**NATIONAL JUNIOR COLLEGE**
**SH2 PRELIMINARY EXAMINATION**
Higher 2

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|---|---|---|---|
| CANDIDATE NAME | | | |
| SUBJECT CLASS | | REGISTRATION NUMBER | |

# CHEMISTRY

**9729/03**
Paper 3 Free Response
**13 September 2022**
**2 hours**

Candidates answer on Question Paper.
Additional Materials: Data Booklet

**READ THE INSTRUCTIONS FIRST**

Write your subject class, registration number and name on all the work you hand in.
Write in dark blue or black pen.
You may use a soft pencil for any diagrams or graphs.
Do not use staples, paper clips, glue or correction fluid.

**Section A**
Answer **all** questions.

**Section B**
Answer **one** question.

A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.

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

| For Examiner's Use | |
|---|---|
| **Section A** | |
| **1** | **/18** |
| **2** | **/19** |
| **3** | **/23** |
| **Section B (*circle the question you attempt)** | |
| **4** | **/20** |
| **5** | **/20** |
| **Paper 3 Total** | **/80** |

## Section A

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

**1 (a)** Amines can be synthesised from methylbenzene, shown by the following steps.

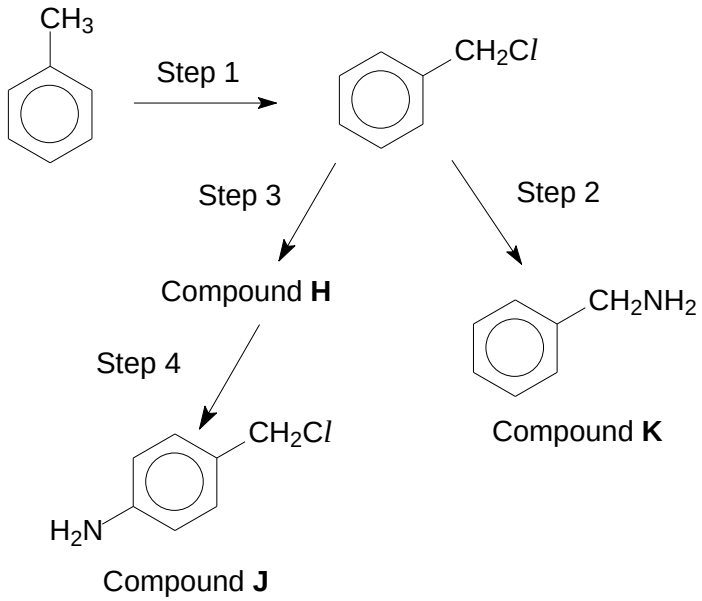


**Fig. 1.1**

**(i)** Suggest the structure for compound **H**. [1]

**(ii)** Suggest reagents and conditions for steps 1, 2, 3 and 4 in Fig. 1.1. [4]

**(iii)** Suggest why the yield for step 2 is not high. [1]

The $K_b$ values of three bases, at 25 °C, are shown in Table 1.2.

**Table 1.2**

| base | $K_b$/mol dm$^{-3}$ |
|---|---|
| ammonia | $1.8 \times 10^{-5}$ |
| compound **K** | $4.5 \times 10^{-4}$ |
| compound **J** | $7.4 \times 10^{-10}$ |

**(iv)** Explain the relative magnitudes of the $K_b$ values in Table 1.2. [2]

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**(b)** The rate of reaction for step 2 in Fig. 1.1 can be followed by measuring the change in concentration of $C_7H_7Cl$ with time. The reaction was carried out with the other reactant in large excess.

Fig. 1.2 shows the concentration of $C_7H_7Cl$ monitored against time for step 2.

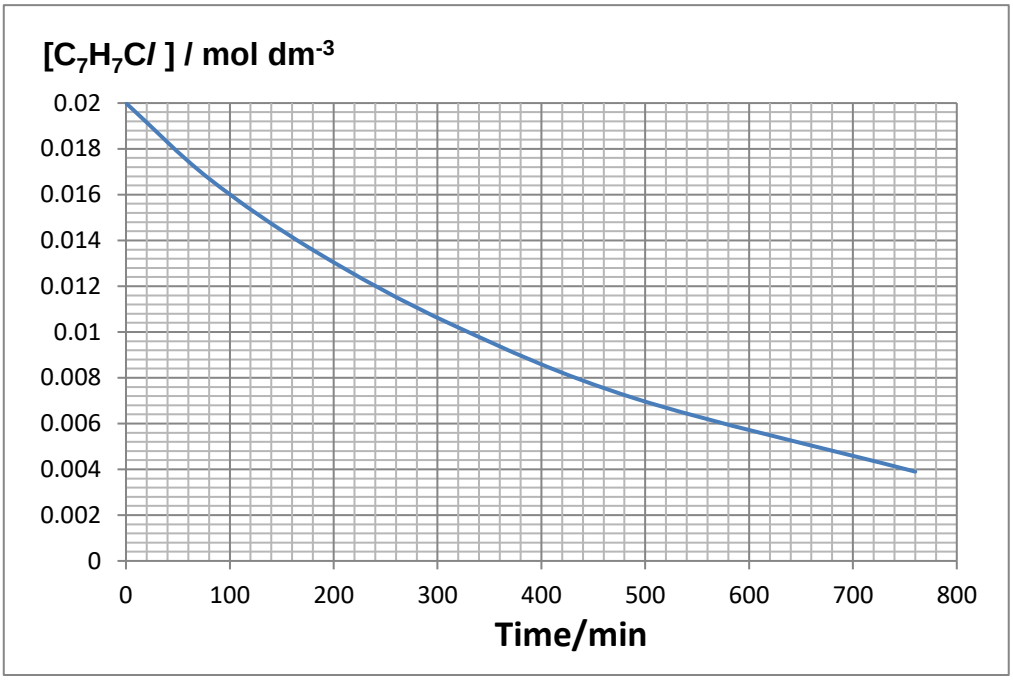


**Fig. 1.2**

Showing all your working and drawing clearly any construction lines, use Fig.1.2 to determine:

**(i)** The order with respect to $C_7H_7Cl$. Explain your reasoning. [2]

**(ii)** The initial rate, in mol $dm^{-3}$ $min^{-1}$ [1]

Given that the half-life magnitude of $C_7H_7Cl$ is not affected by the change in concentration of the other reactant.

**(iii)** Write the rate equation for step 2 in Fig.1.1, and calculate a value for the rate constant, stating its units. [2]

**(iv)** Hence, outline a mechanism for step 2 in Fig.1.1 to form all the products.

Show all charges and relevant lone pairs and show the movement of electron pairs by using curly arrows. [3]

**(v)** Explain why step 2 proceeds via the mechanism you describe in **b(iv).** [1]

**(vi)** Suggest and explain the difference in reactivity when 4-bromomethylbenzene undergoes the same reaction. [1]

[Total : 18]

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**PLEASE TURN OVER**

**2** Hydrogen cyanide, HCN, is extremely toxic and with sufficient concentrations it leads to rapid death. During the Second World War, a form of hydrogen cyanide known as *Zyklon B* was used in the Nazi gas chambers.

**(a)** **(i)** Draw a dot–and–cross diagram to illustrate the bonding in HCN. [1]

HCN can be oxidised to cyanogen, $C_2N_2$.

$$C_2N_2(g) + 2H^+(aq) + 2e^- \rightleftharpoons 2HCN(g) \quad E^\ominus = +0.37\ V$$

**(ii)** Suggest a suitable oxidant to oxidise HCN to $C_2N_2$ in acidic solution, using the *Data Booklet*.

Write an equation for the reaction and calculate the $E^\ominus_{cell}$. [2]

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**(b)** The synthesis of HCN was developed in the early 1900s. The most commonly used procedure is the *Andrussow* process. A less common method is the *BMA* process.

*Andrussow* process:

$CH_4\,(g) + NH_3\,(g) + \frac{3}{2}O_2\,(g) \longrightarrow HCN\,(g) + 3H_2O\,(l)$ $\quad \Delta H = -506\ kJ\ mol^{-1}$

*BMA* process:

$CH_4\,(g) + NH_3\,(g) \longrightarrow HCN\,(g) + 3H_2\,(g)$

**(i)** Using information from the *Data Booklet*, calculate the enthalpy change of reaction for the *BMA* process given above. [2]

**(ii)** By considering the spontaneity of reaction, suggest why the *Andrussow* process is the preferred procedure at low temperature. [2]

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**(c)** The *BMA* process is a reversible reaction at 500 $^{o}$C. Starting with equal amounts of $CH_4$ and $NH_3$, the reaction is allowed to reach equilibrium at 500 $^{o}$C under a constant pressure of 1 atm.

*BMA* process: $CH_4\,(g) + NH_3\,(g) \rightleftharpoons HCN\,(g) + 3H_2\,(g)$

**(i)** Write an expression for the $K_p$ of *BMA* process, stating its units. [1]

**(ii)** Given that the equilibrium partial pressure of $H_2$ is 0.3 atm, calculate the value of $K_p$ at 500 $^{o}$C.

[2]

**(iii)** Discuss the effect of increase in total pressure on

- the proportion of HCN,
- $K_p$ value,
- rate of reaction .

[3]

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**(d)** HCN (aq) has p$K_a$ = 4.79 at 25 $^oC$.

**(i)** Calculate the concentration of $CN^-$ ion at pH 4, when the concentration of HCN(aq) is 0.06 mol $dm^{-3}$. [1]

Zinc cyanide, $Zn(CN)_2$, is sparingly soluble in water.
The numerical value of $K_{sp}$ is $8.0 \times 10^{-12}$ at 25$^oC$.

**(ii)** Write an expression for the $K_{sp}$ of $Zn(CN)_2$, stating its units. [1]

**(iii)** By considering your answer to **(d)(i)**, determine the minimum concentration of $Zn^{2+}$ required to cause precipitation of $Zn(CN)_2$ at pH 4. [2]

**(iv)** Describe and explain how the solubility of $Zn(CN)_2$ is affected:

- by adding HC*l*(aq)
- by adding concentrated Zn$Cl_2$(aq)

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[Total:19]

**3 (a)** GABA, a naturally occurring neurotransmitter, has the condensed formula of $HOOCCH_2CH_2CH_2NH_2$. It can be synthesised from 2-bromoethanal, $CH_2BrCHO$, shown by the following steps.

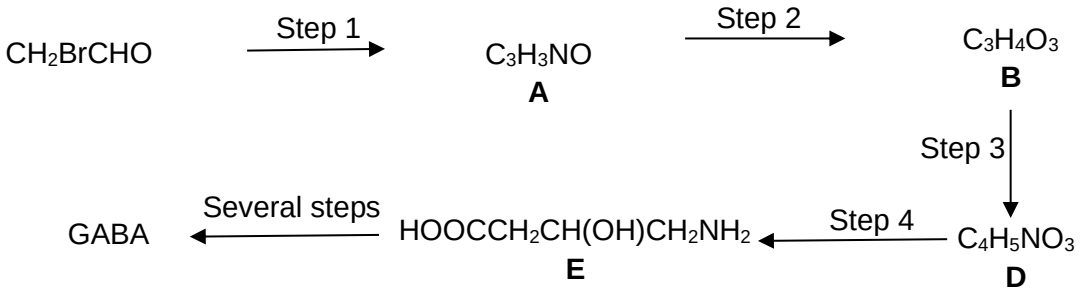


**Fig. 3.1**

Compound **B** gives effervescence with $Na_2CO_3(aq)$ and it gives a brick red precipitate with warm Fehling's solution.

**(i)** Suggest what these observations indicate about the functional groups in **B.** [1]

**(ii)** Give the structures for compounds **A** and **D**. [2]

**(iii)** Suggest reagents and conditions for steps 1, 2, 3 and 4 in Fig. 3.1. [4]

**(iv)** Suggest why the yield for step 3 is very low. [1]

**(v)** The conversion of **B** to **D** involves a nucleophilic addition. Suggest why only 50% of compound **D** can be used in drug synthesis. [2]

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**(b)** Compound **E** undergoes intramolecular condensation reaction under suitable conditions. Isomer **F** is produced instead of isomer **G**.

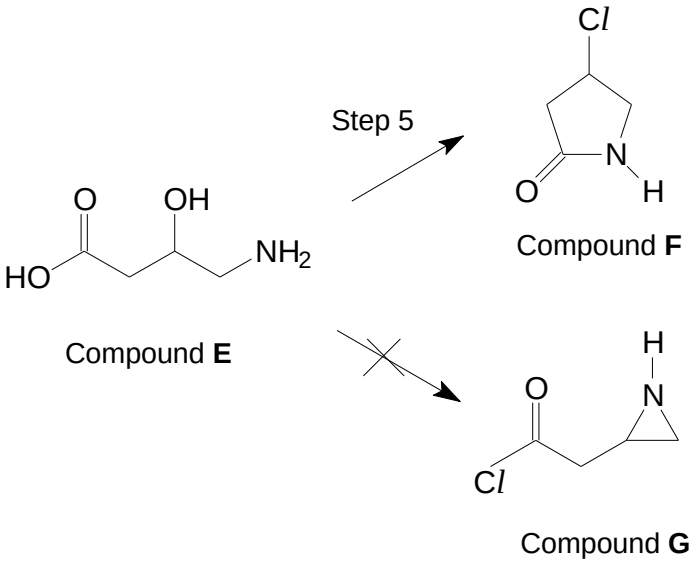


**Fig. 3.2**

**(i)** Suggest the reagents and conditions for step 5 in Fig. 3.2. [1]

**(ii)** Give two reasons why isomer **F** is preferentially formed. [2]

**(iii)** Explain why compound **F** is neutral. [2]

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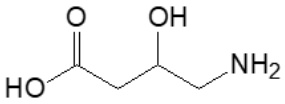
**(c)** Table 3.3 shows the p$K_a$ values of different functional groups present in compound **E** and GABA.

**Table 3.3**

| | p$K_{a1}$ of carboxyl group | p$K_{a2}$ of amino group |
|---|---|---|
| $HOOCCH_2CH_2CH_2NH_2$<br>GABA | 2.45 | 9.10 |
|  <br>Compound **E** | 2.05 | 9.80 |

**(i)** Suggest a reason why p$K_{a1}$ value of compound **E** is of lower value than p$K_{a1}$ of GABA. [1]

**(ii)** Calculate the initial pH of 25.0 $cm^3$ of 0.050 mol $dm^{-3}$ of compound **E**. [1]

**(iii)** Calculate the volumes of 0.10 mol $dm^{-3}$ of NaOH required to form a buffer mixture with compound **E** at pH 2.05 and 9.80 respectively. [2]

**(iv)** Sketch the pH-volume added curve you would expect when compound **E** is titrated against 0.10 mol $dm^{-3}$ of NaOH. Include the volume and pH values given or calculated in **(c)(ii)** and **(c)(iii)** as well as the volumes required for each equivalence point.

You may assume that the graph tends towards pH 13 upon addition of excess NaOH. [2]

**(v)** The working range for thymolphthalein is 9.3 to 10.5, comment on whether thymolphthalein is a suitable indicator for identifying the first endpoint. [1]

**(vi)** Write two equations to describe how the buffer mixture at pH 9.80 from **(c)(iii)** can act as a buffer when small amounts of $H^+$ or $OH^-$ is added. [1]

[Total: 23]

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**PLEASE TURN OVER**

## Section B

Answer **one** question from this section.

**4** **(a)** State the electronic configuration of chromium. [1]

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**(b)** Chromium(VI) ions commonly exist as oxo-anions such as $CrO_4^{2-}$, which is yellow in color and $Cr_2O_7^{2-}$,which is orange.

**(i)** Explain why chromium(VI) ions exist as oxo-anions instead of $[Cr(H_2O)_6]^{6+}$. [1]

**(ii)** Write the equation for the conversion of $CrO_4^{2-}$ to $Cr_2O_7^{2-}$ in acidic medium. Predict the observation when NaOH is added to this solution at equilibrium. [2]

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**(c)** **E** is a hydrated salt containing 13.0 % of Cr, 27.0 % of $H_2O$ and 60.0 % of Br by mass. When 0.400 g of **E** is dissolved in water, an octahedral complex cation is formed. When treated with aqueous silver nitrate, this solution **immediately** gives 0.188 g of cream precipitate.

**(i)** Calculate the mole ratio of Cr: $H_2O$: Br in the hydrated salt **E**. [1]

**(ii)** Identify the cream precipitate and hence, determine the formula of the complex cation formed when **E** is dissolved in water.

[2]

**(iii)** Draw the structure of the complex cation present in **E**, showing clearly how the ligands are arranged around chromium cation. Indicate the overall charge of this complex ion. [1]

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**(d)** When a current of 1.0 A was passed through aqueous potassium maleate ($KO_2CCH=CHCO_2K$) for 15 minutes, it was found that 110 $cm^3$ $H_2$, measured at r.t.p, was collected at the cathode. The following reaction took place.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$$

Ethyne, $C_2H_2$, and $CO_2$ gas were produced at the anode. In order to determine the stoichiometry of the anode reaction, the volume of the gases collected at the anode was measured. The anode gas was first passed through aqueous NaOH before being collected in a gas syringe. The following data was collected :

- mass of bottle containing NaOH before experiment = 10.501 g
- mass of bottle containing NaOH after experiment = 10.904 g
- initial reading on syringe = 10.0 $cm^3$
- final reading on syringe = 120.0 $cm^3$

**(i)** Using the data *obtained from the cathode* and the *Data Booklet*, calculate a value for Faraday constant.

[2]

**(ii)** Calculate the volume of $CO_2$ produced at the anode, assuming r.t.p conditions.

[2]

**(iii)** State the volume of ethyne gas and hence suggest an ion-electron equation for the reaction that occurred at the anode.

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**(e)** Ethanal used to be manufactured from ethyne. These days, ethene is being used as the reactant instead. Widely known as the Wacker-Tsuji Oxidation, ethene and oxygen are bubbled together through an aqueous solution containing $CuCl_2$ and $PdCl_2$ catalysts:

$$CH_2{=}CH_2 \ + \ \tfrac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

The Wacker-Tsuji Oxidation is also useful for the synthesis of ketone:

$$RCH{=}CH_2 \ + \ \tfrac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} RCOCH_3$$

Compound **A**, $C_9H_{10}$, is used as a reactant in the Wacker-Tsuji oxidation reaction to give compound **B**, $C_9H_{10}O$. **B** gives a yellow precipitate when warmed with aqueous alkaline $I_2$. When **B** is reacted with $LiAlH_4$ in dry ether, compound **C** is formed. **A**, **B** and **C** all reacted with hot acidified $KMnO_4$ to give compound **D**, $C_7H_6O_2$.

Suggest the structures of compounds **A** to **D** and explain the reactions described.

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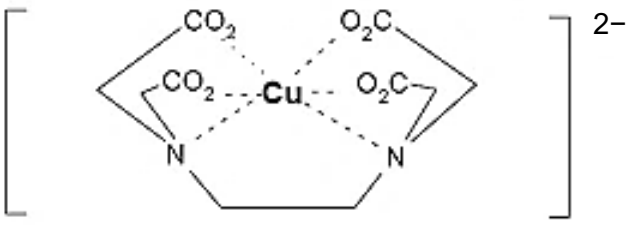
[Total: 20]

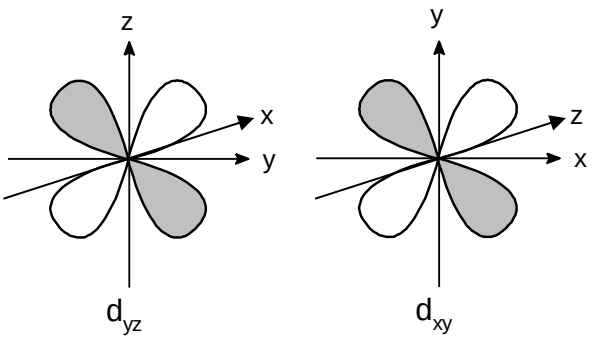
**5** **(a)** Copper and its compounds have a wide variety of uses.
Copper-EDTA complexes are commonly used in cosmetics and it gives the blue colour in many shampoos.

The structure of the copper-EDTA complex is given below.




**(i)** State the electronic configuration of the copper ion in the copper-EDTA complex. [1]

**(ii)** Two of the d orbitals are given below. Sketch the shapes of the other three d orbitals present in copper, labelling your orbitals clearly.




[2]

**(iii)** Explain why the copper-EDTA complex is blue. [3]

**(iv)** Cobalt and copper are both common transition elements.

Comment on the similarity of the atomic radii between cobalt and copper. [1]

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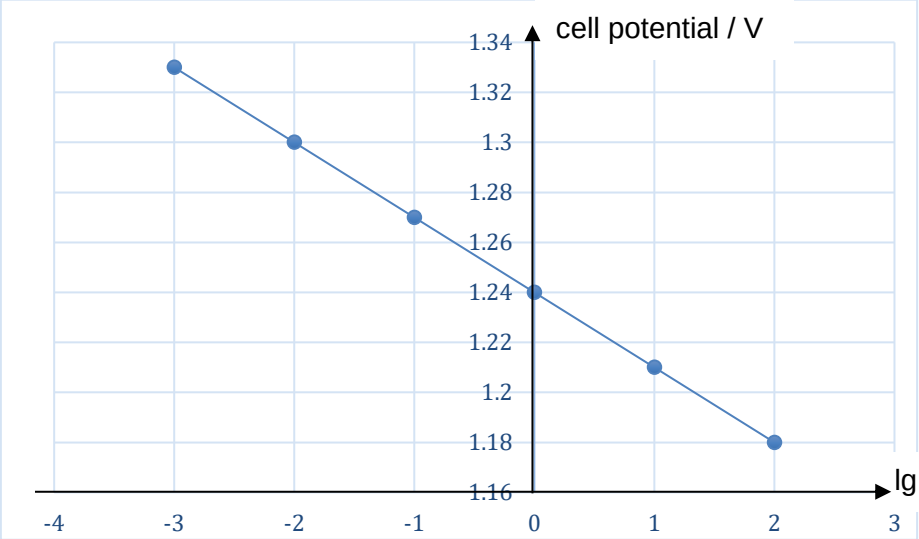
**(b)** An experiment was set up to investigate how the cell potential of a cell containing a metal, **M**, in contact with an aqueous solution of its ions, $\mathbf{M}^{n+}(aq)$, changed as $\mathbf{M}^{n+}(aq)$ was diluted.
As a Standard Hydrogen Electrode was not available, a half-cell consisting of $Cl^-/ClO^-$ in alkaline medium under standard conditions was used to connect to the half-cell with **M** in contact with $\mathbf{M}^{n+}(aq)$.

**(i)** Draw a fully labelled diagram of the electrochemical cell set-up as described above, in order to measure the changes in cell potential.

[3]

**(ii)** The cell potential was measured for various concentrations of $\mathbf{M}^{n+}(aq)$ and the results of cell potential against lg $[\mathbf{M}^{n+}]$ obtained are plotted in the graph as shown below.




Given that the cell potential of a cell, $E_{cell}$, is related to the standard electrode potential, $E^{\ominus}_{cell}$, by the equation:

$E_{cell} = E^{\ominus}_{cell} - \dfrac{0.06 \lg[M^{n+}]}{n}$, use your graph to determine

(I) the charge, n, of the $\mathbf{M}^{n+}$ ions

(II) the $E^{\ominus}_{cell}$

[2]

**(iii)** Given that the standard electrode potential for $Cl^-/ClO^-$ in alkaline conditions is +0.80 V, calculate the standard electrode potential of the half cell containing $\mathbf{M}^{n+}(aq)$ and **M**(s).
Suggest the identity of **M**.

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**(c)** In the presence of $HClO_4$, alcohols react with nitriles to form *N*–alkylamides. This is known as the *Ritter reaction*, as shown in Fig. 5.1.

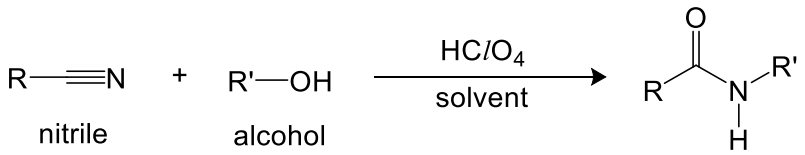


**Fig. 5.1**

Compounds **A** and **B** react in the presence of $HClO_4$ to give compound **C** via the *Ritter reaction.*

Compound **A** has the molecular formula $C_4H_{10}O$. When heated under reflux with acidified $K_2Cr_2O_7$, it gives a product that gives a yellow precipitate when warmed with aqueous alkaline iodine.

Compound **D** is a 6-membered ring molecule and has the molecular formula $C_7H_{12}O$. When heated with acidified $KMnO_4$, it forms $CH_3COCH_2CH_2COCH_2CO_2H$. **D** reacts with $PCl_5$ followed by hot ethanolic KCN to give **B**.

Suggest the structures of compounds **A** to **D** and explain the reactions described. [6]

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**Additional answer space**

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