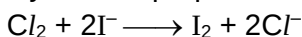


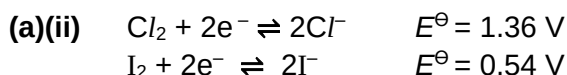
2021 H2 Chemistry Prelim Paper 3 Suggested Solutions

- C1 (a)(i)** $\text{Cl}_2(\text{aq})$ is added to solution of KI, followed by hexane. The mixture is shaken and the hexane layer turns purple, indicating the presence of I_2 .



Examiner Comments

- This question was poorly attempted as many students were unable to properly describe a redox reaction involving the two halogens. In order to show the relative oxidizing abilities of Cl_2 and I_2 , you **must** choose a redox reaction.
- It is also necessary to describe the use of hexane for a visual observation of the reaction.



$$E^\ominus_{\text{cell}} = 1.36 - 0.54 = +0.82 \text{ V}$$

Since the $E^\ominus_{\text{cell}}$ value is positive, the reaction is spontaneous.

OR

Since the $E^\ominus$ value for Cl_2 is higher than that of I_2 , chlorine has a higher tendency for reduction and is hence, a stronger oxidising agent.

Examiner Comments

- Many students were able to quote the correct $E^\ominus$ to use and/or calculate the correct $E^\ominus_{\text{cell}}$ value. However, do remember to compare them and state a conclusion.
- Unfortunately, many students did not apply this knowledge into answer part (1).

- (a)(iii)** Half-equation for iodine: $\text{I}_2(\text{aq}) + 2\text{e}^- \rightleftharpoons 2\text{I}^-(\text{aq})$
Hence, ascorbic acid and iodine react in a 1:1 mole ratio.

$$\text{Amount of iodine titrated} = 0.005 \times 0.02205 = 1.1025 \times 10^{-4} \text{ mol}$$

$$\text{Amount of ascorbic acid present in } 10.0 \text{ cm}^3 = 1.1025 \times 10^{-4} \text{ mol}$$

$$\begin{aligned} \text{Amount of ascorbic acid present in } 100 \text{ cm}^3 &= 10 \times 1.1025 \times 10^{-4} \\ &= 1.1025 \times 10^{-3} \text{ mol} \end{aligned}$$

$$\text{Mass of ascorbic acid present} = 1.1025 \times 10^{-3} \times 176.0 = 0.194 \text{ g}$$

$$\text{Mass of ascorbic acid present in } 100.0 \text{ g of candy} = 0.194 \text{ g}$$

$$\% \text{ by mass of ascorbic acid} = \frac{0.194}{100.0} \times 100\% = 0.194\%$$

Examiner Comments

- Generally well done.
- Students are reminded to include units in the intermediate steps of your working.

- (b)** Add equal amounts of bromopropane, chloropropane and iodopropane in separate test tubes and warm the test tubes in a water bath maintained at 50°C .

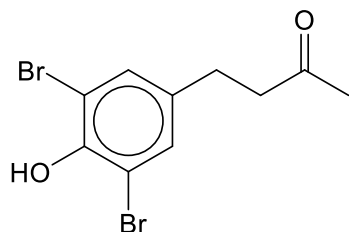
Then add 5.0 cm^3 of silver nitrate solution in ethanol to each compound and note the time taken for the precipitates to first appear.

The mixture containing iodopropane will form a yellow ppt of AgI first, followed by the mixture containing bromopropane with a pale cream ppt of AgBr and in the mixture containing chloropropane with a white ppt of AgCl.

Examiner Comments

- Many students who attempted this question gave reasonable answers but left out important details, and hence, did not earn full credit. While this is not a full planning question as you would see in Paper 4, your experiment outline must still include steps to ensure the aim of the experiment can be achieved.
- For instance, many students left out the heating step so the reaction did not even take place. Note that **heating in a water bath** is recommended for this experiment as temperature should be kept constant for all three reactions (since this experiment is used to determine rate of reaction).
- Most answers used equal volumes of the RX compounds, but in order to observe the rate of the reaction, you must start with equal **amounts** of the compound. Since the three compounds have different densities, using the same volume or mass will not equal the same amount.
- A number of students did not measure the time taken for the precipitate to first appear. Since there are three reactions, it's impossible to start the three reactions and a stopwatch simultaneously. Hence, you must use a stopwatch to **record time** (instead of a visual observation of which is faster).
- Many students did not include the expected sequence of formation of ppt as part of the expected observations.
- Many incorrect answers used NaOH(aq) as the reagent with heat, followed by neutralization with HNO₃ before adding AgNO₃. This will not work because the hydrolysis reaction would be complete by the time the acid is added. Adding AgNO₃ would then give an immediate ppt for all three compounds.
- Some answers suggested carrying out the hydrolysis for a fixed interval of time and then weighing the mass of ppt form. This will not work because the molar mass of each ppt is different!

(c)(i)

*Examiner Comments*

- Generally well done.

(c)(ii) NaBH₄ / H₂, Ni, heat / LiAlH₄ in dry ether
Reduction reaction

Examiner Comments

- Generally well done, although some students read the question wrongly and gave for reagents and conditions for the oxidation of alcohol instead.
- Students are reminded to use the correct conditions for the reaction.

(c)(iii) There are two functional groups on rhododendrol: phenol and aliphatic alcohol.

When added to sodium hydroxide, only phenol will react to form phenoxide.

This is because phenol is a stronger acid than the aliphatic alcohol. In the phenoxide ion, the p-orbital of the O atom overlaps with the π -electron cloud of the benzene ring and the negative charge/lone pair on the O atom is delocalised into the ring. Hence, the phenoxide ion is resonance-stabilised and more stable than the alkoxide ion. **OR**

This is because the aliphatic alcohol is a weaker acid than phenol. The O atom on the alkoxide ion is bonded to two electron donating alkyl groups which intensifies the negative charge on the O atom. The alkoxide ion is less stable than the phenoxide ion.

Examiner Comments

- Most students who attempted this question gave good answers which correctly explained the stability of the two conjugate bases. However, students wrote too much or were too detailed in their explanations, which would lead to insufficient time for the rest of the paper.
- Students need to be clear in their answers whether they are referring to the acid or the conjugate base.

(c)(iv) Add 2,4-dinitrophenylhydrazine/2,4-DNPH to each compound in a test tube.

- For RK, orange ppt is formed
- For rhododendrol, no ppt is formed

Add $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$, $\text{H}_2\text{SO}_4(\text{aq})$ to each compound in a test tube and heat in a hot water bath.

- For rhododendrol, orange acidified $\text{K}_2\text{Cr}_2\text{O}_7(\text{aq})$ turns green
- For RK, the solution remains orange

Examiner Comments

- Generally well done.
- Oxidation using acidified KMnO_4 will not distinguish the two compounds as both will undergo side-chain oxidation.
- The iodoform test also will not distinguish the two compounds as both will give positive tests (RK has a $-\text{COCH}_3$ group, and rhododendrol has a $-\text{CH}(\text{OH})\text{CH}_3$ group at the end of the chain).
- Students should give the observations for both compounds.

(d)(i) The reaction is acidic hydrolysis.

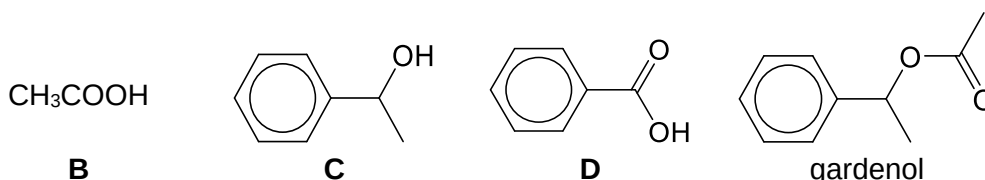
- Gardenol is an ester
- **B** is a carboxylic acid
- **C** is an alcohol/phenol

Examiner Comments

- Generally well done.
- Many students did not name the functional group in gardenol, but were not penalized.

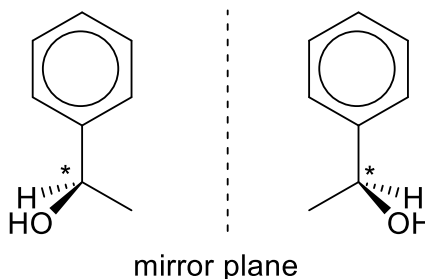
(d)(ii)

Gardenol has formula $C_{10}H_{12}O_2$	C:H ratio $\approx 1:1 \Rightarrow$ benzene ring present
Gardenol reacts with acidified $KMnO_4$ to give B and D	Gardenol undergoes oxidation and acidic hydrolysis. C undergoes oxidation to form D C is not phenol OR C is an alcohol D is a ketone / carboxylic acid
C reacts with acidified $KMnO_4$ to give D	C undergoes side-chain <u>oxidation</u> D is benzoic acid

*Examiner Comments*

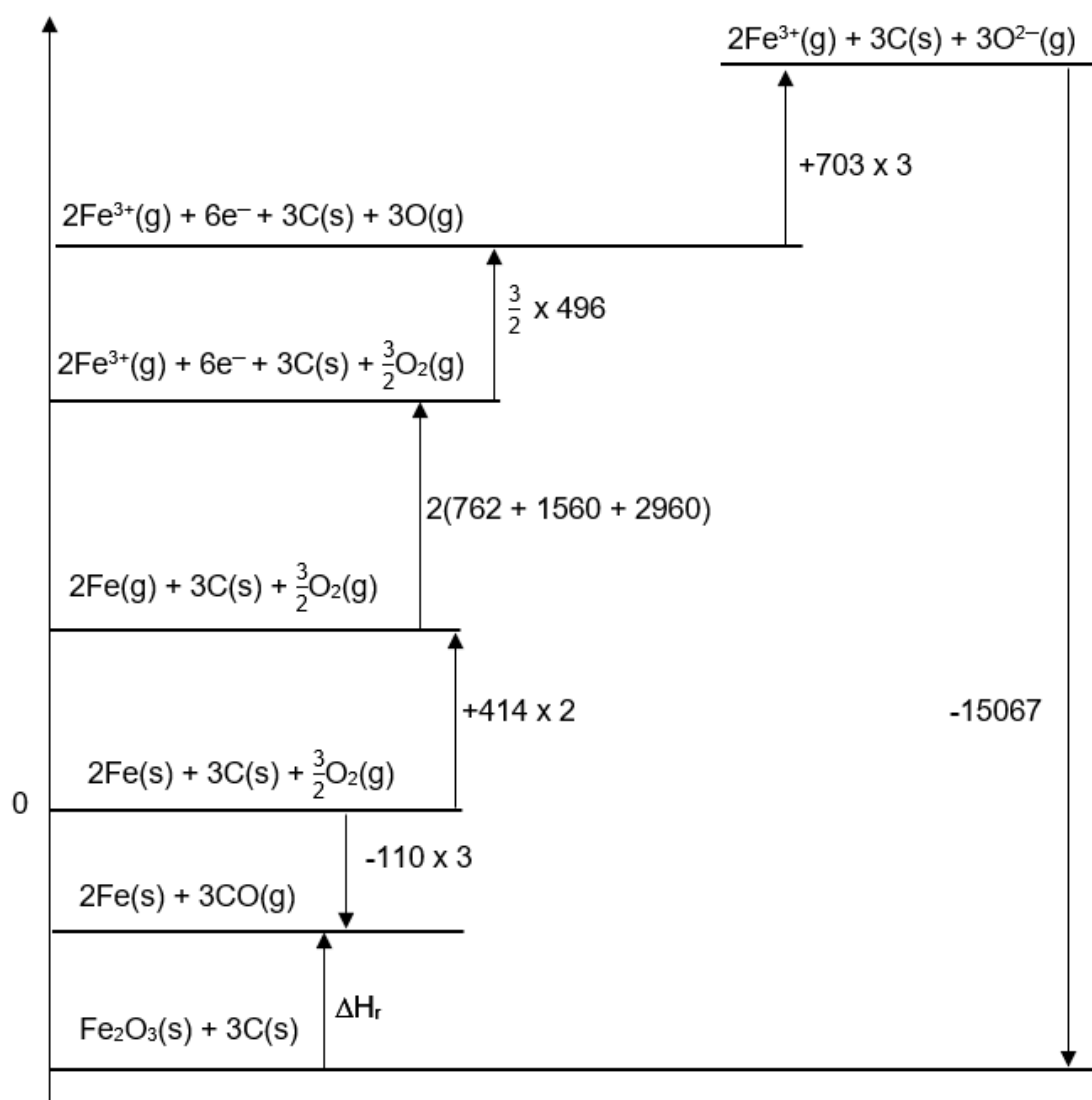
- Although many students were able to identify **B** from its chemical formula, the rest of the structures proved challenging.
- Students should use the information already deduced in part (i) to help in the elucidation without having to repeat those deductions (i.e. the hydrolysis reaction or the acid-carbonate reaction).
- Since gardenol is $C_{10}H_{12}O_2$ and the hydrolysis reaction involves H_2O (opposite of condensation), given that **B** is $C_2H_4O_2$, the chemical formula of **C** is $C_8H_{10}O$. Understanding that **C** is an alcohol with a chiral centre, there is only one possible structure for **C**.
- Many students forgot that **C** will undergo side-chain oxidation to form benzoic acid, not a ketone.
- Like in part (i), some students did not draw the structure of gardenol.
- Many students incorrectly deduced that the reaction with acidified $KMnO_4$ was the oxidative cleavage of $C=C$ bonds. Students should use the chemical formula of gardenol to deduce the presence of a benzene ring. Hence, there should be no alkene present.
- Students are reminded to draw your correct structures clearly and in pen. You must cross out all other structures which were part of your working but should not be marked, whether in pen or pencil.

(d)(iii) The carbon bonded to the -OH group is chiral because it is bonded to four different groups.

*Examiner Comments*

- Many students forgot to explain why the indicated C is chiral, or did not draw the tetrahedral angles properly.

C2 (a)

Energy / kJ mol⁻¹

$$\Delta H_r = -(-15067) - (+703 \times 3) - \left(\frac{3}{2} \times 496\right) - 2(762 + 1560 + 2960) - (+414 \times 2) + (-110 \times 3) = +492 \text{ kJ mol}^{-1}$$

Examiner Comments

- This question was poorly done with these main issues:
 - Many students combined several steps into one arrow. This is unacceptable unless the steps are of the same nature. e.g. atomisation of metal and non-metal/ ionisation energies. IE and EA should not be combined into one arrow/one row of arrows as the production and consumption of electrons would not be observable.
 - A huge number of students performed EA before IE. This doesn't make sense as EA takes in electrons, which are produced from the IE step. As such, **IE must happen before EA**. The omission of electrons produced in the IE steps was commonly observed as well.
 - 3rd IE of Fe was omitted by a handful of students. Fe₂O₃ contains Fe³⁺, not Fe²⁺.
 - The atomisation of oxygen using O=O bond energy was omitted by many as well. Students have to be aware that BE data can be found in the data booklet and may not be provided as additional data in the question. As such, knowing the enthalpy changes definitions well would remind them that they need to retrieve such data from the data booklet and **not** convert O₂ molecules to O²⁻ directly via EA.
 - Good knowledge of the enthalpy changes definitions is also necessary for arrows to be drawn in the correct direction (from correct reactant species to correct product species) and for enthalpy changes to be multiplied by the correct coefficients.

- Students are reminded to include state symbols and to balance equation written for each step.
- For students drawing energy level diagrams, please be reminded that the ΔH_r arrow has to be pointing in the correct direction based on their calculated value. E.g. it shouldn't be pointing down (suggesting exothermic) when the calculated value is positive. As such, do check and correct the diagram after your calculation.

- (b)(i) Nanoparticles have relatively large surface area (when compared to the same volume of material made up of bigger particles) resulting in more / faster adsorption of the SeO_3^{2-} ions.

Examiner Comments

- This question was poorly done with many being unaware that nanoparticles provide a large surface area to volume ratio (hint in question: extremely small particles that have nanometer-sized dimensions).
- Among those who noted the larger surface area, a handful continued with a faster rate of reaction. There was however no reaction, just mere adsorption, as stated in the question.
- Many students gave a lengthy description of how the adsorption of toxic substances on the nanoparticles facilitates the removal, however they did not address **how** the **use of nanoparticles** will **improve** the removal. Students should consider how a property of nanoparticles is relevant in this context.

- (b)(ii) At high alkaline pH, the OH^- ions will compete with SeO_3^{2-} to be adsorbed on the surfaces of the nanoparticles. OR
 $\text{Fe}(\text{OH})_2$ gets oxidised to $\text{Fe}(\text{OH})_3$ in an alkaline medium. As such, there are less $\text{Fe}(\text{OH})_2$ available for adsorption/ SeO_3^{2-} adsorbs less effectively on the surfaces of $\text{Fe}(\text{OH})_3$ nanoparticles.

Examiner Comments

- The question was poorly done as well. Many students wrote the OH^- reacted with $\text{Fe}(\text{OH})_2$ to form $\text{Fe}(\text{OH})_3$. This statement is flawed because
 - 1) 'react' is too vague. Students learn it in QA that such a reaction is oxidation.
 - 2) the oxidising agent is O_2 (in air or dissolve in water), not OH^- . The oxidation of $\text{Fe}(\text{OH})_2$ to $\text{Fe}(\text{OH})_3$ by O_2 can take place in an alkaline medium.
- A significant number of students mentioned that SeO_3^{2-} and OH^- would repel each other, thus hindering the adsorption. This may not be true as the adsorption may not be obstructed, unless the OH^- is adsorbed onto the surface and repelled SeO_3^{2-} away, which leads to the first answer on competition.
- Students who suggested that $\text{Fe}(\text{OH})_2$ forms a complex ion with OH^- should note that $\text{Fe}(\text{OH})_2$ is insoluble in excess NaOH (covered in QA), so complex formation does not occur.
- The toxic substances adsorb on the surfaces of the **solid** $\text{Fe}(\text{OH})_2$ nanoparticles. Students who discussed how the increased $[\text{OH}^-]$ decreases solubility of $\text{Fe}(\text{OH})_2$ and hence $[\text{Fe}^{2+}]$ were not given credit.

- (b)(iii) $\text{SeO}_3^{2-} + 3\text{H}_2\text{O} + 4\text{e}^- \rightarrow \text{Se} + 6\text{OH}^-$

Examiner Comments

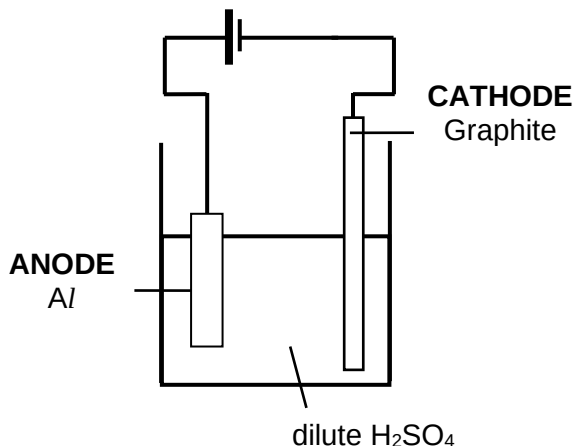
- This part is generally well done.
- Students should read the question carefully and balance the reduction half equation in alkaline medium.

- (b)(iv) $\text{Fe}(\text{OH})_2$ gets oxidised by air/ O_2 / SeO_3^{2-} to form red-brown $\text{Fe}(\text{OH})_3$.

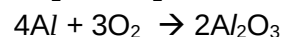
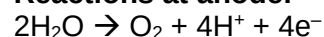
Examiner Comments

- This part is generally well done.
- The main reason for not scoring here is concluding that the red-brown colouration is due to Fe^{3+} instead of $\text{Fe}(\text{OH})_3$. Students should be aware that Fe^{3+} is yellow/orange and soluble in solution (and would not appear red-brown on the surfaces of the nanoparticles).

(c)



Reactions at anode:



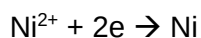
Examiner Comments

- The main issue for this part is that despite being guided in the question to draw an electrolytic cell, many students drew an electrochemical cell instead. Do note that anodising is the process of coating aluminium objects with aluminium oxide via electrolysis (with only 1 tank and use of an electrical source such as a battery).
- A significant number of students also wrote the oxidation half equation of Al instead of the overall equation for the formation of Al_2O_3 . Note that oxygen evolved at the anode reacts with Al at the anode, oxidising it to Al_2O_3 .

- (d)(i) Number of moles of HF in solution **E** = $2 \times \frac{19.90}{1000} \times 0.40 = \underline{0.0159 \text{ mol}}$

$$Q = It = n_e F$$

$$n_e = \frac{0.40 \times (32 \times 60)}{96500} = 0.0079585 \text{ mol}$$



$$\text{Number of moles of Ni}^{2+} = \frac{0.0079585}{2} = 0.0039793 \text{ mol}$$

$$\text{Number of moles of NiF}_2 \text{ in solution } \mathbf{E} = 2 \times 0.0039793 = \underline{0.00796 \text{ mol}}$$

Examiner Comments

- A significant number of students were careless and overlooked this point: 'Solution **E** was divided into **two equal parts**'. It is important to multiply the amount of HF and NiF_2 in one part of solution **E** by 2 to answer the question.
- Students who showed clear working to determine the n_e , and hence the amount of Ni^{2+} , did better for this question.
- Do express the final answer to 3.s.f.

- (d)(ii) Number of moles of $O_2 : HF : NiF_2 = 0.004 : 0.0159 : 0.00796$
 $= 1 : 4 : 2$



Considering the number of F, $12 = 2x + 4 + 4 \Rightarrow x = 2$

Examiner Comments

- As the question requirement was to **deduce** the value of x, logical deduction must be presented.
- The information on 0.004 mol of O_2 produced along with solution **E** must be taken into consideration to write a balanced equation for the reaction between K_xNiF_6 & H_2O . Students should check their working in (i) for any errors if a balanced equation cannot be written.

- (e)(i) $pV = nRT$
 $(100 \times 10^3) V = \left(\frac{300}{170.7} \times 4\right) \times 8.31 \times (170+273)$
 $V = 0.259 \text{ m}^3$

Examiner Comments

- Note that mole ratio of $Ni(CO)_4 : CO = 1 : 4$. Many students mistakenly substituted amount of $Ni(CO)_4$ as amount CO.
- As the volume of CO is not determined at r.t.p nor s.t.p, the molar gas volumes ($24.0 \text{ dm}^3 \text{ mol}^{-1}$, $22.7 \text{ dm}^3 \text{ mol}^{-1}$) at these conditions cannot be used.

- (e)(ii) The sign of $\Delta S_r^\ominus$ is positive because the reaction leads to an increase in the number of gaseous particles in the system such that the system becomes more disordered than before.

Examiner Comments

- This part is generally well done.

- (e)(iii) At 70°C , $Ni(CO)_4$ is formed as a gas and can be separated from the solid impurities. It also ensures rate of reaction is sufficiently high to make it practical on an industrial scale.

Examiner Comments

- A large group of students had the misconception that high temperatures would favour an exothermic reaction, thus increasing yield. On the contrary, **high temperatures favour endothermic reactions** and would decrease yield in this reaction.
- It is not true that the reaction in step 1 is spontaneous at 70°C and not at room temperature. Since $\Delta H_r^\ominus < 0$ and $\Delta S_r^\ominus < 0$, reaction is spontaneous at low temperatures (room temperature).
- Some students gave an elaborate, yet unnecessary, explanation of how a substance exist as a gas above its boiling point and as a liquid below its boiling point. Students should focus on how $Ni(CO)_4$ as a gas is beneficial in this application to purify Ni.

- (e)(iv) For the reaction in step 2 to be spontaneous,

$$\Delta G_r^\ominus < 0$$

$$\Delta H_r^\ominus - T\Delta S_r^\ominus < 0$$

$$+160.9 - T(+410/1000) < 0$$

$$T > 392 \text{ K (or } 119^\circ\text{C)}$$

Alternatively,

At 170°C ,

$$\Delta G_r^\ominus = \Delta H_r^\ominus - T\Delta S_r^\ominus$$

$$= +160.9 - (170+273)(+410/1000)$$

$$= -20.7 \text{ kJ mol}^{-1} < 0$$

At 70°C ,

$$\Delta G_r^\ominus = \Delta H_r^\ominus - T\Delta S_r^\ominus$$

$$= +160.9 - (70+273)(+410/1000)$$

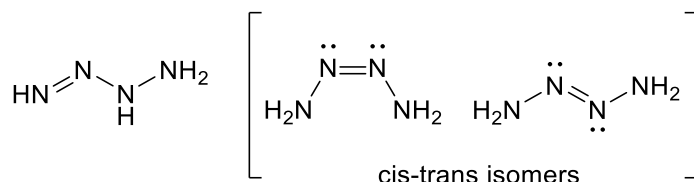
$$= +20.3 \text{ kJ mol}^{-1} > 0$$

Increasing the temperature from 70°C to 170°C (which is $> 119^\circ\text{C}$) ensures that the reaction is spontaneous.

Examiner Comments

- The first step to getting this question right is to recognise that step 2 is the reverse of step 1 and so $\Delta H_r^\ominus$ of reaction in step 2 = +160.9 kJ mol⁻¹.
- Students were expected to **show relevant calculations** as required by the question. Either calculation of minimum T for reaction to be spontaneous OR $\Delta G_r^\ominus$ at 70 °C and 170 °C was accepted. Qualitative comparison of the signs and the magnitude of ΔH and $-T\Delta S$ is inconclusive and was not accepted.
- Do include units for the $\Delta G_r^\ominus$ calculated.

C3 (a)

*Examiner Comments*

- When drawing the structures, quite a number of students forgot that N cannot expand its octet. Many erroneously drew structures containing N with 4 or even 5 bonds. The correct number of bonds around N should be 3.
- When showing cis-trans isomers, it is important to show them with the proper spatial arrangement showing clearly the bond angle around N=N, including the presence of the lone pair of electrons on N. Drawing the cis-trans isomers as shown below is also an incorrect way of representation as the angle of 90 degree around N=N is wrong.



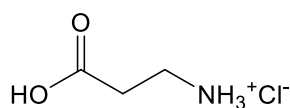
- (b)(i) NH_3 is a nucleophile and is repelled by the electron-rich C=C bond in ethene / there are no electron deficient sites in ethene.

Due to presence of electronegative N / electron-withdrawing -CN group, electron density is withdrawn away from the C=C bond. This causes the carbon of the terminal alkene to be more electron deficient, hence more susceptible to nucleophilic attack by NH_3 .

Examiner Comments

- Despite the fact that the question clearly required students to explain Fig. 3.1, many chose to focus only on the second reaction that produces 3-aminopropanenitrile, resulting in a penalty of marks. You should explain both reactions shown in Fig 3.1.
- Many students used the words “electronegative” and “electron-withdrawing” interchangeably. Be rigorously unambiguous in your answer. Students must know the difference – “Nitrogen is electronegative” while “-CN group is electron-withdrawing”.
- Some students identified the wrong carbon atom that is electron deficient. By referring to Fig. 3.1, it is not difficult to identify the electron deficient C as C3. Nucleophilic attack by NH_3 occurs at C3.
- One last point for all to note. It is not advisable to represent ethene as =. This is an ambiguous answer. It is better to write ethene as $\text{CH}_2=\text{CH}_2$.

(b)(ii)

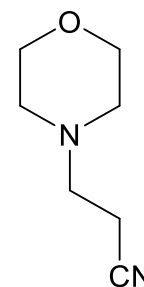
*Examiner Comments*

- This was generally well done. Many noted that the -CN group was hydrolysed while the -NH₂ group was protonated by dilute HCl.

(b)(iii) Morpholine has reacted.

There are 2 electron-donating alkyl groups bonded to N of morpholine which increases the electron density on N making the lone pair of electrons on N more available for nucleophilic attack. OR

The lone pair of electrons on N of phenylamine delocalises into the π electron cloud of benzene, making it less available for nucleophilic attack.



Examiner Comments

- This is another question that distinguished students who were conscientious in learning how to describe and explain their answers with accurate details and concepts from those who learned them haphazardly. Merely stating that the “electrons in phenylamine are delocalised and the negative charge is dispersed, thereby giving the C-N bond a partial double bond character” helps markers identify students who simply crammed random words without any understanding during their learning process. The statement quoted has the following flaws.
 1. Unclear – Be clear to state that the *lone pair of electrons on N* is delocalised into the π electron cloud of benzene.
 2. Incorrect – There is *no negative charge* to be dispersed in phenylamine.
 3. Irrelevant – A C-N bond with a partial double bond character is totally irrelevant in answering this question.
- Despite having identified that Fig. 3.1 involves a nucleophilic attack to form 3-aminopropanenitrile, many students now changed their minds and stated that the lone pair of electrons on N in morpholine is more available for reaction with a *proton (instead of electron-deficient C)*. The pitfall of memorizing answers or statements from other questions without clear understanding tend to result in students failing to contextualize their answers to the questions asked.
- Quite a large proportion of students got carried away in their explanation and forgot to draw the structure of the product.

(c)(i) $R_1R_2(CH_3)N$ is more basic than R_1R_2NH .

$R_1R_2(CH_3)N$ has an additional electron donating methyl / alkyl group bonded to N, making the lone pair of electrons on N more available for forming a dative bond to a proton.

Examiner Comments

- This is a direct recall question. It is surprising to see that there are students who fail to make the connection between the presence of an *additional* methyl group and the increased availability of lone pair of electrons on N.
- The answer is only complete when students recognize that having an *additional* methyl group causes the lone pair of electrons on N to be more available for forming a dative bond to a *proton*.

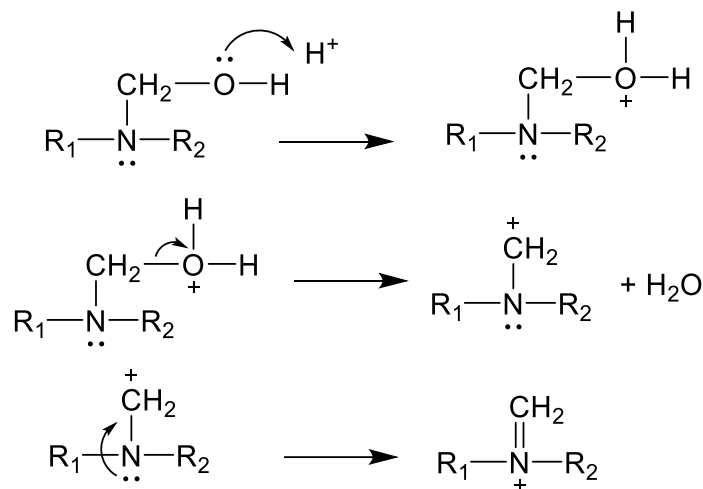
(c)(ii) ① NaBH_3CN is a weaker reducing agent. $-\text{CN}$ is an electron-withdrawing group / N is electronegative, making the H less electron rich / less δ^- in NaBH_3CN .

② If NaBH_4 is used, methanal would also be reduced.

Examiner Comments

- Since the question stated that both reducing agents are sources of H^- ions, it is only logical to relate the effect of the electron withdrawing $-\text{CN}$ group in making the H less electron rich, hence a weaker reducing agent.
- There are students who forgot the organic reactions that they have learnt when they encountered unfamiliar contexts. Some students erroneously wrote that NaBH_4 is too weak to reduce methanal. This shows the need to constantly revise organic reactions prior to the exams so that they can be confidently applied to unfamiliar contexts as well.

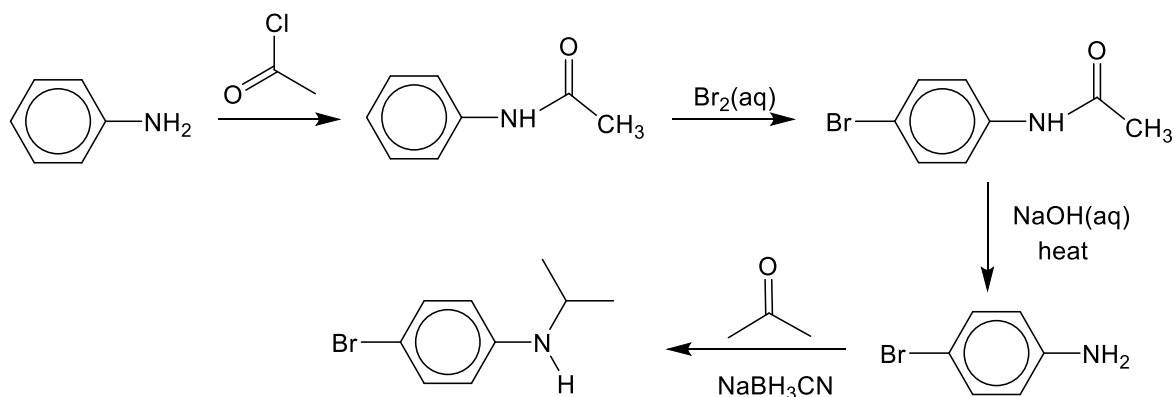
(c)(iii)



Examiner Comments

- Students who have understood the concept of arrow pushing in organic reaction mechanisms scored very well in this question.
- In step 1, when the $-\text{OH}$ group is protonated, the lone pair of electrons on O forms a dative bond with H^+ . This results in 3-bonded oxygen which bears a *positive charge*, and not H. Hence, this understanding has to be clearly demonstrated in the structure drawn.
- Step 2 states “Heterolytic fission of the C–O bond occurs.” There are students who drew arrows to represent homolytic fission instead. Many also failed to show the loss of a water molecule in this step.
- In step 3, the lone pair of electrons on N is pushed to form the C–N π bond. It is incorrect to draw the curly arrow from N to the carbon bearing the positive charge, which was commonly observed. This does not show the formation of the C–N π bond. The curly arrow should point to the middle of the C–N to illustrate the formation of the π bond.

(c)(iv)



Examiner Comments

- In order to produce a mono-brominated phenylamine, the amine group has to be converted to an amide, a less activating group. This explains the reaction between phenylamine and an acyl chloride in step 1.
- Subsequently, the amide has to be hydrolysed with an alkali to regenerate the amine.
- A handful of students left out this statement "You should include a suitable carbonyl compound in one of the steps and consider information given in Fig. 3.2.". As a result, they mistakenly chose to carry out nucleophilic substitution as their last step. This does not fulfil the requirement of the question.

- C4 (a)(i)** The order of reaction with respect to a given reactant is the power to which the concentration of that reactant is raised in the rate equation.

Examiner Comments

- A number of students could not quote the definition correctly. Some students had vague recollections and included incorrect unnecessary details – no credit was awarded in such cases. Students are reminded to learn the definitions from the *Reaction Kinetics* notes.

- (a)(ii)** ($V_{\infty} - V_t$) refers to the volume of N_2 yet to be evolved OR
 ($V_{\infty} - V_t$) is proportional to the amount / concentration of $C_6H_5N_2Cl$ remaining.

Examiner Comments

- Generally well done.
- Students should use the correct words to represent the relationship between the terms. For example, ($V_{\infty} - V_t$) is proportional (not "equal") to the amount / concentration of $C_6H_5N_2Cl$ remaining.

- (a)(iii)** As ($V_{\infty} - V_t$) decreased from 190 cm^3 to 95 cm^3 , half-life was 17 min.
 As ($V_{\infty} - V_t$) decreased from 180 cm^3 to 90 cm^3 , half-life was 17 min.
 Since ($V_{\infty} - V_t$) $\propto [C_6H_5N_2Cl]$, reaction is 1st order with respect to $C_6H_5N_2Cl$.

Examiner Comments

- Since ($V_{\infty} - V_t$) $\propto [C_6H_5N_2Cl]$, the graph can be used to show that the reaction is 1st order with respect to $[C_6H_5N_2Cl]$.
- Two values of half-life need to be quoted in order to deduce a first order reaction. An example of a clear statement quoting one half-life value is:
As ($V_{\infty} - V_t$) decreased from 180 cm^3 to 90 cm^3 , half-life = $20 - 2.75 = 17.25\text{ min}$.
 This statement clearly shows the values used to determine half-lives.
- An alternative to writing the above statement would be to have clearly drawn construction lines (dotted lines) linking the graph drawing and x-axis and y-axis, and double-headed arrows labelling each half-life value. Please refer to the lecture examples in *Kinetics* notes to revise how to draw the construction lines for half-lives.
- Students are also reminded to use a pen or a dark and sharp pencil to draw the lines and labels.

- (a)(iv)** H_2O is a solvent and is in excess. The concentration of H_2O does not change during the reaction.

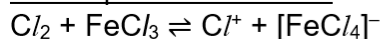
$$\text{rate} = k[C_6H_5N_2Cl]$$

Examiner Comments

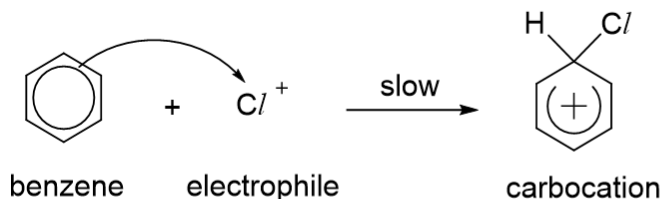
- Generally well done.

(b)(i) A suitable catalyst is $\text{FeCl}_3 / \text{AlCl}_3$.

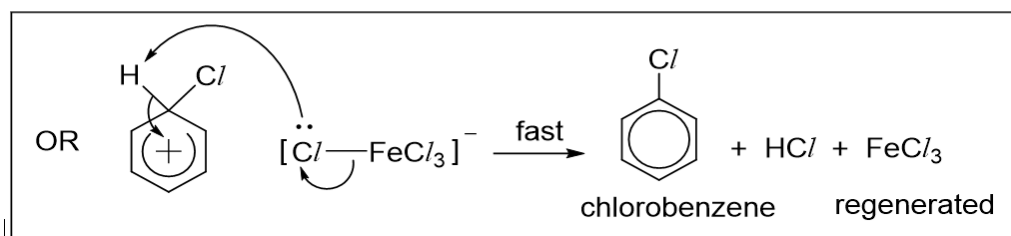
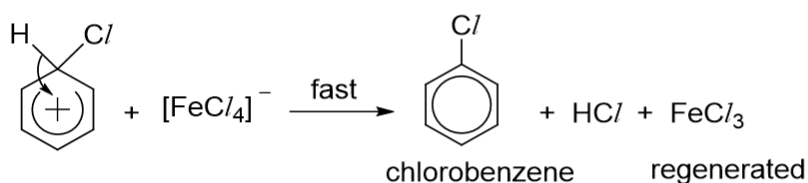
Electrophilic substitution



Step 1:



Step 2:



Examiner Comments

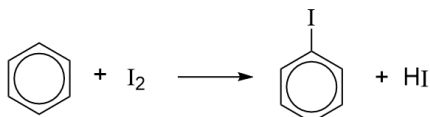
- Some students neglected to state the identity of the catalyst, as required by the question. It must be explicitly stated for credit to be awarded.
- Students are reminded to label the *slow* and *fast* steps in reaction mechanisms.
- The arrow in step 2 starts from the C–H bond, and not from the H atom, since the bond pair in the C–H bond are donated back to the carbocation.
- It is also necessary to show, in step 2, how the FeCl_3 is regenerated in the reaction.

(b)(ii) ΔH_{rxn} for iodination of benzene
 $= \text{BE}(\text{I}-\text{I}) + \text{BE}(\text{C}-\text{H}) - \text{BE}(\text{C}-\text{I}) - \text{BE}(\text{H}-\text{I})$
 $= +151 + 410 - 240 - 299 = +22.0 \text{ kJ mol}^{-1}$

Since ΔH_{rxn} is positive and ΔS_{rxn} is approximately 0, ΔG_{rxn} will be positive. Therefore, iodination of benzene is not spontaneous.

Examiner Comments

- The equation for the iodination of benzene is shown below:

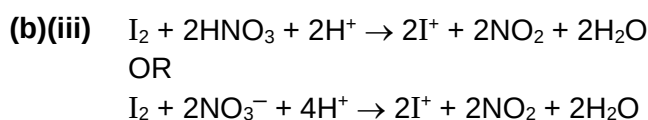


Bonds broken	C–H I–I	Bonds formed	C–I H–I
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Since the question allows us to assume that all reactants and products are the gaseous state during the reaction,

$$\begin{aligned} \Delta H_{\text{rxn}} &= \sum \text{BE}(\text{bonds broken}) - \sum \text{BE}(\text{bonds formed}) \\ &= \text{BE}(\text{I}-\text{I}) + \text{BE}(\text{C}-\text{H}) - \text{BE}(\text{C}-\text{I}) - \text{BE}(\text{H}-\text{I}) \end{aligned}$$

- A portion of the student population did not understand that when asked to comment on the *spontaneity* of a reaction, students need to immediately know that it refers to whether ΔG is positive or negative. It is then necessary to gather information about ΔS and ΔH .
- To comment on the spontaneity of a reaction: since we are assuming that reactants and products are in the gas phase, the change in number of gas particles during the reaction is zero, thus $\Delta S \approx 0$.
Since $\Delta G = \Delta H - T\Delta S$, $\Delta G \approx \Delta H$.
- $\Delta H > 0$ from our ΔH_{rxn} calculation, $\therefore \Delta G > 0$ and the reaction is non-spontaneous.
- There was inappropriate use of terms which led to marks lost. In this case, the absolute entropy before and after reaction remains the same, so some students explained that the entropy remained constant – that is alright. However, the entropy *change* is not constant, the entropy change is zero since there was no change in entropy.



Examiner Comments

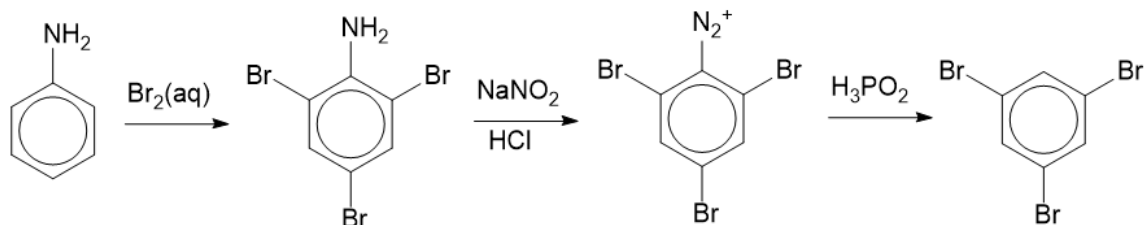
- Students are reminded to read the question carefully for the given reactants and products. Many students formed products like HOI, which was not given as a product.
- Some students also gave half-equations, instead of a balanced chemical equation. Please be aware of the difference! Half-equations describe either reduction or oxidation and have electrons in them to balance the charges. Chemical equations and ionic equations do not have electrons in them! Read the question carefully.
- To derive the overall equation, students need to first write the reduction and oxidation half-equations, before combining them to obtain the overall equation. You should not try to balance the equation just by trial and error, as you might not balance the charges correctly.
- The two half-equations are:
 $\text{I}_2 \rightarrow 2\text{I}^+ + 2\text{e}^-$ --- (1)
 $\text{HNO}_3 + \text{H}^+ + \text{e}^- \rightarrow \text{NO}_2 + \text{H}_2\text{O}$ --- (2)
 Hence the overall equation is given by (1) + 2×(2):
 $\text{I}_2 + 2\text{HNO}_3 + 2\text{H}^+ \rightarrow 2\text{I}^+ + 2\text{NO}_2 + 2\text{H}_2\text{O}$

(c)(i)

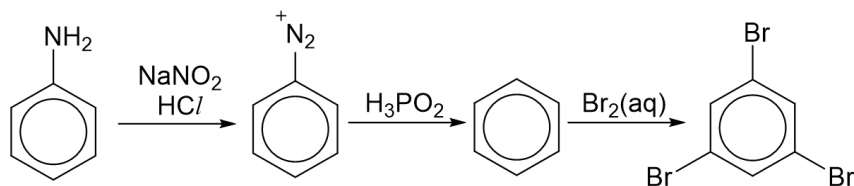
P	Q	Reagents and conditions
		Step 1: conc HNO_3 , conc H_2SO_4 , heat Step 2: Sn, conc. HCl , heat, followed by aq. NaOH Step 4: CuCN Step 5: $\text{H}_2\text{SO}_4(\text{aq})$, heat

Examiner Comments

- Students are reminded to read and use the given information in the question. A number of students tried to use ethanolic KCN in step 4 to obtain **Q**, instead of using the Sandmeyer reaction. The use of ethanolic KCN is limited to nucleophilic substitution in halogenoalkanes.
- In step 2, note that the reduction of phenylamine using Sn, conc. HCl must be followed up with neutralisation of the protonated ammonium salt formed, since amines are basic and get protonated in acidic medium.
- In step 5, hydrolysis of the $-\text{CN}$ group occurs and must be done in aqueous medium, in the presence of heat.

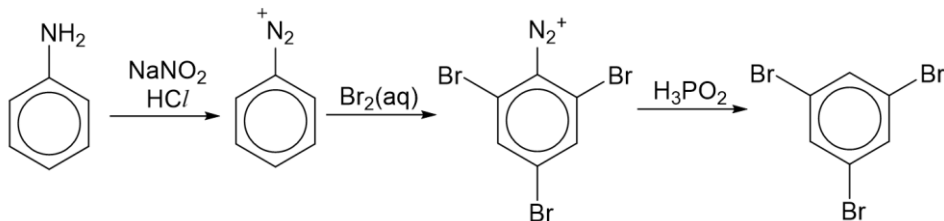


- Generally well done.
- Some common wrong answers are shown below.
 - Incorrect answer 1



- In step 3, benzene cannot be brominated using $\text{Br}_2(\text{aq})$. A catalyst such as FeBr_3 needs to be used together with Br_2 in a non-aqueous medium. Phenylamine reacts with $\text{Br}_2(\text{aq})$ directly because the $-\text{NH}_2$ group is highly activating, which makes the benzene ring of phenylamine more reactive, thus no catalyst is required for phenylamine. Using FeBr_3 , Br_2 in step 3 does not allow tri-bromination to be achieved.

- Incorrect answer 2

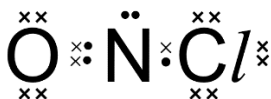


- The proposed reaction in step 2 cannot occur because the $-N_2^+$ group is highly deactivating. A mild reaction condition like $Br_2(aq)$ will not allow any reaction to take place.

In summary, the bromination step must be carried out as the first step, so that the major product of the synthesis has three –Br atoms substituted in the desired positions.

- This is a synthesis question. The structures of products of intermediate steps must always be included as part of your answer for any credit to be awarded.

C5 (a)(i)



- This was generally well done, except for a handful of candidates who forgot to indicate the lone pairs on O, Cl and even N. Do remember that all valence electrons (bonding or non-bonding) need to be shown in a dot-cross diagram. There were a few who miscounted the number of valence electrons on N, and even ended up with a lone electron on N.

(a)(ii) bent, 110°

Examiner Comments

- This was generally well done, except for a handful of candidates who incorrectly gave the shape as trigonal planar. The lone pair on N should repel the bond pairs to a greater extent such that the bond angle is less than 120°. Any value such that 90° < bond angle < 120° was accepted.
- Note that a value needs to be given, as required by the question, and not a range i.e., "<120°" is not acceptable.

(a)(iii) There are four electrons in the N=O bond as compared to only two electrons in the N–Cl bond and hence there is greater electrostatic attraction between the bonding electrons and the N and O nuclei, which causes these nuclei to be closer together in the N=O bond. The nitrogen-oxygen bond length would be shorter.

Examiner Comments

- Candidates should always identify the most significant factor(s) for discussion, which in this case, is that there is a double bond present compared to the single bond. However, candidates, by just stating this factor alone, did not show an understanding of why a double bond is stronger (and hence the bond length is shorter).
- Some candidates merely stated: "more effective orbital overlap" but did not go further to show understanding that there are actually two regions of overlap that need to be discussed: a *more effective* overlap between N's 2sp² orbital with O's 2p orbital compared to with Cl's 3p orbital (more diffuse) for the σ bond, as well as an *additional* region of overlap between N's 2p orbital with O's 2p orbital for the π bond.
- Some candidates incorrectly deduced that the double bond is weaker because the additional electrons experience greater repulsion. Please do not confuse what is tested here with the additional inter-electronic repulsion between the paired electrons in a ns²np⁴ vs ns²np³ configuration for the first IE discussion under Atomic Structure.

(a)(iv) NOCl is polar and the permanent dipole-permanent dipole interactions (and instantaneous dipole-induced dipole interactions) between NOCl molecules are stronger than the instantaneous dipole-induced dipole interactions between non-polar Cl₂ molecules.

More energy is required to overcome the attraction between NOCl molecules and hence NOCl has a higher boiling point.

Examiner Comments

- Please do not use "pd-pd" or "id-id" without defining them explicitly.
- Some candidates incorrectly wrote "id-id" as instantaneous dipole–*instantaneous* dipole.
- Note that in this case, as NOCl and Cl₂ have a similar number of electrons, and NOCl is *not* significantly more cylindrical in shape than Cl₂, their id-id is largely similar. Hence it is more important to highlight the pd-pd present.

(b)(i) $K_p = p_{\text{NO}}^2 p_{\text{Cl}_2} / p_{\text{NOCl}}^2$

Examiner Comments

- This is K_p , not K_c , and hence there should be no terms using concentration or [] here.

(b)(ii)

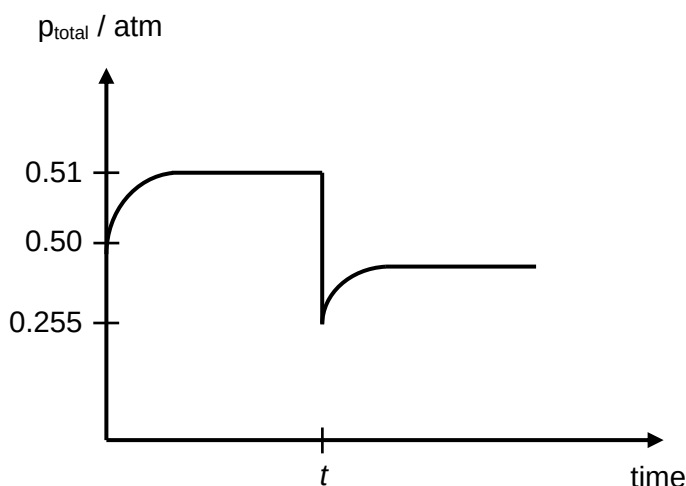
	$2\text{NOCl(g)} \rightleftharpoons 2\text{NO(g)} + \text{Cl}_2\text{(g)}$			
$p_{\text{initial}} / \text{atm}$	0.50	-	-	
$p_{\text{change}} / \text{atm}$	-0.02	+0.02	+0.01	
$p_{\text{final}} / \text{atm}$	0.48	0.02	0.01	$p_{\text{total}} = 0.51 \text{ atm}$

$$K_p = (0.02)^2 (0.01) / (0.48)^2$$

$$= 1.74 \times 10^{-5} \text{ atm}$$
Examiner Comments

- A handful of candidates converted the units to Pa (by using $1 \text{ atm} = 101325 \text{ Pa}$, as given in the Data Booklet) although there was no need to do so here.

(b)(iii)

*Examiner Comments*

- Many candidates misread the question and drew the individual graphs for the partial pressures of the three gases instead.
- Some candidates missed out on indicating the values on the p_{total} -axis.
- Students need to calculate the first equilibrium total pressure at 0.51 atm (instead of using the initial total pressure of 0.50 atm) for K_p on graph.
- Do take note that a distinct horizontal line is required to show that equilibrium is reached eventually (for both changes that took place.)

(b)(iv) When the volume was doubled, the total pressure was decreased (halved). The partial pressures of the 3 gases would also be halved initially/decrease.

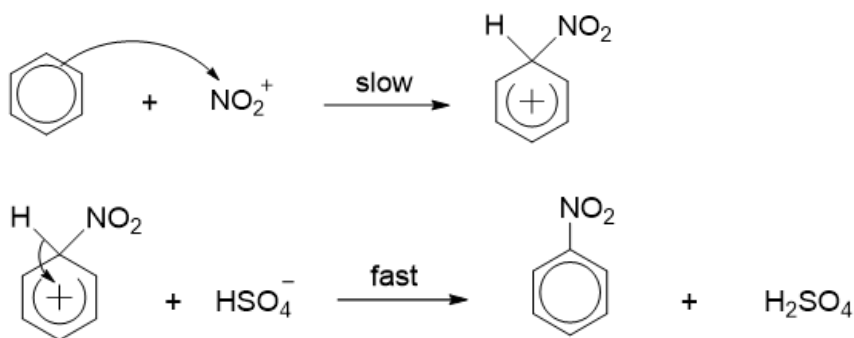
To increase the total pressure / increase the total number of gaseous particles in the system, by Le Chatelier's Principle, the position of equilibrium would shift to the right.

The partial pressure of NOCl would then decrease further while that of NO and Cl_2 would increase until equilibrium is re-established.

Examiner Comments

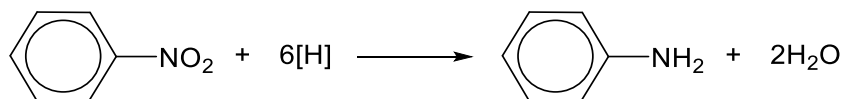
- In such discussions involving Le Chatelier's Principle, the following should be included:
 - the change/disturbance to the equilibrium,
 - how system responds, and the shift in the position of equilibrium, and
 - why the system responds in such a manner (to increase number of moles of gaseous particles)
- Some students misinterpreted the question as asking for the change in the partial pressures at time t , but the question asked for the changes from time t .

(c) Electrophilic substitution

*Examiner Comments*

- This was surprisingly not well-attempted. Many candidates did not give the equation for the generation of the electrophile correctly. Some missed out on writing “fast” and/or “slow”. Many forgot the HSO_4^- and H_2SO_4 in the final equation. Others made mistakes in arrow pushing.
- A few candidates wrote this entire answer in prose. Please note that such questions on mechanisms are to be answered using balanced equations, and with all the relevant details.

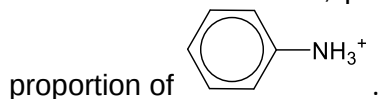
(d)(i)

*Examiner Comments*

- A large number of candidates incorrectly balanced the $[\text{H}]$, and/or wrote O_2 as a product instead.

(d)(ii)

Under acidic conditions, phenylamine undergoes acid-base reaction to produce a high

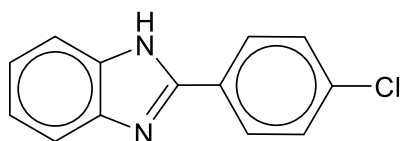


The $-\text{NH}_3^+$ is 3-directing and hence a large proportion of the 3-isomer is produced.

Examiner Comments

- Note: a deactivating group does not necessarily mean it is 3-directing. You can refer to your Data Booklet to confirm this.
- Incoming substituents do not direct their own final positions, it is the substituent *which is already on the benzene ring* that is 2,4- or 3-directing to the incoming substituents.
- A quick check with the Data Booklet would have alerted candidates that the $-\text{NH}_2$ group is 2,4-directing, not 3-directing.

(d)(iii)

*Examiner Comments*

- This was generally well done. Some candidates missed out the “H” attached to the N.