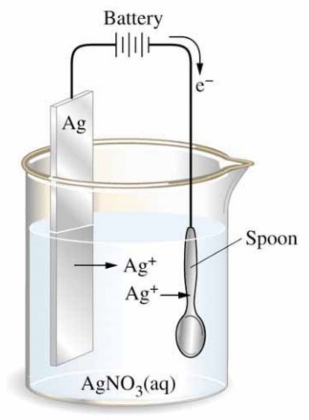
Hence, the anode, consisting of impure copper, becomes smaller and smaller while the cathode, consisting of pure copper, becomes bigger and bigger. However, the $CuSO_4$ solution remains unchanged in concentration.

The impurities are either left on the anode or will fall off to collect below the anode. These impurities are usually other metals, like silver or gold.

Electroplating

This is a method of coating the surface of one metal with another metal. Electroplating is used to give objects an attractive appearance, a good decorative finish, and for protection against corrosion. Common examples include copper plating, tin plating for food cans, silver and gold plating.

For example, let us look at the silver plating of a spoon.



Objects to be electroplated are made the cathode while the metal used to plate is made the anode. The electrolyte must contain the cations of the metal used to plate the spoon, which in this case are Ag+ ions.

During electrolysis, the Ag metal at the anode is oxidised and dissolves to form Ag^+ ions. These ions migrate to the cathode where they are discharged and deposited as a layer on the object. Thus the concentration of the metal's ions in the electrolyte remain unchanged.

The equations at the cathode and anode are as such:

Equation at anode: $Ag (s) \rightarrow Ag^+ (aq) + e^-$

Equation at cathode: $Ag^+ (aq) + e^- \rightarrow Ag (s)$

Sometimes, a series of plating may be necessary. For example, chromium does not adhere well to steel, and so the steel is first plated with copper, providing adhesion, and then a layer of nickel for sacrificial protection against corrosion before being plated fully with chromium for a tarnish-free finish.

Electroplating a non-conducting materials requires the material to either be first sprayed with metallic paint or coated with graphite powder so electricity can be conducted. (Don't say this in your exam if this comes out, talk also about how electricity is necessary for the process of electrolysis and redox reactions)

Extraction of Elements

Aluminium is extracted from bauxite ore, which contains aluminium oxide, Al_2O_3, mixed with impurities such as iron (III) oxide, Fe_2O_3, and silica, SiO_2.

Bauxite if first purified to obtain alumina (pure aluminium oxide). Electrolysis of the molten aluminium oxide will yield aluminium.

*Pure aluminium oxide has a very high melting point of 2045°C, and this is very expensive and dangerous to carry out (because of the high temperature). Hence, aluminium oxide is mixed with a compound called cryolite, Na_3AlF_6, forming a mixture that melts at a much lower temperature of about 950°C – cryolite acts as the solvent.

The equations that occur are as follows:

Equation at cathode: $Al^{3+}\ (l) + 3e^{-} \rightarrow Al\ (l)$

Equation at anode: $2O^{2-}\ (l) \rightarrow O_2\ (g) + 4e^{-}$

Overall equation: $4Al^{3+}\ (l) + 6O^{2-}\ (l) \rightarrow 4Al\ (l) + 3O_2\ (g)$

Note: Oxygen gas attacks the carbon anodes at high temperature to form gaseous products, mainly CO_2 gas. This causes the carbon anodes to burn away, so they must be replaced regularly.

Chlorine is obtained from common salt by electrolysing brine, which is a concentrated solution of sodium chloride.

Anodizing

This is the process of making the oxide layer on the surface of aluminium thicker. This will protect the aluminium better.

The aluminium object is made the anode while the cathode could be copper, lead r aluminium. The electrolyte is usually dilute sulphuric acid. During electrolysis, O_2 gas is evolved at the anode and this O_2 combines with the aluminium at the anode, thus the oxide layer become thicker.

*Note: Anodizing is not tested.

Organic Chemistry

Introduction

Organic Chemistry is the chemistry of carbon compounds, especially when it pertains to compounds of plant or animal origin.

Definitions

Organic Compound: Compounds made up of strikingly few elements. Apart from carbon, which must be present, hydrogen and oxygen are usually found. Moreover, nitrogen, the halogens, phosphorus, sulfur and some metals are sometimes present. However, the number of organic compounds far outnumbers the compounds of all other elements added together, because of the ability of carbon atoms to bond to other carbon atoms to form long chains.

Carbon atoms are able to form 4 single covalent bonds by sharing electrons with neighbouring atoms. The four single covalent bonds are directed symmetrically in space in a tetrahedral arrangement. (What this means is that the bonds point towards the corners of a regular tetrahedron when the carbon atom is placed in its centre.

Properties of Organic Compounds

1. Most organic compounds are covalent in nature and are largely non-polar and thus generally do not ionise in solution
2. They are generally insoluble in water. However, organic molecules that contain polar groups can dissolve in water (e.g.: alcohols contain O-H group, amines, amino acids, and carboxylic acids)
3. Most organic compounds mix well with non-polar solvents like hexane/tetrachloromethae
4. Organic compounds generally have lower melting and boiling points than inorganic compounds (because they are generally non-polar – therefore only have weak id-id interactions – and they have SMS – simple molecular structure)
5. Many organic compounds are thermally unstable, decomposing into smaller/simpler molecules when heated
6. Most organic compounds are inflammable and burn exothermically in plentiful supply of air to yield CO_2 gas and water (H_2O).
7. Reactions involving organic compounds tend to take place at a lower rate than the ionic compounds of inorganic chemistry. They then usually require heating, thorough mixing and the use of a catalyst to speed up the reactions.
8. A homologous series is a family of organic compounds which follows a regular structured pattern. An example is the alkanes, a series of hydrocarbons with the general formula C_nH_{2n+2} with members such as methane, ethane, propane and butane. All members of a homologous series share a general molecular formula.
9. Members of a homologous series exhibit similar physical and chemical properties, with gradual changes as the molecular size increases.
10. A functional group is an atom, a radical (a group of atom) or a bond common to a homologous series, and which determines the main chemical properties of the series. For example, the members of the alcohol series all have the hydroxyl, O-H group.
11. A saturated organic compound contains carbon atoms bonded only by 1 covalent bond, while an unsaturated one contains carbon atoms joined by double or triple covalent bonds.

12. Structural formulae are very important in organic chemistry. It indicates how atoms are arranged within the molecule of a substance, and shows which and how atoms are linked together

*Note: The structural formula is usually shown as planar for convenience and does not necessarily imply a flat molecule.

Alkanes

Definitions

Alkanes are saturated hydrocarbons and are the main constituent of petroleum.

General formula: C_nH_{2n+2}

The first four members are: methane (CH_4), ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}).

Note that alkanes do not have a functional group defining them.

Properties

Most alkanes are gases or liquids at room conditions, because they have SMS – simple molecular structures. The first 4 members are gases.

Chemically, alkanes are inert. They only undergo few reactions, mainly combustion and substitution reactions.

Combustion

In plentiful supply of oxygen, methane burns to produce CO_2 gas and water (H_2O).

As an example, let's look at the combustion of methane:

$CH_4 + 2O_2 \rightarrow CO_2 + H_2O$

Substitution

Let's look at substitution with chlorine.

Methane reacts with chlorine in sunlight (UV light acts as a catalyst) to give a mixture of products. Each hydrogen atoms in methane can be substituted by a chlorine atom.

If one hydrogen atom is replaced the product formed is chloromethane (CH_3Cl).

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

If two hydrogen atoms are replaced, the product is dichloromethane (CH_2Cl_2); if three, trichloromethane ($CHCl_3$), and if four, tetrachloromethane (CCl_4).

Alkenes

Definition

Alkenes are unsaturated hydrocarbons with a C=C double bond.

General formula: C_nH_{2n} (*Note: Only for alkenes with 1 C=C double bond)

The first 3 members are ethene (C_2H_4), propene (C_3H_6) and butene (C_4H_8). (Ethene is sometimes referred to also as ethylene)

The defining functional group of alkenes is the C=C double bond.

Properties

Most alkenes are also gases or liquids at room temperature, because of SMS.

Chemically, alkenes are far more reactive than alkanes, because of the presence of the C=C bond that allows alkenes to undergo addition reactions (will be explained later).

Combustion

This is similar to alkanes, where products are CO_2 gas and water.

As an example, let's look at the combustion of ethene.

$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$

Addition

Definition

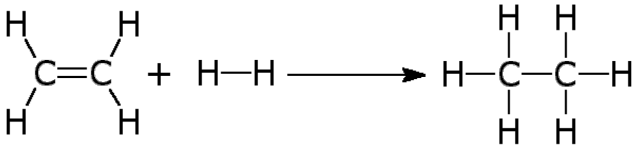
Addition reactions are reactions in which two or more molecules react to give a single molecule.

Addition of Hydrogen (Hydrogenation)

Let's look at ethene once again for this.

In the reaction, nickel is used as a catalyst. Ethane is produced.

$C_2H_4 + H_2 \rightarrow C_2H_6$



You can expand this knowledge and use it on bigger alkenes. However, note that the addition of hydrogen can ONLY occur at the carbon atoms where the C=C double bond is present, because carbon can only be covalently bonded to 4 atoms at the max.

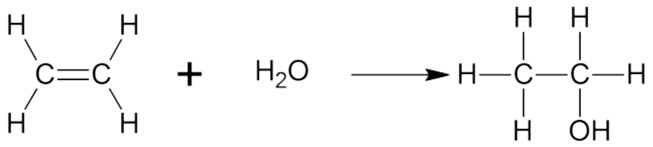
Hydrogenation is really important in making margarine. Vegetable oil is polyunsaturated (consisting of many C=C bonds) and is thus liquid. The addition of hydrogen to the oil creates a more "solid" substance. (This is a process known colloquially as "hardening")

Addition of Water (Hydration)

What happens here is that an alkene and water combine to produce an alcohol.

Let's look at ethene again.

$C_2H_4 + H_2O \rightarrow C_2H_5OH$

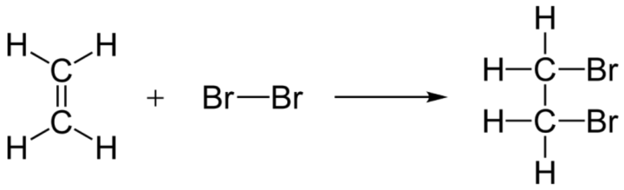


The reaction takes place under high temperature (300°C) and pressure (60 atm). Water, in the form of steam and the catalyst – phosphoric acid (H_3PO_4) are used.

Addition of Bromine

Let's look at ethene again (again).

$C_2H_4 + Br_2 \rightarrow C_2H_4Br_2$ (this compound is known as 1,2-dibromoethane – note that nomenclature will be discussed later)

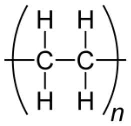


This reaction is very useful as it serves as a test for unsaturation. When liquid or aqueous bromine is added to an alkene and shaken, the brown colour of bromine decolourises quickly, because it forms 1,2-dibromoethane. However, this does not happen with saturated compounds.

Polymerisation

Many small alkene molecules can link together (also known as polymerise) to form a long chain.

For example, ethene become polyethene.



Alkynes

*Note: This isn't tested.

Definition

Alkynes are unsaturated hydrocarbons with a C≡C triple bond.

The general formula of an alkyne is C_nH_{2n-2}.

The first 3 members are ethyne (C_2H_2), propyne (C_3H_4) and butyne (C_4H_6).

Incomplete Combustion of Hydrocarbons

Complete combustion of a hydrocarbon occurs when sufficient oxygen is present. This will produce CO_2 gas and water.

However, when insufficient oxygen is present, incomplete combustion occurs instead. This produces carbon monoxide (CO) and carbon (soot).

For a Bunsen burner, complete combustion occurs when the air hole is opened. This will result in. a non-luminous, clean flame.

However, when the air hole is closed, the flame is orange/yellow, and soot is produced due to incomplete combustion.

*Note: A substance with a greater percentage carbon by mass will have a sootier flame.

Alcohols

Definition

Alcohols are organic compounds that contain the hydroxyl group, the O-H group.

Alcohols all end with the suffix –ol.

The first four members are methanol (CH_3OH), ethanol (C_2H_5OH), propanol (C_3H_7OH) and butanol (C_4H_9OH).

*Note: Alcohols with two –OH groups are called diols and with three –OH groups are called triols.

General formula is $C_nH_{2n+1}OH$.

**Note:We will be using ethanol as a primary example for all the reactions in this segment.

Preparation

Preparation from Ethene

The equation for this is $C_2H_4 + H_2O \rightarrow C_2H_5OH$ (hydration – ring a bell?)

A mixture of ethene and steam is passed over phosphoric acid (which is a catalyst) at a high

temperature of 300°C and a high pressure of 60 atm.

Preparation by Fermentation

Definition

Fermentation: The slow decomposition of organic compounds induced by microorganisms like yeast.

How does it work?

The active factors actually responsible for the chemical reaction are the enzymes present in the microorganisms.

The underlying reaction in the production of ethanol by fermentation is the catalytic conversion of sugar, glucose, into ethanol by the enzyme zymase present in yeast. The process is carried out in an oxygen-free environment as the reaction is anaerobic.

The sugar can be obtained from a variety of sources, such as fruit, honey, or molasses.

The ethanol solutions obtained after fermentation are usually concentrated and purified by fractional distillation.

Properties

All alcohols are colourless liquids at room temperature and pressure. The four above-mentioned alcohols are soluble in water.

They also are able to undergo reactions.

Combustion

The equation is $C_2H_5OH + 3O_2 \rightarrow 3H_2O + 2CO_2$.

Dehydration

This is the reverse of hydration.

$C_2H_5OH \rightarrow C_2H_4 + H_2O$

This is done by heating ethanol with concentrated sulphuric acid, H_2SO_4 (the dehydrating agent).

Oxidation

$C_2H_5OH + 2[O] \rightarrow CH_3COOH + H_2O$

A carboxylic acid is formed as a result.

*Note: the [O] represents the oxygen that comes from an oxidising agent. In the above example, ethanol is oxidised to form ethanoic acid. Acidified potassium dichromate (VI) is a good oxidising agent. Moreover, oxygen from the air can also serve as oxidising agents for the reaction.

**Note: This is why beer or wine left exposed to air turns sour (because ethanol is oxidised by the oxygen in the air to form ethanoic acid, and acids taste sour – this is why lemons are sour).

Esterification

Alcohols react with carboxylic acids to produce an ester and water. This will be expounded upon later in the section of esterification under carboxylic acids.

Applications

Alcohols are especially useful, and not in the context of food and beverage. Ethanol, for example, is incredibly versatile, and is used as a solvent, and as fuel for motor vehicles in some countries, such as Brazil.

Carboxylic Acids

Definition

Carboxylic acids: Organic compounds contain the carboxyl group, -COOH, as a functional group.

*Note: All the names of carboxylic acids end with –oic acid. (Acids with two carboxyl groups have names ending with –dioic)

General formula:$C_nH_{2n+1}COOH$

*Note: the first member has n=0, and methanoic acid has the formula HCOOH.

The first four members are methanoic acid (HCOOH), ethanoic acid (CH_3COOH), propanoic acid (C_2H_5COOH) and butanoic acid (C_3H_7COOH).

Ethanoic acid is sometimes also called acetic acid. Vinegar is a solution of ethanoic acid in water.

Preparation

Ethanoic acid can be produced in a few ways.

From alcohols

The equation is $C_2H_5O + 2[O] \rightarrow CH_3COOH + H_2O$. (This is also known as the oxidation of ethanol)

Properties

The above-mentioned carboxylic acids are liquids at room conditions. The acids do not completely dissociate in water and are hence weak acids.

Oxidation and Reduction in Organic Compounds

As it is rather difficult to apply traditional definitions of oxidation and reaction to organic compounds, it is defined in different terms.

Oxidation	Reduction
Gain of oxygen atom	Loss of oxygen atom
Loss of hydrogen atom	Gain of hydrogen atom

*Note: A method to remember this that I'd recommend is to first associate oxidation with gain in the number of oxygen atoms, and just remember that it is the opposite with hydrogen.

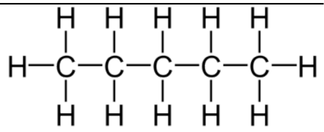
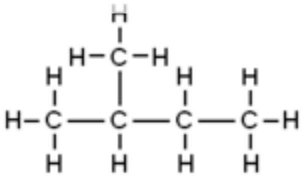
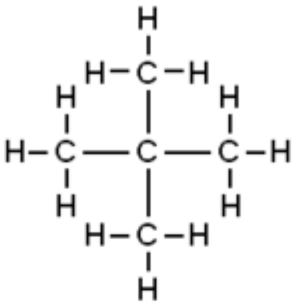
Isomerism

Definition: Isomers are molecules that have the same molecular formula, but have different arrangements of the atoms in space.

Structural Isomerism

Chain Isomerism

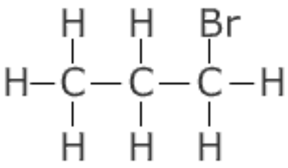
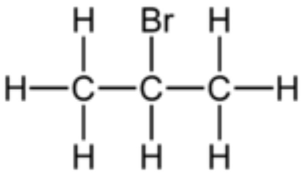
In chain isomerism, the components of the carbon skeleton (the main chain) are rearranged, giving rise to branching. A clear example is pentane, which has 3 chain isomers in total: pentane, 2-methylbutane, and 2,2-dimethylpropane.

pentane	2-dimethylbutane	2,2-dimethylpropane
		

As you can see, all 3 molecules have the same molecular formula, but as there is the possibility of branching off of the main chain, chain isomers do exist.

Position Isomerism

In position isomerism, the basic carbon skeleton remains the same, but important functional groups are moved around the skeleton. Let's look at position isomers of bromopropane; 1-bromopropane and 2-bromopropane.

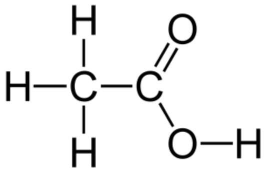
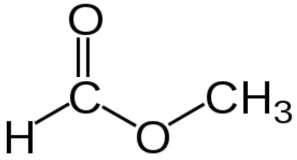
1-bromopropane	2-bromopropane
	

Notice that while the number of carbon atoms in the main chain remains unchanged, the bromine functional group assumes 2 positions; one attached to the first carbon, and one attached to the second.

*Note: There is no 3-bromopropane because it will essentially be 1-bromopropane flipped around, and in naming convention for organic chemistry, we seek to use the lowest number when identifying functional groups. (You do not need to know this)

Functional Group Isomerism

In this type of structural isomerism, the molecules are of entirely different homologous groups. A clear example of this is ethanoic acid and methyl methanoate.

ethanoic acid	methyl methanoate
	

While one is a carboxylic acid, the other is an ester.

Stereoisomerism

*Note: This is not tested.

This is isomerism in which isomers are joined in the same order, but still have a different spatial arrangement.

There are two types: optical isomerism and cis-trans isomerism.

Optical Isomerism

A

B

Let us look at the two molecules above, A and B. Each colour represents an element, let's say. No matter how you rotate B, you will never be able to get A. When rotating them around, this is what you get:

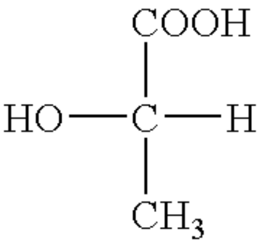
A

B

Molecules such as this are described as non-superimposable mirror images of each other. This is similar to your hands, where the left and right hands are mirror images of one another, and look similar, but their images cannot be superimposed on one another. Molecules such as these are termed chiral molecules, and their central atom is called a chiral centre.

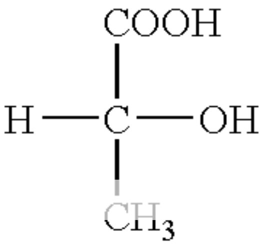
These molecules are called optical isomers because of their effect on plane polarised light. Simple substances that show optical isomerism, exist as two isomers called enantiomers. A solution of one enantiomer rotates the plane of polarisation in a clockwise direction, while a solution of another will rotate the plane of polarisation in an anti-clockwise direction. The enantiomer that rotates the plane of polarisation in a clockwise direction is the (+) form while the enantiomer that rotates the plane of polarisation in an anti-clockwise direction is the (-) form.

An example is lactic acid, $CH_3CHOHCOOH$, which has 2 enantiomers.



$$\begin{array}{ccc} & \mathrm{COOH} & \\ & | & \\ \mathrm{HO} - & \mathrm{C} & - \mathrm{H} \\ & | & \\ & \mathrm{CH_3} & \end{array}$$

L(+) lactic acid



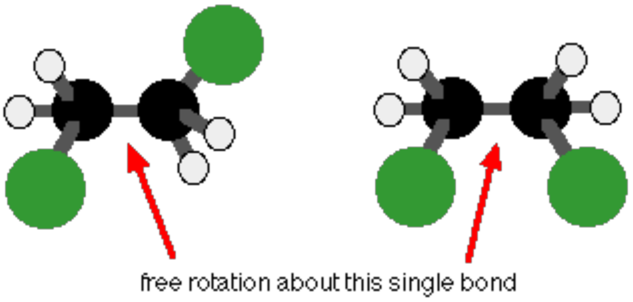
$$\begin{array}{ccc} & \mathrm{COOH} & \\ & | & \\ \mathrm{H} - & \mathrm{C} & - \mathrm{OH} \\ & | & \\ & \mathrm{CH_3} & \end{array}$$

D(-) lactic acid

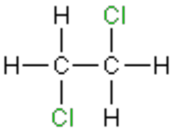
Cis-Trans Isomerism

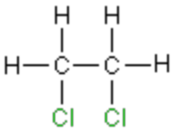
This is another form of stereoisomerism in which the atoms are attached in the same way but their spatial arrangement differs.

Cis-trans isomerism occurs when there is restricted rotation somewhere in a molecule. In organic chemistry, this means the presence of carbon-carbon double bonds.

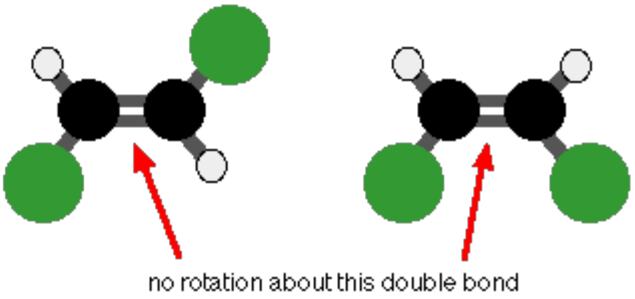


This model shows how cis-trans isomerism cannot exist in compounds with only a carbon-carbon single bonds, as there is free rotation about that bond. Hence, the compounds shown below are exactly the same thing, 1,2-dichloroethane.



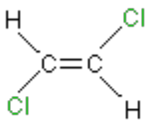


However, with carbon-carbon double bonds, rotation is restricted about the bond, as is described by the diagram below.

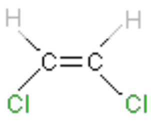


Hence, two possible configurations exist, the trans- and cis- “versions” of the molecule. The trans-version is the one in which the green atoms exist, locked on opposite sides of the bond. The cis-version is the one in which the green atoms are on the same side of the bond.

Let us look at 1,2-dichloroethene as an example.



trans-1,2-dichloroethene



cis-1,2-dichloroethene

Applications of Organic Chemistry – Petrochemical Industry

Definitions

Petroleum: A mixture of hydrocarbons that needs to be refined to make useful fuels and chemicals.

Fractional Distillation of Petroleum

Petroleum is heated in a furnace where it vaporises, and is passed up fractionating columns. Fuels of different boiling points come out of the column at different heights. Generally, smaller molecules have lower boiling points and so come out at the top of the column. Larger molecules tend to have higher boiling points and so come out at the bottom of the column.

This is a table of the different fractions that constitute petroleum.

Fraction	**Approximate no. of carbon atoms per molecule**	**Approximate b.p./°C**	**Uses**
Petroleum gases	1 – 4	Below r.t.p.	Bottled gas for gas cooker
Petrol/Gasoline	5 – 10	35 – 75	Fuel for motor vehicles
Naptha	8 – 12	70 – 170	Petrochemicals
Kerosene/Paraffin	10 – 14	170 - 250	Fuel for jet aircraft; fuel for oil stoves
Diesel	15 – 25	250 – 340	Fuel for diesel engines
Lubricating oil	19 – 35	340 – 500	Lubricant in engines; for making waxes and polishes
Bitumen	> 70	Over 500	To surface roads

Cracking

Definition: The process of breaking large hydrocarbons into smaller hydrocarbons (in terms of molecular size).

Cracking is especially important because lighter fractions tend to be more in demand than heavier ones (e.g.: petrol has higher demand than lubricating oil), and cracking allows heavier fractions to be converted into smaller ones.

Let us look at a few reactions that decane ($C_{10}H_{22}$) can undergo, which can be considered cracking:

1. $C_{10}H_{22}\ (l) \rightarrow C_7H_{16}\ (l) + C_3H_6\ (g)$
2. $C_{10}H_{22}\ (l) \rightarrow C_{10}H_{20}\ (l) + H_2\ (g)$
3. $C_{10}H_{22}\ (l) \rightarrow C_4H_{10}\ (g) + C_3H_8\ (g) + C_2H_4\ (g) + C\ (s)$

There are 2 types of cracking: thermal cracking and catalytic cracking.

Thermal cracking is when alkanes are heated to temperatures of about 800°C to 850°C under high pressure.

Catalytic cracking is when alkanes are passed over a catalyst, at about 300°C. The catalysts used are alumina (Al_2O_3) and silica (SiO_2).

*Note: After cracking, the products are separated via fractional distillation.

Applications of Cracking

There are 3 important applications of cracking:

1. Changing heavy fractions such as lubricating oil which are in less demand into lighter fractions such as petrol which are in higher demand.
2. Changing naptha into alkenes (especially ethene)
3. To make hydrogen gas

Chemical Conversion

Many important molecules are derived from hydrocarbons made from petroleum. Lower alkenes, such as ethene, are useful as starting materials to make these molecules. For example:

- Ethene is used to make plastics such as polyethene
- Chloroethene is used to make PVC
- 1,2-ethanediol is an antifreeze, a hydraulic fluid, and is also used in the production of polyesters such as Terylene
- Phenylethene – used to make polyphenylethene, a plastic
- Ethanol – A very important solvent
- Propene – To make polypropene, a plastic, and the solvent propan-2-ol

*Note: Chemical conversion is not tested