

Ocean Acidification

Explain how an increase in atmospheric carbon dioxide levels can cause a change in the pH of our oceans.

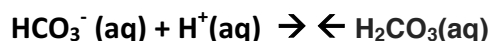
Some atmospheric carbon dioxide dissolves in ocean water to produce the weak carbonic acid. The carbonic acid then ionises to produce H_3O^+ . Since $\text{pH} = -\log(\text{H}_3\text{O}^+)$, the presence of additional H_3O^+ in our oceans lowers the pH and causes acidification.

- How might industrial waste affect the pH of a river or lake?

The presence of a high concentration of H^+ or OH^- in the wastewater will affect the H^+ ion concentration of the lake. This will affect the lake or river water pH as $\text{pH} = -\log \text{H}^+$.

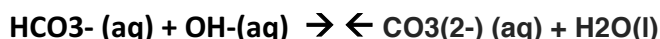
Explain how the presence of these dissolved minerals (dissolved salts like sodium or potassium hydrogen-carbonate) helps to keep the pH of these environments fairly constant.

The presence of hydrogen-carbonate ions, HCO_3^- in these lakes and rivers is able to cause a buffering effect. If some strong acid solution enters the lake or river then the presence of the weak base HCO_3^- , reacts with it as shown:



Neutralising the introduced waste acid this way helps to keep the lake water pH fairly constant.

If any basic waste solution enters the lake or river then the hydrogen-carbonate ions act as a weak acid and reacts:



This has the effect of neutralising the base present in the industrial waste water added to the lake. Consequently, the pH remains fairly constant.

- Explain how an increase in the level of atmospheric carbon dioxide can cause ocean acidification. Use relevant chemical equations to support your answer.

Atmospheric $\text{CO}_2(\text{g})$ dissolves in the ocean where it forms carbonic acid. This weak acid partially ionises to produce H^+ ions thus raising the H^+ ion concentration which in turn lower pH. As the atmospheric $\text{CO}_2(\text{g})$ concentration increases so does the degree of ocean acidification.

$\text{CO}_2 (\text{g, atmosphere}) \rightarrow \leftarrow \text{CO}_2 (\text{aq, ocean})$ atmospheric carbon dioxide dissolves in ocean water

$\text{CO}_2 (\text{aq, ocean}) + \text{H}_2\text{O} (\text{l}) \rightarrow \leftarrow \text{H}_2\text{CO}_3(\text{aq})$ Formation of carbonic acid

$\text{H}_2\text{CO}_3 (\text{aq}) \rightarrow \leftarrow \text{H}^+(\text{aq}) + \text{HCO}_3^- (\text{aq})$ Ionisation of carbonic acid to produce H^+

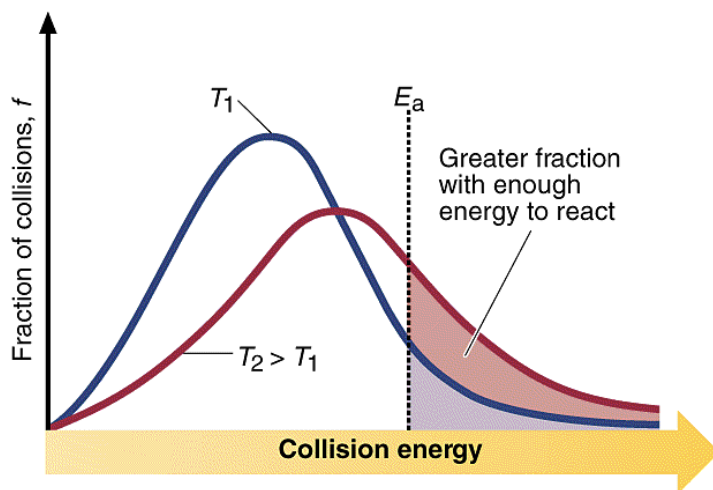
- Explain how ocean acidification could lead to a decrease in the rate of calcification in aquatic organisms. State two consequences of this decreased calcification rate.



The increasing H^+ concentration; as occurs in ocean acidification, would shift the $\text{HCO}_3^-/\text{CO}_3^{2-}$ equilibrium to the left (reverse reaction is favoured). This results in decreased sea water concentration of CO_3^{2-} . Calcifying species absorb CO_3^{2-} ions in the production of their skeletal material. As its concentration is reduced they are less able to do so. This can impact their survival and reduce their population. This would result in weakening or damaging of coral reefs, which provide shelter for our coastlines, as well as impacting the populations of other dependent marine life.

Collision Theory, Reaction Rates, Equilibrium, Le Chatelier's Principle

- Use the temperature distribution graph to explain the effect of raising temperature on reaction rate. Your answer should also make reference to the collision theory as a basis for explaining the effect of temperature on the rate of this reaction.



For this reaction to occur the reacting particles must collide with sufficient energy (activation energy). At the higher temperature (T_2), a higher percentage of the colliding molecules have a kinetic energy greater than the E_a . This is indicated by the pink shaded area which is larger than the purple. Thus a greater percentage of the collisions are successful at the higher temperature of T_2 than at T_1 and hence the reaction rate increases at the higher temperature.

- Effect of increase in temperature.**

Temperature increase, endothermic reaction favoured, (forward/reverse)

If forward reaction is favoured, concentration of products increases, thus K_a value increases

Acid-base Theories

- Briefly state the main developments different scientist made in the field of acid-base theory.

DAVY- It was previously thought that acids must contain oxygen and therefor “oxides” were all acidic. Davy demonstrated HCl was composed of hydrogen and chlorine, thus proposed that acids must contain hydrogen.

- Difference between Bronsted-Lowry and Arrhenius theory. What are the limitations of the Arrhenius theory?

According to the Arrhenius theory, an acid is a substance that ionises in water to produce H⁺ ions, while a base dissociates in water to produce OH⁻ ions.

The Arrhenius theory does not account for the basic nature of carbonates, oxides and salts (Na₃PO₄, KCH₃COO) that do not contain OH⁻.

Bronsted-Lowry

Acid is a substance that donates a proton

Base is a substance that accepts a proton

- Explain the definition of an acid and a base as proposed by Arrhenius and why it is that these two substances are able to neutralise each other.

According to Arrhenius, acids are substances that contain H in their formula and produce H⁺ ions in solution. Bases are substances that have OH in their formula and produce OH⁻ ions in solution. They are able to neutralise each other because $H^+ + OH^- \rightarrow H_2O$.

- What is a “weak, diprotic acid”?

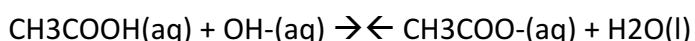
“Weak” indicates ionisation does not go to completion. “Diprotic” indicates each molecule contains 2 acidic hydrogen atoms.

Buffers

- Explain how a buffer system works.

Buffers are solutions that resist changes in hydrogen ion or hydroxide ion concentration. They are able to do this as they consist of a solution of a weak acid and its conjugate weak base. If excess acid is added to a buffer solution, then most of the acid is neutralised as it reacts with the weak base present in the buffer. Similarly any excess base added to the buffer will be mostly neutralised by the weak acid present in the buffer solution.

When NaOH is added to the buffer system, it reacts with the ethanoic acid present according to the following equation,



As can be seen, the presence of the weak acid prevents the additional hydroxide ion from changing the pH to any great extent. **The ability of a buffer to maintain a constant pH when a strong acid or strong base is added to it is known as its buffer capacity.** The buffer capacity depends on the amount of weak acid and weak base present in the solution. As NaOH was continuously added to the system, more CH_3COOH would be used up. Eventually, the solution reaches the limit of its buffer capacity and is unable to neutralise any further addition of NaOH. This would result in a sharp increase in pH corresponding to the presence of the extra OH^- ions.

For a buffer system to be most effective, it should have a high concentration in equimolar amounts of both the weak acid and weak base to ensure neither will be significantly depleted or reduced in concentration on the addition of either OH^- or H_3O^+ ions. Buffers are also most effective when the weak acid and weak base have similar concentrations.

Titration

- **What are the characteristics of a primary standard?**
 - High purity consistent to its known formula
 - Stable enough so it does not react with air to change water content or react with other gases (hygroscopic/deliquescent)
 - Reasonably high molar mass
 - Soluble in water
- **What are some substances NOT suitable for a primary standard?**
 - X H_2SO_4 , NaOH, KOH are not available in its pure forms. It is deliquescent, absorbs moisture from the air and can form a solution in this moisture
 - X $\text{NaOH}_{(s)}$ and $\text{KOH}_{(s)}$ are affected by exposure to air as they absorb water vapour and react with CO_2 , forming Na_2CO_3 and K_2CO_3 . This alters their purity
 - X HCl is not available in its pure form; it is a gas. Weighing out the mass would involve many technical difficulties and inaccuracies. It would be more efficient and accurate to use it as a secondary standard.
- **What are the systematic and random errors of titration?**

RANDOM ERRORS- slight variations in results which are inevitable and difficult to eliminate. This error does not cause results to be consistently high or lower than actual. (e.g. careless attention to colour change, poor technique, dirty apparatus, grease in the burette can cause traces of liquid to remain, so giving a false larger than actual titration reading (inconsistent rinsing technique)

SYSTEMATIC ERROR- consistently high/lower than the actual value. (e.g. wrong indicator used, fault apparatus)

- **Distinguish between the terms "precise" and "accurate".**

"Precise"-results that are close together and show little variation
"Accurate" closeness of results to actual/accepted value.

- **How would repeating trials improve accuracy?**

Repeat trials allow an average titre to be calculated rather than one single value. Averaging the data **reduces the effects of random errors** on the results and **improves reliability**.

- **How do you calculate the average titre and explain why averaging provides a more accurate result.**

All measurements contain some degree of **random error**. This causes some results to be slightly higher than the actual value and others will be slightly lower than actual. Averaging multiple trials reduces the effect of this type of error and produces a more **reliable** result.

- Elaborate on the laboratory processes the student could use to standardise the HCl using Na_2CO_3 as the primary standard. In your answer you should consider the preparation of the primary standard, performing the titration and processing the data. Consider the equipment, techniques and reagents needed as well as the concentrations and quantities involved. Include the techniques that minimise experimental error.

Preparation of 250mL of primary standard solution

Weigh accurately, add distilled water, stir, add to volumetric flask, shake, storage bottle, calculate concentration of primary standard

Standardising the HCl solution

Clean burette with soap, then water, then HCl. Set up burette. Rinse pipette with primary standard solution, use pipette to deliver aliquots into conical flask. Add indicator. Perform one quick titration. Take note of values. Swirl flask continuously. Repeat carefully, adding HCl dropwise when nearing end point. Calculate titre volumes, ($\pm 0.20\text{mL}$), disregard any outliers and determine average volume of HCl.

Calculate the concentration

- Distinguish between the “equivalence point” and the “end point”.

Equivalence point is where stoichiometrically equivalent amounts of reactant have been mixed. End point is where the indicator colour change occurs. In a titration these two points need to coincide as closely as possible for accurate results.

Acid-base indicators

- What types of substances are acid-base indicators? Use the Bronsted-Lowry theory to explain the colour change.

Indicators are weak acids or bases (they are capable of accepting or donating a proton according to the Bronsted-Lowry theory. A substance is an indicator if there is a colour change associated with its protonation/deprotonation.

As pH changes rapidly at equivalence it causes a strong shift in the indicator acid-base equilibrium. This alters the predominant form of the indicator present in the titration reaction mixture thus causing a **colour change** that is the end point of the titration.

- Explain how a litmus indicator works.

Litmus works because the acidic form is a different colour than the basic. In acidic solution the reverse reaction is favoured due to presence of hydronium ions (red form of litmus dominates). In basic solution the equilibrium shifts to the right due to the presence of hydroxide ions and the blue form dominates.

Electrochemical cells (Galvanic)

- Describe the production of an electrochemical cell. Include a sketch of your apparatus.
- State the role of a salt bridge in the galvanic cell.

The salt bridge completes the circuit allowing ions to move between the cathode and anode. This prevents a build up of negative charge at the cathode and positive charge at the anode. It also prevents direct contact between the oxidant and reductant.

- State the role of an electrolyte in the galvanic cell.

The electrolyte allows for the migration of ions and thus completes the circuit through the electrolyte.

BACKGROUND: An electrolyte is a substance that produces ions in solution. These ions move in an electrochemical cell that becomes the current. The cations and anions conduct the current in the solution. The flow of current in the external circuit is by electrons from the anode to the cathode and, the ions in the internal circuit.

- State the role of the hydrogen half-cell in determining the emf.

The voltage of an electrochemical cell is the difference in the reduction potentials for the two metals making up the cell. A measure of the reduction potential for a half cell can only be obtained by joining it with a common reference couple. The selected reference is the H⁺/H₂ couple. For this reference half cell, a E value of exactly zero volt is assigned. The standard reduction potentials for other half cells are obtained by measuring the total cell voltage when attached to a standard hydrogen half cell.

EX) Compared to hydrogen, cadmium has a higher tendency to oxidise, indicated by its half-cell potential, -0.40V. When a cadmium half cell is connected to a hydrogen half cell, cadmium is oxidised and hydrogen is reduced and the voltmeter reading (at standard 25C and 1.00atm) will be 0.40V.

- Why does the rate of production of electrical current from a Galvanic cell decrease as it operates?

As the reaction proceeds, the ions are used up and their concentrations fall which decreases the cell voltage as well. The cell emf is a function of the electrolyte concentrations.

- During the operation of a Galvanic cell, why is it important that the anode and cathode do not come into contact with each other?

If the anode and the cathode come into contact, electrons will transfer directly from the anode to cathode rather than flowing through the external circuit. This short circuiting robs the electrical energy that will otherwise be available by rerouting the electrons. This prevents a current flow through the external circuit where it can be used. It is important to note that the essential and the principal role of an electrochemical cell is to make the electrons flow through an external circuit first, prior to eventually completing the circuit and completing the reactions.

- **What is the key difference between fuel cells and other galvanic cells?**

Fuel cells require a continuous input of reactants and therefore have the ability to produce a continuous voltage. Other galvanic cells contain a fixed amount of reactant and once this is used up the cell will cease to produce a voltage.

1. Primary Cells

These are **non-rechargeable** galvanic cells. It contains a fixed amount of oxidant and reductant which once consumed cannot be replaced or generated.

2. Secondary Cells

Rechargeable galvanic cells. Once flat, they are recharged by applying a DC voltage that forces the spontaneous discharge reactions to be reversed and regenerate the oxidant and reductant originally present. (electrolysis)

There is a limit to the number of recharge cycles until electrodes are physically degraded.

3. Fuel Cell

The oxidant and reductant are **continuously fed into the cell**.

Reductant: fuel (combustible substance e.g. hydrogen, methane, methanol)

Oxidant: oxygen gas

They have a very long life and can theoretically operate without limit as long as oxidant and reductant are supplied in the cell.

- **Describe the chemical principles behind an electrochemical cell and explain why different cells are able to produce different voltages.**
- Different voltages are produced by different cells because oxidation and reduction half reduction have different E values.
- The greater the different in the E value, the greater the voltage produced by the cell.
- Electrochemical cells use a redox reaction where the oxidation happens in a physically different location to the reduction
- The electrons are forced to divert through an external pathway to move from the reductant to the oxidant, creating an electrical current.
- **Give a brief description of how a hydrogen-oxygen fuel cell operates and how it differs from primary and secondary cells.**

Fuel cells do not store the oxidant or reductant like the primary and secondary cells do. They require a continuous input of reactants. As the oxidant and reductant are fed into the cell, an electric current is produced. In the hydrogen-oxygen fuel cell, hydrogen enters at the anode and oxygen enters at the cathode.

- **Explain why many consider the PAFC to be a “clean” source of energy. Use a chemical equation to support your answer.**

The only product of this cell reaction is water, completely harmless

The overall cell reaction: $2 \text{H}_2(\text{g}) + \text{O}_2(\text{g}) \rightarrow 2 \text{H}_2\text{O}(\text{l})$

- Explain the role of the porous membrane in the function of the cell.

The porous membrane separates the two solutions from directly coming into contact and reacting and transferring electrons directly. However, the membrane allows the migration of ions to complete the circuit. Electrical neutrality is maintained by the migration of ions through the membrane.

- The role of standard hydrogen half cell in determining the table of the Standard Reduction Potentials.

Standard Reduction potentials (E°) are measured with solutions of 1.0 mol L^{-1} concentrations (gases at 100 kPa) and at a temperature of 25°C . They are a measure of the relative capacity of the more oxidisable form of the couple to gain electrons, and are called reduction potentials. The hydrogen half cell is assigned a E° value of exactly zero volt because this is used as a reference reaction. Standard reduction potentials for all other reduction reactions are obtained by measuring the total cell voltage or emf when attached to a standard hydrogen half cell. Thus H half cell acts as a standard reference for all other cells. In the SRP table, the half reactions are arranged in the order of decreasing reduction potentials.

- Limitations of the Reduction Potential table

- The half-reactions given in the table apply to aqueous solutions only
- The E° values are given for concentrations of 1.0 mol L^{-1}
- The electrode reactions depend on the nature of the electrode surface
- The table does not provide any information on the rate of reactions
- Experimentation is the only way to make sure that a reaction will occur

- Concentration changes in Galvanic cells

In any electrochemical cell, in the concentration of reactants increases, the reaction becomes more spontaneous and cell emf increases.

- Concentration of reactants increases, FRR increases, emf increases.
- Concentration of products increases, RRR increases (FRR decreased), emf decreases

As the cell operates, the concentration of the reactant ions decreases. Thus, FRR decreases, cell emf decreases.

Electrolytic cells

- **Differences between Galvanic Cells and Electrolytic Cells**

In an electrolysis cell the applied **DC voltage** determines the flow of electrodes and this determines the cathode and anode (non-spontaneous reaction)

In a galvanic cell it is the **spontaneous reaction** occurring inside the cell that determines the flow of electrons and hence which electrode is the cathode and anode.

- **What is the reason why solids cannot undergo electrolysis?**

Electrolysis requires **ions** taking part in the reaction to be **mobile**. In solid state, ions are in fixed positions within an ionic lattice and are not free to move.

- **Why do electrolytes need to be in liquid/molten states for the electrolysis process to work?**

- 1) Electrolysis requires the **movement of charge** around the complete circuit and ions in the electrolyte.
- 2) In solid state, the ions are **not free to move** so no current can flow.
- 3) When dissolved in water, the ions are now free to move through the electrolyte and so **complete the circuit**.

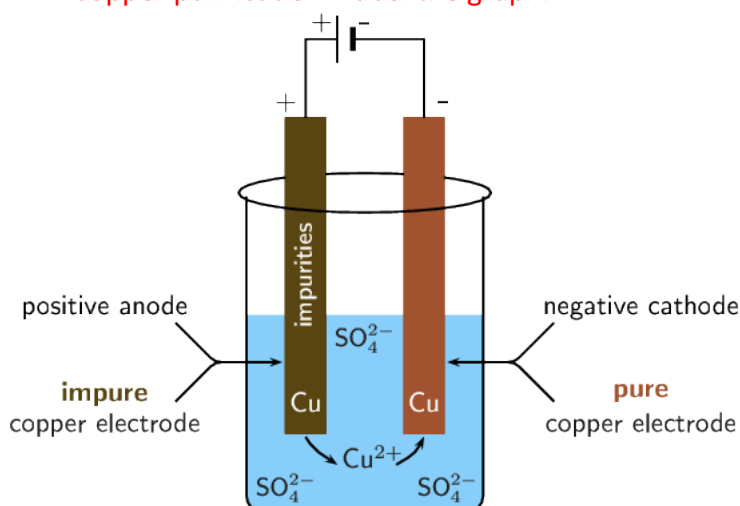
- **List 3 potential hazards associated with the electrolysis of molten potassium fluoride.**

- High temperature
- Use of electricity
- Use of high current flows for "good" reaction rate
- Toxic fluorine gas
- Molten metal

- **State one safety precaution that workers using electrolysis to extract potassium from molten potassium fluoride should take.**

- Breathing apparatus, gloves, protective clothing
- Ventilation
- Dry environment
- Extraction/safe storage of fluorine gas

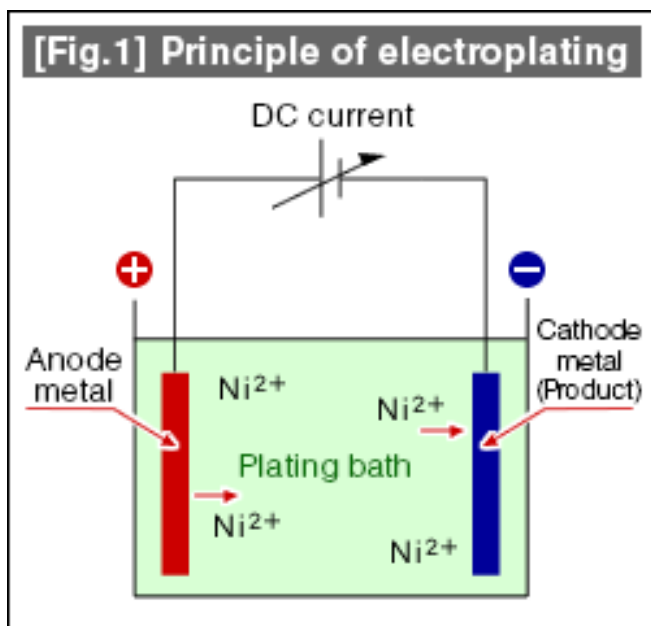
- **Copper purification- Label the graph.**



- Explain how impurities in copper are removed during the electrolytic process and prevented from contaminating the pure electro-refined copper.

The less reactive metals are not oxidised and do not move into the electrolyte solution. Instead, as the anode disintegrates, these metals fall to the bottom of the cell where they form an anode slime. This sludge is periodically removed from the bottom of the cell and the metals recovered.

- Electroplating



Haber-Bosch process

- Comment on the conditions used in the Haber-Bosch process, in terms of the effect on reaction rate and yield of ammonia.

CHANGE	RATE (NH_3)	YIELD	REASON	BENEFITS/COSTS
Iron/iron catalyst	Rate of production of NH_3 increases	No effect on yield	Provides alternative pathway with lower E_a , allowing greater proportion of particles to exceed E_a .	Catalysts reduce costs as they can be recycled and allow lower temperature to be used
High pressure	Increases	Increases	More collisions between reactants. Favours forward reaction (less moles)	
Moderate temperature	High temperature-high rate	Low temperature-high yield (exothermic)	E_k increases, higher percentage	Compromise of high rate and high yield

- Suggest why industrial processes can never actually have a yield of 100% and comment on some of the specific factors that would contribute to a loss of yield in the production of ammonia.

1. Loss of reagent due to unwanted side reactions that consume reagents
2. Physical loss of product due to inability to completely separate or purify product from final mixture
3. Equilibrium reactions don't go to completion
4. Presence of impurities in reagents means the amount of reagent added is less than amount measured.

- (c) State two (2) safety considerations the students would have to take into account when conducting this experiment. (2 marks)

any 2 acceptable precautions such as...

- wear safety glasses / take precautions when using electrical devices / avoid contact with copper sulfate electrolyte / keep voltage low to prevent electrolysis of water and production of flammable hydrogen etc

- (e) What factors or problems with an experiment can cause; (2 marks)

(i) random error?

- Uncontrollable (unpredictable or unknown) effects of equipment, procedure or environment (minimised by multiple trials and averaging)

(ii) systematic error?

- identifiable and quantifiable uncertainty, i.e. consistent bias or faults in measuring instruments or consistent errors in experimental techniques or procedure (minimised by using correct scientific technique)

- (b) If the temperature of the system was decreased, explain the effect this would have on the equilibrium in terms of reaction rates. (3 marks)

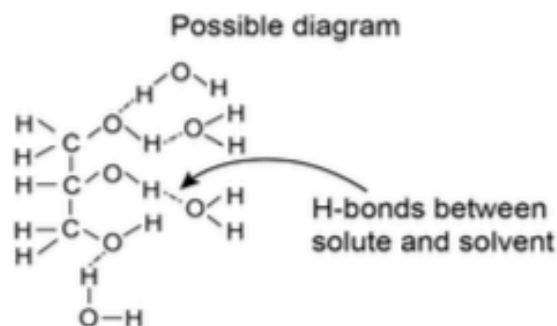
- both forward and reverse reaction rates would decrease, due to a decreased average kinetic energy of particles
- the endothermic direction (forwards) is always affected to a greater extent by temperature change, and is therefore decreased more than the reverse rate
- results in reverse reaction being favoured until the system re-establishes equilibrium, where the forward and reverse rates are again equal (but lower than initially)

Select from the list below to complete the 'Property' column of the table. A property may only be used **once**. State a different use for each polymer.

- hydrophobic
- high tensile strength
- biodegradable
- rigid
- chemically inert
- heat resistant

Plastic	Type of polymer (addition or condensation)	Property	Use related to property
High density polyethene (HDPE)	addition	high tensile strength	furniture
Polytetrafluoroethene (Teflon)	addition	heat resistance	coating on frypans and other cookware
Polyethylene terephthalate (PET)	condensation	chemically inert	drink bottles

- (d) The glycerol produced can be used as anti-freeze due to its high water solubility. Explain, with the aid of a diagram, why glycerol has water solubility. (5 marks)



Description	Marks
1 mark for recognition that both water and glycerol have H-bonding as their predominant type of IMF	1
1 mark for showing that their similar IMFs leads to a high degree of interaction between solvent and solute molecules/formation of H-bonding	1
1 mark for recognising that solubility arises due to the strength of attraction between solute and solvent molecules being sufficient to overcome attraction between solute-solute and solvent-solvent molecules (see note)	1-2
1 mark for a suitable, labelled diagram representing H-bonding between water and glycerol molecules	1
question incorrectly answered or not attempted	0
Total	5
<p>Note: An explanation in terms of the competing forces of attraction between solute-solute molecules, solvent-solvent molecules and between solvent-solute molecules is also acceptable. Students may also discuss the energy released when solvent-solute molecules attract being sufficient to overcome the energy to separate solute-solute molecules and solvent-solvent molecules.</p> <p>'Like dissolves like', contains no chemistry and should not be awarded any marks.</p>	

- (a) What types of substances are acid-base indicators? (2 marks)
- **weak acids or weak bases**
 - **where the acidic form is different colour to basic form**
- (a) Explain the chemical principles of an electrolytic cell. (2 marks)
- **electrolytic cells utilise an external applied voltage**
 - **this drives a non-spontaneous redox reaction to occur**

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.

Description	Marks
recognition that 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	1
recognition that the cells will need an electrolyte (eg. NaCl dissolved in water or 0.1 mol L ⁻¹ HCl)	1
recognition of role of ions as electrolyte to complete the circuit	1
recognition that voltmeter needs to be connected in the external circuit to measure potential difference between electrodes	1
recognition E(A/B), E(A/C) and E(B/C) is the data that needs to be collected	1
recognition that 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	1–2
labelled diagram to show typical Galvanic cell (electrodes, voltmeter, salt bridge if 2 beakers used)	1–2
Recognition of variables to control. any 2 variables e.g. temp, conc. of electrolyte soln, surface area of electrodes in contact with electrolyte	1
question incorrectly answered or not attempted	0
Total	10

- (a) Explain the chemical principles of an electrolytic cell. (2 marks)
- **electrolytic cells utilise an external applied voltage**
 - **this drives a non-spontaneous redox reaction to occur**

4. Fuel Cell

The oxidant and reductant are **continuously fed into the cell**.

Reductant: fuel (combustible substance e.g. hydrogen, methane, methanol)

Oxidant: oxygen gas

They have a very long life and can theoretically operate without limit as long as oxidant and reductant are supplied in the cell.

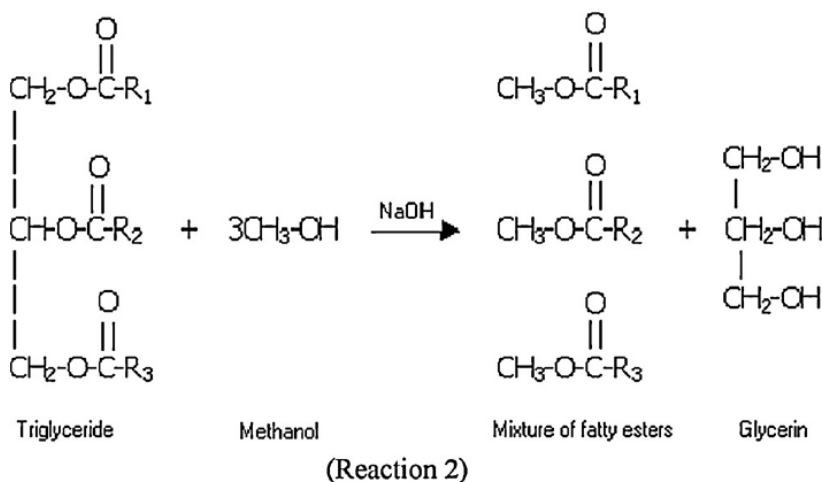
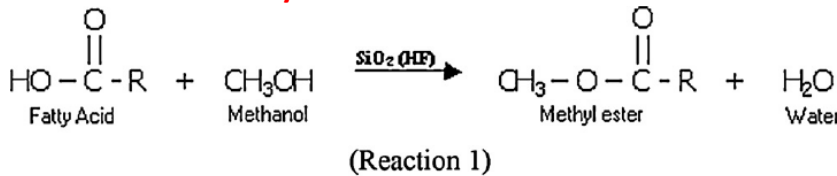
Fuel Cells

Fuel cells do not store the oxidizing or reducing agent. These reactants are constantly fed into the cell to generate electricity. Chemical by-products of the cell reactions are expelled from the cell as it operates.

BIODIESEL

- **biodiesel is produced from renewable biomass**
- **less pollution /not adding to CO₂ in atmosphere/fits into the natural carbon cycle**

Biodiesel: Base catalysed transesterification of TGs



REACTION 1

Chosen feedstock is filtered to remove foreign matter and treated to remove water. (water results in undesirable side reaction involving conversion of esters into soap).

This is undesirable as it wastes valuable reagent and reduces the yield of biodiesel. Also its presence in the final reaction mixture causes biodiesel and its co-product glycerol to form an **emulsion** making the much harder to separate.

If free fatty acid FFA content exceeds 4% then oil is treated to reduce FFA content (or soap formed when NaOH added).

- One method is to treat FFA's with methanol and an acid catalyst prior to transesterification
- Converts FFA'S to FAME fatty acid methyl ester (biodiesel)

Explain how this soap-producing reaction can occur. (Chemical equations are **not** required in your answer). (2 marks)

- **the NaOH catalyst can react directly with the oil**
- **this results in a saponification reaction where the oil forms soap instead of biodiesel**

REACTION 2 (Trans-esterification)

- Strong base (KOH, NaOH)
- Moderate temperature (60)
- Add methanol in excess to increase concentration and favour high yield
- Equilibrium (sealed vessel to prevent loss of volatile alcohol; methanol has low BP)

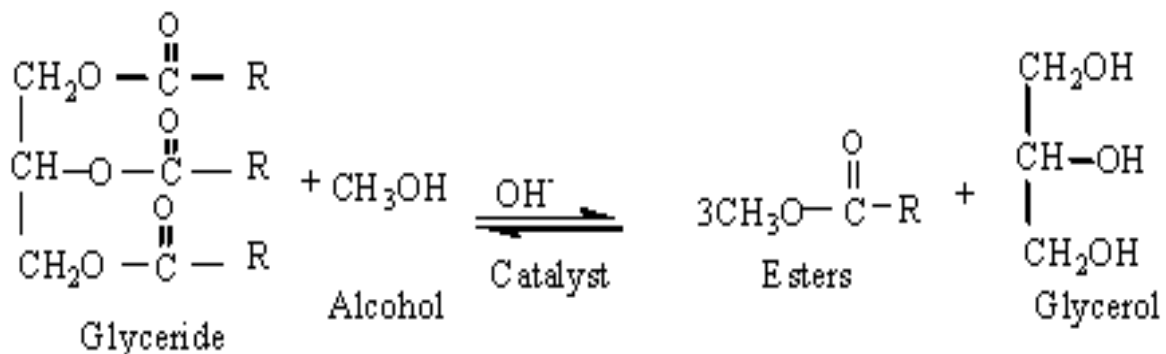
Methanol + Tristearin (a TG) → FAME (methyl esters, i.e. biodiesel) + glycerol

Biodiesel and glycerol are insoluble so they form two separate layers. Biodiesel is separated from the top layer while the denser glycerol forms a bottom layer. Any excess methanol, base catalyst and soap remain in the glycerol layer, with small amounts in biodiesel. The biodiesel is washed with warm water to remove any residual catalyst, methanol or soap, and is then dried, ready for use.

Any methanol recovered from glycerol is recycled in trans-esterification process.

ROLE OF NaOH (catalyst)

- Increases rate of reaction
- Alternative pathway (lower activation energy)
- Greater percentage of collisions with energy greater than or equal to activation energy
- Presence of ions increases the difference in polarity of the reactant molecules thus increasing reaction rate



- After suitable preparation the oil then undergoes transesterification to produce biodiesel
- Very slow equilibrium process so a **catalyst** is used to achieve reasonable rate

- Most biodiesels use a strong base (**NaOH or KOH**) to catalyse
- Further increase speed **moderate temp 60°C**
- Typically methanol or ethanol are **mixed with base to prevent loss of volatile alcohol**
- The required stoichiometric ratio is 3:1 but **alcohol is added in large excess 6:1** as higher concentration favours high yield (98%)
- Biodiesel and glycerol **insoluble** in one another so separation is easy
- Biodiesel is washed with warm water to remove any residual catalyst, methanol or soap, then dried
- Glycerol layer is also treated for further use

Biodiesel: Lipase catalysed transesterification of TGs

- Replaces strong base with enzymes known as lipases (naturally occurring enzyme found in cellular materials of living things)
- Advantages :
 - Milder temperatures and pH
 - Eliminates need to use corrosive and hazardous catalyst NaOH
 - Higher yield, higher purity of biodiesel product that is more easily separated from the by-product glycerol
 - No need to treat FFA's
 - Simultaneously catalyse transesterification of TGs and the esterification of FFAs into biodiesel
 - Do not cause side reactions (soap formation)
 - Simplify product purification, reduce waste
 - Use less energy (lower temp) to produce
- Disadvantages
 - Slower acting (higher catalyst concentration required)
 - Lipase catalysts quite expensive
 - Lipase recovery from final process is difficult

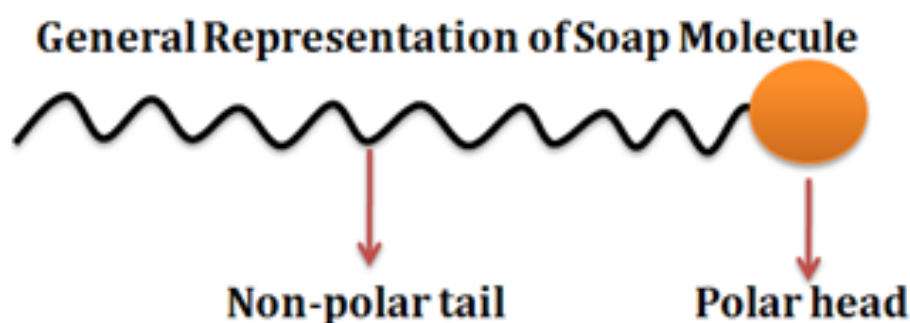
Saponification, structure and cleaning action of soaps and detergents

The triglyceride molecule (fat) is a naturally occurring ester composed of three fatty acids attached to a glycerol. The TG molecules found in fats and oils can be used to produce soap in a reaction called saponification.

This involves reacting the fat with a strong base, usually NaOH or KOH. This produces soap as well as the by-product glycerol. Soap being defined as the sodium or potassium salt of a fatty acid. The soap that would be produced from this TG has the formula $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^- \text{Na}^+$.

When soap is used for cleaning, it dissociates forming Na^+ and $\text{CH}_3(\text{CH}_2)_{16}\text{COO}^-$, which is known as the “surfactant ion”. The surfactant ion consists of a polar, hydrophilic head (COO^-) and a non-polar, hydrophobic tail ($\text{CH}_3(\text{CH}_2)_{16}$). The polar head of the surfactant ion interacts strongly with water through hydrogen bonds and ion-dipole forces. The non-polar tail interacts with non-polar dirt and grease by dispersion forces.

With agitation, the surfactant ion is able to remove non-polar dirt and grease from a surface. It does this by forming small spherical structures called a micelle. The non-polar dirt and grease, along with the hydrophobic part of the soap ion, form the inside of the micelle while the hydrophilic ends of the soap ions form the outer surface of the micelle. This allows the hydrophobic parts of the soap ions to interact strongly with the non-polar dirt and grease while the hydrophilic parts are able to interact strongly with the surrounding water molecules.



Cleaning action of soaps and detergents

A soap molecule or detergent molecule is made up of two components:

- Hydrocarbon component
- Carboxylate component (for soaps)
- Sulfonate component (for detergents)

The hydrocarbon is the hydrophobic end. The other component is hydrophilic.

In dirt, the hydrophobic end attaches itself to the oil molecule with strong dispersion forces. The hydrophilic end attaches itself to water with strong dipole-dipole forces. Agitation of water detaches oil from the surface.

Detergents have an advantage over soap when it comes to hard water contained dissolved Ca^{2+} or Mg^{2+} ions. These salts produce scum with soap. The sulfonate part of the

detergent does not react with the calcium or magnesium ions in hard water.

- (a) Note one similarity and one difference between the structure of this detergent molecule and a soap molecule. (2 marks)

Similarity	soaps and detergents both have <ul style="list-style-type: none">- a non-polar hydrophobic hydrocarbon tail- polar hydrophilic head –charged head- ionic
Difference	main difference <ul style="list-style-type: none">- detergents have charged polar <u>sulfonate</u> group (SO_3^-)- soaps have a charged polar carboxylate group (COO^-)- Detergent structure reacts with hard water : soap does not

- (b) Describe the cleaning action of detergents. Include in your answer a discussion of the advantage detergents have over soaps when used in hard water. (5 marks)

- ionic (polar) hydrophilic head of molecule remains dissolved in polar water
- non-polar hydrophobic tail dissolves in non-polar fats/oil/grease/dirt
- micelle formation
- these interactions take place due to the similar intermolecular forces
- ion/dipole and dispersion present
- with agitation, this allows the detergent molecule to remove the fats/oil/grease/dirt from the object
- soaps form an insoluble ppt (scum) with the Ca^{2+} or Mg^{2+} ions present in hard water but detergents do not