Catholic Junior College

JC2 Preliminary Examination

Higher 2

CANDIDATE NAME	
CLASS	**2T**

CHEMISTRY

9729/03

Paper 3 Free Response

September 2021

2 hours

Candidates answer on the question paper.

Additional Materials: Data Booklet

MARK SCHEME

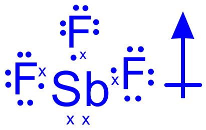
This document consists of **24** printed pages.

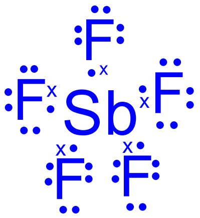
Section A

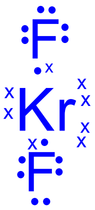
Answer **all** the questions in this section.

1 Fluorine is the most electronegative element and forms many interesting compounds. Antimony, Sb, is in Group 15 of the periodic table and forms two covalent fluorides that exist as simple molecules in gas phase, SbF_3 and SbF_5.
Krypton, Kr, is in Group 18 of the periodic table and its first compound discovered is KrF_2.

(a) Draw 'dot-and-cross' diagrams showing the electrons (outer shells only) in SbF_3, SbF_5, and KrF_2. Use the VSEPR (valence shell electron pair repulsion) theory to predict their shapes and hence state whether the species is polar or non-polar. [8]

	**3 bond pairs** of electrons, **1 lone pair** of electrons around Sb, **trigonal pyramidal** shape (CAO) **Polar**

	**5 bond pairs** of electrons, no lone pair of electrons around Sb, **trigonal bipyramidal** shape. (CAO) **Non-polar.**

	**2 bond pairs** of electrons, **3 lone pair** of electrons around Kr, **linear** shape. (CAO) **Non-polar.**

[1] x3 For each molecule, correct dot & cross
(–1 if incorrect valence electrons shown for F, –1 if 'orbit' used)

[1] x3 correct shape (CAO, –1 if number/type of electron pairs not stated)

[2] All 3 correct polar/non-polar stated (CAO, 1m if 2 correct)

Diagrams were generally drawn well, though can do better with a relatively larger central atom, so that the electrons are more clearly differentiated.
Critically, several missed out lone pairs on F or Kr and mistakenly showed dative or double bonds in KrF_2.

Majority of the candidates could not score well for predicting shapes, answer as if it was to "state" or "suggest", hence missed the number and type of electron pairs. On the other hand, some answers were as if it was to "explain" (see 2019/P3/Q1) and stated the full VSEPR principles.
Incorrect answers include trigonal planar, tetrahedral and even shapes for 3 bond pairs for KrF_2 when clearly 2 bond pairs were drawn.

(b) SbF_5 can react as shown in the following reaction and is a useful reagent as an exceptionally strong Lewis Acid.

$$SbF_5 + F^- \rightarrow [SbF_6]^-$$

Explain the term *Lewis Acid*, and suggest the reason why SbF_5 is a *strong* Lewis Acid. [2]

A Lewis acid is an **electron pair acceptor.** [1]

Sb is **highly electron-deficient** as it is bonded to five very/highly **electronegative F** atoms, and it will strongly attract electrons from other species. [1]

The first mark was designed as an easy recall question, and most who attempted knew that Lewis acid involves electrons, but the keyword of "pair" was frequently missing. Candidates should note that by not stating pair, it could be incorrectly suggesting redox or free radical reactions.

Attempts for the 2nd mark were often as if answering only why it can act as a Lewis acid but not the "STRONG" Lewis acid.

(c) SbF_3 exists as gaseous molecules at a temperature of 700 K.

(i) Calculate the volume of 0.10 mol of an ideal gas at a temperature of 700 K, at a pressure of 1.01×10^5 Pa. [1]

(ii) The volume of 0.10 mol of SbF_3 measured at 700 K and 1.01×10^5 Pa in a gas syringe was significantly different from your answer in **(i)**.
Suggest **two** possible reasons why this might be the case in terms of the properties of SbF_3. [2]

(i)

$pV = nRT$

$(1.01 \times 10^5) V = (0.1)(8.31)(700)$

$V = \mathbf{5.76 \times 10^{-3}}\ m^3$ [1, with correct units]

(ii) SbF_3 molecules are polar and the **intermolecular** permanent-dipole permanent-dipole forces between the molecules are **significant**. [1]
Furthermore, the SbF_3 **molecules** are large, and the **volume of the molecule is not negligible** **compared to the volume of the gas syringe**. [1]

(i) Unfortunately, although almost all answers had the correct formula, wrong units were often given for this straightforward question.

(ii) This was about assumptions of ideal gas, and majority scored credit only for the first mark as 2nd point had missing keywords and/or poor conceptual understanding.

The most common error was to state that "SbF_3 or the gas do not have negligible size/volume compared to the size of the container" – and missed the keyword of molecules of SbF_3.
Size/volume of a gas is the same as the size/volume of the container, and it is the size of the gas particles that should be compared.

Another incorrect response was 'low temperature and high pressure', which are conditions of the experiment/surrounding and not intrinsic properties of a gas.

(d) KrF_2 is a very reactive compound, undergoing thermal decomposition to give Kr and F atoms at very low temperature.

(i) Suggest what information this gives about the Kr–F bond. [1]

(ii) KrF_2 is a strong oxidising agent, with a standard redox potential of +3.5 V.

State how the reactivity of the halogens as oxidising agents varies down the group. Using relevant data from the *Data Booklet,* arrange KrF_2 and the halogens in increasing order of oxidising power. [2]

(iii) Given the reduction half-equation for krypton fluoride, KrF_2, is as follows:

$$KrF_2 + 2e^- \rightarrow Kr + 2F^-$$

When krypton fluoride, KrF_2, is added to an aqueous solution containing bromide ions, effervescence is observed. The mixture of gas contains Kr gas and another gas that relights a glowing splint.

State another expected observation and suggest a balanced equation for the reaction. [2]

(i)

The Kr–F bond is very weak/ low bond energy. [1, BOD long bond length, or small extent of orbital overlap, unstable]

(ii) Down the group, **reactivity of halogens decreases** [1] as the oxidising power decreases.

Oxidising power increases in the following order, **I_2, Br_2, Cl_2, F_2, and KrF_2** [1]

(iii) The solution turns **orange** as Br_2 (aq) is produced. [1]

$3KrF_2 + 2H_2O + 2\,Br^-(aq) \rightarrow 3Kr + O_2 + 4H^+ + 6F^- + Br_2(aq)$ [1]

O: $2\,Br^- \rightarrow Br_2 + \mathbf{2e^-}$

O: $2\,H_2O \rightarrow O_2 + 4H^+ + \mathbf{4e^-}$

R: $(\,KrF_2 + \mathbf{2e^-} \rightarrow Kr + 2F^-\,)\ x3$

(i) A variety of answers were accepted for this relatively simple "suggest" question, but some continue to incorrectly relate IMF to thermal stability (about chemical reaction).

(ii) Many candidates tried to "Explain why and how the reactivity varies" rather than simply "State" for the first mark.

Many incorrect answers were given for the 2nd mark, such as stating halogens as monoatomic molecule, and puzzlingly gave oxidising power of Kyrpton dihalides such as $KrBr_2$ and even mistook noble gases for halogens. It should be noted that this can be solved. The order can derived from redox potential values.

(iii) This proved most challenging as candidates had to use the redox potential values from data booklet, analyse and work out the balanced equation.

2 **(a)** The mineral fluorspar consists mainly of calcium fluoride, CaF_2, which is a principal source of hydrogen fluoride.

(i) Using calcium fluoride, CaF_2, as an example, define the term *standard enthalpy change of formation*. [1]

(ii) Using the following data and relevant data from the *Data Booklet*, construct a Born-Haber cycle and use it to calculate the enthalpy change of formation of CaF_2(s), stating its units. [2]

	Value / kJ mol^{-1}
lattice energy of CaF_2(s)	–2640
electron affinity of fluorine	–328
enthalpy change of atomisation of calcium	+184

(iii) The solubility product values, K_{sp}, of some Group 2 fluorides, at 25 °C, are given in the table below. Identify the least soluble fluoride from the table and calculate its solubility, in mol dm^{-3}, at 25 °C. [2]

Group 2 fluorides	K_{sp} / mol^3 dm^{-9}
CaF_2	3.9×10^{-11}
SrF_2	2.8×10^{-9}
BaF_2	1.7×10^{-6}

(iv) State and explain how the solubility of the fluoride identified in **(iii)** would change if it is added to an aqueous solution containing sodium fluoride, NaF. [1]

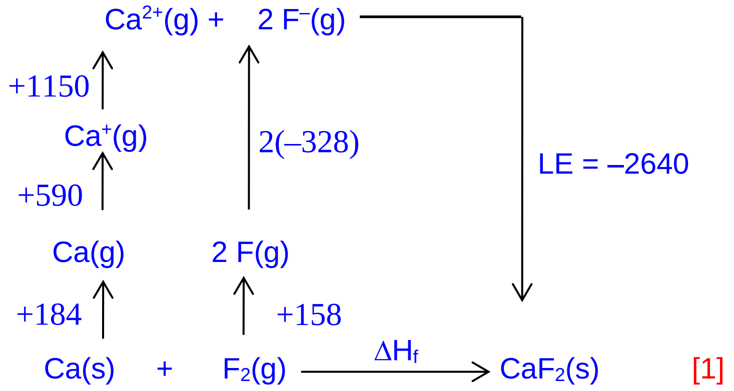
(v) Solution **X** contains 0.100 mol dm^{-3} strontium chloride and 0.100 mol dm^{-3} barium chloride. Predict and explain, with the aid of relevant calculations, what would happen when equal volumes of solution **X** and 0.00500 mol dm^{-3} of sodium fluoride, NaF, are mixed together. [2]

(i) The **standard enthalpy change of formation, $H_f^\ominus$**, of calcium fluoride, CaF_2, is defined as the enthalpy change when **one mole of CaF_2 (s)** is **formed** from its **elements**, Ca (s) and F_2 (g) under **standard conditions of 298 K and 1 bar**. [1]

Common Errors:

1. **Not stating 1 mole of substance/compound formed.**
2. **Not stating standard conditions 298K & 1bar.**

(ii)



[1]

By Hess' Law, $\Delta H_f^\ominus$ = 184 + 158 + 590 + 1150 + 2(–328) + (–2640)

= –1214 kJ mol^{-1} [1, with units, 3 or 4sf accepted]

Common Errors:

1. **Bond Energy of F_2(g) was either missing of halved.**
2. **Electron Affinity of 2F(g) did not multiply by 2.**
3. **Missing or wrong state symbols for some species in Born Haber Cycle.**

(iii) Least soluble fluoride: CaF_2 [1]

Let solubility of CaF_2 be x

CaF_2 (s) ⇌ Ca^{2+}(aq) + $2F^-$ (aq) …..(1)

$$x \qquad\qquad 2x$$

$K_{sp} = x(2x)^2 = 4x^3 = 3.9\times10^{-11}$

Solubility of CaF_2 at 25°C = $x = 2.14\times10^{-4}$ mol dm^{-3} [1]

(iv) Solubility of CaF_2 will decrease due to common ion effect [1]. The common ion, F^-, from NaF will shift the equilibrium position in (1) to the left and reduce the solubility of CaF_2.

(v) In the mixture,

$[Ba^{2+}] = [Sr^{2+}]$ = (0.100 / 2) mol dm^{-3} & $[F^-]$ = (0.005 / 2) mol dm^{-3}

Ionic product of SrF_2 = $(0.05)(0.0025)^2 = 3.13 \times 10^{-7}$ $mol^3\ dm^{-9}$ [1]

= Ionic product of BaF_2

Ionic product (SrF_2) > K_{sp} (SrF_2) ⇒ SrF_2 is precipitated

Ionic product (BaF_2) < K_{sp} (BaF_2) ⇒ BaF_2 is not precipitated [1, both correct]

Common Errors:

1. **Wrongly identified BaF_2 as least soluble salt in (iii) despite all 3 salts having same formula type and BaF_2 having highest K_{sp} value. Did not square coefficient 2 for $[F^-]$ in calculation of solubility.**

Common Errors:

2. **In (iv), many did not mention common ion effect decreasing solubility, but were given credit for explaining in terms of position of equilibrium shifting as a result of increased [F$^-$].**
3. **Part (v) was poorly attempted as many did not halve the concentrations of [F$^-$] and [Sr^{2+}] and [Ba^{2+}] in their calculations due to equal volumes used. Some answers were incomplete as there was no mention of whether BaF_2 was precipitated despite the question mentioning the presence of X containing equal concentrations of strontium chloride and barium chloride.**

(b) Morphine, denoted as Mor, is a weak monoacidic alkali and used in small quantities for pain relief.

When 30 cm^3 of 0.30 mol dm^{-3} of morphine solution was titrated against 0.20 mol dm^{-3} hydrochloric acid at room conditions, the end-point was determined using a suitable indicator.

(i) Write the K_b expression for morphine. Use Mor and MorH$^+$ to denote morphine and its conjugate acid respectively. [1]

(ii) Calculate the initial pH of the morphine solution. (Given K_a of MorH$^+$ = 2.09 x 10^{-12} mol dm^{-3}) [2]

(iii) Determine the concentration of the salt that was formed at the equivalence point. [3]

(iv) Explain, using an appropriate equation, why the end point of the titration is not neutral. Hence, by using your answer in **(iii)**, determine the pH at the equivalence point. [2]

(v) By using your calculations in **(i)**, **(ii)** and **(iii)**, sketch and label the graph of pH against volume of hydrochloric acid used, indicating the region where the mixture acts as a buffer. [2]

(i) $K_b = \frac{[\mathrm{MorH^+}][\mathrm{OH^-}]}{[\mathrm{Mor}]}$ [1]

(ii) Let [OH$^-$] at eqm be x mol dm^{-3}

	Mor (aq) + H_2O (l) $\rightleftharpoons$	MorH$^+$ (aq) +	OH$^-$(aq)
Initial conc:	0.30	0	0
Δ in conc:	-x	+x	+x
Eqm conc:	0.30 – x	+x	+x

Assume that x is so small that $0.30 - x \approx 0.30$

$K_b = \frac{[\mathrm{MorH^+}][\mathrm{OH^-}]}{[\mathrm{Mor}]} = \frac{x^2}{0.30}$

Since $K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{2.09 \times 10^{-12}}$

x = [OH$^-$] = 0.037887 mol dm^{-3} [1]

pOH = -log$_{10}$(0.037883) = 1.42

pH = 14 – 1.42 = **12.6** [1]

Common Errors:

1. **K_b is BASE dissociation constant but some gave K_b expression with $[H^+]$.**
2. **In (ii), many attempted to find pH using K_a of $MorH^+$ which is the salt or conjugate acid of weak base Mor, not realizing that no salt is present initially before any reaction has taken place.**

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(iii) $Mor\ (aq) + HCl\ (aq) \rightarrow MorH^+Cl^-\ (aq) + H_2O\ (l)$

No. of mol of salt formed = No. of mol of morphine in solution

= 30/1000 x 0.30 = 9.00×10^{-3} mol [1]

Since mol of acid reacted = 9.00×10^{-3} mol

Vol acid added = $(9.00 \times 10^{-3}) / 0.20 = 0.045$ dm^3 [1]

Hence conc of salt = $(9.00 \times 10^{-3}) / (0.045 + 0.030)$ = **0.120 mol dm^3** [1]

(iv) At equivalence point, salt hydrolysis occurs.

$MorH^+\ (aq) \rightleftharpoons Mor\ (aq) + H^+\ (aq)$ [1]

Since $[H^+] > [OH^-]$ in the solution, pH < 7 at end point.

Since $K_a = \frac{[Mor][H^+]}{[MorH^+]}$

$2.09 \times 10^{-12} = \frac{[H^+]^2}{0.120}$

$[H^+] = 5.01 \times 10^{-7}$ mol dm^{-3}

pH = $-\log(5.09 \times 10^{-7})$ = **<u>6.30</u>** [1]

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Common Errors:

1. **For (iii), concentration of salt at equivalence point, the moles of salt formed and the total volume at equivalence point is required. The difficulty seems to be finding the volume of HCl added which requires the concentration of HCl (given) and moles of HCl reacted (from amt of Mor reacted & mole ratio between Mor : HCl).**
2. **For (iv), equation to show salt hydrolysis and formation of H^+ or H_3O^+ from conjugate acid $MorH^+$ was missing or incorrect. Hence, the K_a expression for $MorH^+$ could not be established and pH cannot be determined.**

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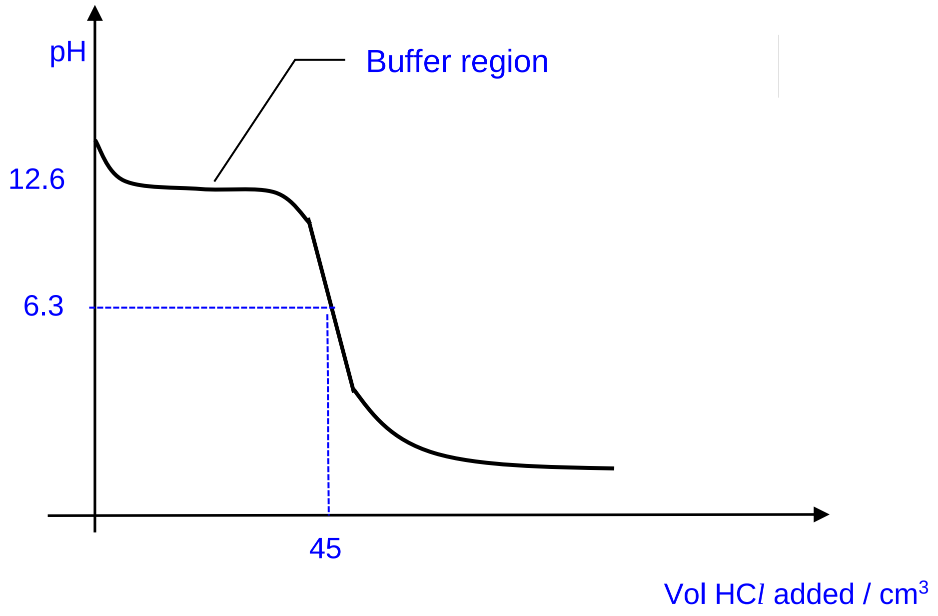
(v) Graph of pH against volume of hydrochloric acid used



[1] for initial and equivalence point pH & volume

[1] for buffer region

Common Errors:

1. **Buffer region was either not indicated or wrongly located.**
2. **Shape of graph was wrong and pH & volume for initial and equivalence points were either missing or not indicated correctly.**

(c) 1 mole of methane reacts with 1 mole of steam to form carbon monoxide and another gas. The enthalpy change of this reaction is +210 kJ mol^{-1} and the entropy change of this reaction is +216 J mol^{-1} K^{-1}.

Write a balanced chemical equation with state symbols for the above reaction, and explain why the entropy change is positive and why the reaction is spontaneous only at high temperatures.

Hence, determine the minimum temperature, T_s, when the reaction is spontaneous.

[4]

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2]

CH_4 (g) + H_2O (g) $\rightarrow$ CO (g) + $3H_2$ (g) [1]

$\Delta S^\ominus$ is positive because there is an **increase in number of gaseous molecules (2 mol to 4 mol)** produced. [1]

Since $\Delta H^\ominus$ and $\Delta S^\ominus$ is positive, **$-T\Delta S^\ominus$ is negative.**
At high temperatures, magnitude of **$-T\Delta S^\ominus > \Delta H^\ominus$**.

Since $\Delta G^\ominus = \Delta H^\ominus - T\Delta S^\ominus$, hence **$\Delta G^\ominus$ becomes negative** at high temperatures and reaction becomes spontaneous. [1]

At T_s, $\Delta G^\ominus < 0 \Rightarrow \Delta H^\ominus - T_s\Delta S^\ominus < 0$

$-210 \times 10^3 \ \ -T_s(-216) < 0$

$T_s >$ **972.22 or 973 K** [1]

Common Errors:

1. **Did not mention SIGNIFICANT reason for $\Delta S > 0$ is due to increase in number of GASEOUS molecules after reaction.**
2. **Did not compare $|\Delta H|$ against $|-T\Delta S|$ to explain the resultant effect of high temperature on $|-T\Delta S|$ and hence $\Delta G < 0$ for spontaneous reaction. Quoting $\Delta G = \Delta H - T\Delta S$ and stating therefore a high temperature is needed for $\Delta G < 0$ without considering the signs of ΔH and ΔS results in no credit due to vague and incomplete answer.**
3. **Did not convert either ΔH to J mol^{-1} (multiply by 1000) or ΔS to kJ mol^{-1} K^{-1} (divide by 1000) in calculating minimum temperature for reaction to be spontaneous. The minimum temperature should be > 972.22 and hence 973 K could be stated.**

3 **(a)** State the electronic configuration of a copper atom. [1]

^{29}Cu: $1s^22s^22p^63s^23p^63d^{10}4s^1$ or $[Ar]3d^{10}4s^1$ [1]

Common Error:

1. **Gave $[Ar]3d^94s^2$, forgetting the extra stability of half or fully-filled $3d^5$ or $3d^{10}$ (expected knowledge from Atomic Structure)**

~~**(b)** Explain why the 1st ionisation energy of the first row transition metals are relatively invariant across the period.~~ [2]

~~1st I.E. involves the removal of 4s valence electrons.~~

- ~~Across the 1st row transition metals, nuclear charge **increases.**~~
- ~~**Inner 3d electrons** provide effective **shielding effect between the nucleus and valence 4s electrons**.~~
- ~~Increase in nuclear charge **slightly outweighs/ is balanced out by** the increase in shielding effect. [1]~~
- ~~**Effective nuclear charge increases slightly/ remains relatively invariant**.~~
- ~~Hence, **attraction between the valence electron and the nucleus increases slightly/ remains relatively invariant**. [1]~~
- ~~Energy required to remove the valence electron increases slightly/ remains relatively invariant.~~

~~**(c)** Copper forms a variety of complex ions, eg. blue $[Cu(H_2O)_6]^{2+}$ which has an octahedral shape.~~

~~**(i)** In the gas-phase transition metal ion, the 5 d orbitals are degenerate, but in the octahedral complex, the d orbitals are split into 2 energy levels.~~

~~State and explain which d orbitals have the higher energy level in the complex ion.~~ [2]

- ~~From the shape of the *d* orbitals, the **$d_{x^2-y^2}$ and d_{z^2} orbitals have their lobes pointing directly at the ligands along the x, y and z axes**, hence they experience **greater inter-electronic repulsion** from the ligands. [1]~~
- ~~Hence the **$d_{x^2-y^2}$ and d_{z^2}** orbitals have **higher energy** than the d_{xy}, d_{yz} and d_{xz} orbitals. [1]~~

~~**(ii)** When excess ammonia is added to aqueous copper(II) ions, the blue solution turns deep blue. Describe the reaction that has occurred, and write a balanced equation for the reaction. [2]~~

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~~When excess ammonia is added to aqueous copper(II) ions, a <u>ligand exchange reaction</u> occurs, where stronger NH_3 ligands displace H_2O ligands, to form a deep blue complex $[Cu(NH_3)_4(H_2O)_2]^{2+}$. [1]~~

~~$[Cu(H_2O)_6]^{2+}$ (aq) + $4NH_3$ (aq) ⇌ $[Cu(NH_3)_4(H_2O)_2]^{2+}$ (aq) + $4H_2O$ (l) [1]~~

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(d) Glycine, $H_2NCH_2CO_2H$, is the simplest stable amino acid, with a single hydrogen atom as its side chain.

Glycinate anions can act as ligands, forming complexes such as copper glycinate, $[Cu(H_2NCH_2CO_2)_2]$, which is used as a source of dietary copper in animal feed.

A synthesis route to form copper glycinate is shown.

$$CH_3CH_2OH \xrightarrow{\text{I}} CH_3CO_2H \xrightarrow{\text{II}} [Cu_2(CH_3CO_2)_4] \xrightarrow{\text{III}} [Cu(H_2NCH_2CO_2)_2]$$

(i) State reagents and conditions for step I. [1]

~~Step II can be carried out by heating the ethanoic acid, CH_3CO_2H, with copper(II) hydroxide, $Cu(OH)_2$, to form $[Cu_2(CH_3CO_2)_4]$.~~

~~**(ii)** State the oxidation number of copper in $[Cu_2(CH_3CO_2)_4]$. [1]~~

~~**(iii)** Step III is often carried out by adding $[Cu_2(CH_3CO_2)_4]$ in aqueous alcohol to glycine. Given that the shape of copper glycinate is square planar, draw and label the 2 *cis-trans* isomers of copper glycinate that can be formed in step III. [2]~~

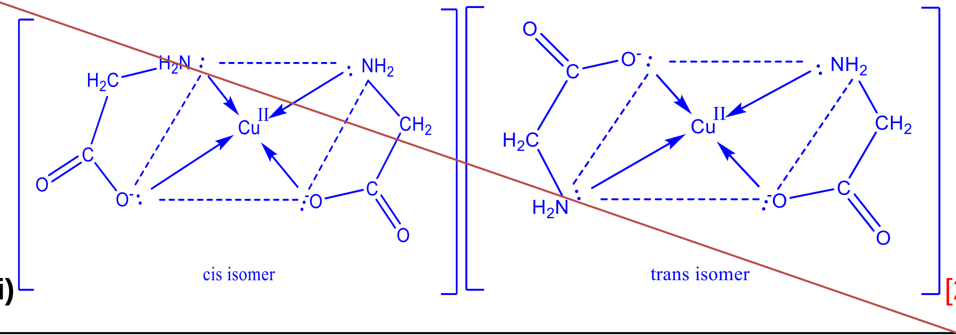
(i) <u>**Acidified**</u> **(H_2SO_4)** <u>**$K_2Cr_2O_7$ or $KMnO_4$**</u>**,** <u>**heat**</u> under reflux [1]

Common Error:

1. **Some students missed out the acid, or used HCl or HNO_3 which may interfere with the redox reaction, or stated "acidified $K_2Cr_2O_7$, heat with distillation", which would form the aldehyde rather than carboxylic acid.**

~~**(ii)** +2 [1]~~

(iii)



[2]

(e) Glycine can be synthesized from ethanoic acid in the following synthesis route:

$$CH_3CO_2H \xrightarrow{\text{I}} ClCH_2CO_2H \xrightarrow{\text{II}} H_2NCH_2CO_2H$$

(i) In step I, Cl_2 reacts with ethanoic acid in the presence of a catalyst to form chloroethanoic acid.

Suggest a chemical test to distinguish between ethanoic acid and chloroethanoic acid. Include the reagents and conditions used, and the observations for each compound. [2]

(ii) Give reagents and conditions for step II and state the type of reaction that is occurring. [2]

(i) Heat separate samples of the compounds in $NaOH(aq)$, allow to cool, then add $HNO_3(aq)$ followed by $AgNO_3(aq)$. [1] White ppt will be formed for chloroethanoic acid but no ppt for ethanoic acid. [1]

(ii) (excess) NH_3 in alcohol eg. ethanol, heat in sealed tube [1]
Nucleophilic substitution reaction [1]

Common Errors:
(i) -Many students forgot that the C-Cl bond needs to be hydrolysed with NaOH(aq) and heat first, then any excess NaOH neutralized with HNO_3 (not other acids as they may form other ppts), and then $AgNO_3$ added to form white AgCl ppt.
-observations for both compounds must be stated, and should be the positive and negative (white ppt vs no ppt), not "no visible observation".
(ii) -Some students wrote $NH_3(aq)$ which is the wrong solvent
-Some students wrote heat under reflux, but NH_3 would escape. Also, it is not a sealed "test tube" but a bigger and more durable tube, made of glass or quartz etc.
-A worrying number of students stated "electrophilic substitution", which is for benzene/arenes, but this is clearly a nucleophilic substitution of an alkyl chloride to form an amine.

(f) Another transition element compound, vanadium(V) oxide, V_2O_5, is used as a catalyst in the Contact process to manufacture sulfuric acid.

Sulfur dioxide and oxygen in a 1:1 ratio are passed over the heated V_2O_5 catalyst to form sulfur trioxide. During the reaction, the brown-yellow catalyst changes colour to dark blue, but returns to the original brown-yellow colour at the end of the reaction.

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) \qquad \Delta H = -196 \text{ kJ mol}^{-1} \qquad \textit{reaction 1}$$

(i) *Reaction 1* takes place via *heterogeneous* catalysis. State what is meant by *heterogeneous* catalysis. [1]

~~**(ii)** The mode for this catalysis is unusual, as the catalyst reacts with the reactants that are adsorbed onto its surface. However, throughout *reaction 1*, no vanadium complexes are involved. Suggest a reason for the colour change of the catalyst. [1]~~

(iii) Use Le Chatelier's principle to explain the optimum temperature and pressure conditions for *reaction 1* in order to maximize yield, and suggest one other consideration in deciding the temperature for *reaction 1* to be carried out commercially. [3]

(i) Heterogeneous catalysis means that the reactants and catalyst are in different phases, ie. vanadium(V) oxide is solid but the reactants are gaseous. [1]

~~**(ii)** Vanadium undergoes a **change in oxidation state**, but is regenerated at the end of the reaction. [1] (Since no complexes are involved, the colour change cannot be due to ligand exchange reaction)~~

(iii) Since forward reaction is exothermic, Le Chatelier's principle predicts that low temperature and high pressure will be ideal [1], as equilibrium position lies to the right as heat energy is released by the forward exothermic reaction, and fewer number of moles of gas are present on the right hand side, hence higher yield. [1] [or 1m for 1 correct condition plus explanation]

However, at low temperatures, rate of reaction will be slow, hence, a moderate/higher temperature is used commercially. [1]

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Common Errors:

(i) **-Many students did not read the question carefully and explained a "heterogeneous catalyst" instead of "catalysis"**
-Many students misspelled "heterogeneous" as "heterogenous"
-A number of students outlined the mode of action (adsorption, desorption, doesn't take part in the reaction etc), instead of defining "heterogeneous"

(iii) **-Some students explained temperature affecting pressure and vice versa, but should have kept the explanations separate.**
-Many answers were vague or had circular reasoning in explaining low temperature or high pressure would shift position of eqm to the right "to increase yield" or "to increase temperature" or "to decrease pressure".
-Some students explained the optimum temperature and pressure that would increase rate rather than equilibrium yield.

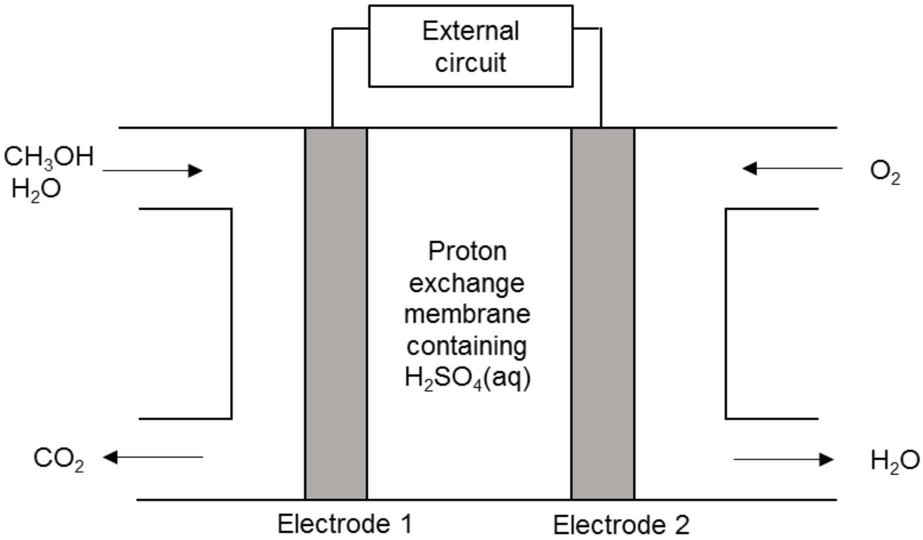
-Some students did not state another consideration in deciding temperature at all, or stated cost to maintain the temperature, which does not show key Chemistry understanding that rate is slow at low temperatures, or application of similar conditions from the Haber process.

……………………………………………………………………………………………… [Total: ~~20~~ **10**]

Section B

Answer **one** question from this section.

4 **(a)** The following diagram illustrates the parts of the direct methanol fuel cell (DMFC). Methanol is supplied to Electrode 1 where methanol and water react to form carbon dioxide. Oxygen is supplied to Electrode 2 simultaneously and reacts with the protons at the cathode to form water.



The overall cell reaction of a DMFC can be expressed as follow.

$$CH_3OH(l) + \frac{3}{2}O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

Research has shown that the DMFC is an appropriate alternative to rechargeable batteries. The electrons are transported through an external circuit from anode to cathode, providing power to connected devices like mobile phones and laptop computers.

(i) Write the half–equations for the reactions which take place at Electrode 1 and Electrode 2. [2]

Electrode 1: $CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-$ [1]

Electrode 2: $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$ [1]

Most candidates were able to pick the correct equation for electrode 2, from the Data Booklet. However, there was a small handful of students who were still unable to balance the half-equations.

(ii) A DMFC is capable of producing a voltage of 1.18 V at standard conditions. Hence, calculate the standard Gibbs free energy change, $\Delta G^{\ominus}$, for the **given** overall cell reaction. [1]

□$\Delta G^{\ominus} = -nFE^{\ominus}cell$

$= -(6)(96500)(1.18)$

$= -683\ 000$ J mol^{-1} [1]

This question was well done. Common mistakes included using the wrong no of mole of electrons e.g. 4 or 12. Note that question requested for the given overall cell reaction, i.e. 6 mole of electrons for 1.5 mol of O_2.

(iii) Predict how the voltage of this cell would change if the [CH_3OH] was decreased. [2]

When [CH_3OH] is decreased, by Le Chaterlier's Principle, the equilibrium position for $CO_2 + 6H^+ + 6e^- \rightleftharpoons CH_3OH + 2H_2O$ shifts to the right. Thus, $E_{CO2/CH3OH}$ becomes less negative/more positive. [1, based on direction of half-equation given] This will cause cell potential (E_{cell}) to be less positive [1] since $E_{cell} = E_{red} - E_{CO2/CH3OH}$

Few candidates were given full credit and most answers had incomplete reasoning. Since the change of decreasing concentration of methanol was applied for the half-cell, students had to first explain the impact on equilibrium position for the half-equation involving methanol and CO_2. Students are reminded to avoid writing the term Eox. There were some candidates who referred to $E_{CO2/CH3OH}$ as Ecell or voltage of cell. Also, most scripts merely referred to a decrease in Ecell. Although benefit of doubt was given, students ought to be clearer and state Ecell becomes less positive or decrease to less that 1.18V. Other common mistakes included referring to E°cell instead of Ecell despite this no longer under standard conditions. There were many scripts which had no reference to the equation or referred to the equation in (a)(i) when applying Le Chaterlier's equation. Students are reminded to state the equation first (with reversible arrows) before proceeding to explain how the equilibrium position would shift.

(b) The electricity generated by the DMFC can be used to electroplate taps with nickel to give a high lustre finish and resistance to wear and corrosion. The electrolyte used was a solution of nickel(II) sulfate.

Calculate the current produced by the DMFC when a total of 3 hours was used to plate 15 g of nickel. [2]

$Ni^{2+} + 2e^- \rightarrow Ni$

Amount of Ni = $\frac{15}{58.7}$ = 0.256 mol

Amount of e^- = 0.256 x 2 = 0.512 mol

Q = nF

=0.512 x 96500 [1]

= 49408 C (or 49318 C)

Q = It

49408 = I x (3 x 60 x 60)

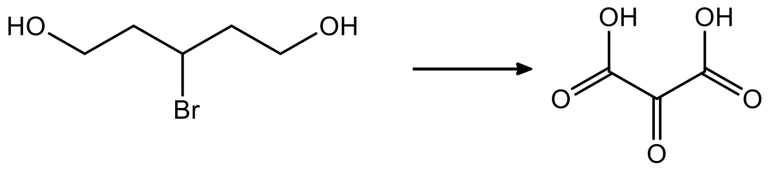
I = 4.57 A [1, ecf]

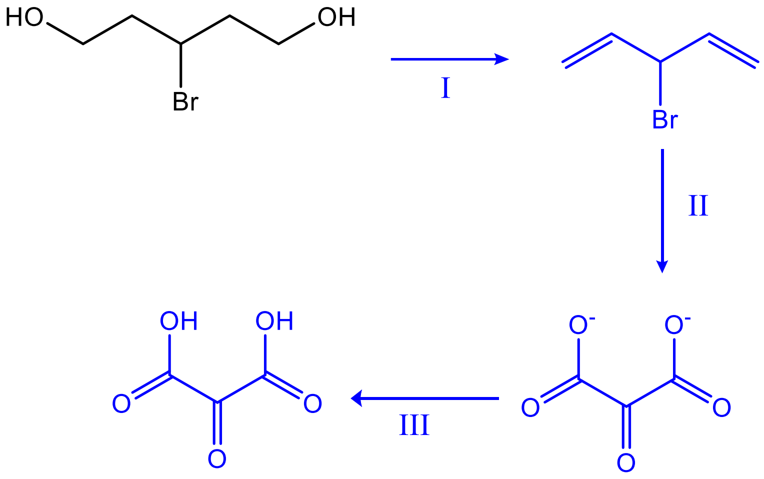
This part was well done. Common mistake is omitting the mole ratio of Ni to electrons. There were also students who had difficulty calculating Q from ne.

(c) Alcohols can undergo various reactions to form other class of organic compounds like carboxylic acids and esters. Suggest how the following products can be formed from the corresponding alcohol in **three steps**.

You are required to state the reagents and conditions for each step and give the structures of the intermediate compounds.

(i) [3]



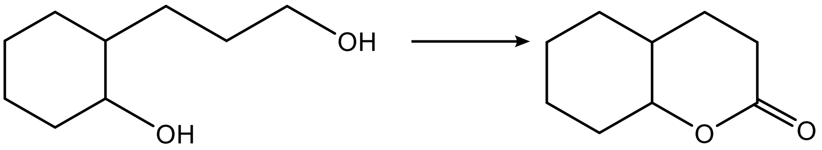


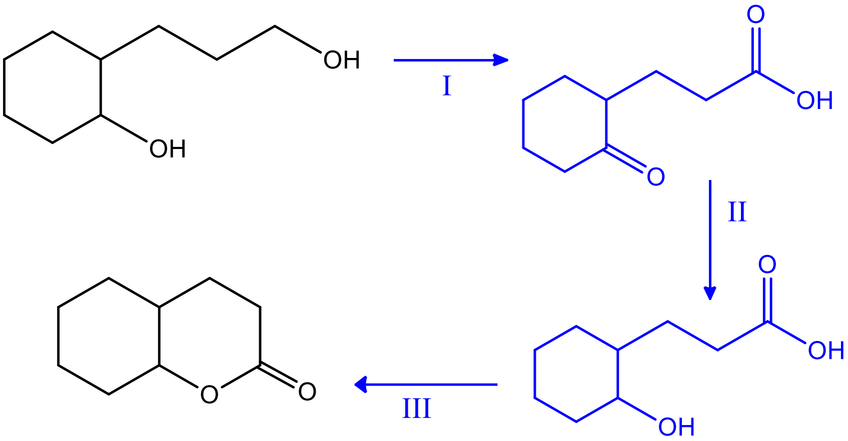
I: excess conc H_2SO_4, heat under reflux/ 170°C [1, including intermediate compound]
II: $KMnO_4$, NaOH(aq), heat under reflux [1, including intermediate compound]
III: H_2SO_4(aq) or HC*l*(aq) [1, including final product]

Few students were able to get full credit for this question. Many failed to see that the number of carbon atoms decreased by two hence a step-down reaction involving alkenes i.e. oxidative cleavage is involved.

OR
II: NaOH(aq), heat under reflux
III: $KMnO_4$(aq), H_2SO_4(aq), heat under reflux

(ii) [3]





I: KMnO$_4$, dilute H$_2$SO$_4$, heat under reflux [1]
II: NaBH$_4$ in methanol, or H$_2$, Pt/Pd, rt or Ni catalyst, heat [1]
III: conc H$_2$SO$_4$, heat under reflux [1]

Only a small handful of students was able to get the correct synthesis. Note that an ester was present in the product and hence students needed to generate a carboxylic acid and alcohol as one of the intermediates. Many students were unfamiliar with the reducing agents for specific types of functional groups e.g. NaBH$_4$ or H$_2$ is needed to selectively reduce the ketone but not the carboxylic acid.

(d) Chemists and biochemists use pK_a values to compare the strengths of acids. The use of pK_a values is more convenient for comparing acid strengths than the K_a values.

The pK_a values of two naturally occurring acids are shown below.

name	structural formula	pK_a (at 25 °C)
benzoic acid	C_6H_5COOH	4.19
phenylmethanol	$C_6H_5CH_2OH$	15.1

Explain in terms of their molecular structures why benzoic acid and phenylmethanol have significantly different pK_a values. [2]

s

Benzoic acid has a lower pK_a value; is a stronger acid than phenylmethanol.

$C_6H_5CO_2^-$ is **more stable** as the p orbital of the oxygen atom overlaps with the electron cloud of the –C=O bond and the lone pair of electrons on the oxygen atom delocalise into the –C=O. The **negative charge is delocalised over the carbon atom and the two electronegative oxygen atoms**, stabilising the $C_6H_5CO_2^-$ ion. **[1]**

$C_6H_5CH_2O^-$ is destabilised as the **negative charge is localised** and the **electron-donating alkyl group intensifies the negative charge** on oxygen. **[1]**

Most students were able to identify that delocalisation can occur for the benzoate ion. However, some students thought that the negative charge can delocalise into the benzene ring which is incorrect. The delocalisation is across the C=O bond instead. Note that as there are 2 distinct functional groups, students ought to give the explanation for each functional group.

(e) Compound **A**, with molecular formula C_5H_8O, decolourises aqueous bromine and gives off white fumes when reacted with PCl_5. Upon heating **A** with acidified potassium manganate(VII), a symmetrical product **B**, $C_5H_6O_5$, is formed.

B does not give a red precipitate with Fehling's solution but an orange precipitate is observed with 2,4-dinitrophenylhydrazine. 1 mol of **B** also reacts with 1 mol of Na_2CO_3 with effervescence observed.

Deduce the structures of compounds **A** and **B**, explaining the chemistry of the reactions involved.

Observation	**Type of reaction**	**Functional group present**
A decolourises aqueous bromine	**Electrophilic addition**	**C=C present**
A reacts with PCl_5 to give off white fumes of HCl	**Nucleophilic substitution**	**alcohol present**
A undergoes oxidation with $KMnO_4$ to give a symmetrical product B with no loss in C atoms ☐	**Oxidative cleavage and oxidation of secondary alcohol**	**C=C is in a ring and A is a cyclic compound**
B does not give a red precipitate with Fehling's solution but forms an orange precipitate with 2,4-dinitrophenylhydrazine ☐	**B cannot be oxidised but can undergo condensation reaction with 2,4-DNPH.**	**B is a ketone**
1 mole of B also reacts with 1 mole of Na_2CO_3	**Acid-base reaction**	**B contains 2 $-CO_2H$ groups**

7 (reasoning and structures) max 5

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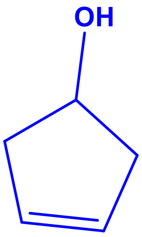
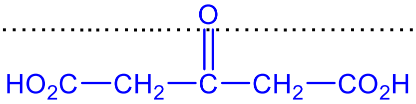


A

……

B



$HO_2C-CH_2-\overset{\overset{O}{\|}}{C}-CH_2-CO_2H$

……[5]

[Total: 20]

Few students were able to get the structure of A. Many students did not give complete reasoning i.e. both reaction types and functional groups. Some scripts were vague in the identification of functional groups. They only identified that A has an –OH group or hydroxy group which was not specific. Most students also failed to deduce that B had 2 carboxylic acid groups from the mol ratio given.

$2RCO_2H + Na_2CO_3 \rightarrow CO_2 + H_2O + 2RCO_2^-Na^+$

5 **(a)** The pH values of the solutions of two Period 3 chlorides are given below.

compound	pH of a 1.0 mol dm^{-3} solution
Na*Cl*	7.0
$MgCl_2$	6.0

By using suitable data from the *Data Booklet*, suggest explanations for the pH values of the two chloride solutions. Include appropriate equations in your answer. [4]

Ionic radii: **0.095 nm (Na^+), 0.065 nm (Mg^{2+})** **[1] quote correct Data Booklet values**

NaCl dissolves in water to form Na^+ ions and Cl^- ions. These ions do not hydrolyse in water as the Na^+ charge density is not high. Thus, the solution gives a pH of 7.

$NaCl(s) + aq \rightarrow Na^+(aq) + Cl^-(aq)$ **[1]**

When $MgCl_2(s)$ dissociates completely in water, the equation is:

$MgCl_2(s) + 6H_2O(l) \rightarrow [Mg(H_2O)_6]^{2+}(aq) + 2Cl^-(aq)$

$[Mg(H_2O)_6]^{2+}(aq)$ is a weak acid. Mg^{2+} has **high charge density**, hence **$[Mg(H_2O)_6]^{2+}(aq)$** undergoes **slight hydrolysis** **[1]** (reaction with water) to give H_3O^+ to give a slightly acidic solution (pH 6.5).

$[Mg(H_2O)_6]^{2+}(aq) + H_2O(l) \rightleftharpoons [Mg(H_2O)_5OH]^+(aq) + H_3O^+(aq)$ **[1]**

A number of candidates have the misconception of using Na^+/Na and Mg^{2+}/Mg half-cell equations to explain the pH values of chloride solutions.

A few candidates have the misconception that the dissolution of $MgCl_2$ will result in the formation of HCl.

Many candidates failed to read the question carefully that they need to quote data from data booklet.

Many candidates failed to use the term "slight" or "partial" to describe the hydrolysis of $[Mg(H_2O)_6]^{2+}(aq)$.

Many candidates failed to relate partial hydrolysis of $[Mg(H_2O)_6]^{2+}(aq)$ to its high charge density.

Many candidates failed to use reversible arrow for the equation for the Partial Hydrolysis of $[Mg(H_2O)_6]^{2+}(aq)$.

(b) Other Period 3 compounds such as $Mg(OH)_2$ and $Al(OH)_3$ are sparingly soluble in water. Their solubility products at 298 K are given in the table below:

compound	numerical value of K_{sp}
$Mg(OH)_2$	1.80×10^{-5}
$Al(OH)_3$	1.80×10^{-11}

Calculate the solubilities of the two compounds, and hence deduce which of the two compounds is more soluble in water at 298 K. [3]

$$Mg(OH)_2\,(s) \rightleftharpoons Mg^{2+}\,(aq) + 2OH^-\,(aq)$$

K_{sp} of $Mg(OH)_2 = [Mg^{2+}][OH^-]^2$

$1.80 \times 10^{-5} = (s)(2s)^2$

$s = \sqrt[3]{\frac{1.80 \times 10^{-5}}{4}}$ **[1]** $= 1.65 \times 10^{-2}$ mol dm^{-3}

$$Al(OH)_3\,(s) \rightleftharpoons Al^{3+}\,(aq) + 3OH^-\,(aq)$$

K_{sp} of $Al(OH)_3 = [Al^{3+}][OH^-]^3$

$1.80 \times 10^{-11} = (s')(3s')^3$

$s' = \sqrt[4]{\frac{1.80 \times 10^{-11}}{27}}$ **[1]** $= 9.04 \times 10^{-4}$ mol dm^{-3}

Based on the calculated solubilities, **$Mg(OH)_2$ is more soluble than $Al(OH)_3$.** **[1]**

A few candidates only compare the solubility products of both compounds to evaluate on the solubilities of both compounds.

A few candidates have the misconception of taking the solubility product, Ksp of the compound as its solubility, s.

A number of candidates uses $(s)(s)^2$ as Ksp of $Mg(OH)_2$ and $(s)(s)^3$ as Ksp of $Al(OH)_3$. They forgot to use the mole ratios of $Mg(OH)_2 \equiv 2OH^-$ & $Al(OH)_3 \equiv 3OH^-$ when calculating the solubility, s for each compound.

(c) A zinc-air battery uses oxygen gas in the air as an oxidising agent and zinc metal as a reducing agent. Zinc is oxidised to a soluble zincate, $Zn(OH)_4^{2-}$. The electrolyte circulated through the battery is NaOH(aq).

(i) Write the equations for the reactions that occur at the anode and cathode respectively. [2]

Anode: $Zn + 4OH^- \rightarrow [Zn(OH)_4]^{2-} + 2e^-$ **[1]**

Cathode: $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ **[1]**

Most candidates failed to balance the half-equations for alkaline medium condition.

Some candidates failed to use the given product, $Zn(OH)_4^{2-}$ as the product for the oxidation half-equation.

A number of candidates mistakenly use reversible arrow for the oxidation and reduction half-cell equations.

(ii) Given that the $\Delta G^{\ominus}$ for the reaction is –636.9 kJ mol^{-1}.

1. Calculate the standard standard cell potential, $E^{\ominus}_{cell}$. [2]

$Zn + 4OH^- \rightarrow [Zn(OH)_4]^{2-} + 2e^-$ … (1)

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ … (2)

Overall Equation: (1) × 2 + (2)

$2Zn + 4OH^- + O_2 + 2H_2O \rightarrow 2[Zn(OH)_4]^{2-}$

$\Delta G^{\ominus} = -nFE^{\ominus}$

$E^{\ominus}$ cell = **$-636.9 \times 10^3 / (-4 \times 96500)$** **[1]** = **+1.65 V** **[1]**

Most candidates failed to use the correct no of moles of electrons, n and/or failed to convert 636.9 kJ mol^{-1} correctly to 636900 J mol^{-1}.

A number of candidates failed to use the equation, $\Delta G^{\ominus} = -nFE^{\ominus}$ to calculate E_{cell}. Instead they tried to use $E_{red} - E_{oxid}$ to do so.

2. Hence, by the use of suitable data from the *Data Booklet*, calculate a value for the $E^{\ominus}$ of the $Zn(OH)_4^{2-}$ / Zn electrode reaction. [1]

$E^{\ominus}$ cell = $E^{\ominus}$ red – $E^{\ominus}$ oxid

1.65 = 0.40 – $E^{\ominus}$ of $Zn(OH)_4^{2-}$ / Zn

$E^{\ominus}$ of $Zn(OH)_4^{2-}$ / Zn = 0.40 – 1.65 = **–1.25 V** **[M1] allow ecf for wrongly calculated E°cell**

Some candidates mistaken the calculated E_{cell} derived from part 1 as E_{red} or E_{oxid} when calculating $E^{\ominus}$ of the $Zn(OH)_4^{2-}$ / Zn electrode reaction.

A number of candidates are careless when doing arithmetic calculation of $E^{\ominus}$ of the $Zn(OH)_4^{2-}$ / Zn electrode reaction.

(d) An aromatic compound **C** has the molecular formula, $C_{10}H_{14}N_2O_2$, and is an amine that dissolves readily in aqueous HC*l*. Decolourisation is observed when aqueous Br_2 is added to **C** and a new product **D**, $C_{10}H_{13}BrN_2O_2$, is formed.

C does not give orange precipitate upon reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH) but reacts with excess concentrated H_2SO_4 to form an alkene. **C** also reacts with hot alkaline aqueous iodine to form a yellow precipitate.

Reaction of **C** with hot aqueous sodium hydroxide produces ammonia gas and a salt.

When **C** is subjected to hot acidified $KMnO_4$ followed by a suitable extraction technique, compound **E**, $C_9H_7NO_6$ is obtained. 1 mol of compound **E** requires 1.5 mol of aqueous sodium carbonate for complete neutralisation.

Deduce the structures of compounds **C**, **D**, and **E**, explaining your reasoning. [8]

C undergoes **electrophilic substitution** with aqueous Br_2 to form **D.**
⇒ **C** contains **phenylamine group** with **2 out of the 2,4,6, positions occupied by 2 subtituents/ only 1 position out of 2,4,6 free for substitution**. **[1]**

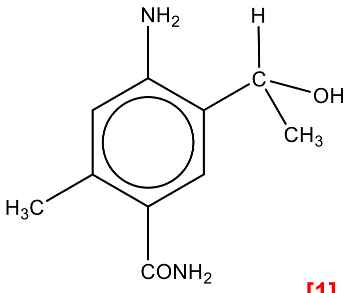
C does not undergo condensation with 2,4-DNPH.
⇒ **C** contains **no aldehyde and ketone (or carbonyl)** group. **[1]**

C undergoes **elimination** with excess concentrated H_2SO_4.
⇒ **C** contains **alcohol** group. **[1]**

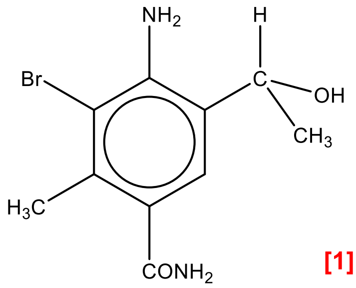
C undergoes **basic hydrolysis** with hot NaOH (aq) to form ammonia gas**.**
⇒ **C** contains **primary amide** group. **[1]**

C undergoes **oxidation** with hot alkaline iodine.
⇒ **C** contains the **$–CH(CH_3)OH$** group **[1]** and the yellow ppt is CHI_3.

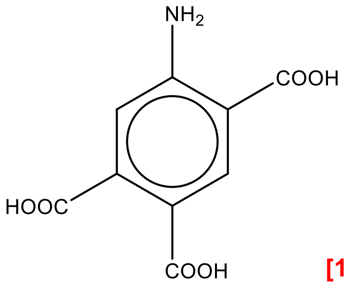
E undergoes **acid-carbonate/ acid-base reaction** with 1.5 moles Na_2CO_3
⇒ **E** contains **3 -COOH or carboxylic acid group**. **[1] Total 9 max 8**



Compound **C** **[1]**



Compound **D** **[1]**



[1]

Compound **E**

Most candidates never state Reaction Type for their elucidative statements.

Most candidates mistaken the reaction with Br_2 as Electrophilic Addition instead of Electrophilic Substitution. Hence they made the deduction of “C is an Alkene”.

Most candidates can deduce correctly from the reaction with 2,4 DNPH.

Most candidates mistaken the reaction with Hot NaOH as Acid-Base instead of Alkaline Hydrolysis. Hence, they made the deduction of “C is an amine”.

Most candidates can deduce correctly from the reaction with Concentrated H_2SO_4.

Some candidates made the mistake of including $-COCH_3$ as one of the deduced structures for the reaction with “Hot Alkaline Iodine”. They forgot that they had made the previous deduction that C is not Carbonyl.

Most candidates never include the Number of Carboxylic Acid groups in E when writing the elucidative statement for the reaction with Sodium Carbonate.

Most candidates forgot to account for the mono-substitution of Br for the reaction of C with Br_2 when deducing the structure of C. Hence, the substituent groups for C are placed on the wrong positions of the benzene ring.

Most candidates forgot to account for the 9 Carbon Atoms of E when deducing on the structure of E. Hence, the deduced structure of E either has 8 or 10 carbon atoms.

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[Total: 20]

Additional answer space

If you use the following pages to complete the answer to any question, the question number must be clearly shown.