CHEMISTRY IN INDUSTRY AND TECHNOLOGY

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As one of the most important roles of chemistry is to make forms of matter that have never existed before, it plays a central role in any material revolution. The Industrial Revolution of the 18th century was the result of the large-scale extraction of iron, but the material revolution continues the development of new materials with structures and properties that serve the technologies of today. The consideration of how the materials benefit society makes this option particularly relevant to aim 8 (raising awareness of the moral, ethical, social, economic and environmental implications of using science and technology).

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INTRODUCTION

The chemical industry can take raw materials and turn them into much more valuable products such as sulfuric acid, ammonia, ethene, sodium hydroxide, and chlorine amongst others. Technology is used extensively in the chemical industry to produce biofuels or manufacture polymers with different properties. The importance of chemistry in industry and technology rests on the food, clothes, medicines and the great variety of consumer articles that it produces. One sign of the economic development of a country is the state of its chemical industry. For example, the commercialization of the Haber process likely prolonged World War I by at least one year. Almost a century later, "the emerging fields of nanoscience and nanotechnology are leading to unprecedented understanding and control over the fundamental building blocks of all physical things. This is likely to change the way almost everything - from vaccines to computers to automobile tires to objects not yet imagined - is designed and made."

(Nanotechnology shaping the world atom by atom, National Science and Technology Council Report, September 1999, Washington, D.C.)

OPTION

C1 IRON, STEEL AND ALUMINIUM

The main sources of iron include iron ores and scrap iron. Iron ores are mined as oxides, Fe_2O_3, (haematite), Fe_3O_4, ($FeO\cdot Fe_2O_3$, magnetite, a mixed oxide) and the sulfide FeS_2, (iron pyrites). The latter is roasted in air to form the oxide and sulfur dioxide.

$$4\ FeS_2\ (s) + 11\ O_2\ (g) \longrightarrow 2\ Fe_2O_3\ (s) + 8\ SO_2\ (g)$$

A mixture of the raw materials limestone (calcium carbonate, $CaCO_3$), coke (C) and iron ore (for example iron(III) oxide, Fe_2O_3) is fed into the blast furnace from the top (called the **hopper)**. The mixture is called '**solid charge**'. A large volume of air is introduced under pressure near the bottom of the furnace where coke is oxidized exothermically to carbon dioxide as follows:

$$C\ (s) + O_2\ (g) \longrightarrow CO_2\ (g) + heat$$
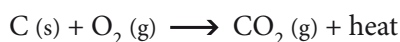
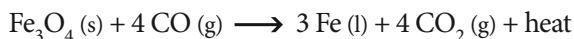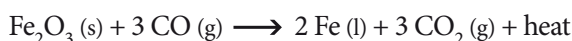The furnace is at about 2200 K temperature in this lower region. Higher up the furnace, carbon dioxide reacts with coke to form carbon monoxide. This reaction is endothermic, with the furnace in this region cooling to 1400 K:

$$CO_2\ (g) + C\ (s) + heat \rightarrow 2\ CO\ (g)$$
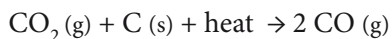
If natural gas methane, CH_4 is injected with the hot air, incomplete combustion can occur to form carbon monoxide and less coke is required:

$$2\ CH_4\ (g) + O_2\ (g) \longrightarrow 2\ CO\ (g) + 4\ H_2\ (g)$$

It is carbon monoxide that plays the largest part in the reduction of the ore towards the top of the furnace. Iron oxides are reduced exothermically:

$$Fe_2O_3\ (s) + 3\ CO\ (g) \longrightarrow 2\ Fe\ (l) + 3\ CO_2\ (g) + heat$$

$$Fe_3O_4\ (s) + 4\ CO\ (g) \longrightarrow 3\ Fe\ (l) + 4\ CO_2\ (g) + heat$$

If methane is injected, the hydrogen gas produced on partial oxidation can also act as a reducing agent:

$$Fe_3O_4\ (s) + 4\ H_2\ (g) \longrightarrow 3\ Fe\ (l) + 4\ H_2O\ (g)$$
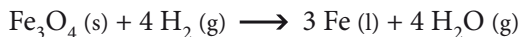
Coke can also reduce the oxide, for example:

$$Fe_2O_3\ (s) + 3\ C\ (s) \longrightarrow 2\ Fe\ (l) + 3\ CO\ (g)$$

The iron produced sinks to the bottom of the furnace where the temperature is high enough to keep it molten. At the same time, because of the high temperature, the limestone in the charge decomposes to form calcium oxide and carbon dioxide:
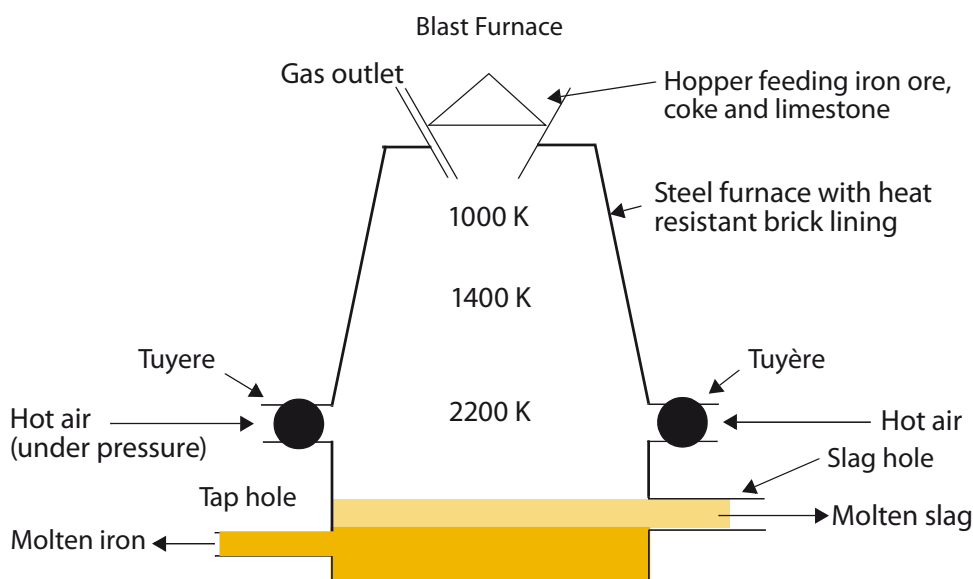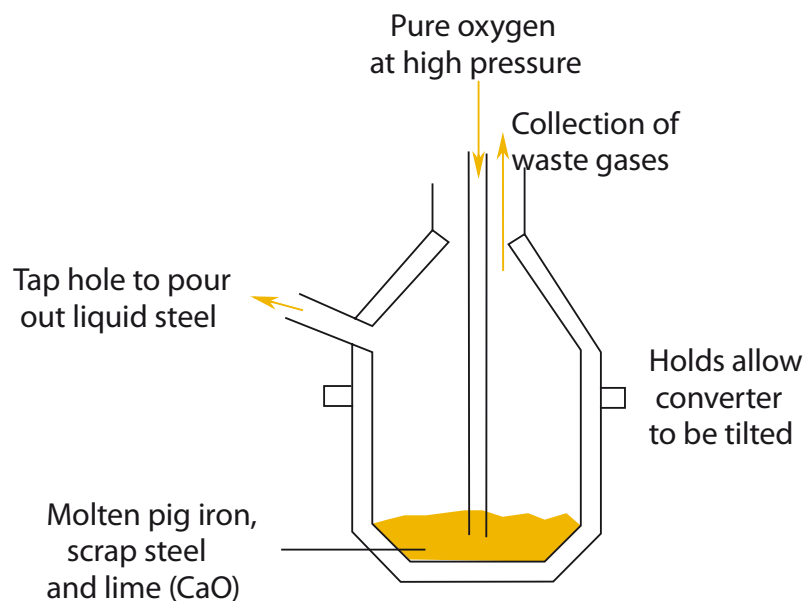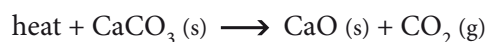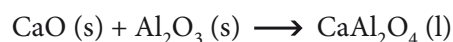

Figure 1401   Blast Furnace

Figure 1402   A basic oxygen converter

$$heat + CaCO_3 \text{ (s)} \longrightarrow CaO \text{ (s)} + CO_2 \text{ (g)}$$
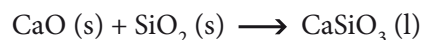
The highly basic calcium oxide combines with the acidic silicon(IV) oxide present as sand in the impure ore and the amphoteric aluminium oxide (which can behave as an acid or a base). These impurities in the ore form a molten slag of calcium silicate(IV) and calcium aluminate(III), which trickles down the stack:

$$CaO \text{ (s)} + SiO_2 \text{ (s)} \longrightarrow CaSiO_3 \text{ (l)}$$

$$CaO \text{ (s)} + Al_2O_3 \text{ (s)} \longrightarrow CaAl_2O_4 \text{ (l)}$$
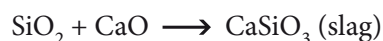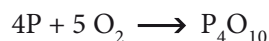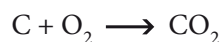
The molten iron, called pig iron, is impure and not so strong. It contains about 4 – 5% carbon, 1 – 2% silicon and smaller amounts of elements such as manganese, phosphorus and sulfur. The more dense pig iron lies at the bottom of the furnace and the lighter slag forms an immiscible layer above it; the molten iron and slag are tapped off every few hours. Slag is used for road making and in the manufacture of cement. A furnace can operate continuously for several years before it needs relining. See Figure 1401.

THE BASIC OXYGEN PROCESS:

The most common method of making steel is to blast pure oxygen through the impure molten iron. Scrap steel is placed in the converter, which is then tilted and molten pig iron is transferred from the blast furnace. The oxygen and powdered calcium oxide (lime) are blown onto the surface of the metal at high pressure through water cooled pipes. The oxygen penetrates into the molten iron and oxidizes the impurities rapidly. Acidic oxides of carbon, sulfur, phosphorous and silicon are formed, which escape from the melt as gases or combine with lime to form slag:

$$C + O_2 \longrightarrow CO_2$$

$$S + O_2 \longrightarrow SO_2$$

$$4P + 5\,O_2 \longrightarrow P_4O_{10}$$

$$Si + O_2 \longrightarrow SiO_2$$

$$SiO_2 + CaO \longrightarrow CaSiO_3 \text{ (slag)}$$

Slag forms a layer above the crude steel (containing less than 1.5% carbon) and remains behind as liquid steel which is poured off. The oxidation of the impurities is an exothermic process and the heat evolved as the impurities are oxidized keeps the contents of the furnace in a molten state, despite a rise in the melting point as impurities

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are removed (recall: impurities lower and broaden the melting point of a substance). Alloying elements such as manganese and cobalt are then added to the molten metal to form alloys with specific properties.

C.1.4	Describe alloys.
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An **alloy** is a mixture of two or more elements at least one of which is a metal; thus it is a homogeneous mixture of metals or a mixture of a metal and non-metal in which the metal, called the base metal, is in the much larger amount resulting in metallic properties. The alloy is made by mixing the alloying element(s) with the base metal when molten and allowing the mixture to cool to form the alloy.

C.1.5	Explain how alloying can modify the properties of metals.
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Metals contain a lattice of cations in a sea of electrons with an orderly arrangement of the atoms and with no rigid or directional bonds present in the metallic crystal structure (unlike, for example, in covalent macromolecular structures). As a result, metal layers are able to slide over each other when a stress is applied to it and are soft, ductile and malleable – properties typical of metals. The presence of another element, with differently sized atoms/cations, modifies the micro-structure of the base metal by disrupting the regular, repeating lattice. This now makes it difficult for one layer to slide over another. With atoms such as carbon, which are very much smaller than the metal cations, they can fit into the holes of the metal lattice disrupting the bonding between metal atoms and again impacting on the structure.

Alloying can modify physical properties such as hardness and malleability, as well as engineering properties such as tensile strength and chemical properties such as resistance to corrosion. For example, stainless steel and bronze are stronger and more corrosion resistant than their base metals iron and copper respectively. Addition of different amounts of metals to steel changes its hardness, resistance to oxidation and strength. Similarly when a low percentage of carbon is added to iron, there is less disruption in the lattice structure of the base metal. The steel can still be bent and shaped and thus used to make automobiles. As the percentage of carbon is increased, the disruption in the crystal lattice increases, the layers experience greater difficulty in sliding over each other and a stronger steel is formed that can be used to build bridges. Further increase in carbon (to about 1%) makes steel very hard and it can be used in drill bits. If the amount of carbon becomes higher still, to about 4% as in pig iron, it is so difficult for the layers to slide over each other that it becomes brittle and of little use for construction.

C.1.6	Describe the effects of heat treatment of steel.
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Steel obtained from the basic oxygen converter may not have the desired properties and often requires further heat (or mechanical) treatments. These lead to changes at the micro-crystal structure level that result in the desired effect. Thermal treatments include annealing, quenching and tempering:

Annealing is the process of slowly heating steel and holding it at a particular temperature (sometimes about half its melting point) to modify crystal structure, and then cooling it. The rate of heating and cooling and the temperature it is raised to depend on the type of steel and the desired properties. Annealing is used to soften steel (that is make it more ductile and malleable), remove stress caused by uneven heating or mechanical treatment, change its electrical or other physical properties as well as remove trapped gases (which if not removed, weaken the steel making it susceptible to cracking).

OPTION

Stress applied to metallic structure

Layers are able to slide over each other when a stress is applied

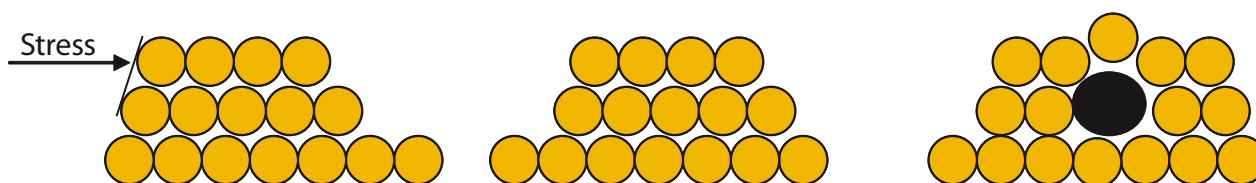Larger element disrupts regular metal lattice structure

Stress

*Figure 1403 How alloying can modify the properties of metals*

Quenching refers to rapid cooling and involves the sudden immersion of hot metal in cold water or oil. Quenching allows the crystal structure which is stable at high temperatures to exist at low temperatures. These crystal structures tend to be harder than those stable at room temperature since the alloying elements are trapped within the crystal lattice making the sliding of layers very difficult. For example, carbon steel (containing nearly 1% carbon) is used for the production of cutting tools.

If the quenched steel is too brittle, it has to be made more ductile through a heat treatment called **tempering** which leads to a loss of some hardness but which makes the steel less brittle. Tempering is the process of re-heating hardened steel to certain temperatures (in the 200 °C to 600 °C range) depending on the type of steel and then cooling it (and is done subsequent to quenching). Tempering allows some of the carbon atoms to diffuse to form a different structure, making the steel softer and more ductile.

Iron is a shiny, soft, ductile, malleable metal of high strength which can be shaped into objects. Iron rusts to form hydrated iron(III) oxide which crumbles easily:

$$4\,Fe\,(s) + 3\,O_2\,(g) + x\,H_2O\,(l) \longrightarrow 2\,Fe_2O_3\,.\,x\,H_2O\,(s)$$
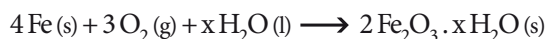
Unlike aluminium oxide, rust is porous, allowing oxygen and water to penetrate it and continue the corrosion process.
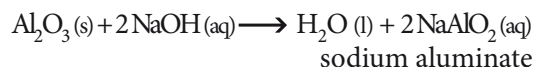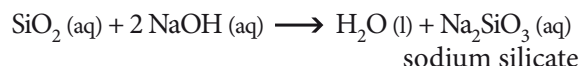
Uses of iron include tin cans (mild steel coated with a layer of tin), ornamental gates, bridges, reinforcing concrete with steel and use as a catalyst in the Haber process. Most iron produced is used to make steel. Many different steels are made, with different properties for different uses. The amount of carbon and the alloying metals mixed with the iron largely determine the nature of the steel such as its tensile strength and other useful mechanical properties. Small amounts of elements such as manganese, are added to give desirable qualities such as toughness so that it can be used as tool steel. The presence of chromium as an additive to steel inhibits rusting and produces stainless steel. It also contains some nickel; formation of a coating of chromium(III) oxide, Cr_2O_3 prevents the iron from rusting. Other important steel alloys, their properties and some uses are given below:

Aluminium is obtained industrially by the electrolysis of molten aluminium oxide, Al_2O_3. This is obtained from bauxite, impure hydrated aluminium oxide, $Al_2O_3 \cdot xH_2O$. The main impurities in bauxite are iron(III) oxide, Fe_2O_3 and silicon(IV) oxide, SiO_2. The amphoteric nature of Al_2O_3 is an essential feature on which its purification is based. When the impure bauxite is treated with hot concentrated sodium hydroxide, silicon(IV) oxide and aluminum oxide dissolve:

$$SiO_2\,(aq) + 2\,NaOH\,(aq) \longrightarrow H_2O\,(l) + Na_2SiO_3\,(aq)$$
sodium silicate

$$Al_2O_3\,(s) + 2\,NaOH\,(aq) \longrightarrow H_2O\,(l) + 2\,NaAlO_2\,(aq)$$
sodium aluminate

Iron(III) oxide and other basic materials remain insoluble and are removed by filtration. The solution is diluted and seeded with solid sodium hydroxide to reverse the

Iron + other metals	Important Properties	Some uses
Titanium steel	Withstands high temperatures	Gas turbines, spacecraft
Chromium steel	Hard	Ball bearings
Cobalt steel	High magnetic permeability	Magnets
Manganese steel (10 - 18% Mn)	Tough tool steel; resistant to wear	Earthmoving machinery, railway lines
Stainless steel containing about 20% chromium and 10% nickel	Non-rusting	Cutlery, sinks, car accessories, surgical instruments

Figure 1404 Properties and uses of some iron alloys

reaction and precipitate aluminium hydroxide (sodium silicate stays in solution):

$$2H_2O(l) + NaAlO_2(aq) \longrightarrow Al(OH)_3(s) + NaOH(aq)$$
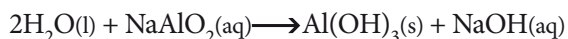
Finally, the aluminium hydroxide is heated to obtain pure aluminium oxide:

$$2\,Al(OH)_3\,(s) \longrightarrow Al_2O_3\,(s) + 3\,H_2O\,(g)$$

Aluminium is so reactive that it is obtained by electrolysis of molten salts, requiring high temperatures to maintain the molten state. The melting point of Al_2O_3 is > 2000 °C

(the cation Al^{3+} and the anion O^{2-} both have high charge densities due to their relatively small sizes and large charges, leading to very strong electrostatic interactions, high lattice energy and a very high melting point; in addition there is a high degree of covalent character to the bonding so the molten substance is also a poor conductor). Alumina is mixed with molten cryolite, Na_3AlF_6, as a solvent which lowers the melting point to about 900 °C and improves the conductivity. The electrolyte is maintained at this temperature by the current through it and thus the process is energy intensive. The mixture of cryolite and alumina is electrolyzed in a cell with graphite (carbon) positive electrodes (anodes) and a graphite cell lining that serves as the negative electrode (cathode). As the electrolysis takes place, molten aluminium (melting point 660 °C) sinks to the bottom of the cell and is run off into molds.
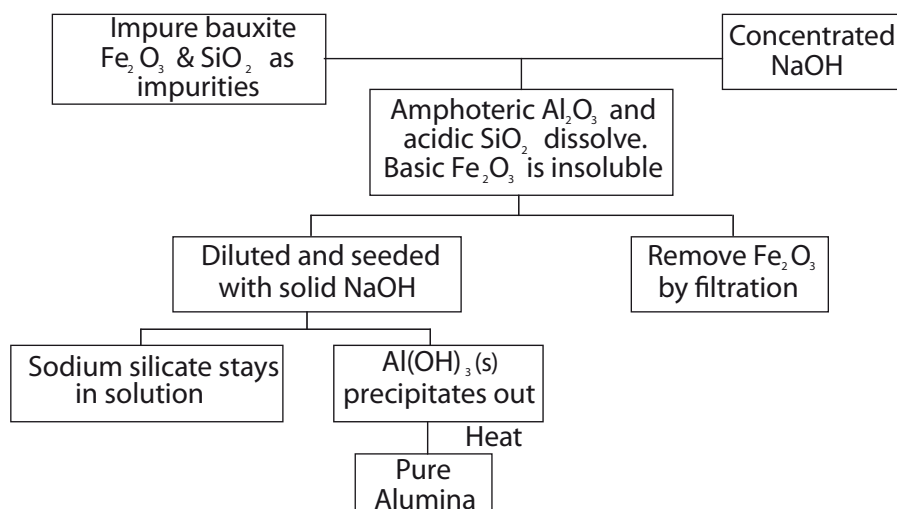

Figure 1405   Treatment of bauxite to obtain pure Al_2O_3
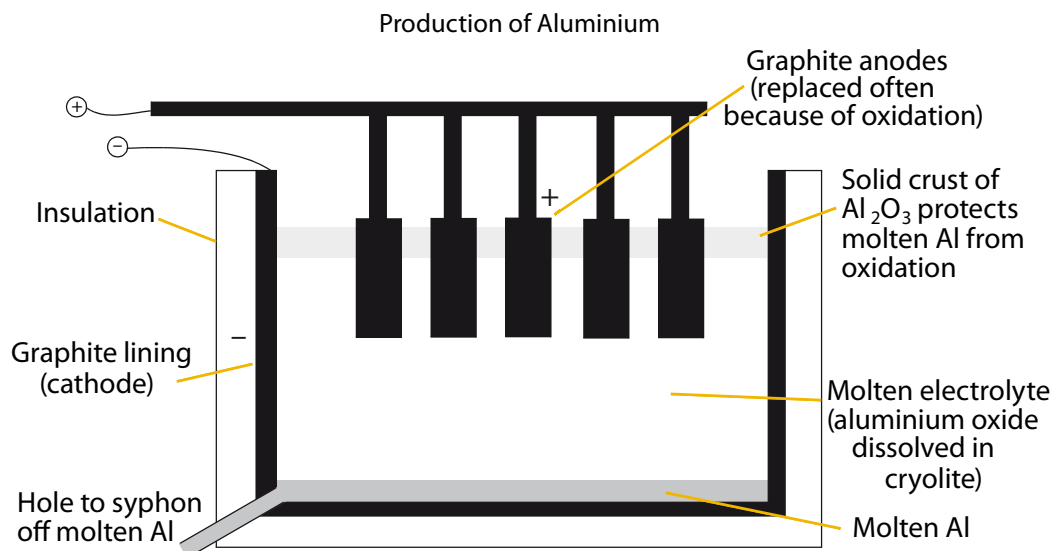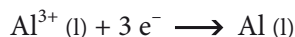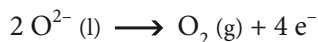
Production of Aluminium

Figure   1406 Production of Aluminium

(–) electrode half reaction (cathodic reduction; molten aluminium produced):

$$Al^{3+} \text{ (l)} + 3\ e^- \longrightarrow Al \text{ (l)}$$

(+) electrode half reaction (anodic oxidation; oxygen gas evolved):

$$2\ O^{2-} \text{ (l)} \longrightarrow O_2 \text{ (g)} + 4\ e^-$$

The overall reaction is:

$$4\ Al^{3+} \text{ (l)} + 6\ O^{2-} \text{ (l)} \longrightarrow 4\ Al \text{ (l)} + 3\ O_2 \text{ (g)}$$

The O_2 produced reacts with the graphite positive electrodes (anodes) to form oxides of carbon:

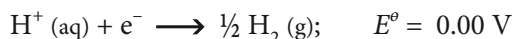$$C \text{ (s)} + O_2 \text{ (g)} \longrightarrow CO_2 \text{ (g)}$$
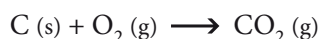
Thus the anodes gradually burn away and are replaced regularly. Every ton of aluminium requires half a ton of carbon.

> **C.1.9** Describe the main properties and uses of aluminium and its alloys.
>
> © IBO 2007

The position of aluminium in the electrochemical series and its electrode potential suggest it should react with oxygen to form its oxide and react with dilute acids to produce hydrogen:

$$Al^{3+} \text{ (aq)} + 3e^- \longrightarrow Al \text{ (s)}; \qquad E^{\ominus} = -1.66 \text{ V}$$

$$H^+ \text{ (aq)} + e^- \longrightarrow \tfrac{1}{2}\ H_2 \text{ (g)}; \qquad E^{\ominus} = 0.00 \text{ V}$$

The high chemical reactivity of the element is offset by rapid formation of a very thin, hard, non-porous film of aluminium oxide, Al_2O_3, over the surface, which protects the metal from further oxidation by oxygen or moisture (iron, on the other hand, forms a porous oxide rust layer allowing further rusting to continue underneath the rusted surface).

Aluminum is a light-weight, corrosion resistant metal with good electrical and thermal conductivity; it is also a versatile, malleable metal that can be made into a variety of shapes. Many of its alloys are very strong. Hence, aluminum is an excellent choice when a strong, but lightweight, metal is required. It is used both as a structural and decorative metal and as an electrical conductor in high voltage transmission lines.

Most of the uses of aluminum such as saucepans, aircraft and vehicle bodywork are possible because of the protective oxide coating. The thickness of the oxide layer can be increased by an electrolytic proces known as **anodizing**. This is done by making aluminium the anode during the electrolysis of sulfuric acid. Water is oxidized to oxygen at the anode:

$$2\ H_2O \text{ (l)} \longrightarrow O_2 \text{ (g)} + 4\ H^+ \text{ (aq)} + 4\ e^-$$
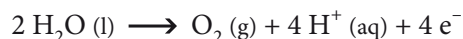
Oxygen combines with the aluminium and thickens the oxide layer, thus protecting it even further. The electrolytic anodizing process can be carried out in the presence of dyes which are absorbed by the oxide layer, thus coloring the anodized material to make it suitable for different uses such as window frames, kettles and drink cans. Light-weight aluminum alloys for different needs are made by the addition of elements such as copper, magnesium, manganese, silicon and zinc amongst others:

Aluminum alloy with:	Properties	Uses
Copper	Increased strength	Automobiles
Iron and silicon	Increased strength; heat resistant	Foil
Up to 12% silicon	Lowers the melting range	Welding
Magnesium	Hardened alloy; corrosion resistant	Marine work
Zinc (with smaller amounts of Mg, Cu and Cr)	High strength	Airplane frames

Figure 1407   Properies and uses of some aluminium alloys

OPTION

C.1.10 Discuss the environmental impact of iron and aluminium production.

All of the processes in steel making, from the blast furnace to the final heat treatment and the production of aluminium by electrolysis, use tremendous quantities of energy. In the production of a ton of steel, approximately one ton of coal is consumed and a ton of slag produced! About ten times more energy is needed to produce a ton of aluminium than to produce a ton of steel. The environmental effects of mining the ore depend on the extraction method used as well as the geographic area in which the ore is found. The mined areas can be scars on the landscape unless the mining company decides to revegetate the area. The waste products of mining, '**tailings**', and the metal wastes from these can be very damaging to the environment. The purification of bauxite produces considerable waste of iron(III) oxide, the disposal of which, as it is a vivid colour, can result in visual pollution.

Recycling: Recycled aluminium from aluminium cans requires approximately 5% of the energy needed to produce the metal from the ore. Thus, recycling is essential because it saves money, energy and fuels; it saves the environment and the reserves of materials and it reduces the problem of waste disposal. However, recycling is not always economically feasible as it can be labor intensive to collect, sort and process. The higher the value of the material, the more economical it is to recycle. Thus, virtually all gold is recycled, but only about half of the aluminium produced is recycled and a still lesser percentage of scrap iron and steel is recycled.

C2 THE OIL INDUSTRY

C.2.1 Compare the use of oil as an energy source and as a chemical feedstock.

By supplying a large part of the world's energy needs, crude oil has become the most important modern raw material. Although only about 10% of the refined products of crude oil are used as **chemical feedstock**, the raw materials required for an industrial process to produce petrochemicals, it is still the most significant source of organic chemicals. By itself, crude oil is not a very useful resource. However, it consists of a mixture of very useful hydrocarbons which are sources of energy such as petrol and other fuels for transport and oil heating systems.

Petrochemicals are organic compounds found in, or derived from, petroleum and are used in the manufacture of products other than fuels. Examples include polymers, drugs, cosmetics, paints, fertilizers, pesticides, detergents and dyes. Fractional distillation of crude oil produces lubricating oils, wax candles, ointments, polishes and chemicals which, in turn, are used to produce fibers, agricultural chemicals, synthetic rubber and solvents. Benzene from crude oil is converted to aminobenzene used in the preparation of drugs and dyestuffs; methylbenzene is nitrated to produce TNT and also to produce polyurethane foams for upholstery, insulation and flotation devices.

C.2.2 Compare catalytic cracking, thermal cracking and steam cracking.

The petroleum fractions with 1 to 12 carbon atoms in the molecule are in greater demand than other fractions. **Cracking** is the breaking up of larger, less useful, hydrocarbon fractions into shorter chain, more useful alkanes and alkenes which are used as fuels and petrochemical feedstock. Thus, cracking is a critically important process in the oil industry. Cracking can be achieved under different conditions of temperature, pressure and the presence or absence of a catalyst, steam or hydrogen gas. Thermal cracking is also called **pyrolysis**. For example, the presence of a catalyst reduces the temperature at which cracking occurs. In the absence of a catalyst, higher temperature (and pressure) is required.

Steam cracking requires pre-heating and vapourising the feedstock and mixing it with steam at still higher temperatures to form low molar mass alkenes.
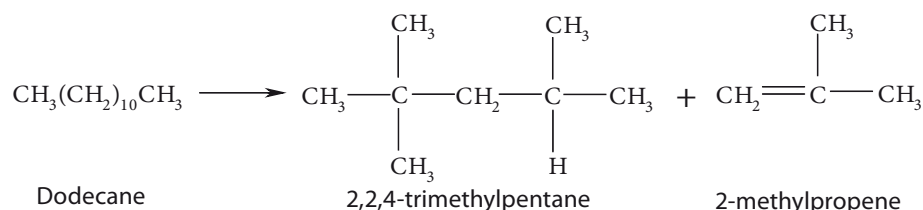

Figure 1408   The thermal cracking of dodecane

The smaller alkanes are more easily vaporized and are more useful fuels. Cracking can also produce more branched hydrocarbons that are better as fuels as they have higher **octane numbers** and thus cause less **knocking** in the automobile engine. The alkenes are feedstock for other petrochemicals and form polymers with extensive uses. Use of different feedstocks, temperatures and catalysts produce different products.

	Catalytic cracking (Cat cracking)	**Thermal cracking Pyrolysis: breaking using heat**	**Steam cracking**
Feedstock: reactant molecules	Gas oil: 14 – 20 carbon chain liquids (250 – 350 °C boiling point range)	Kerosene: 10 – 16 carbon chain liquids (190 – 250 °C boiling point range)	Naphtha: 5 – 10 carbon chain liquids (40 – 190 °C boiling point range) ;
Reaction conditions	Lower temperatures of about 500 °C Moderately low pressures Catalyst: Powdered zeolite (aluminum silicate)'*'; historically silica and alumina used Short contact time	Moderate temperature range: 500 – 750 °C High pressure of about 70 atm. No catalyst Longer contact time	Higher temperature range: 800 – 900 °C Moderately low pressures No catalyst Very short contact time
Mechanism of reaction	Ionic intermediate; catalyst behaves as an electron pair acceptor forming carbocations	Free radicals formed; C—C bonds break so each atom has one unpaired electron	Free radicals formed; C—C bonds break so each atom has one unpaired electron
Products example	$C_{16}H_{34} \longrightarrow C_8H_{18} + C_8H_{16}$ Branched alkanes and alkenes	$C_{12}H_{26} \longrightarrow C_8H_{18} + C_4H_8$ Branched alkanes and alkenes	$C_6H_{14} \longrightarrow C_3H_6 + C_3H_8$ $C_4H_{10} \longrightarrow 2\,C_2H_4 + H_2$ Alkanes and alkenes (+ hydrogen)
Uses of products	High grade gasoline (branched chain alkanes increase fuel octane rating)	Lighter fractions used as fuel	Low molar mass alkenes used in polymer manufacture; hydrogen used in hydrocracking

Figure   1409 Comparison of different methods of cracking

The powdered catalyst in catalytic cracking is treated to give it fluid-like characteristics for greater contact with the reactants. As a result of the decomposition of hydrocarbons, carbon deposits on the catalyst reduce its activity. From time to time air is passed through the reactor so the coke is burnt off to regenerate the catalyst. The combustion of coke produces energy which is used for further cracking.

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C3 ADDITION POLYMERS

Polymers are long chain macromolecules made by joining together many smaller repeating units called **monomers**. **Polyethene**, a typical addition polymer, is a giant molecule made of hundreds of thousands of ethene monomers joined together to make a long chain polymer, polyethene, represented by $-(C_2H_4)_n-$. The empirical formula for polyethene is CH_2, just as it is for ethene.

$$nCH_2\!=\!CH_2 \longrightarrow -(C_2H_4)_n-$$
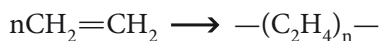
This is an example of addition polymerization in which all the monomer's atoms are present in the polymer, a double bond is converted to a single bond and two extra single bonds are formed. Other alkenes can also undergo polymerisation, the general equation for these reactions is:

$$nCHX\!=\!CH_2 \longrightarrow -(CHX\!-\!CH_2)_n$$

The greater the average chain length, the greater are the intermolecular forces and hence higher the strength and melting point of a polymer. Besides chain length and IMFs, three other structural features are generally important in determining the properties of addition polymers:

1. Branching: Depending on reaction conditions, polyethene can be made either as a high–density polyethene (HDPE) or low–density polyethene (LDPE) polymer. HDPE has little branching. Thus it is a 'linear' polymer in which the carbon backbone of the chain takes up a zig–zag pattern due to the tetrahedral structure for carbon bonded to four other atoms. Such a 'straight' chain polymer can pack closer together. Thus, it is strong and quite rigid with a comparatively high melting point (about 135 ˚C) and is used for making rigid articles such as buckets, milk bottle crates, disposable syringes, etc. However, in the low density polymer, side chains are present off the main chain. The presence of branches in LDPE limits how close polymer chains can come to each other, thus lowering intermolecular forces, leading to lower density and melting point (about 100 ˚C). LDPE is used to make plastic bags, wrappers, squeeze bottles, plastic bowls, etc.

2. Orientation (or position) of the alkyl groups along a polymer backbone chain: Different properties arise from the stereochemistry of the polymer chains. For example polypropene is made by the polymerisation of propene as shown in Figure 1411.

$$n\ CH_2\!=\!CH\!-\!CH_3 \longrightarrow \left(\!CH_2\!-\!\underset{\underset{CH_3}{|}}{\overset{\overset{H}{|}}{C}}\!\right)_n$$
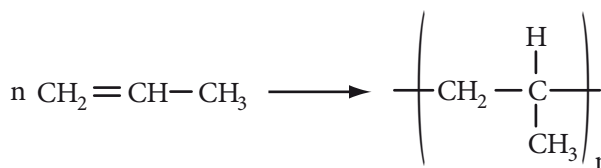
Figue 1411   The formation of polypropene

The carbon atoms in the polymer backbone are arranged in a in a zig-zag manner (with tetrahedral angles) as shown in Figure 1412.

X	Monomer	Polymer
H	Ethene	Poly(ethene)
CH_3	Propene	Poly(propene)
C_6H_5	Phenylethene	Poly(phenylethene), also called polystyrene
If X and H atoms replaced by F	Tetrafluoroethene	Poly(tetrafluoroethene); commercial name: Teflon

Figure 1410   Examples of addition polymerization of CHX=CH$_2$

Figure 1412   The arrangement of the carbon 'backbone'

The hydrogen atom and the methyl side chain ($—CH_3$) can appear on either side of the backbone. If the methyl groups are all on the same side and the hydrogen atoms on the opposite side, that is the methyl groups are ordered with the same orientation, the polymer is said to be **isotactic**. Polymers with regular isotactic arrangements can pack more closely with stronger intermolecular forces. Thus these polymers are tough and are used to make fibres, ropes, carpets and automobile bumpers. If the arrangement is random, that is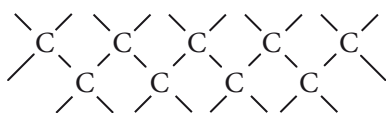 without any order to the orientation of the methyl groups (which is the more likely), the polymer is called **atactic**. Polymer chains in atactic polypropylene cannot pack as closely and are not held very tightly making polypropylene soft and flexible, with a low melting point and not very strong. It is, for example, used in making sealants and water-proofing materials. Refer to Figure 1413.
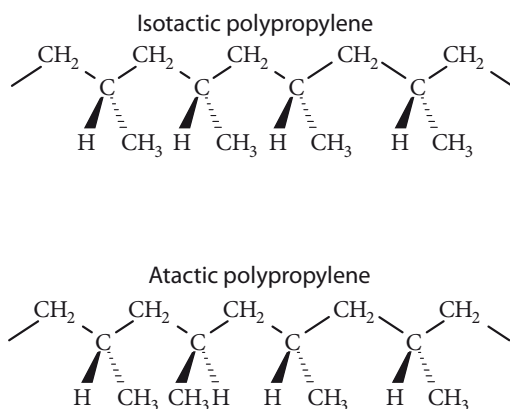

Figure 1413   Isotactic and atactic arrangements

> **C.3.2   Describe ways of modifying the properties of addition polymers.**
>
> © IBO 2007

Plasticizers in polyvinyl chloride: The stronger dipole-dipole intermolecular forces between chains in the polymer polyvinyl chloride (PVC) lead to a rigid plastic. Plasticizers are small molecules added to a polymer. These reduce IMFs and allow polymer chains to slide over each other, producing a softer plastic. Medical products such as blood bags and intravenous drip tubes tend to be made of polyvinyl chloride containing a (diethylhexyl phthlate)

plasticizer. A 10% concentration of the plasticizer produces a semi-rigid PVC and higher concentrations produce the more flexible polymers.

Volatile hydrocarbons in the formation of expanded polystyrene: This involves the polymerisation of styrene in the presence of a volatile hydrocarbon of low boiling point such as pentane, C_5H_{12}. This produces polystyrene containing the volatile hydrocarbon which, as it vaporises, causes the polystyrene to expand to several times its original size and hence have a reduced density. These expanded polystyrenes are very good thermal insulators and are used, for example, in making disposable coffee cups.

> **C.3.3   Discuss the advantages and disadvantages of polymer use.**
>
> © IBO 2007

Polymers are light, impermeable to water and can be pigmented, giving rise to articles with a wide variety of attractive colors. Since weak van der Waals' forces exist between polymer chains, most polymers become soft and melt on heating so they can be molded to form thin films and sheets as well as rods and tubes. Polymers contain strong covalent bonds within the polymer chains making them resistant to chemical reactions and they also generally have good electrical insulation properties. The advantage of polymers is that they can be specially made to exhibit different properties such as:

- Strength and high density: Examples include HDPE, rigid PVC, polystyrene.

- Flexibility and low density: Examples include LDPE, flexible PVC.

- Insulators: Polymers such as expanded polystyrene, and polytetrafluoroethene (PTFE) are excellent examples.

Disadvantages of plastics: The source of most synthetic polymers is petroleum, a non–renewable resource, so using plastics further depletes this. Other disadvantages include the volume occupied by plastics in landfills. These can have a substantial environmental impact as non-degradable materials collect and toxic fumes, caused by the burning plastics are released. Some other disadvantages appear under disposal of plastics.

Disposal of plastics is of key importance since currently a great deal of it ends up in landfills. There are four possible approaches to reducing this:

OPTION

INCINERATION

Buried plastics represent a high energy content in landfills. Products of complete combustion of plastics are primarily carbon dioxide and water and can lead to a large reduction in plastic waste while producing useful energy. However, incineration does present problems namely: (i) carbon dioxide produced is a greenhouse gas, (ii) chlorinated polymers such as PVCs produce hydrogen chloride on combustion, leading to acid rain, (iii) if the incineration temperature is not high enough, toxic chemicals such as dioxins are formed and (iv) some printed plastic contains heavy metals such as lead and cadmium, which are toxic. Also, polyurethane foams produce toxic vapours (hydrogen cyanide and nitriles) when burnt.

BIODEGRADABILITY

The use of bacteria and fungi to break down plastics: Microorganisms are able to break down natural polymers such as cellulose and starch into simpler molecules using enzymes. Thus, starch can be incorporated into a plastic to make it biodegradable. The question of biodegradability is complicated by the fact that landfills are often lined to stop leaching into the water table. Unfortunately, such covering produces anaerobic (oxygen–free) environments where biodegradation by aerobic micro-organisms occurs very slowly or cannot take place.

RECYCLING

Recycling can reduce the amount of new plastics manufactured. The amount of plastic recycled ranges from very little to as much as 50% depending on government policies. There is a clear increase in the recycling of plastic bottles made of PET (**p**oly**e**thylene **t**erephthlate) which is easy to melt and reuse. This is true of any polymer that is not extensively cross–linked. The molten polymer can either be used in the manufacture of new products if the waste is made of similar monomers or it can be used to make plastic of lower quality with appropriate uses such as cheap plastic lumber. However, the sorting of plastic waste can be quite labour intensive.

CONSERVATION

As a society we have become voluminous users of plastics which are made from a non–renewable resource. Conservation, recycling and minimal use of plastics should be a key strategy in extending the life of non–renewable resources (Reduce, Reuse, Recycle).
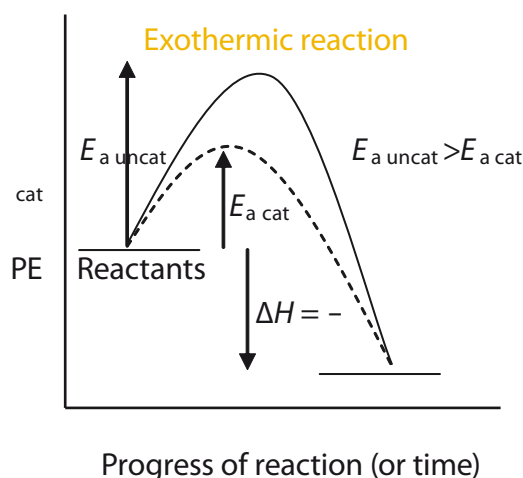
C4 CATALYSTS

C.4.1:   Compare the modes of action of homogeneous and heterogeneous catalysts.

C.4.2:   Outline the advantages and disadvantages of homogeneous and heterogeneous catalysts.

C.4.3:   Discuss the factors in choosing a catalyst for a process.

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Catalysts are of vital importance in biochemistry (known as enzymes which are protein based), environmental chemistry (such as platinum and rhodium based catalytic converters), and industrial chemistry. Examples include iron in the manufacture of ammonia, vanadium(V) oxide in the Contact process for the manufacture of sulphuric acid, Zeigler-Natta organometallic catalysts in the production of high density polyethene, powder silica/alumina in catalytic cracking, nickel in the hydrogenation of vegetable oils to manufacture margarine amongst many others.

As discussed in Chapter 5, a catalyst is a substance that increases the rate of a chemical reaction without being chemically changed. It is usually required in small amounts and is not used up in the reaction (inhibitors or negative catalysts decrease the reaction rate). A catalyst speeds up a reaction by lowering the activation energy of a reaction involving different transition state(s) and providing an alternate path for it to occur (like a tunnel through a mountain). With lower activation energy, a larger number of particles can now react successfully. However, ΔH of the reaction is not affected (it remains the same); neither is the position of equilibrium; a catalyst increases the rate of both the forward and reverse reactions equally.

Exothermic reaction

$E_{a\ uncat} > E_{a\ cat}$
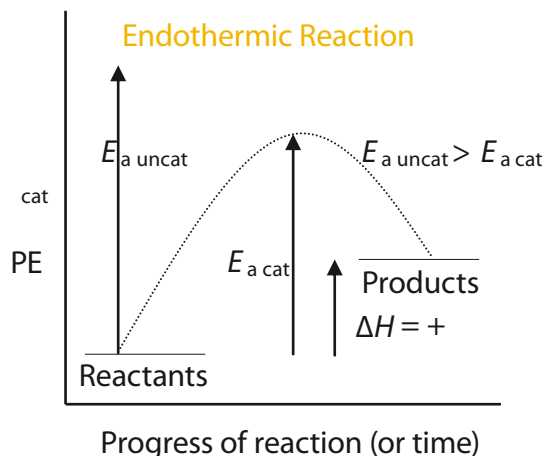
Progress of reaction (or time)

Figure 1414 Exothermic and endothermic reactions

The effect of a catalyst can also be shown on a Maxwell-Boltzmann distribution curve: In the presence of a catalyst, activation energy, E_a is lowered via an alternate pathway. Many more particles now have the minimum energy to react and rate increases. Refer to Figure 1415.
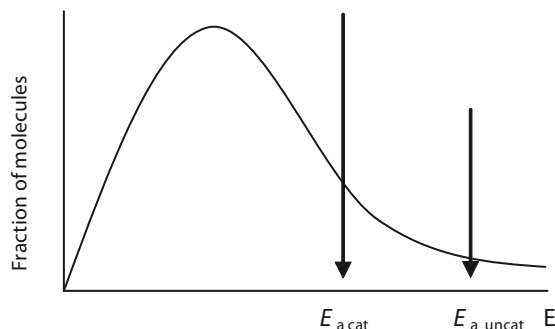

Figure 1415 A Maxwell-Boltzmann distribution curve

Catalysts can react at the surface or participate in the reaction. In surface catalysts such as nickel in the hydrogenation of alkenes, the surface of the catalyst provides active sites on which the reaction can occur with reduced activation energy. d block metals such as iron and nickel behave as surface catalysts. Intermediate catalysts such as aluminium chloride, $AlCl_3$, used in the halogenation and alkylation of benzene react with a reactant to form an intermediate ($AlCl_4^-$) and are regenerated at the end of the reaction.
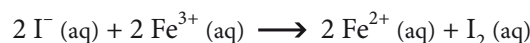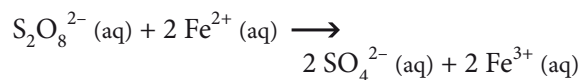
Catalysts can be classified as homogeneous or heterogeneous catalysts:

In **homogeneous catalysis**, the reactants and the catalyst are in the same phase; the catalyst allows the reaction to take place by a different mechanism, with lower E_a, thus increasing reaction rate. In this process the catalyst reacts
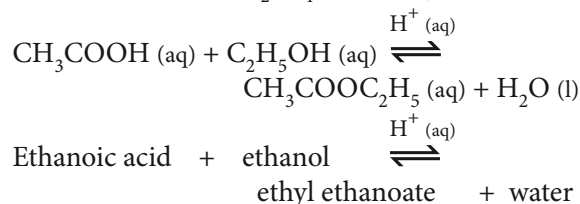
in a step of the mechanism and is regenerated at a later step. An example in aqueous solution is the reaction between $S_2O_8^{2-}$ (aq) and I^- (aq) in the presence of Fe^{2+} (aq) as a catalyst:

$$S_2O_8^{2-} \text{ (aq)} + 2\ I^- \text{ (aq)} \longrightarrow 2\ SO_4^{2-} \text{ (aq)} + I_2 \text{ (aq)}$$

Fe^{2+} (aq) behaves as an intermediate catalyst: it is oxidized to Fe^{3+} (aq) and reduced to Fe^{2+} (aq) in the subsequent step:

$$S_2O_8^{2-} \text{ (aq)} + 2\ Fe^{2+} \text{ (aq)} \longrightarrow$$
$$2\ SO_4^{2-} \text{ (aq)} + 2\ Fe^{3+} \text{ (aq)}$$

$$2\ I^- \text{ (aq)} + 2\ Fe^{3+} \text{ (aq)} \longrightarrow 2\ Fe^{2+} \text{ (aq)} + I_2 \text{ (aq)}$$

Another example is the formation of esters (sweet smelling compounds) used in the perfume and food industry (such as the smell of bananas, peaches, perfumes) that use concentrated sulfuric acid, H_2SO_4, as a catalyst:

$$CH_3COOH \text{ (aq)} + C_2H_5OH \text{ (aq)} \underset{}{\overset{H^+ \text{ (aq)}}{\rightleftharpoons}}$$
$$CH_3COOC_2H_5 \text{ (aq)} + H_2O \text{ (l)}$$

$$\text{Ethanoic acid} \ + \ \text{ethanol} \ \underset{}{\overset{H^+ \text{ (aq)}}{\rightleftharpoons}}$$
$$\text{ethyl ethanoate} \ \ + \ \text{water}$$

The forward reaction is the acid-catalysed formation of the ester, and the reverse reaction is the acid-catalysed hydrolysis of the ester; both are examples of homogeneous catalysis.

In **heterogeneous catalysis**, the reactants and the catalyst are in different phases, typically a solid catalyst with the reactants being in the gas or liquid phase where the catalyst provides the reactive surface upon which the reaction can take place. Examples include:

1. The **Contact Process**: Production of SO_3 for the manufacture of sulfuric acid, the 'king' of chemicals:

$$2\ SO_2 \text{ (g)} + O_2 \text{ (g)} \overset{V_2O_5 \text{ (s)}}{\rightleftharpoons} 2\ SO_3 \text{ (g)}$$
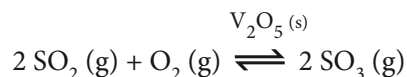
2. The **Haber Process**: Manufacture of ammonia for fertilizers, explosives (TNT), etc.

$$N_2 \text{ (g)} + 3\ H_2 \text{ (g)} \overset{Fe \text{ (s)}}{\rightleftharpoons} 2\ NH_3 \text{ (g)}$$
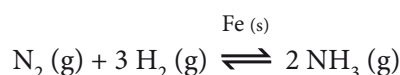
3. Hydrogenation of an alkene containing $C=C$ bonds (an example of an addition reaction):

$$C_2H_4 \text{ (g)} + H_2 \text{ (g)} \overset{Ni \text{ (s)}}{\longrightarrow} C_2H_6 \text{ (g)}$$

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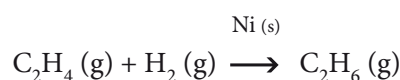
This type of reaction is used in the food industry to produce partially saturated compounds, for example, margarine.

Enzymes have some characteristics of both homogeneous and heterogeneous catalysts. Like homogeneous catalysts most enzymes occur in the same phase as the reactants, but like heterogeneous catalysts the reactants bind to an active site on the surface of the enzyme molecule. Enzymes are unique in that these are very specific, efficient and work best at body temperature. Enzymes can catalyse only one particular reaction unlike inorganic catalysts such as alumina, which catalyses many reactions. Enzymes differ from inorganic catalysts in their incredibly higher catalytic activity. In mammals and birds respiration occurs at 37 ºC and requires numerous steps, each one catalysed. In the lab, the reaction occurs above 600 ºC.
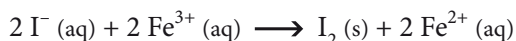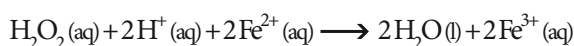
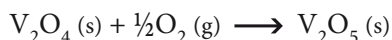# MODES OF ACTION OF HOMOGENEOUS AND HETEROGENEOUS CATALYSTS

Ability to form a range of oxidation states by transition metal compounds

Transition metal ions exhibit relatively stable multiple oxidation states by gaining or losing electrons in redox reactions. An example of homogeneous catalysis is the role of Iron(II)/(III) in speeding up the slow reaction between acidified hydrogen peroxide and iodide ions. The iron(II) is oxidised by the peroxide to iron(III) which is then reduced by the iodide ions to regenerate iron(II):

$$H_2O_2 \text{(aq)} + 2H^+ \text{(aq)} + 2Fe^{2+} \text{(aq)} \longrightarrow 2H_2O \text{(l)} + 2Fe^{3+} \text{(aq)}$$

$$2\,I^- \text{(aq)} + 2\,Fe^{3+} \text{(aq)} \longrightarrow I_2 \text{(s)} + 2\,Fe^{2+} \text{(aq)}$$

These reactions occur more rapidly because both have lower activation energies than the reaction without the use of the catalyst.

An example of a heterogeneous catalyst involving change in oxidation number of the transition metal ion catalyst is the use of vanadium(V) oxide in the Contact process. In the first step, sulfur dioxide is oxidised to sulfur trioxide and the vanadium(V) is reduced to V(IV); subsequently, V(IV) is oxidised by oxygen to regenerate the catalyst:

$$SO_2 \text{(g)} + V_2O_5 \text{(s)} \longrightarrow SO_3 \text{(g)} + V_2O_4 \text{(s) (or 2 VO}_2)$$

$$V_2O_4 \text{(s)} + \tfrac{1}{2}O_2 \text{(g)} \longrightarrow V_2O_5 \text{(s)}$$

The shape of the catalyst

Enzymes are very complex in structure. The three dimensional shape of the globular protein molecules is crucial to the catalytic activity of enzymes. Enzymes and substrates are only effective if they have specific three–dimensional shapes which complement one another (the lock and key model). If the enzyme changes its shape or arrangement, the substrate will no longer be able to bind to the active site and the enzyme is rendered non-functional. This **denaturation** can take place when the surrounding environment changes even slightly. This may be brought about in several ways such as a variation in the temperature or pH of the solution, or by the presence of heavy metal ions (see Chaper 13, Section B 7.7).

For example, an increase in temperature increases enzymatic reaction rates up to a certain point as the substrates collide with active sites more frequently as the molecules move faster. However, the speed of the reaction drops sharply when the temperature reaches a certain point. Here, the thermal agitation of the enzyme disrupts the hydrogen bonds, ionic bonds and other non–covalent interactions that stabilize its active structure. If the three–dimensional structure is changed as a result of temperature, the enzyme activity is affected. All enzymes have an optimum temperature at which they are not yet denatured and the substrates collide fastest with the enzyme. In humans, enzymes have an optimum temperature of about 37°C, about the same as the internal body temperature. Beyond this temperature, the change in the enzyme structure affects the active site (usually irreversibly) and the rate drops sharply. Figure 1416 shows the variation of reaction rate with temperature when the substrate concentration and pH and other factors are held constant.

Figure 1416   The effect of temperature on enzyme activity

Proteins contain groups such as —NH$_2$ and —COOH and are susceptible to pH changes. Extreme changes in pH values denature such ionisable enzymes rendering them ineffective. For such enzymes, a similar trend is observed to that of the effect of temperature. At low or high pH values, the enzyme is irreversibly denatured and the rate drops sharply. Within a narrow pH range, the enzyme structure changes reversibly and each such enzyme works

	Homogeneous catalysts	Heterogeneous catalysts
Advantages	High activity as all the catalyst is exposed to the reactants High selectivity for single product as the catalyst has unique active sites	Solid catalysts are easy to remove and recover from products by filtration Long catalytic life
Disadvantages	Difficult to recover from reaction mixture for reuse	Only effective on the surface – hence most of the solid is not used; also, any coating on surface reduces activity

Figure 1418   Advantages and disadvantages of various catalysts

optimally at a specific pH. Thus the maximum rate for the enzyme chymotrypsin occurs around pH 8 and for pepsin this occurs at pH 2. However, the enzyme invertase which catalyzes the hydrolysis of the neutral sucrose molecule has a constant rate in the pH range 3.3 to 7.5. Thus, if an enzyme is acting on an electrically neutral substrate molecule, or where the charge plays no role in the catalyzed reaction, changes in pH have little effect on the rate of this reaction. Figure 1417 shows the variation of reaction rate with pH when the substrate concentration, temperature and other factors are held constant.
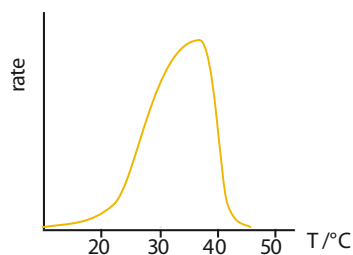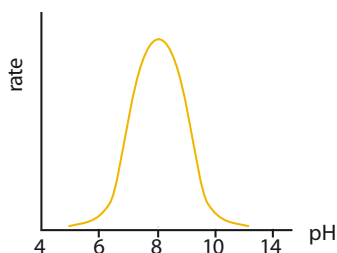

Figure 1417   The effect of pH on enzyme activity

Heavy metal ions can also disrupt some enzyme activity. When a heavy metal ion is present at the active site, substitution of a different metal ion for the original ion causes the enzyme to malfunction and denature, particularly where heavy metal ions can bind or chelate to the –S–H groups in proteins to form –S–M–S– type arrangement (see, also Chapter 13 Option B).

Availability of active sites
The region of the catalyst which binds to one or more reactants is called the **active site**. For enzymes the lock and key model illustrates how the substrate molecule binds reversibly to the active site to form the enzyme-substrate complex (in which the substrate forms weak bonds), the reaction is catalysed to form the enzyme-product complex and the products leave to make the active sites available for further catalytic activity. Refer also to Option B.

Heterogeneous catalysts contain active sites that are able to adsorb one or more reactants onto it to facilitate the reaction and reduce the activation energy. Adsorption is an increase in the concentration of one substance, the reactant, at the surface of another, the catalyst (it is different to absorption). Consider the hydrogenation of an alkene at the surface of nickel catalyst: on adsorption, the electron pair that holds the two hydrogen nuclei together in hydrogen and the electron pair in alkene forming the π bond of the double bond are attracted to the catalyst. This weakens the H—H bond and the C=C double bond making the reaction between the two faster. Once the product is formed it has weaker attraction for the active site and leaves, freeing the active site to adsorb other reactant molecules to its surface.

Good heterogeneous surface catalysts such as nickel, platinum and rhodium adsorb the reactants(s) sufficiently to lower the activation energy for reaction to take place but do not adsorb the product molecule which is released, allowing the process to continue. Metals such as silver adsorb reactant molecules too weakly (or tungsten which adsorbs too strongly) to be useful as surface catalysts. Figure 1418 shows the advantages and disadvantages of homogeneous and heterogeneous catalysts.

FACTORS IN SELECTING A CATALYST

Selectivity
Enzymes are highly selective and catalyse only one type of reaction. Good selectivity means only the desired product is produced and unwanted by-products are not formed. If a catalyst leads to unwanted products, it exhibits poor selectivity. Zeolites are examples of solid catalysts with regular molecular size porous holes (also called pores and channels). Zeolites are more selective as only molecules of the specific size can enter the holes and only products of size smaller than the holes can exit.

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A good example of a zeolite catalyst in action is to compare the methylation of methylbenzene using $AlCl_3$ or zeolite as a catalyst. Since the methyl group is ortho, para (2,4-) directing, the products are 1,2- and 1,4-dimethylbenzene. When $AlCl_3$ is used, the 1,2-isomer is formed in the larger amount as there are two ortho positions on benzene, but only one para position. A small amount of 1,3-isomer is also formed. However, using zeolite of specific sized pores, the product is almost entirely the 1,4-isomer since the other two isomers have a larger cross-section than the diameter of the pores.

1,2-dimethylbenzene
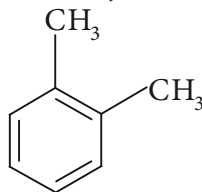
1,3-dimethylbenzene
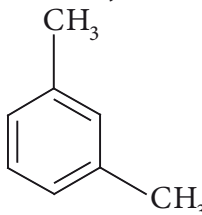
1,4-dimethylbenzene

Figure 1419   The use of zeolite catalyst
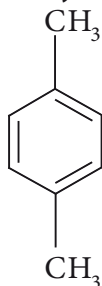
Efficacy (or effectiveness)

This tells us how rapidly the catalyst forms the desired product. For example, zeolites expose a much larger surface area to reactants producing greater efficacy than $AlCl_3$. Hydrogen peroxide is decomposed by a variety of catalysts including manganese(IV) oxide, silver, platinum and iodide ion as well as the enzyme catalase. The enzyme, which contains iron at its active site, is, however, the most effective.

Ability to work under mild/severe conditions

One of the disadvantages of enzymes is that they work under narrow temperature and pH ranges and are easily denatured beyond these ranges. On the other hand, heterogeneous catalysts such as iron are effective under vastly different conditions of temperature and pressure, for example in the Haber process.

Environmental impact

Catalysts are in great demand with estimates of 80% of all chemical industries using catalysts. This raises the concern over their environmental impact. For example, the demand for the platinum group elements (platinum, rhodium, palladium) used in catalytic converters since the 1970s has increased greatly. Some of these metals are lost to the environment and raise the issue of potential health risks since, although cisplatin and other platinum based drugs are used in the treatment of cancer, these exhibit severe side effects and toxicity to living cells. Disposal of spent catalysts is a concern though the cost of the platinum group of elements makes a convincing argument for recycling. Also, research is providing new catalysts in place of acid catalysts to reduce environmental impact.

Catalyst poisoning

A catalyst can be poisoned or rendered ineffective. The efficiency of a catalyst usually decreases with time as it becomes inactive due to impurities in the reaction mixture, side reactions, or if its active surface becomes coated and unavailable for activity such as the coke coating on alumina or silica in catalytic cracking. The coke can, however, be burnt off to regenerate the catalyst. Enzymes denature by the effect of temperature, pH and heavy metal ions such as Hg^{2+} and Pb^{2+} if their structures are altered.

C5 FUEL CELLS AND RECHARGEABLE BATTERIES

A fuel cell is a device that converts the chemical energy of fuels directly into electrical energy. Normally fuels are burnt converting chemical energy to heat which can be converted to electricity by generating steam to turn turbines. This is a highly inefficient method; fuel cells lead to a much more efficient conversion of chemical energy directly into electrical energy to generate power.

In a hydrogen-oxygen fuel cell, the negative electrode (anode) is made of porous carbon impregnated with the catalyst Pd or Pt; the positive electrode (cathode) is also made of porous carbon containing the catalyst Pt. These electrodes are separated by aqueous hydroxide electrolyte (KOH or NaOH) and the oxidation of hydrogen gas by oxygen gas takes place in a controlled manner.
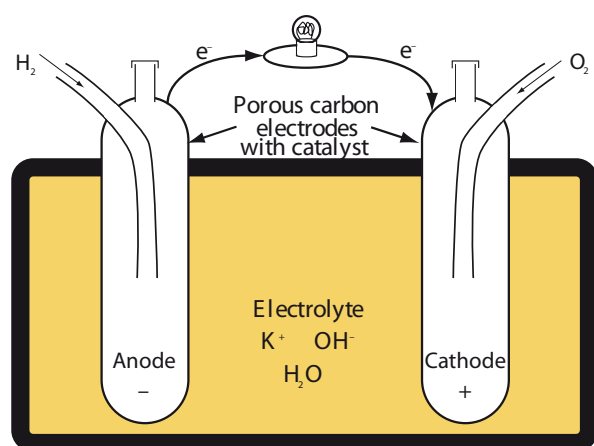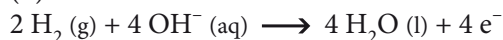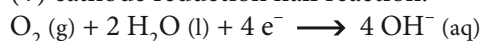

Figure 1420 Hydrogen-oxygen fuel cell

The oxidation process leads to the loss of electrons by the hydrogen gas, H_2 at the negative electrode (anode). The electrons flow out of the fuel cell and back to the positive electrode (cathode), via an external circuit to reduce the oxygen gas, O_2 to hydroxide ions, OH^-. Most commonly, the reactions take place in basic solution:
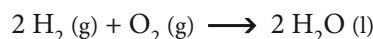
(–) anode oxidation half reaction:
$$2\ H_2\ (g) + 4\ OH^-\ (aq) \longrightarrow 4\ H_2O\ (l) + 4\ e^-$$

(+) cathode reduction half reaction:
$$O_2\ (g) + 2\ H_2O\ (l) + 4\ e^- \longrightarrow 4\ OH^-\ (aq)$$

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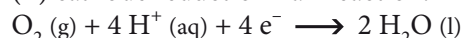$$2\ H_2\ (g) + O_2\ (g) \longrightarrow 2\ H_2O\ (l)$$

The net result is the oxidation of H_2 at the (–) anode electrode and and the reduction of O_2 at the (+) cathode electrode.

Half reactions in acidic conditions are also possible:

(–) anode oxidation half reaction:
$$2\ H_2\ (g) \longrightarrow 4\ H^+\ (aq) + 4\ e^-$$

(+) cathode reduction half reaction:
$$O_2\ (g) + 4\ H^+\ (aq) + 4\ e^- \longrightarrow 2\ H_2O\ (l)$$

Advantages and disadvantages of fuel cells: Fuel cells are highly efficient (70-80%) since they convert the chemical energy of the fuels directly to electrical energy. Thus these greatly reduce thermal pollution, as well as being less polluting in general as water is the product, so there is no release of greenhouse gases from the combustion of fossil fuels, though note that if electrolysis of water is used as a source of hydrogen gas for the fuel cell, the power for the electrolysis may well have come from fossil fuel plants. Fuel cells also tend to be light weight. On the other hand, fuel cells can experience technical problems ranging from leaks to corrosion and catalytic failures. The dangers of storing and transporting hydrogen gas also have to be considered. Fuel cells are used in the space program. These usually operate at about 70-140 °C, generate about 0.9 V and the water produced can be purified and used for drinking. Some fuel cells are used for commercial production of electricity in Japan. A great deal of research has taken place to make fuel cells for the auto industry in order to reduce the dependence on non-renewable fuel. Also, the production of carbon dioxide greenhouse gas is reduced and less is released into the environment. A combination of fuel cell and electrically powered hybrid solutions are also being developed.

Rechargeable batteries are examples of secondary cells. These electrochemical cells are reversible, and can be recharged; the reactant concentration can be restored by

applying an external source of electricity in the opposite direction.

Lead-acid storage battery

These are used in automobiles and are an important example. They use lead plates (in practice an alloy) and moderately concentrated sulfuric acid as the electrolyte. The lead reacts with the acid to produce a coat of lead(II) sulfate on both electrodes. When the battery is charged up, at the electrode into which electrons flow, the lead(II) sulfate is reduced to lead metal (oxidation state = 0):

$$PbSO_4 \text{ (s)} + 2 \text{ e}^- \longrightarrow Pb \text{ (s)} + SO_4^{2-} \text{ (aq)}$$

and at the electrode that loses electrons the lead(II) sulfate is oxidised to lead(IV) oxide:

$$PbSO_4 \text{ (s)} + 2 H_2O \text{ (l)} \longrightarrow$$
$$PbO_2 \text{ (s)} + 4 H^+ \text{ (aq)} + SO_4^{2-} \text{ (aq)} + 2 \text{ e}^-$$
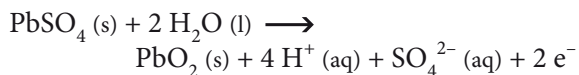
This removes water and produces sulfuric acid, so the concentration of the acid electrolyte increases.

When the battery is used to power an external load these reactions are reversed, so at the electrode that behaves as the negative terminal, the lead anode is oxidised to lead(II) sulfate:

$$Pb \text{ (s)} + SO_4^{2-} \text{ (aq)} \longrightarrow PbSO_4 \text{ (s)} + 2 \text{ e}^-$$

At the electrode that acts as the positive terminal, the lead(IV) oxide cathode is reduced to lead(II) sulfate

$$PbO_2 \text{ (s)} + 4 H^+ \text{ (aq)} + SO_4^{2-} \text{ (aq)} + 2 \text{ e}^- \longrightarrow$$
$$PbSO_4 \text{ (s)} + 2 H_2O \text{ (l)}$$
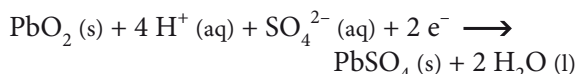
The overall reaction for the discharging process is:

$$Pb \text{ (s)} + PbO_2 \text{ (s)} + 2 H_2SO_4 \text{ (aq)} \longrightarrow$$
$$2 PbSO_4 \text{ (s)} + 2 H_2O \text{ (l)}$$
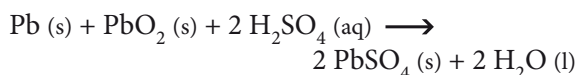
This consumes sulfuric acid so the concentration of the acid decreases. Thus, the state of a battery can be determined from the density of the electrolyte solution using a hydrometer.

The battery is charged by the alternator while under operation in an automobile; a flat battery can be charged by a battery charger and the reverse reaction takes place:

$$2 PbSO_4 \text{(s)} + 2 H_2O \text{(l)} \rightleftharpoons Pb \text{(s)} + PbO_2 \text{(s)} + 2 H_2SO_4 \text{(aq)}$$
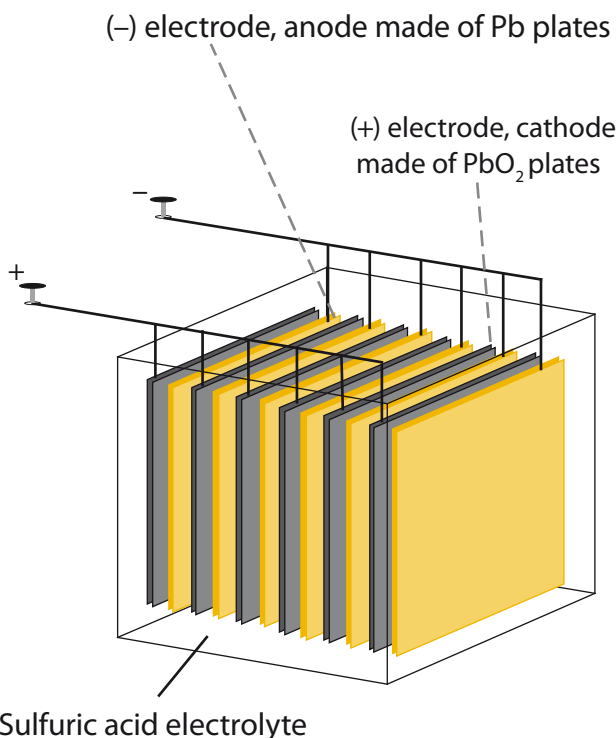
Figure 1421   The lead-acid storage battery

The voltage produced per cell is 2V. Thus, for a 12V car battery, six 2V cells are arranged in series. This produces 12 volts but internal resistance also increases, thus producing less current than six single cells.

Advantages of lead acid battery: It can deliver large amounts of energy for short time periods and is rechargeable. Disadvantages: Owing to the high density of lead, there is a high mass to charge ratio (heavy) and acid spillage is a possibility, although car batteries now tend to come in sealed containers.

Nickel–Cadmium ('NiCad') Batteries

These batteries are rechargeable, light–weight dry cells that produce a constant potential of 1.4V:

At the negative cadmium electrode (the anode), an oxidation half reaction takes place in the presence of hydroxide ions and Cd is oxidized to Cd^{2+}:

$$Cd \text{ (s)} + 2 OH^- \text{ (aq)} \longrightarrow Cd(OH)_2 \text{ (s)} + 2 \text{ e}^-$$
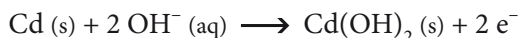
At the positive nickel electrode (the cathode), a reduction half reaction occurs where Ni^{3+} in NiO(OH) is reduced to Ni^{2+}:

$$e^- + NiO(OH) \text{ (s)} + H_2O \text{ (l)} \longrightarrow Ni(OH)_2 \text{ (s)} + OH^- \text{ (aq)}$$

OPTION

The overall reaction is:
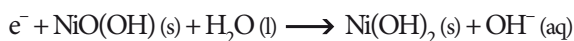
$$Cd_{(s)} + 2\ NiO(OH)_{(s)} + 2\ H_2O_{(l)} \longrightarrow$$
$$Cd(OH)_{2\ (s)} + 2\ Ni(OH)_{2\ (s)}$$
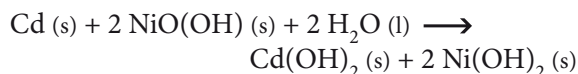
Oxidation numbers:
$$0 \qquad +3$$
$$\qquad\qquad +2 \qquad\qquad +2$$

Cadmium is being oxidized from 0 to +2; nickel is reduced from +3 to +2. Insoluble hydroxides of cadmium and nickel deposit on the electrodes and half reactions are easily reversed during charging. The reducing agent cadmium and oxidizing agent $NiO(OH)$ are regenerated on recharging:

$$Cd(OH)_{2\ (s)} + 2\ Ni(OH)_{2\ (s)} \longrightarrow$$
$$Cd_{(s)} + 2\ NiO(OH)_{(s)} + 2\ H_2O_{(l)}$$

Ni-Cd battery

A Ni-Cd battery experiences the 'memory" effect which occurs when it is charged after being incompletely discharged (this happens as a result of unreactive surface formed on the electrodes that stops reactions during recharging). It is thus best to completely discharge the battery before being re-charged. The nickel and cadmium are more expensive, produce a lower voltage, but have longer life than lead-acid accumulators. Cadmium is toxic to many life forms and there are environmental concerns about the disposal of toxic cadmium containing batteries.

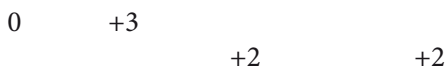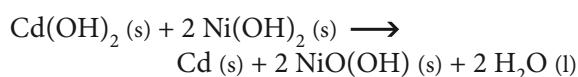| Fuel cells and rechargeable batteries	
Similarities	**Differences**
Both devices convert chemical energy directly into electrical energy using spontaneous redox reactions. Both have similar modes of operation, namely, negative anode electrodes where an oxidation half-reaction takes place and positive cathode electrodes where a reduction half-reaction takes place.	Fuel cells are energy conversion devices whereas rechargeable batteries are energy storage devices. Fuel cells require a constant supply of reactants (an example of an open system) and produce electrical energy only as long as fuel is made available to the cell. Batteries on the other hand have stored chemical energy in a closed system and provide power until the stored chemicals are used up. Batteries can be recharged; this uses electrical energy to carry out the reverse reaction. Recharging takes a battery out of operation. A fuel cell, on the other hand, does not need recharging like a battery. Rather, it can have a continuous supply of fuel (by replacing empty fuel containers with full ones) providing longer operating life. The electrodes in fuel cells are made of inert materials (such as porous carbon impregnated with platinum and palladium as a catalyst) which allow the movement of hydrogen, oxygen and water. Fuel cells are currently more expensive than rechargeable batteries.

Figure 1422   Comparing fuel cells and rechargeable batteries

OPTION

Lithium-ion battery

The very high activity of lithium metal means an oxide layer forms over the metal easily reducing the contact with the electrolyte in a battery. This is overcome in the lithium-ion battery which contains no metal and involves the movement of lithium ions between the negative anode and the positive cathode electrodes through the electrolyte, a lithium salt in an organic solvent. Such cells use carbon graphite as the negative electrode (anode). Lithium ions can enter (insert) into the graphite lattice with an approximate LiC_6 composition. The positive electrode (cathode) is a metal compound, for example of formula MO_2, such as manganese(IV) oxide (MnO_2), cobalt (IV) oxide (CoO_2) or nickel (IV) oxide (NiO_2). Oxidation occurs at the negative electrode (anodic oxidation):

$$LiC_6 \longrightarrow Li^+ + 6\,C + e^-$$

Lithium ions in solution enter the oxide positive electrode where reduction occurs (cathodic reduction):

$$Li^+ + e^- + MnO_2 \longrightarrow LiMnO_2$$
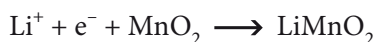
The net result is the movement of lithium ions from the negative anode to the positive cathode: The overall reaction is:

$$LiC_6 + MnO_2 \longrightarrow 6\,C + LiMnO_2$$

It is the difference in the free energy of lithium between LiC_6 and $LiMnO_2$ that powers the cell. The electrodes are called insertion electrodes as small lithium ions can be inserted (and removed) into the electrode lattice. On recharging, the reverse reaction takes place. The lithium-ion battery does not suffer from the 'memory' effect that Ni-Cd batteries do.

C6 LIQUID CRYSTALS

C.6.1   Describe the meaning of the term liquid crystals.

C.6.2   Distinguish between *thermotropic* and *lyotropic* liquid crystals.

C6.3   Describe the liquid-crystal state in terms of the arrangement of the molecules and explain thermotropic behaviour.

C.6.4   Outline the principles of the liquid-crystal display device.

C.6.5   Discuss the properties needed for a substance to be used in liquid-crystal displays.

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LIQUID CRYSTALS

The states of matter depend on the mobility of particles and typically include solid, liquid and gas which depend on temperature. For example, 'water' is ice below 0 °C, water between 0 and 100 °C and water vapour above 100 °C (at 1 atmosphere pressure). In solids, particles have an orderly, three dimensional arrangement in which molecules are fixed in position and orientation (pointing in the same direction) and are arranged in a repeating pattern to give a particular crystal lattice. In liquids, the molecules are free to move about randomly and can change their orientation (typically, liquids occupy a little more space than solids; water and ice are an exception due to hydrogen bonding in ice that gives rise to holes in the crystal structure). Ordinary liquids are called **isotropic** (meaning independent of direction) as the molecules are randomly arranged, have no orientation order and exhibit no long range order. The distribution of the particles is such that, overall, ordinary liquids have the same physical properties such as optical, magnetic and electrical properties when viewed from any direction.

On the other hand, some substances exist in what is called the *mesophase* (meso meaning between), sometimes called the 'fourth state'. For example, cholesterol myristate is a solid below 71 °C and a clear liquid above 86 °C. In between, it exists as a cloudy liquid. Such liquid crystals (LCs) have some order but also some ability to flow, namely these are in a phase with order between that of a liquid and a solid. There is a degree of orientation of molecules in LCs like a solid, but molecules also move to different

positions, that is, a loss of order in the position takes place similar to a liquid, thus the apparent contradiction in the name: 'liquid crystal' (LC).

LCs are fluids that have physical properties (such as electrical, optical and elasticity) that are dependent on the molecular orientation relative to some fixed axis in the material, making them unique in their properties and uses.

Elongated, moderate size organic molecules tend to form liquid crystals that orient on their longer axis, although liquid crystals are not restricted to elongated molecules; disc-like and banana-shaped molecules of liquid crystals are also possible. One example of an elongated organic liquid LC is called MBBA in which the benzene rings form a planar skeleton as shown in Figure 1423.
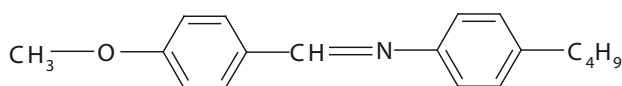
$$CH_3\!-\!O\!-\!\bigcirc\!-\!CH\!=\!N\!-\!\bigcirc\!-\!C_4H_9$$

Figure 1423   MBBA

Examples of LCs include biological materials such as cell membranes (for example, phospholipids), aqueous polymeric DNA solutions, some viruses such as the tobacco mosaic virus, the solution extruded by a spider to form silk threads, micelles such as soap solution, colloidal solutions, graphite and cellulose amongst others. Note that liquid crystal materials may not always be in the liquid phase just as water is not always in the liquid phase.

Thermotropic and lyotropic lcs

Thermotropic LC materials are pure substances that occur as LCs over a certain temperature range between the solid and liquid phases such as the example of cholesterol myristate given above. At the temperature below the range, the substance forms a solid crystal; above the temperature range, it turns into the liquid phase. The biphenyl nitriles (cyanobiphenyls) are common examples of thermotropic LCs, for example 5CB, which is crystalline below 18 °C, an isotropic liquid above 36 °C and LC between the two temperatures. See Figure 1424.
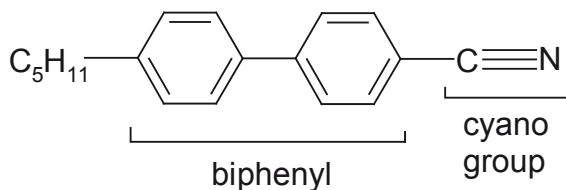
$$C_5H_{11}\!-\!\bigcirc\!-\!\bigcirc\!-\!C\!\equiv\!N$$

biphenyl   cyano group

Figure 1424   A thermotropic LC

Lyotropic LCs, on the other hand, are solutions that show the liquid crystal state at certain concentrations, that is as a function of the concentration of the molecules, such as soap or detergent, in a solvent such as water (in this case leading to the formation of micelles LC example). Above a certain soap concentration, a LC phase is formed in which the the carbon chain hydrophobic tail of the soap molecules point away from the polar water while the hydrophilic soap components point toward the water.
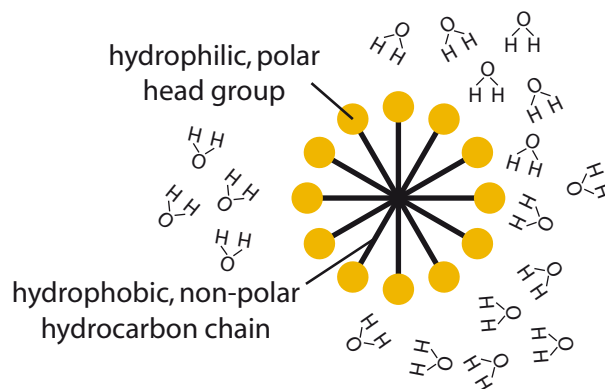

hydrophilic, polar head group

hydrophobic, non-polar hydrocarbon chain

Figure 1425   A lyotropic LC

Thermotropic behaviour in terms of arrangement of molecules in LC state:

In the crystalline solid, the rod-shaped molecules are fixed in position and direction: these are parallel, arranged in layers and the layers positioned one over the other (as shown in Figure 1426) in a three-dimentional arrangement. The intermolecular forces present in a solid lattice of a LC are different in various directions. As the solid crystal is heated, first the weak forces are overcome; the heating disturbs the precise order of molecules giving rise to random arrangement in some direction, but the stronger forces are still at play and this provides regular arrangement in other directions. In **smectic LCs**, layers still exist (the molecules centred are still arranged in layers) with movement within layers so that the molecules are roughly parallel. See Figure 1426.

Further heating disrupts the long range positional order to form **nematic LCs** in which the layer arrangement no longer exists. See Figure 1426. In nematic LCs, the rod-shaped molecules are distributed randomly but, on average, point in the same direction; this is typically used in LCDs. On still further heating, the increased thermal agitation disrupts this directional order until it is lost when the isotropic (normal) liquid phase is formed with loss of directional order as well. It is the ability of molecules in a LC to point in a particular axis, called the director, that is its distinguishing feature:

OPTION

| | Crystal | Smectic LC | Nematic LC | Isotropic liquid |
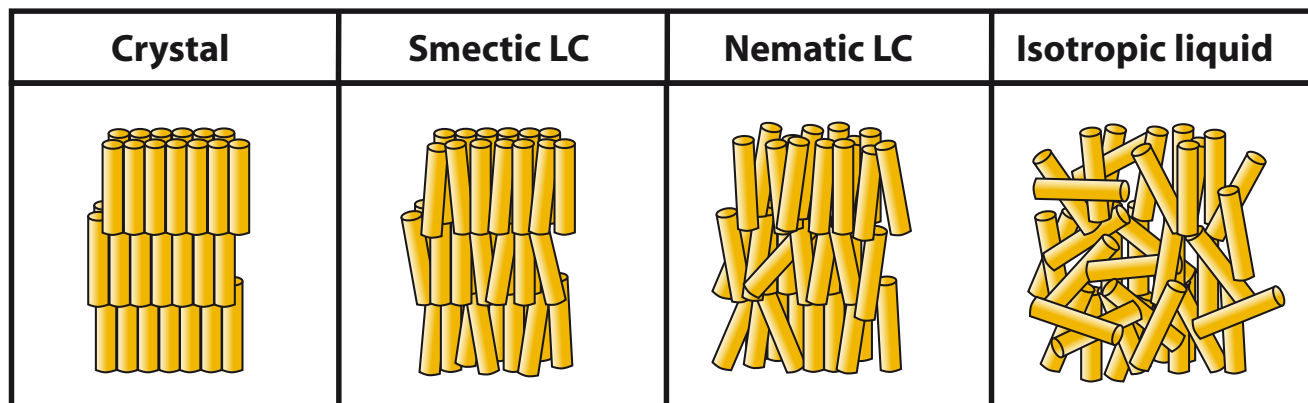
Figure 1426   Order in crystals, smectic LC, nematic LC and isotropic liquids

	Crystalline Solid: highly ordered	Liquid Crystal		Isotropic Liquid: No long range order
		Smectic	Nematic	
Positional order	Yes	Some	No	No
Directional (orientational) order	Yes	Yes	Yes	No

Figure 1427   A comparison of LC forms

Principles of liquid-crystal display devices

A polarizer allows light in which the electric field vibrates in only one direction to pass through as shown in Figure 1428 (a) and (b) at right.

In crossed polarizers, where one polarizer is perpendicular to the other one in its direction of propagation, no light transmission takes place after the second polarizer, as shown in Figure 1429.

a)   Polarizer in the *x* direction

Light vibrating in all directions

Light vibrating in only one direction - *x*
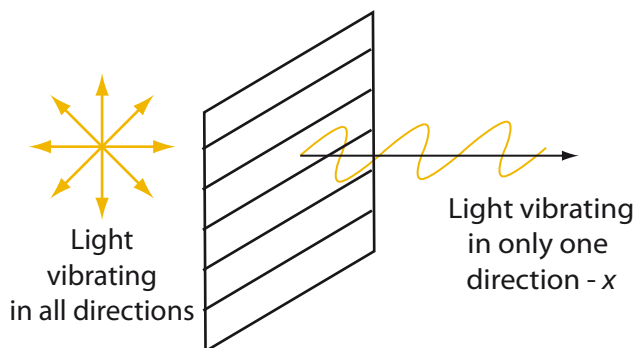
b)   Polarizer in the *z* direction

Light vibrating in all directions

Light vibrating in only one direction (*z*), perpendicular to the *x* direction

Light vibrating in all directions

No transmission of light

Figure 1429   The principle of cross-polarization

Figure 1428 (a) and (b)   The principle of a polarizer

Figure 1430   The use of an LC with a polarizer

If, however, a liquid crystal is placed between the above two crossed polarizers, transmission of light can occur after the second polarizer as shown in Figure 1430.

This suggests that a LC is able to rotate or twist the plane of polarization of the light propagating through it. As stated earlier, it is the ability of molecules in a LC to point in a particular axis, its director, that allows LC molecules to transmit light depending on t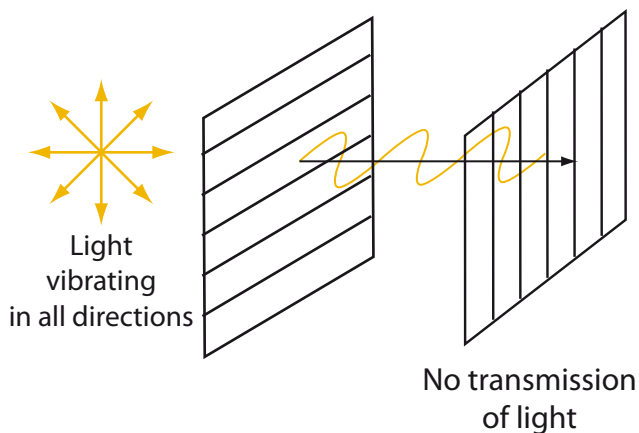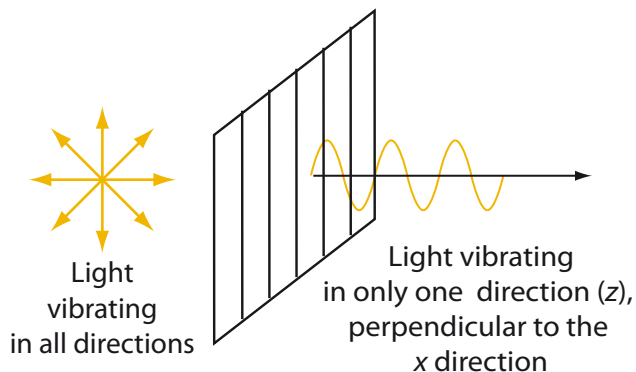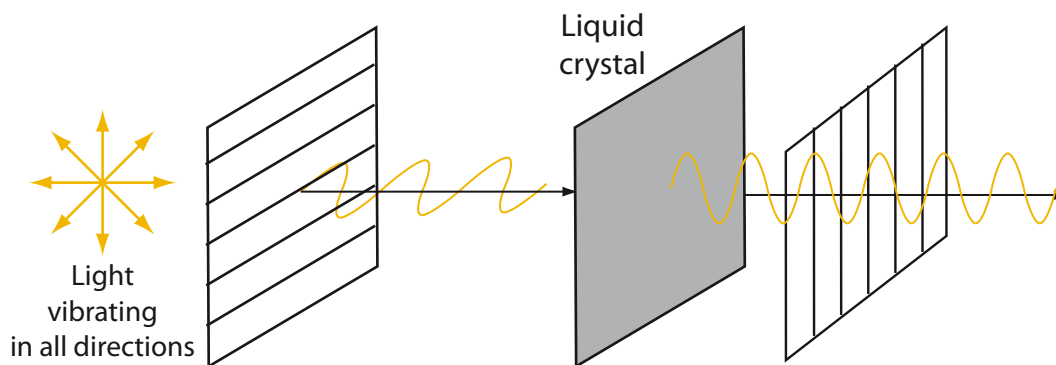he orientation of the molecules. The orientation of the polar LC molecules can be controlled by the application of a small voltage across a thin film of the material. The areas of the display that are light and dark can be controlled in this way.

LCDs use very little electrical power and are thus ideal for use in battery operated electronic devices such as calculators, radios, digital watches, laptop notebooks, mobile phones, flat panel displays (LCD TVs), etc. leading to a multi-billion dollar industry.

Properties needed for a substance to be used in liquid-crystal displays:

The earliest LC materials, the cyanobiphenyls were found to be ideal for use in LCDs because these molecules possess a number of important properties: Their chemical stability means they do not decompose in the instruments; they are operational at room temperature and the LC phase is stable over a wide and suitable temperature range (for example, from about –10 °C to 60 °C). Additionally, the materials have dipoles (polar or easily polarizable). This is essential as the application of an electrical field leads to a change in the orientation of the molecules. Also, LCs must have a rapid switching speed between orientations so there is no lag when a small voltage is applied, that is, they must have a fast response time to the applied electric field.

C7
NANOTECHNOLOGY

C.7.1   Define the term nanotechnology.

C.7.2   Distinguish between physical and chemical techniques in manipulating atoms to form molecules.

C.7.3   Describe the structure and properties of carbon nanotubes.

C.7.4   Discuss some of the implications of nanotechnology.

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"Nanotechnology has given us the tools … to play with the ultimate toy box of nature – atoms and molecules. Everything is made from it… The possibilities to create new things appear limitless."

Horst Stormer (Nobel laureate)

Figure 1431   Atomic art?

Figure 1431 shows the Japanese Kanji, which means 'atom', written literally with atoms, each just a few nanometres across.

OPTION

Nanotechnology involves measurements in the nanometre scale, namely 10^{-12} m range which is the size of a group of atoms; DNA molecules are about 2.5 nm wide, the smallest bacterium is about 200 nm wide whereas human hair is about 100,000 nm wide. **Nanoparticles** often have physical and chemical properties that are quite different and novel since a large proportion of the small group of atoms are at the surface, that is they have a large surface area to volume ratio compared to bulk matter. For example, gold is known for its chemical inertness. However, at the nanoscale it is reactive, catalytic and its melting point is much lower (in fact a liquid at about room temperature) compared to the macroscale element. Particles of gold can also appear red, blue or gold, depending on their size. Thus at nanoscale, properties do not depend only on composition and structure of the matter as they do at the macroscale.

Definition of the term nanotechnology: "Nanotechnology involves research and technology development at the 1 nm to 100 nm range. (It) creates and uses structures that have novel properties because of their small size. Nanotechnology builds on the ability to control or manipulate at the atomic scale."

(Definition from IBO Guide as quoted from the Nanotechnology Initiative.)

C.7.2   Distinguish between physical and chemical techniques in manipulating atoms to form molecules.

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Scanning probe microscopes (such as the scanning tunnelling microscopes, STMs) are able to move individual atoms one atom at a time, or allow the controlled deposition of single atomic or molecular layers one on top of another. Metals can be vaporized and atomic layer deposition leads to nanoparticles when cooled. These are examples of physical techniques which allow atoms to be manipulated and positioned to specific requirements. On the other hand, chemical techniques position atoms in molecules using chemical reactions. Thus whereas a STM can be used to move a carbon monoxide molecule to an iron atom, a voltage can be used to chemically bind these together. Similarly, a voltage activated platinum-rhodium tip on a STM can catalyse the homolytic fission of hydrogen gas and deposit the hydrogen atoms across a C=C alkene double bond placed on a surface. The result is selective hydrogenation of the double bond.

C.7.3   Describe the structure and properties of carbon nanotubes.

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A **carbon nanotube** (CNT) is made of rolled graphite (graphene) along an axis consisting of carbon hexagons and closed at the ends by hemispherical (half-size) fullerene-like caps or domes requiring carbon pentagons to close the structure at the ends. Nanotubes are hollow cylinders made of carbon atoms and can be one atom thick (single-wall carbon nanotubes - typically about 1 nm wide, but wider ones can be formed) or multi-walled carbon nanotubes consisting of concentric nanotubes with a smaller one in a larger one, like a set of Russian matryoshka dolls. Typically the sides of the tubes contain hexagons, the caps hexagons and pentagons. The latter are rather more susceptible to chemical reactions and the reactivity allows particles of metals, metal oxides, metal salts amongst others to be inserted into the nanotubes. Figure 1432 shows a single-walled carbon nanotube
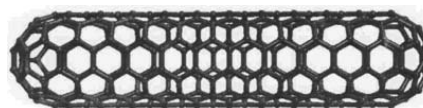

Figure 1432   A single-walled carbon nanotube

The structure of a nanotube determines its properties such as electrical and thermal conductivity. Whereas graphite is

soft and somewhat malleable, CNTs are structurally rigid and extremely strong, many times stronger than steel. Like graphite, carbon atoms are bonded by strong covalent bonds with sp^2 hybridization along the nanotube length. They also exhibit unique electrical properties, and can act either as excellent electrical conductors or semiconductors depending on the length and multi-walls present. The narrower the diameter of the nanotube, the less it behaves like graphite. As the diameter gets wider, the more its bulk properties are similar to those of graphite; this is typical of the nanoscale materials mentioned earlier.

> ### C.7.4   Discuss some of the implications of nanotechnology.
>
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Possible applications

Current applications include invisible suncreens comprising titanium or zinc oxides, bacteriocidal bandages with silver nanoparticles, production of spill-proof, water repellent and wrinkle free garments (requiring infrequent cold water cleaning), heterogeneous catalysis and microcircuits, amongst many others. Progress in nanotechnology research and development is rapid as governments, research institutions and industry are investing heavily in it. Potential uses range from development of vaccines and drugs to faster, cheaper and more powerful electronics with much higher storage capacities, to light weight, longer lasting materials for construction, transportation and everyday uses that require less energy and resources and cause less pollution.

Nanomedicine and bionanotechnology are examples of new multidisciplinary fields with developments in, for example, drug delivery methods. If drugs can be targeted just to cancer cells in the correct dosage, the benefit would be tremendous to society in terms of reduced costs and fewer possible side effects. Similarly the possibility of using nano-amounts as catalysts in catalytic converters, fuel cells, oil refineries and chemical industries can go a long way to reducing pollution. Incredible possibilities are being suggested for nanotechnology – no doubt it will lead to beautiful successes and spectacular failures. It certainly has lead to "Nano-Buzz" and "Nano-Hype".

Heath and environment effects and concerns

It is possible that the combination of small size and distinctive properties may pose environmental and or health risks. The small size means it is easy to inhale nanoparticles. For example, the ultra thin soot particles from industrial activity are known to have adverse effects on the respiratory system of humans. What about possible cancer causing risks if nanoparticles can change the genetic makeup of cells? Will nanoparticles be able to cross the blood-brain barrier and if they can, what will the effects be? What about the use of metal oxide nanoparticles in sunscreens; is there any potential hazard as a result of absorption through the skin? Nanoparticles have been found to be harmful to animals. If these can enter the lymphatic system, the body's immune system, by passing through the skin's top layer, there could be health concerns.

Toxicity concerns

The field of **nanotoxicology** is concerned with various aspects of the toxicity of nanoparticles, since such materials have properties quite different from their macro counterparts. For example, an inert material may become very reactive at the nanoscale and the current standards of toxicity for that substance may no longer apply. Thus a determination of the harmful effects of nanoparticles to humans and the environment presents a great challenge since there are many variables involved such a size, shape, surface area to volume ratio etc. Nanoparticles tend to aggregate and the properties of these nanoclusters tends to be different from nanoparticles, further complicating toxicity issues. The website www.nanotoxicity.php makes several references to the toxicity of nanotubes and this is an area that requires more research and data in order to establish toxicity standards. As more data is available, nanotechnology will require international regulations and restrictions on the production and use of harmful products.

Responsibilities of industries

If nanotechnology does not require heavy industry, scarce natural resources and massive capital, it has the potential for exponential growth of manufacturing systems leading to fast acceleration in manufacture and improvement of products and use of inexpensive raw materials (as much smaller amounts will be required). The responsibility of industries to rise to the challenges posed by nanotechnologies will require working to the highest ethical and social standards while balancing between global and self interest.

Ethical and political issues

The implications of nanotechnology are many and these have given rise to new interdisciplinary areas of study ranging from **nanoethics** (the ethical and social uses in developing nanotechnology, for example the military uses such as cheaper, more powerful weapons) to **nanopolitics**, (such as the need for public education, for informed debate and for public involvement in policy discussions). The nano-divide is the concern of the increase in the gap between the poor and the rich; could nanotechnology help reduce the divide by making smaller and cheaper technology available to a larger number of people around

the world? Nanotechnology is still at an early stage and the science behind it is not fully understood. It is of global importance and successful use of nanotechnology for the benefit of humans will require a joint effort by governments, industry, academia and businesses from around the world.

TOK Science versus Politics

Who should determine priorities in the funding of research?

Can anything ever be 'values free'? As humans we inevitably have values and cannot help regarding everything in the light of these values. These values of course are the fundamentals of moral judgements and differ from person to person. There are various moral codes such as Utilitarianism, "Might is right", "Do unto others as you would have them do to you", "Cultural relativism".

I suppose, pragmatically, the basic principle guiding research has to be "He who pays the piper calls the tune". If you don't want any money to do it, then you can probably research into what you like – as long as it's legal. Again I don't think there is much question about this with regard to private research institutions; if ICI is paying for the research then nobody questions them telling their scientists what to investigate. With research that takes place in state institutions then it is not quite clear who is paying the piper. Sometimes industrial companies will sponsor a research worker and again probably they have the right to direct that research, but what about the others? Maybe there shouldn't be any others, maybe those who are likely to profit should pay like industry does, but who then would be likely to profit? In the short term, shall we pay for better mapping of the Earth's magnetic field by an expensive satellite? It might never get done even though in the long term there could be lots of benefits, generally impossible to predict at the outset. The laser is a good example of a discovery that has transformed so many things and which came out of some "blue sky" research. I suspect we (at least if you are a taxpayer) are the "payers". Maybe I have 10 minutes of a scientist's time as a result of what I pay in taxes – I wonder what I'm going to get him/her to do? Not a problem, the government, in its wisdom, as well as taking our money away from us in taxes because it knows better how to spend it, also relieves us of the burden of research decisions. Once upon a time academics were trusted just to research into whatever they found interesting. Nowadays money is a little tighter, so that usually they have to submit proposals to research councils who award funding. Unfortunately that means that many spend as much time writing research proposals and going through all the involved "follow up", as they do actually carrying out any research! Who are on these research councils anyway? Usually it is other scientists in a similar field who, supposedly, have the expertise to decide which projects deserve support and which do not. But what should their decisions rest on – something that looks likely to "pay off" in 5-years or something that, just possibly, might revolutionise everything 50 years down the track? Somebody who is working in a prestigious university, somebody who has published a lot of academic papers (though maybe of dubious interest) recently, the guy who bought you a beer in the bar at the last conference? Lack of funding might even be a stimulus; I think it was Ernest Rutherford who said "Our request for funding hasn't been granted, so we'll have to think instead".
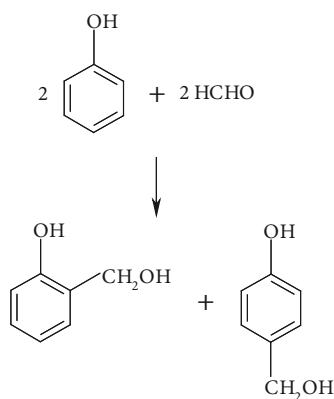
C8 CONDENSATION POLYMERS (HL)

C.8.1   Distinguish between addition and condensation polymers in terms of their structures.

C.8.2   Describe how condensation polymers are formed from their monomers.

C.8.3   Describe and explain how the properties of polymers depend on their structural features.

C.8.4   Describe ways of modifying the properties of polymers.

C.8.5   Discuss the advantages and disadvantages of polymer use.

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There are two main types of polymers – addition and condensation polymers.

In **addition polymerization**, monomers are unsaturated organic compounds such as ethene, $CH_2 {=} CH_2$ and chloroethene $CH_2{=}CHCl$ (vinyl chloride). Monomer units add together without the elimination of any atoms to form the polymer. Addition takes place across the double bond. After polymerization, the double bond is converted to a single bond. Typically, a single monomer is involved.

In **condensation polymerization**, the monomer units have two reacting sites on them for polymerization to take place such as dicarboxylic acids, diols and diamines (called bifunctional monomers). These undergo condensation reactions to produce a larger molecule with the elimination of a smaller molecule such as water. Typically two monomers are involved, though there are examples of condensation polymers (such as nylon-6) which only involve a single monomer with different functional groups at the two ends of it. Butanedioic acid, ethane-1,2-diol and 1,2-diaminoethane are examples of bifunctional monomers as shown in Figure 1433.

Figure 1433   Examples of bi-functional polymers

Thus, the repeating unit of the polymer made from the condensation of the two monomers butanedioic acid and ethane-1,2-diol is shown in Figure 1434.

Figure 1434   The repeating unit

EXAMPLES OF CONDENSATION POLYMERS

Phenol-methanal plastics

The —OH group on the phenol is 2,4-directing. Thus, the intial reaction between phenol and methanal involves substitution at both the 2- and 4-positions on the benzene ring as shown in Figure 1435.

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Figure 1435

It is the reaction of the substituted products from the above reaction with phenol that undergo condensation with the elimination of water, as shown in Figure 1436.
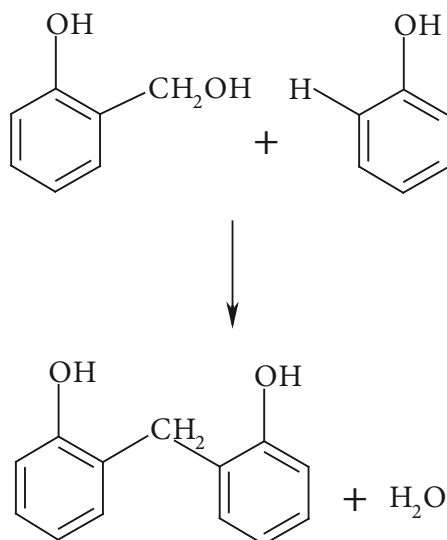

Figure 1436

Subsequent condensation reactions with hydrogen on the 2- and 4- positions produce the phenol-methanal plastic (commercially called Bakelite) with extensive cross-links. As shown in Figure 1437.
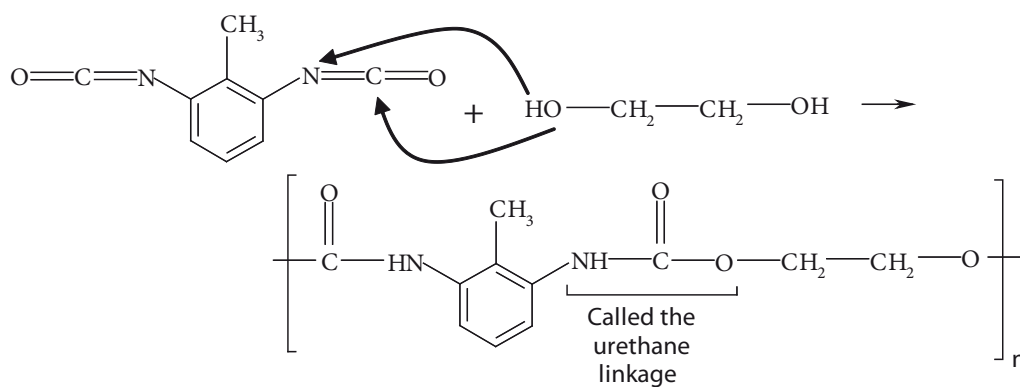

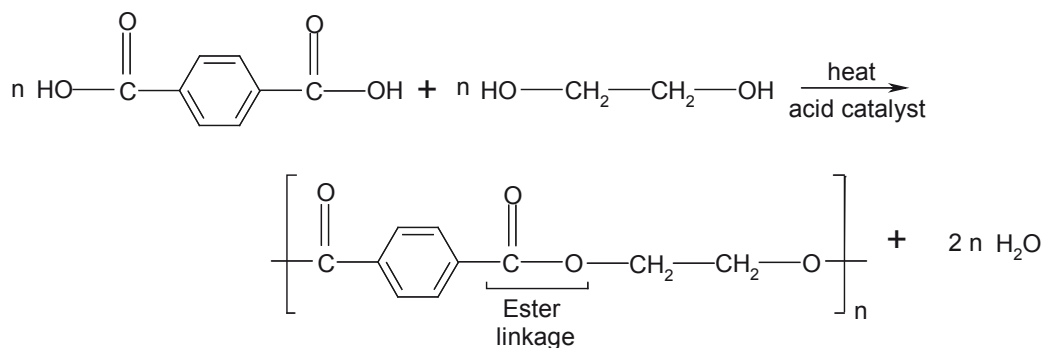*Figure 1438 (a)   The urethane linkage*

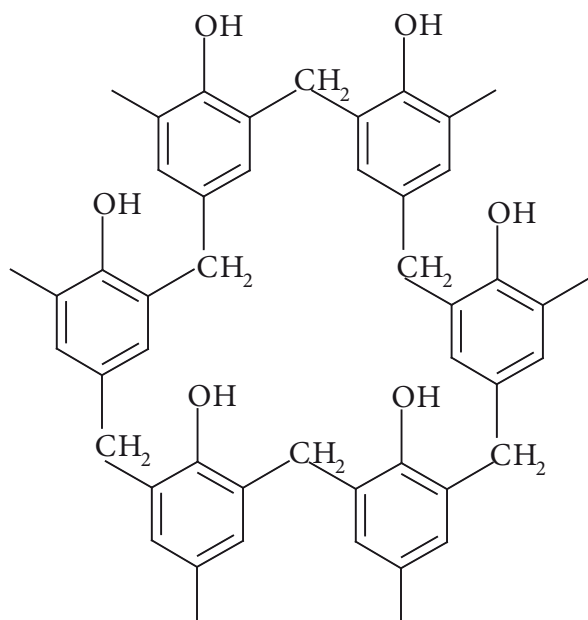*Figure 1438 (b)   The ester linkage in the polymer PET*

Figure 1437

Polyurethanes

Polyurethanes are used extensively in making polyurethane fibres and foams. Polyurethane is made by the reaction of di-isocyanates in which an oxygen atom is bonded to the cyano group at either end of the carbon chain containing monomer: OCN—(carbon chain)—NCO. The other bifunctional monomer for the condensation reaction is a diol, for example, ethane-1,2-diol as shown in Figure 1438 (a).

Polyethylene terephthalate (PET)

PET is the polymer of choice in the blow-moulded bottling industry because unlike glass it is light weight and does not shatter. It is a polyester made by the condensation of benzene-1,4-dicarboxylic acid (called terephthalic acid) with ethane-1,2-diol (called ethylene glycol) – hence the name of the polymer: polyethylene terephthalate, PET. (Fig 1438 (b)).

FACTORS DETERMINING THE PROPERTIES

OF CONDENSATION POLYMERS

Chain length

The greater the average chain length, the greater are the intermolecular forces and hence the higher the strength and melting point.

The way groups are arranged or orientated along a polymer backbone chain

Different properties can arise from different stereochemistries of polymers. **Kevlar** is an excellent example of a condensation polymer where the trans orientation of the chain allows it to be a straight chain polymer with close approach between chains, allowing strong hydrogen bonding between them, which gives it great strength. The cis-orientation however produces bent chains and does not allow close approach for strong bonding between chains.

Cross–linking

In **cross-linked polymers**, two different chains are connected by short lengths of another chain which in some cases may be only two or three atoms long. A cross-linked polymer is found to be more rigid than a linear or branched polymer. The amount of cross–linking determines how rigid the final structure becomes. A good example of this is the vulcanization of rubber. Natural rubber is a soft, sticky substance which hardens to a useless material unless it is treated with sulfur, or some other chemical. Rubber is built from isoprene (2–methyl–1,3–butadiene) monomers. When rubber is heated with sulfur it maintains its spring for longer periods of time than natural rubber. The sulfur atoms create strong covalent links between the chains so that treated rubber retains the shape into which it was molded. This led to the development of rubber tires and the use of rubber in hoses, shoes and balls.

The phenol-methanal plastic is an example of a polymer where the benzene ring is bonded to CH_2 in three positions with extensive 3-D cross-links that produce rigid plastics with high melting points which are high enough that it undergoes decomposition before melting (that is, a thermosetting rather than a thermoplastic polymer). Thus phenol-methanal plastics are excellent electrical insulators, non-flammable and chemically inert. These plastics are used in electrical plugs, sockets, switches, casings for electronic equipment, etc.

WAYS OF MODIFYING THE PROPERTIES

OF POLYMERS

Air in the manufacture of polyurethane foams

A 'blowing agent' such as air produces a polyurethane foam that is soft and has a low density. Such foams are used as cushioning materials for furniture. More often, in the case of polyurethane, water is used to produce the foaming agent carbon dioxide since the isocyanate group reacts with water to produce CO_2.

$$—NCO + H_2O \longrightarrow —NH_2 + CO_2$$

Doping a polymer

A polymer such as polyethyne, made by the polymerization of ethyne, can produce two types of polymers: one containing the cis-arrangment in the polymer chain containing the C=C double bond and the other containing the trans-arrangement. It is found that the trans-polymer

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is not an insulator like polyethene, but more like a semi-conductor because of the presence of the conjugated system of alternate C—C single and C=C double bonds. Addition of the oxidant iodine as vapour increases the level of conductivity to that of metals. Thus doping polyethyne with iodine vapour produces an organic polymer that can conduct electricity.

Blending of polyester fibres

For example, a blend of aromatic polyamide with polyester fibre produces a flame-resistant garment material. Similarly, soft blended polyester fibres are used to manufacture comfortable mattress pads, and polyblend fibres can produce strong and durable fabric materials. Blending of polyester fibres with particular molecular groups or charges (such as sulfonic acid radical or anionically modified nylon) make these materials easy to dye due to a strong attraction for dyes with the opposite electrical charge (called the affinity method of dyeing).

C9 MECHANISMS IN THE ORGANIC CHEMICALS INDUSTRY (HL)

C.9.1   Describe the free-radical mechanism involved in the manufacture of low-density polyethene.

C.9.2   Outline the use of Ziegler–Natta catalysts in the manufacture of high-density polyethene.

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A **free-radical mechanism** is involved in the manufacture of LDPE: recall the addition polymerization to form polyethene from ethene:

$$nCH_2{=}CH_2 \longrightarrow -(CH_2{-}CH_2)n{-}$$

The weaker π-bond in each ethene breaks to give the two bonds at the end of the molecule to form the macromolecular polymer. Evidence from kinetic studies of polymerization reactions is, however, necessary to elucidate the mechanisms for such reactions. Low density polyethene is made at very high pressure (≈1500 atm), a temperature of about 200 °C and in the presence of organic peroxides which are a source of free radicals. See Figure 1439.

$$nCH_2{=}CH_2 \xrightarrow[\text{peroxides}]{200°C;\ 1500\ atm} -(CH_2{-}CH_2)_n{-}$$
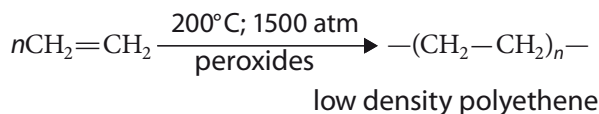
low density polyethene

Figure 1439

A free radical mechanism involves initiation, propagation and termination steps; also, peroxides contain a very weak O—O bond in the R—O—O—R functional group.

MECHANISM

Initiating step

Peroxides decompose to form alkoxy free radicals as the O—O covalent bond in the peroxide is broken. This is shown in Figure 1440.
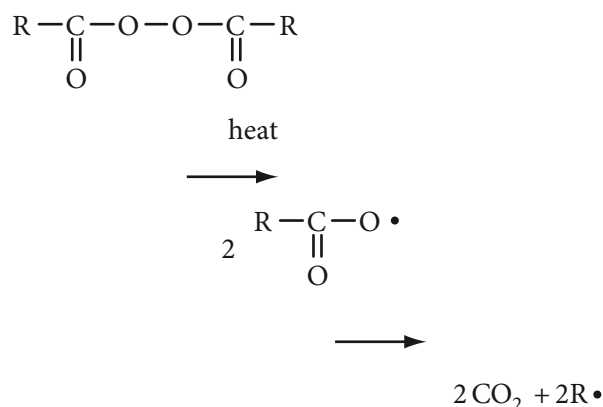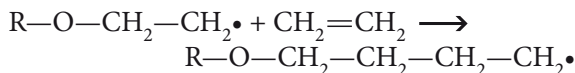

Figure 1440   R—O—O—R ⟶ 2R—O•

Propagating step

The alkoxy free radicals react with the alkene to produce a longer alkyl free radical:

$$RO• + CH_2{=}CH_2 \longrightarrow R{-}O{-}CH_2{-}CH_2•$$

The chains add successive ethene units to produce longer free radicals:

$$R{-}O{-}CH_2{-}CH_2• + CH_2{=}CH_2 \longrightarrow$$
$$R{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_2•$$

Also the following reaction takes place that leads to chain branching:

$$R{-}O{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}O{-}R +$$
$$•O{-}R \longrightarrow$$
$$•R{-}O{-}CH_2{-}•CH{-}CH_2{-}CH_2{-}O{-}R +$$
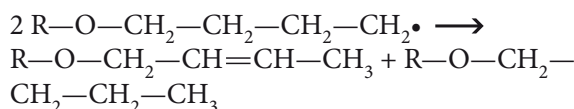$$R{-}O{-}H$$

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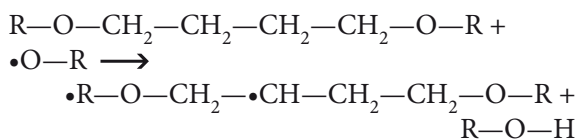
It is this branching that gives polyethene its low density as the chains cannot pack very closely, giving it a comparatively low melting point.

Terminating step

The free radicals either combine to form a longer chain molecule or the transfer of a hydrogen atom occurs to form a combination of an alkane and alkene:

$$2 \; R—O—CH_2—CH_2—CH_2—CH_2\bullet \longrightarrow$$
$$(R—O—CH_2—CH_2—CH_2—CH_2)_2—$$

or

$$2 \; R—O—CH_2—CH_2—CH_2—CH_2\bullet \longrightarrow$$
$$R—O—CH_2—CH=CH—CH_3 + R—O—CH_2—$$
$$CH_2—CH_2—CH_3$$
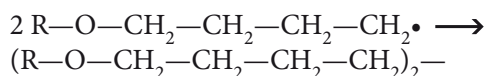
The use of **Ziegler-Natta catalysts** in the manufacture of HDPE: High–density polyethene is formed at much lower pressures (5–7 atm) and lower temperatures (about 75°) in the presence of special catalysts. The Ziegler–Natta catalysts used in the production of high–density polymers are not soluble in alkane solvents. The reaction mixture is thus a heterogeneous one and polymerization takes place at the surface of the catalyst which is a suspension of titanium (III) or (IV) chloride and an alkyl-aluminium compound. As a result the process is also called **coordination polymerization** (because of the coordination/bonding between the unsaturated reactive center of the monomer and the transition metal). This polymerization uses an ionic mechanism.

The typical compounds used as catalysts are: titanium(IV) chloride, $TiCl_4$, and triethylaluminium, $(C_2H_5)_3Al$ in which the aluminium is electron deficient. They react together to give an organotitanium compound $Ti—CH_2—CH_3$ which is believed to play a key role in which the $Ti—C$ bond is quite polar. The titanium is the site for the coordination with the alkene. Bonding between the partially positive metal and the alkene's π bond develops. This is followed by insertion of the alkene into the hydrocarbon chain bonded to the titanium atom. See Figure 1441.

$$Ti \overset{\delta+}{—}CH_2—CH_3$$
$$CH_2=CH_2 \qquad Ti \overset{\delta+}{—}CH_2—CH_2—CH_2—CH_3$$
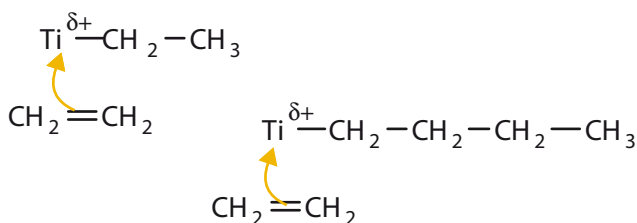$$CH_2=CH_2$$

Figure 1441   Formation of the growing hydrocarbon chain attached to the catalyst:

The polymerization produces linear, regular arrangements of groups along the chains with no branching of the polymer chain, which fit together much better in a crystal structure. These rigid high density polymers thus have stronger van der Waal's forces and higher melting point than LDPE.

C10 SILICON AND PHOTOVOLTAIC CELLS (HL)

C.10.1 Describe the doping of silicon to produce p-type and n-type semiconductors.

C.10.2 Describe how sunlight interacts with semiconductors.

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Silicon is the most important element used in the semiconductor industry without which it would be impossible for the industry to exist. Silicon contains 4 valence electrons. As each atom forms four tetrahedrally directed covalent bonds to other silicon atoms, a macromolecular crystal structure in three dimensions is built up. Carbon in the form of diamond, with a similar tetrahedral structure to silicon, is a non-conductor of electricity. Carbon is smaller than silicon in size and all valence electrons are held tightly by forming strong covalent C-C bonds in three dimensions, making diamond extremely hard. Because of the larger bond length in silicon, electrons are not as tightly held allowing it to be a semi-conductor. Semiconductors are a special class of materials which have an electrical resistance between those of electrical conductors and electrical insulators and are better conductors under certain circumstances. For example, they conduct electricity better as the temperature rises.

According to **band theory**, in giant non-ionic structures the valence atomic orbitals interact to give allowed electron energy bands. If these bands are completely filled (as in diamond) then electrons cannot move within the solid and it is an insulator. If the band is only partially filled (as in copper) then electrons can move throughout the structure and it is an electrical conductor. Silicon is a semiconductor because, even though it has a filled lower electron band, it has unfilled bands at a level that electrons can reach by thermal excitation.   As the temperature increases, more electrons can move into the conduction band and hence

the conductivity increases with temperature, unlike metals.

"Doping" a semiconductor with a trace of another element can increase conductivity. If a trace of an element from group 5/15 of the periodic table is added to the silicon (for example phosphorus) then the extra electrons have to go into the upper unfilled band and this increases the conductivity. This is known as an n-type semiconductor (n for negative as the current is carried by negative electrons). Conversely if the doping element is from group 3/13 (for example boron), then there are gaps or "holes" in the filled band and this too enhances conductivity. A doped semiconductor of this type is known as a p-type semiconductor (p for positive as the current is carried by positive holes).

Doping of silicon to produce n-type and p-type semiconductors

Doping is the incorporation of minute amounts of impurities within the crystal lattice of silicon so as to increase its conductivity. Typically, doping of semiconductors is carried out by adding certain substances to molten silicon. This can be done by exposing the semiconductor to the vapor of the substance which is added in the furnace. The chosen substance is added in carefully controlled amounts to bring its content up to only a few parts per million. The atoms of the added substance are therefore well spaced out in the semiconductor so that its crystal structure is not weakened. The process is called doping and the added substances are called **dopants**. In surface doping, a solid silicon surface is exposed to the vapour of the dopant.

There are two types of doped semiconductors: **n–type** and **p–type**. In n–type semiconductors, the dopants are Group V (or 15) elements, such as arsenic and antimony which have 5 electrons in the outer shell. When an arsenic dopant atom replaces an atom of silicon in the structure, it uses four of its five valence electrons to form covalent bonds with silicon atoms. The fifth electron is supplied to

the material, creating a negative charge. These are called n–type semiconductors. The added atoms are called **donor atoms** because they donate electrons to the material. The addition of donor atoms leaves the crystal uncharged overall because the additional electrons are associated with additional positive charges on the donor nuclei. See Figure 1442

In p–type semiconductors, the dopants are Group III (or 13) elements, such as boron (B), gallium (Ga), or indium (In), which have three electrons in the outer shell. When a boron atom replaces a silicon atom, it forms three electron pair bonds with three silicon atoms, but the fourth bond is incomplete as it has only one electron. The vacancy is called an **electron hole** and is positively charged, producing a p–type semiconductor. The added atoms are called **acceptor atoms** because they can accept electrons to fill the holes in the bonds.

A typical solar (photo–voltaic) cell consists of two layers of almost pure silicon; one has a trace of arsenic (n–type) and the other a trace of boron (p–type). The n–type has atoms with an extra electron which is relatively free to move whereas the p–type layer has atoms short of an electron. When the two layers are placed together, the extra electrons from the n–type move to the p–type layer giving the p-type a net negative charge at its junction with the p-type. This means that electrons can therefore move from the p-type to n-type but the negative charge on the p-type prevents them moving the other way around. This therefore operates as a **diode**. When sunlight strikes such a surface, the sun's energy is able to give electrons the energy to move, but because of the diode, they can only move from the p-type to the n–type layer. If an external circuit is present, the electron can flow back through it from the n-type layer to the p–type layer.

The advantages of solar cells are many. These include no moving parts, no liquids and no corrosive chemicals. They generate electricity as long as the sun is shining. The
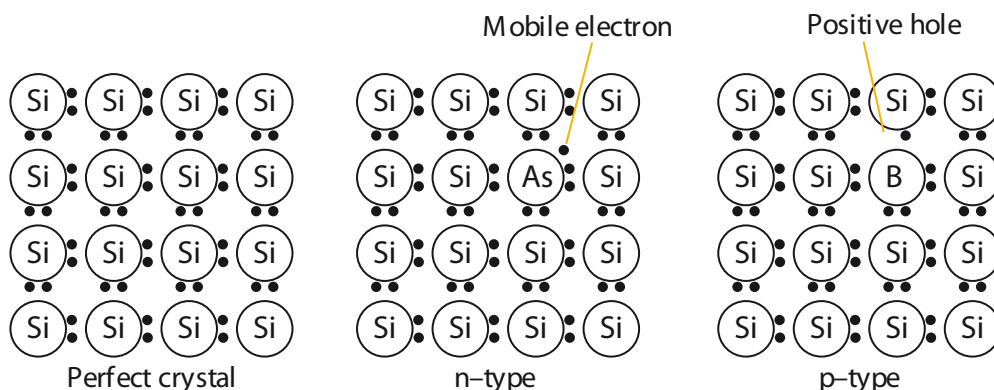

Figure 1442   Structure of semi-conductors

disadvantages include the need for large surfaces, the fact that pure silicon is very expensive and that the solar cells only work when the sun is shining and produce low power outputs.

C11 LIQUID CRYSTALS (HL)

C.11.1 Identify molecules that are likely to show liquid-crystal properties, and explain their liquid-crystal behaviour on a molecular level.

C.11.2 Describe and explain in molecular terms the workings of a twisted nematic liquid crystal.

C.11.3 Describe the liquid-crystal properties of Kevlar, and explain its strength and its solubility in concentrated sulfuric acid.

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Molecules that show LC properties, and their LC behaviour on a molecular level:

A mixture of cyanobiphenyls (biphenyl nitriles) that operate over a wide enough temperature range are used in LCDs. See Figure 1443
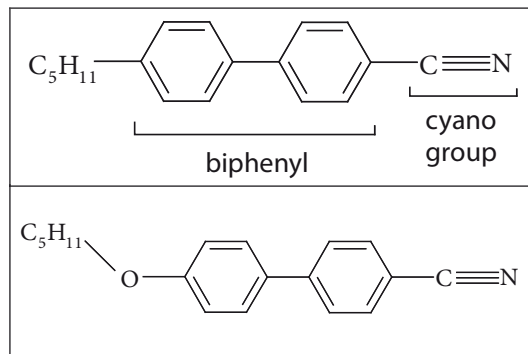

Figure 1443   Examples of cyanobiphenyls

These molecules have three key chemical/structural features

- The polar cyano (nitrile) group allows an electric field to control the orientation of the molecules as well as creating strong intermolecular forces for the molecules to be oriented in the same direction.
- The biphenyl groups contain two planar benzene rings bonded by a single covalent bond. These are chemically stable, make the molecule rod-like and rigid.
- The long hydrocarbon chain affects the melting point as the molecules cannot pack together as closely and can maintain the LC phase. The size and shape of the alkyl group can be changed to alter the melting range.

The workings of a twisted nematic liquid crystal

Many common **liquid crystal displays** (LCDs) use twisted nematic liquid crystals, TNLCs. A TNLC is naturally twisted and can be untwisted depending on the voltage
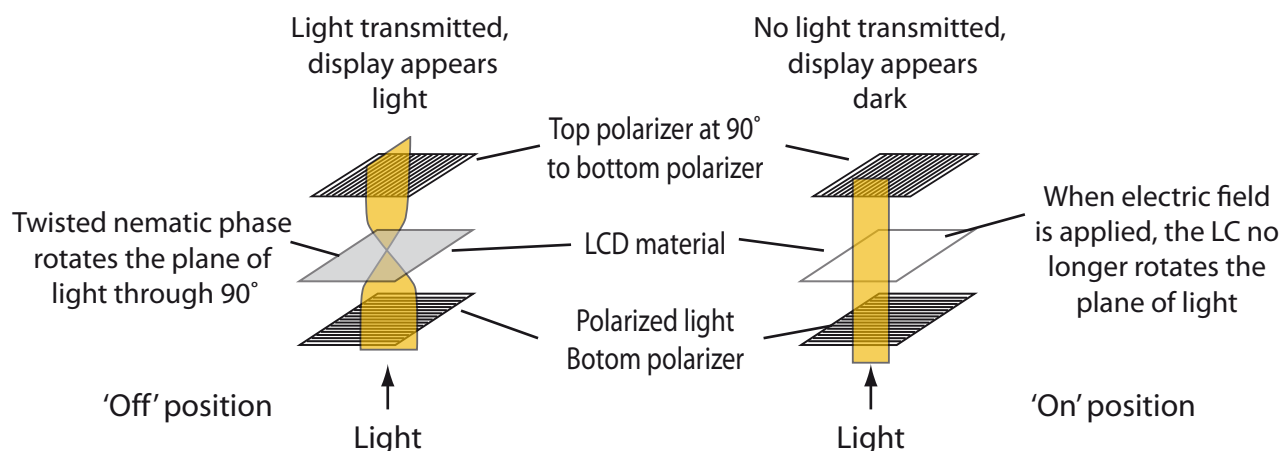

Figure 1444 (a), (b)   How an LCD works

applied. That is, its effect on polarized light is influenced by an electric current. An LCD contains a collection of pixels (tiny sections containing single points in an LCD image) which can be controlled using an electric field. The principle behind the TNLC display is that the twisting or rotation of polarized light by the TNLC molecules can be removed by the application of an appropriate amount of voltage.

An LCD is made of multiple layers consisting of glass sheets coated with transparent indium tin oxide (ITO). A metal oxide film above and below which act as electrodes that apply the voltage to untwist the LC. In between, an LCD contains an LC material placed between a pair of crossed polarizers that are perpendicular to each other. These can be made by creating scratches on glass (or transparent plastic) plates at 90° to each other. The LC molecules in contact with the glass line up with the scratches, and molecules form a twisted arrangement between the plates due to intermolecular forces.

Light vibrating in the plane of the first polarizer passes through. When it comes in contact with the TNLC molecules, it is rotated by the molecules through 90° as it passes through the LC film. Since the second polarizer is at 90° to the first one, the polarized light emerging from the LC is aligned with the scratches. Light will pass through the film and the pixel will appear bright when no electric field applied to it (thus called the 'off' position) as shown in Figure 1444 (a).

If a voltage is applied across the film, the polar molecules align with the electric field and the twisted structure is lost. Plane-polarized light is no longer rotated, and so the pixel appears dark as in Figure 1444 (b). Thus regions in which an electric field of sufficient magnitude is applied appear dark. If the electric field is switched off, the twist is re-established and bright light pixel appears. For example, the numbers on a calculator are based on seven sections; applying voltages to different sections produce different numbers, for example if sections 1, 3, 4, 5 and 7 are in the on position, the number 2 appears whereas sections 1, 3, 4, 6, and 7 in the on position gives the number 3 as shown in Figure 1445.
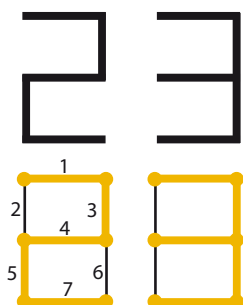

Figure 1445   An LCD display

Liquid-crystal properties of Kevlar, its strength and its solubility in concentrated sulfuric acid

Kevlar is a rod-like polyaromatic amide. It is a condensation polymer of 1,4-diaminobenzene and 1,4-benzenedicarboxylic acid with the repeating unit as shown in Figure 1446.
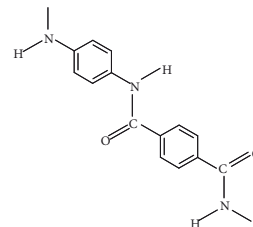

Figure 1446   The repeating unit of Kevlar

Kevlar is a very strong, light-weight synthetic fibre spun like a spider's web in which the trans-polymer chains are arranged parallel to each other. The carbon-based polymer does not corrode and is several times stronger than steel! Thus it has many uses including in bullet-proof vests and radial tyres. Kevlar's strength comes from the strong intermolecular hydrogen bonding between the polar amide groups in the adjacent chains. This is due to the attraction of the highly electronegative oxygen atom in one chain and the tiny partially positive hydrogen atom bonded to the highly electronegative nitrogen atom on the other chain, shown by dashed lines in the structure below. The strength also comes from the interaction that results from the arrangement of the π bonds in the benzene rings in the adjacent chains. See Figure 1447.
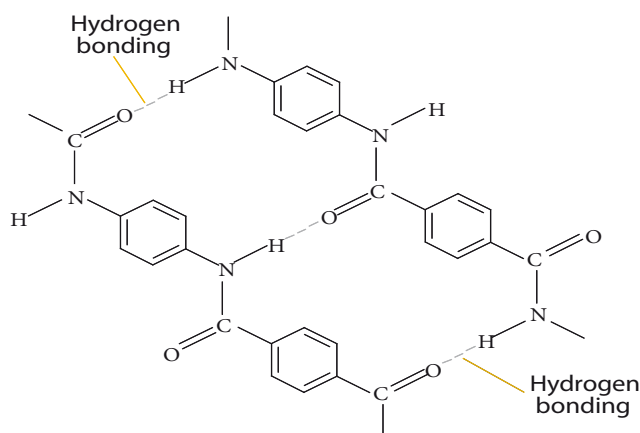

Figure 1447   The structure of Kevlar

These interactions give rise to a highly ordered and strong polymer, of unidirectional orientation and structural rigidity, which is resistant to dilute acids and bases. However, Kevlar degrades on exposure to concentrated sulphuric acid as the hydrogen bonds can be broken between the chains by the protonation of the oxygen and the nitrogen atoms. Hydrolysis of the amide linkage takes

place to form a lyotropic liquid crystal solution in moderate concentration of the acid containing rigid rod-shaped molecules due to the linked benzene rings. The long range order (the alignment of the molecules) is maintained depending on the concentration of LC molecules in the concentrated acid solution.

Molecular Modelling

Kevlar is a good example of a polymer that can be studied through molecular modelling which involves making and visualizing large molecules in three dimensions using computer simulations. A quick look at the chain structure of Kevlar suggests that its cis-arrangement (conformation) around the amide group will lead to bent chains which will not line up to form strong interactions between the chains; the trans arrangement, on the other hand, will be able to. Also, on making a 3-D structure, the instability of the cis arrangement becomes clear as it reveals that there is not enough space for the hydrogen atoms on the adjacent benzene rings on the 2-positions to fit within the narrow space between the two rings. See Figure 1448.
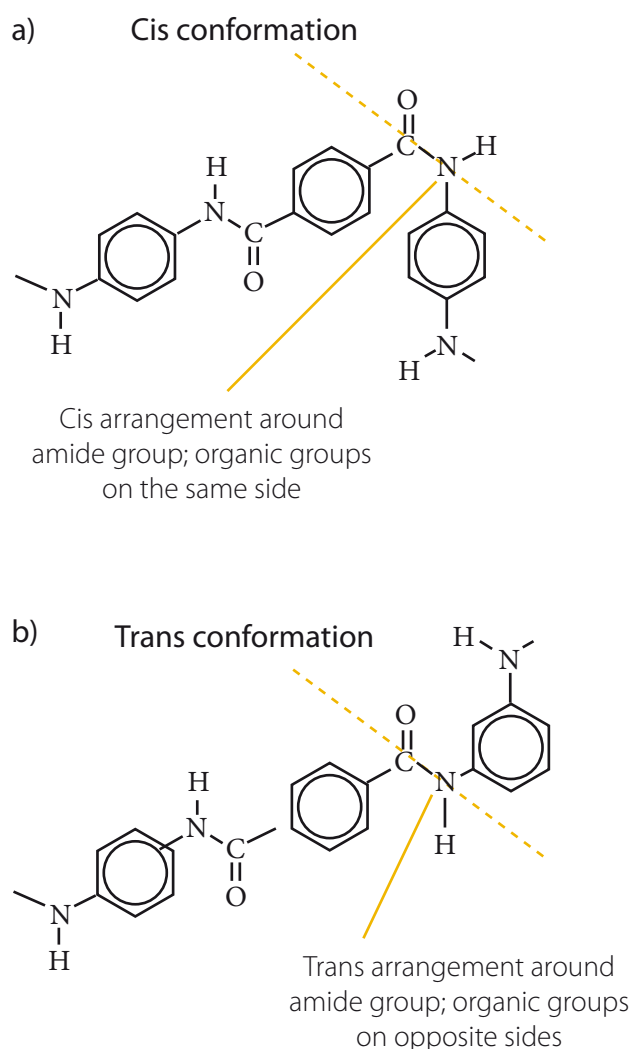

Figure 1448 (a) and (b)   Cis and Trans conformations

Molecular modelling has become an important tool in the hands of chemists in many branches of the subject ranging from the study of biologically important molecules to drug research. Numerous resources are available on the subject, including on the world wide web (www).

C12 THE CHLOR–ALKALI INDUSTRY (HL)

C.12.1 Discuss the production of chlorine by the electrolysis of sodium chloride.
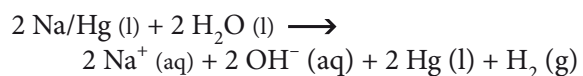
© IBO 2007

The **chlor–alkali industry** is the name given to a group of related industries that produce chlorine, sodium hydroxide and sodium carbonate. These chemicals are used in huge quantities in many different chemical processes. Chlorine and sodium hydroxide are made from the electrolysis of brine solution (salt water; aqueous sodium chloride) by various commercial methods including mercury, diaphragm and membrane cells which produce hydrogen gas as a useful by product.

The mercury cell process: Brine is continuously passed into a cell that has positive graphite electrodes, the anodes where chloride ions are discharged in preference to the hydroxide ions in water (because of the much higher concentration of chloride ions present). A moving layer of mercury acts as the negative electrode, the cathode where sodium ions are discharged in preference to water or hydrogen ions. Although sodium is higher than hydrogen in the activity series, sodium's discharge is due to the use of mercury as the negative cathode where sodium reacts with the mercury, making a liquid alloy known as an amalgam (Na/Hg (l)).

$$Na^+ \text{ (aq)} + e^- + Hg \text{ (l)} \longrightarrow Na/Hg \text{ (l)}$$
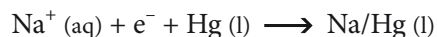
The amalgam travels out of the cell into a chamber containing water. It is at this stage that sodium hydroxide solution and hydrogen gas are produced:

$$2 \, Na/Hg \text{ (l)} + 2 \, H_2O \text{ (l)} \longrightarrow$$
$$2 \, Na^+ \text{ (aq)} + 2 \, OH^- \text{ (aq)} + 2 \, Hg \text{ (l)} + H_2 \text{ (g)}$$

This is catalysed by the presence of steel grids. The mercury is then recycled to the electrolysis cell.

OPTION

The mercury cell

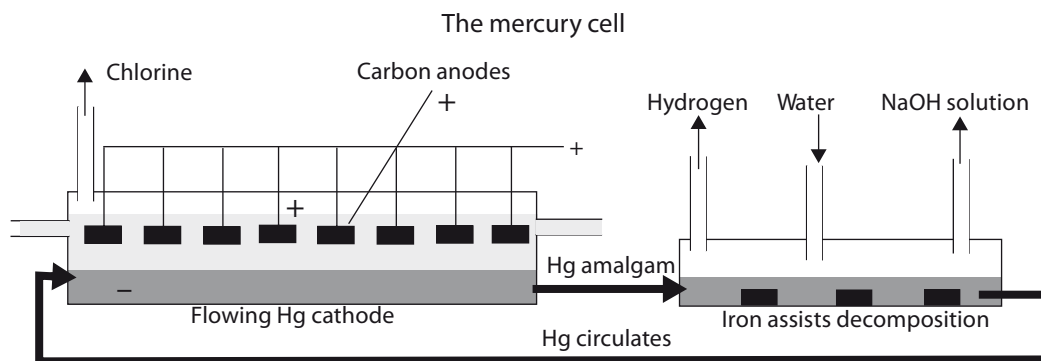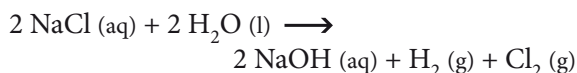Figure 1449   The mercury cell

Oxidation takes place at the positive graphite electrode, the anode to form chlorine gas:

$$2\ Cl^- \longrightarrow Cl_{2\ (aq)} + 2\ e^-$$

The overall equation for the reactions taking place is:

$$2\ NaCl_{(aq)} + 2\ H_2O_{(l)} \longrightarrow$$
$$2\ NaOH_{(aq)} + H_{2\ (g)} + Cl_{2\ (g)}$$

The chlorine gas produced by the oxidation of chloride ions at the (+) graphite anode electrode is slightly impure owing to it being mixed with water vapor. The latter is removed by drying the gas with concentrated sulfuric acid. See Figure 1449.

Diaphragm and membrane cell process: In a diaphragm cell, the positive electrode, the anode, and the negative electrode, the cathode, are in two compartments separated by a diaphragm. Diaphragms were made of asbestos. Asbestos fibres, however, scar lung tissue and cause asbestosis. Membrane cells, on the other hand, use ion-selective membrane technology which does not use asbestos; an organic flouropolymer, similar to PTFE, is

used instead as a membrane in these cells. The positive anode is made from titanium, sometimes with a coating of platinum, and the negative cathode is made from steel. See Figure 1450.

In the (+) anode compartment, chlorine is given off by the oxidation of chloride ions:

$$2\ Cl^-_{(aq)} \longrightarrow Cl_{2\ (g)} + 2\ e^-$$

In the (−) cathode compartment, water is reduced to hydrogen gas and hydroxide ions are formed:

$$2\ H_2O_{(l)} + 2\ e^- \rightarrow 2\ OH^-_{(aq)} + H_2_{(g)}$$
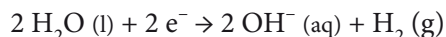
The overall result is that the brine loses its chloride ions and becomes richer in hydroxide ions as a result of electrolysis:

$$2\ NaCl_{(aq)} + 2\ H_2O_{(l)} \longrightarrow$$
$$Cl_{2\ (g)} + H_{2\ (g)} + 2\ NaOH_{(aq)}$$
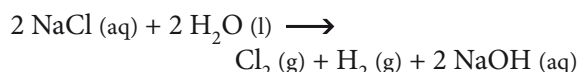
Several reactions, however, can occur unless the separation of the electrolytes in the two compartments is effective. In

The diaphragm cell

Figure 1450   The diaphragm cell

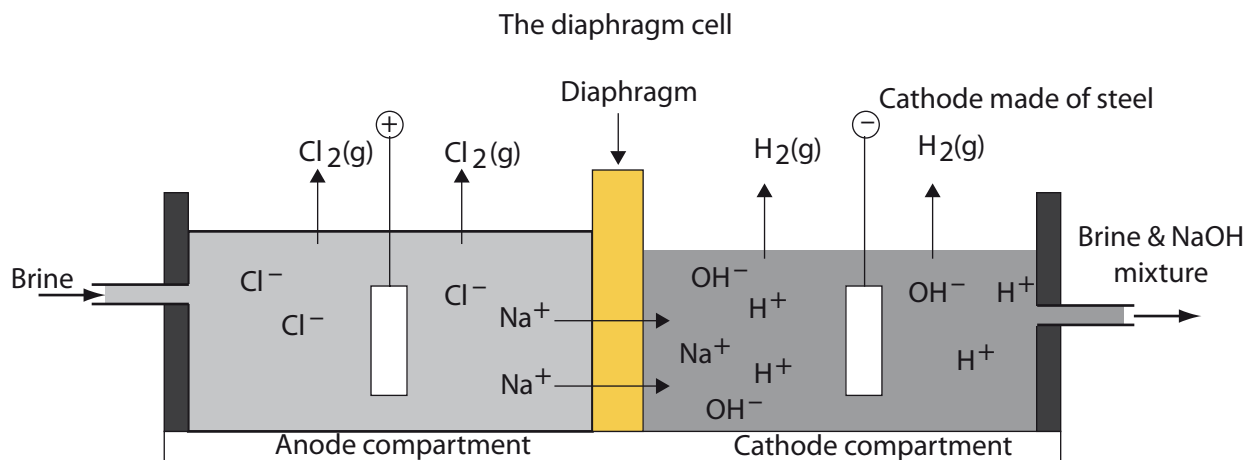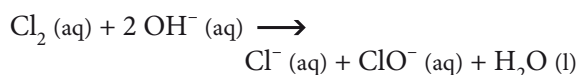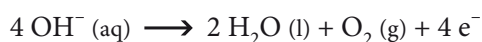the cold, chlorine reacts with hydroxide ions to produce chlorate(I) ions, ClO^- ions:

$$Cl_2 \text{ (aq)} + 2\ OH^- \text{ (aq)} \longrightarrow$$
$$Cl^- \text{ (aq)} + ClO^- \text{ (aq)} + H_2O \text{ (l)}$$

In some cells however this is promoted because the product is a liquid bleach. Also if hydroxide ions reach the (+) anode, these can be discharged. If this happens, oxygen is given off due to oxidation of hydroxide ions.

$$4\ OH^- \text{ (aq)} \longrightarrow 2\ H_2O \text{ (l)} + O_2 \text{ (g)} + 4\ e^-$$

A similar reaction occurs if the concentration of the chloride ions falls too low so that water is oxidised at the (+) anode:

$$2\ H_2O \text{ (l)} \longrightarrow O_2 \text{ (g)} + 4H^+ \text{ (aq)} + 4\ e^-$$
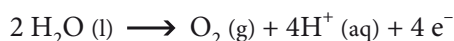
These contaminate the chlorine and makes the isolation of pure chlorine more difficult. To avoid these problems, the brine in the (+) anode compartment is kept at a slightly higher pressure than in the (–) cathode compartment. This makes it less likely that the solution around the (–) cathode will reach the (+) anode.

In membrane cells the membrane only allows cations to pass and, because of its structure, it is impermeable to anions. This prevents the anions in the two compartments from mixing, whilst allowing cations to move between them, thus keeping the current flowing.

Electrolysis of an aqueous solution of sodium chloride produces three very important chemicals, chlorine gas, hydrogen gas and sodium hydroxide. Their uses are outlined in Figure 1451.

The amount of mercury escaping around a mercury cell plant is always controlled and minimised, but almost inevitably some mercury enters the environment. Mercury reacts with many organic molecules to form organo–mercury compounds. Intake of organo-mercury compounds results in a sickness called Minamata disease (because it was first identified in this Japanese town). Mercury is converted to methyl–mercury ions by bacterial action which can enter the food chain and end up in fish, leading to biological magnification when fish is the main diet for people. Methyl–mercury compounds can form strong covalent bonds to sulfur atoms in the —SH groups present in the cysteine units in some proteins, thus seriously altering their properties. Mercury poisoning can cause inflammation of gums, nausea, diarrhoea, kidney failure, blindness, damage to the brain and damage to the central nervous system.

Some uses of chlorine	Some uses of sodium hydroxide	Some uses of hydrogen
Manufacture of solvents	Inorganic chemicals	Hydrogenation of unsaturated oils - margarine
PVC manufacture	Organic chemicals	HCl manufacture
Bleaching paper products	Paper products - converting wood to pulp	Future potential use in fuel cells
Disinfecting drinking and swimming pool water	Aluminium industry	
Production of inorganic chemicals	Soap manufacture	

Figure 1451   Some important uses of products

OPTION

Minamata disease has been largely responsible for the replacement of the mercury cell by the diaphragm cell. However, the use of an asbestos diaphragm presents problems of its own as it has been identified as causing respiratory tract cancer and asbestosis. Thus asbestos is no longer the only diaphragm material and is replaced with an organic polymer instead as a membrane in these cells.

Amongst its many uses, chlorine is used in the manufacture of chlorine–containing solvents and CFCs. Besides their use as solvents, they are used as aerosol propellants, refrigerants in automobiles, home and commercial air conditioners, in refrigerators and freezers and in fire extinguishers. It is the high strength of the C–Cl (and the C–F) bonds that makes these molecules stable. This and their low densities make it possible for the substances to reach the upper atmosphere without decomposing. This is where a major concern arises because of the interference of CFCs with the ozone layer. The presence of CFCs and other gases have been found to be responsible for the destruction of ozone in the ozone layer. As a result of the Montreal Protocol, the use of chlorinated solvents has been greatly curtailed.

Chlorine is also used in large quantities in the production of chlorine containing polymers, such as PVC. Other major uses of chlorine are to kill bacteria in the treatment of drinking water and as a bleach.

Sodium hydroxide has many uses as a general alkali in the chemical industry, for example in the purification of bauxite in the production of aluminium. Large quantities are also used in the treatment of woodpulp for paper making.

OPTION C: CHEM IN IND & TECH

QUESTIONS

C1 Iron, steel and aluminium

1. (a) Different chemical methods are used to extract aluminium and iron. State a method for the extract each metal, briefly describe the chemical principle behind each method and explain your reasoning.

(b) (i) State the main sources of iron.

(ii) Using appropriate equations, state two reasons why coke is used in the manufacture of iron.

(iii) State two other chemicals required in a blast furnace. One of the chemicals added leads to the formation of iron, the other to slag. Write relevant equations for the formation of iron and slag and suggest three possible uses for slag.

(iv) With the help of two equations, outline how addition of methane to the pre-heated air in a blast furnace forms the reducing agent that also forms iron.

(v) State and explain one serious environmental problem associated with the production of iron.

2. (a) (i) State the main aluminum ore.

(ii) Write the formula of cryolite and explain why it is used in the manufacture of aluminum.

(iii) State the main impurities in the aluminium ore and describe how the impurities are removed.

(iv) Write equations for half reaction at the positive anode and negative cathode, and the over all reaction during the manufacture of aluminium.

(b) Explain the effect of the product on the positive anode and how the effect is addressed.

3 (a) (i) State the name given to the molten iron formed in a blast furnace.

(ii) Name the two major impurities in the molten iron.

(b) Describe and explain the conversion of iron into steel using the basic oxygen converter.

(c) (i) State the meaning of the term *alloy* and describe how an alloy may be made.

(ii) Explain how alloying can modify the structure of a metal and state properties it can affect.

(iii) Steel obtained from the basic oxygen converter may not have the desired properties and often requires further heat treatments. Describe the three common heat treatment processes used in the making of steel.

(iv) Describe the main properties and uses of aluminum and its alloys.

(d) (i) Discuss the environmental impact of iron and aluminum production.

(ii) Suggest two reasons why it is advisable to recycle aluminium.

C2 The oil industry

4. (a) (i) Compare the use of oil as an energy source and as a chemical feedstock and suggest why it is better to search for new energy sources.

(ii) Define the term *cracking* as it is applied to the oil industry.

(iii) Cracking can be achieved under different conditions of temperature, pressure the presence or absence of a catalyst, and steam. State and compare the conditions used in catalytic cracking, thermal cracking and steam cracking, giving appropriate equations. State the use of products from each of the cracking processes listed above.

C3 Addition polymers

5. (a) (i) Define the term *polymer*.

(ii) At the molecular level, describe what happens in addition polymerization and give the name and formula of a organic compound other than ethene that undergoes addition polymerization.

(b)   Describe and explain how the physical properties of an addition polymer depend on the structural features listed below and state the type of polymer that arises as a result:

(i)   branching, and

(ii)   orientation (or position) of the alkyl groups along a polymer backbone chain:

(iii)   State conditions under which low-density and high-density polyethylene is formed.

(c)   Discuss the advantages and disadvantages of polymer use.

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C4 Catalysts

</div>

6. (a) (i) Define the term *catalyst*, explain its effect on the rate of the forward and reverse reactions and on the activation energy, change in enthalpy and position of equilibrium of the reaction.

(ii)   Outline the advantages and disadvantages of industrial catalysts.

(b)   Compare the modes of action of homogeneous and heterogeneous catalysts and give an example of a chemical reaction for each.

(c)   Outline the advantages and disadvantages of homogeneous and heterogeneous catalysts.

7. (a) Describe how enzymes have some characteristics of both homogeneous and heterogeneous catalysts. Describe how enzymes are unique and how they differ from inorganic catalysts.

(b)   Describe the modes of action of homogeneous and heterogeneous catalysts in terms of:

(i)   ability to form a range of oxidation states by transition metal compounds.

(ii)   the shape of the catalyst, and

(iii)   availability of active sites.

8.   Outline factors involved in selecting a catalyst and give an example of each.

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C5 Fuel cells and rechargeable batteries

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9. (a) Define the term *fuel cell* and explain why fuel cells are more efficient than the ways in which electricity is normally produced.

(b)   State the electrodes and the electrolyte in a hydrogen–oxygen fuel cell and describe how it works in (i) an acidic and (ii) a basic condition. Write balanced equations to show the chemical reactions taking place at the electrodes in each case.

(c)   List the advantages and disadvantages of fuel cells.

10. (a) Write balanced equations for the reaction at each electrode taking place in the following batteries:

(i)   lead-acid

(ii)   NiCad, and

(iii)   Lithium ion.

(b)   Discuss two similarities and two differences between fuel cells and rechargeable batteries.

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C6 Liquid crystals

</div>

11. (a) Describe the meaning of the term liquid crystals.

(b)   Distinguish between thermotropic and lyotropic liquid crystals.

(c)   Use an example to describe the liquid-crystal state in terms of the arrangement of the molecules and explain thermotropic behaviour and explain the terms smectic and nematic LCs.

12.   (a) Outline the principles of the liquid-crystal display device.

(b)   Discuss the properties needed for a substance to be used in liquid-crystal displays.

OPTION

C7 Nanotechnology

13. (a) Define the term nanotechnology.

(b) Distinguish between physical and chemical techniques in manipulating atoms to form molecules.

(c) Describe the structure and properties of carbon nanotubes.

(d) Discuss some of the implications of nanotechnology including possible and potential uses. Include examples of new multidisciplinary fields, potential health and environmental effects, toxicity concerns and potential ethical and political issues.

[HL] C8 Condensation polymers

14. (a) Distinguish between addition and condensation polymers in terms of their structures.

(b) Describe and explain how the properties of polymers depend on their structural features.

(c) Describe ways of modifying the properties of polymers.

(d) Discuss the advantages and disadvantages of condensation polymer use.

[HL] C9 Mechanisms in the organic chemicals industry

15. (i) State the conditions used in the manufacture of low density polyethene.

(ii) State the three steps common to free-radical mechanisms and describe this mechanism in terms of the movement of electrons involved in the manufacture of low-density polyethene.

(iii) State the conditions used in the manufacture of high density polyethene.

(iv) Outline the use of Ziegler–Natta catalysts in the manufacture of high-density polyethene.

[HL] C10 Silicon and photovoltaic cells

16. (a) List the number of valence electrons in silicon and suggest why it is a semiconductor.

(b) Describe the doping of silicon to produce p-type and n-type semiconductors.

(c) Describe how sunlight interacts with semiconductors.

[HL] C11 Liquid crystals

17. (a) Identify molecules that are likely to show liquid-crystal properties, and explain their liquid-crystal behaviour on a molecular level.

(b) Describe and explain in molecular terms the workings of a twisted nematic liquid crystal.

(c) Describe the liquid-crystal properties of Kevlar, and explain its strength and its solubility in concentrated sulfuric acid.

OPTION

[HL] C12 The chlor-alkali industry

18. Discuss the production of chlorine by the electrolysis of sodium chloride, write the appropriate half equations and the equation for the overall reaction and explain why it is important to keep the products apart.

19. Describe the mercury cell process for the manufacture of chlorine, write equations for reactions at the electrodes and the overall reaction and outline the advantage and disadvantage of this method.

20. Describe the diaphragm cell process for the manufacture of chlorine, write equations for reactions at the electrodes and the overall reaction and outline the advantage and disadvantage of this method.

21. Outline some important uses of the products of the electrolysis of sodium chloride process.