HWA CHONG INSTITUTION
C2 Preliminary Examinations
Higher 2

CANDIDATE NAME		**CT GROUP**	20S
CENTRE NUMBER		**INDEX NUMBER**	

CHEMISTRY

9729/03

Paper 3 Free Response

16 September 2021

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Centre number, index number, name and CT group in the spaces at the top of this page.

Write in dark blue or black pen.

You may use an HB pencil for any diagrams or graphs.

Do not use staples, paper clips, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question Paper. If additional space is required, you should use the pages at the end of this booklet. The question number must be clearly shown.

No. of sheets of writing paper submitted (write 0 if none)	

Section A

Answer **all** questions.

Section B

Answer **one** question.

A Data Booklet is provided.

The use of an approved scientific calculator is expected, where appropriate.

At the end of the examination, fasten all your work securely together.

The number of marks is given in brackets [ ] at the end of each question or part question.

For Examiner's Use	
1	**/ 21**
2	**/ 18**
3	**/ 21**
Circle your option below	
4 / 5	**/ 20**
Deductions	
Total	**/ 80**

This document consists of **27** printed pages and **1** blank page.

Section A

Answer **all** the questions in this section.

1 (a) With the aid of the Boltzmann distribution, explain how an increase in temperature will affect the rate constant of a reaction. [3]

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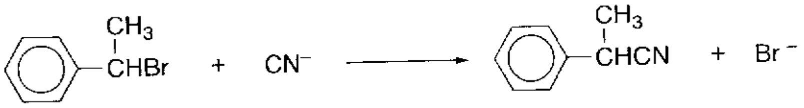
(b) Bromoalkanes can react with sodium cyanide to form nitriles. Depending on the structure of the bromoalkane, the reaction can proceed via the S_N1 or S_N2 mechanism.

Reaction 1 follows the S_N1 mechanism under certain conditions.

reaction 1



(i) Describe the mechanism for *reaction 1*. In your answer, show all relevant charges, lone pairs, dipoles and show the movement of electron pairs by using curly arrows. [2]

(ii) Hence, write the rate equation for *reaction 1*. [1]

(iii) What is meant by the term *order of reaction*? [1]

(iv) An experiment is carried out to study the kinetics of *reaction 1*. The concentration of the bromoalkane is monitored at timed intervals, with sodium cyanide present in large excess.

Sketch a suitable graph and show clearly on the graph how the results of the experiment can be used to confirm the reaction is first order with respect to the concentration of the bromoalkane. [2]

(v) The reaction below follows the same mechanism as *reaction 1*.

reaction 2

$C_6H_5CH(CH_3)Cl + CN^- \longrightarrow C_6H_5CH(CH_3)CN + Cl^-$

Predict the relative rates of *reaction 1* and *reaction 2* under identical conditions, giving your reasoning. [1]

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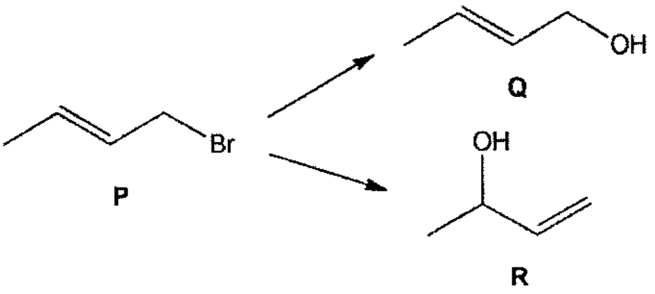
(c) When another bromoalkane, **P**, reacts with aqueous sodium hydroxide, the reaction could occur via both S_N1 and S_N2 mechanisms. Two products, **Q** and **R**, are obtained.



(i) Name compound **P**. [1]

(ii) Explain why compound **P** can react via the S_N1 mechanism, even though it is a primary bromoalkane. Hence suggest how product **R** may be formed in the reaction. Use the concept of delocalisation in your answer. [2]

(iii) State the type of stereoisomerism shown by product **R** and draw its stereoisomers. [2]

(iv) Compound **P** can react with ethylamine to form compound **S**, $C_6H_{13}N$. Draw the displayed formula of compound **S**. [1]

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(d) Although they have similar formulae, the following two compounds have differently shaped molecules.

PBr_3 ClF_3

Use the Valence Shell Electron Pair Repulsion (VSEPR) theory to predict the shape of each molecule. Draw appropriate diagrams to illustrate the shapes and label the bond angles in your diagrams. [5]

[Total: 21]

For Examiner's use

2 (a) (i) State the relative charges and relative masses of protons, neutrons and electrons. [2]

(ii) Describe the distribution of mass and charges within an atom. [1]

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(b) (i) Explain the general trend in ionic radii down Group 2. [2]

(ii) Describe and explain the trend in the thermal stabilities of the Group 2 carbonates. [3]

(iii) Write an equation, with state symbols, for the thermal decomposition of calcium carbonate. [1]

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For Examiner's use

(c) Define the term *mole*. [1]

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(d) 0.15 g of a solid mixture containing only $MgCO_3$ and $BaCO_3$ was shaken with excess aqueous hydrochloric acid. 35.00 cm^3 of carbon dioxide was collected at 30.0°C and 1 bar.

(i) Calculate the amount of carbon dioxide, in moles, that was collected. [2]

(ii) Hence, determine the mole fraction of $MgCO_3$ in the mixture. [3]

(iii) The mole fraction of $MgCO_3$ in the solid mixture can also be determined by indirect (back) titration.

Outline how you would determine the mole fraction of $MgCO_3$ using the indirect titration method.

No details regarding quantities, use of specific glassware, or calculations are required. [3]

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3 (a) Describe and explain the acid-base behaviour of aluminium oxide, Al_2O_3.

Write equations for all the reactions you choose to illustrate your answer. [4]

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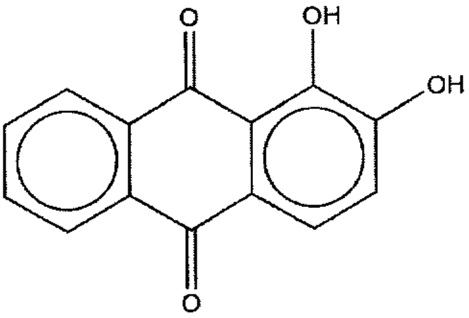
(b) Alizarin is a red dye with the structure shown below.



alizarin

Alizarin is used to dye cotton red in the presence of aluminium ions. Fig. 3.1 shows how Al^{3+} is bonded to alizarin and the hydroxyl groups of cotton.

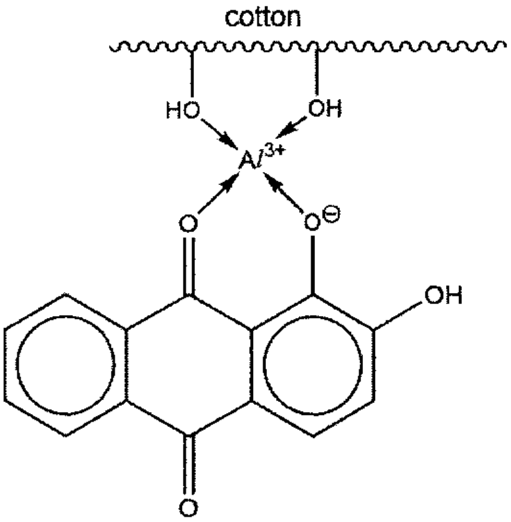


Fig. 3.1

(i) Explain how Al^{3+} behaves as an acid when forming the structure in Fig 3.1. [1]

(ii) Explain why alkaline conditions are needed for alizarin molecules to bond with Al^{3+} ions. [2]

(iii) A piece of cloth dyed red with alizarin was placed in a basin containing boiling water. It was observed that very little red dye enters the water.

Suggest a substance that could be added such that more dye enters the water. [1]

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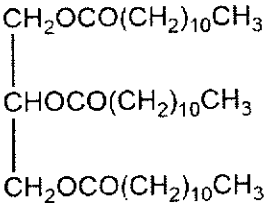
(c) Coconut oil contains a large amount of compound **G**.



$$\begin{array}{l} CH_2OCO(CH_2)_{10}CH_3 \\ | \\ CHOCO(CH_2)_{10}CH_3 \\ | \\ CH_2OCO(CH_2)_{10}CH_3 \end{array}$$

G

G can be converted into soap by heating it with aqueous sodium hydroxide, $NaOH$, to form a sodium salt, **H**, which remains dissolved in the solution. **H** is precipitated out as a solid by adding sodium chloride, $NaCl$.

(i) Give the structural formula of **H**. [1]

You may represent **H** as Na^+A^- for the rest of this question.

(ii) The solubility of **H** in water is 0.108 mol dm^{-3} at 24 °C.

Calculate a value for the solubility product, K_{sp}, of **H** at 24 °C. [1]

(iii) Explain why adding $NaCl$ to a solution of **H** causes solid **H** to precipitate out. [1]

(iv) Use your answer in **(c)(ii)** to determine the minimum mass of solid $NaCl$ that is needed to precipitate solid **H** when added to 500 cm^3 of a 1.00×10^{-2} mol dm^{-3} solution of **H** at 24 °C. [2]

(v) Explain why the solubility of **H** in water is lower than the solubility of $NaCl$ in water. [1]

For Examiner's use

(d) Double bonds that alternate with single bonds are said to be conjugated. For example, 1,3-butadiene is a conjugated diene, whereas 1,4-pentadiene is a non-conjugated diene.

$CH_2{=}CH{-}CH{=}CH_2$ 1,3-butadiene $\quad$ $CH_2{=}CH{-}CH_2{-}CH{=}CH_2$ 1,4-pentadiene

An electrocyclic reaction involves the cyclisation of a conjugated alkene. Fig. 3.2 shows the movement of electron pairs, represented by curly arrows, when 1,3,5-hexatriene undergoes this reaction. During this reaction, a new σ bond is formed, the number of π bonds decreases by one, and the remaining π bonds change position.

1,3,5-hexatriene $\quad$ 1,3-cyclohexadiene

Fig. 3.2

(i) 2-methyl-1,3-butadiene is a conjugated alkene and undergoes the electrocyclic reaction to form compound **J**.

2-methyl-1,3-butadiene

Suggest the structure of compound **J**. [1]

(ii) Compound **K**, C_8H_{12}, is a conjugated alkene and undergoes the electrocyclic reaction to form compound **L** which contains a 6-membered ring.

One mole of **K** reacts with 3 moles of liquid bromine in the dark. On treatment with hot concentrated potassium manganate(VII), $KMnO_4$, **K** forms CO_2 and compound **M**, $C_2H_4O_2$.

$$\underset{\textbf{K}}{C_8H_{12}} \xrightarrow{KMnO_4} \underset{\textbf{M}}{2C_2H_4O_2} + 4CO_2$$

When **L** was treated with hot concentrated $KMnO_4$, it forms CO_2 and compound **N**, $C_6H_{10}O_4$. **N** does not give an orange precipitate with 2,4-dinitrophenylhydrazine.

$$\underset{\textbf{L}}{C_8H_{12}} \xrightarrow{KMnO_4} \underset{\textbf{N}}{C_6H_{10}O_4} + 2CO_2$$

K, **L** and **N** are symmetrical molecules.

Use the information above to suggest structures for compounds **K**, **L**, **M** and **N**, explaining the reactions described. [6]

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[Total: 21]

Section B

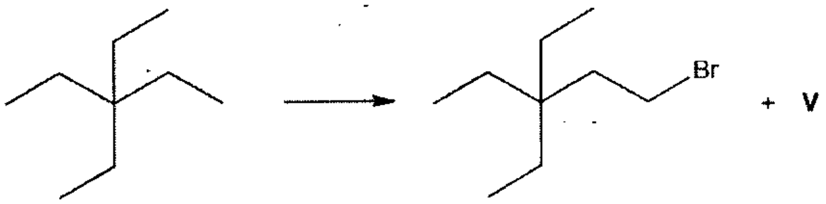
Answer **one** question from this section.

For Examiner's use

4 (a) Bromine reacts with alkanes in the presence of light.

(i) Outline the mechanism of the reaction between propane and bromine to form 2-bromopropane. [4]

3,3-diethylpentane reacts with bromine to give two monobromoalkanes, **U** and **V**.



3,3-diethylpentane **U**

(ii) Draw the structure of **V** and state its isomeric relationship to **U**. [2]

(iii) Predict the relative proportions of **U** and **V** formed in the above reaction. Explain your answer. [2]

(iv) When the bromination is carried out and the products are analysed, it is found that the mole ratio of **U** : **V** is about 1:1.

Suggest an explanation for the difference between this ratio and the one you gave in **(a)(iii)**. [1]

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(b) An equimolar mixture of bromine and hydrogen was heated at 700 K until equilibrium was established. The equilibrium mixture was found to contain 77.65 % by mass of HBr.

$$H_2(g) + Br_2(g) \rightleftharpoons 2HBr(g) \quad \Delta H < 0$$

(i) Write an expression for the equilibrium constant, K_c, for this reaction and calculate its value. [5]

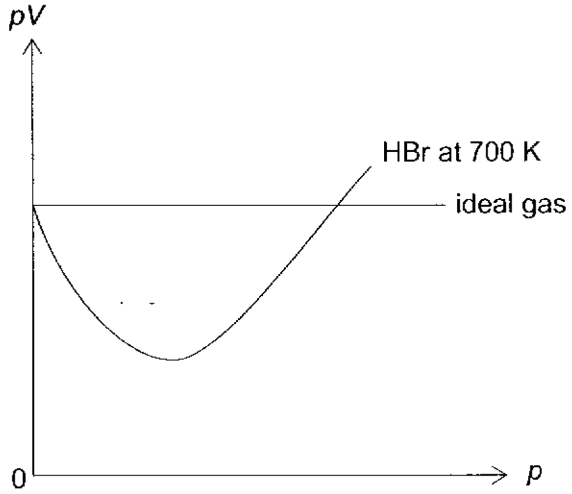
(ii) State and explain how the composition of the equilibrium mixture would change if there were an increase in

I the pressure at constant temperature

II the temperature [2]

(c) **(i)** Explain, in terms of intermolecular forces and molecular size, the conditions necessary for a gas to approach ideal behavior. [2]

(ii) The value of pV is plotted against p for HBr gas at 700 K, where p is the pressure and V is volume of the gas.



Copy the diagram and sketch the corresponding graphs for the ideal gas and HBr gas when the temperature is raised to 800 K. [2]

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5 **(a)** Describe the mode of action of iron as a heterogeneous catalyst in the Haber Process. [3]

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(b) State **two** d-block elements whose isolated gaseous **atoms** in the ground state have the same number of electrons in the 3d subshell as an isolated gaseous Fe^{3+} ion. [1]

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(c) When solid hydrated iron(III) salts containing $[Fe(H_2O)_6]^{3+}$ ions are dissolved in water, an acidic solution is obtained due to the following equilibrium.

$$[Fe(H_2O)_6]^{3+} + H_2O \ll [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

(i) State the relationship between $[Fe(H_2O)_6]^{3+}$ and $[Fe(H_2O)_5(OH)]^{2+}$ ions. [1]

(ii) A 0.15 mol dm^{-3} solution of aqueous iron(III) chloride has a pH of 1.78. Calculate the acid dissociation constant, K_a, of $[Fe(H_2O)_6]^{3+}$. [2]

(iii) When 0.10 g of solid sodium hydroxide is added to 50 cm^3 of the solution in **(c)(ii)**, a buffer solution of pH 2 to 3 is obtained and no precipitation occurs.

Use your answer in **(c)(ii)** to calculate the pH of this buffer solution. [3]

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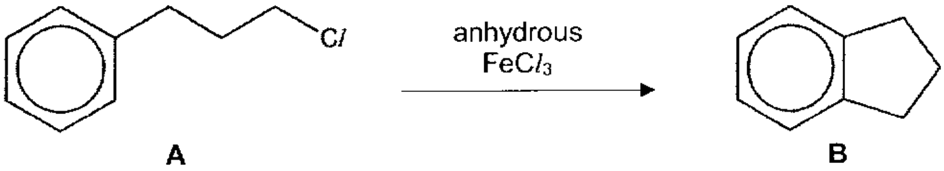
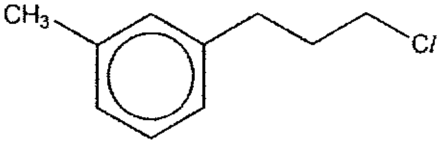
(d) **(i)** When anhydrous iron(III) chloride is added to compound **A**, an intramolecular electrophilic substitution occurs to form **B**.



Describe the mechanism for the formation of **B** from **A**. In your answer, you should show all charges and lone pairs and show the movement of electrons by curly arrows. [3]

(ii) Compound **C** also undergoes the above reaction in the presence of anhydrous iron(III) chloride.



C

Predict the reactivity of **C** in this reaction compared to that of **A**, giving your reason. [1]

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(e) Compound **D**, $C_9H_{11}Cl$, is an isomer of **A**. Warming **D** with NaOH(aq) produces alcohol **E**, which does not react with excess acidified $Na_2Cr_2O_7$.

Compound **F** can be formed from **D** or from **E** in one step. The M_r of **D** is 30.9% larger than the M_r of **F**.

(i) Draw the structures of **E** and **F**, giving your reasoning. [4]

(ii) State the reagents and conditions required to convert **D** to **F**, and **E** to **F**. [2]

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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.

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SUGGESTED SOLUTIONS

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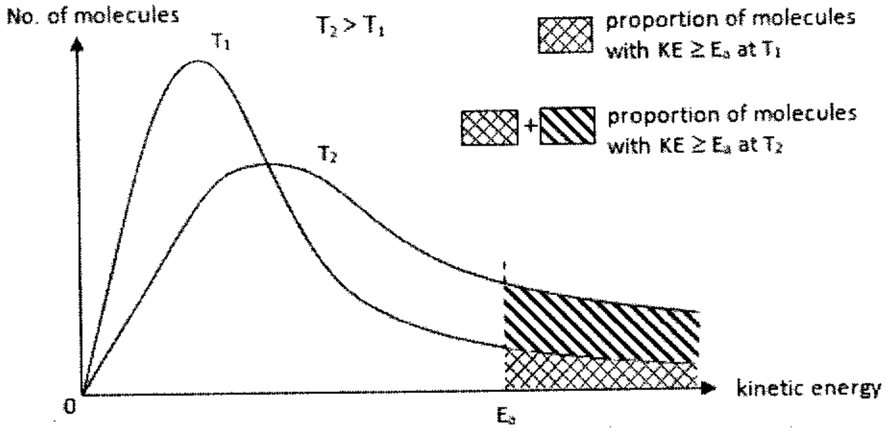
1 (a)



[1] – correctly drawn curve

When temperature is increased, the reactant particles have greater average kinetic energy. They move more quickly and so collide more frequently. The **proportion** of particles that have **kinetic energies greater than or equal to the activation energy increases**. **[1]** **Frequency of effective collisions** hence rate of reaction and **rate constant increases**. **[1]**

The question requires that you use the Boltzmann distribution to explain why an increase in temperature will affect the rate constant of a reaction. In order to do this, you must sketch the Boltzmann distribution curve and show how the kinetic energy of the particles in the reaction mixture changes with an increase in temperature.

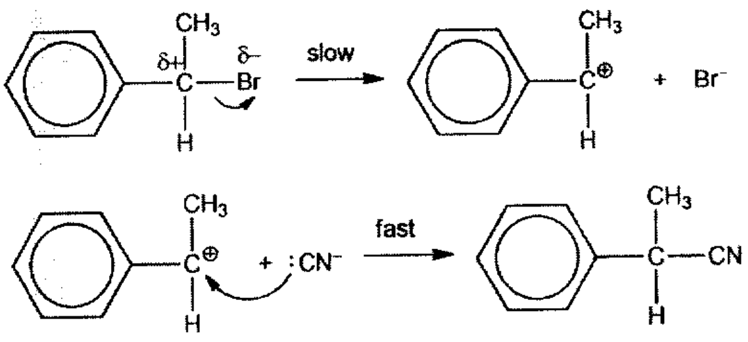
When drawing the graph, please ensure that the axes label are correct. Also, ensure that the shape of the curve is correct where it flattens out at higher kinetic energy.

It is not sufficient to state in your answer that the average kinetic energy of the reactant particles increase. In order for the rate of the reaction to increase, the particles need to have kinetic energy greater than or equal to activation energy. This phrase is essential.

Because of this, we can then conclude that the frequency of effective collision between the reactant particles increase and hence the rate of reaction would increase.

For this question, we ask how temperature would affect the rate constant of the reaction. You need to explicitly tell us that the rate constant will increase with increasing temperature.

(b) **(i)**



1 mark for each step
(deduct ½ for missing arrows, partial charges, lone pairs, slow fast step)

The question states that *Reaction 1* follows the S_N1 mechanism. As such, it is not necessary to name the mechanism.

Please ensure that the arrows that represent the movement of electrons start from a bond or a lone pair, and end at the atom where the new bond is formed.

(ii) Rate = k[$C_6H_5CHBrCH_3$] **[1]**

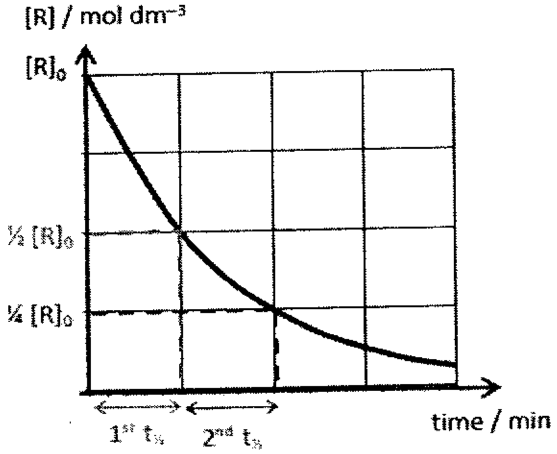
For the S_N1 mechanism, the only reactant in the rate determining step is the halogen derivative.

Please ensure that the name of the compound is correct if you choose to use the name of the compound when writing the rate equation.

(iii) Order of reaction with respect to a reactant is the power on its concentration term in the experimentally determined rate equation. **[1]**

This is a definition question. Please study your definitions.

(iv)



[1]

Show constant half-life on the graph **[1]**

Based on the design of the experiment given in the question, the variables being monitored are the concentration of the bromoalkane at various times. As such, the logical graph to plot is the [bromoalkane] against time.

The question requires that you show clearly on the graph how the results obtained can be used to confirm that the reaction is first order with respect to the [bromoalkane]. The graph need not be drawn to scale, but this means that you need to label both axes with values to illustrate that the half-life are constant. Written explanations are not required. No credit is given for answers that only consist of written explanations without any annotations on the graph.

(vi) Reaction 2 is **slower** as the **C–Cl bond is a stronger bond than C–Br** and requires more energy to break. **[1]**

The rate determining step in the S_N1 reaction involves the breaking of the C-Halogen bond. A direct answer on the relative strength of the bonds (you could even quote the bond energy values from the *Data Booklet*) would suffice here.

(c) **(i)** 1-bromobut-2-ene **[1]**

When naming a molecule, start by finding the longest chain of carbon atoms. For compound **P**, this would be a 4 carbon chain. Since the C=C is on C2 and C3, this is a but-2-ene. There is a bromo group on the terminal carbon. This terminal carbon could either be considered C1 or C4. Since IUPAC nomenclature requires that we use the smallest number to name the compound, we should assign the carbon connected to the bromine atom as C1.

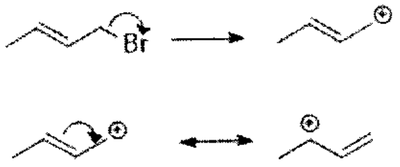
The name of compound **P** is therefore 1-bromobut-2-ene. Please note that hyphens are used only between number and letter. As the C=C in this compound shows the trans configuration, the more complete naming of the compound is *trans*-1-bromobut-2-ene.

(ii) The carbocation formed when **P** undergoes S_N1 mechanism is stabilised due to the delocalisation of the positive charge over C=C **OR** due to the delocalisation of the pi electrons of the C=C to the C^+. **[1]**

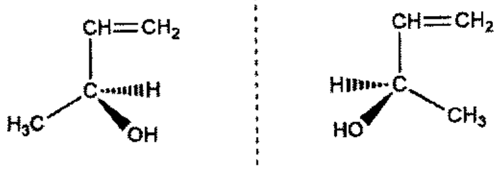
Due to the delocalisation, the positive charge shifts to the third carbon to form  OR the position of the C=C can shift to form  that forms **R**. **[1]**

The question directs you to think about why this primary bromoalkene is able to undergo the S_N1 reaction. Given that it is a primary halogen derivative, arguments for the R group causing steric hindrance and not favouring the S_N2 will be invalid. This R group is not very big and would not do much to block the pathway of attack of the nucleophile.

Instead, you should be thinking about how the carbocation can be stabilised. The question directs you to think about the concept of delocalisation in your answer. When you inspect the carbocation formed, you will realise that the carbocation is adjacent to the C=C, so there are 3 adjacent p orbitals where delocalisation can occur, hence the electrons in the C=C can delocalise to disperse the positive charge on the carbocation.



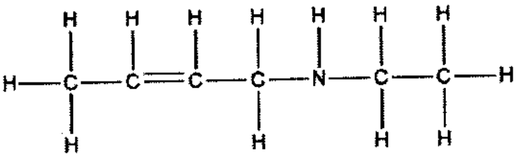
(iii) **Q**: enantiomerism **[1]**



[1] for correctly drawn pair of enantiomers

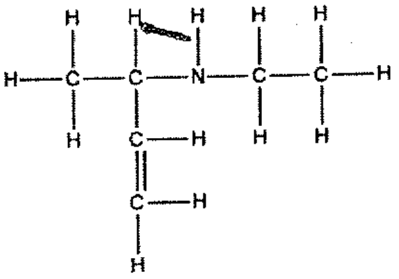
When drawing the enantiomers, please make sure that you have drawn the 3D representation (this means using the solid wedge and hash lines in your answer) on the chiral carbon. While it is not necessary to draw the displayed formula here, you should ensure that you have written out clearly the different substituent groups around the chiral carbon, showing correctly how each group is connected to the chiral carbon.

(iv)

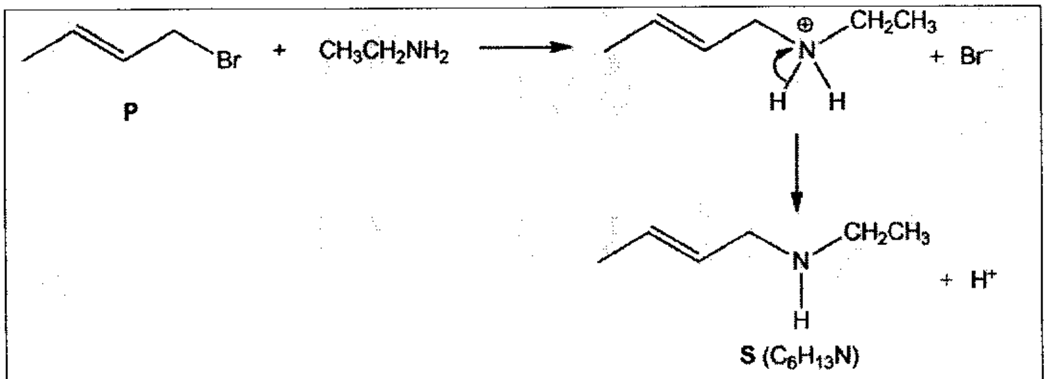


[1]

OR



From the earlier parts, we know that **P** can undergo nucleophilic substitution. Hence when **P** is reacted with ethylamine, ethylamine which has available lone pair on N can act as a nucleophile to substitute the Br atom on **P**. The subsequent loss of H^+ produces **S** which fits $C_6H_{13}N$.



Just like how **R** is formed, ethylamine can also attack the carbocation that has the positive charge on C3 after the position of C=C shifts. This is how the alternative answer above is derived.

Please read the question carefully. The question is asking for the <u>displayed formula</u> of the product formed from the reaction. So after you figured out how the product is formed, you need to draw it as a displayed formula.

(d) PBr_3 is <u>trigonal pyramidal</u> **[1/2]** as there are <u>3 bond pairs and 1 lone pair</u> around P **[1/2]**

ClF_3 is <u>T-shaped</u> **[1/2]** as there are 3 bond pairs and 2 lone pairs around Cl **[1/2]**

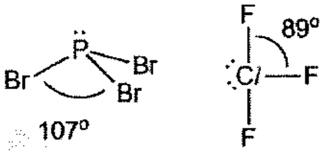


Diagram with correct number of bond pairs and lone pairs **[1/2]** each, showing shape **[1/2]** each
Bond angle labeled between two bond pairs **[1/2]** each

The question requires that you do a few things:

1. Use VSEPR to predict the shape of each molecule.

This means that you need to count and state the number of bond pairs and lone pairs around the central atom of the molecule, and use it to deduce the shape of the molecule. You need NOT state the principles of VSEPR as it is not asked for in the question.

2. Draw diagrams to illustrate the shape

This means that you need to draw a diagram to show the shape of the molecule. This diagram required is a Lewis structure. If the question requires a dot-and-cross diagram, the question will tell you to draw a dot-and-cross diagram.

3. Label the bond angles in your diagrams

This means that the bond angles need to be labeled on the diagram, and not merely stated in your answer. "Bond angle" refers to the angle between two bond pairs (**not** between lone pairs nor between a bond pair and lone pair!). A range of bond angles were accepted as reasonable. Please note that since the question requires that you label the bond angle, you need to state a value that the bond angle will take.

2 (a) (i)

	Relative Mass	Relative Charge
Proton	1	+1
Electron	1/1833	−1
Neutron	1	0

Accept 1/1800, 1/1830, 1/1836, 1/1840, 1/2000 for the relative mass of electron
[1] All relative charges are correct
[1] All relative masses are correct

> The question asked for the relative mass and the relative charge of protons, neutrons and electrons, which means that you are to find the ratio for mass, and the ratio for charge.
>
> The Data Booklet is very helpful here, but note that it lists the **absolute** rest mass of the three species, and the **absolute** charge of the electron.

(ii) The **mass of an atom is concentrated in the nucleus** of an atom. The electrons are of negligible mass.

The **nucleus is positively charged**(due to the protons), and the **negatively charged particles**(electrons) **surround the nucleus**.

[1/2] Distribution of mass
[1/2] Distribution of charge

> Many students didn't answer the question: the question is not asking how masses and charges are calculated/determined. Instead, the question is asking about the distribution of mass and charge, i.e. where they are located within the atom.
>
> Also, your description needs to be specific, accurate, and make use of good grammar. The following statements are not accepted.
>
> "The nucleus is heavier than the electron cloud" ×
> The above statement is **not specific**. It does not tell us how mass is concentrated in the nucleus.
>
> "The negative charges are around the atom" ×
> The above statement is **not accurate**. The electrons are found around the nucleus, not the atom.

(b) (i) Down the group, nuclear charge and shielding effect increases, thus **effective nuclear charge differs little**. However, the **number of quantum shells increases**, and the **outermost electrons are further away from the nucleus / the attraction between the nucleus and the outermost electron is weaker [1]**. Thus, the **number of quantum shells is the more important factor [1]** and ionic radii decreases down the group.

> As mentioned, effective nuclear charge differs little down the group. Hence effective nuclear charge is unable to explain the trend in ionic radii. Instead,

the increasing number of quantum shells is the main explanation as the distance between the valence electrons and the nucleus must increase with more quantum shells. Nevertheless, there is a need to compare all three factors (nuclear charge, shielding effect and number of principal quantum shell) when explaining trend in ionic radius down the Group as required by the syllabus.

Technical terms need to be used judiciously. The following statements are not accepted.

"*nuclear* charge of the cation remains constant at +2" ×
The above statement is incorrect. Nuclear charge is not the same as charge of an ion!

"there is an increase in number of *valence* shells" ×
The above statement is incorrect. Valence shell refers to the outermost quantum shell, and there is only one valence shell regardless of the atom/ion.

"the number of principal *subshells* increases" ×
The above statement does not explain the trend in ionic radius accurately. Down the group, the principal quantum number increases, not the number of subshells in each principal quantum shell. Note that while shielding effect will still increase due to an increase in the number of subshells, the increase in shielding effect will be less as compared to the shielding afforded by an increase in the number of principal quantum shells.

Finally, the charge of ion is not relevant to the trend in ionic radii. Be mindful of the fundamental basis of the concepts you apply.

(ii) Down the group, the thermal stability of Group 2 carbonates **increases**. **[1]**

The charge of the Group 2 ions is constant, but the ionic radii increases down the group. Hence, **charge density, and hence polarizing power decreases down the group**. As such, the **electron cloud of the carbonate ion is distorted to a smaller** extent down the group, and **more energy is required to break the covalent bonds in the carbonate ion**. Therefore, the temperature required for thermal decomposition increases down the group.

Key ideas: Charge density, polarizing power, distortion of the electron cloud, energy required to break covalent bonds.

[0] 1 key idea
[1] 2 or 3 key ideas
[2] 4 key ideas

This question is generally well done, and most students are able to state and explain the trend in thermal decomposition of Group 2 carbonates.

Common misconceptions are as follows:
1) It is incorrect to say that thermal decomposition of group 2 carbonates involves overcoming the ionic bonding that exists between group 2 cations and carbonate anions. Thermal decomposition involves breaking covalent

bonds within the carbonate anion, **not** the ionic bonds between the cation and anion.

2) It is incorrect to refer to polarisability (of an anion) when you meant polarising power (of a cation).

3) It is incorrect to use effective nuclear charge to explain the trend in charge density – the two concepts are different!

(iii) $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ **[1]**

This question is generally well done.

(c) One mole contains exactly **<u>6.02 x 10^{23}</u>** elementary entities. **[1]**

Students are highly encouraged to commit this definition to memory in its entirety. Most responses were inaccurate and inadequate, and less ideal alternatives were grudgingly accepted.

Do note that while atoms/molecules were accepted, they are not ideal because they are too specific and 'mole' is a more general measurement of quantity.

(d) **(i)** $pV = nRT$

$100000 \times (35.00 \times 10^{-6}) = n \times 8.31 \times (273 + 30)$

$n = 1.39 \times 10^{-3}$ mol

[1] correct conversion and substitution

[1] answer

This calculation is generally well done.

(ii) Let the mass of magnesium carbonate be x g

Mass of barium carbonate is (0.15 – x) g

$$\frac{x}{84.3} + \frac{0.15-x}{197.3} = 1.39 \times 10^{-3}$$

[1] correct reasoning regarding stoichiometric relationship

x = 0.0927 g

Amount of magnesium carbonate = $0.0927 \div 84.3 = 1.10 \times 10^{-3}$ mol

[1] correct amount in moles

Mole fraction of magnesium carbonate = $1.10 \times 10^{-3} \div 1.39 \times 10^{-3} = 0.791$

[1] calculates mole fraction

There are many approaches to solving this question, and there were a fair number of efficient and elegant responses.

The crux of this calculation is to recognise that the amount of carbon dioxide determined in **(d)(i)** is formed from unequal amounts of each carbonate, and writing an equation that connects the answer in **(d)(i)** to the mass of each carbonate in the mixture.

(iii)

- Weigh a **known mass** of the mixture
- React the mixture with a **known** amount of **excess** hydrochloric acid.
- Titrate an aliquot with a **standard solution of sodium hydroxide**

[1] Stated general approach – to titrate acid with an aqueous base
[1/2] uses a known mass of the mixture / uses all of the sample mixture
[1/2] uses excess acid
[1/2] amount of acid is known / concentration and volume of the acid is known
[1/2] titrates using a standard solution / titrant is of known concentration

Many students are unfamiliar with the term indirect (back) titration. You can refer to your lecture notes, 04 Reactions and Stoichiometry, Section 3.3, for a recap.

The question asked for an outline, and it was stated that details regarding quantities, glassware, and calculations are not needed. Thus, the focus is to describe the most crucial features of the experimental procedure, without which, the experiment will fail. These features are highlighted in the answer above.

The question specifically asked for indirect titration to be used. Therefore, all other approaches will receive no credit (even if it works). Titrations of solid carbonate directly in the conical flask are not accepted.

It was noted that many students thought that the acid-base reaction of magnesium carbonate or barium carbonate will result in a residue that requires filtration. If hydrochloric acid or nitric acid was used, the resulting products are water soluble.

3 **(a)** Al_2O_3 is an amphoteric oxide / has both acidic and basic property **[1]**

Reaction with acid: $Al_2O_3 + 6H^+ \rightarrow 2Al^{3+} + 3H_2O$ **[1]**
(accept equation using $HCl/H_2SO_4/HNO_3$ but must be balanced)

Reaction with base: $Al_2O_3 + 2OH^- + 3H_2O \rightarrow 2[Al(OH)_4]^-$ **[1]**
(accept equation using NaOH but must be balanced)

<u>Al^{3+}</u> has a **<u>high charge density</u>** (or Al^{3+} has high charge and small ionic radius) **[1/2]** and hence it **<u>polarizes O^{2-}</u>** anion, result in **<u>covalent character</u>** in Al_2O_3 **[1/2]**

This is a recall question. Refer to Section 4.3.3 of Periodicity notes.

Do note that Al_2O_3 **<u>does not</u>** react with water.

Many students were unable to write the equation for reaction of Al_2O_3 with strong base. Do pay attention to the product as well as the stoichiometric coefficient.

Read the question carefully. In addition to describing the amphoteric property of Al_2O_3, you need to **<u>explain why</u>** Al_2O_3 is amphoteric. Ionic oxides are basic while covalent oxide are acidic. Al_2O_3 is amphoteric as it is an ionic oxide with covalent character and you should explain why Al_2O_3 has covalent character. It is not sufficient to just talk about Al^{3+} having high charge density. You need to go on to explain the polarization of O^{2-} that results in covalent character.

(b) **(i)** Al^{3+} acts as a Lewis acid by **<u>accepting lone pair of electrons / electron pair</u>** from OH groups on cotton and alizarin. **[1]**

You can see from Fig. 3.1 that dative bonds are formed from OH groups on cotton to Al^{3+}. Similarly, dative bonds are formed from O atoms on alizarin to Al^{3+}. This means Al^{3+} is accepting lone pair of electrons from OH groups on cotton and from O atom on alizarin which makes it a Lewis acid (*not* Bronsted acid). Do take note of the definition of a Lewis acid which is an **<u>electron pair</u>** acceptor. Inaccurate answer such as Al^{3+} accepts electrons did not gain credit.

Read the question carefully, it is not asking "why", but **<u>how</u>** Al^{3+} acts as an acid in this structure, hence answers about Al^{3+} having high charge density etc. are irrelevant.

(ii) **<u>Phenol</u>** is acidic and hence **<u>deprotonated in alkaline medium,</u>** to form phenoxide. **[1]**

Reject alizarin is deprotonated. Must identify OH group / phenol / mention to form O^-.

<u>Phenoxide is more electron rich than phenol</u> and is able to **<u>better donate its lone pair</u>** to Al^{3+}. **[1]**
OR **<u>Phenoxide is negatively charged</u>** and is **<u>attracted more strongly to Al^{3+}</u>** than electrically neutral phenol.

Comparison of phenoxide to phenol must be made to get second mark.

Comparing the structure of alizarin on page 12 and the structure in Fig 3.1, you will see that one of the phenol functional group on alizarin is deprotonated and the O^- group forms dative bond with Al^{3+}. Since phenol is acidic (apply your organic chemistry concept), the alkaline medium helps to convert phenol to phenoxide. Phenoxide is better able to donate an electron pair to Al^{3+} as its O atom is more electron rich than in phenol. The lone pair on O of phenol is delocalized over the benzene ring which makes the lone pair less available for donation to Al^{3+}. Do note that it is incorrect to say that phenol does not have lone pair to donate to Al^{3+}. The lone pair on O of phenol is less available but not totally unavailable.

Alternatively, you can explain your answer in terms of stronger electrostatic attraction between positively charged Al^{3+} and negatively charged O^- part of phenoxide that allows the deprotonated alizarin to be more strongly attracted to Al^{3+} compared to alizarin with electrically neutral OH group. Do note that when the deprotonated alizarin is sufficiently close to Al^{3+}, a dative bond will be formed where phenoxide donates lone pair to Al^{3+}. The interaction between Al^{3+} and phenoxide is not an ionic bond.

Do answer the question given. Addressing what happens in the "acidic" condition is not relevant since the question is about alkaline conditions.

(iii) HCl / H_2SO_4 / HNO_3 **[1]**
(accept compound with transition metal ion)

Al^{3+} helps to bond the dye to cotton by forming dative bond with both cotton and dye. For more dye to enter the water, it means some alizarin is no longer bonded to cotton i.e. the dative bond between alizarin and Al^{3+} is disrupted.

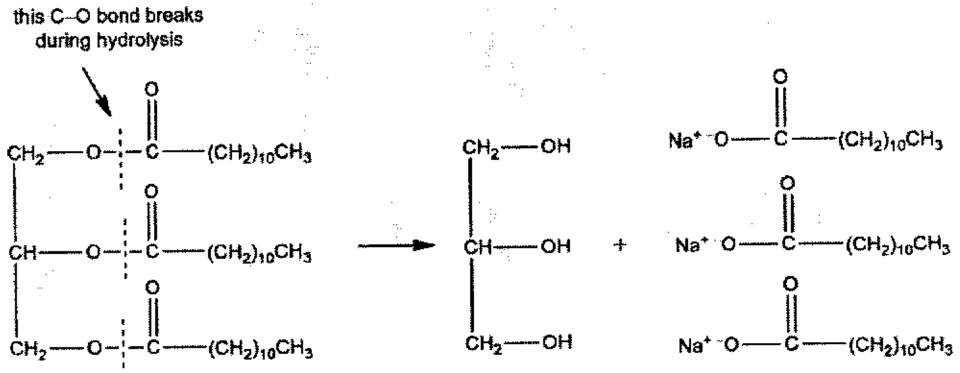
From **(ii)**, we know that alkaline medium is needed to form the structure in Fig. 3.1. Hence the substance added should be a strong acid such as HCl or H_2SO_4 that will protonate the phenoxide to reform phenol. Heat from the boiling water can cause some dative bond to break and when HCl is added, H^+ will protonate the phenoxide to reform phenol. Phenol does not bind so well to Al^{3+} and hence alizarin is no longer bonded to cotton through Al^{3+} and it enters the water.

Compounds with transition metal ion such as Fe^{3+} can also be added as the transition metal ion will compete with Al^{3+} and form dative bond with alizarin. When alizarin is no longer bond to Al^{3+}, it will not bond to cotton and hence enters water. Since the formation of complex ion by transition metal ion is no longer in the syllabus, you need not know this although it was acceptable as an answer.

(c) **(i)** $CH_3(CH_2)_{10}CO_2^-Na^+$ **[1]**

You need to know how to interpret the structural formula of compound **G**. Read the structural formula from left to right and draw out its structure.

Recognise that **G** contains three **ester** groups: "OCO" which means -O-C=O group so **G** will undergo alkaline hydrolysis:



sodium salt **H**

The ester functional group is hydrolysed in the presence of NaOH to form the alcohol (with 3OH groups) and the carboxylate salt, which is the sodium salt **H**.
Note that the alcohol group will not be deprotonated in NaOH.

(ii) $NaA(s) \rightleftharpoons Na^+(aq) + A^-(aq)$
$K_{sp} = 0.108^2 = 0.0117$ mol^2 dm^{-6} **[1]**

With the given solubility of NaA, substitute into the K_{sp} expression to obtain its value.

(iii) Addition of NaC*l* **increases [Na⁺]** which **increases ionic product of NaA such that IP > K_{sp}** / causes the **equilibrium position for $NaA(s) \rightleftharpoons Na^+(aq) + A^-(aq)$ to shift to the left**. **[1]**

Since **H** can be precipitated as a solid, you should see it as a sparingly soluble salt that is made up of Na^+ and A^-. Addition of NaC*l* will increase $[Na^+]$ and hence ionic product (IP) increases. When IP > K_{sp}, precipitation occurs. You can also explain your answer in terms of shift in equilibrium position but the correct equilibrium equation must be given.

(iv) $NaA(s) \rightleftharpoons Na^+(aq) + A^-(aq)$

At the moment when NaA precipitates, IP = K_{sp}
$[Na^+](1.00 \times 10^{-2}) = 0.0117$ **[1/2]**
$[Na^+] = 1.17$ mol dm^{-3} **[1/2]**

$[Na^+]_{\text{from NaCl}} + [Na^+]_{\text{from NaA}} = [Na^+]_{\text{total}}$
$[Na^+]_{\text{from NaA}} = 1.00 \times 10^{-2}$ mol dm^{-3}
$[Na^+]_{\text{from NaCl}} + 1.00 \times 10^{-2} = 1.17$
$[Na^+]_{\text{from NaCl}} = 1.16$ mol dm^{-3}
η(NaC*l*) required = $500 \times 10^{-3} \times 1.16 = 0.580$ mol **[1/2]** *(ecf allowed)*
Mass of NaC*l* required = $0.580 \times (23.0 + 35.5) = 33.9$ g **[1/2]** *(ecf allowed)*

Alternative
Assume $[Na^+]_{\text{from NaA}} << [Na^+]_{\text{from NaCl}}$,
$[Na^+]$ added = 1.17 mol dm^{-3}
η(NaC*l*) required = $500 \times 10^{-3} \times 1.17 = 0.585$ mol **[1/2]** *(ecf allowed)*
∴ Mass of NaC*l* required = $0.585 \times (23.0 + 35.5) = 34.2$ g **[1/2]** *(ecf allowed)*

Precipitation first occurs at the point when IP = K_{sp}.
IP = $[Na^+][A^-]$

A^- can only come from **H**. Hence $[A^-] = 1.00 \times 10^{-2}$ mol dm^{-3}. Substitute this value into IP = $[Na^+][A^-] = K_{sp}$ to get $[Na^+]$ at equilibrium. Note that you must substitute **concentrations** into the K_{sp} expression, *not* the number of moles!

There are two sources of Na^+: from NaA and from NaC*l*. $[Na^+]$ is thus the sum of $[Na^+]$ from NaA and $[Na^+]$ from NaC*l*.

Alternatively, you can also assume that $[Na^+]$ from NaA << $[Na^+]$ from NaC*l* given the low solubility of NaA.

From here, work out $[Na^+]$ from NaC*l*. With 500 cm^3 of solution, work out number of moles and hence mass of NaC*l*.

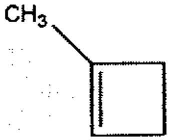
(v) $CH_3(CH_2)_{10}CO_2^-$ (A^-) has a **larger anionic radius** and hence **less energy is released when it forms ion-dipole interaction with water / weaker ion-dipole interaction**. **[1]**

OR: Long **hydrophobic / non-polar / alkyl chain** of $CH_3(CH_2)_{10}CO_2^-$ **interferes with the formation of ion-dipole interaction** with water.

An ionic compound is soluble in water due to formation of ion-dipole interaction between the ions and water molecules. The difference here is the anion, $CH_3(CH_2)_{10}CO_2^-$ (A^-) and C*l*$^-$. If **H** is less soluble in water, it means that the ion-dipole interaction form between its ions and water molecule is weaker. This is due to the much larger anionic radius of $CH_3(CH_2)_{10}CO_2^-$. Recall enthalpy change of hydration is proportional to q/r. With larger size of anion, less energy is released from formation of ion-dipole interaction with water and hence enthalpy change of solution will be less exothermic. Alternatively, you can also consider the long carbon chain of $CH_3(CH_2)_{10}CO_2^-$ that disrupts ion-dipole interaction with water.

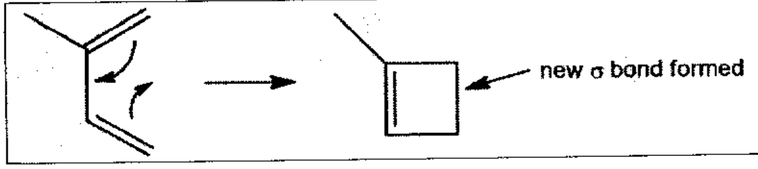
Do note that while $CH_3(CH_2)_{10}CO_2^-$ (A^-) has a long non-polar alkyl chain, A^- still has a $-CO_2^-$ group that can form ion-dipole interaction with water, hence the main reason for the solubility of **H** in water is about the strength of this ion-dipole interaction. It is incorrect to say **H** or A^- forms dispersion forces with water without recognizing its ability to also form ion-dipole interaction with water. Several students also wrongly refer to **H** as a "molecule".

(d) (i)



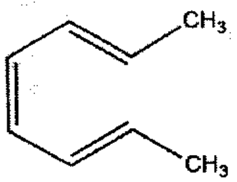
[1]

Draw in the curly arrows on 2-methyl-1,3-butadiene and follow the pattern given to work out the structure of compound **J**.

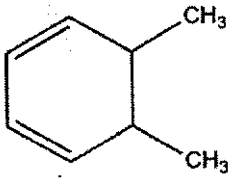


(ii)
- **K** undergoes **electrophilic addition** with $Br_2(l)$.
- Since the product contains 6 Br atoms, **K** contains **3 C=C**. *(can mark for this in the structure of* **K** if the correct deduction based on reaction with Br_2 is made)
- Both **K** and **L** undergoes **oxidative cleavage** with hot concentrated $KMnO_4$. (strong oxidation / oxidation are not accepted. Side-chain oxidation cannot be correct since there is no benzene ring.)
- Since **N** does not give orange precipitate with 2,4-DNPH, it **does not contain carbonyl functional group / does not contain ketone** (product of oxidative cleavage cannot be aldehyde).

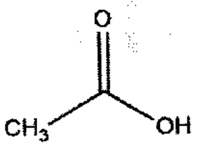
[1/2] for each bullet.



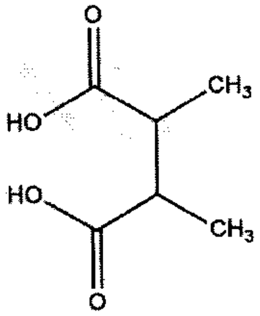
K



L



M

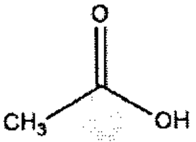


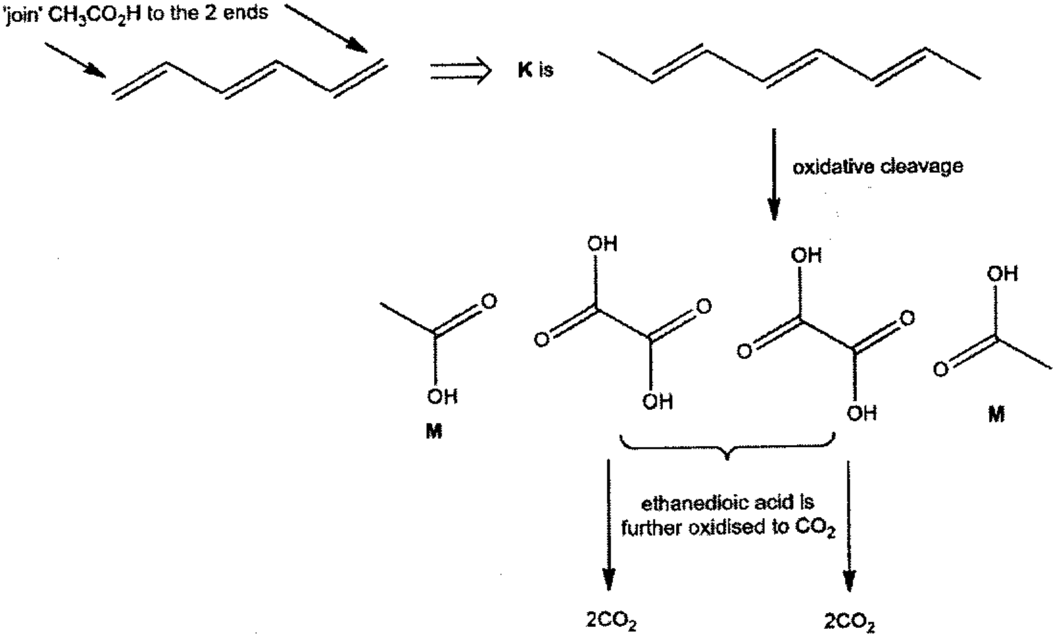
N

[1] for each structure

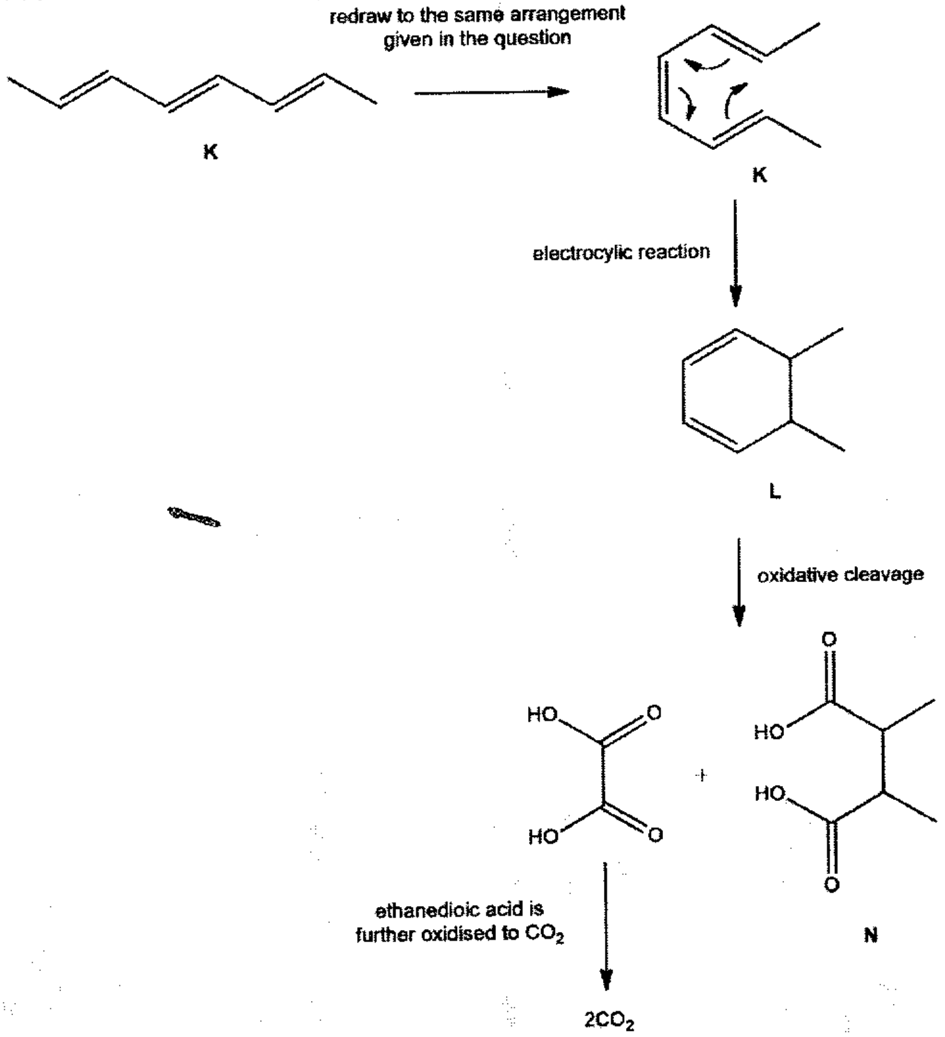
First, you should recognise that **K** is a conjugated alkene, i.e. it has C=C that alternates with C–C. From the reaction of **K** with liquid bromine, you should deduce that **K** has 3 C=C. From here, you know **K** has the following fragment:

You need to add in 2 more carbon atoms to fit C_8H_{12}. On reaction with hot concentrated $KMnO_4$, oxidative cleavage takes place to form CO_2 and **M** ($C_2H_4O_2$).

With 2 carbon atoms, **M** ($C_2H_4O_2$) can only be . Use 2 of these molecules and the above structure with 3 C=C that you have deduced above, you should be able to work out the structure of **K**:



From the structure of **K**, work out the structure of **L** and hence structure of **N**:



Remember to state the type of reaction involved and functional group deduced for each reaction mentioned.

4 (a) (i) **Free radical substitution [1]**

Initiation

$Br—Br \longrightarrow 2Br\cdot$ (half arrow must be drawn for homolytic fission)

Propagation

$CH_3CH_2CH_3 + Br\cdot \longrightarrow CH_3\dot{C}HCH_3 + HBr$

$CH_3\dot{C}HCH_3 + Br_2 \longrightarrow CH_3CHBrCH_3 + Br\cdot$

Termination

$2Br\cdot \longrightarrow Br_2$

$CH_3\dot{C}HCH_3 + Br\cdot \longrightarrow CH_3CHBrCH_3$

$2CH_3\dot{C}HCH_3 \longrightarrow (CH_3)_2CHCH(CH_3)_2$

[1] for each stage of mechanism

This was a straightforward mechanism question. More work is needed to recall the details of the mechanism unerringly as too many students did not obtain full marks for this part.

Common errors include:

1. Not reading the question carefully to note that the product asked for is 2-bromopropane and **not** 1-bromopropane.

2. Assuming that the alkane was 3,3-diethylpentane instead of propane

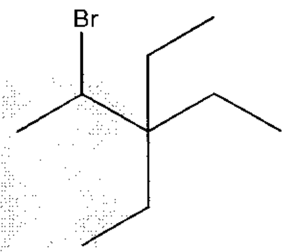
3. Not including the name of the mechanism. It was not given in the question so it must be written down.

4. Not including the stage names: initiation, propagation and termination

5. Forgetting the 2^nd^ step in the propagation stage.

6. Not including all the 3 equations in the termination stage of the mechanism

(ii)



[1]

Constitutional isomer **[1]**

Positional isomer was accepted but not preferred as the syllabus states constitutional or structural isomer.

Note that the question asked for the isomeric relationship between **U** & **V**. Hence the answer should be **U** & **V** are constitutional isomers. It should not be expressed as constitutional isomerism as that implies the type of isomerism. Although no penalty was imposed in this part for this exam, it may not always be the case at the A levels, so greater care with the use of terms should be observed.

(iii) There are **12 1° H atoms & 8 2° H atoms** **[1]** that may be substituted hence the **ratio of U to V** = 3 : 2 **[1]**.

**Ensure the ratio matches the correct compounds. Accept 12 : 8 or 60 : 40 or percentages.*

The question asked for a prediction of the proportion of **U** to **V**. Hence it is expected that a ratio should be worked out. Note that without further information, prediction of proportions of various substituted products in FRS is solely based on the probability of substituting different H atoms. It is not expected of students to predict proportions based on relative stabilities of the different radicals formed when no data is given.

(iv) A 2° alkyl radical is **more stable** than the 1° alkyl radical as it has **more electron donating alkyl groups** to stabilize the radical. **[1]**

Formation of 2-bromopropane is more favourable as it involves the formation of 2° alkyl radical intermediate, while a 1° alkyl radical (intermediate) is formed when 1-bromopropane is formed.

Hence 2-bromopropane will be formed in larger quantities than 1-bromopropane.

Note that having more electron-donating alkyl groups helps stabilize the radical as the carbon carrying the unpaired electron is electron deficient.

(b) **(i)** $K_c = \frac{[HBr]^2}{[H_2][Br_2]}$ **[1]**

Solution 1

Let the initial mass of the mixture be 100 g. (Conservation of matter means that the final total mass of mixture is also 100 g)

% mass of H_2 + Br_2 at equilibrium = 22.35 %

Hence mass of H_2 + Br_2 at equilibrium = 22.35 g

Let equilibrium number of moles of H_2 = x mol. Hence equilibrium number of moles of Br_2 = x mol.
Note that the equilibrium mole ratio of H_2 : Br_2 must be equimolar like initially.

Hence 2.0x + 159.8x = 22.35 **[1]**
x = 0.138 mol **[1]**
Number of moles of HBr = 77.65 ÷ 80.9 = 0.9598 mol **[1]**

$$K_c = \frac{(0.9598/V)^2}{(0.138/V)(0.138/V)} = \mathbf{48.4}$$

[1]

Solution 2

Let the initial mass of the mixture be 100 g. (Any starting mass is acceptable)

initial number of moles of H_2 = initial number of moles of Br_2 = *x* mol

2(79.9)*x* + 2*x* = 100
***x* = 0.618 mol** (initial amount of H_2 & Br_2) **[1]**

The mass before and after the reaction should be 100 g. (Conservation of matter)

Therefore equilibrium mass of HBr = 77.65 g
equilibrium number of moles of HBr = 77.65 ÷ (79.9 +1) = **0.9598 mol** **[1]**

	H_2 (g)	+ Br_2 (g)	⇌ 2HBr (g)
I / mol	0.618	0.618	–
C / mol	– 0.4799	– 0.4799	+ 0.9598
E / mol	0.138	0.138	0.9598

[1]

$$K_c = \frac{(0.9598/V)^2}{(0.138/V)(0.138/V)} = \mathbf{48.4}$$

[1]

Solution 3

	H_2 (g)	+ Br_2 (g)	⇌ 2HBr (g)
I / mol	x	x	–
C / mol	– y	– y	+ 2y
E / mol	x – y	x – y	2y

Mass of H_2 = 2.0 (x – y)
Mass of Br_2 = 159.8 (x – y)
Mass of HBr = 2y(80.9) all mass expressions **[1]**

Since % mass of HBr at equilibrium = 77.65%,

$$\frac{2y(80.9)}{2y(80.9)+2.0\,(x-y)+159.8\,(x-y)} = \frac{77.65}{100}$$

[1]

y = 0.7765x **[1]**

$$K_c = \frac{(2y/V)^2}{((x-y)/V)^2} = \frac{(2\times0.7765x)^2}{(x-0.7765x)^2} = \mathbf{48.3}$$ **[1]**

In this solution, the initial amount (x mol) cancel off and could be substituted with any value like 1 mol.

Solution 4

Let the initial mass of the mixture be 100 g. (Conservation of matter means that the final total mass of mixture is also 100 g)

At equilibrium, % mass of HBr = 77.65 % & % mass of H_2 + Br_2 = 22.35 %

Hence equilibrium mass of HBr = 77.65 g
Equilibrium number of moles of HBr = 77.56 ÷ 80.9 = 0.9598 mol

Hence equilibrium mass of H_2 + Br_2 = 22.35 g

Using Mr ratio to find the mass of H_2 & Br_2 by proportion:

equilibrium mass of H_2 = $\frac{2}{2+159.8} \times 22.35 = 0.276\ g$
equilibrium number of moles of H_2 = 0.276 ÷ 2.0 = 0.138 mol

equilibrium mass of Br_2 = 22.35 – 0.276 = 22.074 g
equilibrium number of moles of Br_2 = 22.074 ÷ 159.8 = 0.138 mol

$$K_c = \frac{(0.9598/V)^2}{(0.138/V)(0.138/V)} = \mathbf{48.4}$$

The expression for *K*c was also very badly done by a number of students. The subscript 'c' in *K*c refers to concentration. Hence the expression should be written in concentration terms. Too many students were confused by the gas state symbols given in the chemical equation. A gas may have concentration as well. For a fixed number of moles of gas in a given volume, the concentration of the gas may be calculated by taking the number of moles of gas divided by the volume. This is reflected in rearranging the ideal gas equation:

$$pV = nRT$$

$$\frac{n}{V} = \frac{p}{RT}\text{, where } \frac{n}{V} = \text{concentration}$$

The calculation for this part was very badly done by a significant number of students. There was confusion between number of moles and mass. Many equated the mole ratio to the mass ratio which is wrong. To equate both would require that the mole ratio be multiplied by the relevant *M*r.

There are 4 possible ways to solve this question.

Solution 1, 2 & 4 fixes the total mass of the reactants at 100 g. Any mass could be used but 100 g was used for simplicity as % mass was used. Using this, many students fix the initial number of moles of H_2 and Br_2 as 1 mol. This is wrong as the combined mass of H_2 & Br_2 (100g) will not give 1 mol of either. This was a very common error and highlighted a poor grasp of stoichiometry.

Note also that there is equimolar amount of H_2 and Br_2 initially. Hence it's incorrect to assume starting mass of H_2 and mass of Br_2 that will not give 1:1 mole ratio. Likewise, there is equimolar amount of H_2 and Br_2 at equilibrium. Hence it is incorrect to calculate equilibrium mass of H_2 or Br_2 as 22.35/2 g.

Solution 3 fixes the initial amount of reactants as x mol. Any starting number of moles could be used. Many students were confused as they tried to incorporate the 77.65% by mass into the ICE table by fixing the mass (most often at 100 g). In this case, the starting number of moles pre-determines the total mass of each substance and hence the masses cannot be fixed like for Solution 1 & 2.

There were a significant number of students who simply substituted the mass % into the ICE table and the *K*c expression without realizing that they should be using no. of moles.

A final note to all students is to flesh out the working in your answer. There were too many answers where only a set of numbers were written in the ICE table with no working to account for how the student arrived at those numbers. These answers were not given any credit if the final *K*c value was wrong. No method marks could be awarded.

(ii) **I** The **composition would not change** as the pressure increases, as there are **equal number of moles of gas on each side** of the equilibrium. **[1]**

II The **forward reaction is exothermic** and as the temperature increases, the **equilibrium position will shift to the LHS to absorb the heat** and the composition will have **less HBr / more reactants**. **[1]**

A common mistake in this part was not stating what would happen to the composition of the equilibrium mixture.

Part I was well-answered. There is no shift in the equilibrium position since both sides of the equilibria had the same number of moles of gas.

Part II was not as well answered as many students either forgot to explain that the equilibrium position shifted to the left or the backward endothermic reaction was favoured. Note that the endothermic reaction absorbs heat and thereby helps counteract the rise in temperature. The idea of absorbing heat energy must be clearly explained in the answer before full credit is given.

An alarming number of students were unable to tell that $\Delta H < 0$ means that the forward reaction is exothermic.

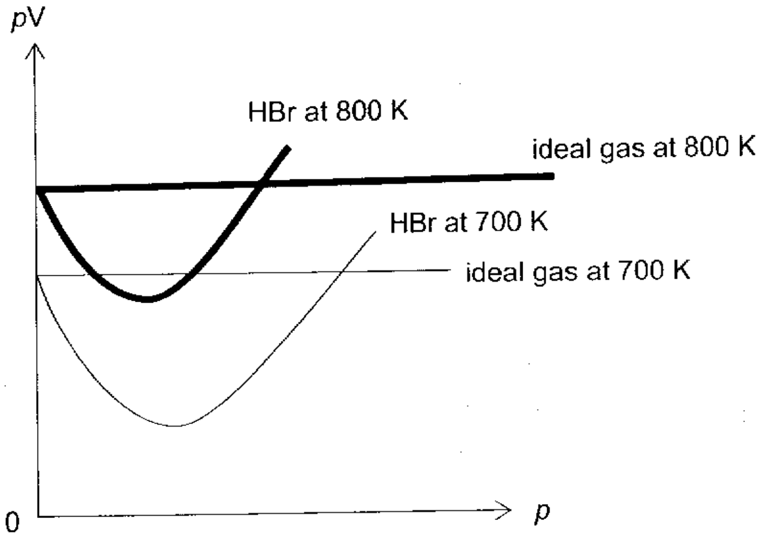
(c) **(i)** At high temperature, **gas particles have higher kinetic energy**. **[½]**
Hence the gas particles have enough energy to **overcome intermolecular forces which is considered negligible** and hence the gas approaches ideal behaviour. **[½]**

At low pressure, the **gas particles are further apart**. [½]
This causes the **molecular size of the gas particles to be negligible relative to the volume of the container** and hence the gas approaches ideal behaviour. [½]

This part was very badly done. Many students gave the properties of the gas, that is, small molecular size and weak intermolecular forces of attraction which would allow the gas to behave ideally. Too many also stated the 3 assumptions of the kinetic theory of gases which the question didn't ask for. Students should distinguish between the terms: conditions vs properties vs assumptions.

Note that the question asks for the conditions by which a gas may behave ideally. Conditions refer to temperature and pressure. For example, standard conditions refer to 298 K, 1 bar & 1 mol dm^{-3} (for solutions). So comment on temperature and pressure when asked for conditions.

(ii)



[1] for ideal gas (horizontal line above 700 K)
[1] for HBr (dip from new ideal must be smaller than original dip from 700 K, ignore part of curve above ideal gas line)

Too many students ignored the instructions to copy the diagram in the space below.

For answers which only had lines drawn for HBr at 800 K, no credit was given. Both sets of lines (for HBr and ideal gas at 700 K and 800 K) must be present in order for the comparison of the size of the dip below the ideal gas line (deviation from ideal behaviour) for each temperature to be made.

The gas should deviate less from ideal behaviour at 800 K as indicated in part **(i)**. Students should translate their understanding of the conditions to how the graph should look like.

The ideal gas graph at 800 K should be higher than that for 700 K. The ideal gas equation: $pV = nRT$. Hence, the value of pV depends on the value of nRT. Since n & R are constants, the value of nRT therefore depends solely on T in this case. Hence pV at 800K will be a bigger value than pV at 700 K.

5 (a) Reactant molecules diffuse towards the catalyst surface and are adsorbed onto the active sites. **[0.5]**

The bonds in the reactant molecules weaken**[0.5]**, and the activation energy is lowered. **[0.5]**

Reactant molecules are brought closer together **[0.5]** (concentration of reactants on the surface of the catalyst increase) and are correctly orientated. **[0.5]**

When the product is formed, it desorbs and diffuses away from the catalyst surface freeing up the active sites. **[0.5] either desorb or free up active sites.**

> The question asks for the mode of action of the metal catalyst. What this means is that students are expected to describe the processes involved when the metal catalyst helps to increase the rate of reaction. There are 3 main things that the catalyst helps to do: weaken bonds in reactants, increase reactant concentration on the surface of the catalyst and correctly orientates the molecules. Answers should capture these points and describe the process of adsorption and desorption.
>
> In reality, the solid catalyst is not pure. Students need to recognise that the reactant must be adsorbed onto the active site, **not** other parts of the catalyst, for the reaction to be catalysed."

(b) chromium **[1/2]** and manganese **[1/2]**

> Electronic configuration of Fe^{3+} : [Ar] $3d^5$
> Electronic configuration of Mn : [Ar] $3d^5 4s^2$
> Electronic configuration of Cr : [Ar] $3d^5 4s^1$
>
> Please note that Vanadium has an electronic configuration of [Ar] $3d^3 4s^2$ rather than [Ar] $3d^5$.

(c) (i) conjugate acid-base pair OR $[Fe(H_2O)_5(OH)]^{2+}$ is the conjugate base of $[Fe(H_2O)_6]^{3+}$**[1]**

> A conjugate acid-base pair constitutes two species which differ from each other by a proton.

(ii) $[H^+] = 10^{-1.78} = 0.0166$ mol dm^{-3} **[1]**
$K_a = (0.0166)^2 / 0.15 = 0.00184$ mol dm^{-3} **[1]**

Accept $K_a = (0.0166)^2 / (0.15 - 0.0166) = 0.00207$ mol dm^{-3} **[1]**

(iii)	$[Fe(H_2O)_6]^{3+}$ +	OH^- →	$[Fe(H_2O)_5(OH)]^{2+}$ + H_2O
Initial/mol	0.15 x 0.050 = 0.0075	0.10/40 =0.0025 **[1]**	
Final/mol	0.0050	0	0.0025 **[1] ratio**

$0.00184 = [H^+] \times 0.0025 / 0.0050$
$[H^+] = 0.00368 \text{ mol dm}^{-3}$

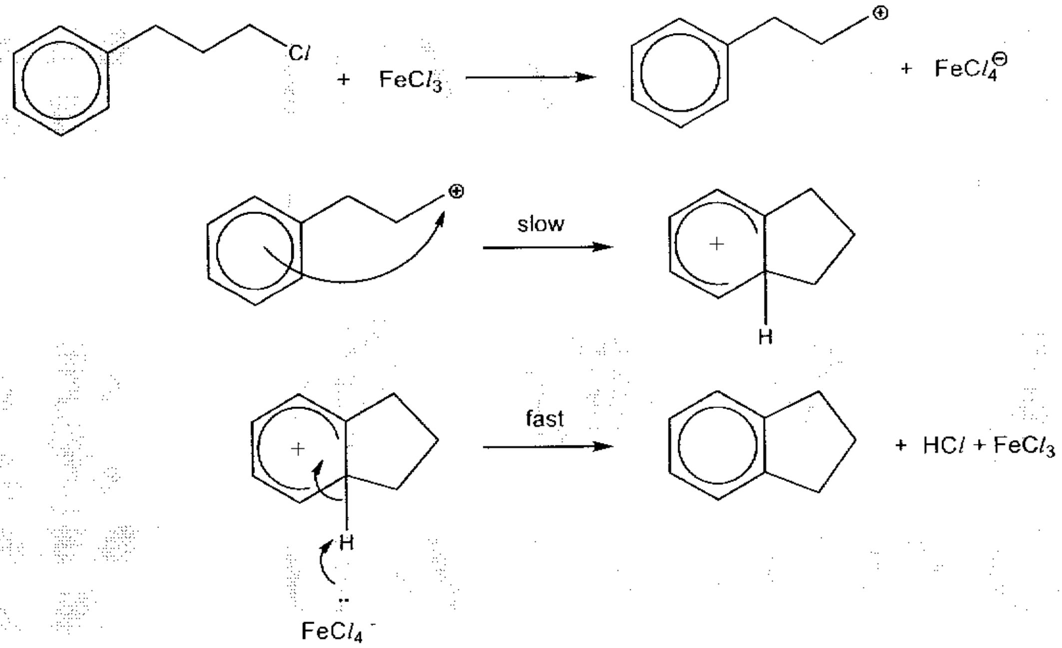
pH = 2.43 **[1] ecf**

If $K_a = 0.00207 \text{ mol dm}^{-3}$, then pH = 2.38

Some students mistakenly subtract amount in moles from initial concentration of 0.15 mol dm^{-3}. Others did not consider that the original amount of $[Fe(H_2O)_6]^{3+}$ would have decreased due to the neutralization reaction.

While the original solution contains $0.0166 \times 0.050 = 8.30 \times 10^{-4}$ mol of H^+, it is in an equilibrium with $[Fe(H_2O)_6]^{3+}$. This means that when the sodium hydroxide is added, the position of equilibrium will shift right as OH^- removes H^+. So, the initial amount of acid reacting should remain to be 0.0075 mol and not $(0.0075 - 8.30 \times 10^{-4})$ mol.

(d) (i)



[1] for every step, **[-0.5]** for every mistake in each step

Name of mechanism is given. Thus, no credit is given for it.

The C–Cl bond in **A** will not break on its own. The Lewis catalyst must be introduced to allow this to occur.

Arrow must start from ring / bond and end at the atom where the new bond will be formed. For the slow step, arrow must end on carbon atom and not at + charge. For the fast step, arrow must point back to the ring to form the delocalised pi system.

Slow step must be indicated in a mechanism

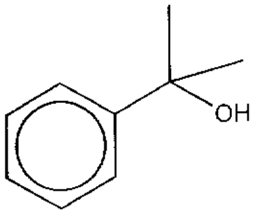
Commonly, the HC*l* in the last step was left out, which will leave the equation unbalanced.

(ii) The electron-donating methyl group increases electron density of the benzene ring, causing **C** to be more susceptible to electrophilic substitution and increasing the reactivity. **[1]**
(deduct 0.5 m if no mention of increase electron density of benzene)

A clear answer must involve how an alkyl group being electron-donating will result in an increase in reactivity of an electrophilic substitution reaction. In this case, it must have resulted in an increase in electron density in the benzene ring and attract the electrophile (electron deficient species) more easily.

(e) **(i)** **E** is a tertiary alcohol which does not undergo oxidation. **[1]**

E:

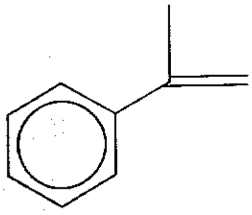


[1]

M_r of **C** or **D** = 154.5
M_r of **F** = 154.5/130.9 x 100 = 118.0 **[1]** (or words to the effect)

OR **D** undergoes **nucleophilic substitution** to give **E**. Both **D** and **E** undergo **elimination** to give **F**.

F:



[1]

A handful of students thought that a phenol is an alcohol. Please note that alcohols and phenols are two different functional groups, and they are collectively known as hydroxyl compounds.

When M_r of D is 30.9% larger than the M_r of F, it means that:
For every 100g of F, there will be 130.9g of D.
NOT for every 100g of D, there will be 130.9g of F.
Likewise, an increase in 30.9% of M_r should be taken with reference to M_r of **F** and not **D**.

Some students successfully worked out a loss in 30.9% will result in the elimination of HC*l* with M_r of 36.5 and deduced compound **F**.

Quite a number of students thought that **F** was benzoic acid. Firstly, the M_r of benzoic acid is 26.6% more than M_r of **D** (it will not be rounded off to 30.9%). Discounting the 6 carbons required to form the benzene ring, there are 3 remaining carbons for **E**. All 3 carbon atoms must be used to form a tertiary alcohol, since this alcohol does not oxidise in the presence of acidified potassium dichromate. With no other hydrogen atoms attached to the carbon with the -OH group, **E** could not have undergo side-chain oxidation to form benzoic acid too.

(ii) **D** to **F**: ethanolic NaOH, heat **[1]**
E to **F**: conc sulfuric acid, heat OR aluminium oxide, heat **[1]**