

Analytical Essays, Mini Essays and Others

Chapter
15

Chapter

Note: Questions in this section will no longer be in the form set in previous TEE papers, which was an essay spanning several pages. The WACE examinations will encompass the same kinds of topics, but questions will be in smaller parts

1. [20 marks] (2009.01)

In Kwinana, Western Australia, the Alcoa company uses waste carbon dioxide from another industrial company to neutralise alkaline waste from the Bayer process.

Bayer Process

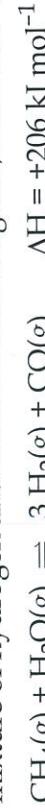
Bauxite, an ore of aluminium, contains mainly gibbsite ($\text{Al}(\text{OH})_3$) and impurities such as Fe_2O_3 and SiO_2 . The bauxite is treated with hot sodium hydroxide solution to separate the gibbsite from the impurities. After removal of the gibbsite, the waste is pumped into residue beds in the form of a 'red mud'. This red mud is highly alkaline because of the excess sodium hydroxide.

Treatment of Red Mud

Waste CO_2 from hydrogen production (see below) is used by Alcoa to neutralise the excess sodium hydroxide in the red mud that is pumped to its residue beds. The CO_2 passed into the red mud produces sodium carbonate and sodium hydrogencarbonate. This assists the rehabilitation of the land recovered from the red mud by lowering the pH from approximately 11 to 8.5.

Waste CO_2 from Hydrogen Production for the Haber Process

The hydrogen gas used for the Haber process is produced from two reactions. The first is the reaction of methane with water at temperatures from 700 to 1000°C to produce a mixture of hydrogen and carbon monoxide gases, known as 'syngas':



The syngas from this reaction is separated through a membrane which preferentially allows the hydrogen gas to pass through it, leaving a syngas mixture with a reduced ratio of hydrogen to carbon monoxide. This syngas, with the lower hydrogen concentration, is then pumped to a chamber where the carbon monoxide and steam at approximately 130°C react with the aid of a catalyst as shown in the following reaction:



The gaseous products are passed through a membrane filter to give a stream of gas with mainly hydrogen and a second stream of waste gases where the carbon dioxide can be collected in concentrations of up to 95%.

From the information provided and your understanding of chemical principles:

For the Bayer process, explain, with the support of equations, how the sodium hydroxide solution is able to separate the gibbsite from impurities. Explain, in detail, what can be done to increase the efficiency of the reaction involving the sodium hydroxide and therefore minimise the amount of excess sodium hydroxide.

Describe, with the support of equations, the reactions occurring between the carbon dioxide and excess sodium hydroxide in the red mud. Explain how the efficiency of this process can be maximised and explain, using equations, why the pH of the red mud will not be lowered below 8.5 by this method.

For the hydrogen production process, discuss the conditions needed for maximising hydrogen production. An aspect your answer needs to address is the importance of passing the syngas through a separation membrane before the second reaction.

2. [10 marks]

(2010:42)

Nitric acid is manufactured by the Ostwald process.

In the first step, ammonia gas reacts with oxygen gas to produce nitric oxide in the presence of a catalyst such as platinum with 10% rhodium. This reaction is carried out at a temperature of approximately 900°C and at a pressure of approximately 10 atmospheres.



The nitric oxide is next oxidised at approximately 50°C.



The nitrogen dioxide then enters an absorption tower, where water is added through a sprinkler system in the presence of air to give nitric acid.



Use your understanding of reaction rates and chemical equilibrium to explain the conditions used in the Ostwald process. Your answer should include at least three (3) paragraphs, and should be 1 to 1½ pages in length.

3. [10 marks]

(2011:41)

Soaps and detergents are common organic substances. Discuss the chemistry of these two classes of organic substances, including their structure, manufacture and how they act as cleaning agents.

Your answer should

- include relevant chemical content. [8]
- display coherence and clarity of expression. [2]

A comprehensive answer should consist of at least three (3) paragraphs and be at least one page in length.

4. [12 marks]

Using examples, describe 'condensation' and 'addition polymerisation'.

Your answer should include:

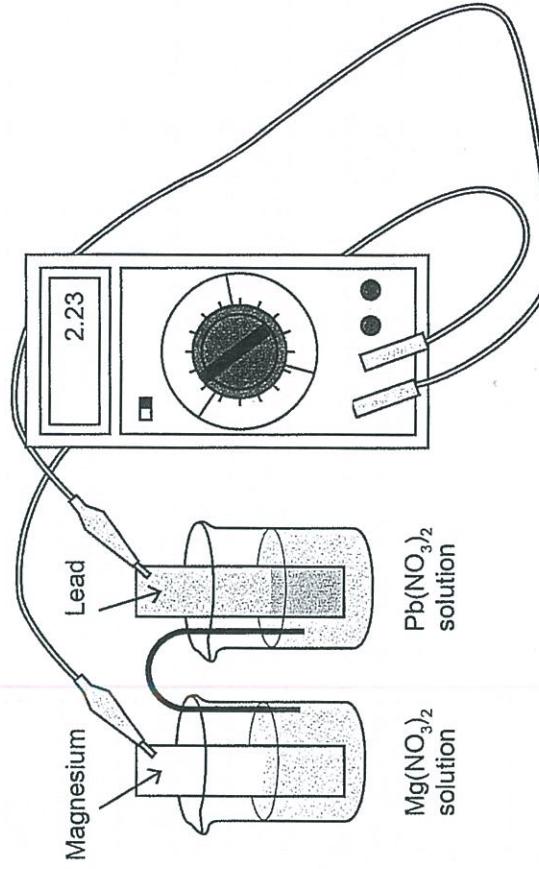
- an explanation of the term 'polymer'
 - the structure and name of each polymer type
 - structures of starting materials for the production of each example of a polymer type
 - polymerisation reactions

5. [8 marks]

(2014:42)

Using the diagram below, explain the role of the following in the operation of an electrochemical (galvanic) cell:

- anode process
- cathode process
- lead(II) nitrate electrolyte
- salt bridge
- electron flow in external circuit.



6. [10 marks]

You are supplied with strips of three unknown metals, **A**, **B** and **C**, and are required to determine the order in which they are reduced, from most easily to least easily.

Using a voltmeter, electrical leads and clips, standard laboratory glassware and the typical range of chemicals found in most laboratories, design an investigation and describe the procedures to be followed to determine the order of reduction for the metals. Use a labelled diagram to support your description. Ensure that you explain the purposes of substances or equipment (excluding beakers or other glassware) used.

Indicate the data you will collect and explain how these data give the order of reduction.

3.3 (2016 SP:41)

7. [16 marks]

3.3 (2016 SP:42)

Use the following information about bleaching to answer the questions that follow.

Many chlorine-based compounds, such as sodium hypochlorite (NaOCl), chlorine (Cl_2) and chlorine dioxide (ClO_2), are used as bleaches in household cleaning products and for industrial processes.

Their uses include:

- removing colour (for example, stain removal from clothes)
- whitening paper pulp in the process of making paper
- sterilising substances (for example, swimming pool water).

These compounds act by oxidising the compounds with which they come into contact. When chlorine gas is used for bleaching, the active ingredient is hypochlorous acid (HOCl). This is produced by reaction of the chlorine gas with water. Hydrochloric acid is also produced in the reaction.

To increase the amount of hypochlorous acid produced in this reaction, the water through which the chlorine is bubbled is usually made alkaline by the addition of a small amount of hydroxide ions. Chlorine-based bleaches react well at room temperatures.

A disadvantage of chlorine bleaches is the potential for highly poisonous dioxins to be produced by reaction with organic compounds. Peroxide bleaches are environmentally more acceptable because they produce only oxygen and water.

Hydrogen peroxide is a liquid, but sodium percarbonate ($2 \text{Na}_2\text{CO}_3 \cdot 3 \text{H}_2\text{O}_2$) and sodium perborate ($\text{NaBO}_3 \cdot \text{H}_2\text{O}$) are solid peroxide bleaches that release hydrogen peroxide when dissolved in water. A disadvantage of peroxide bleaches is the need for high temperatures for them to react.

The development of molecules known as tetra-amido macrocyclic ligand-activators (TAMLs) that function as catalysts has enabled the hydrogen peroxide bleaching reaction to occur at much lower temperatures.

(a) Write the balanced equation for the reaction of chlorine gas with water. [1]

(b) Explain briefly how the addition of hydroxide ions to the water through which the chlorine is bubbled will increase the amount of hypochlorous acid produced. [3]

- (c) Give the oxidation state of chlorine in hypochlorous acid and the oxidation state of chlorine in hydrochloric acid. [2]

Oxidation state of Cl in hypochlorous acid	Oxidation state of Cl in hydrochloric acid

- (d) Identify the species oxidised and the species reduced when chlorine gas reacts with water. [2]

Species oxidised	Species reduced

- (e) Write the half-equation for the reduction of hypochlorous acid to chloride ion. [1]

- (f) For every one mole of formula units of sodium percarbonate, how many mole of hydrogen peroxide are released when it is dissolved in water? [1]

- (g) Compare the activation energy for oxidation reactions involving chlorine-based bleaches to those using peroxide-based bleaches (in the absence of catalysts). Explain the reasons for your answer. [2]

- (h) Draw a fully labelled energy profile diagram showing the progress of the decomposition of hydrogen peroxide with and without TAML molecules. [4]

The equation for the reaction is $2 \text{H}_2\text{O}_2 \rightarrow 2 \text{H}_2\text{O} + \text{O}_2 + \text{energy}$.

g) Determining the concentration of nitrogen in g L⁻¹ in the phosphorus depleted urine.

$$n((\text{NH}_4)_2\text{SO}_4) = (\text{m} \div M) = (72.65 \div 132.144) = 0.5498 \text{ mol}$$

$$\text{m}(\text{N}) = n((\text{NH}_4)_2\text{SO}_4) \times 2 = 0.5498 \times 2 = 1.0996 \text{ mol}$$

m (N) obtained at 78% efficiency = $1.096 \times 14.01 = 15.405 \text{ g}$

Therefore, m (N) at 100% efficiency = $(15.405 \div 78) \times 100 = 19.75 \text{ g}$

Concentration in mol L⁻¹ = $(\text{m} \div v) = (19.75 \text{ g} \div 5.00 \text{ L}) = 3.95 \text{ g L}^{-1}$.

15.(2016 SP:40) a) lipase

$$\text{b) } n(\text{veg oil}) = 1.50 \times 10^6 / 855.334 = 1.754 \times 10^3 \text{ mol}$$

$$n(\text{CH}_3\text{OH}) = 3 \times n(\text{veg oil}) = 5.261 \times 10^3 \text{ mol}$$

$$m(\text{CH}_3\text{OH}) = 5.261 \times 10^3 \times 32.042 = 1.69 \times 10^5 \text{ g}$$

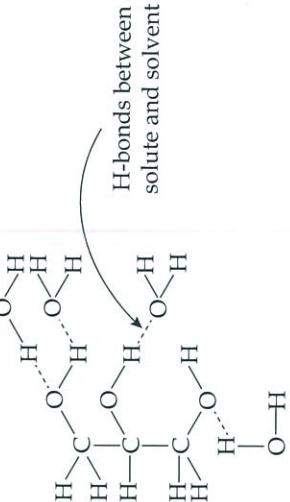
$$\text{c) for 100% efficient: } n(A) = n(\text{veg oil}) = 1.754 \times 10^3 \text{ mol}$$

78% efficient, thus $n(A) = 0.78 \times 1.754 \times 10^3 = 1.368 \times 10^3 \text{ mol}$

MF Ester A is C₁₇H₃₄O₂ thus M(A) = 270.442 g mol⁻¹

$$m(A) = 1.368 \times 10^3 \times 270.442 = 3.70 \times 10^5 \text{ g}$$

d) Possible diagram



- e) i) soap/sodium salt of long chain fatty acid
ii) sodium salt for long chain fatty acid component of either A, B or C

Chapter 15: Analytical Essays, Mini Essays and Others

1.(2009:01) This extended answer question requires you to analyse the set of chemical reactions in the metallurgical processes of gibbsite and associated processes from the point of view of equilibrium and rates of chemical reactions. You are asked to provide the analytical discussion in three areas, viz. the Bayer Process, the treatment of red mud and the production of hydrogen, as outlined in the question.

Bayer Process: Al(OH)₃ is amphoteric in nature and as such dissolves in sodium hydroxide, whereas the impurities such as Fe₂O₃ and SiO₂ do not.



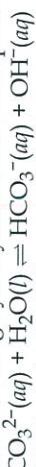
These impurities are separated from the solution by filtering. The process is speeded up by pulverising the ore mixture (which increases the surface area for reaction), increasing the reaction temperature (which provides more energy for the colliding molecules) as well as by increasing the concentration of the sodium hydroxide used (which increases the number of molecules in a given volume thus increasing the chances of effective collisions). An increase in the concentration of NaOH will inevitably lead to an increase in the pH of the red mud produced. On the other hand, the presence of excessive bauxite would leave a large amount of untreated bauxite. These problems can be kept under control by mixing molar equivalent quantities of gibbsite with NaOH. Pure alumina (Al₂O₃) is obtained by the process of seeding and subsequent filtration and evaporation.

Treatment of the red mud: Red mud is the leftover residue after gibbsite is removed. This mixture is first cooled, then the CO₂ is bubbled through the cool mixture, which increases its solubility. With an increased partial pressure (to increase concentration) and agitation (which makes more collisions possible), CO₂ reacts with NaOH to produce Na₂CO₃ which continues to react with CO₂ to produce NaHCO₃ as shown below:



The presence of NaHCO₃ renders the red mud slightly less basic, keeping the pH below 8.5.

The following hydrolysis reactions take place when the basic anions CO₃²⁻ and HCO₃⁻ react with water:



Production of Hydrogen: Hydrogen gas is used for the Haber process and is produced by two reactions: firstly, when methane gas reacts with water and, secondly, when CO gas reacts with water. The two reactions are:
 CH₄(g) + H₂O(g) ⇌ 3 H₂(g) + CO(g) H = +206 kJ mol⁻¹ (1)
 CO(g) + H₂O(g) ⇌ H₂(g) + CO₂(g) H = -42 kJ mol⁻¹ (2)
 The first reaction is endothermic and an increase in temperature will increase both the rate and the yield. The use of an appropriate catalyst would bring the reaction to equilibrium sooner. Periodical injection of methane and

removal of hydrogen gas from the system would continue to produce the products at a steady rate, reducing the rate of the reverse reaction.

The second reaction is exothermic and an increase in temperature would reduce the yield. However, to provide the required activation energy and keep the reaction going at a desirable rate, a compromise would be necessary and an optimum temperature would be needed. All the other changes for reaction 1 are applicable for reaction 2. In both these reactions, though the yield is unaffected, the use of a suitable catalyst would increase the rate of the reaction and also reduce the time factor.

Removing the hydrogen gas produced through the membrane filter would keep the reaction going forward and minimise the extent of the reverse reaction. The by-product, carbon dioxide, produced at a high concentration, is used to neutralise the alkaline waste from the Bayer process.

2.(2010:42) This is a mini-essay question which requires you to analyse the Ostwald process of producing nitric acid from the point of view of rates of reactions and chemical equilibrium principles. There are three steps in this process.

Step 1 occurs at 900°C and at 10 atmospheric pressure:



Step 2 occurs at 50°C: $2 \text{NO}(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}_2(\text{g}) + \text{heat.}$

Step 3 is a dissolving//reacting process which produces the acid:



Step 1 is an exothermic reaction. According to the Le Châtelier's principle, an increase in temperature (viz., 900°C) will favour the formation of reactants. However, the rate of both the forward and the reverse reaction will increase. The advantage of an increase in temperature is the increase in the rate of effective collisions with adequate energy to form both reactants and the products in equal amounts. An increase in pressure (viz., 10 atmosphere) will also increase the reaction rate and, the application of pressure brings the molecules closer and increase the rate of collisions as well as the rate of both forward and the reverse reactions. However, the reactant side of the equation has less gaseous moles and hence the equilibrium will shift to the reactant side and decrease the yield of the products. The catalyst (viz., platinum with rhodium) lowers the activation energy barrier by providing an alternate pathway by removing the relatively higher rate determining step of the uncatalysed reaction. The overall effect is a sustained, but slow yield of the product.

Step 2 is also an exothermic reaction. The temperature used (50°C) is a low enough temperature to shift the equilibrium forward and increase the yield. The downside is the decrease in rate of the yield. This step is the slowest of the three steps in the Ostwald process. The yield from this process will increase under high pressure as the molecules come closer and increase the rate of effective collisions.

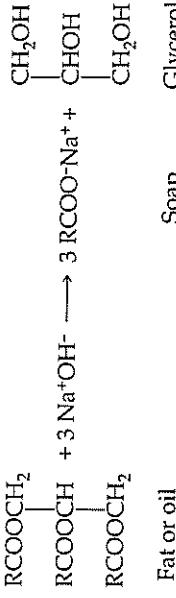
Step 3 involves the dissolving of NO_2 in water. And its reaction with the oxygen in the air. The use of sprinklers in this step, which sprays water on to the gas, is to increase the surface area of the particles that come into contact which increases the rate of effective collisions. Oxygen is also added through air at this stage. The 20% content of oxygen in air will reduce the rate and the yield as the concentration of the reactant (oxygen) is less than if it had been available pure. The NO_2 gas with the air-mixture introduced at the bottom of the tower rises to react with the sprinkler water coming from the top. This produces nitric acid. (In the industrial process, however, all the NO_2 does not get converted to HNO_3 . Some NO in the reaction mixture is left over and this is separated and sent back to the bottom of the tower again for its complete oxidation to nitric acid.)

The Ostwald process is a good example of an industrial chemical process where a simplistic application of the Le Châtelier's principle cannot predict the actual conditions for the maximum yield of nitric acid. Some conditions need to be compromised in order to obtain the optimum yield at the best conditions that favour this.

3.(2011:41) The Chemistry of Soaps and Detergents

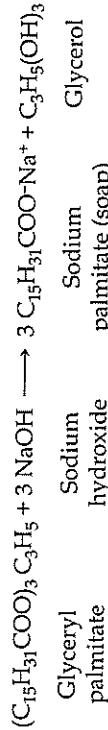
This is a straight forward question which requires you to discuss the manufacture, cleaning process and the effectiveness of detergents compared with soaps.

Soaps are substances prepared by the hydrolysis of animal fat and hardened oils with sodium hydroxide or potassium hydroxide. The hydrolysis of fats and oils (and esters) by alkalis is known as saponification. The general structural equation of a saponification reaction is:



General equation of a saponification reaction

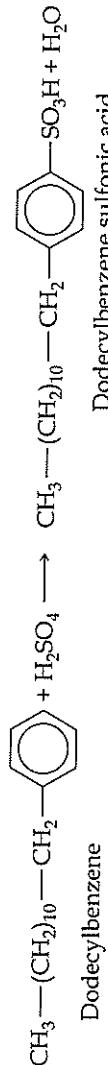
As an example, the hydrolysis of palm oil (glycerol palmitate) with sodium hydroxide is shown below:



The hydrolysis of glyceryl palmitate

The oil is mixed with sodium hydroxide solution and is heated with steam. Sodium chloride is added to salt out the soap. The soap is washed and mixed with substances like perfume and anti-septic chemicals. Distillation of the aqueous solution produces glycerol.

Sodium dodecylbenzene sulfonate is an example of a common detergent. It is first prepared from the polymerisation of propene. It is then reacted with benzene to form dodecylbenzene. Reaction with concentrated sulfuric acid produces dodecyl[benzyl] sulfonic acid.

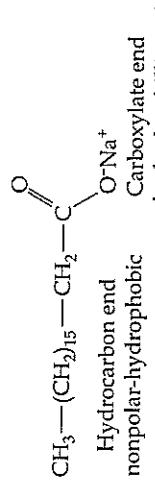


The production of dodecylbenzyl sulfonic acid

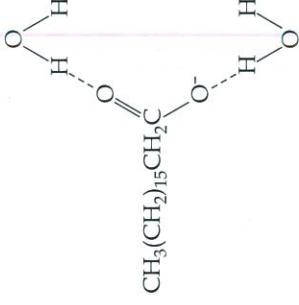
This is neutralised with sodium carbonate or sodium hydroxide to produce the detergent, dioctylbenzyl sulfonate.

Cleaning action of soaps and detergents:

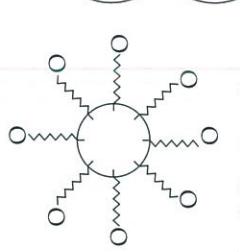
A soap molecule or a detergent molecule is made up of two components, a hydrocarbon component and a carboxylate component in the case of soap and, a hydrocarbon component and a sulfonate component, in the case of detergent. The hydrocarbon component is the hydrophobic or water repelling end and the other component is the hydrophilic component or water attracting component. The following diagrams show the formation of hydrogen bond between water molecules and at the carboxylate ion by showing



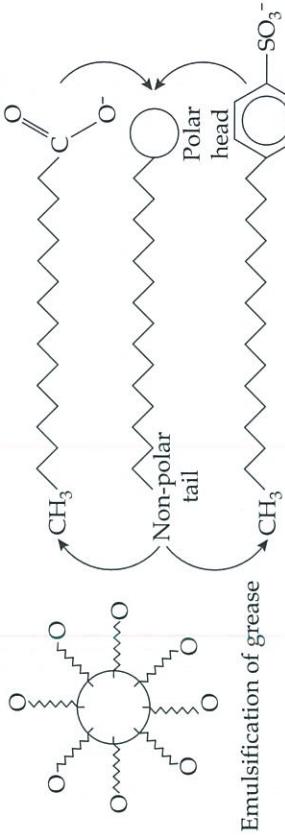
When a soap or detergent is added to water which has a fabric with an oil stain, the hydrophobic ends attaches itself to the oil molecule with strong dispersion forces and the hydrophilic end attaches itself to water with strong dipole-dipole forces. Agitation of water detaches oil from the fabric surface and the emulsification of oil increase as shown by the following chart.



Carboxylic end bonding with H₂O



Sulfonate end bonding with H₂O



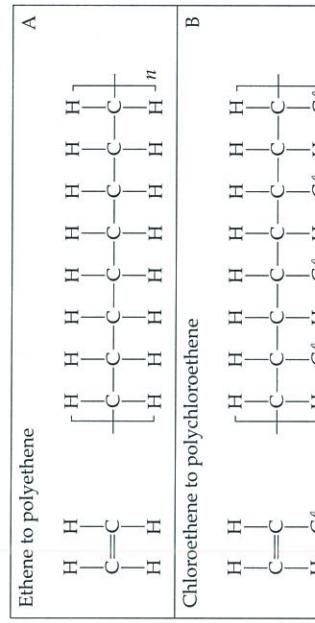
A detergent has an advantage over soap when it comes to hard water which contains dissolved Ca²⁺ and Mg²⁺ ions in the form of hydrogen carbonate, chlorides or sulfate salts. These salts produce a sticky solid with soap which is generally called scum. This reaction not only uses up soap, but also leaves scales in containers where this water is used, such as boilers and kettles. The sulfonate part of the detergent does not react with the calcium or magnesium ions in hard water. Due to this property of detergents, the problem of hard water no longer occurs when a detergent is used.

4.(2013:42) This is a mini-essay question. You are asked to explain what a polymer is and the different types of polymerisation reactions with examples.

Polymers are very large molecules made up of small repeating units called monomers. Natural substances such as rubber, silk, cotton and synthetic substances such as PVC, teflon, rayon etc. are all polymers. The ability of monomers to combine to form a long chain compound is called polymerisation. The long chain molecule is called a polymer or macromolecule.

Polymerisation reactions are of two kinds: addition polymerisation and condensation polymerisation.

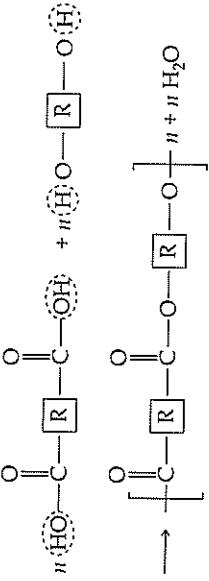
Addition polymerisation: Certain small organic molecules containing carbon-carbon double bond can undergo addition polymerisation. In this type of reaction one of the bonds in the C=C double bond is broken and resulting parts join up to form a long chain. Breaking up the double bond gives each carbon with additional bonding capacity which is used to form bonds between carbon atoms to form long, continuous chain. The number of monomer units can vary from 100 to 10,000 and more. This type of reaction requires an initiator to start the reaction. Two examples are shown below:



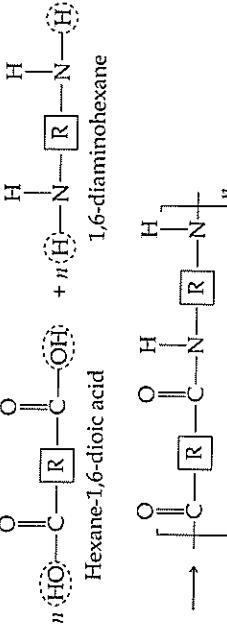
In addition to polymerisation, the polymer has the same empirical formula as the monomer. These kinds of polymers are also called plastics and are very durable. They are easily shaped and moulded and are inexpensive. They do not corrode, rust or decay. They are lighter. But, many are non-biodegradable and produce poisonous fumes when they burn.

Condensation polymerisation: This kind of polymerisation involves a reaction between two different monomers in which a molecule of water is condensed out and the two molecules link together. It can also occur between the same kind of molecule which contain two different functional groups at either ends. The two most common type of condensation polymerisation occurs between a carboxylic group and an alcohol or an amine group. Three examples are provided below:

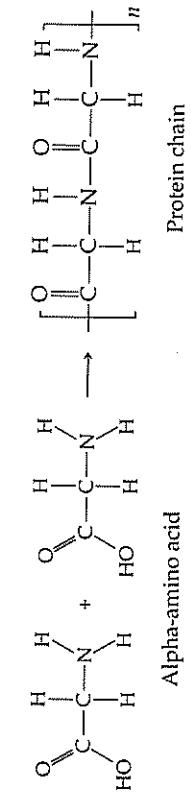
A dicarboxylic acid and a diol



A dicarboxylic acid and a diamine

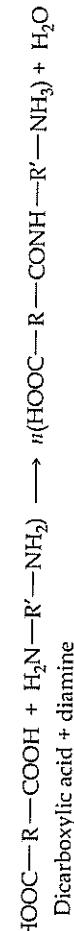


Between amino acid molecules



Polyamides, commonly known as nylons are condensation polymers formed by dicarboxylic acids and diamines. These are extensively used in hosiery, clothing, fibres, ropes and bearings. There are different types of nylons used for different purposes. The general reaction for the formation of a polyamide is given below:

A general reaction for the formation of polyamides



卷之三

Polyurethane Foams 111

question which requires an explanation of the

Anode process: Since Mg has the lower reduction potential of the two, it oxidises in preference to the lead electrode and supplies electrons. Mg^{2+} ions have a lesser tendency to gain electrons than Pb^{2+} ions. Therefore, the reaction for $Mg-Cu$ cell is:

$$Mg(s) + Pb^{2+}(aq) \rightarrow Mg^{2+}(aq) + Pb(s)$$

cathode which is lead. As a result, the mass of the anode decreases.

Cathode process: Pb has the higher reduction potential of the two and stays in the reduced metallic form. However, the Pb^{2+} ions in the electrolyte ($\text{Pb}(\text{NO}_3)_2$), are reduced at the cathode forming Pb atoms which adhere to the Pb cathode. As a result, the mass of the Pb cathode increases.

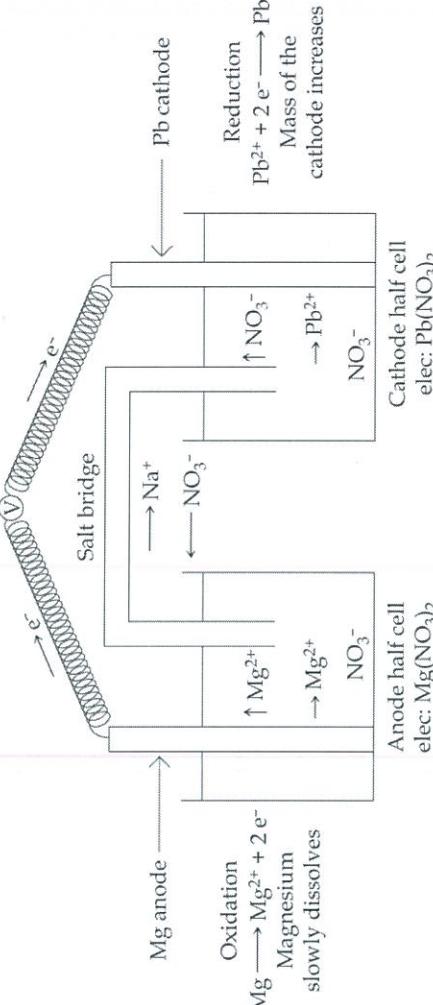
Their ions. Electrolytes are electrically neutral, but contains ions which are free to move. There are two electrolytes in the $Mg/Mg^{2+} / Pb/Pb^{2+}$ cell. $Pb(NO_3)_2$ supplies the Pb^{2+} ions for current flow and $Mg(NO_3)_2$ supplies the Mg^{2+} ions for migration and current flow. The electrolytes allow the passage of ions through them. The concentration of the electrolyte is an important factor in determining the cell potential. Temperature is another important variable. Electrical neutrality is maintained by the migration of cations (Pb^{2+}) and anions (NO_3^-) from one solution or molten form to another through the electrodes.

The salt bridge: A salt-bridge has a general design consisting of a 'U-tube' that contains an electrolyte solution such as NaNO_3 . The ends of the U-tube are plugged with porous ceramic neutrals that are maintained by the migration of cation (Fe^{2+}) towards the lead half cell and anions (Mg^{2-}) away from the Mg half cell.

out. Electrical neutrality is maintained by the migration of ions through the bridge. The solution used in the salt bridge should be such that it does not react with any of the other ions in the cell. The salt bridge also serves to complete the circuit.

Electron flow in the external circuit: In an electrochemical cell, electrons released at the anode travel through the external circuit to the cathode half cell due to the potential difference that exists between the two electrodes.

Cell emf: At 1.00 mol L⁻¹ concentration of the electrolytes and at 25°C, the cell will yield an emf of 2.23 V.



6.(2016 SP:41)

- 3 Galvanic cells with A and B as electrodes, then A and C as electrodes and B and C as electrodes need to be constructed
- cells will need an electrolyte (eg. NaCl) dissolved in water or 0.1 mol L⁻¹ HCl
- role of ions as electrolyte to complete the circuit
- voltmeter needs to be connected in the external circuit to measure potential difference between electrodes
- E(A/B), E(A/C) and E(B/C) is the data that needs to be collected
- direction of current flow can be used to identify the anode and cathode in each of the cell couples and the magnitude of voltage can be used to order the 3 metals from most easily to least easily reduced
- labelled diagram to show typical Galvanic cell (electrodes, voltmeter, salt bridge if 2 beakers used)
- variables to control. any 2 variables e.g. temp, conc. of electrolyte soln, surface area of electrodes in contact with electrolyte

7.(2016 SP:42) a) $\text{Cl}_2 + \text{H}_2\text{O} \rightarrow \text{HOCl} + \text{HCl}$

- b)
- recognition that the hydroxide will react with the H^+
 - recognition that removal of H^+ will prevent reverse reaction from occurring
 - recognition that the forward reaction will thus continue until close to completion thus increasing yield of HOCl

c)

Oxidation state of Cl in hypochlorous acid +1

Oxidation state of Cl in hydrochloric acid -1

d) Identify the species oxidised and the species reduced when chlorine gas reacts with water.

Species oxidised Cl_2

Species reduced Cl_2

e) $\text{HOCl} + \text{H}^+ + 2\text{e}^- \rightarrow \text{Cl}^- + \text{H}_2\text{O}$

f) 3 moles

- g) activation energy for oxidation of peroxides is higher than E_a of chlorine based bleaches the oxidation of peroxide based bleaches requires higher temperatures than for oxidation of chlorine based bleaches

