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

CHEMISTRY

Paper 3 Free Response

9729/03

19 September 2018

2 hours

Candidates answer on separate paper.

Additional Materials: Answer Paper
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.

Section A
Answer **all** questions.

Section B
Answer **one** question.

Begin **each question** on a **fresh** piece of answer paper.

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

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.

Section A

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

1 This question concerns acid-base properties of organic compounds and compounds of some elements in the Periodic Table.

(a) The behaviour of a molecular specie as an acid or base is dependent of the surrounding medium and its interaction with another reacting specie.

Using the symbol **HZ** to represent a Brønsted-Lowry acid and the symbol $\mathbf{B}^-$ to represent a Brønsted-Lowry base, write equations to show the following:

(i) CH_3OH acting as a Brønsted-Lowry base. [1]

(ii) NH_3 acting as a Brønsted-Lowry acid. [1]

(b) In an acid-base reaction, conjugate acid-base pairs can be determined. Copy the table below onto your writing paper and complete it by writing the formula of the conjugate acid-base pairs of the species listed, assuming the acids/bases are monobasic/monoacidic in nature respectively.

	acid	**base**
I		H_2O
II	H_2	

[1]

(c) A particular weak monobasic acid HA has a dissociation constant, K_a, of 1.0×10^{-5} mol dm^{-3}. The un-ionised acid molecules are blue and the anions are yellow.

(i) Calculate the pH at which a solution containing HA molecules and A^- ions is green, *i.e.* midway between blue and yellow. [1]

(ii) Describe qualitatively how the answer in **(c)(i)** would be affected by the addition of solid sodium salt of the acid, NaA. [2]

A solution mixture is prepared by adding 50 cm^3 of 0.10 mol dm^{-3} of the acid HA to 50 cm^3 of 0.10 mol dm^{-3} of the sodium salt NaA.

(iii) Calculate the final pH of the above solution mixture if 0.04 g of NaOH(s) was added. [3]

(d) Elements and their compounds of the Periodic Table display varied chemical and physical properties.

(i) The peroxide ion has the formula O_2^{2-}. Group 2 peroxides, on heating, decompose to the oxides and oxygen as exemplified by barium peroxide below:

$$BaO_2(s) \longrightarrow BaO(s) + \tfrac{1}{2}O_2(g)$$

Predict how the temperature of decomposition of calcium peroxide would differ from that of barium peroxide. Support your prediction with a brief explanation. [2]

(ii) Explain why the melting point of Al_2O_3, is higher than that of P_4O_{10}, but lower than that of SiO_2. [3]

(e) Bromine occurs as bromide ion in low concentration in sea-water. It is extracted commercially by the following series of steps.

I Chlorine is passed into acidified sea-water and bromine is then removed in a stream of air. The concentration of bromine in the gas phase is too low at this stage for it to be condensed efficiently.

II Therefore it is converted to hydrogen bromide by reaction with added sulfur dioxide and a small excess of water vapour:

$$Br_2(g) + SO_2(g) + 2H_2O(g) \rightarrow 2HBr(g) + H_2SO_4(g)$$

A moderately concentrated, aqueous mixture of hydrobromic and sulfuric acids is obtained when the vapour is cooled and condensed.

III The concentrated mixture of acids is treated with chlorine and steam, producing a bromine vapour from which liquid bromine is obtained through condensation on cooling. The sulfuric acid remains in the solution.

IV The crude bromine is purified by fractional distillation.

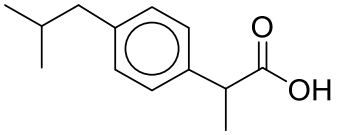
(i) Explain in terms of the relevant standard electrode potentials the feasibility of the reactions taking place in Steps **I** and **II**. [3]

(ii) Discuss the difference between the polarity of SO_2 and Br_2. [2]

(iii) Explain in terms of bonding, why, in Step **III**, the sulfuric acid remains in the solution. [1]

[Total: 20]

2 (a) Ibuprofen is a nonsteroidal anti-inflammatory drug (NSAID) that is commonly used as a painkiller and for fever reduction. The structure of ibuprofen is as shown below.



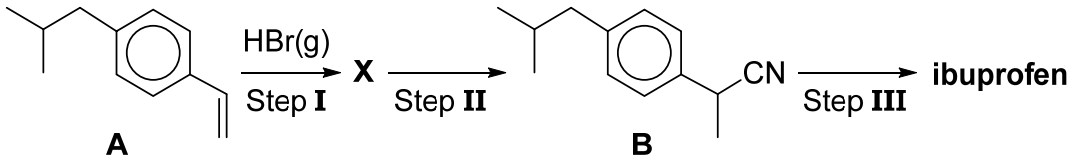
(i) Describe what is a chiral carbon. [1]

(ii) Draw the pair of enantiomers of ibuprofen. You may represent the aryl substituent using **Ar**. [2]

In the laboratory, the enantiomers of ibuprofen have been separated into their enantiomerically pure forms. However, the bottles containing these pure enantiomers were not labelled.

(iii) State a suitable physical property that you could use to identify the two different enantiomers. Explain your answer. [2]

There are a few routes that can be used to synthesis ibuprofen. Below is a reaction scheme proposed by a student to synthesise ibuprofen from the hydrocarbon **A**, *via* two intermediates **X** and **B**.



(iv) Suggest the identity of intermediate **X**. [1]

(v) Name and outline the mechanism for Step **I**, including curly arrows, showing the movement of electrons, and all charges. [3]

(vi) State the reagents and conditions for Step **II** and Step **III**. [2]

(b) Methylbenzene, an important starting material in synthetic chemistry, can be manufactured from heptane *via* catalytic reforming:

$$C_7H_{16}(l) \rightarrow C_7H_8(l) + 4H_2(g)$$

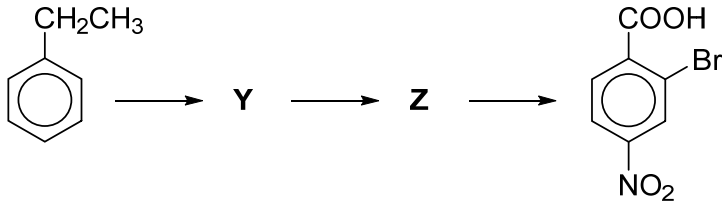
At T = 27 ºC, the enthalpy of reaction, $\Delta H^{\ominus}$, is +211 kJ mol^{-1}, and the change in Gibbs free energy of reaction, $\Delta G^{\ominus}$, is +110 kJ mol^{-1}.

(i) Using the information above, calculate for $\Delta S^{\ominus}$ in J mol^{-1} K^{-1}. [2]

(ii) Calculate for $\Delta G^{\ominus}$ at T = 627 ºC, in kJ mol^{-1}. [1]

(iii) Hence, comment on the effect of temperature on the spontaneity of the reaction. State any assumption that must be made for your comment to be valid. [2]

(c) The position of an incoming electrophile in electrophilic substitution is dependent upon nature and position of the substituent(s) already bonded to the benzene ring. Ethylbenzene undergoes a three-step reaction as shown below.



(i) Suggest the structures of intermediate **Y** and **Z**. [2]

(ii) With reference to the substituents on the benzene ring, explain the rationale behind the order of substitution in determining the identity of **Y** and **Z**. [2]

[Total: 20]

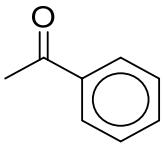
3 Ethanal used to be manufactured from ethyne, HC≡CH. This process is now being replaced by a method based on ethene. Widely known as the Wacker Oxidation, the overall process amounts to oxidation. Ethene and oxygen are bubbled together through an aqueous solution containing $CuCl_2$ and $PdCl_2$ catalysts:

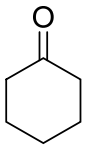
$$CH_2{=}CH_2 \ + \ \tfrac{1}{2}O_2 \xrightarrow[CuCl_2]{PdCl_2} CH_3CHO$$

The laboratory scale modification – the Wacker-Tsuji Oxidation – is useful for the synthesis of various ketone:

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

(a) (i) Draw the structure of the starting material to manufacture the following ketones using the Wacker-Tsuji Oxidation:

(**I**) acetophenone, 

(**II**) cyclohexanone,  [2]

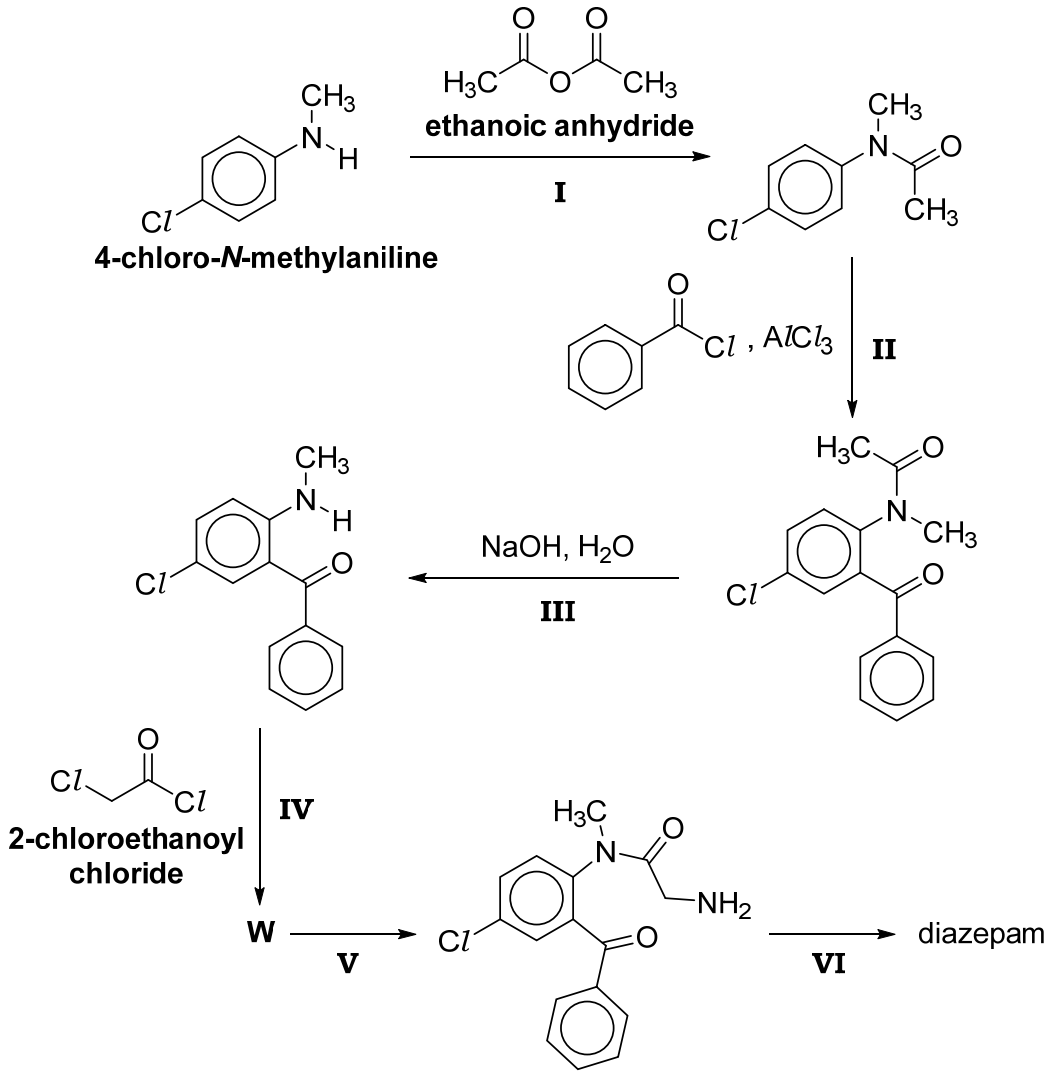
(ii) Describe one simple chemical test to distinguish between the above two ketones. You should state the reagents, conditions and the expected observations with each compound. [2]

(b) Ethanal is often used in the manufacture of 2-chloroethanoyl chloride, $ClCH_2COCl$.

(i) Propose a 3-step synthetic route for the formation of 2-chloroethanoyl chloride from ethanal, stating clearly the reagents and conditions for each step. [3]

2-chloroethanoyl chloride is an important reagent in the manufacture of diazepam, a drug that is commonly used to treat a range of conditions including anxiety and alcohol withdrawal syndrome.

The following reaction scheme shows the synthesis of diazepam from 4-chloro-*N*-methylaniline.

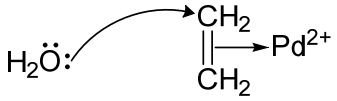


(ii) The mechanism for Step **II** is similar to that of Friedel-Crafts alkylation. Suggest the mechanism for this step, including curly arrows, showing the movement of electrons, and all charges. [2]

(iii) Draw the structure of compound **W** and state the reagent for Step **V**. [2]

(iv) Step **VI** occurs spontaneously at room temperature, without the need of any reagents. This reaction is similar to the reaction of carbonyl compounds with 2,4-dinitrophenylhydrazine. Draw the structure of diazepam. [1]

(c) The suggested mechanism of the Wacker Oxidation involves the formation of a complex between ethene and Pd^{2+}, whereby ethene acts as a *ligand*. This is then followed by nucleophilic attack of water at the complexed ethene molecule:



The resulting complex breaks down by a number of stages to form ethanal and palladium metal. The palladium metal is oxidised back to Pd^{2+} by oxygen. The $CuCl_2$ is a catalyst for this oxidation.

(i) What is meant by the term *ligand* in the context of transition element chemistry? [1]

(ii) Suggest a reason why the formation of this complex renders ethene attractive to nucleophiles rather than the usual electrophiles. [1]

(iii) Aqueous $CuCl_2$ is commonly observed as a blue solution. Explain this phenomenon. [3]

(d) A mixture containing 0.200 mol dm^{-3} Cu^{2+} and 0.200 mol dm^{-3} Pd^{2+} is treated with solid potassium hydroxide in attempt to separate the two cations, by precipitating out $Pd(OH)_2$.

The numerical values of the solubility products of $Cu(OH)_2$ and $Pd(OH)_2$ are given in the table below.

hydroxide	**solubility product, K_{sp}**
$Cu(OH)_2$	2.20×10^{-20}
$Pd(OH)_2$	1.00×10^{-31}

Maximum separation of the two ions is achieved when $Cu(OH)_2$ is just about to precipitate out from solution.

(i) Determine the hydroxide ion concentration at maximum separation. [1]

The two ions are said to be *selectively* separated when a maximum of 0.01% of the precipitated compound still remains as the aqueous ions.

(ii) By calculating the concentration of Pd^{2+} remaining in solution at maximum separation, determine whether Pd^{2+} can be selectively separated from Cu^{2+}. [2]

[Total: 20]

Section B

Answer **one** question from this section.

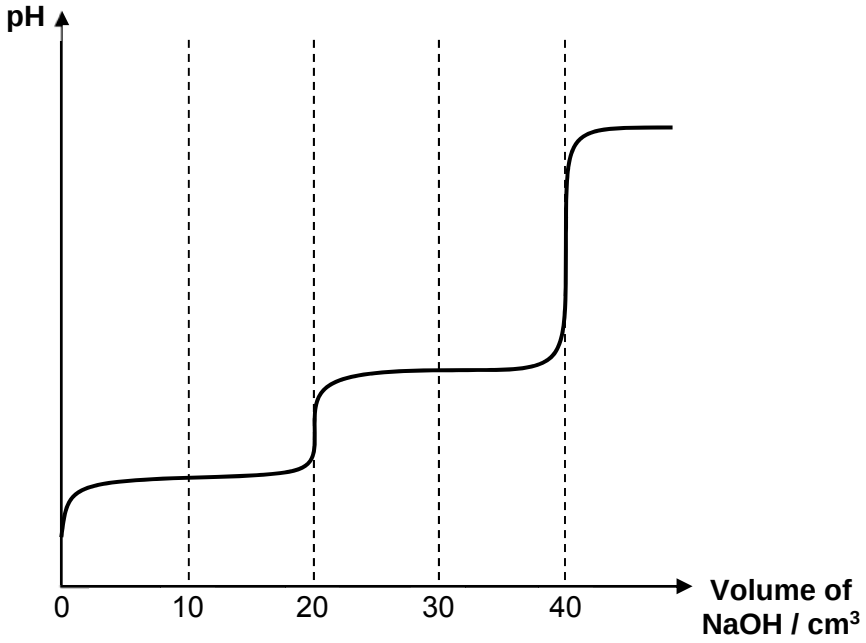
4 (a) The pK_a values of some weak acids are given below.

acid	formula	pK_{a1}	pK_{a2}
peroxyethanoic acid		*y*	–
ethanoic acid		4.76	–
malonic acid		2.83	5.69

(i) Suggest, with reasoning, whether the pK_{a1} of peroxyethanoic acid, *y*, is larger or smaller than the pK_{a1} of ethanoic acid. [2]

(ii) Explain why pK_{a2} of malonic acid is higher than pK_{a1} of ethanoic acid. [1]

(iii) 25.0 cm^3 of a sample containing malonic acid was titrated with 0.800 mol dm^{-3} of a solution of NaOH. The following titration curve was obtained.



You may represent malonic acid as H_2A.
Calculate the concentration of malonic acid in the sample. [1]

(iv) Calculate the initial pH of malonic acid, explaining any assumptions made. [2]

(v) From the list of indicators below, state a suitable indicator that can be used to detect the first equivalence point for the titration of malonic acid with NaOH, giving a reason for your choice.

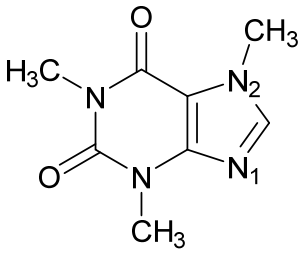
indicator	pH at which colour changes
methyl violet	0−1.6
bromocresol green	3.8−5.4
cresol purple	7.6−9.2

[1]

(vi) The experiment in **(a)(iii)** was repeated with ethanoic acid of the same concentration as malonic acid. Explain whether the pH at equivalence point would be higher or lower than the first equivalence point of the titration with malonic acid. [1]

(b) Describe and explain how the ease of hydrolysis of $CH_3CH_2C\mathit{l}$ differs from that of $CH_3COC\mathit{l}$. [2]

(c) Caffeine is a component of many over the counter analgesics.



caffeine

(i) Predict the products when caffeine undergoes prolonged heating with aqueous sodium hydroxide. [3]

(ii) Caffeine is monobasic. Given that both N_1 and N_2 are sp^2-hybridised, suggest why N_1 is basic while N_2 is neutral. [2]

(d) A zinc-air electrochemical cell is operated by the reaction of zinc with the oxygen in air under an alkaline condition. At the anode, zinc is converted to aqueous zincate ions, $Zn(OH)_4^{2-}$, by air.

(i) Construct an equation for the anode reaction. [1]

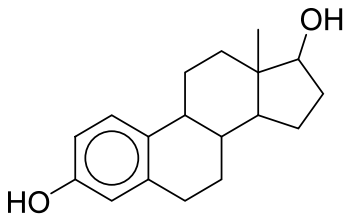
(ii) At 298 K, the standard e.m.f. of a zinc-air electrochemical cell is +1.65 V. By using suitable data from the *Data Booklet*, suggest the standard electrode potential of the $Zn(OH)_4^{2-}(aq)\,|\,Zn(s)$ half-cell at 298 K. [2]

(iii) Determine the effect of using pure oxygen instead of air on the e.m.f. of the zinc-air electrochemical cell at 298 K. [2]

[Total: 20]

5 Many hormones in the human body contain hydroxy or carbonyl compounds.

(a) Estradiol, an estrogenic hormone, can be synthesized from *Testosterone*. The structure of estradiol is shown below.



estradiol

Draw the structure of the organic product formed when estradiol is reacted with each of the following under suitable conditions:

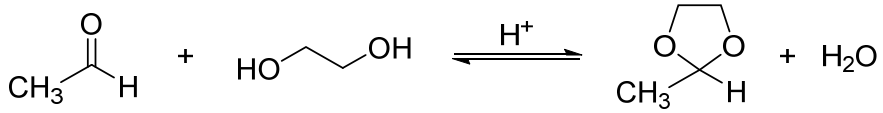
(i) Cl_2(aq) [1]

(ii) $SOCl_2$ [1]

(iii) Sodium metal [1]

When aldehydes or ketones are reacted with an alcohol and an acid catalyst, acetals are formed.

The reaction between ethanal and ethane-1,2-diol was studied in the inert solvent dioxane.



ethanal **ethane-1,2-diol** **acetal**

(b) When the initial rate of this reaction was measured at various concentrations of the two reactants with H^+ concentration of 0.05 mol dm^{-3}, the following results were obtained.

experiment	$[CH_3CHO]$ / mol dm^{-3}	$[HOCH_2CH_2OH]$ / mol dm^{-3}	relative rate
1	0.20	0.10	1.00
2	0.25	0.10	1.25
3	0.25	0.16	2.00

(i) Determine the order of reaction with respect to the following reactants, explaining how you arrive at your answer.

- CH_3CHO
- $HOCH_2CH_2OH$ [2]

(ii) Hence, write the rate equation for the reaction, including units of the rate constant. [2]

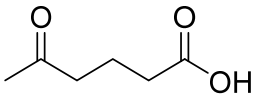
(iii) When the H^+ concentration used in experiment 2 was increased to 0.10 mol dm^{-3}, the relative rate had a value of 2.50.

State the value of the relative rate when the concentrations of CH_3CHO, $HOCH_2CH_2OH$ and H^+ used are 0.20 mol dm^{-3} each. [1]

(c) The acetal group does not react with bases or reducing agents, which the carbonyl group is susceptible to. For instance, both $NaBH_4$ and $LiAlH_4$ do not react with the acetal group.

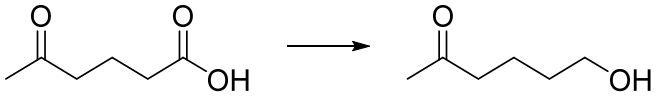
Hence it is possible to use the formation of acetals from carbonyl compounds as a way to protect the carbonyl groups from these reagents. Subsequently one can restore the carbonyl functional group by acidic hydrolysis since the formation of acetals is a reversible reaction.

(i) Draw the structure of the product formed when the following compound is reacted with $NaBH_4$ and $LiAlH_4$ respectively.



[1]

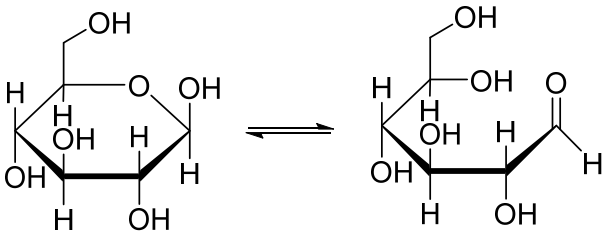
(ii) By using ethane-1,2-diol, $HOCH_2CH_2OH$, as the alcohol to form an acetal group in the inert solvent dioxane as a first step, suggest a suitable synthesis route for the following conversion.



[2]

Copper is used widely in electrical equipment, the minting of coins and for decorative purposes such as in jewellery. Pure copper could be obtained from the electrolysis of a solution containing Cu^{2+} ions, or from electrolysis involving impure copper.

(d) Copper ions are present in Fehling's solution and can be used to test for "reducing sugars". Glucose, a basic form of sugar, has the following structure.



cyclic form of glucose open-chain form of glucose

Glucose gives a positive test with Fehling's solution.

(i) Identify the functional group involved in the reaction and describe what is observed when Fehling's solution is added to glucose with heating. [1]

(ii) Explain why glucose is classified as a "reducing sugar". [1]

(e) In an electrolytic cell, a current of 0.25 A is passed through solution of concentrated copper(II) chloride using platinum electrodes.

(i) Write the equation for the half-cell reaction taking place at the anode. [1]

(ii) When the cell operates for 2.00 hours, 0.496 g of copper is deposited at one electrode. Determine the percentage efficiency of the electrolytic cell. [2]

(f) A sample of impure copper was composed mainly of copper, but with silver and chromium as impurities.

Draw a fully labelled diagram and with reference to relevant $E^{\ominus}$ values, explain how pure copper could be obtained from the impure sample. [4]

[Total: 20]

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Suggested Answer

1 (a) (i) $\underset{\text{base}}{CH_3OH} + \underset{\text{acid}}{\mathbf{HZ}} \longrightarrow CH_3OH_2^+ + \mathbf{Z^-}$ **[1m]**

(ii) $\underset{\text{acid}}{NH_3} + \underset{\text{base}}{\mathbf{B^-}} \longrightarrow NH_2^- + \mathbf{BH}$ **[1m]**

(b)

	acid	base
I	**H_3O^+**	H_2O
II	H_2	**H^-**

[1m] for both correct

(c) (i) $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Midway between blue and yellow indicates that $[H^+] = [HA]$

Hence, $K_a = \dfrac{[H^+]\cancel{[A^-]}}{\cancel{[HA]}} = [H^+]$

$\therefore\ pH = pK_a = -\lg K_a = -\lg(1.0\times10^{-5}) = \underline{\mathbf{5.0}}$ **[1m]**

(ii) $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Upon addition of NaA (a strong electrolyte) to the solution, it undergoes complete dissociation and **[A^-] in the solution is thus momentarily increased**. In accordance to Le Chatelier's principle, the **equilibrium position of the above reaction would shift to the left** **[1m]** to remove the additional A^- ions added. Hence the **[H^+] would decrease** **[1m]** and the pH of the solution would correspondingly **increase**. **Accept alternative explanation using HH equation**

(iii) Before addition of NaOH at pH = 5:

System: Acidic buffer

pH 5 is the point of maximum buffering capacity where pH = pK_a = 5

Thus $[HA] = [A^-] =$ 0.050 mol dm^{-3}

$$\boldsymbol{n_{HA} = n_{A^-}} = \frac{50}{1000}\times0.10 = \underline{\mathbf{5.00\times10^{-3}\ mol}}$$

On addition of NaOH:

n_{OH^-} added $= 1.00\times10^{-3}$ mol

When small amount of OH^- is added to the buffer:

$OH^- + HA \rightarrow A^- + H_2O$

n_{A^-} after addition of $OH^- = 5.00\times10^{-3} + 1.00\times10^{-3} = \underline{\mathbf{6.00\times10^{-3}\ mol}}$

n_{HA} after addition of $OH^- = 5.00\times10^{-3} - 1.00\times10^{-3} = \underline{\mathbf{4.00\times10^{-3}\ mol}}$

$$pH = pK_a + \lg\frac{[A^-]}{[HA]}$$

$$= 5.00 + \lg\frac{\left(\frac{6.00\times10^{-3}}{V}\right)}{\left(\frac{4.00\times10^{-3}}{V}\right)}$$ **[1m] for correct substitution into formula**

$$=$$ **5.18** **[1m] for ans in 3 s.f., ecf**

(d) (i) Temperature of decomposition for CaO_2 is **lower than** that of BaO_2. **[1m]** **Charge density of Ba^{2+} < Ca^{2+}** thus **polarising power of Ba^{2+} < Ca^{2+}** because Ba^{2+} has a larger ionic size but both have the same charge. Since Ca^{2+} is more polarising, the **O–O bond in O_2^{2-} is weakened** to greater extent. **[1m]** Hence CaO_2 decomposes more readily into CaO and O_2 as compared to BaO_2.

(ii) Al_2O_3 has a **giant ionic structure** with **strong electrostatic forces of attraction** between the oppositely charged Al^{3+} and O^{2-} ions. Melting Al_2O_3 involves overcoming the **strong ionic bonding** in the lattice which requires a large amount of heat energy. **[1m]**

P_4O_{10} has a **simple molecular structure**. It consists of discrete molecules with **instantaneous dipole–induced dipole interactions** existing between the molecules. Melting P_4O_{10} involves overcoming these relatively **weak** intermolecular forces and requires less heat energy than in the case of melting Al_2O_3. Hence P_4O_{10} has a lower melting point than Al_2O_3. **[1m]**

SiO_2 has a **giant covalent structure** (or macromolecular structure) with each Si atom covalently bonded to four O atoms tetrahedrally. Melting SiO_2 involves breaking the **strong Si–O covalent bonds** and this requires more heat energy than in the case of melting Al_2O_3. Hence the melting point of SiO_2 is higher than that of Al_2O_3. **[1m]**

(e) (i) For Step I: $\mathbf{Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)}$

$$E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation} = +1.36 - (+1.07) =$$ **+0.29 V** **[1m]**

Since the $E^{\ominus}_{cell} > 0$, the oxidation of the Br^- ion by Cl_2 is a thermodynamically / energetically spontaneous process under standard conditions.

For Step II: $Br_2(aq) + SO_2(g) + 2H_2O(l) \rightarrow 2HBr(g) + H_2SO_4(g)$

$$E^{\ominus}_{cell} = E^{\ominus}_{reduction} - E^{\ominus}_{oxidation} = +1.07 - (+0.17) =$$ **+0.90 V** **[1m]**

Since the $E^{\ominus}_{cell} > 0$, the oxidation of SO_2 by Br_2 is a thermodynamically / energetically spontaneous process under standard conditions.

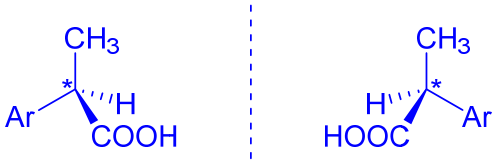
Both correct conclusions on energetically spontaneous reactions **[1m]**

(ii) SO_2 is a **bent** molecule, whereas Br_2 is a linear molecule **[1m]**. SO_2 is **polar** as it has a **net dipole moment**, whereas Br_2 is non-polar. **[1m]**

(iii) The sulfuric acid remains in the solution because it is significantly less volatile than bromine. This is so because it exists as an aqueous ionic mixture consisting of H^+, HSO_4^- and SO_4^{2-} ions solvated by water molecules (through **ion-dipole interactions**) **[1m]** and is hence not volatile.

2 (a) (i) A chiral carbon is an asymmetrical **carbon attached to four different substituents**. **[1m]**

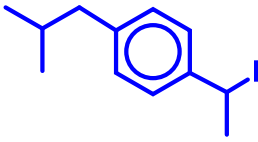
(ii)



[1m] for correct 3D configuration
[1m] for correct chiral carbon identification and pair of enantiomers

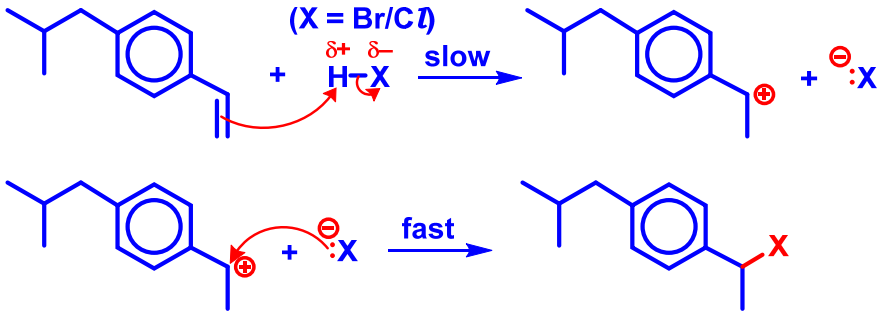
(iii) **Optical activity / Optical rotation** **[1m]** of the enantiomers can be used. Since the pair of enantiomers will **rotate plane-polarised light in different directions** **[1m]** this can be used to identify the pure enantiomer.

(iv)



[1m]

(v) Type of Reaction: **Electrophilic addition** **[1m]**



[1m] arrow pushing, balanced equation
[1m] partial charges, charges, carbocation intermediate

(vi) Step **II** – Reagent: **ethanolic KCN**
Condition: **heat with reflux**
[1m] for both reagent and conditions
Step **III** – Reagent: **dilute H_2SO_4**
Condition: **heat with reflux**
[1m] for both reagent and conditions

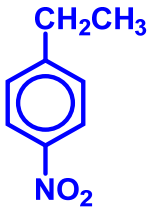
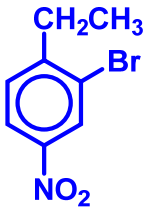
(b) (i) $\Delta G_r^{\ominus} = \Delta H_r^{\ominus} - T\Delta S_r^{\ominus}$

$$\Delta S_r^{\ominus} = \frac{\Delta H_r^{\ominus} - \Delta G_r^{\ominus}}{T} = \frac{+211-(+110)}{300}$$ **[1m] for correct equation and sub**

$= +0.3367 \text{ kJ mol}^{-1} \text{ K}^{-1} =$ **$+337 \text{ J mol}^{-1} \text{ K}^{-1}$** **[1m] for answer and units**

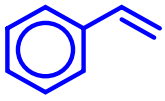
(ii) $\Delta G_r^{\ominus} = \Delta H_r^{\ominus} - T\Delta S_r^{\ominus} = +211-(900\times 0.3367) =$ **$-92.0 \text{ kJ mol}^{-1}$** **[1m]**

(iii) As the temperature of the reaction increases, **$\Delta G_r^{\ominus}$ becomes more negative**. Therefore, reaction becomes **more spontaneous**. **[1m]** This will hold true if **$\Delta H_r^{\ominus}$ and $\Delta S_r^{\ominus}$ remains constant/are unaffected by temperature change**. **[1m]**

(c) (i) Y is  ; Z is  **[1m] for each structure**

(ii) Ethylbenzene **cannot be oxidised to benzoic acid first** as the benzoic acid has a **3-directing COOH group**. **[1m]**

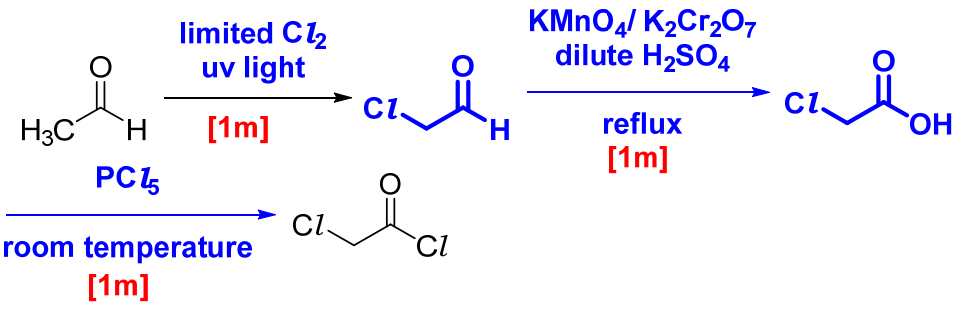
Starting with ethylbenzene which has a **2,4-directing ethyl group**, nitration will occur at the 4-position, forming **Y**. **[1m]** Subsequently, **Y** has a 2-directing ethyl group and a 3-directing NO_2 group, bromination will be direct to the 2-position relative to ethyl, to form **Z**.

3 (a) (i) (I)  **[1m]** (II)  **[1m]**

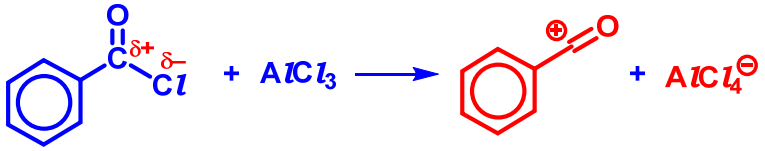
(ii) **Reagents and conditions:** Add aqueous iodine in sodium hydroxide to a solution of acetophenone and cyclohexanone separately. Heat the solution. **[1m]**

Observations: Pale yellow precipitate of triiodomethane (CHI_3) will be observed for acetophenone but not for cyclohexanone. **[1m]**

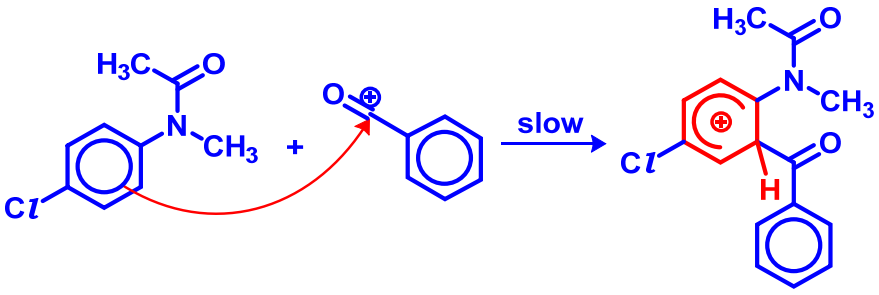
(b) (i)



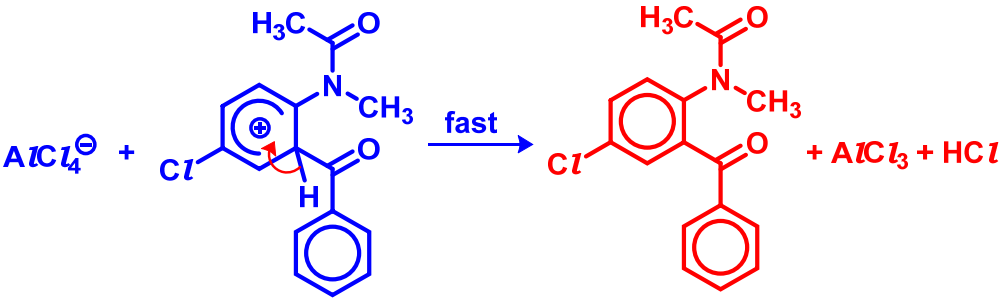
(ii) **Step 1:** Generation of electrophile



Step 2: Electrophilic attack

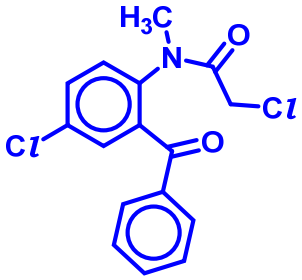


Step 3: $AlCl_4^-$ abstracts H^+ from arenium ion



[1m] curly arrows, charges and partial charges (for C–C*l* bond)
[1m] slow step; correct arenium intermediate and balanced equations

(iii)

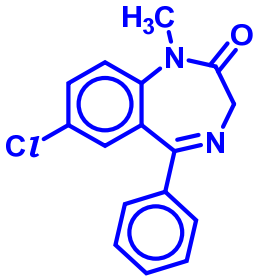


[1m]

W

Reagent for Step **V** : **Ethanolic NH_3 [1m]**

(iv)



[1m]

diazepam

(c) (i) A *ligand* is a neutral **molecule or an anion** which possesses **at least one lone pair of electrons** which can be used to form **dative bonds** with the central atom or ion. **[1m]**

(ii) The Pd^{2+} cation forms a complex with ethene, **decreasing the electron density** in the double bond of ethene, making the molecule prone to nucleophilic attack. **[1m]**

(iii) $CuCl_2(aq)$ contains the $[Cu(H_2O)_6]^{2+}$ ion. Cu^{2+} has a **d^9 configuration/partially unfilled d orbitals** so **electron transition between d orbitals** is possible. **(✓1)**
In an octahedral Cu(II) complex ion, the presence of **ligands causes the d orbitals to split into 2 (different) energy levels (✓2)**.
Energy gap/ΔE corresponds to the radiation in the visible light spectrum (✓3).
When radiation from the visible light spectrum is absorbed, **an electron transits from a d orbital of LOWER energy to a d orbital of HIGHER energy**. **(✓4)**
Hence, the **colour seen is the complement of the colours absorbed OR the colour seen is the colours that are not absorbed**. **(✓5)**
5(✓): [3m] ; 4–3(✓): [2m] ; 1–2(✓): [1m]

(d) (i) When $Cu(OH)_2$ is about to precipitate out, $IP(Cu(OH)_2) = K_{sp}(Cu(OH)_2)$

$[OH^-]$ at maximum separation $= \sqrt{\dfrac{2.20\times10^{-20}}{0.200}} = \underline{\mathbf{3.32\times10^{-10}\ mol\ dm^{-3}}}$ **[1m]**

(ii) $[Pd^{2+}]$ at maximum separation $= \dfrac{1.00\times10^{-31}}{\left(3.32\times10^{-10}\right)^2} = \underline{\mathbf{9.07\times10^{-13}\ mol\ dm^{-3}}}$ **[1m]**

$\%[Pd^{2+}]$ remaining $= \dfrac{9.07\times10^{-13}}{0.200}\times100\% = 4.54\times10^{-10}\% < 0.01\%$ **[1m]**

Therefore Pd^{2+} **<u>can</u>** be selectively precipitated from Cu^{2+}.

4 (a) (i) The pK_{a1} of peroxyethanoic acid, *y*, is **<u>larger</u>** **[1m]** than pK_{a1} of ethanoic acid. The negative charge on the oxygen of the peroxyethanoate ion is stabilised by the **<u>electron-withdrawing</u>** inductive effect of the **<u>neighbouring electronegative oxygen</u>**, while the negative charge on the oxygen of the ethanoate ion is much more stabilised by **<u>effective delocalisation over the C=O</u>**. Since the ethanoate ion is **<u>resonance stabilised</u>** and is more stable than the peroxyethanoate ion, ethanoic acid is more acidic than peroxyethanoic acid. **[1m]**

(ii) The pK_{a2} of malonic acid is higher because it is **<u>more difficult to remove an H^+ ion from an already negatively charged species than from a neutral ethanoic acid molecule</u>**. **[1m]**

(iii) Concentration of $H_2A = \dfrac{\dfrac{20.00}{1000}\times0.800}{\dfrac{25.00}{1000}} = \underline{\mathbf{0.640\ mol\ dm^{-3}}}$

(iv) Assumption: Since $K_{a1} >> K_{a2}$, it can be assumed that the H_3O^+ from the second dissociation is negligible and can be ignored, and all the H_3O^+ in the solution comes from the first dissociation. **[1m]**

$$K_{a1} = \frac{\left[H^+\right]^2}{\left[H_2A\right]-\left[H^+\right]} = 10^{-2.83}$$

$$\frac{\left[H^+\right]^2}{0.640-\left[H^+\right]} = 1.479\times10^{-3}$$

$$\frac{\left[H^+\right]^2}{0.640} \approx 1.479\times10^{-3}\left(\text{since } 0.640 ?\ \left[H^+\right]\right)$$

$$\left[H^+\right] = 0.03077\ \text{mol dm}^{-3}$$

$$\text{initial pH} = \underline{\mathbf{1.51}}\ \textbf{[1m]}$$

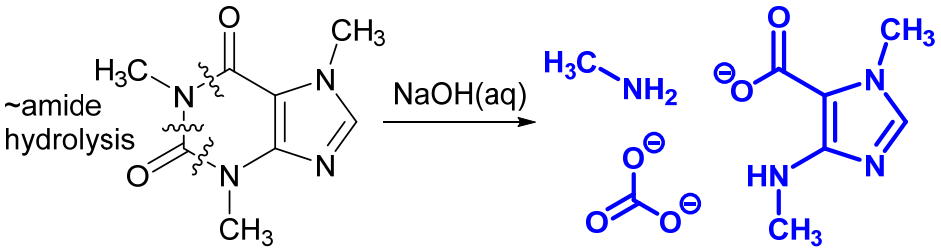
(v) **<u>Bromocresol green</u>** because the **<u>pH at equivalence point falls within the region of rapid pH change</u>**. **[1m]**

(vi) Since ethanoic acid has a larger pK_{a1} than malonic acid, its **<u>conjugate base has a higher K_b (or is a stronger base)</u>** than that of the monoanion of malonic acid. Hence, conjugate base of ethanoic acid hydrolyses to a greater extent, **<u>resulting in pH at equivalence point being higher</u>**. **[1m]**

(b) CH_3COCl **hydrolyses more readily** than CH_3CH_2Cl as the acyl carbon is **more electron-deficient** (or has a larger δ+ charge) compared to the α-carbon, as it is **bonded to another electronegative atom O** besides Cl **[1m]**, hence more susceptible to nucleophilic attack by water or HO^-.

In addition, the acyl carbon is **trigonal planar** (sp^2-hybridised) while the α-carbon is **tetrahedral** (sp^3-hybridised), hence CH_3COCl experiences **less steric hindrance** **[1m]** compared to CH_3CH_2Cl for approach of the nucleophile.

(c) (i)



[1m] for each structure

(ii) The **lone pair of electrons on N_1 is located in one of the sp^2-hybridised orbital which is perpendicular to the unhybridised p orbitals of the neighbouring sp^2-hybridised carbon atoms**, thus **this lone pair is not delocalised into the neighbouring C=C bond** and available for protonation. **[1m]**
On the other hand, the **lone pair of electrons on N_2 is located in the remaining unhybridised p orbital which is parallel to the unhybridised p orbitals of the neighbouring sp^2-hybridised carbon atoms**, thus **this lone pair is delocalised into the neighbouring C=C bonds** and unavailable for protonation. **[1m]**

(d) (i) $\mathbf{Zn(s) + 4OH^-(aq) \rightarrow Zn(OH)_4^{2-}(aq) + 2e^-}$ **[1m]**

(ii) From *Data Booklet*, cathode equation is

$$O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq) \qquad E^\ominus = +0.40\ V \text{ [1m]}$$

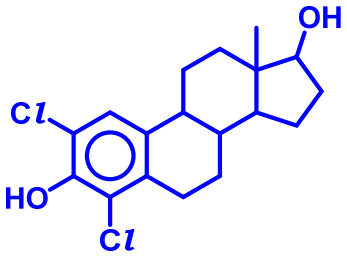
$$E^\ominus_{cell} = E^\ominus_{reduction} - E^\ominus_{oxidation} = E^\ominus\left(O_2|OH^-\right) - E^\ominus\left(Zn(OH)_4^{2-}|Zn\right)$$

$$+1.65 = +0.40 - E^\ominus\left(Zn(OH)_4^{2-}|Zn\right)$$

$$E^\ominus\left(Zn(OH)_4^{2-}|Zn\right) = +0.40 - (+1.65) = \underline{\mathbf{-1.25\ V}} \text{ [1m]}$$

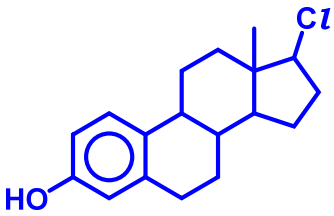
(iii) The use of pure air increases partial pressure of oxygen gas, thus equilibrium position of $O_2(g) + 2H_2O(l) + 4e^- \quad 4OH^-(aq)$ shifts to the **right** **[1m]**, causing cell **e.m.f. to increase** **[1m]** **(Since e.m.f. $= E^\ominus\left(O_2|OH^-\right) - E^\ominus\left(Zn(OH)_4^{2-}|Zn\right)$)**.

5 (a) (i)



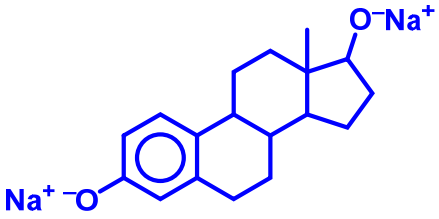
[1m]

(ii)



[1m]

(iii)



[1m]

(b) (i) **CH_3CHO**

Comparing **expt 1 & 2**,
when **concentration of CH_3CHO was increased 1.25 times**, keeping the concentration of CH_3OH constant, the **relative rate was 1.25 times the original value**.
Hence **order of reaction w.r.t. CH_3CHO is 1**. **[1m]**

$HOCH_2CH_2OH$

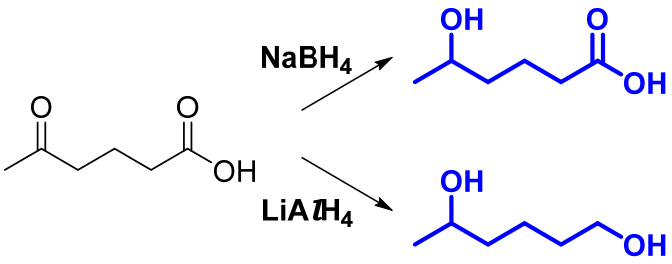
Comparing **expt 2 & 3**,
when **concentration of $HOCH_2CH_2OH$ was increased 1.6 times**, keeping the concentration of CH_3CHO constant, the **relative rate was 1.6 times the original value**.
Hence **order of reaction w.r.t. $HOCH_2CH_2OH$ is 1**. **[1m]**

(ii) **Rate = $k[CH_3CHO][HOCH_2CH_2OH]$ [1m]**
Units of k: **$mol^{-1}\ dm^3\ time^{-1}$** **[1m] units for time can be s, min, h**

(iii) rate = $k'[H^+]^n[CH_3CHO][HOCH_2CH_2OH]$, where n is the order of reaction w.r.t. H^+.
When $[H^+]$ doubles from 0.05 mol dm^{-3} to 0.10 mol dm^{-3},
relative rate doubles from that in expt 2.
Hence, order of reaction w.r.t. H^+ is 1.

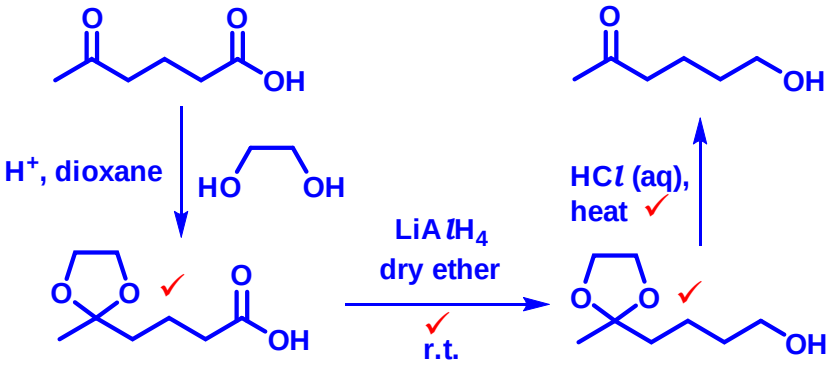
rate = $k'[H^+][CH_3CHO][HOCH_2CH_2OH]$
If $[H^+] = [CH_3CHO] = [HOCH_2CH_2OH] = 0.20$ mol dm^{-3}, compared to expt 1,
i.e. $[H^+]$ is 4× Expt 1, $[HOCH_2CH_2OH]$ is 2× Expt 1,
relative rate should be 8 times that of Expt 1,
i.e. **relative rate = 8** **[1m, accept 1 to 3 sf]**

(c) (i)



[1m] for both

(ii)



4✓ : [2m] ; 2–3✓ : [1m]

(d) (i) (Aliphatic) **Aldehyde**
Brick-red ppt of Cu_2O formed **[1m] for both**

(ii) **Cu^{2+}** (Cu in oxidation state +2) in Fehling's solution is **reduced** by glucose to **Cu(I) oxide** (Cu in oxidation state +1). **[1m]**

(e) (i) **$2Cl^-(aq) \rightarrow Cl_2(g) + 2e^-$ [1m] including state symbols**

(ii) $Cu^{2+}(aq) + 2e^- \rightarrow Cu(s)$

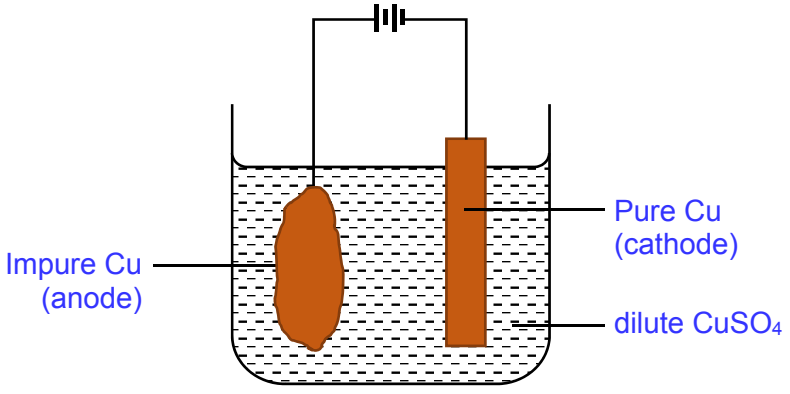
Assuming 100% efficiency,

$$n_{Cu}\text{ expected} = \frac{q}{n \times F} = \frac{I \times t}{n \times F} = \frac{0.25 \times (2 \times 60 \times 60)}{2 \times 96500}\ \textbf{[1m]} = 9.326 \times 10^{-3}\ \text{mol}$$

$$n_{Cu}\text{ deposited} = \frac{0.496}{63.5} = 7.811 \times 10^{-3}\ \text{mol}$$

$$\text{Percentage efficiency} = \frac{7.811 \times 10^{-3}}{9.326 \times 10^{-3}} \times 100\% = 83.76\% \approx \underline{\textbf{83.8\%}}\ \textbf{[1m]}$$

(f)



[1m]

$Ag^+ + e^- \quad Ag \qquad E^{\ominus} = +0.80\ V$
$Cu^{2+} + 2e^- \quad Cu \qquad E^{\ominus} = +0.34\ V$

Since the $\boldsymbol{E^{\ominus}\left(Cu^{2+}|Cu\right)}$ **is less positive**, Cu is preferentially oxidised at the anode.

Thus **Ag impurities will not be oxidised** **[1m]** and they fall to the bottom as 'sludge'.

$Cr^{3+} + 2e^- \quad Cr \qquad E^{\ominus} = -0.74\ V$
$Cu^{2+} + 2e^- \quad Cu \qquad E^{\ominus} = +0.34\ V$ **[1m] for quoting all 3 $E^{\ominus}$ values**

Since the $E^{\ominus}\left(Cr^{3+}|Cr\right)$ is less positive, Cr is preferentially oxidised at the anode and goes into the solution (as Cr^{3+} ions) first, followed by Cu. At the cathode, however, since the **$E^{\ominus}\left(Cu^{2+}|Cu\right)$ is more positive, Cu^{2+} is preferentially reduced** and deposited on the pure Cu rod. **Cr^{3+} ions remain in the electrolyte [1m]** and are not plated onto the cathode.