Class Adm No

Candidate Name: _____

H

millennia institute

# 2019 Preliminary Exams
## Pre-University 3

**H2 CHEMISTRY** **9729/03**

Paper 3 Free Response **20 Sept 2019**

**2 hours**

Candidates answer on separate paper.

Additional materials: Answer Paper
Data Booklet
Graph Paper

**READ THESE INSTRUCTIONS FIRST**

**Do not turn over this question paper until you are told to do so**

Write your name, class and admission number on all 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 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.

You are reminded of the need for good English and clear presentation in your answers.

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.

| Question | Section A | | | Section B | | Total |
|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | 5 | |
| Marks | /19 | /19 | /22 | /20 | /20 | /80 |

## Section A

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

**1** **(a)** 3–chloropropanoic acid, $CH_2ClCH_2CO_2H$, is a weak Brønsted acid. A 0.100 mol $dm^{-3}$ solution of $CH_2ClCH_2CO_2H$ has a pH of 2.49.

**(i)** Calculate the p$K_a$ of 3–chloropropanoic acid. [3]

Since pH = 2.49, $[H^+] = 10^{-2.49}$

$$K_a = \frac{[CH_2ClCH_2CO_2^-][H^+]}{[CH_2ClCH_2CO_2H]}$$

$$= \frac{[10^{-2.49}][10^{-2.49}]}{[0.100]}$$

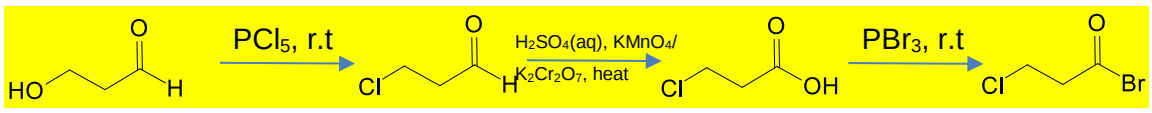
$$= 1.05 \times 10^{-4}$$

$pK_a = -\lg(1.05 \times 10^{-4}) = 3.98$

**(ii)** State and explain the differences in the relative acid strength between 3–chloropropanoic acid and propanoic acid. [2]

3–chloropropanoic acid is a stronger acid than propanoic acid. Due to the presence of the electron withdrawing group, C*l*, the negative charge of O on the carboxylate anion is dispersed. ; This causes the conjugate base of 3–chloropropanoic acid to be more stable. Hence, acidity increases. ;

**(iii)** 3-chloropropanoyl bromide is the acid derivative of 3–chloropropanoic acid. Propose a 3-step synthetic route for the formation of 3-chloropropanoyl bromide, using 3-hydroxypropanal as the starting reagent. State clearly the reagents and conditions used for each step. [5]




1m x 3 reagents and conditions

1m x 2 correct intermediates

**(b)** A student investigated the rate of reaction between 3–chloropropanoic acid and aqueous sodium carbonate.

The rate of the reaction may be determined by measuring how long it takes for the gas to be completely released.

A series of experiments were carried out to study the order of reaction with respect to 3–chloropropanoic acid and sodium carbonate. The following results were obtained.

| Experiment Number | Volume / $cm^3$ | | | Time / s |
|---|---|---|---|---|
| | 3–chloropropanoic acid | $Na_2CO_3$ | $H_2O$ | |
| 1 | 20.0 | 40.0 | 40.0 | 78 |
| 2 | 20.0 | 30.0 | 50.0 | 100 |
| 3 | 5.0 | 20.0 | 25.0 | 75 |

**(i)** Write an equation, including state symbols, for the reaction between sodium carbonate and 3–chloropropanoic acid. [1]

$2CH_2ClCH_2CO_2H(aq) + Na_2CO_3(aq) \rightarrow 2CH_2ClCH_2CO_2^-Na^+(aq) + CO_2(g) + H_2O(l)$

**(ii)** State the relationship between time and rate. [1]

Inverse relationship

**(iii)** Determine the order of the reaction with respect to 3–chloropropanoic acid and sodium carbonate. [2]

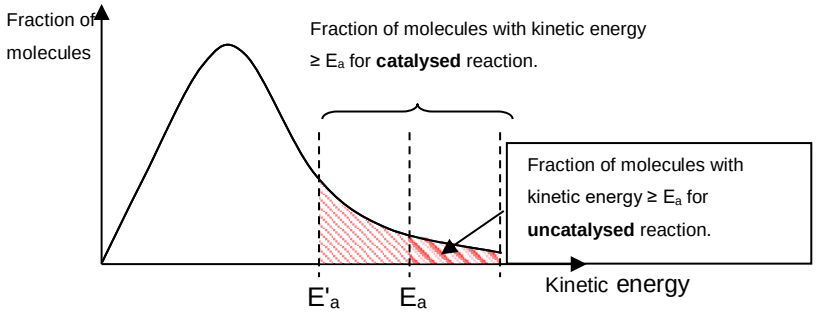
Comparing Expt 1 and 2, while volume of 3–chloropropanoic acid is kept constant and volume of $Na_2CO_3$ is 4/3 times, rate is 100/78 times. Order with respect to $Na_2CO_3$ is 1.

Comparing Expt 1 and 3, while volume of $Na_2CO_3$ is kept constant after multiplying the volume by two, volume of 3–chloropropanoic acid is halved, rate stays relatively constant. Order with respect to 3–chloropropanoic acid is 0.

**(iv)** Hence, write the rate equation, stating the units of k. [2]

Rate = $k[Na_2CO_3]$
$k = s^{-1}$

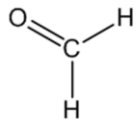
**(v)** With the aid of an appropriate diagram, explain how the addition of a catalyst can increase the rate of a reaction between 3–chloropropanoic acid and sodium carbonate. [3]



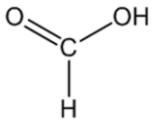

A catalyst provides an alternative pathway for the reaction, lowering the activation energy required. Hence, there is a greater fraction of molecules with energy greater than activation energy. Frequency of effective collisions increases, leading to increase rate of reaction. (2m for diagram, 1m for explanation)

[Total: 19]

**2** **(a)** Using only the elements C, H and O, draw the structural formulae of **two** different **organic** compounds, each containing a **single** carbon atom with an oxidation state of 0 and +2 respectively. [2]



O.S. = 0



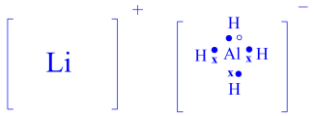
O.S. = +2

**(b)** A symmetrical organic compound **A**, $C_2H_4N_2O_2$, upon reacting with hot dilute NaOH(aq) produces a colourless, pungent gas that turns moist red litmus paper blue.

**(i)** Draw the structure of compound **A** and state the functional group present. [2]

$(CONH_2)_2$ , amide

**(ii)** The functional group present in compound **A** can be reduced by lithium aluminium hydride, Li*Al*$H_4$. Draw the dot-and-cross diagram for Li*Al*$H_4$. [1]



**(iii)** Other than Li*Al*$H_4$, $NaBH_4$ can also be used for the reduction of certain functional groups. Li*Al*$H_4$ is able to produce hydride ion, $H^-$ more readily than $NaBH_4$. Suggest why Li*Al*$H_4$ is a more powerful reducing agent than $NaBH_4$. [1]

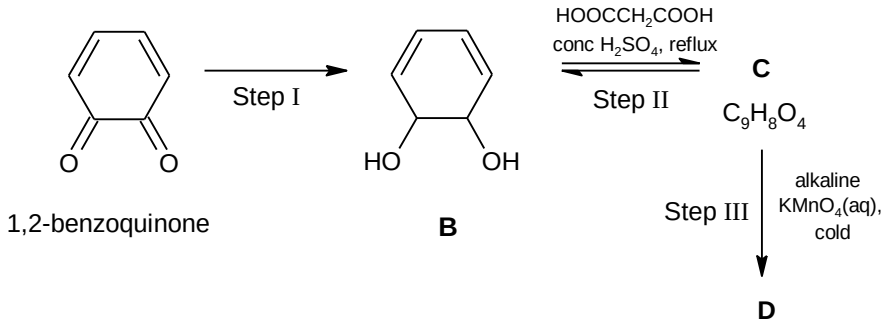
The electronegativity of Al is lesser than that of B. Hence, H bonded to Al can produce $H^-$ more readily than H bonded to B. Thus, reduction occurs more readily for $LiAlH_4$, proving that it is a stronger reducing agent.

OR

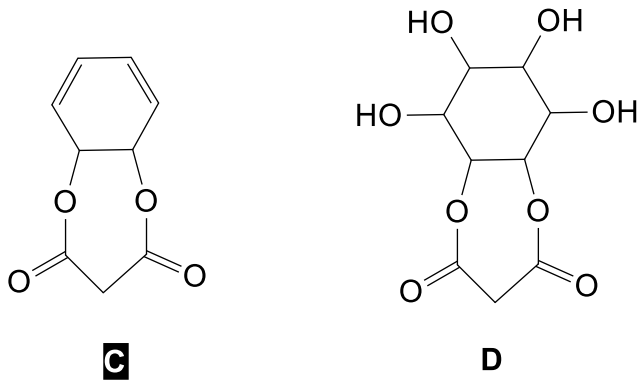
The size of A*l* atom is larger compared to B, thus the orbital overlap between A*l* and H is less effective. Therefore the bond length of A*l*–H bond is longer than that of B–H bond. ; Less energy is required to break the weaker A*l*–H bond, resulting in a greater ease of generating $H^-$ for the reduction process.

**(c)** Quinones are used in photography as a reducing agent. Quinone compounds are multifunctional as they exhibit properties of both ketones and alkenes.

The following scheme involves 1, 2-benzoquinone, where step I involves the use of $LiAlH_4$.

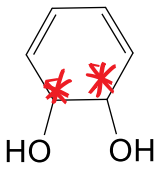



**(i)** Draw the structures of **C** and **D**. [2]



**C** **D**

**(ii)** Identify the chiral centres on **B**. Hence, explain why it does not display optical activity.[2]



It does not display optical activity as there is a plane of symmetry in the compound.

**(iii)** Using a simple chemical test, suggest how 1,2-benzoquinone can be distinguished from compound **B**. In your answer, state all reagents and conditions used and the expected observations. [2]

2,4-DNPH, warm.

Orange ppt observed for 1,2-benzoquinone, no orange ppt observed for **B**.

OR

$PCl_5$, r.t.

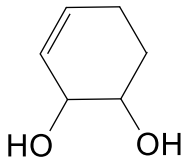
White fumes observed for **B**, no white fumes observed for 1,2-benzoquinone.

OR

$K_2Cr_2O_7/H_2SO_4$(aq), heat.

Orange $K_2Cr_2O_7$ turns green for **B**, orange $K_2Cr_2O_7$ remains orange for 1,2-benzoquinone.

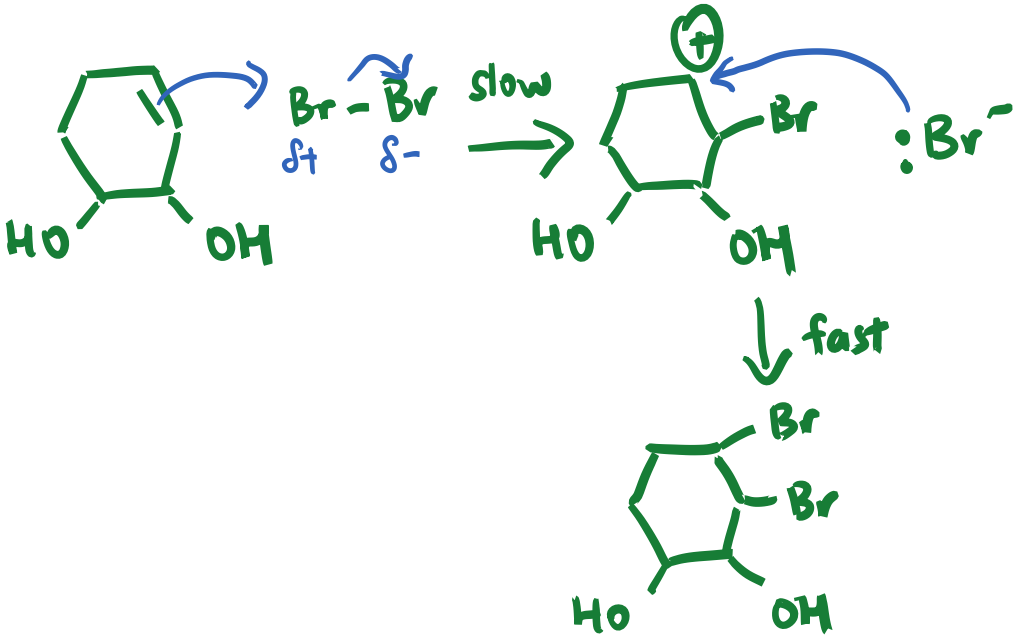
**(iv)** When compound **B** undergoes partial hydrogenation, it forms compound **E**.




**E**

Describe the mechanism of the reaction when compound **E** reacts with $Br_2$ in $CCl_4$ in the dark. In your answer, show all relevant charges and movement of electrons clearly. [3]

Electrophilic addition




*1m for correct intermediate, 1m for name of mechanism, 1m for correct movement of electrons*

**(d)** $K_2Cr_2O_7$ and $KMnO_4$ are common oxidising agents used in organic synthesis where $KMnO_4$ is the more powerful of the two. Compound **F**, $C_4H_8O$, reacted with $K_2Cr_2O_7$ and $KMnO_4$ separately to yield different products as shown in the reactions below.

$$\underset{\textbf{F}}{C_4H_8O} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{} \underset{\textbf{G}}{C_4H_6O_2}$$

$C_4H_8O \xrightarrow{KMnO_4/H_2SO_4} C_2H_4O_2$

**F** **H**

Given the following information,

- All three compounds, **F**, **G** and **H** react with sodium metal.
- **G** and **H** react with $Na_2CO_3$, but **F** does not.
- **F** and **G** decolourise aqueous bromine.

Suggest the structures of compounds **F**, **G** and **H**, explaining the chemistry involved. [4]

**F**: $CH_3CH=CHCH_2OH$ ;

**G**: $CH_3CH=CHCOOH$ ;

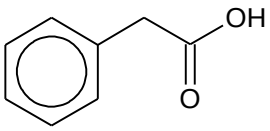
**H**: $CH_3COOH$ ;

*1m for explanation*

| | |
|---|---|
| All three compounds, **F**, **G** and **H** react with sodium metal | All 3 compounds contain the -OH functional group |
| **G** and **H** react with $Na_2CO_3$, but **F** does not | Presence of carboxylic acid in C and D |
| **F** and **G** decolourise aqueous bromine. | Presence of alkene |

[Total: 19]

**3** **(a)** Phenylethanoic acid is used as a treatment for hyperammonemia, a condition where there is an accumulation of ammonia in the human body.




phenylethanoic acid

**(i)** In a titration experiment, 60 $cm^3$ of 0.10 mol $dm^{-3}$ of sodium hydroxide was added to 20 $cm^3$ of 0.20 mol $dm^{-3}$ of phenylethanoic acid in a conical flask. Calculate the pH of the final solution when all 60 $cm^3$ of sodium hydroxide was added to the flask. [3]

Amount of acid present = 20/1000 x 0.2 = 0.004 mol
Volume of NaOH required at equivalence point = 0.004 / 0.1 = 40 $cm^3$ ;

When 60 $cm^3$ of NaOH is added:

$$[OH^-] = [NaOH] = \frac{\text{moles of excess NaOH}}{\text{new volume of solution}} = \frac{[(60-40)/1000] \times 0.10}{(20+60)/1000}$$

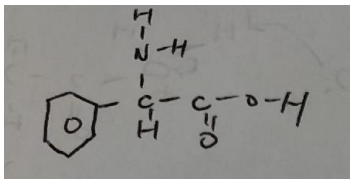
$$= 0.0250 \text{ mol } dm^{-3} \ ;$$

$$pOH = -\log_{10} 0.0250 = 1.60$$

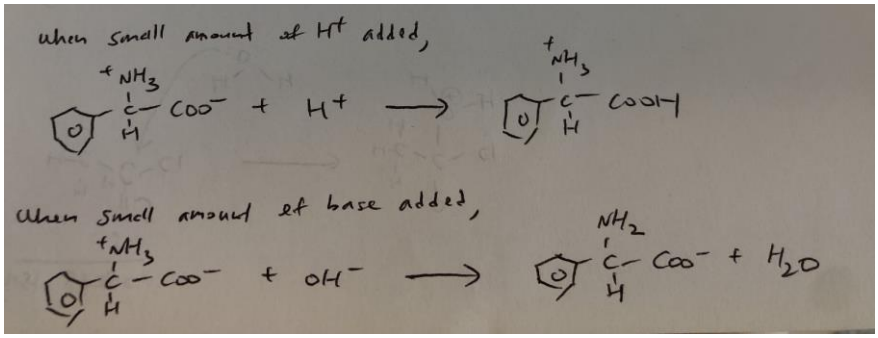
$$pH = 14 - pOH = 14 - 1.60 = 12.4 \ ;$$

**(ii)** 2-amino-2-phenylethanoic acid can be synthesised from phenylethanoic acid through a series of substitution reactions.

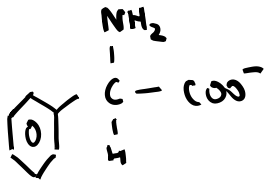
Draw the displayed formula of 2-amino-2-phenylethanoic acid. [1]



**(iii)** Write two equations to show how an aqueous solution of 2-amino-2-phenylethanoic acid is able to resist the change in pH upon addition of small amounts of acid and base. [2]




**(iv)** Draw the structure of the predominant form when 2-amino-2-phenylethanoic acid is in an aqueous solution of pH 10. [1]



**(b)** **(i)** Predict and explain whether phenylethanoyl chloride or phenylethanoic acid has a higher reactivity towards nucleophilic reagents. [2]

Phenylethanoyl chloride is more reactive as the reactive carbon is more electron deficient since it is attached to two highly electronegative atoms (Cl and O) which results in the nucleophiles to attack it more readily.

**(ii)** Given that phenylethanoyl chloride has a boiling point of 95 °C and phenylethanoic acid has a boiling point of 266 °C, explain this difference in terms of structure and bonding. [2]

Phenylethanoic acid will have a higher boiling point ; due to the presence of strong intermolecular hydrogen bonding between its molecules, compared to the weaker permanent dipole-permanent dipole forces of attraction between molecules of phenylethanoyl chloride. ; More energy is required to overcome the stronger H-bonding between phenylethanoic acid, resulting in a higher boiling point.

**(iii)** State the number of $sp^2$ and $sp^3$ hybridised carbon atoms found in one molecule of phenylethanoic acid. [1]

7 $sp^2$ and 1 $sp^3$ C

**(iv)** State the number of sigma and pi bonds in one molecule of phenylethanoic acid. [1]

18 sigma and 4 pi

**(c)** Acid chloride reacts instantly with cold water. The reaction is very exothermic in which steamy white fumes of hydrogen chloride gas are released and the carboxylic acid is formed. The mechanism of the reaction takes place in two stages as described below.

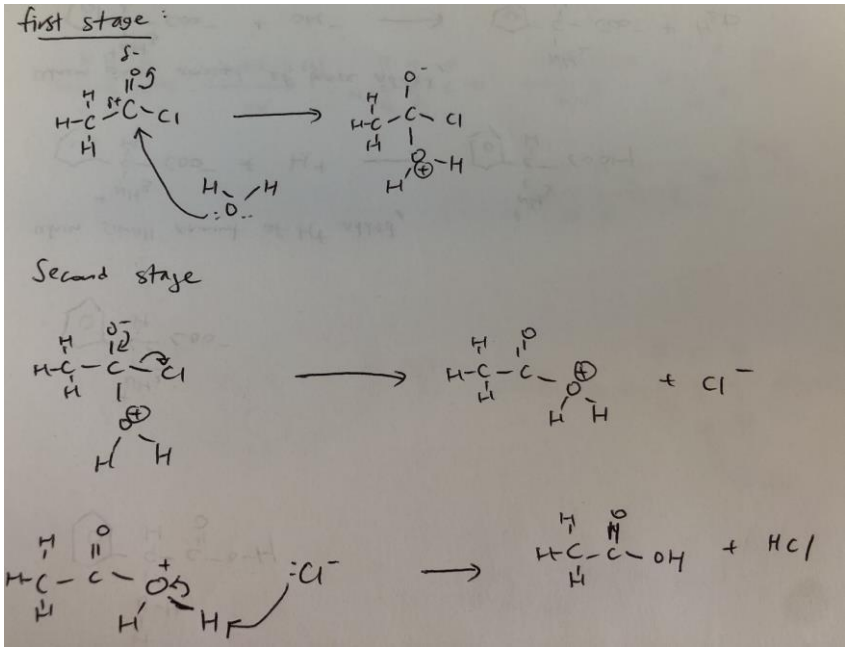
**First stage**

- The lone pair on the oxygen atom of water molecule attacks the electron deficient carbon atom of the acid chloride, causing the $\pi$ bond of the C=O bond to break.

**Second stage**

- The carbon-oxygen double bond reforms and a chloride ion is released.
- As a result, a hydrogen ion is removed by the chloride ion to give the carboxylic acid and hydrogen chloride.

**(i)** Using ethanoyl chloride as an example, illustrate the mechanism of the reaction when ethanoyl chloride reacts with cold water. [3]



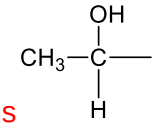
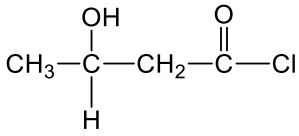
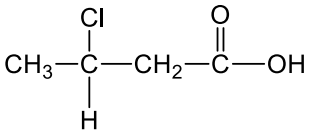

1m for each step

**(ii)** State the type of reaction occurring in the first stage of the mechanism. [1]

Nucleophilic addition

**(d)** Compounds **Y** and **Z** are isomers of molecular formula $C_4H_7O_2Cl$. When **Y** and **Z** are added to separate portions of water, solutions are formed with pH values of 0.5 and 2.5 respectively. White precipitate is observed when aqueous silver nitrate is added to **Y**, but not **Z**. Both **Y** and **Z** gives yellow precipitate when heated with aqueous sodium hydroxide and iodine.

Suggest the structures of compounds **Y** and **Z**. Explain your answers. [5]

- Compound Y is an acyl chloride that undergoes hydrolysis in water, giving a solution of lower pH value since HC*l* is formed. ;
- White precipitate of AgC*l* is formed when Y is added to aqueous silver nitrate, Y is an acyl chloride. No white precipitate of AgC*l* is formed when Z is added to aqueous silver nitrate, Z contains a chloroalkane. ;
- Compound Z is a carboxylic acid as it gives an acidic solution upon partial dissociation of $H^+$ ions in water. ;
- Both Z and Y contains  .
- Y is  ;
- Z is  ;

[Total: 22]

## Section B

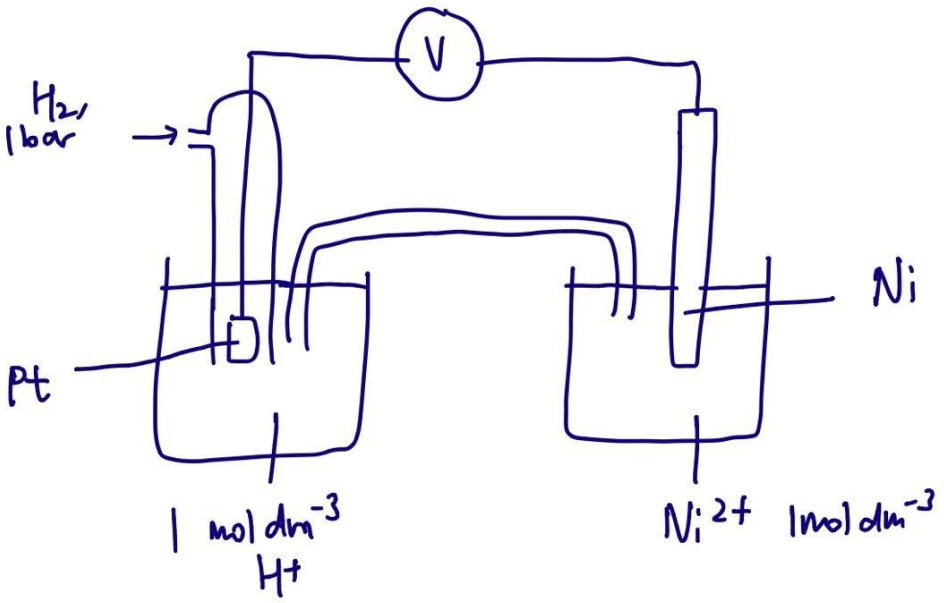
Answer **one** question from this section.

**4** **(a)** Nickel is a transition metal and can exhibit variable oxidation states. The reducing power of Ni can be determined through its oxidation to $Ni^{2+}$.

**(i)** Define the term standard electrode potential. [1]

The **Standard electrode potential, $E^{\ominus}$ ,** of an electrode, is the relative potential of this electrode under standard conditions compared with the standard hydrogen electrode whose electrode potential is assigned as zero.

**(ii)** Draw a fully labelled diagram of the electrochemical cell that you would set up in order to measure the standard reduction potential of $Ni^{2+}$/Ni under standard conditions. [3]




**(iii)** Hence or otherwise, suggest what happens to the value of the voltmeter reading when a more concentrated nickel(II) solution is used in part **(ii)**. [1]

The reading will become less positive.

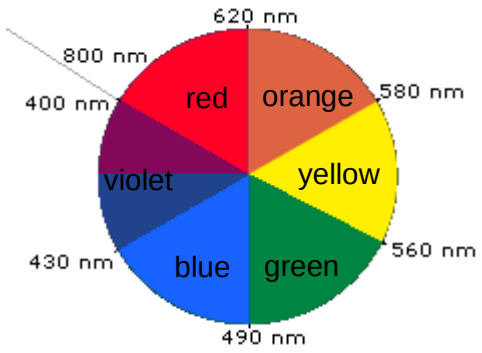
**(iv)** An electrolytic cell contains $Ni(NO_3)_2$ and $Mn(NO_3)_2$ in an aqueous electrolyte uses graphite as the electrodes. Determine the products discharged at the cathode and anode and write the overall balanced equation for the electrolytic cell. [3]

Cathode: Ni discharged, $Ni^{2+} + 2e \longrightarrow Ni$

Anode: $O_2$ discharged, $2H_2O \longrightarrow O_2 + 4H^+ + 4e$

Overall: $2Ni^{2+} + 2H_2O \longrightarrow 2Ni + O_2 + 4H^+$

**(b)** Aqueous nickel salts are coloured. $[Ni(NH_3)_6]^{2+}$ ions absorb at 600 nm, whereas $[NiCl_4]^{2-}$ ions absorbed at 420 nm. The colour and the respective wavelengths are given in the colour wheel below.




**(i)** State the oxidation number of nickel in $[NiCl_4]^{2-}$. [1]

+2

**(ii)** Suggest the colour of:

**I**: $[Ni(NH_3)_6]^{2+}$

**II**: $[NiCl_4]^{2-}$ [2]

$[Ni(NH_3)_6]^{2+}$ is blue, while $[NiCl_4]^{2-}$ is yellow

**(iii)** Explain why the two complexes are coloured. [3]

In the presence of an octahedral ligand field, the degenerate d-orbitals will split into two energy levels. In the partially-filled d orbitals (d4), electrons are able to promote from the lower to the higher level by absorbing energy in the visible spectrum (blue-green). The colour shown is the complementary colour (orange-red or yellow).

**(c)** The stability of complexes can be determined by the stability constant of the complexes. Consider the formation of $[Ni(NH_3)_6]^{2+}$ from $[Ni(H_2O)_6]^{2+}$. The stability constant, $K_{stab}$, is given by

$$K_{stab} = \frac{[[Ni(NH_3)_6]^{2+}]}{[[Ni(H_2O)_6]^{2+}][NH_3]^6}$$

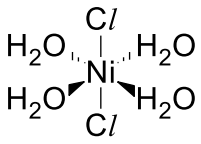
| Complex | Stability constant |
|---|---|
| $Ni(H_2O)_6]^{2+} + 6NH_3 \rightleftharpoons [Ni(NH_3)_6]^{2+} + 6H_2O$ | $4.8 \times 10^7$ |
| $Ni(H_2O)_6]^{2+} + 3\ en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O$ | $2.0 \times 10^{18}$ |

State and explain if the en ligand will replace the $NH_3$ ligand for the nickel complexes. [2]

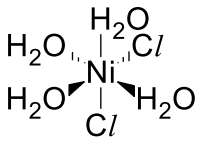
Yes, ligand exchange will take place as the stability constant for $[Ni(en)_3]^{2+}$ is higher than that of $[Ni(NH_3)_6]^{2+}$. Hence this implies that $[Ni(en)_3]^{2+}$ is more stable and will tend to be formed more.

**(d)** **(i)** The coordination compound $NiCl_2(H_2O)_4$ has an octahedral geometry. Draw and identify the type of isomerism present in the compound. [2]

Cis-trans isomerism




Trans



cis

**(ii)** Explain why $[Ni(en)_3]Cl_2$ can dissolve in water. [2]

$[Ni(en)_3]Cl_2$ is ionic in nature. The energy evolved in the formation of ion-dipole interaction is sufficient to overcome the ionic bonds between the oppositely charged ion and hence it is soluble in water.

[Total: 20]

**5 (a) (i)** State the structure and describe the bonding present in the chlorides of sodium and aluminium respectively. [2]

Sodium chloride – giant ionic structure with strong electrostatic forces of attraction between the opposite charged ions ;

Aluminium chloride – simple covalent structure with id-id between the molecules and covalent bonds between Al and Cl atoms;

**(ii)** Construct a fully labelled energy level diagram for the formation of sodium chloride using the following values and relevant values from the *Data Booklet* and calculate the standard enthalpy change of formation of sodium chloride. [3]

| **Thermochemical term** | **ΔH / kJ mol$^{-1}$** |
|---|---|
| Lattice energy of NaCl(s) | -788 |
| Enthalpy change of atomisation of Na(s) | +108 |
| First electron affinity of Cl(g) | -349 |

$\Delta H_f$ = (+108) + ( +494) + (+122) + (-349) + (-788) = -413 kJ mol$^{-1}$ ;

2m for correct energy level diagram

**(iii)** Describe what happens when the chlorides of aluminium and silicon are dissolved in water. Write the relevant equations and state the observation when Universal Indicator is added. [4]

$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^-$

$[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightleftharpoons [Al(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$ ;

$AlCl_3$ undergoes partial hydrolysis to produce a pH 3 solution which appears red in the presence of universal indicator. ;

$SiCl_4$ (*l*) + $2H_2O$ (*l*) $\rightarrow$ $SiO_2$ (s) + 4HCl (aq) ;

$SiCl_4$ undergoes complete hydrolysis to produce a pH 2 solution which appears red in the presence of universal indicator.;

**(b)** The reactions of different halogens with hydrogen differ due to their reactivity. Explain the relative stability of the hydrogen halides with reference to the Data Booklet. [3]

As the **size of the Halogen increases down the Group;** , **the H–X bond becomes longer and weaker due to the less effective overlap of the orbitals** ; and so it is easily broken. Thus, the thermal stability of the hydrides decreases down the Group, due to the decrease in strength of the H–**X** bond.

| **Bond** | **Bond energy / kJ mol$^{-1}$** |
|---|---|
| H–F | 568 |
| H–Cl | 431 |
| H–Br | 366 |
| H–I | 299 |

**(c)** The iodine clock reaction involves 2 reactions.
First reaction involves peroxydisulfate ($S_2O_8^{2-}$) and excess iodide ions. The second reaction involves thiosulfate ($S_2O_3^{2-}$) ion reacting with the iodine produced.

**(i)** Write the equations for the two reactions of the clock reaction. [2]

$S_2O_8^{2-} + 2I^- \longrightarrow 2SO_4^{2-} + I_2$

$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$

**(ii)** If 30 $cm^3$ of 0.002 mol $dm^{-3}$ of $S_2O_3^{2-}$ is used in the reaction, determine the mass of potassium peroxydisulfate needed for the first step. [2]

Amount of $S_2O_3^{2-}$ = 0.00006 mol

Amount of $K_2S_2O_8$ = 0.00003 mol

Mass of $K_2S_2O_8$ = 0.00003 mol x 270.4 = 0.00811g

**(iii)** Iron(II) ions are sometimes added to the reaction between peroxydisulfate and iodide. Write the equations to show how iron(II) ions aid in the speeding up the rate of reaction.

[2]

$2Fe^{2+} + S_2O_8^{2-} \rightarrow 2Fe^{3+} + 2SO_4^{2-}$

$2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

**(d)** Iron is also used in other reactions, such as the Haber Process. State the role of iron in the Haber Process and explain why iron is suitable for this role. [2]

It acts as a heterogenous catalyst. It has partially-filled d-orbitals that can accept electron pairs from reactant particles.

[Total: 20]