EUNOIA JUNIOR COLLEGE
JC2 Preliminary Examination 2018
General Certificate of Education Advanced Level
Higher 2

CANDIDATE NAME							
CIVICS GROUP	1	7	–			INDEX NUMBER	

CHEMISTRY

9729/02

Paper 2 Structured Questions

13 September 2018

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, civics group and registration number on the work you hand in.
Write in dark blue or black pen.
You may use an HB pencil for any diagrams or graphs.
Do not use paper clips, highlighters, glue or correction fluid.

Answer **all** questions in the spaces provided on the Question paper.
The use of an approved scientific calculator is expected, where appropriate.
A Data Booklet is provided.

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	
2	
3	
4	
5	
6	
Total	

This document consists of **21** printed pages and **1** blank page.

Answer **all** the questions in the spaces provided.

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1 The table below shows the melting points of some oxides of Period 3 elements.

compound	chemical formula	melting point / °C
sodium oxide	Na_2O	1132
aluminium oxide	Al_2O_3	2980
sulfur trioxide	SO_3	16

(a) (i) Briefly relate the melting points of these oxides to their structure and bonding.

Both Al_2O_3 and Na_2O **are of giant ionic lattice structure**. During melting, a lot of energy is required to break **strong electrostatic forces of attraction between oppositely charged ions [both, 1m]** in these two compounds, resulting in their high melting points. Al_2O_3 has higher melting point than Na_2O as Al_2O_3 has a larger magnitude of lattice energy (since Al^{3+} ion has higher charge and is smaller in size compared to Na^+ ion).

SO_3 has **covalent simple molecular structure** that has **weak intermolecular instantaneous dipole-induced dipole (id-id) interactions [both, 1m]** between SO_3 molecules, **requiring little amount of energy to overcome** during melting. Thus, SO_3 has the lowest melting point. [2]

(ii) Describe the reactions, if any, of these oxides with water, stating the approximate pH of any solution formed.
Write equations for all the reactions that take place.

Na_2O is an ionic oxide that reacts with water to form strongly alkaline solutions.

$Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ [1m] (**pH ≈ 13–14**).

Al_2O_3 **does not dissolve in water** because its lattice energy is highly exothermic **[1m]**. (**pH = 7**)

SO_3 is an acidic oxide that react readily with water to form strongly acidic solutions.

$SO_3(l) + H_2O(l) \rightarrow H_2SO_4(aq)$ [1m] (**pH ≈ 1–2**)

[all three pH's correct – 1m] [4]

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(b) Suggest a reason for each of the following observations:

(i) Effervescence is observed when aqueous sodium carbonate is added to an aqueous solution of aluminium chloride. Write equations for the reactions involved.

Al^{3+} has a **high charge density** and **further polarises** and **weakens the O–H bonds** of the water ligands **[1m]**. Hence $[Al(H_2O)_6]^{3+}$ undergoes **appreciable hydrolysis**, giving an acidic solution that reacts with sodium carbonate to give carbon dioxide.

$[Al(H_2O)_6]^{3+}(aq) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$

$CO_3^{2-}(aq) + 2H^+(aq) \rightarrow CO_2(g) + H_2O(l)$ [both eqns – 1m]

..... [2]

(ii) Silicon tetrachloride, $SiCl_4$, hydrolyses in water while carbon tetrachloride, CCl_4, remains insoluble in water.

Carbon in CCl_4, unlike silicon in $SiCl_4$, **does not have low-lying vacant orbitals** to accommodate the lone pair from water during hydrolysis.

In addition, **steric hindrance** from the 4 bulky chlorine atoms prevents approach/attack of water nucleophiles at the carbon atom in CCl_4.

[both, 1m]

..... [1]

(c) Gaseous N_2O_5 dissociates to form NO_2 and O_2 as shown in the following reaction equilibrium:

$$2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$$

The value of the equilibrium constant, K_p, is 1.80×10^4 atm^3 at 750 K and 3.23×10^3 atm^3 at 700 K.

(i) Write an expression for K_p for the above dissociation.

$$K_p = \frac{p_{O_2} \times (p_{NO_2})^4}{(p_{N_2O_5})^2}$$ **[1m]**

[1]

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(ii) Calculate the equilibrium constant in terms of pressure at 700 K for the reaction represented below:

$$\frac{1}{2}O_2(g) + 2NO_2(g) \rightleftharpoons N_2O_5(g)$$

$$K_p = \frac{p_{N_2O_5}}{(p_{O_2})^{\frac{1}{2}} \times (p_{NO_2})^2} = \left(\frac{1}{\frac{p_{O_2} \times (p_{NO_2})^4}{(p_{N_2O_5})^2}} \right)^{\frac{1}{2}}$$

$$= \left(\frac{1}{3.23 \times 10^3} \right)^{\frac{1}{2}} = \underline{\mathbf{1.76 \times 10^{-2}\ atm^{-\frac{3}{2}}}}\ \mathbf{[1m]}$$

[1]

(iii) Will the enthalpy change for the dissociation be a positive or negative value? Justify your answer briefly.

The enthalpy change will have a **positive value [1m]**.

The value of K_p for the dissociation **increases** with **increasing** temperature.

Therefore **the amounts of products (O_2 and NO_2) will increase while the amount of reactant (N_2O_5) will decrease [1m]** when temperature increases.

According to Le Chatelier's Principle, the forward reaction must be endothermic as it is favoured when temperature increases.

..... [2]

(iv) State and justify the effect on the position of equilibrium if the total volume of the system at equilibrium is increased at constant temperature.

Increasing the volume decreases the total pressure of the system.

This shifts the position of equilibrium to the **right [1m]** to **form more gaseous particles** to **increase pressure** as there are **more gaseous particles on the right [1m]**.

.....

..... [2]

[Total: 15]

For Examiner's Use

2 Halogens have a wide range of uses, such as in water purification and as antiseptics. Halogens form compounds, such as halides and oxoanions which are used in photography and as oxidising agents respectively.

(a) State and explain the variation of the first ionisation energy of the halogens from chlorine to iodine.

From chlorine to iodine,

- Valence electrons are **further away** from the nucleus.
- **Weaker electrostatic attraction** between nucleus and the valence electrons.
- **Less** energy is required to remove the valence electron. **[1m] for explanation**

Hence, first ionisation energy generally **decreases** down the group. **[1m]** [2]

(b) Halogens react with hydrogen gas to form hydrogen halides.
State and explain the trend in the thermal stability of hydrogen halides from HC*l* to HI.

From HC*l* to HI,

- Covalent **bond length of H—X increases**
- Covalent **bond strength decreases** *or* **bond (dissociation) energy decreases**

[1m] for both

- **Thermal stability decreases [1m]** [2]

(c) Halogens react with the thiosulfate ion, $S_2O_3^{2-}$. In acidic medium, bromine reacts with $S_2O_3^{2-}$ to form SO_4^{2-} and bromide ions, while iodine reacts with $S_2O_3^{2-}$ to form $S_4O_6^{2-}$ and iodide ions.

(i) Write an ionic equation for the reaction between iodine with the thiosulfate ion.

$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$ **[1m] ss optional** [1]

(ii) By quoting suitable values from the *Data Booklet*, explain the difference in the products formed.

$I_2 + 2e^- \; f \; 2I^-$ $\qquad E^{\ominus} = +0.54$ V

$Br_2 + 2e^- \; f \; 2Br^-$ $\qquad E^{\ominus} = +1.07$ V

As $E^{\ominus}(Br_2|Br^-)$ is **more positive** than $E^{\ominus}(I_2|I^-)$, **I_2 is the weaker oxidising agent [1m, with correct $E^{\ominus}$ values]** and oxidation number of S **increases** from **+2** in $S_2O_3^{2-}$ to **+2.5** in $S_4O_6^{2-}$. Bromine is the stronger oxidising agent and oxidation number of S **increases** from **+2** in $S_2O_3^{2-}$ to **+6** in SO_4^{2-}. **[1m]** [2]

For Examiner's Use

(d) 5.0×10^{-4} mol of a bromate salt containing the BrO_4^{n-} anion was added to 25.0 cm^3 of acidified KI present in excess to yield iodine and bromide ions.

The resultant solution required 40.0 cm^3 of 0.10 mol dm^{-3} sodium thiosulfate, $Na_2S_2O_3$, for complete reaction.

Determine the value of ***n***.

Iodometric equation: $2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

n_{I_2} formed $= n_{I_2}$ reacted with $S_2O_3^{2-}$

$$= \frac{1}{2}\times(0.0400\times0.10)$$

$$= \underline{\mathbf{2.00\times10^{-3}\ mol}}$$ **[1m] ecf from eqn in (c)(i)**

$$\frac{n_{I_2}}{n_{BrO_4^{n-}}} = \frac{2.00\times10^{-3}}{5.0\times10^{-4}} = 4$$

Oxidation: $2I^- \rightarrow I_2 + 2e^-$

Mole ratio: $\mathbf{BrO_4^{n-} \equiv 4I_2 \equiv 8e^-}$

1 mole of BrO_4^{n-} gains 8 moles of electrons.

Oxidation number of Br in BrO_4^{n-} decreases by 8 to –1 in Br^-

Oxidation number of Br in BrO_4^{n-} = +7

+7 + 4(–2) = ***n***(–1)

n = **1** **[1m] with logical working to deduce this**

[2]

(e) When chlorine reacts with magnesium, magnesium chloride, $MgCl_2$ is formed in preference of magnesium(I) chloride, MgCl. Attempts to isolate MgCl have not been successful. It is proposed that the MgCl formed undergoes disproportionation to form $MgCl_2$ and Mg.

$$2MgCl\,(s) \rightarrow MgCl_2\,(s) + Mg\,(s)$$

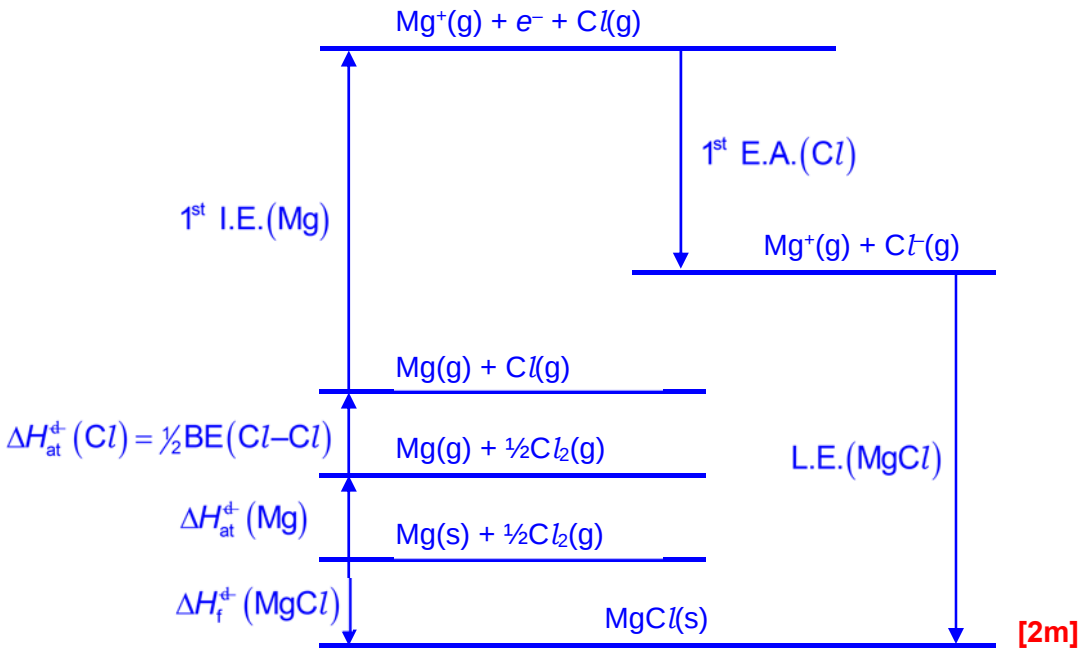
(i) Define the standard enthalpy change of formation of MgCl.

The enthalpy change when **1 mole of MgCl** is formed from its **constituent elements in their standard states** at 298 K and 1 bar **[1m]** [1]

For Examiner's Use

(ii) Using appropriate data from the *Data Booklet* and the information given below, construct a Born-Haber cycle to predict the lattice energy of magnesium(I) chloride, MgCl.

Enthalpy change of atomisation of magnesium = +148 kJ mol^{-1}
First electron affinity of chlorine = –349 kJ mol^{-1}
Standard enthalpy change of formation of magnesium(I) chloride = –130 kJ mol^{-1}



[2m]

By Hess' Law,

$$\Delta H_{at}^{\ominus}(\text{Mg}) + \frac{1}{2}\text{BE}(\text{Cl–Cl}) + 1^{\text{st}}\ \text{I.E.}(\text{Mg}) + 1^{\text{st}}\ \text{E.A.}(\text{Cl}) + \text{L.E.}(\text{MgCl}) = \Delta H_{f}^{\ominus}(\text{MgCl})$$

$$\text{L.E.}(\text{MgCl}) = -130 - (+148) - \frac{1}{2}(+244) - (+736) - (-349)$$ **[1m]**

$$= \underline{\textbf{–787 kJ mol}^{-1}}$$ **[1m]**

[4]

(iii) The preferential formation of MgCl_2 can also be explained through the use of lattice energy of both MgCl_2 and MgCl and the relevant ionisation energies of magnesium.

Given that the experimental lattice energy of MgCl_2 is –2526 kJ mol^{-1}, explain why MgCl_2 is formed preferentially and MgCl is not.

- The ionisation energy required to produce Mg^{2+} (1^{st} IE(Mg) = +736 kJ mol^{-1} and 2^{nd} IE(Mg) = +1450 kJ mol^{-1}) can be compensated reasonably well by the higher magnitude of lattice energy (higher amount of energy (–2526 kJ mol^{-1}) is released during the formation of MgCl_2). **[1m]**

or

- Whereas the ionisation energy required to produce Mg^{+} is only merely compensated by the formation of MgCl due to its lower lattice energy (–787 kJ mol^{-1}). **[1m]**

Therefore MgCl_2 is formed preferentially. [1]

[Total: 15]

For Examiner's Use

3 The Haber Process is one of the landmark discoveries that converts nitrogen from the atmosphere to ammonia via a reversible reaction with hydrogen gas. This allows the agricultural industry to flourish due the increased accessibility of ammonia to synthesise nitrogen-containing fertilisers.

(a) (i) Write an equation, including state symbols, for the Haber Process.

N_2 (g) + $3H_2$ (g) $2NH_3$ (g) **[1m]** [1]

(ii) Using the information in **(a)(i)**, predict and explain the sign of the entropy change for the conversion of nitrogen to ammonia.

In the reaction in **(a)(i)**, there is a **decrease in the number of gas molecules**, **reducing** the number of ways that the **particles and energy can be distributed**. **[1m] for gas molecules and particles/energy distributed**

Hence, there is a **decrease in entropy**. The sign of the entropy change should **be negative**. **[1m] for entropy and sign of entropy change**

[2]

(b) Often the behaviour of gases can be estimated using the ideal gas equation, which is based on the laws of Boyle, Charles and Avogadro. However, this is assuming that all gases behave ideally. These assumptions are based on the kinetic theory of gases.

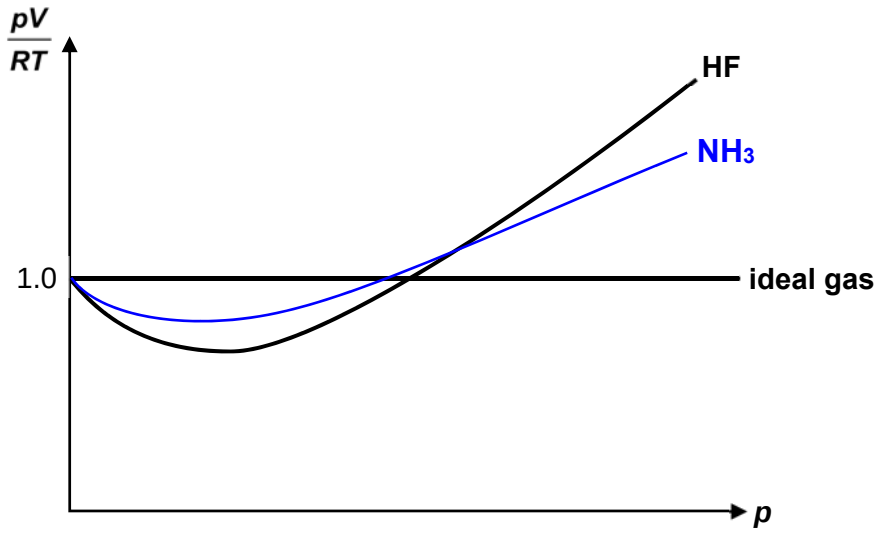
(i) State **two** assumptions of the kinetic theory of gases.

- There are **no/negligible intermolecular forces of attraction** between the gas molecules.
- Gas molecules **does not occupy any volume**. (volume is negligible compared to the volume of container)
- Collisions between gas molecules are **"perfectly elastic"**.

[2m] any 2 [2]

For Examiner's Use

(ii) The plot of $\frac{pV}{RT}$ against p for one mole of an ideal gas and one mole of hydrogen fluoride gas at 300 K is given below.



Sketch on the graph above to show how one mole of ammonia gas (NH_3) will behave at 300 K. Explain your answer.

The **hydrogen bonds** between NH_3 are **weaker** than that between HF molecules since **N–H bond is less polar than H–F bond**. **[1m] for concept of weaker hydrogen bonding between molecules**

Hence, NH_3 **deviates less** from ideal gas behaviour. **[1m] for correct sketching of line** [2]

(iii) Under what conditions of temperature and pressure would ammonia behave like an ideal gas? Explain your answer.

Under **low pressure and high temperature**. **[1m] for stating both conditions**

At lower pressure, NH_3 molecules are **far apart**, such that **volume of gas molecules becomes insignificant compared to the volume of the container** **[1m]** in which the gas is held.

At high temperature, NH_3 molecules **moves faster** (or have higher average kinetic energy). As such, **the intermolecular forces of attraction between the molecules become negligible [1m]**.

[3]

[Total: 10]

For Examiner's Use

4 Trimethylamine, $(CH_3)_3N$, is a base which is used as a starting material for the preparation of insecticides and pharmaceuticals.

(a) A 10.0 cm^3 of an aqueous solution of trimethylamine was placed in a conical flask. The pH of the solution was found to be 11.85. When a titration was performed, 16.00 cm^3 of 0.250 mol dm^{-3} dilute sulfuric acid was required to neutralise this base.

(i) Calculate the concentration of trimethylamine in the conical flask.

$$\text{Concentration of triethylamine} = \frac{2\times\left(\frac{16.00}{1000}\times 0.250\right)}{\frac{10.0}{1000}} = \underline{\mathbf{0.800\ mol\ dm^{-3}}}\ \mathbf{[1m]}$$

[1]

(ii) Use your answer in **(a)(i)** and the above data to show that trimethylamine is a weak base. Explain your answer.

pOH = 14 – 11.85 = 2.15

$[OH^-(aq)] = 10^{-pOH} = 7.079\times10^{-3}$ mol $dm^{-3} \approx$ **$\underline{7.08\times10^{-3}\ mol\ dm^{-3}}$ [1m]**

Since $[OH^-(aq)]$ is **less than** [trimethylamine (aq)], trimethylamine is **not fully ionised** in solution **[1m]** and hence is a weak base.

[2]

(iii) Write an expression for the base dissociation constant, K_b, for trimethylamine. Hence determine its pK_b value.

$$K_b = \frac{\left[(CH_3)_3NH^+(aq)\right]\left[OH^-(aq)\right]}{\left[(CH_3)_3N\ (aq)\right]}\ \mathbf{[1m]}$$

$$= \frac{\left(7.079\times10^{-3}\right)\left(7.079\times10^{-3}\right)}{\left(0.800 - 7.079\times10^{-3}\right)} = 6.321\times10^{-5}\ \text{mol}$$

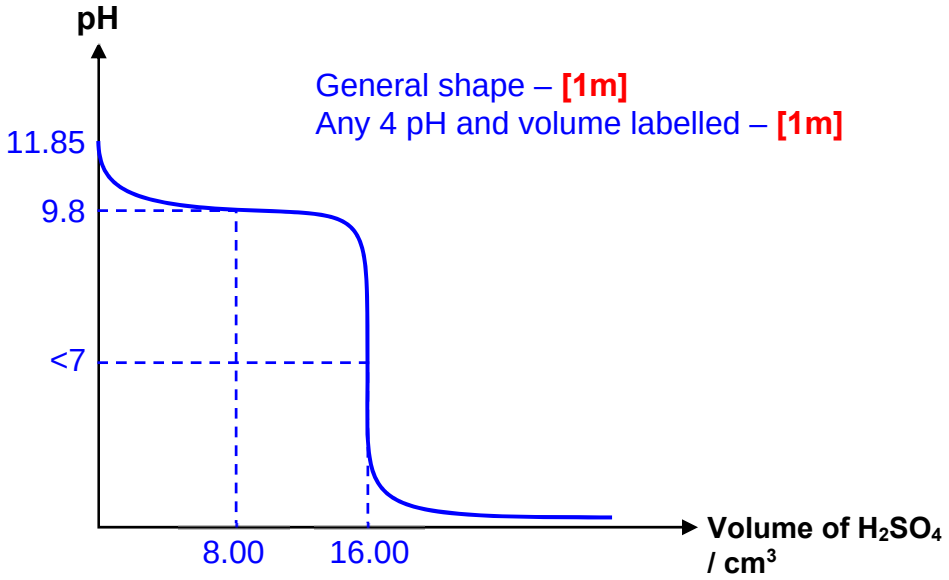
pK_b = –log (6.321×10^{-5}) = 4.199 = **$\underline{4.20}$** (3 sf) **[1m]**

[If assuming the dissociation to be very small, and approximating $0.800 - 7.079\times10^{-3} \approx 0.800$, then p$K_b$ = **4.203** or **4.20** (3sf)]

[2]

For Examiner's Use

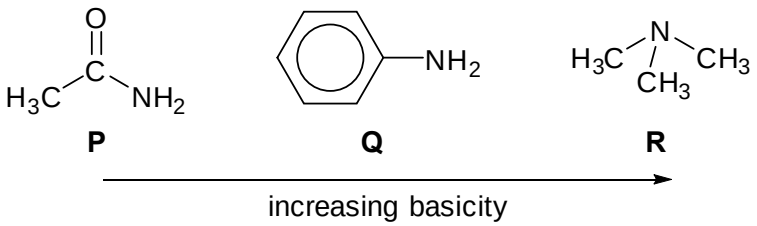
(b) Sketch the pH curve that would be obtained for the titration reaction mentioned in **(a)**. Label clearly **any significant co-ordinates** on your sketch.



[2]

(c) The basicity of trimethylamine is different in comparison with other nitrogen organic compounds.

Account for the trend in basicity as shown below.



amide P: lone pair of electrons on N is delocalised into the neighbouring carbonyl group with δ+ C and highly electronegative O due to overlap of p orbital of N with the π electron cloud of C=O

⇒ not readily available for donation **[1m]**

aryl amine Q: lone pair of electron delocalised into the benzene ring

⇒ less readily available for donation **[1m]**

tertiary amine R: alkyl groups are electron donating, increases the electron density around N

⇒ lone pair of electrons more easily donated, increased basic strength **[1m]**

[3]

[Total: 10]

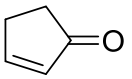
For Examiner's Use

5 (a) This question is about Grignard reagents, compounds that are of great use in organic synthesis for forming carbon–carbon bonds.

Grignard reagents are compounds of general formula RMgX where X = Br or I. They are very reactive, giving rise to the highly nucleophilic ion R^-. When a solution of a Grignard reagent in dry ether is added to a carbonyl compound, the R^- attacks the carbonyl group.

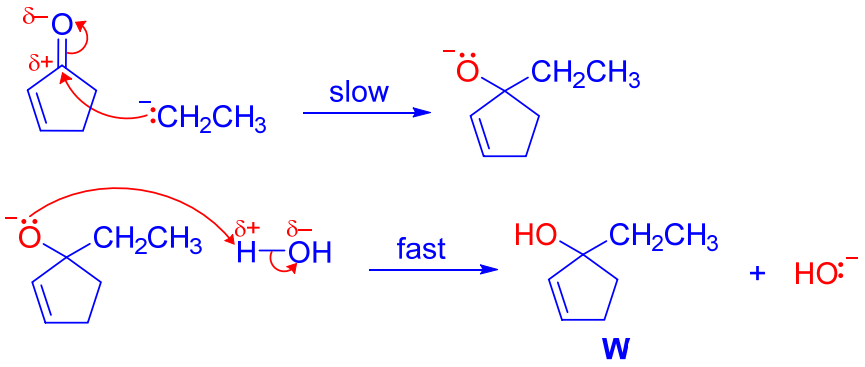
The mechanism of this reaction involves **two steps**:

- The first step is the rate determining step which involves a nucleophilic attack of nucleophilic ion **R^-** on the carbonyl carbon to form a tetrahedral intermediate.
- The second step involves an acid-base reaction with water.

(i) 2-cyclopentenone,  , is treated with the Grignard reagent ethyl magnesium bromide, CH_3CH_2MgBr, followed by water. An organic compound **W**, $C_7H_{12}O$, is formed.

Name and draw the mechanism of the above reaction.

Nucleophilic addition **[1m]**



[1m] curly arrows, partial charges, lone pair
[1m] intermediate and slow step products

[3]

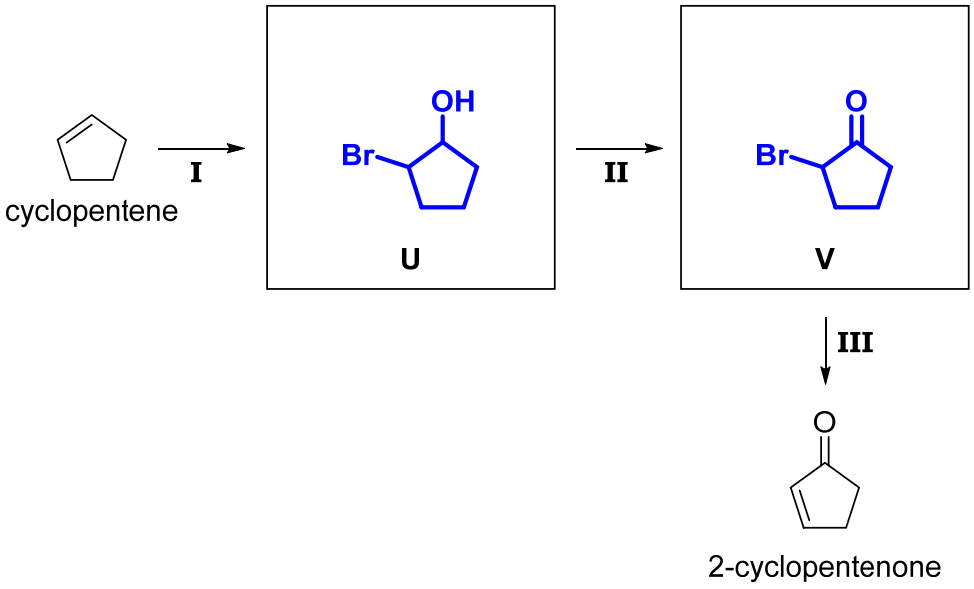
(ii) Does 2-cyclopentenone exhibit *cis-trans* isomerism? Explain your answer.

No. There is no *cis-trans* isomerism as the C=C is in a small cyclic ring, so only the *cis* isomer is present due to **ring strain**. **[1m]**

[1]

For Examiner's Use

(iii) 2-cyclopentenone can be formed from cyclopentene. Propose a three-step synthetic route to obtain 2-cyclopentenone from cyclopentene. State the reagents and conditions required, and draw the structures of the intermediates **U** and **V** obtained in the boxes below.



Step I: Br_2 (aq), room temperature

Step II: $KMnO_4$(aq) or $K_2Cr_2O_7$(aq), H_2SO_4(aq), heat

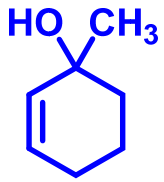
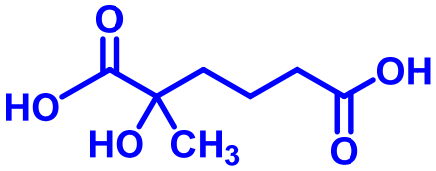
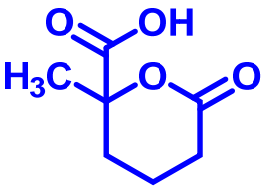
Step III: ethanolic KOH, heat ..... [3]

[1m] for each step and intermediate

For Examiner's Use

(b) A six-membered cyclic compound **X**, an isomer of **W**, $C_7H_{12}O$, reacts with gaseous HBr at room temperature to form chiral compounds with molecular formula $C_7H_{13}OBr$. Compound **X** is readily oxidised by hot acidified potassium manganate(VII) to form an acidic compound **Y**, $C_7H_{12}O_5$. 1 mole of **Y** is exactly neutralised by 2 moles of sodium hydroxide. When **Y** is warmed with concentrated sulfuric acid, a sweet-smelling compound **Z**, $C_7H_{10}O_4$ is isolated.

Suggest the structures for compound **X**, **Y** and **Z**.

X	
Y	
Z	

[1m] for each compound

[3]

[Total: 10]

For Examiner's Use

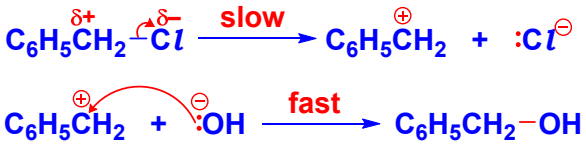
6 Halogenoalkanes are compounds in which one or more hydrogen atoms in an alkane have been replaced by halogen atoms (fluorine, chlorine, bromine and iodine). They serves as important intermediates in organic synthesis due to the ease of cleavage of the polar C–X bond (X = C*l*, Br or I), leading to substitution of the halogen atom by a wide variety of nucleophiles.

(a) The reaction between the primary halogenoalkane, benzyl chloride, $C_6H_5CH_2Cl$, and sodium hydroxide is known follow the rate equation:

rate = *k* [benzyl chloride]

(i) Draw the mechanism of the reaction which is consistent with the rate equation.

S_N1 Nucleophilic substitution



[1m] curly arrows, partial charges, lone pair
[1m] benzyl cation intermediate and slow step products

[2]

(ii) Suggest a possible reason why despite being a primary halogenoalkane, benzyl chloride adopts the mechanism you have drawn in **(a)(i)**.

The benzyl cation, **$C_6H_5CH_2^+$, intermediate** formed although is a primary cation, is **stabilised by delocalisation of the electrons from the benzene ring** **[1m]** onto the carbocationic carbon, hence favouring the S_N1 mechanism instead of S_N2 mechanism.

[1]

(b) Unlike halogenoalkanes, halogenoalkenes such as vinyl bromide, CH_2=CHBr, are inert towards nucleophilic substitution. Suggest a possible explanation for this inertness.

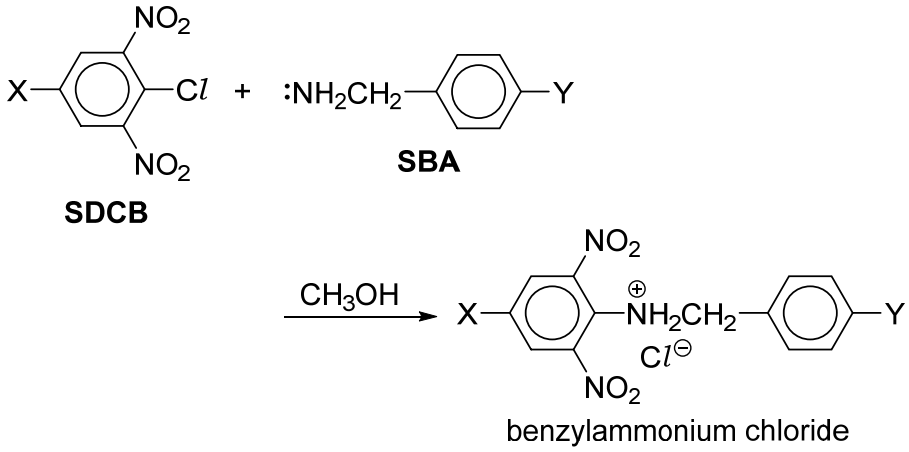
The **lone pair of electrons on Br is delocalised into the C=C**, imparting **partial double bond character** to the C–Br, and **strengthening the C–Br bond**, hence rendering cleavage of the C–Br bond difficult. **[1m]** In addition, this lowers the electron-deficiency of the α-carbon, making vinyl bromide less susceptible to nucleophilic attack.

[1]

Like halogenoalkenes, halogenoarenes are also usually inert towards nucleophilic substitution reaction.

Nonetheless, when suitably tuned, halogenoarenes can be made to undergo nucleophilic substitution too, although the mechanism is different from the S_N1 and S_N2 mechanisms of aliphatic halogenoalkanes.

(c) 4-X-Substituted-2,6-dinitrochlorobenzenes (SDCB) react with 4-Y-substituted-benzylamines (SBA) in methanol to give benzylammonium chloride salt:



SDCB **SBA**

benzylammonium chloride

In the reaction, SDCB is regarded as the substrate, while SBA is the nucleophile.

(i) Suggest how it can be shown *chemically* that substitution reaction had indeed taken place with SDCB?

Addition of **aqueous silver nitrate** to the reaction mixture will produce an **immediate white precipitate of AgCl** if the substitution reaction had taken place. Otherwise, no precipitate will be observed. **[1m] for both reagent and immediate ppt** [1]

(ii) Suggest, with reason, one physical property which may be used to follow the progress of the reaction.

Since the reaction **produces an ionic product** from electrically neutral reactants, the **electrical conductivity [1m]** of the mixture will increase with the amount of the product formed, allowing the progress of the reaction to be followed.

[1]

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The reaction was found to follow overall second-order kinetics, with rate equation:

$$\text{rate} = k[\text{SDCB}][\text{SBA}]$$

The rate constant, k ($\text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$), for the reaction of three 4-X-substituted-2,6-dinitrochlorobenzenes with four 4-Y-substituted-benzylamines in pure methanol at 25 ºC is given in Table 6.1 below.

Table 6.1

X (SDCB substrate)	**4-Y-benzylamine (SBA nucleophile)**			
	4-OCH_3	**4-CH_3**	**H**	**4-C*l***
NO_2	3.12	2.47	2.34	1.66
CN	0.748	0.563	0.498	**0.357**
CF_3	0.100	0.0902	0.0744	0.0479

The values of the rate constant, k, can be obtained from suitable concentration–time plots such as those shown in Figure 6.1 on the next page.

Figure 6.1 is obtained by monitoring changes in the concentration of the nucleophile, 4-chlorobenzylamine, with time, using an **excess** of the three substrates separately. The initial concentrations of the three substrates are indicated on Figure 6.1.

(iii) With the aid of Figure 6.1, determine the rate constant, k, when X = CN, using 4-chlorobenzylamine as nucleophile, and fill in the blank in Table 6.1.

From the graph,

$$\text{initial rate} = \left|\frac{0.010 - 0}{0 - 8}\right| = 1.25 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$ **[1m]**

$$\text{Hence, } k = \frac{\text{rate}}{[\text{SDCB}][\text{SBA}]} = \frac{1.25 \times 10^{-3}}{0.350 \times 0.010} = 0.3571 \approx \underline{\mathbf{0.357}}\ \text{mol}^{-1}\ \text{dm}^3\ \text{s}^{-1}$$ **[1m]**

[2]

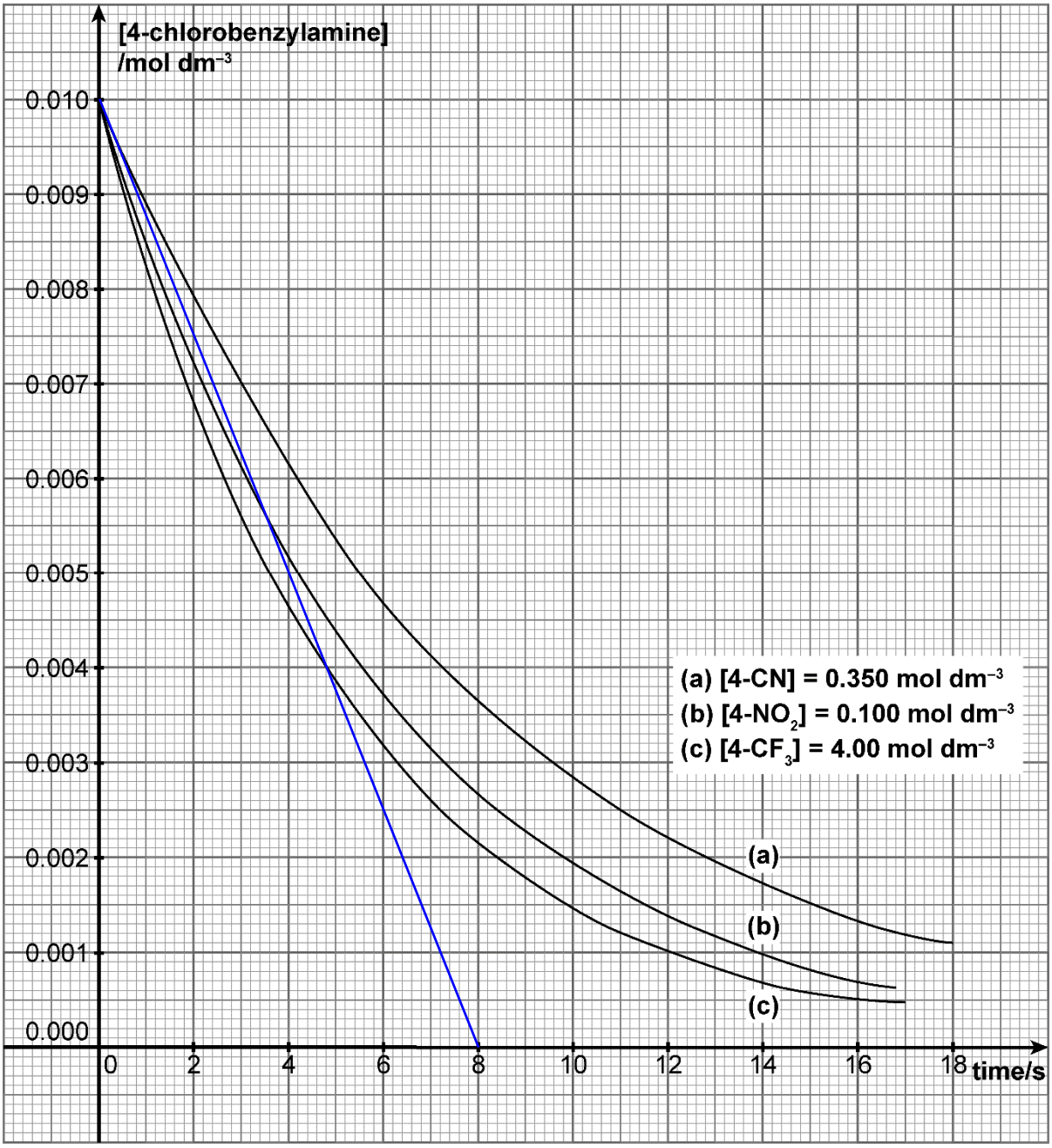

Figure 6.1

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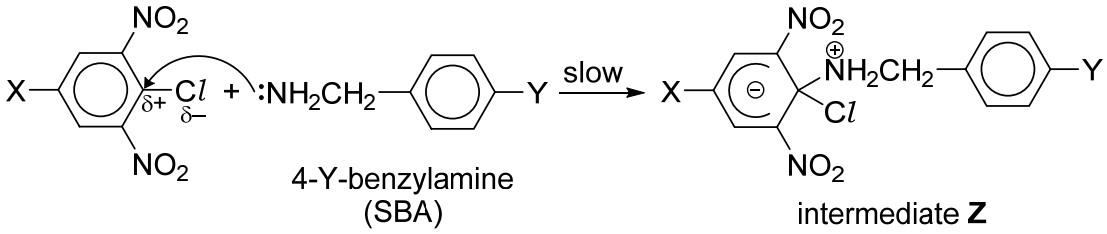
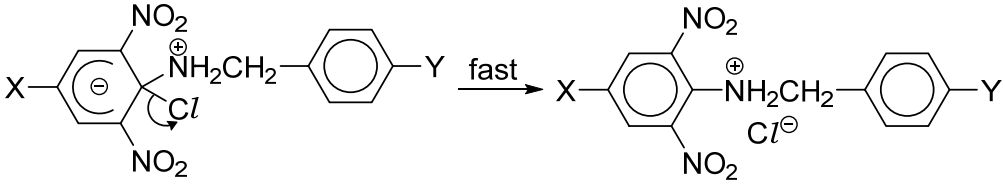
(d) Although the reaction is second-order, however, it is **not** a single-step reaction. Instead, SBA performs a rate-determining nucleophilic attack at the electrophilic C–C*l* carbon of SDCB, leading to the formation of resonance-stabilised intermediate **Z**:



4-Y-benzylamine (SBA)

intermediate **Z**

Subsequently, intermediate **Z** rapidly expels a chloride ion to give the desired benzylammonium chloride:



intermediate **Z**

benzylammonium chloride

This two-step mechanism is known as the S_NAr mechanism.

Using the mechanism given above and the data in Table 6.1, explain which of the three substituents X = NO_2, CN or CF_3, is the strongest electron-withdrawing group.

From the mechanism, since the slow step involves the formation of intermediate **Z**, the **more stable Z** is, the **faster** the reaction will be. The **negative charge** of intermediate **Z** will be **stabilised** by the presence of **electron-withdrawing substituents**. Since the reaction is fastest (largest *k*) with X = NO_2, **NO_2** must be the strongest electron-withdrawing group. **[1m]** [1]

(e) The magnitude of the rate constant *k* can be used as a direct measure of the nucleophilicity of the 4-Y-benzylamine (SBA) nucleophile, that is, the larger the rate constant *k*, the more nucleophilic is the 4-Y-benzylamine.

Using the mechanism of the S_NAr mechanism described, explain why there is a positive correlation between the magnitude of the rate constant *k* and the nucleophilicity of the 4-Y-benzylamine.

From the mechanism, since the **slow step** involves the **nucleophilic attack** of the 4-Y-benzylamine at the electrophilic carbon of the benzene ring, the **more nucleophilic** the 4-Y-benzylamine, the **lower** will be the **activation energy**, and hence **larger** the **rate constant** *k*. **[1m] for nucleophilic attack being slow step and lower activation energy** [1]

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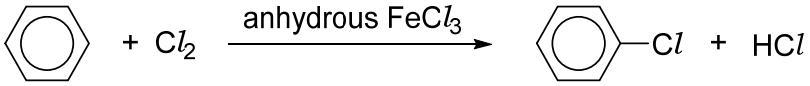
Chloroarenes can be prepared by the reaction of benzene and chlorine in the presence of anhydrous $FeCl_3$ as a Lewis acid catalyst:



(f) Describe the role of anhydrous $FeCl_3$ in the reaction, illustrating with an equation.

The role of anhydrous $FeCl_3$ is to serve as a halogen carrier to **generate the strong electrophile**, the chlorine cation, from chlorine:

$$Cl_2 + FeCl_3 \rightarrow Cl^+ + FeCl_4^-$$

[1m] for strong electrophile and equation [1]

Anhydrous iron(III) chloride, $FeCl_3$, is an almost black crystalline solid and is very hygroscopic; it forms a series of hydrates when exposed to moist air. The common hydrate is yellow $FeCl_3 \cdot 6H_2O$, which contains $[FeCl_2(H_2O)_4]^+$. This is very soluble in water, and gives a strongly acidic solution.

The $[Fe(H_2O)_6]^{3+}$ ion exist only in strongly acidic solution in the absence of coordinating anion. The ion is violet in solution, although some hydrolysis may colour the solution yellow-brown.

(g) (i) Explain why $[FeCl_2(H_2O)_4]^+$ and $[Fe(H_2O)_6]^{3+}$ have different colours despite both containing iron(III).

Despite containing iron(III), the two complexes possesses **different ligands** and hence, the 3d orbitals of iron(III) is **split** into two different energy levels by **different extent**, resulting in **different energy gaps** between the two levels. **[1m]** [1]

(ii) Explain why the violet $[Fe(H_2O)_6]^{3+}$ ion is stable only in highly acidic solution.

Due to the high charge density of the Fe^{3+} ion, $[Fe(H_2O)_6]^{3+}$ undergoes **hydrolysis** readily: **$[Fe(H_2O)_6]^{3+}(aq)$ $[Fe(H_2O)_5(OH)]^{2+}(aq) + H^+(aq)$**
Hence, a **high concentration of $H^+(aq)$** is needed to **suppress the hydrolysis**, to stabilise the $[Fe(H_2O)_6]^{3+}$ ion. **[1m]** [1]

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(h) On the other hand, anhydrous iron(III) iodide, FeI_3, had only been prepared recently in non-aqueous medium via the reaction of 6-coordinated $Fe(CO)_4I_2$ in hexane:

$$Fe(CO)_4I_2 + \tfrac{1}{2}I_2 \xrightarrow[\text{hexane}]{\text{uv light}} FeI_3 + 4CO$$

(i) State and explain the type of reaction involved in the synthesis of iron(III) iodide.

Redox reaction. The oxidation state of iron in $Fe(CO)_4I_2$ is +2, which is increased to +3 in FeI_3, while the oxidation state of iodine in I_2 is 0 which is decreased to –1 in FeI_3 **[1m] with correct explanation**

[1]

A non-aqueous medium is required for the above synthesis as iron(III) iodide is completely decomposed in aqueous solution.

(ii) Using the *Data Booklet*, suggest possible products from the decomposition of iron(III) iodide in water.

Since $E^{\ominus}(Fe^{3+}|Fe^{2+}) = +0.77\ V > E^{\ominus}(I_2|I^-) = +0.54\ V$, Fe^{3+} is capable of oxidising I^- to I_2, while itself reduced to Fe^{2+}:

$$FeI_3 \rightarrow FeI_2 + \tfrac{1}{2}I_2$$

The possible products are **FeI_2** and **I_2**. **[1m] for both products** [1]

[Total: 15]

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