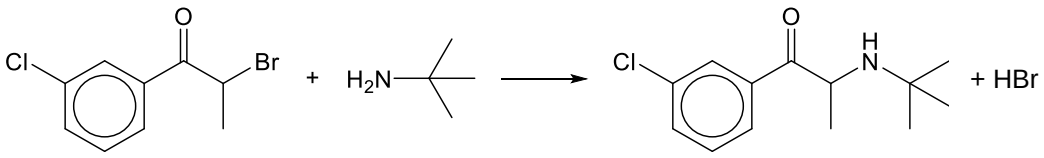
2019 Y6 H2 Chemistry Preliminary Exams Paper 3 Suggested Solutions

Section A

1 **(a)** **(i)**



Examiner's Comments
- Most students were able to correctly draw the structure of the amine. However, many did not balance the equation with HBr.

(ii) The p orbital of the C*l* atom overlaps with the π electron cloud of the benzene ring. This allows the lone pair of electrons in the p orbital of the chlorine atom to delocalise into the benzene ring and results in partial double bond character in the C–C*l* bond. This bond is strengthened and hence not easily broken.

Sterically, nucleophilic attack at the electron-deficient carbon atom from the side directly opposite the C*l* atom is blocked by the benzene ring. In addition, the pi-electron cloud of the benzene ring will repel the lone pair of electrons of an incoming nucleophile, rendering attack of the nucleophile difficult.

Examiner's Comments
- Many students gave incomplete answers, either omitting the C*l* p-orbital overlapping with the π electron cloud of benzene or omitting the delocalisation of electrons.
- Students should phrase their answers clearly. For example, it is the C-C*l* bond that has partial double bond character and not the C*l* atom.
- Most students did not discuss the steric hindrance effect of the benzene ring.

(iii) Add NaOH(aq) to each sample in a test-tube and heat each mixture in a hot water bath. Cool each mixture and acidify each one with dilute HNO_3. Then add $AgNO_3$(aq) to each mixture.

For compound H, a pale cream precipitate of AgBr will be observed.
For bupropion, no cream precipitate is observed.

Alternative answer: Br_2(aq) – compound H will decolourise orange Br_2(aq)

Examiner's Comments
- Most students were able to correctly state the distinguishing test and accompanying observations. Do remember to refer to the Data Booklet for the correct colour of the silver halides.
- When describing observations, avoid stating "no observable change" and instead, state the opposite of the positive test.
- Students should also take note to specify the solvent used. For example, NaOH(aq), Br_2(aq), HNO_3(aq).

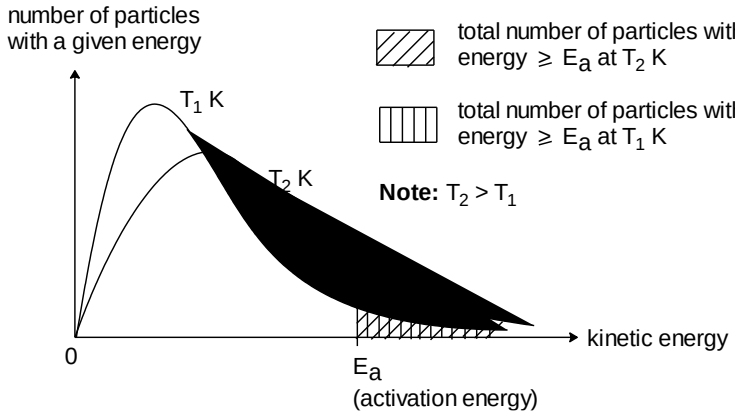
(b) **(i)** To quench the reaction / to stop the reaction at one minute / to neutralise the unreacted amine from the reaction mixture.

Examiner's Comments
- Statements such as "slow down" the reaction, no matter how "drastically" or "significantly", were not accepted.

(ii) The rate of the reaction is dependent on temperature. Having the two solutions at the same temperature before the start of the reaction will minimise any temperature changes during the mixing of solutions.

Examiner's Comments
- This question was poorly done. Many answers did not address the question.
- For example, "…so that temperature will not affect the rate of the reaction." Nothing you can do experimentally will stop temperature from affecting the rate of a reaction.
- Another example, "…so that temperature is the only independent variable in the experiment." This would be correct if the question asked, "Why was the reaction mixture kept in a temperature-controlled water bath?"

(iii) **Maxwell-Boltzmann distribution of kinetic energies at two different temperatures.**



At 60 °C, the average kinetic energy of the reactant particles increases. As such, significantly more reactant particles have energy greater than or equal to the activation energy of the reaction. This results in an increase in effective collision frequency and hence an increase in the rate of the reaction.

Examiner's Comments
- Students must be careful to replicate the shape of the distribution curve exactly.
- The T_2 curve must peak at a lower maximum than the T_1 curve and be broader.
- The area under both curves must be about the same, and they should pass through the origin, without intersecting the x axis.
- The point that more reactant particles have energy ≥ E_a must be clearly stated or shown in the diagram.

(c) Initial rate = $-\frac{(0.05-0)}{(0-180)}$ = 2.78×10^{-4} mol dm^{-3} min^{-1}

Also accepted: 4.63×10^{-6} mol dm^{-3} s^{-1}

Examiner's Comments
- A range of initial rate values were accepted due to a certain level of subjectivity in drawing a tangent to the curve at $t = 0$. Values outside of the range were not accepted.
- Many students neglected the units or stated incorrect units (such as s^{-1} instead of min^{-1}).
- Although the gradient is negative, students should note that initial rate is a positive value.

(d) Using experiment 1 and 2:
When [triethylamine] is doubled (0.10/0.05), the relative initial rate is also doubled (1/0.5).
Hence order of reaction w.r.t. triethylamine is 1.

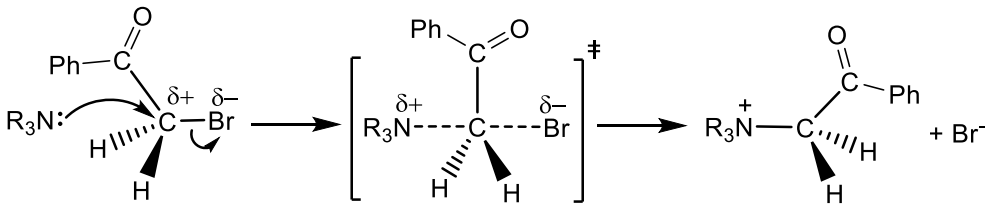
Using experiment 2 and 3:
When [$PhCOCH_2Br$] is doubled (0.10/0.05), the relative initial rate is also doubled (1/0.5).
Hence order of reaction w.r.t. $PhCOCH_2Br$ is 1.

The reaction is overall second order.

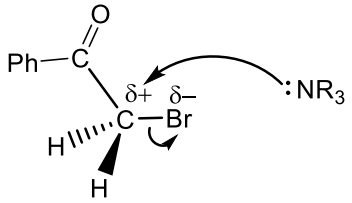
Rate = k[$PhCOCH_2Br$][triethylamine]
units of rate constant: $mol^{-1}\ dm^3\ min^{-1}$ or $mol^{-1}\ dm^3\ s^{-1}$

Examiner's Comments
- This question was generally well done. However, reasoning must be shown in determining the orders of the reaction.
- Also, students should take note of the correct form of the rate equation.

(e) Mechanism: S_N2



Examiner's Comments
- The name of the mechanism must be stated, as required in the question. Please also note the correct format of writing S_N2 – note which are terms are in subscript.
- All partial charges and arrows were required for full credit.
- Many students omitted the positive charge on the N in the product.
- Students should also note that in a S_N2 mechanism, the nucleophile should attack the R-X from the "backside" (see above) and not the "front side" (see below).



THIS IS WRONG!!!

(f) **(i)** Using $PhCOCH_2I$ will result in a <u>higher rate</u> than Experiment 1 because the <u>C-I bond is weaker</u> than the C-Br bond.

Examiner's Comments
- Generally well done. However, many students went on to explain why the bond was weaker. This was not necessary since the question was only given 1 mark.

(ii) Using compound **G**, which is a secondary RX, will result in a slower rate than Experiment 1.

During the S_N2 reaction, the nucleophile attacks the electron-deficient carbon atom from the side directly opposite the halogen atom (i.e. a backside attack). For compound **G**, this approach and attack is sterically hindered by the methyl group on the C-Br carbon.

Examiner's Comments

- Many students were able to identify the difference in Compound **G** being that this was a secondary RX with a methyl group on the C-Br carbon.
- However, a large number of students stated that the "electron-donating methyl group decreased the $\delta+$ partial charge on the C-Br carbon". This was not accepted. In the S_N2 mechanism, the nucleophile must be able to attack the $\delta+$ carbon, i.e., the steric effect is the key factor here.
- Note that the electron donating effect is important in the S_N1 mechanism to stabilise the carbocation.
- Marks were not awarded for answers which were vague in describing the position of the methyl group, e.g. "additional methyl group in **G**" or "methyl group on the carbon atom".

(iii) Using $PhCH_2CH_2Br$ will result in a slower rate than Experiment 1.

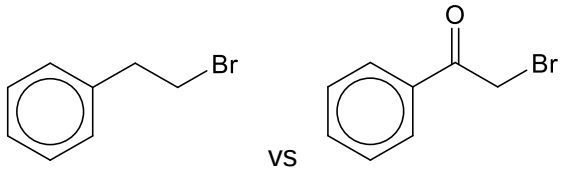
Compared to $PhCOCH_2Br$, (2-bromoethyl)benzene does not have an additional C=O electron withdrawing group on the C-Br carbon. This decreases the intensity of the $\delta+$ charge on the carbon atom, making it less susceptible to nucleophilic attack.

-or-

The C-Br carbon in $PhCOCH_2Br$ is bonded to two electron withdrawing groups (-Br and the C=O group), hence the carbon is more electron deficient and more susceptible to nucleophilic attack. Therefore, $PhCOCH_2Br$ will react faster.

Examiner's Comments

- Many students likely drew the wrong structure for (2-bromoethyl)benzene. Therefore, all discussions related to the benzene ring are incorrect as the benzene ring is the same distance away from the C-Br carbon in both cases.



- The difference in the two structures lie in the -C=O group, which many students were able to identify. However, describing the effect of the electron-withdrawing group was poorly done. As above, students need to be clear in describing the position of the group.

2 **(a)** The electron cloud of I_2 is larger and more polarisable than that of F_2, Cl_2 and Br_2, resulting in I_2 having stronger instantaneous dipole-induced dipole (id-id) interactions. At room temperature, there is insufficient energy to overcome the id-id interactions between molecules of I_2.

Examiner's Comments

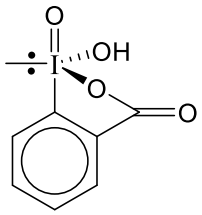
- Students often failed to discuss the polarisability of the electron cloud before deducing the relative strength of the id-id interactions.
- It is necessary to compare iodine with the other halogens in your answer due to the phrasing of the question.

(b) **(i)** Fluorine. Its valence shell does not possess low-lying vacant d-orbitals to accommodate additional electrons.

Examiner's Comments

- The question clearly stated "**unable** to exhibit hypervalency". Students should answer to the question instead of giving the opposite to what is required.

(ii)



This arrangement minimizes / has the lowest lone pair-bond pair repulsions.

Examiner's Comments

- Other arrangements of groups around the central iodine atom were accepted as long as the lone pair on iodine is on the equatorial position and the iodine-benzene bond and iodine-oxygen-of-ester bond were not both axial.
- Students were sloppy in their diagram of IBX, often missing out the hash/wedge or lone pair of electrons on iodine.
- Some students only draw the immediate atoms surrounding the central iodine atom. The entire structure must be drawn to gain any credit.
- Students should avoid representing a double bond with the hash or wedge.
- This arrangement of groups is to minimise all lone pair-bond pair repulsions. No credit was awarded for answers which focus on only some of the bond pairs.

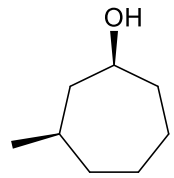
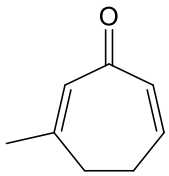
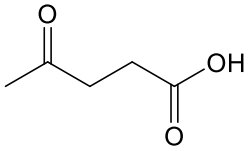
(c) **(i)** +3 to +1

Examiner's Comments

- +5 to +3 was also accepted because the examiners decided that the relative electronegativities of carbon and iodine were difficult to predict. Such kindness is once-off, on a case-by-case basis and is not an entitlement.
- The most popular incorrect answer (+4 to +2) was obtained when students forget to consider the carbon-iodine bond in their calculation of oxidation state.
- Many students were unable to calculate the oxidation states of iodine in IBX and IBA, leading to incorrect answers. Please refer to notes on *Introduction to Organic Chemistry* to find out how to calculate oxidation states using electronegativities.

(ii)

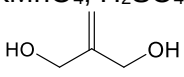
Evidence	Deductions
Alcohol **J** is optically active and is one of four stereoisomers.	• J contains at least 1 chiral centre.
K and **L** are not optically active.	• K and L do not possess any chiral centres.
K → **L** + **M**	• Oxidation of C=C occurred.
K and **L** give orange ppt with 2,4-DNPH, but no silver mirror with Tollen's reagent.	• Condensation reaction occurred. • Not oxidised by Tollens' reagent. • K and L contain ketones.
L gives a yellow ppt of CHI_3 when heated with aq alkaline I_2.	• Oxidation occurred. • L contains the $–COCH_3$ group.
L produces effervescence of CO_2 with aq Na_2CO_3.	• Acid-carbonate reaction occurred. • L contains a –COOH group.
J → K	• Loss of 6 H atoms, means it is an oxidation reaction

 (or any of the other 3)		
J	**K**	**L**

Examiner's Comments

- Students who had ample practice with elucidation and learnt from the lessons of the previous examinations this year presented their work adequately and gained high marks for this question! Well done to those!
- It has been mentioned on numerous occasions that the type of reactions for each reaction must be mentioned, along with any deductions of the functional groups of the reactants and products.
- Most students did not manage to draw a stereoisomer of **J**, as required in the question. The 3D representation is necessary to show which stereoisomer of **J** is shown, i.e. the use of hash and wedge. Since **J** has two chiral centres (hence the four stereoisomers), the 3D representation of BOTH chiral centres must be shown.

(d) Step 1: NaOH(aq), heat
Step 2: $KMnO_4$, H_2SO_4, heat

Q : 

Examiner's Comments

- Students were careless when suggesting a structure for **Q**. They should have double checked their answer with the molecular formula of **Q** given in the question.
- It is important to specify the medium for Step 1, i.e. either the mention of "dilute" or "(aq)", so as to differentiate with the use of alcoholic medium, where elimination will take place instead.

(e) **(i)** Order of reaction is negative.

Examiner's Comments
- Quite a few students gave their answer as "less than 1" or "not zero". These answers are ambiguous and inconsistent with the kinetics observed.

(ii) Amount of iodide ions produced = 2(0.10) = 0.20 mol
Anode: $2I^- \rightarrow I_2 + 2e^-$
Amount of electrons = 0.20 mol

$$n_e F = It$$

$$t = \frac{n_e F}{I} = \frac{(0.20)(96500)}{0.5} = 38600 \text{ s}$$

Examiner's Comments
- The electrolytic setup is to **remove the iodide produced**. Many students misunderstood the information given and thought it was to produce iodide ions. So they calculated the amount of electrons incorrectly.

3 **(a)** Capable of oxidising quinol, choose either one of the following:

$F_2 + 2e^- \rightleftharpoons 2F^- \quad +2.87V$
$Cl_2 + 2e^- \rightleftharpoons 2Cl^- \quad +1.36V$
$Br_2 + 2e^- \rightleftharpoons 2Br^- \quad +1.07V$

F_2 and quinol: $E^\ominus_{cell} = +2.87 - (+0.70) = +2.17V > 0$
Cl_2 and quinol: $E^\ominus_{cell} = +1.36 - (+0.70) = +0.66V > 0$
Br_2 and quinol: $E^\ominus_{cell} = +1.07 - (+0.70) = +0.37V > 0$
Conclude that $E^\ominus_{cell} > 0$, the reaction is spontaneous.

Unable to oxidise quinol, choose:
$I_2 + 2e^- \rightleftharpoons 2I^- \quad +0.54V$

I_2 and quinol: $E^\ominus_{cell} = +0.54 - (+0.70) = -0.16V < 0$
$E^\ominus_{cell} < 0$, the reaction is not spontaneous.

Examiner's Comments
- Generally well done.
- Students are reminded to deduce the spontaneity of reactions by calculating $E^\ominus_{cell}$.

(b) Ethene: in the dark; Benzene: In the presence of $FeBr_3$ / Fe

Ethene is unsaturated and not resonance stabilised, hence it requires a milder condition for electrophilic addition to occur. Benzene is resonance-stabilised due to the presence of six delocalised π electrons. Hence, benzene requires a Lewis Acid to generate the stronger Br^+ electrophile for electrophilic substitution to occur.

Examiner's Comments
- Most students are able to state the reagents and conditions for the two reactions. A few students, however, failed to realise that electrophilic substitution of benzene requires an anhydrous condition to prevent hydrolysis of the Lewis Acid, $FeBr_3$.
- Accounting for the difference in conditions was less well done. Many students were unable to clearly articulate the fact that benzene, a resonance-stabilised molecule, only

undergoes electrophilic substitution in the presence of a stronger electrophile Br^+, which was generated by $FeBr_3$.

- $FeBr_3$ serves as a Lewis Acid as it accepts a lone pair of electrons from Br_2 to generate the electrophile Br^+. Most students chose to label $FeBr_3$ as the catalyst. While it is not totally wrong to do so, it is also important to realise that $FeBr_3$ acts as the Lewis Acid. This will enable a better appreciation of the role of $FeBr_3$ in the electrophilic substitution mechanism. Students are strongly discouraged from using the phrase '$FeBr_3$ acts as the halogen carrier' as it does not translate to any meaningful understanding of the mechanism.

(c) (i) An electrophile is an **<u>electron-pair acceptor</u>** which is attracted to an electron-rich site.

<u>Examiner's Comments</u>
- Not done well.
- It is not sufficient to simply state that an electrophile is electron deficient.

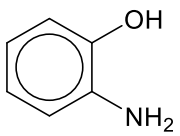
(ii) Increasing reactivity: benzene < phenol < phenylamine

1. Phenol and phenylamine are more reactive than benzene. The oxygen in the –OH group and the nitrogen in the $–NH_2$ group each has a lone pair of electrons that can be delocalised into the π electron cloud of the benzene ring by resonance. This makes the benzene ring in phenol and phenylamine more electron rich and hence more susceptible to electrophilic attack.

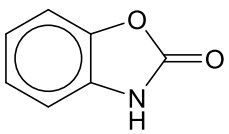
2. Phenylamine is more reactive than phenol. Nitrogen is less electronegative than oxygen. Hence, the benzene ring in phenylamine is more electron rich than that in phenol. Phenylamine is more susceptible to electrophilic attack than phenol.

<u>Examiner's Comments</u>
- This question requires students to explain the reactivity of the compounds by considering electronic effects. Hence, a clear description and comparison of the impact of resonance effect and inductive effect on the relative relativities of the compounds is needed to gain full credit.
- There was attempt to discuss this question in terms of resonance and inductive effect. However, the discussions were usually confusing to the examiners or contained points which contradicted one another. Students are reminded to learn how to describe or compare these two effects clearly.
- It is important to note that the lone pair of electrons on both the –OH group and the $–NH_2$ group delocalise into the π electron cloud of the benzene ring by resonance. However, as nitrogen is less electronegative than oxygen, the lone pair on N is more readily delocalised into the benzene ring of phenylamine, the benzene ring in phenylamine is more electron rich than that in phenol. Thus, phenylamine is more reactive than phenol, which in turn is more reactive than benzene.

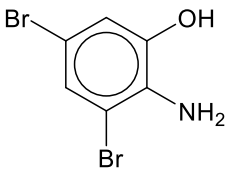
(iii)



U



V

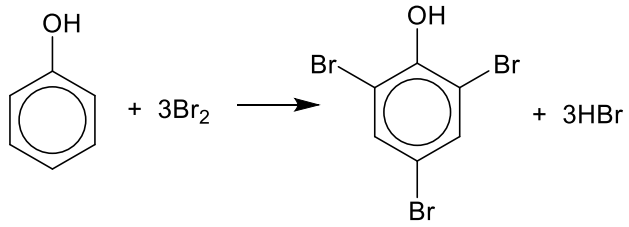


W

Examiner's Comments

- Different positional isomers of **U** were drawn as anwers. However, the only way to obtain an acylated compound V with the correct molecular formula was to begin with 2-aminophenol for **U**.
- To obtain the correct positional isomer for **W**, students need to refer to the data given in the question. In **(c)(ii)**, students recognise that the $–NH_2$ group is a stronger activating group than the –OH group. Hence, the –bromo group must be substituted into positions which are 2- or 4- w.r.t to the $–NH_2$ group. In addition, monobrominated products are not accepted as phenylamine reacts with Br_2 to form 2,4,6–tribromophenylamine, as shown in the table.

(d) (i)

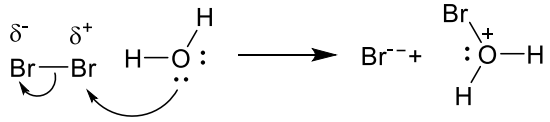


Examiner's Comments

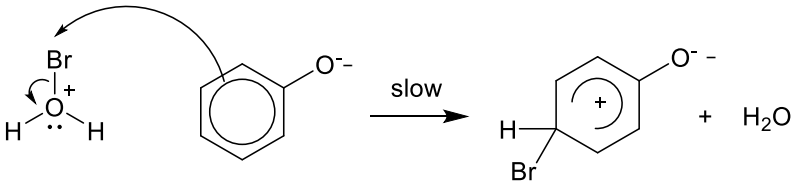
- This is surprisingly very poorly done.
- Many students seem to have forgotten that phenol reacts with aqueous Br_2 to form 2, 4, 6–tribomophenol. Many students failed to balance their equation with HBr as the by-product.

(ii)

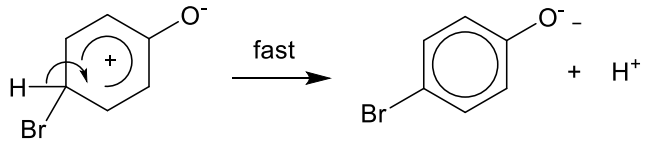
Step 1



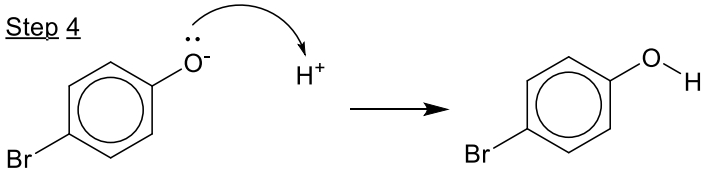
Step 2



Step 3



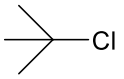
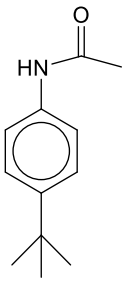
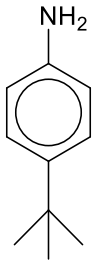
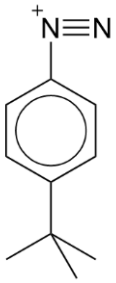
Step 4



Examiner's Comments

- Not well done.
- Students have to be mindful that they are expected to show charges, relevant lone pairs of electrons, displayed formulae of relevant compounds and curly arrows. Curly arrows must also originate from a pair of electrons.
- Quite a number of students mistakenly drew structures of other positional isomers, instead of 4–bromophenol, as required by the question.

(e) (i)

Step	Reagents and conditions	Intermediate compound
Alkylation	 with A*l*C*l*$_3$	
Hydrolysis	NaOH(aq), heat	
Sandmeyer reaction	1) $NaNO_2$, dilute HCl 2) CuBr	

Examiner's Comments

- This question clearly states that the reaction has to proceed via the stated sequence. There were quite a number of students who attempted to swop the sequences around.
- Students have to be mindful when drawing skeletal formulae of compounds. In the first alkylation step, a number of students added an additional carbon to the structure $(CH_3)_3CCl$.
- To obtain 4-(1,1–dimethylethyl)phenylamine, alkaline hydrolysis has to be carried out. Acidic hydrolysis would have resulted in the production of the positively charged conjugate acid.
- As the question requires students to state the reagents and conditions, it is not acceptable for students to state "Sandmeyer reaction" as part of their answers.

(ii) If hydrolysis is done before alkylation, this would produce the amine, which can then react with $(CH_3)_3CCl$ in a nucleophilic substitution reaction.

Examiner's Comments

- Many students mistakenly stated that if hydrolysis were to take place before alkylation, phenylamine will react to form a polyalkylated product. They failed to realise that this will not take place as the $–NH_2$ group of phenylamine will react with $(CH_3)_3CCl$ in a nucleophilic substitution reaction. The $–NH_2$ group of phenylamine will also react with the Lewis Acid, $AlCl_3$, in an Acid–Base reaction.

Section B

4 **(a)** Ionic radius of Ni^{2+}= 0.069nm
Ionic radius of Mg^{2+} = 0.065nm
Ni^{2+} ion has a slightly larger ionic radius than Mg^{2+}. Hence with the same charge, Mg^{2+} ion has a higher charge density than Ni^{2+} ion. Mg^{2+} is more polarising and is able to distort the electron cloud of the carbonate ion in $MgCO_3$ to a greater extent, thereby weakening the covalent bonds within the carbonate ion more. Hence less energy is required to break the weaker covalent bonds in the carbonate ion in $MgCO_3$ and $MgCO_3$ will decompose at a lower temperature than $NiCO_3$. Consequently, $MgCO_3$ is less thermally stable than $NiCO_3$

Examiner's Comments

- Generally well done. Students have indicated the ionic radius of Mg^{2+} and Ni^{2+} to aid them in their explanation.

(b) **(i)** The lattice energy of an ionic compound is the energy released when one mole of the solid ionic compound is formed from its constituent gaseous ions at 298 K and 1 bar.

Examiner's Comments

- Many students left out key words such as 'energy released', '1 mole', 'solid' and 'gaseous ions' and 'standard conditions/298 K and 1 bar' and were not given credit for their answers.

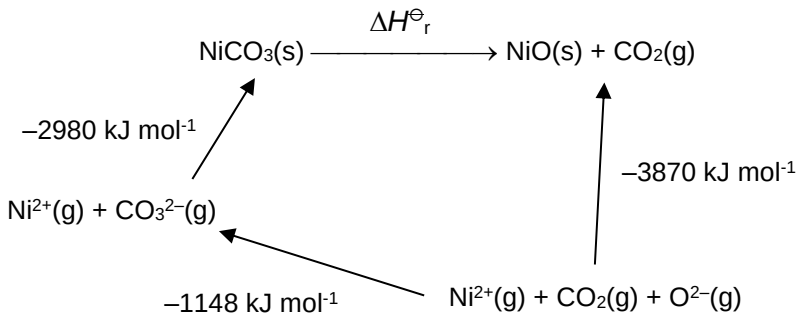
(ii) $$\textbf{|Lattice energy|} \propto \left|\frac{q_+ q_-}{r_+ + r_-}\right|$$

The O^{2-} ion has a smaller radius than the CO_3^{2-} ion. Hence the interionic distance in NiO is smaller than in $NiCO_3$. Therefore the lattice energy of NiO is more negative.

Examiner's Comments

- Generally well done. If students did not specify the formula for L.E, the answer will need to include the phrase 'interionic distance'.

(iii)



By Hess' law

$-1148 - 2980 + \Delta H^{\ominus}_r = -3870$

$\Delta H^{\ominus}_r = -3870 + 2980 + 1148 = +$**<u>258 kJ mol^{-1}</u>**

<u>Examiner's Comments</u>
- Some students did not understand the definition of LE and drew the arrows in the incorrect direction in the energy cycle diagram.
- State symbols need to be included for all species in the energy cycle diagram.
- Students are encouraged not to combine 2 different thermochemical processes into a single arrow to increase clarity in their answers.
- Student should avoid drawing energy level diagram in this case since the question did not ask for it.

(c) (i) $\Delta H^{\ominus} = -603 - 4(-110) = -163$ kJ mol^{-1}

<u>Examiner's Comments</u>
- Generally well done.
- Some students did not multiply the $\Delta H_f^{\ominus}$(CO) by 4 in their calculations.

(ii) The entropy change in step 2 is negative because the reaction resulted in a decrease in the number of moles of gaseous molecules in the system (since 4 moles of gaseous reactant molecules react to form 1 mole of gaseous product molecules). There is a decrease in disorderliness as the reaction takes place.

$\Delta G^{\ominus} = -163 - (298)(-411)/1000 = -40.5$ kJ mol^{-1}

<u>Examiner's Comments</u>
- Students must clearly mention a reduction in the number of **gaseous** molecules in the reaction to be awarded the mark. Marks will not be awarded for merely stating a decrease in number of particles without mentioning the gaseous state.
- In the calculation of $\Delta G^{\ominus}$, students should note that it is necessary to ensure that the units of both $\Delta H^{\ominus}$ and $\Delta S^{\ominus}$ are consistent before carrying out any mathematical manipulation.

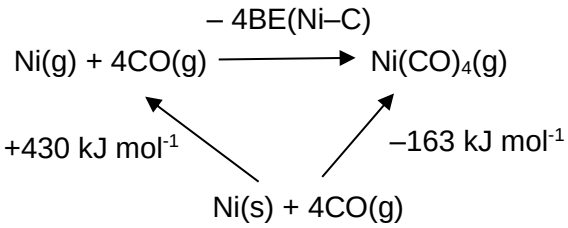
(iii) The reaction in step 3 is the reverse of that in step 2.
Hence for the reaction in step 3, $\Delta H^{\ominus} > 0$ and $\Delta S^{\ominus} > 0$.

$$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$$

In this case, a high temperature T is needed to make the negative $-T\Delta S^{\ominus}$ outweigh the positive $\Delta H^{\ominus}$ such that $\Delta G^{\ominus} < 0$ and the reaction is thermodynamically feasible.

Examiner's Comments
- Students need to clearly indicate **both** the enthalpy change and the entropy change for step 3 are positive.
- A comparison of the $T\Delta S^{\ominus}$ and $\Delta H^{\ominus}$ need to be mentioned to be awarded the full credit.

(iv)



$BE(Ni–C) = (430 + 163)/4 = +148 \text{ kJ mol}^{-1}$

Examiner's Comments
- Generally well done.
- Some students obtained a negative value for BE(Ni–C) and were not aware that it is not correct. These students need to take note that bond formation is exothermic and bond breaking is endothermic.

(d) (i) Cathode (Ni electrode)

$Ni^{2+} + 2e^- \rightleftharpoons Ni$ $\quad E^{\ominus} = -0.25$ V

$Zn^{2+} + 2e^- \rightleftharpoons Zn$ $\quad E^{\ominus} = -0.76$ V

$2H_2O + 2e^- \rightleftharpoons H_2 + 2OH^-$ $\quad E^{\ominus} = -0.83$ V

At the cathode, Ni^{2+} is preferentially reduced to Ni. This is because $E^{\ominus}(Ni^{2+}/Ni)$ is less negative (or more positive) compared to $E^{\ominus}(Zn^{2+}/Zn)$ and $E^{\ominus}(H_2O/H_2)$. Hence the cathode (i.e. Ni electrode) increases in mass/size due to the deposition of Ni.

Anode (Pt electrode)

$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O$ $\quad E^{\ominus} = +1.23$ V

$S_2O_8^{2-} + 2e^- \rightleftharpoons 2SO_4^{2-}$ $\quad E^{\ominus} = +2.01$ V

At the anode, H_2O is oxidised to O_2 gas. This is because $E^{\ominus}(O_2/H)$ is less positive (or more negative) than $E^{\ominus}(S_2O_8^{2-}/SO_4^{2-})$. Hence at the anode (Pt electrode), effervescence of O_2 gas is observed.

Examiner's Comments
- Many students only compared the $E^{\ominus}(Ni^{2+}/Ni)$ and $E^{\ominus}(Zn^{2+}/Zn)$ values and did include $E^{\ominus}(H_2O/H_2)$ when considering the reduction reaction at the nickel electrode.
- Many students did not include the observations at both electrodes, which result in the loss of marks.
- Some students used the $E^{\ominus}(O_2/OH^-)$ instead of $E^{\ominus}(O_2/H_2O)$ for the reaction at the platinum electrode, which is incorrect.
- Some students identified incorrectly the Ni electrode as anode and the Pt electrode as cathode.

(ii) $Ni(OH)_2$

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$
Some water has been reduced at the cathode, forming hydrogen gas and hydroxide ions. Ni^{2+} reacts with the hydroxide ions to produce the green ppt.

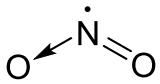
Examiner's Comments
- Some students included species which are not present in the electrolyte, e.g. magnesium or aluminium as the precipitate.
- Many students wrote compounds of zinc as the green precipitate. Zn^{2+} has a full d-subshell and no d-d transiton is possible, which makes most of the zinc compounds colourless or white.
- Students also need to explain where the hydroxide ions come from. Merely saying that Ni^{2+} reacts with OH^- will not be given the credit.

(iii) The pH decreases over time as H^+ is produced from the oxidation of water at the platinum electrode.

The hydrogen ions have diffused throughout the solution and react with the nickel hydroxide produced at the cathode. Hence the green precipitate dissolved.

Examiner's Comments
- Many students did not explain why the pH of the solution decreases, and hence no credit was given.

5 **(a)** **(i)**

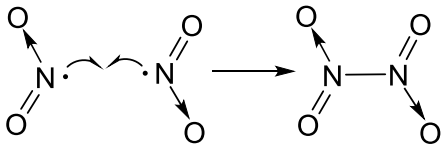


Examiner's Comments
- Many students gave the incorrect number of valence electrons for either O or N in their structure drawn.
- Many did not realise that the repulsion due to the lone electron on N is less than that of a lone pair.
- There were many with two N=O bonds which would lead to N having more than 8 valence electrons even though it is in Period 2.
- Some bond angles were too near 180 º, which basically is a linear shape.

(ii) NO_2 is a polar molecule as its dipole moments do not cancel out / its net dipole moment is non-zero.

Examiner's Comments
- Most were able to deduce / explain why NO_2 is polar.
- A handful wrote about difference in electronegativity without mentioning the net dipole moment of molecule

(iii)



The dimerisation involves only the formation of a N–N covalent bond and bond formation is exothermic.

Examiner's Comments
- Many candidates were able to draw the curly half arrows correctly, while some gave drawings which were not meaningful. Please revise arrow pushing.

(b) When the equilibrium mixture is suddenly expanded in a gas syringe, $[N_2O_4]$ and $[NO_2]$ decrease due to the increased volume, resulting in an immediate lightening of the brown colour.

When the volume increased, total pressure decreased in the syringe. The position of equilibrium will shift left to favour the reaction that produces a greater number of gaseous molecules. Hence, more of the red-brown NO_2 will be produced and the mixture darkens.

Examiner's Comments
- Some explanations were not well crafted even though they were accepted. Please refer to the answer carefully and use the appropriate terms e.g. concentration of NO_2, total pressure etc.
- Reference to the observations such as lightening of colour must be made clearly.
- There should be clear indication that it is the number of gaseous particles that are increased.

(c) **(i)** $K_p = \frac{p_{N_2O_4}}{p_{NO_2}^2}$

Examiner's Comments
- Mostly well done. Please be careful not to use square brackets because in Chemistry, square brackets have the meaning of *concentration* of something.

(ii) $p_{N_2O_4} = \frac{V_{N_2O_4}}{V_{eqm}} \times p = \frac{(V_i - V_{eqm})p}{V_{eqm}}$

Examiner's Comments
- Many were able to do this but some forgot about multiplying by the total pressure, *p*.

(iii) $K_p = \frac{(8-4.77)4.77}{(1)(2\times4.77-8)^2} = 6.50 \text{ atm}^{-1}$

Examiner's Comments
- Generally well done, except some incorrectly used 101 325 Pa (please check the units) instead.

(iv) As temperature increases, K_p decreases. The position of equilibrium shifts to the left/backward reaction is favoured at a higher temperature. This means that the backward reaction is endothermic and hence the dimerisation reaction is exothermic.

Examiner's Comments
- In this context, K_p decreases as a result of an increase in temperature, not the other way around so please phrase properly.

(v) As T increases, total volume of the gas mixture increases.

NO_2 / N_2O_4 is a reacting mixture and as temperature increases, the position of equilibrium 1 shifts to the left to favour the backward reaction.

One molecule of N_2O_4 becomes two molecules of NO_2. The number of particles in the mixture increases. Hence the total volume increases at an increasing rate.

Examiner's Comments
- Most were able to identify the formation of two NO_2 from one N_2O_4 but missed out on the factor of thermal expansion.

(d) (i) Helium has a small atomic size and very weak forces of attraction between the atoms (instantaneous dipole-induced dipole interactions).

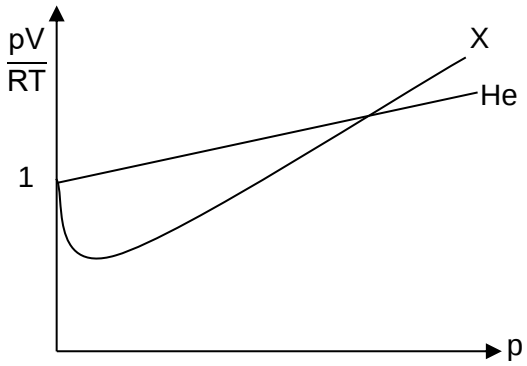
Examiner's Comments
- Helium being a noble gas and not reactive has nothing to do with the question being answered.

(ii) $pV = nRT = (m/M)RT$
$p = (\text{density}/M)RT$
$10^5 = (3.2 \times 10^3)/M \times (8.31)(273)$
$M = 72.6 \text{ g mol}^{-1}$

X is CI_2.

Examiner's Comments
- Some used 101 325 incorrectly (i.e. pressure for r.t.p. instead of s.t.p.).

(iii)



Examiner's Comments
- Some misread the question and plotted the wrong axes.
- Note that the y-intercept is at "1", not "0".