1 Scientific studies have provided strong evidence that lowering salt intake is beneficial in reducing blood pressure. Salt contains 40 % sodium which is essential for the normal functioning of the body. However, when eaten in excess, sodium raises blood pressure especially in individuals who are sodium-sensitive.

The amount of salt in potato chips can be determined by Mohr's Method. It is a direct titration method in which the amount of chloride ions can be determined. The amount of sodium ions can be calculated assuming all the sodium ions are present as sodium chloride.

In this method, the chloride-containing sample solution is titrated with a standard solution of silver nitrate and chromate(VI) ions are added as the indicator. After all of the chloride ions from the solution are precipitated with the silver ions, orange-red precipitate of silver chromate(VI) will be formed with any further addition of silver ions.

The reactions are:

$$Ag^{+}\,(aq) + Cl^{-}\,(aq) \rightarrow AgCl\,(s)$$
$$2Ag^{+}\,(aq) + CrO_4^{2-}\,(aq) \rightarrow Ag_2CrO_4\,(s)$$

(a) You are to plan an experiment to investigate the percentage of sodium chloride in a 5 g sample of potato chips. Give a step-by-step description of how you would carry out the experiment including:

- how you would prepare a solution of sodium chloride from the 5 g sample of potato chips for titration;
- the essential details of titration procedure;
- the appropriate quantities of reagents used.

Your apparatus should only consist of the standard items found in a school laboratory. In addition to the standard apparatus, you are also provided with the following materials:

- 0.10 mol dm^{-3} of silver nitrate;
- 10 % potassium chromate(VI).

1. Weigh accurately 5 g of crushed potato chips into a 250 cm^3 beaker.
2. Add 100 cm^3 boiling water to the beaker.
3. Stir the mixture vigorously for 1 min and let it cool to room temperature.
4. Filter the solution and transfer the filtrate into a 250 cm^3 volumetric flask.
5. **Top up to the mark** with deionised water. **Shake** the volumetric flask to obtain a homogenous solution.
6. **Pipette** 25.0 cm^3 of the filtrate to 250 cm^3 conical flask.
7. Add 1 ml of potassium chromate **indicator**.
8. **Titrate** the solution with 0.10 mol dm^{-3} **$AgNO_3$ from the burette** to the first visible orange-red colour.
9. Record the volume of titrant used.
10. **Repeat** the titration to obtain another consistent reading within ±0.10 cm^3.

[5]

(b) **(i)** In one such titration using the Mohr's Method, the exact concentration of silver nitrate used was determined using commercially available standard solution of sodium chloride.

25.0 cm^3 solutions of silver nitrate were titrated against 0.114 mol dm^{-3} of sodium chloride. The results are reported below:

No.	Volume of Na*Cl* /cm^3
1	22.90
2	27.20
3	22.80

Calculate the exact concentration of silver nitrate.

Average volume of Na*Cl* = $\frac{22.90 + 22.80}{2}$ = 22.85 cm^3

Amount of $AgNO_3$ = Amount of Na*Cl* = $\frac{22.85}{1000}$ x 0.114

= 2.60 x 10^{-3} mol

Concentration of $AgNO_3$ = $\frac{2.60 \times 10^{-3}}{\frac{25}{1000}}$ = 0.104 mol dm^{-3}

(ii) A solution containing sodium chloride was made by adding 100 cm^3 of deionised water to a 5 g sample of potato chips. Using the silver nitrate solution from **(b)(i)**, it was found that 25.0 cm^3 of the salt solution required 8.70 cm^3 of silver nitrate for titration.

Calculate the percentage of sodium chloride in the 5 g sample of potato chips.

Amount of Na*Cl* = Amount of $AgNO_3$ = 8.70 x 0.104/1000

= 9.048 x 10^{-4} mol

Mass of Na*Cl* in 25.0 cm^3 of solution = 9.048 x 10^{-4} x 58.5

= 0.0529 g

Mass of Na*Cl* in 5 g of Na*Cl* = 0.0529 x 100/25 = 0.212 g

Percentage of Na*Cl* in 5 g of potato chips
= $\frac{0.212}{5} \times 100\%$ = 4.23 %

[4]

(c) Mohr's Method using chromate(VI) ions as the indicator can only be conducted under near neutral condition. Explain why the titration cannot be conducted when the pH of the solution is:

(i) too low;

If the pH is low, chromate(VI) will be converted to dichromate. The chromate ion concentration is too low to produce the precipitate at the equivalence point.

(ii) too high.

If the pH is high, brownish white precipitate of silver hydroxide forms and masks the end point. **[3]**

[Total: 12 marks]

2 A student prepared benzoic acid, C_6H_5COOH, by hydrolysis of methyl benzoate, $C_6H_5COOCH_3$ using the following procedure:

Step 1: Dissolve 4 g of sodium hydroxide in water to make 50 cm^3 of an alkaline solution.

Step 2: Add aqueous sodium hydroxide to 2.70 g of methyl benzoate in a 100 cm^3 round bottom flask and set up the apparatus for reflux.

Step 3: Heat the mixture for 30 minutes.

Step 4: Distil the mixture until no more organic liquid is distilled out.

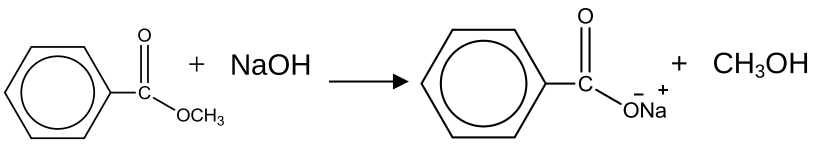
Step 5: Pour the solution from the flask into a beaker and add dilute sulfuric acid until solution is acidic.

Step 6: Filter the crystals obtained and recrystallise from hot water to obtain the benzoic acid.

(a) **(i)** Name the functional group that reacts during this hydrolysis.

Ester

(ii) Give the equation for the hydrolysis of methyl benzoate with sodium hydroxide.



Or $C_6H_5COOCH_3$ + NaOH $\longrightarrow$ C_6H_5COONa + CH_3OH

[2]

(b) The student obtained 1.50 g of benzoic acid.

(i) Calculate the amount of both reactants used and hence identify the limiting reactant.

Amount of methyl benzoate used = $\dfrac{2.7}{(12 \text{x } 6)+5+12+32+15}$
= 0.0199 mol

Amount of NaOH used = 4/40 = 0.100 mol

NaOH is in excess and methyl benzoate is the limiting reactant.

(ii) Calculate the percentage yield of benzoic acid obtained.

theoretical yield of benzoic acid = 0.0199 x 122 = 2.43 g

percentage yield = 1.50/2.43 x 100 = 61.7 %

Alternative method: students use amount to calculate percentage yield **[5]**

(c) Explain why the residue from the flask was acidified in **Step 5** before recrystallising.

With alkaline hydrolysis, acidification is needed to obtain benzoic acid from its carboxylic acid salt
Or to protonate/convert $C_6H_5COO^-$ to C_6H_5COOH **[1]**

(d) **(i)** Identify the organic liquid distilled out in **Step 4**.

Methanol

(ii) Suggest a method to check the purity of benzoic acid after recrystallisation.

Measure the melting point of benzoic acid, it will melt at a fixed temperature if it is pure.
Or melt at a small temperature range

[2]

[Total: 10 marks]

3 This question is about the Contact process and its catalyst, V_2O_5.

The Contact process is an important industrial method of manufacturing sulfuric acid.

The first stage of the Contact process involves the combustion of sulfur dioxide to give sulfur trioxide.

$$SO_2\,(g) + \tfrac{1}{2}\,O_2\,(g) \rightleftharpoons SO_3\,(g)$$

The table below shows how the percentage of sulfur trioxide in the equilibrium mixtures varies with temperature as well as the volume of the reaction vessels.

Temperature /°C	Percentage of sulfur trioxide in the equilibrium mixture for vessel		
	A	**B**	**C**
800	1.68	0.009	0.88
700	2.98	0.016	1.54
600	5.70	0.032	3.02
500	11.9	0.077	6.71

(a) Using the data in the table,

(i) explain whether the forward reaction is exothermic or endothermic.

As temperature decreased, the percentage of SO_3 increased i.e. position of eqm shifted right.
When temperature decreases, system responds to favor the exothermic direction to release heat.
Therefore the forward reaction is exothermic.

(ii) explain and rank the three vessels in order of decreasing volume.

At the same temperature, as volume decreases, total pressure increases, position of equilibrium would lie towards the side with less gaseous molecules. (which happens to be the RHS).

B > C > A

[4]

(b) Write two equations to illustrate how V_2O_5 functions as a catalyst through a proposed two-step mechanism. You are to take V_2O_4 as the catalytic intermediate.

$\mathbf{V_2O_5 + SO_2 \rightarrow V_2O_4 + SO_3}$
$\mathbf{V_2O_4 + \tfrac{1}{2}\,O_2 \rightarrow V_2O_5}$

Comments:

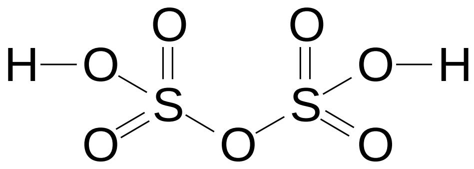
- **No double arrows.**
- **The two equations must add up to the overall equation.**
- **Individual equations must be balanced in mass and charge.**
- **Because V_2O_5 must be reduced (as implied by the catalytic intermediate V_2O_4), the first reagent involved must be sulfur dioxide.**
- **No foreign reagents like S, water, hydrogen and sulfate.** **[2]**

(c) The second stage involves the mixing of the newly formed sulfur trioxide with concentrated sulfuric acid to form oleum, $H_2S_2O_7$. Oleum is then mixed with water to finally form sulfuric acid.

The structure of oleum, which is a dibasic acid, can be described as follows:

- The two sulfur atoms are not bonded together.
- It is tetrahedral with respect to each sulfur atom.

Draw the displayed formula of oleum.



[1]

(d) V_2O_5, the catalyst in the Contact Process, is an interesting compound.

Like phosphorus-based acids and organic acids, V_2O_5 also reacts with thionyl chloride, $SOCl_2$. Two products, sulfur dioxide and **X**, are formed. **X** has a M_r of 173.4.

The disproportionation of **Y** (M_r of 137.9) leads to the formation of **X** and **Z** (M_r of 102.4).

X, **Y** and **Z** are made up of the same group of elements, of varying percentages.

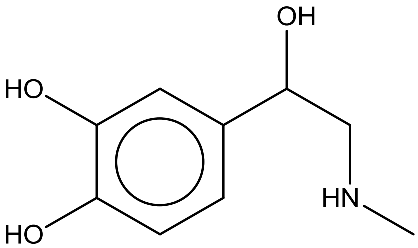
Identify the molecular formulae of **X**, **Y** and **Z**.

X: $VOCl_3$
Y: $VOCl_2$
Z: $VOCl$

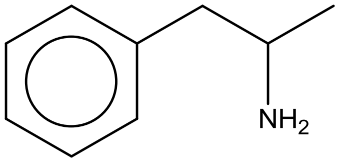
[3]

[Total: 10 marks]

4 Adrenaline is a naturally occurring hormone and stimulant released by the nervous system to prepare the body for immediate physical action during the time of danger or stress. After the discovery of the action of adrenaline, a series of stimulant drugs which are structurally and therapeutically similar to adrenaline were developed by pharmaceutical chemists. One such stimulant is amphetamine as shown below:



Adrenaline



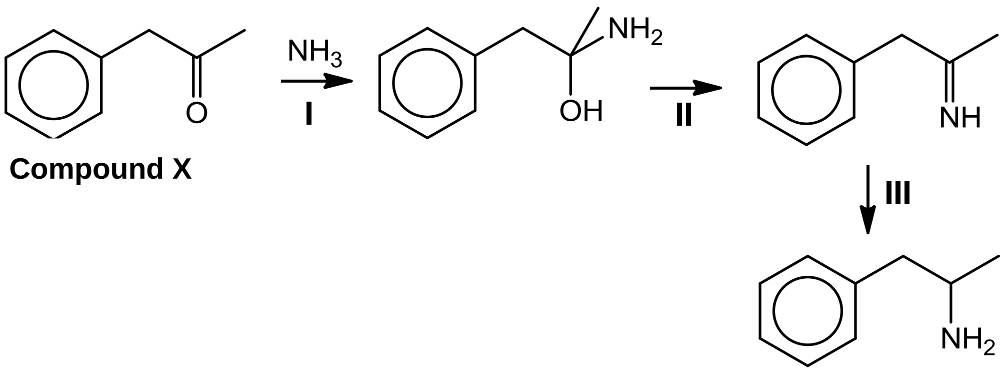
Amphetamine

(a) Even though adrenaline and amphetamine are structurally similar, both of them have different volatilities.
State which compound is less volatile, giving your reasoning.

Adrenaline is less volatile.
Adrenaline forms **more extensive hydrogen bonding** between molecules as it contains three O-H groups.

Or
Hydrogen bonding btw adrenaline molecules stronger than van der Waals forces of attraction btw amphetamine molecules. **[2]**

(b) Amphetamine is prepared commercially from **compound X** via a series of reactions as shown:



What *types of reaction* are reactions **I, II** and **III**?

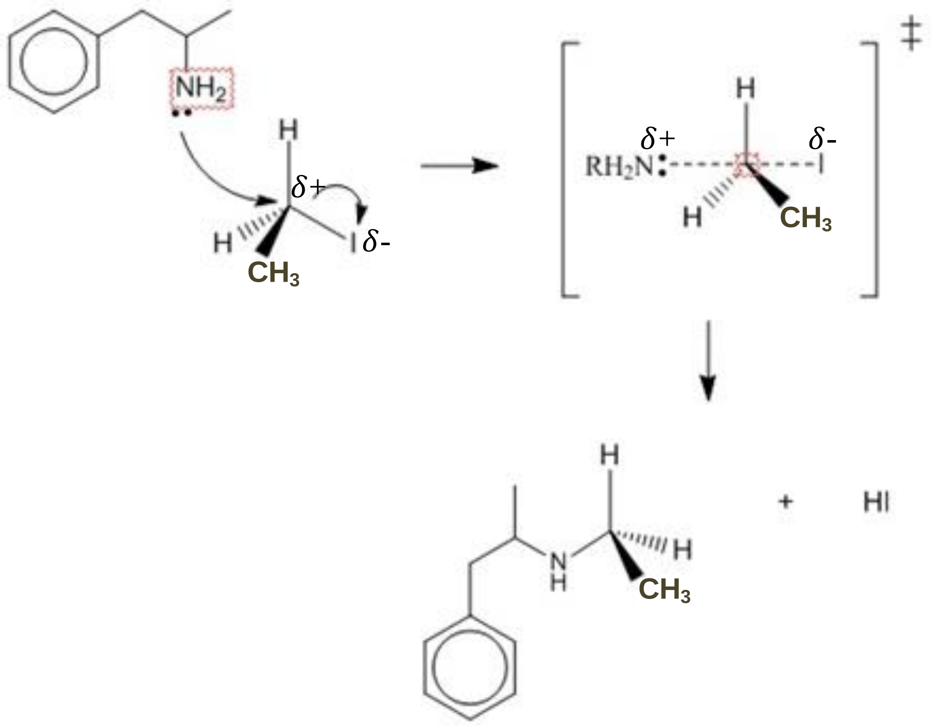
I: Nucleophilic addition
II: Elimination
III: Reduction

[1]

(c) Amphetamine is able to undergo further reactions to form other compounds.

(i) State and describe the mechanism involved in the reaction of amphetamine with limited CH_3CH_2I.

Bimolecular Nucleophilic Substitution

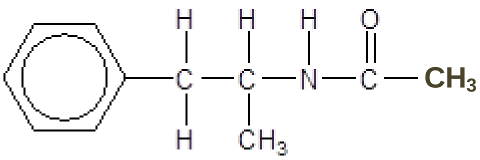


For the transition state, either the partial charges or the transition state symbol needs to be shown.

(ii) The product obtained in **(c)(i)** can be synthesised from amphetamine via a 2-step synthesis pathway. Provide reagents and conditions for each step and give the structural formula of the intermediate formed in the reaction.

Step I: **CH_3COCl**

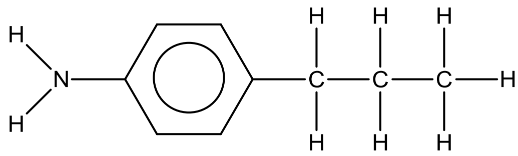
Intermediate:



[6]

Step II: **$LiAlH_4$, dry ether & reflux**

(d) An isomer of amphetamine forms a white precipitate when aqueous bromine is added. When hot acidified $KMnO_4$ is added to this isomer, an ionic product is formed. The formula of the cation in the ionic product is $C_7H_8O_2N^+$. Suggest the full structural formula of the isomer of amphetamine and state the type of isomerism exhibited.

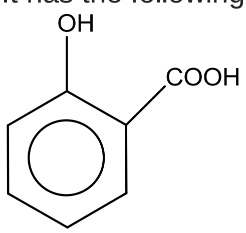


Structural isomerism

Positions 1,2-, 1,3- & 1,4- accepted
side chain as -CH(CH_3)$_2$ accepted

[2]

(e) Salicylic acid is a crystalline solid that is widely used in organic synthesis and functions as a plant hormone. It has the following structure:



Suggest a simple chemical test to distinguish between salicylic acid and adrenaline. State the reagents and conditions used and the expected observation for each compound.

Na_2CO_3 (aq)
Effervescence of colourless, odourless CO_2 gas which gives white ppt in limewater for salicylic acid but no CO_2 gas produced for adrenaline.

OR

$KMnO_4$ /dil H_2SO_4, heat
Purple colour of $KMnO_4$ decolourised for adrenaline but purple colour of $KMnO_4$ remains for salicylic acid.

OR

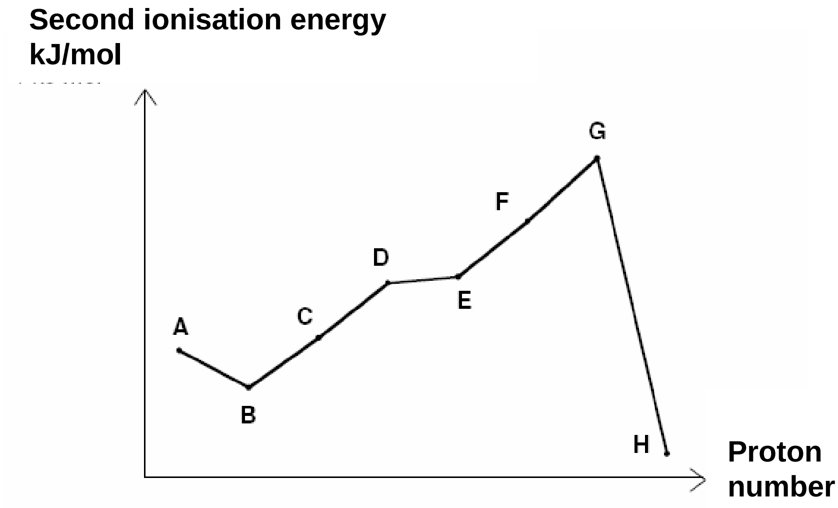
$K_2Cr_2O_7$ /dil H_2SO_4, heat
$K_2Cr_2O_7$ turns from orange to green for adrenaline but $K_2Cr_2O_7$ solution remains orange for salicylic acid.

[2]

[Total: 13 marks]

5 **(a)** **A** to **H** are consecutive elements in the third and fourth period of the Periodic Table.

(i) From the graph below, identify which element **A** to **H** is aluminium. Explain your answer.

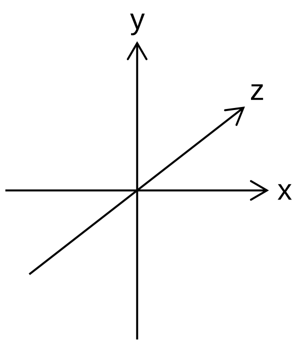


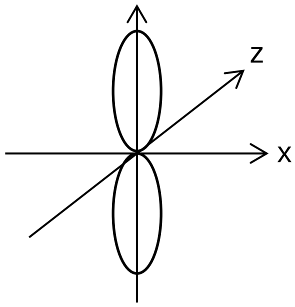
Element A

The **sharp drop in value from G to H indicates that G is from Group I** where the **second ionisation energy involves the removal of an electron from the inner quantum shell**. Hence Element A is in Group III and is Aluminium.

Or
Accept second electron from A or aluminium removed from 3s subshell which is closer to the nucleus than B or silicon where the second electron is removed from 3p subshell. Hence 2nd IE of A higher than that of B.

(ii) On the axes below, sketch the shape(s) of the singly–occupied orbital(s) in an atom of A*l* at ground state.





Can also accept p_x and p_y orbital

[3]

(b) Aluminium and magnesium form compounds with different physical and chemical properties.

(i) Magnesium chloride, $MgCl_2$, is a solid with a melting point of 714 °C whereas aluminium chloride, $AlCl_3$, sublimes at 178 °C.

Explain the above data using the structure and bonding in each of these chlorides.

$MgCl_2$ has a **giant ionic structure** with **ionic bonding** between Mg^{2+} and Cl^- ions.
$AlCl_3$ has a **simple covalent/molecular structure** with **van der Waals' or id-id interactions** between the molecules.
More energy is needed to break the **stronger** ionic bonding in $MgCl_2$ leading to its higher melting point.

(ii) When aqueous sodium hydroxide is added to an aqueous solution of $AlCl_3$, a white precipitate is formed which dissolves in excess sodium hydroxide.

State what you would observe when the above procedure is repeated using $MgCl_2$. Explain the difference(s) in the observations.

With $MgCl_2$, a **white ppt insoluble in excess NaOH** is observed.

$Al(OH)_3$ is **amphoteric** while $Mg(OH)_2$ is **basic**. $Al(OH)_3$ **reacts with NaOH** (to give salt and water), hence dissolves.

OR accept $Al(OH)_3$ forms the complex, $[Al(OH)_4]^-$

[4]

(c) Compounds of aluminium and beryllium share certain chemical properties. Beryllium salts, probably from rocks such as feldspars, may sometimes be found in drinking water.

An aqueous solution of beryllium nitrate is corrosive to the eyes and skin. With the aid of relevant equation(s), explain why that is so.

Solution of beryllium nitrate is **acidic [1/2] or (pH ≈ 3)** thus causing eyes and skin irritations.

$[Be(H_2O)_4]^{2+} + H_2O \rightleftharpoons [Be(OH)(H_2O)_3]^{+} + H_3O^{+}$

The **small, highly polarising beryllium cation or high charge density of Be^{2+}** weakens the O–H bonds of the water molecules in its surrounding sphere of coordination and results in the release of hydrogen ions in solution. **[2]**

(d) The melting points of three oxides are given in the table below:

Oxide	Al_2O_3	ZnO	SeO_2
Melting Point /°C	2080	1975	340

In terms of acid-base characteristics, ZnO is similar to Al_2O_3.

By means of balanced equations, show how ZnO and SeO_2 react with the following:

(i) NaOH(aq),

(ii) HCl(aq).

(i) $ZnO + 2\ NaOH + H_2O \rightarrow Na_2[Zn(OH)_4]$
$SeO_2 + 2\ NaOH \rightarrow Na_2SeO_3 + H_2O$

(ii) $ZnO + 2\ HCl \rightarrow ZnCl_2 + H_2O$

[3]

[Total: 12 marks]

6 Singapore's water is moderately soft and is safe to drink from the tap. Raw water from various sources is conveyed by pipelines to the waterworks where it is chemically treated, filtered and disinfected.

(a) Chemical treatment such as chlorination is used to prevent the spread of waterborne diseases. It is the process of adding chlorine to water to kill certain bacteria and other microbes in tap water as chlorine is highly toxic.

(i) Sodium chlorate(I) is frequently used as a disinfectant. Explain, with the aid of an equation, how sodium chlorate(I) is formed when chlorine is dissolved in an alkaline solution.

$Cl_2 + 2\ OH^- \rightarrow Cl^- + ClO^- + H_2O$

Sodium chlorate(I) is formed by when chlorine undergoes disproportionation reaction with sodium hydroxide.

[2]

(ii) Free chlorine does not combine with other components in the water. For effective chlorination of water, the concentration of free chlorine in water should be at least 5.63×10^{-6} mol dm^{-3}.

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

Given that the equilibrium constant of chlorine in water at 25 °C is 4.5×10^4 mol dm^{-3}. What is the initial concentration of chlorine added to water?

	$Cl_2 + H_2O$	$\rightleftharpoons$	$HOCl$	HCl
I	**x**		**0**	**0**
C	**-y**		**+y**	**+y**
E	**5.63×10^{-6}**		**y**	**y**

$$K_c = \frac{[HOCl][HCl]}{[Cl2]} = \frac{y^2}{5.63 \times 10^{-6}} = 4.5 \times 10^4 \text{ mol dm}^{-3}$$

$y = 0.503$ mol dm^{-3}

Initial concentration of $Cl_2 = 5.63 \times 10^{-6} + 0.503$

$= 0.503$ mol dm^{-3}

[2]

(b) Water samples are regularly collected and tested to ensure that the water is clean and safe. Water described as "hard" is high in concentration of dissolved minerals, specifically calcium and magnesium.

The hardness of water may be reported in parts per million (ppm). The solute concentration of a dilute aqueous solution in units of mg dm^{-3} is called parts per million, or ppm.

Classification	**ppm**
Soft	0 – 17.1
Slightly hard	17.1 – 60
Moderately hard	60 – 120
Hard	120 – 180
Very hard	Above 180

In a sample of water, the concentration of magnesium and calcium ions present are found to be 0.059 mol dm^{-3} and 0.011 mol dm^{-3} respectively. These two ions can be separated by selective precipitation with potassium hydroxide.

The numerical values of solubility product of magnesium hydroxide and calcium hydroxide at 25 °C are 1.5×10^{-11} and 5.5×10^{-6} respectively.

(i) Calculate the total concentration of magnesium and calcium ions in ppm, and hence classify the hardness of water in this sample of sea water.

$[Mg^{2+}]$ in ppm = 0.059 x 24.3 x 1000

= 1433.7 ppm

$[Ca^{2+}]$ in ppm = 0.011 x 40.1 x 1000

= 441.1 ppm

Total $[Mg^{2+}]$ and $[Ca^{2+}]$ = 1433.7 + 441.1 = 1874 ppm

= 1870 ppm (3s.f.)

The sample of water is very hard. (must be supported by working) **[2]**

(ii) Calculate the minimum pH of the solution at which the magnesium ion can be precipitated as magnesium hydroxide.

Ppt is formed when IP ($Mg(OH)_2$) > K_{sp} ($Mg(OH)_2$),

$(0.059)\,[OH^-]^2 > 1.5 \times 10^{-11}$ mol^3 dm^{-9}

$[OH^-] > 1.59 \times 10^{-5}$ mol dm^{-3}

Minimum pH = 14 – pOH

= 14 – (-log 1.59×10^{-5})

= 9.20 (3.s.f.) **[2]**

(iii) The magnesium hydroxide continues to precipitate out of the solution as potassium hydroxide is being added continuously. Eventually, the concentration of the hydroxide becomes high enough to precipitate the calcium ions as well.

What is the concentration of magnesium ions when calcium ions begin to precipitate?

When IP ($Ca(OH)_2$) = K_{sp} ($Ca(OH)_2$),

(0.011) $[OH^-]^2$ = 5.5 x 10^{-6} mol^3 dm^{-9}

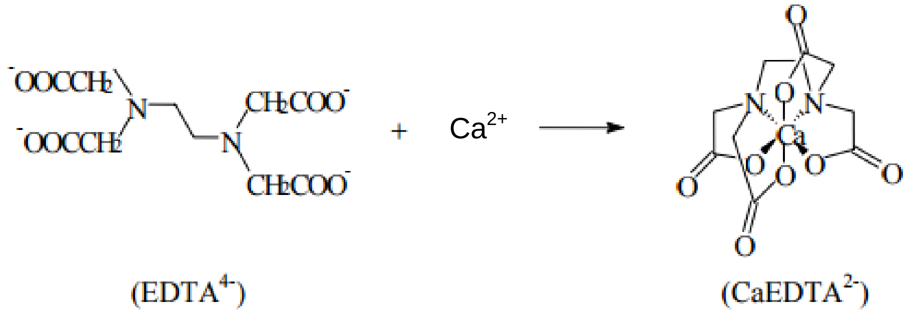
$[OH^-]$ = 0.0224 mol dm^{-3}

When IP ($Mg(OH)_2$) = K_{sp} ($Mg(OH)_2$),

$[Mg^{2+}](0.0224)^2$ = 1.5 x 10^{-11} mol^3 dm^{-9}

$[Mg^{2+}]$ = 2.99 x 10^{-8} mol dm^{-3} **[4]**

(c) Complexometric titration using EDTA (ethylenediamine tetra-acetic acid) solution as the titrant may be used to determine the concentration of the calcium ions in the water.



The reaction between calcium ions and EDTA only occurs at a high pH. Therefore, a buffer solution (pH of 10) has to be added to the water sample. A metal ion indicator, Eriochrome Black T, is used to identify when the reaction is complete.

A supplement tablet containing calcium ion was dissolved in another 50 cm^3 sample of water from **(b)**, filtered, and equal volume of the buffer solution was added. Several 2.00 cm^3 samples of the total solution were titrated with 0.0100 mol dm^{-3} EDTA solution by the method of this experiment. The average titre was 13.65 cm^3.

Calculate the calcium content of the supplement tablet. State the value to the nearest mg.

Amount of EDTA required = Amount of Ca^{2+} in 2.00 cm^3 sample

= 0.0100 x 13.65 ÷ 1000

= 1.365 x 10^{-4} mol

Amount of Ca^{2+} in 50 cm^3 of sample 1.365 x 10^{-4} x $\frac{100}{2}$

= 6.825 x 10^{-3} mol

Amount of Ca^{2+} from the tablet = 6.825 x 10^{-3} - (0.011 x $\frac{50}{1000}$)

= 6.275 x 10^{-3} mol

Calcium content of the supplement tablet in mg

= $6.275 \times 10^{-3} \times 40.1 \times 1000$

= 252 mg **[3]**

[Total: 15 marks]