

CHEMISTRY

9647/01

Paper 1 Multiple Choice

19th September 2016
1 hour

Additional materials: Multiple Choice Answer Sheet
Data Booklet

READ THESE INSTRUCTIONS FIRST

Write in soft pencil.

Do not use staples, paper clips, glue or correction fluid.

1. Enter your **NAME** (as in **NRIC**). _____
2. Enter the **SUBJECT TITLE**. _____
3. Enter the **TEST NAME**. _____
4. Enter the **CLASS**. _____

Write your **name**
and **Civics Group**

Write and shade
your **CG number**
followed by
last 3 digits of **NRIC**

WRITE	SHADE APPROPRIATE BOXES									
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There are **forty** questions on this paper. Answer **all** questions. For each question there are four possible answers **A**, **B**, **C** and **D**.

Choose the **one** you consider correct and record your choice in **soft pencil** on the separate Answer Sheet.

Read the instructions on the Answer Sheet very carefully.

Each correct answer will score one mark. A mark will not be deducted for a wrong answer.

Any rough working should be done in this booklet.

The use of an approved scientific calculator is expected, where appropriate.

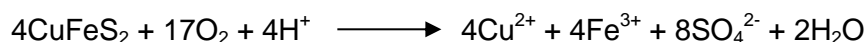
This document consists of **18** printed pages.

Section A

Part 1

For each question there are four possible answers, **A**, **B**, **C** and **D**. Choose the **one** you consider to be correct.

- 1 During the bacterial leaching of low grade copper ores, acidified water is sprayed onto the ore chalcopyrite, CuFeS_2 . Bacteria then convert the insoluble ore into a solution according to the equation shown below:



No change occurs in the oxidation state of copper.

What changes in oxidation state occur for the iron and the sulfur in this reaction?

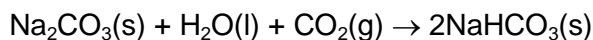
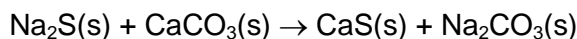
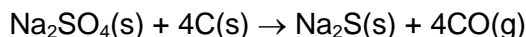
Change in oxidation state

	Fe	S
A	+1	+8
B	+1	-8
C	-1	+6
D	-1	-6

- 2 When cobalt metal is reacted with a solution containing cobalt(III) ions, only cobalt(II) ions are formed. How many moles of Co and $\text{Co}^{3+}(\text{aq})$ would result in a mixture containing both cobalt(II) and cobalt(III) ions in the mole ratio of 3:1 after the reaction had taken place?

	Moles of Co	Moles of Co^{3+}
A	1	2
B	1	3
C	1	5
D	2	3

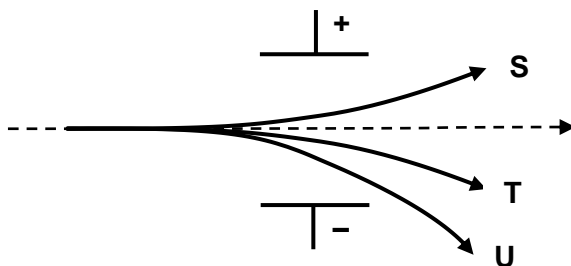
- 3 Sodium hydrogen carbonate, NaHCO_3 , can be prepared from sodium sulfate by a three-step process.



What is the mass of sodium hydrogen carbonate ($M_r = 84.0$), to the nearest kg, that could be formed from 100 kg of the sodium sulfate ($M_r = 142.1$), assuming a 90 % yield in each step?

- A** 43 **B** 86 **C** 106 **D** 118 kg

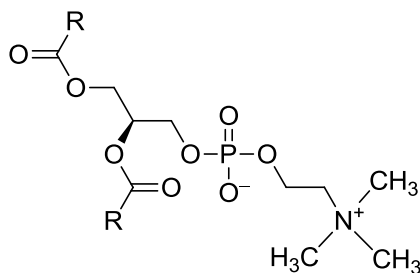
- 4 The following are flight paths of charged particles when accelerated in an electric field.



Which of the following correctly identifies **S**, **T** and **U**?

	S	T	U
A	$^{15}\text{O}^+$	$^{14}\text{C}^+$	$^{14}\text{N}^+$
B	$^{15}\text{O}^-$	$^{14}\text{C}^+$	$^{28}\text{Si}^+$
C	$^{14}\text{N}^-$	$^{16}\text{O}^{2+}$	$^{28}\text{Si}^{2+}$
D	$^{14}\text{N}^-$	$^{14}\text{C}^+$	$^{28}\text{Si}^{4+}$

- 5 Lecithin is used as an emulsifying and stabilising agent in the food, pharmaceutical and cosmetic industries.



lecithin

where R = long hydrophobic carbon chains

Which of the following statements about lecithin is correct?

- A** It can form van der Waals' forces with other non-polar molecules.
- B** It has a low boiling point.
- C** It cannot rotate plane of polarised light.
- D** It can form hydrogen bonds between its own molecules.
- 6 Mixtures of argon and another gas are commonly used during welding. One such gaseous mixture has a density of 1.82 g dm^{-3} at s.t.p.

What could be the other gas in this mixture? [Density of argon = 1.78 g dm^{-3} at s.t.p.]

- A** neon
- B** oxygen
- C** fluorine
- D** carbon dioxide

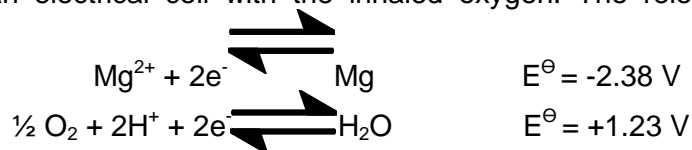
- 7 Which line in the table gives the signs of ΔH , ΔS and ΔG for the melting of ice at room temperature and pressure?

	ΔH	ΔS	ΔG
A	-	+	-
B	-	-	+
C	+	+	+
D	+	+	-

- 8 Which reaction represents standard enthalpy change at 298 K?

- A** $P_4(l) \rightarrow 4P(g)$
B $H_2(g) + Br_2(g) \rightarrow 2HBr(g)$
C $HF(aq) + NaOH(aq) \rightarrow NaF(aq) + H_2O(l)$
D $CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$

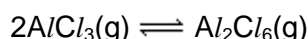
- 9 In the construction of heart 'pacemakers', it is possible to use a tiny magnesium electrode which creates an electrical cell with the inhaled oxygen. The relevant half-cells are as follows:



Under standard conditions, the cell e.m.f. would be +3.61 V, but in the body a potential of +3.25 V is more usual.

What is the best explanation for this lower e.m.f.?

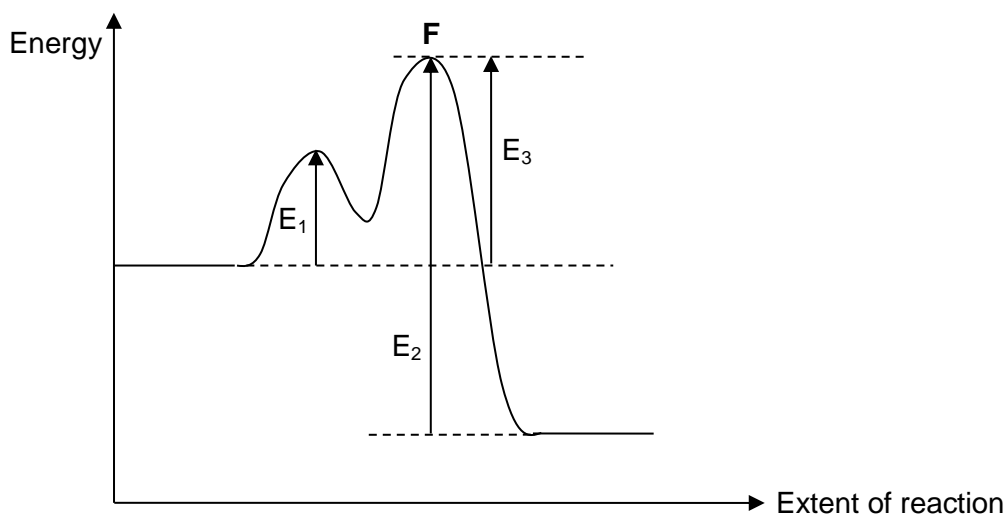
- A** the low concentration of Mg^{2+} ions surrounding the magnesium electrode
B the pH of between 7 and 8 of the body fluid surrounding the electrodes
C the high resistance of the body fluids surrounding the electrodes
D the small size of the magnesium electrode
- 10 Consider the following equilibrium system:



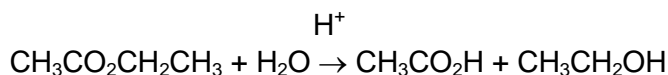
Which of the following statements will cause the position of the above equilibrium to shift to the left?

- A** decreasing the volume of the vessel
B increasing the temperature
C pumping inert gas into the vessel at constant volume
D pumping $AlCl_3$ gas into the vessel

- 11 Which of the following statements is true about the following energy profile for a catalysed reaction?



- A **F** is the intermediate formed.
 B The enthalpy change of the reaction is $E_2 - E_3$.
 C The reaction is catalysed by a heterogenous catalyst.
 D The second step of the reaction is the rate determining step.
- 12 Ethyl ethanoate undergoes a slow acid-catalysed hydrolysis in water where the concentration of acid in the solution remains constant.



The rate equation is found to be

$$\text{rate} = k[\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3][\text{H}^+]$$

In an experiment, when 1.0 mol dm^{-3} HCl was reacted with 0.10 mol dm^{-3} ethyl ethanoate, the half-life was found to be 42 min.

In a second experiment, 2.0 mol dm^{-3} HCl was reacted with 0.20 mol dm^{-3} ethyl ethanoate. What is the half-life of the second experiment?

- A 10.5 min B 21 min C 42 min D 63 min
- 13 Ethanol has a pK_a of 15.5 at room temperature. Sodium ethoxide can be produced by reacting ethanol with sodium metal, and Solution **P** is 0.1 mol dm^{-3} sodium ethoxide. Which of the following statements is **incorrect**?

- A Ethanol is a weak acid.
 B Ethoxide is a strong base.
 C The pH of Solution **P** is 13.
 D The type of reaction between ethanol and sodium is acid-base

17 Which property of the Group II elements (magnesium to barium) and their compounds increases with increasing proton number?

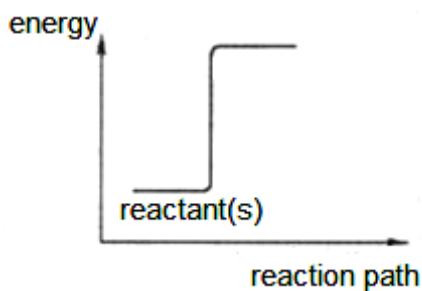
- A the magnitude of the enthalpy change of hydration of the metal ion
- B the solubility of the sulfate
- C the stability of the carbonate to heat
- D the tendency to form complex ions

18 Letters written on paper using aqueous ammonium thiocyanate are invisible until turned blood red by brushing the paper with aqueous iron(III) chloride. If the ammonium thiocyanate is first made alkaline, the letters turned orange brown and are less clear.

Which of the following substances, when formed on the paper in these reactions, best explains these observations?

	with aqueous ammonium thiocyanate	with alkaline aqueous ammonium thiocyanate
A	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$	$\text{Fe}(\text{OH})_3$
B	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
C	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	$\text{Fe}(\text{OH})_3$
D	$[\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+}$	$[\text{Fe}(\text{OH})_4]^-$

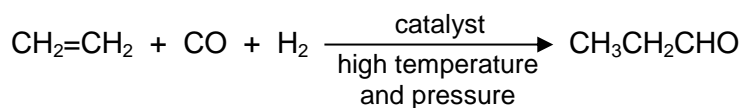
19 An energy profile diagram for a single reaction step is shown below.



To which of the following steps in the reaction of ethane with bromine in the presence of light does this diagram apply?

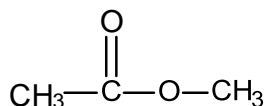
- A $\text{CH}_3\text{CH}_2\cdot + \text{CH}_3\text{CH}_2\cdot \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3$
- B $\text{CH}_3\text{CH}_2\cdot + \text{Br}_2 \rightarrow \text{CH}_3\text{CH}_2\text{Br} + \text{Br}\cdot$
- C $\text{CH}_3\text{CH}_2\cdot + \text{Br}\cdot \rightarrow \text{CH}_3\text{CH}_2\text{Br}$
- D $\text{Br}_2 \rightarrow \text{Br}\cdot + \text{Br}\cdot$

- 20 The oxo reaction is an important industrial process in which an alkene combines directly with carbon monoxide and hydrogen under suitable conditions. The reaction with ethene is shown below.

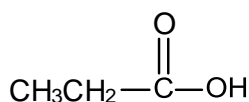


Which of the following structural formulae correctly represents the product of the oxo reaction starting with but-2-ene?

- A $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CHO}$
 B $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CHO}$
 C $\text{CH}_3\text{CH}_2\text{COCH}_2\text{CH}_3$
 D $(\text{CH}_3)_2\text{CHCH}_2\text{CHO}$
- 21 Compounds X and Y are isomers with the molecular formula $\text{C}_3\text{H}_6\text{O}_2$.



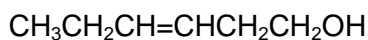
Compound X



Compound Y

Which reagent can be used to distinguish between X and Y?

- A sodium metal
 B 2,4-dinitrophenylhydrazine
 C aqueous alkaline iodine
 D aqueous sodium hydroxide
- 22 The compound hex-3-en-1-ol has a strong 'leafy' smell of newly cut grass and is used in perfumery.



hex-3-en-1-ol

What are the organic products when hex-3-en-1-ol is treated with hot acidic $\text{K}_2\text{Cr}_2\text{O}_7$, followed by hydrogen gas in the presence of platinum?

- A $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}$
 B $\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$ and $\text{HO}_2\text{CCH}_2\text{CO}_2\text{H}$
 C $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ and $\text{HOCH}_2\text{CH}_2\text{CH}_2\text{OH}$
 D $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$

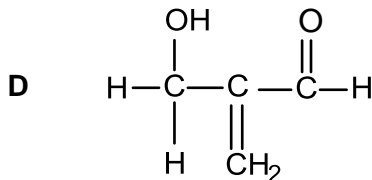
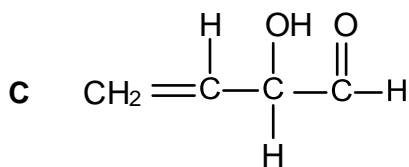
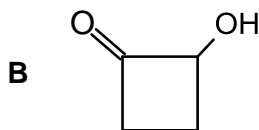
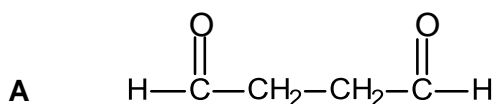
23 Which of the follow reaction produces an organic species that contains deuterium atom?

- A $\text{CH}_3\text{CH}_2\text{Br} \xrightarrow[\text{heat}]{\text{NaOD(aq)}}$
- B $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{heat}]{\text{MnO}_4^-, \text{NaOD(aq)}}$
- C $\text{CH}_3\text{CH}_2\text{OH} \xrightarrow[\text{heat}]{\text{conc D}_2\text{SO}_4}$
- D $\text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{OH} \xrightarrow[\text{heat}]{\text{conc D}_2\text{SO}_4}$

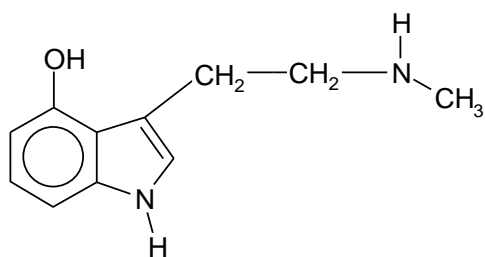
24 Compound Z, $\text{C}_4\text{H}_6\text{O}_2$, undergoes the following reactions.

- It gives a red precipitate with Fehling's solution.
- It gives white fumes with PCl_5 .
- Upon reaction with hydrogen gas and nickel catalyst, an optically active product is obtained.

What is compound Z?



- 25 Psilocin is the pharmacologically active agent in the body after ingestion of some species of psychedelic mushrooms.

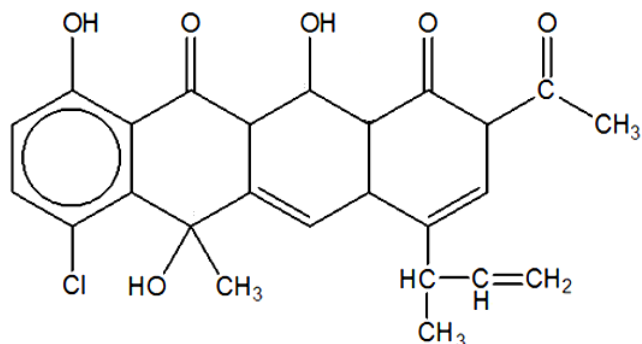


psilocin

Which σ bond formed by the following orbitals overlap is **not** present in psilocin?

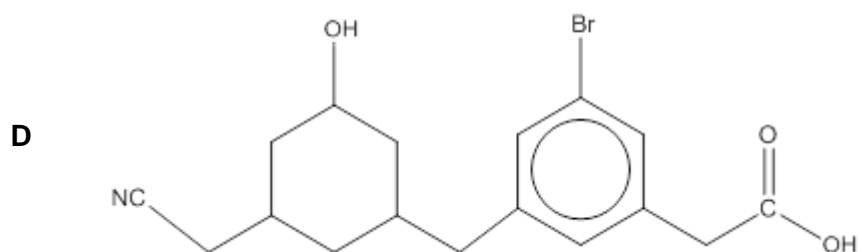
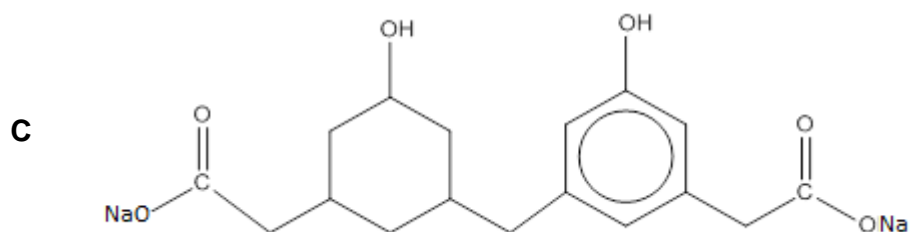
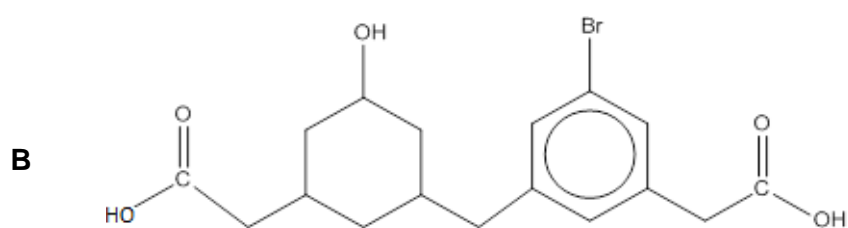
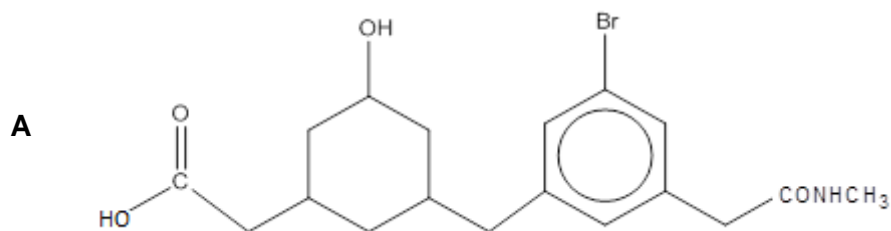
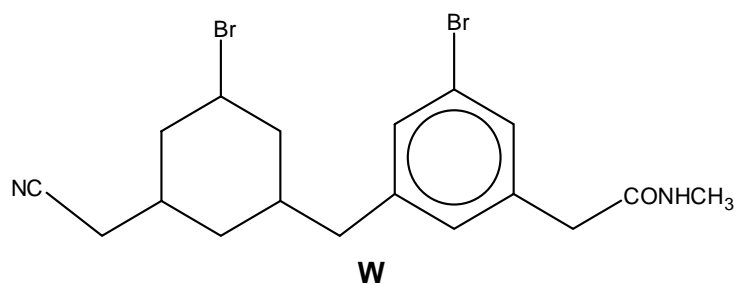
- A sp^3-sp^3 overlap between two C atoms
- B sp^2-sp^2 overlap between two C atoms
- C sp^3-sp^2 overlap between C and N atoms respectively
- D sp^3-sp^3 overlap between C and N atoms respectively

- 26 How many stereoisomers are possible for the following compound?

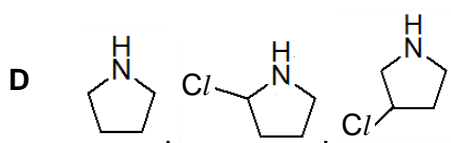
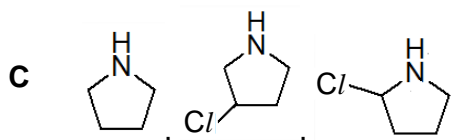
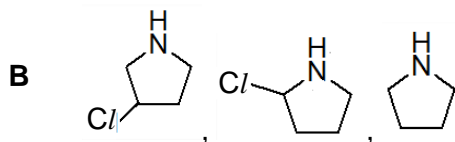
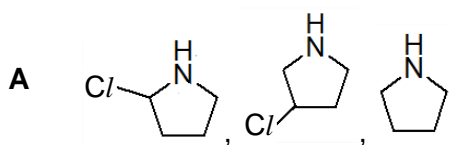


- A 2^3
- B 2^7
- C 2^8
- D 2^{10}

- 27 What is the structure of the compound formed when compound **W** was heated with aqueous sodium hydroxide, followed by acidification?



- 28 Which one of the following shows the given molecules arranged in order of decreasing pK_b values?



- 29 A polypeptide is subjected to hydrolysis.

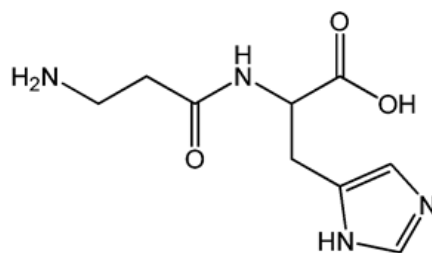
The following was found:

- The enzyme trypsin hydrolyses a peptide bond at the carboxylic end of arginine (arg) to give 2 tripeptides and gly
- The enzyme chymotrypsin hydrolyses a peptide bond at the carboxylic end of tyrosine (tyr) to give 2 dipeptides and a tripeptide
- The chemical cyanogen bromide cleaves the peptide bond at the carboxylic end of methionine (met) to give a tetrapeptide and a tripeptide

What is the primary structure of the polypeptide?

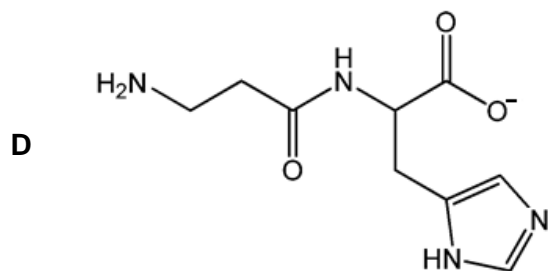
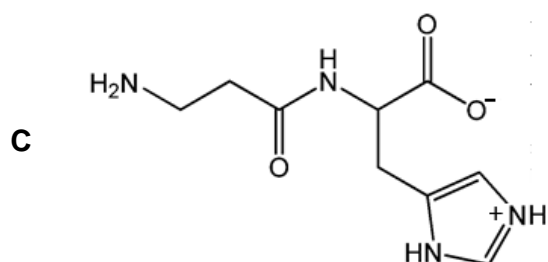
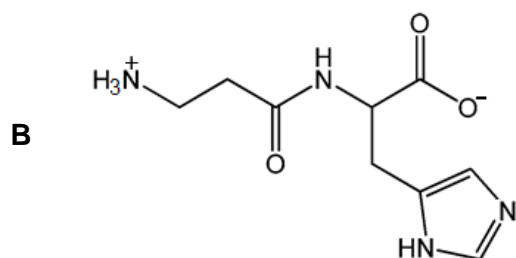
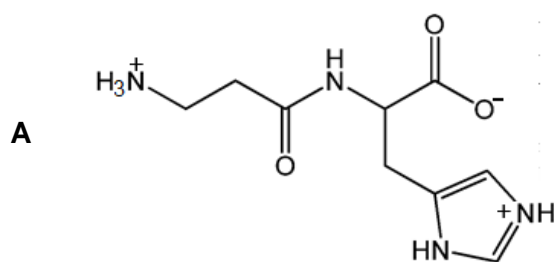
- A pro-tyr-arg-met-tyr-arg-gly
 B gly-arg-tyr-met-arg-tyr-pro
 C pro-tyr-arg-tyr-met-arg-gly
 D gly-arg-met-tyr-arg-tyr-pro

- 30 Carnosine is a dipeptide formed from β -alanine and histidine, and has been documented in recent research as having the ability to prevent many of the detrimental effects of aging.



carnosine

The isoelectric point of carnosine is 6.83. Which of the following is the predominant species present in an aqueous solution at physiological pH 7.4?



Part 2

For each of the questions in this section, one or more of the three numbered statements 1 to 3 may be correct.

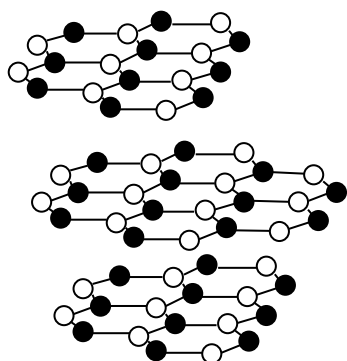
Decide whether each of the statements is or is not correct. (You may find it helpful to put a tick against the statements which you consider to be correct.)

The responses **A** to **D** should be selected on the basis of

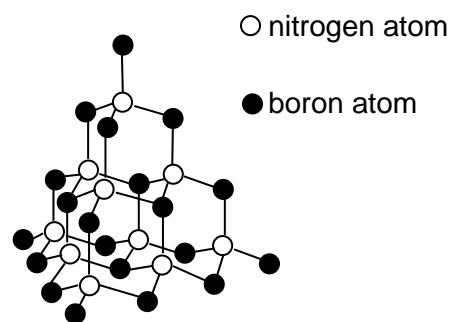
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 31 Boron nitride, BN, exists in two possible forms, hexagonal boron nitride and cubic boron nitride. The structure of hexagonal boron nitride and cubic boron nitride are similar to graphite and diamond respectively.



hexagonal boron nitride



cubic boron nitride

Which of the following statements are correct?

- There is dative bonding in cubic boron nitride.
 - The layers in hexagonal boron nitride are held together by van der Waals' forces.
 - The boron-nitrogen bond in cubic boron nitride is shorter than that in hexagonal boron nitride.
- 32 The standard enthalpy changes of combustion of carbon are as follows:

$$\text{C}(\text{graphite}) = -393.1 \text{ kJ mol}^{-1}$$

$$\text{C}(\text{diamond}) = -395.0 \text{ kJ mol}^{-1}$$

Which of the following deductions can be made from the data above?

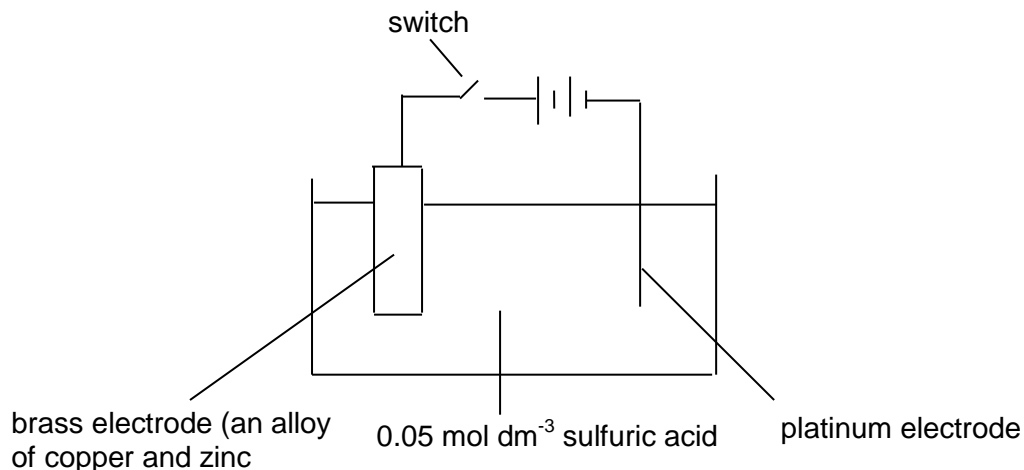
- Graphite is less stable than diamond.
- Graphite has a lower energy content than diamond.
- The conversion of diamond to graphite is exothermic.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

33 The circuit shown in the diagram was set up.

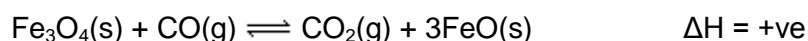


A steady current of 1.00 A was passes through the electrolyte for 10 minutes at room conditions.

Which statements regarding the electrolysis are correct?

- 1 Zinc dissolves preferentially at the anode.
- 2 Effervescence is observed at the cathode.
- 3 pH of the solution increases.

34 Consider the following equilibrium system:



Which of the following statements are correct?

- 1 Increasing the temperature causes the position of equilibrium to shift to the right.
- 2 The equilibrium constant, K_C , for this reaction has no units.
- 3 Adding FeO causes the position of equilibrium to shift to the left.

35 Which of the following shows a general decrease for Period 3 chlorides from MgCl_2 to PCl_5 ?

- 1 pH of the resulting solution when dissolve in water
- 2 maximum oxidation states of the elements in the chlorides
- 3 electrical conductivity in solid state

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

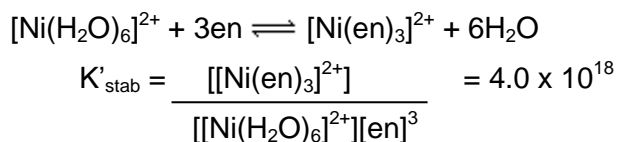
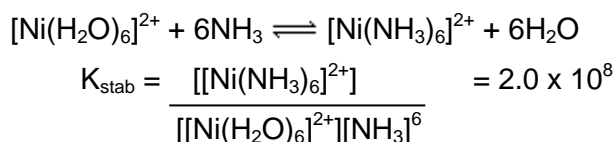
No other combination of statements is used as a correct response.

- 36** The following data refer to copper as a typical transition element and to calcium as an s-block element.

For which property are the data under the correct element?

	property	copper	calcium
1	density/g cm ⁻³	8.92	1.54
2	melting point/° C	1085	842
3	electrical conductivity/ relative units	9.6	85

- 37** Consider the following equilibria shown together with the magnitude of their respective equilibrium constants:



where en represents ethylenediamine, a bidentate ligand.

Which of the following statements are correct?

- Ammonia is a stronger ligand than water.
- Ethylenediamine is a stronger ligand than ammonia.
- The equilibrium constant, K''_{stab} , for the following reaction is equal to $K'_{\text{stab}} / K_{\text{stab}}$:

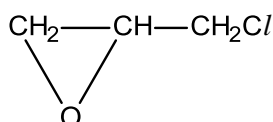
$$[\text{Ni}(\text{NH}_3)_6]^{2+} + 3\text{en} \rightleftharpoons [\text{Ni}(\text{en})_3]^{2+} + 6\text{NH}_3$$

The responses **A** to **D** should be selected on the basis of

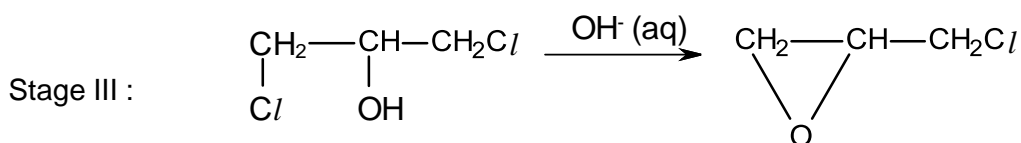
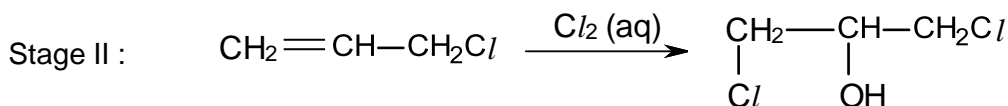
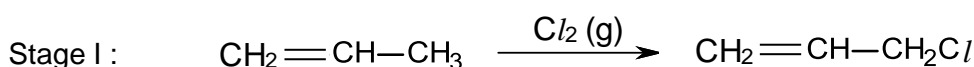
A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 38** Epoxy resins are polymers which are used in adhesives. One monomer used in their manufacture has the following structure:



This monomer is manufactured from propene in three stages:



Which statements are correct for the above synthesis?

- 1 Stage I involves free radical substitution.
- 2 Stage II involves electrophilic addition.
- 3 Stage III involves nucleophilic addition.

- 39** Ovalbumin is the predominant protein in egg white.

A perfect poached egg, with firm white surrounding a velvety yolk, can be made by the addition of vinegar into boiling water, before tipping the egg in and leaving it to cook for 1-2 minutes.

The addition of vinegar allows the egg white to coagulate faster around the yolk, instead of dispersing in the water. Which of the following explains this observation?

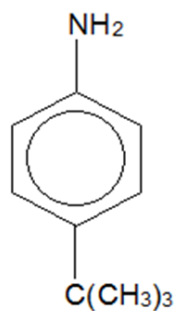
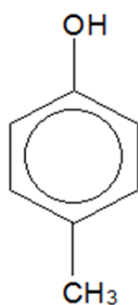
- 1 H^+ in vinegar denatures ovalbumin by protonating the R groups of amino acid residues.
- 2 H^+ in vinegar denatures ovalbumin by protonating the N atom of the peptide linkages.
- 3 H^+ in vinegar denatures ovalbumin by breaking it down to its constituent amino acids.

The responses **A** to **D** should be selected on the basis of

A	B	C	D
1, 2 and 3 are correct	1 and 2 only are correct	2 and 3 only are correct	1 only is correct

No other combination of statements is used as a correct response.

- 40** Which of the following reagents can be used to distinguish between the two compounds shown below?



- 1 aqueous bromine
- 2 acidified KMnO_4 , reflux
- 3 CH_3Br with heating, followed by the addition of AgNO_3

**2016 Preliminary Examination
H2 Chemistry MCQ Solution**

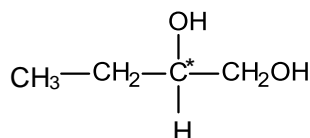
1	2	3	4	5	6	7	8	9	10
A	B	B	D	A	D	D	C	B	B
11	12	13	14	15	16	17	18	19	20
D	B	D	C	C	A	C	C	D	A
21	22	23	24	25	26	27	28	29	30
A	D	A	C	C	B	B	A	A	D
31	32	33	34	35	36	37	38	39	40
B	C	A	B	D	B	A	B	D	C

<p>16. A Observation 1: $\text{H}_2\text{SO}_4 + \text{Cl}^- \longrightarrow \text{HCl} + \text{HSO}_4^-$ HCl bubbled into Br^-, no visible reaction is observed and solution <u>remained colourless</u>. Observation 2: Addition of Ag^+ into solution containing Cl^- and $\text{NH}_3(\text{aq})$ gives a <u>colourless solution containing $[\text{Ag}(\text{NH}_3)_2]^+$</u> as AgCl is soluble in aq NH_3</p>	<p>17. C A: Charge of Group II metal ions is the same but the ionic radius increases down the group. Hence, with decreasing charge density, the magnitude of ΔH_{hyd} decreases down the group. B: Solubility of Group II sulfate decreases down the group. C: Down the group as the charge density of the metal ion decreases, its polarisation power decreases, thus there is less weakening of the C - O bond resulting in greater stability. D: Tendency to form complexes should be decreasing as the charge density of the metal ion decreases down the group.</p>
<p>18. C Blood red seen is due to the complex formed in the following reaction:</p> $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + \text{SCN}^- \rightleftharpoons \text{H}_2\text{O} + [\text{Fe}(\text{H}_2\text{O})_5(\text{SCN})]^{2+} \text{ Blood red}$ <p>In the presence of an alkali, red- brown precipitate of iron(III) hydroxide is formed as well thus diluting the blood red colour making the letters appear orange brown.</p> $[\text{Fe}(\text{H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightleftharpoons 3\text{H}_2\text{O} + [\text{Fe}(\text{OH})_3(\text{H}_2\text{O})_3](\text{s}) \text{ red-brown ppt}$	<p>19. D Energy level diagram indicates in the single reaction step, the reactant(s) undergo bond breaking only ie reactant(s) absorb energy. There is no bond formation taking place. Hence, true for option D only. In options A and C, bond formation only occurs. In option B, there is bond breaking followed by bond formation in the reaction.</p>
<p>20. A Oxo reaction:</p> $\text{CH}_2 = \text{CH}_2 + \text{CO} + \text{H}_2 \rightarrow \begin{array}{c} \text{CH}_2 - \text{CH}_2 \\ \quad \\ \text{H} \quad \text{C} = \text{O} \\ \\ \text{H} \end{array}$ <p>Similarly for but-2-ene,</p> $\text{CH}_3\text{CH} = \text{CHCH}_3 + \text{CO} + \text{H}_2 \rightarrow \begin{array}{c} \text{CH}_3\text{CH} - \text{CHCH}_3 \\ \quad \\ \text{H} \quad \text{C} = \text{O} \\ \\ \text{H} \end{array}$	<p>21. A 2,4-DNPH and $\text{I}_2/\text{NaOH}(\text{aq})$ doesn't react with X and Y. X is an ester, not a carbonyl compound. Y reacts with $\text{NaOH}(\text{aq})$, but it doesn't give observable result. Y reacts with Na to give effervescence of H_2.</p>
<p>22. D $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CH}_2\text{OH}$ $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+ \downarrow$ $\text{CH}_3\text{CH}_2\text{CH}=\text{CHCH}_2\text{CO}_2\text{H}$ which goes through hydrogenation to form $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$.</p>	<p>23. A Nucleophilic substitution gives $\text{CH}_3\text{CH}_2\text{OD}$. B) oxidation to give CH_3CO_2^- C) Elimination to give $\text{CH}_2=\text{CH}_2$ D) Condensation to give $\text{CH}_3\text{CO}_2\text{CH}_3$</p>

24. C

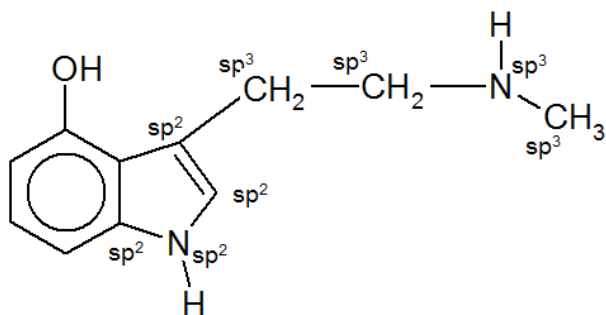
Z is an aldehyde and contains –OH group. Upon reduction by H_2 , **Z** forms a product that contains chiral carbon and no plane of symmetry.

- A) Does not contain –OH
 B) Is not an aldehyde
 C) Contains –OH and aldehyde. Product of reduction reaction is a chiral compound.



- D) Product from reduction $CH_2(OH)CH(CH_3)CH_2OH$ does not have chiral carbon.

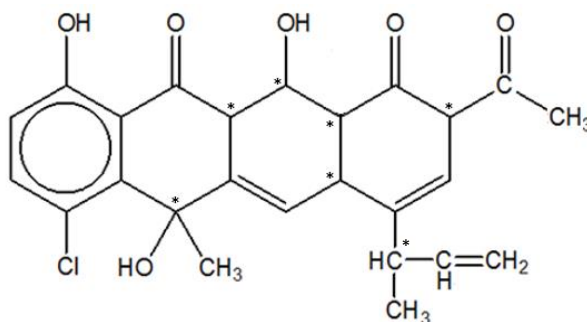
25. C



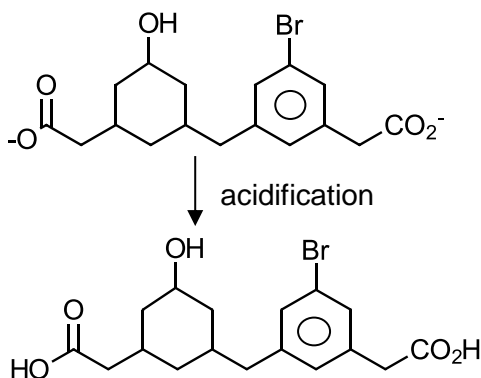
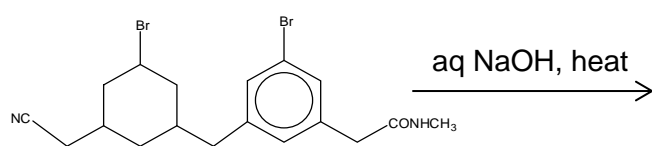
As shown in the diagram above, there is no sp^3 C atom overlapping with sp^2 N atom.

26. B

Maximum number of stereoisomers = $2^{n+m} = 2^{7+0}$
 There are 7 chiral carbons in compound. There isn't any C=C that can display cis-trans isomerism.

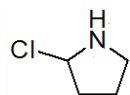


27. B



28. A

The lower the pK_b , the stronger the base. Hence, molecules should be arranged from weakest base to the strongest base.



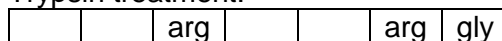
is the least basic due to the close proximity of the electron withdrawing Cl atom, which decreases the electron density on the N atom.



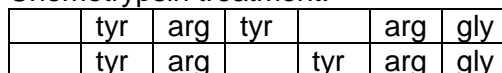
is the most basic due to the presence of two electron release groups, and the absence of any electron withdrawing groups.

29. A

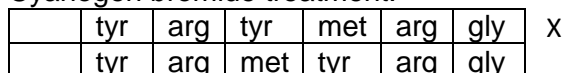
Trypsin treatment:



Chemotrypsin treatment:



Cyanogen bromide treatment:



Primary structure:

pro–tyr–arg–met–tyr–arg–gly

Note: A much faster way would be to analyse the options given, instead of solving in the forward direction.

30. D

General rules

Taking the neutral form of the dipeptide into account,

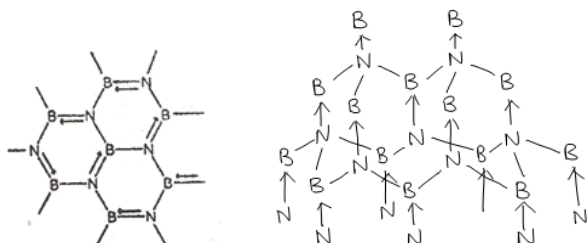
If $\text{pH} > \text{pI}$, $-\text{COOH}$ will be deprotonated, resulting in a negatively charged dipeptide

If $\text{pH} < \text{pI}$, $-\text{NH}_2$ will be protonated, resulting in a positively charged dipeptide

If $\text{pH} = \text{pI}$, the dipeptide is electrically neutral

$\text{pH } 7.4 > \text{pI}$ of carnosine ($\text{pI} = 6.83$) \rightarrow deprotonation

31. B

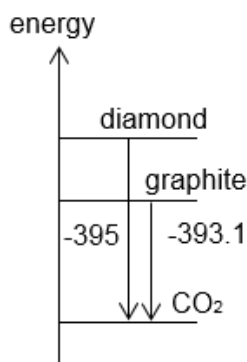


In the cubic structure, each B atom is bonded covalently to 4 N atoms in a tetrahedral manner, where one of the bonds is a dative bond (where N lone pair of electron is donated to B atom).

Like graphite, there are extensive van der Waals forces of attraction between the layers in hexagonal boron nitride.

Option 3 is incorrect. The boron-nitrogen bond in hexagonal boron nitride is shorter and stronger than that in cubic boron nitride, due to the pi bond present. Each B atom uses all its three valence electrons to form covalent bonds with three neighbouring nitrogen atoms. Each nitrogen atom still has a lone pair of electrons which it uses to form a dative pi-bond with an adjacent boron atom.

32. C



33. A

$E^\ominus_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ & $E^\ominus_{\text{Cu}^{2+}/\text{Cu}} = +0.34 \text{ V}$

For anode, oxidation: select E^\ominus that is more negative. Hence, Zn is preferentially discharged. 1 is correct.

For cathode, reduction: select E^\ominus that is more positive.

$E^\ominus_{\text{Zn}^{2+}/\text{Zn}} = -0.76 \text{ V}$ & $E^\ominus_{\text{H}^+/\text{H}_2} = +0.00 \text{ V}$

Hence, H_2 evolved.

$\text{H}^+(\text{aq}) + \text{e}^- \rightarrow \frac{1}{2}\text{H}_2(\text{g})$, effervescence observed. 2 is correct

$[\text{H}^+]$ decreases, pH of solution increases. 3 is correct.

34. B

Statement 1 is correct. Increasing the temperature favours the endothermic (forward) reaction, and by Le Chatelier's principle, the position of equilibrium will shift to the right.

Statement 2 is correct. Since $\text{Fe}_3\text{O}_4(\text{s})$ and $\text{FeO}(\text{s})$ are both in solid states, they are not part of the K_C expression. $K_C = [\text{CO}_2(\text{g})] / [\text{CO}(\text{g})]$ Therefore K_C has no units.

Statement 3 is not correct. Adding a solid reactant or product does not affect the position of equilibrium.

35. D

1. pH of aqueous solution of chlorides decreases from 6.5 (MgCl_2) to 1 (PCl_5).
2. maximum oxidation states of the elements in the chlorides increases from MgCl_2 to PCl_5 .
3. All are insulators in the solid state from MgCl_2 to PCl_5 .

36. B

Option 1: Due to its greater nuclear charge, Cu has a higher atomic mass and smaller atomic volume. Hence, its density is higher than Ca.

Option 2: Metallic bond for Cu is stronger since both 3d and 4s electrons are delocalised compared to the 4s electrons only for Ca. Hence, more energy is needed during melting accounting

	<p>for its higher m pt.</p> <p>Option 3: Electrical conductivity for Cu should be higher since it has a greater number of delocalised electrons (both 3d and 4s) to conduct electricity compared to the 4s electrons only for Ca.</p>
<p>37. A</p> <p>Statement 1 is correct. The magnitude of the equilibrium constant is large ($\gg 100$), which implies the position of equilibrium lies far to the right.</p> <p>Statement 2 is correct. Since K_2 is larger in magnitude than K_1, it implies that en has a higher tendency to replace the water ligands than ammonia.</p> <p>Statement 3 is correct.</p>	$K_{\text{stab}} = \frac{[[\text{Ni}(\text{NH}_3)_6]^{2+}]}{[[\text{Ni}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]^6}$ $K'_{\text{stab}} = \frac{[[\text{Ni}(\text{en})_3]^{2+}]}{[[\text{Ni}(\text{H}_2\text{O})_6]^{2+}][\text{en}]^3}$ $K''_{\text{stab}} = \frac{[[\text{Ni}(\text{en})_3]^{2+}][\text{NH}_3]^6}{[[\text{Ni}(\text{NH}_3)_6]^{2+}][\text{en}]^3}$ $= \frac{[[\text{Ni}(\text{en})_3]^{2+}]}{[[\text{Ni}(\text{H}_2\text{O})_6]^{2+}][\text{en}]^3} \times \frac{[[\text{Ni}(\text{H}_2\text{O})_6]^{2+}][\text{NH}_3]^6}{[[\text{Ni}(\text{NH}_3)_6]^{2+}]}$ $= K'_{\text{stab}} / K_{\text{stab}}$
<p>38. B</p> <p>Statements 1 and 2 are correct.</p> <p>Reactant in stage III is saturated, it cannot undergo addition reaction. Stage III is elimination.</p>	
<p>39. D</p> <p>Option 1 is correct. Protonation of R-groups of the residues in the tertiary structure disrupts existing ionic interactions and hydrogen bonds between them, which results in denaturation.</p> <p>Option 2 is incorrect. The amide functional group in the peptide linkages are neutral, and will not react with H^+</p> <p>Option 3 is incorrect. Primary structure is only affected during hydrolysis. Complete hydrolysis will only occur when ovalbumin is heated for a prolonged period of time under highly acidic conditions, e.g. $6 \text{ mol dm}^{-3} \text{ HCl}(\text{aq})$, heat for a few hours.</p>	<p>40. C</p> <p>Option 1 is incorrect. Both compounds react with aqueous bromine to give a white ppt.</p> <p>Option 2 is correct. The alkyl side chain on the benzene ring will undergo oxidation as long as there is a H atom present at the benzylic position. Purple acidified KMnO_4 will be decolourised.</p> <p>Option 3 is correct. The $-\text{NH}_2$ of the phenylamine will undergo nucleophilic substitution with CH_3Br. The Br^- leaving group will form a cream ppt with AgNO_3.</p>

PRELIMINARY EXAMINATIONS

HIGHER 2

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CHEMISTRY
9647/02

Paper 2 Structured Questions

29th August 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name 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.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use	
1	/ 12
2	/ 15
3	/ 12
4	/ 9
5	/ 24
Paper 1	/ 40
Paper 3	/ 80
Total	

This document consists of **21** printed pages.

Answer **all** the questions

1 Planning (P)

Potentiometric titration is a technique similar to direct titration of a redox reaction and can be used to determine the concentration of a reducing ion such as Fe^{2+} without the use of an indicator. It involves measurement of E_{cell} at intervals as an oxidising titrant is added. The titration is carried out on one side of a cell whose other half is a reference electrode which can be a standard hydrogen electrode or a calomel electrode.

Consider the titration of Fe^{2+} with standard Ce^{4+} , the course of which is monitored potentiometrically as shown in Figure 1 below. The reference electrode used is the calomel electrode shown in Figure 2.

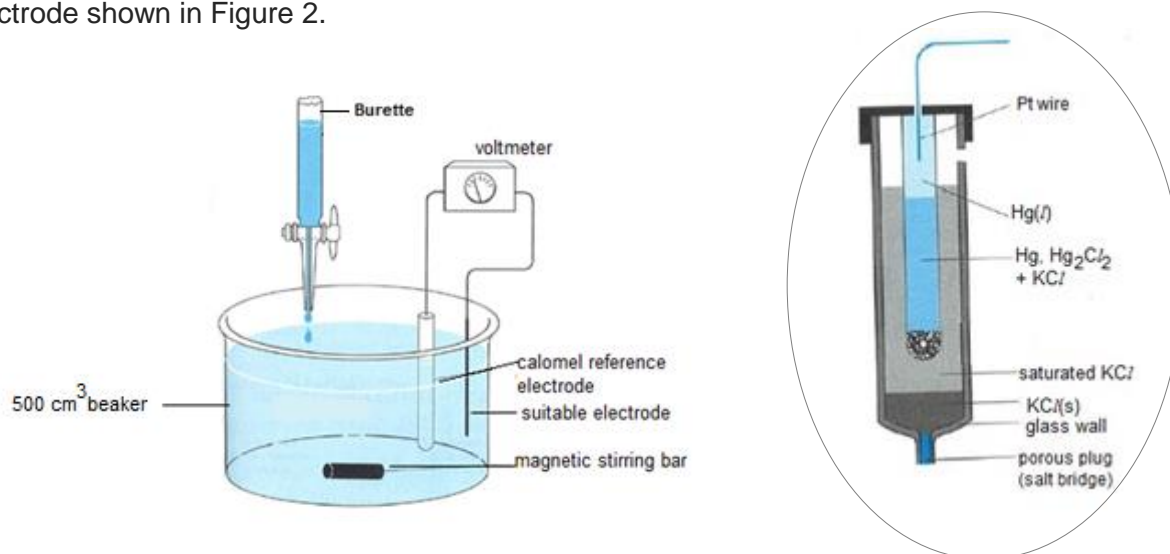
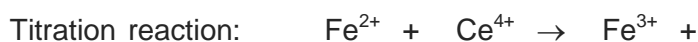


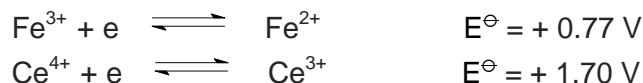
Figure 1: Set-up for potentiometric titration



To follow the course of the reaction, a pair of electrodes is inserted into the reaction mixture. At the calomel reference electrode,



At the suitable electrode, there are two reactions that will come to equilibrium:



As the Ce^{4+} titrant is added, Fe^{2+} is oxidised to Fe^{3+} and the cell potential is controlled by the ratio of reduced and oxidised iron according to the Nernst equation which causes the potential to rise as more iron becomes oxidised.

$$E_{\text{cell}} = \left\{ E^\ominus (\text{Fe}^{3+}/\text{Fe}^{2+}) - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - 0.24 \dots\dots\dots(1)$$

When the equivalence point is reached, the Fe^{2+} will have been totally consumed, and the

potential will then be controlled by the concentration ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$. Thus beyond the end-point the potential rises rapidly to that of a $\text{Ce}^{4+}/\text{Ce}^{3+}$ cell with excess Ce^{4+} .

$$E_{\text{cell}} = \left\{ E^{\ominus}(\text{Ce}^{4+}/\text{Ce}^{3+}) - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - 0.24 \dots\dots\dots(2)$$

A graph of E_{cell} against volume of titrant added can be drawn and the resulting titration curve looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

Solution **FA 1** was prepared by dissolving 0.960 g of 'iron tablets' in 100 cm^3 of 1 mol dm^{-3} HClO_4 acid. By titration method using KMnO_4 , the percentage of iron(II) ions in the iron tablets used to make **FA 1** was found to be 12.5%. A student wishes to verify the percentage of iron(II) ions present in **FA 1** by potentiometric titration using standard 0.100 mol dm^{-3} Ce^{4+} solution.

- (a) Suggest a suitable electrode for the potentiometric titration between Fe^{2+} and Ce^{4+} solution.

Suitable indicator electrode: _____

[1]

- (b) Perform a pre-calculation to estimate the end-point volume for the potentiometric titration of 100 cm^3 of **FA 1** with 0.100 mol dm^{-3} Ce^{4+} solution.

[1]

- (c) Using all the above information including the estimated end-point volume, you are required to write a plan to verify the percentage of Fe^{2+} present in **FA 1** by potentiometric titration.

You may assume that you are provided with the following:

- ◆ 100 cm³ of **FA 1** solution prepared by dissolving 0.960 g of 'iron tablets' in 1 mol dm⁻³ HClO₄ acid.
- ◆ 1.25 mol dm⁻³ Ce⁴⁺ solution
- ◆ a calomel reference electrode
- ◆ a suitable electrode
- ◆ a voltmeter
- ◆ the apparatus normally found in a school laboratory.

Your plan should include details of

- ◆ the preparation of 0.100 mol dm⁻³ Ce⁴⁺ solution
- ◆ how the electrochemical cell set-up in Figure 1 is assembled
- ◆ how you would recognize that the end-point has been reached
- ◆ a table for the recording of readings needed for the plotting of titration curve, showing suitable volumes of titrant added
- ◆ the calculation to verify the percentage of Fe²⁺ in **FA 1** in terms of the end-point volume, V_o cm³ of Ce⁴⁺

E_{cell} :

(ii) $[\text{Ce}^{3+}] = [\text{Ce}^{4+}]$

E_{cell} :

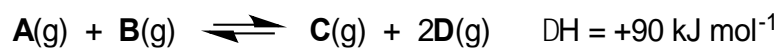
[1]

- (e) If the end-point volume is $V_0 \text{ cm}^3$ of Ce^{4+} , sketch the graph you would expect to obtain. Show clearly in your sketch, the titration volumes in terms of V_0 when you will be obtaining the E_{cell} values calculated in (d)(i) and (d)(ii).

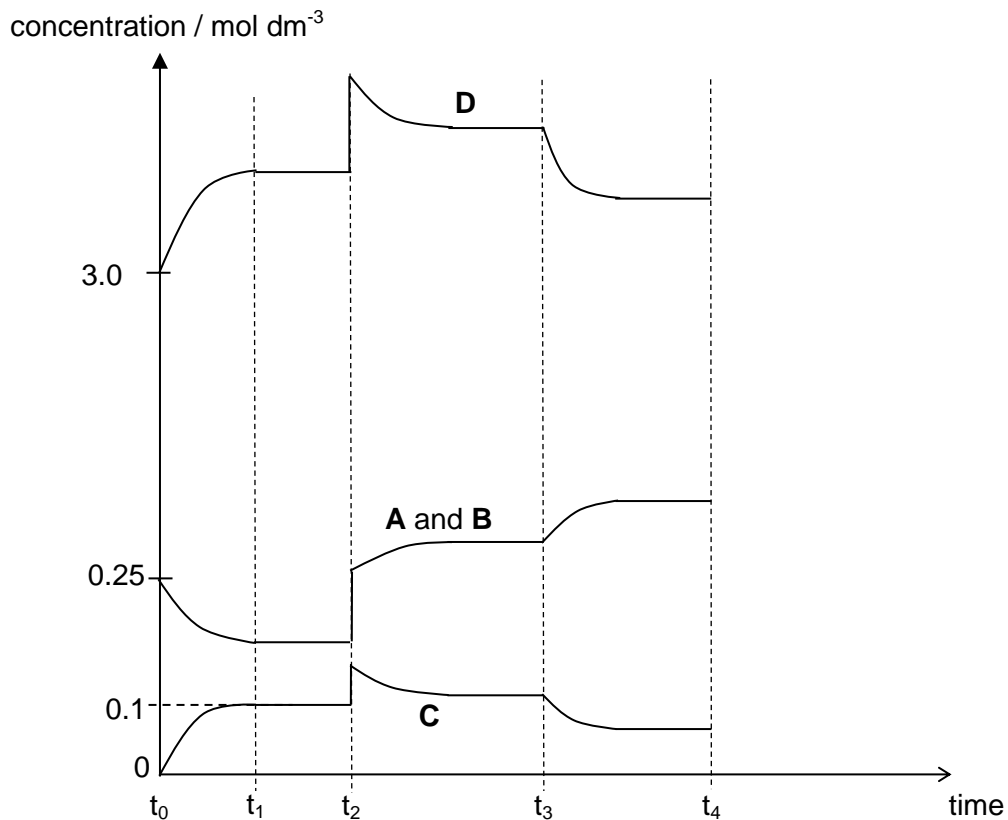
[3]

[Total:12]

- 2 Gases **A** and **B** react as shown in the equation given.



Gases **A**, **B** and **D** were injected into a vessel at 25 °C and allowed to reach dynamic equilibrium. The graph below (not drawn to scale) shows how the concentration of the four gases varies with time.



- (a) (i) Explain what is meant by *dynamic equilibrium*.

.....

.....

.....

.....

[1]

- (ii) Write an expression for K_c for this equilibrium, stating the units.

[1]

- (iii) Calculate the value for K_c at time, t_1 .

[2]

(b) (i) State *Le Chatelier's principle*.

.....

.....

.....

[1]

At time, t_2 , the volume of the system was reduced which lead to an increase in concentration of the gases. This causes the position of the equilibrium to shift.

(ii) Suggest and explain what happens to the system between time t_3 to t_4 .

.....

.....

.....

.....

.....

[2]

(iii) Sketch on the same axes how the concentration of the four gases will change when more gas **C** was introduced at time, t_4 .

[2]

(iv) State and explain the effect of the presence of a catalyst on the equilibrium

position and the value of the equilibrium constant.

[2]

- (c) The standard Gibbs free energy change of reaction, ΔG^\ominus in J mol^{-1} , is related to the equilibrium constant by the following equation.

$$\Delta G^\ominus = -RT \ln (0.02478K_c)$$

- (i) Using your answer in (a)(iii), calculate ΔG^\ominus in kJ mol^{-1} .

[1]

- (ii) Explain the significance of the sign of your answer in (c)(i).

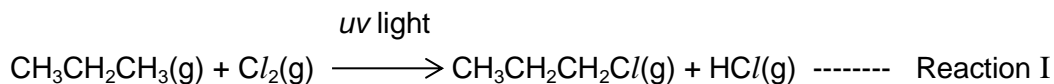
[1]

- (iii) Using your answer in (c)(i) and any other information on page 7, calculate ΔS^\ominus .

[2]

[Total: 15]

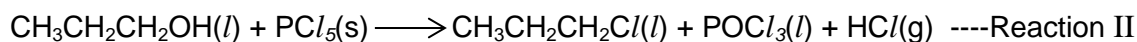
- 3 (a) 1-chloropropane can be synthesized by the following reaction at room temperature.



With reference to the *Data Booklet*, calculate ΔH_r^\ominus of Reaction I.

[1]

- (b) An alternate method of synthesis of 1-chloropropane is as follows:



- (i) Suggest one reason why Reaction II is a better method to produce 1-chloropropane than Reaction I.

.....

.....

.....

[1]

- (ii) Suggest whether the standard change in entropy of Reaction II is likely to be positive or negative, explaining your reasoning.

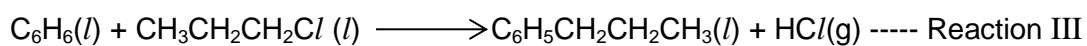
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[2]

(c) 1-chloropropane is an important reactant in the synthesis of propylbenzene:



(i) Define standard enthalpy change of formation.

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[1]

(ii) Using the data listed below,

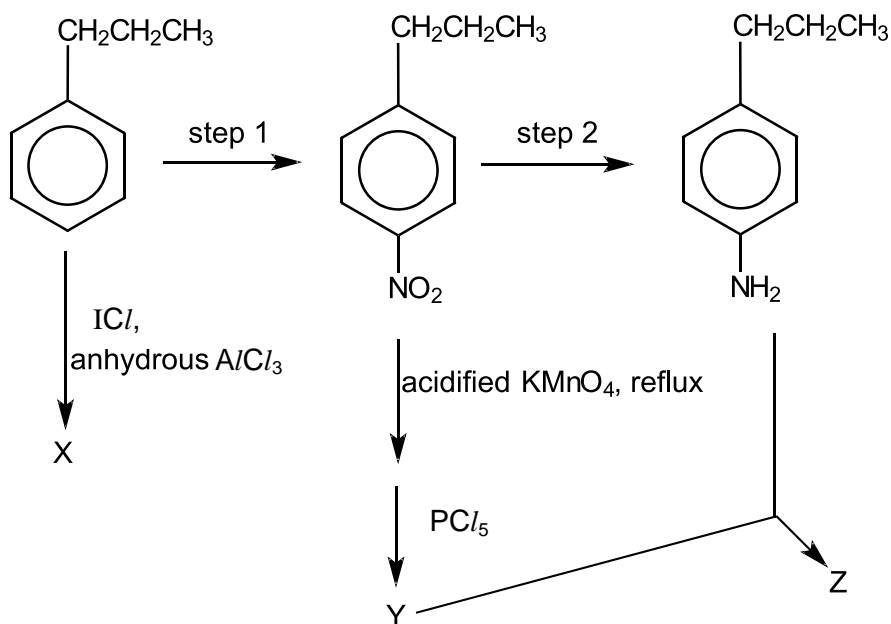
	$\Delta H_f^\ominus / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}(l)$	-161.3
$\text{HCl}(l)$	-167.2
$\text{C}_6\text{H}_6(l)$	+49.0
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3(l)$	-38.4

enthalpy change of vapourisation of HCl is $+74.9 \text{ kJ mol}^{-1}$

construct an energy cycle to calculate ΔH_r^\ominus of Reaction III.

[2]

- (d) Propylbenzene is a fuel additive and solvent. It undergoes the following chemical reactions.



- (i) State the reagents and conditions for the following steps:

Step 1 :

.....

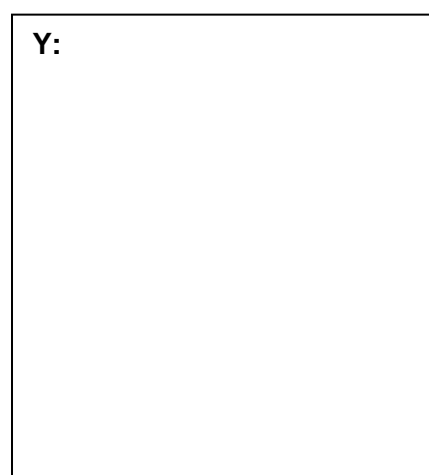
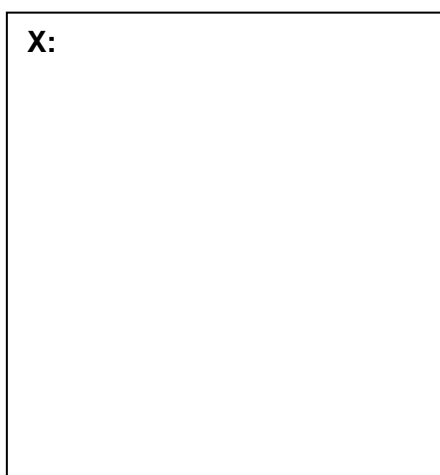
Step 2 :

.....

.....

[2]

- (ii) Draw the structural formula of the organic compounds **X**, **Y** and **Z**.



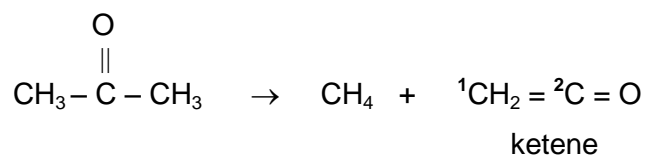
Z:



[3]

[Total:12]

- 4 When propanone vapour is passed over a heated filament, it breaks down into methane and a reactive substance called ketene.



- (a) (i) Draw the hybrid orbitals around each of the 2 carbon atoms, ${}^1\text{C}$ and ${}^2\text{C}$ in ketene molecule. State the type of hybridisation for each carbon atom.

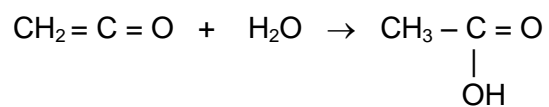
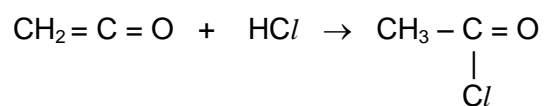
Carbon atom ${}^1\text{C}$	Carbon atom ${}^2\text{C}$
Hybridisation:	Hybridisation:

[2]

- (ii) Draw the displayed formula for the ketene molecule and on it show suggested values of the bond angles around ${}^1\text{C}$ and ${}^2\text{C}$ atoms.

[1]

Ketene is a highly reactive compound. It readily undergoes the reactions shown below.



- (b)** Name and describe the mechanism for the reaction between ketene and water, showing all charges and using curly arrows to show the movement of electron pairs.

[3]

- (c) Ketene reacts with ethanol to form a sweet smelling compound **P**, $C_4H_8O_2$, which reacts with $LiAlH_4$ to give **Q**. Identify **P** and **Q**. Name the type of reaction for the transformation of **P** to **Q**.

P	Q

Type of reaction from **P** to **Q**:

[3]

[Total: 9]

5 Ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, reacts with sodium hydroxide to form sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$. One of the main applications of ethanedioate ions is in rust-removal, as ethanedioate ions form water-soluble derivatives with iron(III) ions.

(a) An electrochemical cell is set up using Cu^{2+}/Cu and $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cells. The electrode in $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell is the negative electrode and the cell potential is +0.77 V.

(i) Using relevant data from the Data Booklet, determine the electrode potential of the $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell.

[2]

(ii) A small quantity of solid potassium iodide is added to the Cu^{2+}/Cu half-cell. Write an equation and state the observations for the reaction that will occur in this half-cell. Hence, predict and explain the effect on the e.m.f. of the electrochemical cell.

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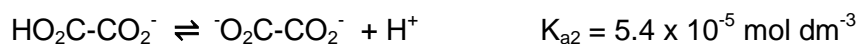
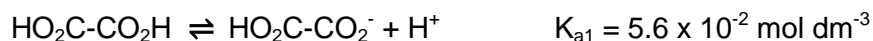
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[3]

- (b) The K_a values for the step-wise dissociation of ethanedioic acid are given below.



Calculate the pH of 0.10 mol dm^{-3} of sodium ethanedioate salt, $\text{Na}_2\text{C}_2\text{O}_4$.

[2]

- (c) Hydrated salt of magnesium ethanedioate has the formula $\text{MgC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. When 6.18 g of hydrated magnesium ethanedioate is heated strongly, a white solid **W** and three gases **X**, **Y** and **Z** are generated. Gases **X**, **Y** and **Z** are passed through anhydrous calcium chloride, followed by aqueous sodium hydroxide. The flasks containing anhydrous calcium chloride and aqueous sodium hydroxide had an increase in mass of 1.50 g and 1.83 g respectively. The residual gas **Z** occupied 1 dm^3 at room temperature and pressure. Gas **Z** is poisonous and can be heated with oxygen to give gas **Y**.

- (i) Suggest the identities of **W**, **X**, **Y** and **Z**.

W:

X:

Y:

Z:

[2]

- (ii) Hence, determine the value of n , showing your working clearly.

.....

[3]

- (iii) Ethanedioate ions form insoluble precipitates with many metal ions, one of which is calcium ethanedioate, a primary constituent of kidney stones.

Calcium ethanedioate decomposes in the same manner as magnesium ethanedioate. Using relevant data from the Data Booklet, deduce whether calcium ethanedioate would decompose at a higher or lower temperature than magnesium ethanedioate. Explain your reasoning.

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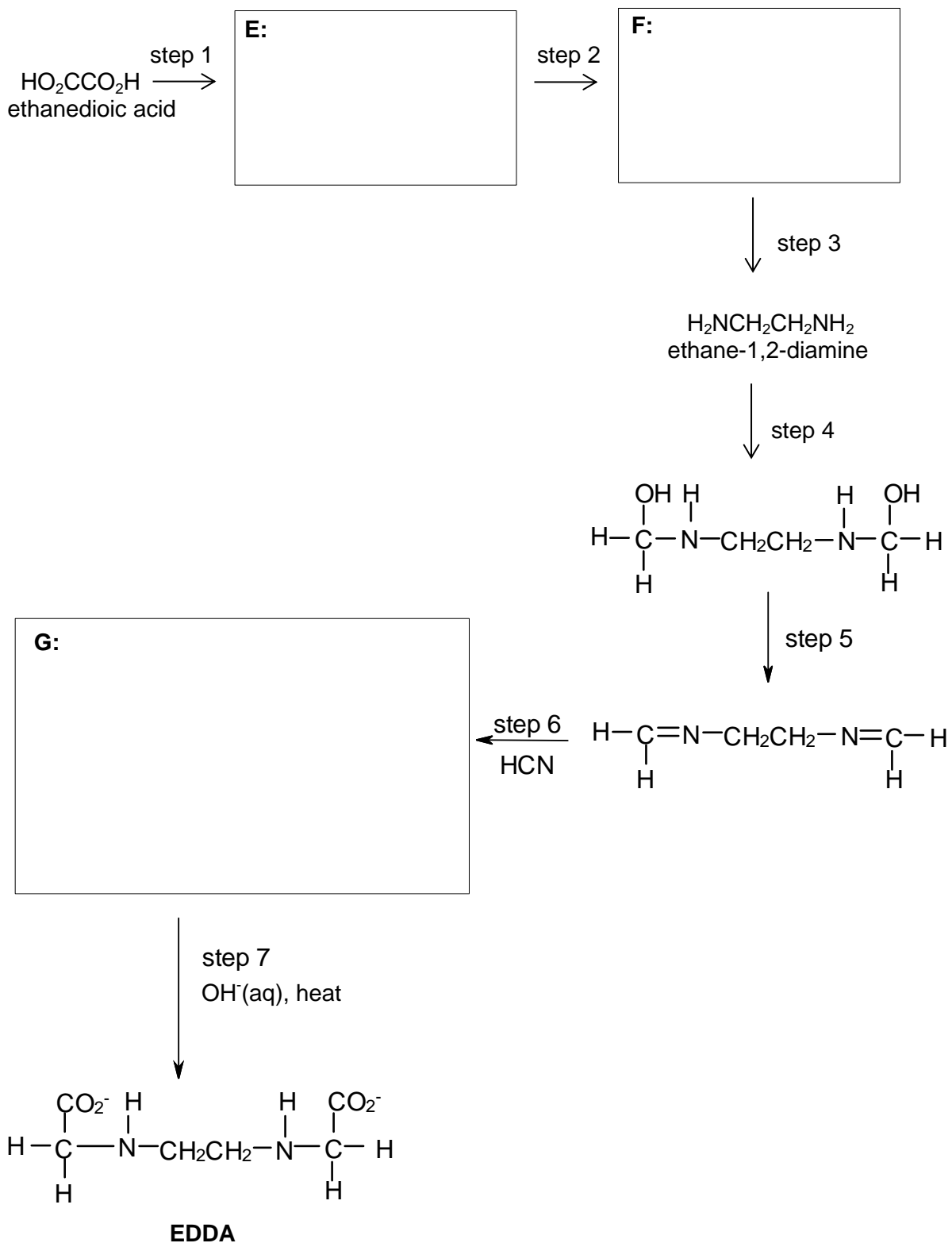
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[3]

- (d) A tetradentate ligand, ethylenediamine-N,N'-diacetate (EDDA) ion, can be synthesised from ethanedioic acid through a series of steps. Ethanedioic acid is first converted to ethane-1,2-diamine through a 3-step synthesis. Steps 4 to 7 represent the mechanism of Skrecker synthesis, which can be used to synthesise amino acids.



- (i) Propose the 3-step synthesis for the formation of ethane-1,2-diamine from ethanedioic acid, naming the reagents and conditions used in each step. Draw the structures of the intermediate compounds **E** and **F** in the spaces provided in the synthetic route.

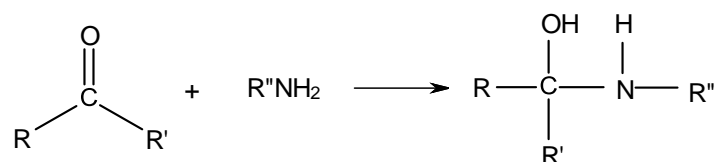
Step 1:

Step 2:

Step 3:

[5]

- (ii) Carbonyl compound and amine react in the following way.



Step 4 of the synthetic route in (d) involves the reaction of ethane-1,2-diamine with 2 moles of a carbonyl compound. Identify the carbonyl compound.

[1]

- (iii) Draw the structure of compound **G** in the space provided. [1]

- (iv) State the types of reaction in step 5 and step 7.

Step 5:

Step 7:

[2]

[Total: 24]

PRELIMINARY EXAMINATIONS

HIGHER 2

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CHEMISTRY
9647/02

Paper 2 Structured Questions

29th August 2016

2 hours

Candidates answer on the Question Paper.

Additional Materials: Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your Civics Group, centre number, index number and name 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.

Answer **all** questions.

The use of an approved scientific calculator is expected, where appropriate.

A Data Booklet is provided.

At the end of the examination, fasten all your work securely together.

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

For Examiner's Use	
1	/ 12
2	/ 15
3	/ 12
4	/ 9
5	/ 24
Paper 1	/ 40
Paper 3	/ 80
Total	

This document consists of **21** printed pages.

Answer **all** the questions

1 Planning (P)

Potentiometric titration is a technique similar to direct titration of a redox reaction and can be used to determine the concentration of a reducing ion such as Fe^{2+} without the use of an indicator. It involves measurement of E_{cell} at intervals as an oxidising titrant is added. The titration is carried out on one side of a cell whose other half is a reference electrode which can be a standard hydrogen electrode or a calomel electrode.

Consider the titration of Fe^{2+} with standard Ce^{4+} , the course of which is monitored potentiometrically as shown in Figure 1 below. The reference electrode used is the calomel electrode shown in Figure 2.

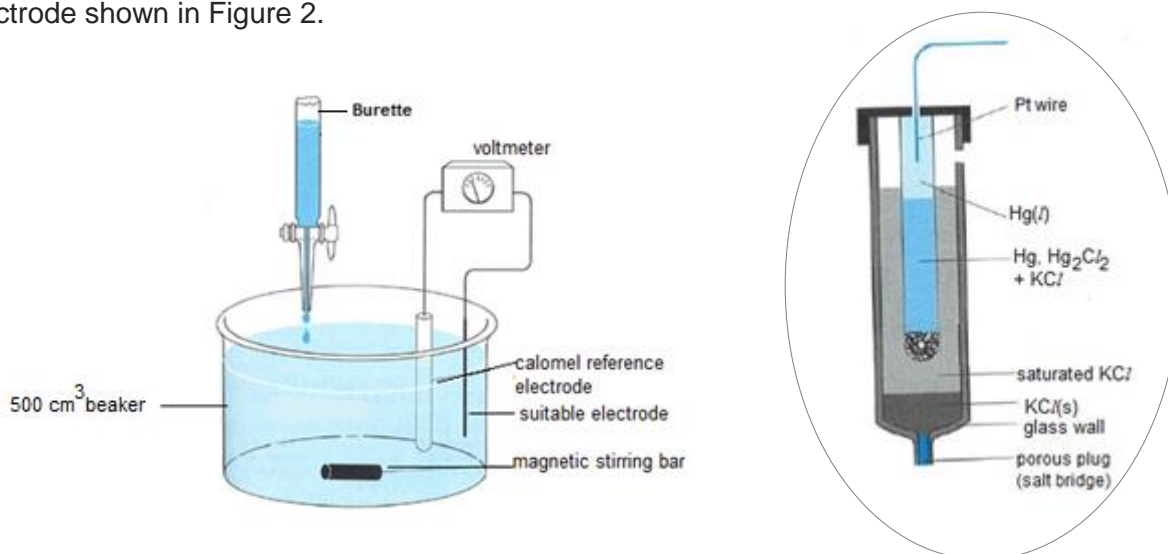
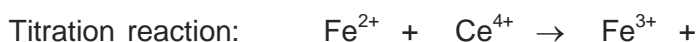


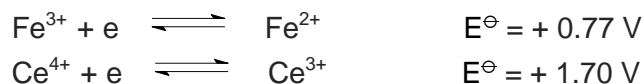
Figure 1: Set-up for potentiometric titration



To follow the course of the reaction, a pair of electrodes is inserted into the reaction mixture. At the calomel reference electrode,



At the suitable electrode, there are two reactions that will come to equilibrium:



As the Ce^{4+} titrant is added, Fe^{2+} is oxidised to Fe^{3+} and the cell potential is controlled by the ratio of reduced and oxidised iron according to the Nernst equation which causes the potential to rise as more iron becomes oxidised.

$$E_{\text{cell}} = \left\{ E^\ominus (\text{Fe}^{3+}/\text{Fe}^{2+}) - 0.05916 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \right\} - 0.24 \dots\dots\dots(1)$$

When the equivalence point is reached, the Fe^{2+} will have been totally consumed, and the

potential will then be controlled by the concentration ratio of $\text{Ce}^{3+}/\text{Ce}^{4+}$. Thus beyond the end-point the potential rises rapidly to that of a $\text{Ce}^{4+}/\text{Ce}^{3+}$ cell with excess Ce^{4+} .

$$E_{\text{cell}} = \left\{ E^{\ominus}(\text{Ce}^{4+}/\text{Ce}^{3+}) - 0.05916 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \right\} - 0.24 \dots\dots\dots(2)$$

A graph of E_{cell} against volume of titrant added can be drawn and the resulting titration curve looks much like the familiar acid-base titration curve. The end point is found not by measuring a particular cell voltage, but by finding what volume of titrant gives the steepest part of the curve.

Solution **FA 1** was prepared by dissolving 0.960 g of 'iron tablets' in 100 cm^3 of 1 mol dm^{-3} HClO_4 acid. By titration method using KMnO_4 , the percentage of iron(II) ions in the iron tablets used to make **FA 1** was found to be 12.5%. A student wishes to verify the percentage of iron(II) ions present in **FA 1** by potentiometric titration using standard 0.100 mol dm^{-3} Ce^{4+} solution.

- (a) Suggest a suitable electrode for the potentiometric titration between Fe^{2+} and Ce^{4+} solution.

Suitable indicator electrode: **Pt**
[1]

- (b) Perform a pre-calculation to estimate the end-point volume for the potentiometric titration of 100 cm^3 of **FA 1** with 0.100 mol dm^{-3} Ce^{4+} solution.

- No of moles of Fe^{2+} in 100 cm^3 of **FA 1** = $(0.125 \times 0.960) \div 55.8 = 0.00215 \text{ mol}$
 - Vol of Ce^{4+} required to reach the end-point = $(0.00215 \div 0.100) \text{ dm}^3 = 21.50 \text{ cm}^3$
- [1]

- (c) Using all the above information including the estimated end-point volume, you are required to write a plan to verify the percentage of Fe^{2+} present in **FA 1** by potentiometric titration.

You may assume that you are provided with the following:

- ◆ 100 cm^3 of **FA 1** solution prepared by dissolving 0.960 g of 'iron tablets' in 1 mol dm^{-3} HClO_4 acid.
- ◆ 1.25 mol dm^{-3} Ce^{4+} solution
- ◆ a calomel reference electrode
- ◆ a suitable electrode
- ◆ a voltmeter
- ◆ the apparatus normally found in a school laboratory.

Your plan should include details of

- ◆ the preparation of 0.100 mol dm^{-3} Ce^{4+} solution
- ◆ how the electrochemical cell set-up in Figure 1 is assembled

- ◆ how you would recognize that the end-point has been reached
- ◆ a table for the recording of readings needed for the plotting of titration curve, showing suitable volumes of titrant added
- ◆ the calculation to verify the percentage of Fe^{2+} in **FA 1** in terms of the end-point volume, $V_0 \text{ cm}^3$ of Ce^{4+}

Preparation of the standard $0.100 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution

1. Using a burette, transfer 20.00 cm^3 of $1.25 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution directly into a 250 cm^3 standard flask.
2. Make up to the mark with distilled water. Stopper and shake well to obtain a homogeneous solution.

1m – correct volume for dilution using burette/pipette for measurement.

1m - using a standard & logical procedure in the preparation

Procedure to record cell potential in the potentiometric titration

1. Transfer the given 100.0 cm^3 of FA 1 solution into a 500 ml beaker.
2. Fill a burette with the prepared $0.100 \text{ mol dm}^{-3} \text{Ce}^{4+}$ solution.
3. Assemble the apparatus as shown in Figure 1.
4. Titrate FA 1 solution with Ce^{4+} solution. Read and record the cell voltage registered on the voltmeter as each aliquot of Ce^{4+} solution is introduced from the burette. Carry out a more careful titration by adding titrant in small increments as the volume gets close to the equivalence point.
5. The end-point volume is reached when the E_{cell} value switches from cell potential based on $\text{Fe}^{3+}/\text{Fe}^{2+}$ to one based on $\text{Ce}^{4+}/\text{Ce}^{3+}$.

Table of readings

Volume of Ce^{4+} solution added / cm^3	$E_{\text{cell}} / \text{V}$
5.00	
10.00	
15.00	
17.00	
19.00	
21.00	
23.00	
25.00	
30.00	
35.00	
40.00	
45.00	

1m – Procedure on the assembly of set-up as in figure 1 and titrating carefully by adding titrant in small increments nearing the end-point

1m - how to recognize that the end-point had been passed

1m – table of readings with volume exceeding 21.50 cm^3 of Ce^{4+} solution

Calculation of % of Fe^{2+} in **FA 1** in terms of end-point volume, $V_0 \text{ cm}^3$ of Ce^{4+} solution

• No of moles of Ce^{4+} used = $0.100V_0 \div 1000 \text{ mol} = 10^{-4} V_0$

= no of moles of Fe^{2+} present in 100 cm^3 of FA 1

Mass of Fe^{2+} present in 0.960 g of iron tablets = $10^{-4} V_0 \times 55.8 = 5.58 \times 10^{-3} V_0 \text{ g}$

Hence % of Fe^{2+} in FA 1 = $(5.58 \times 10^{-3} V_0 \div 0.960) \times 100 = 0.581V_0 \%$

[6]

(d) Use the Nerst equation (1) and (2) to calculate the E_{cell} values when

(i) $[\text{Fe}^{3+}] = [\text{Fe}^{2+}]$ and

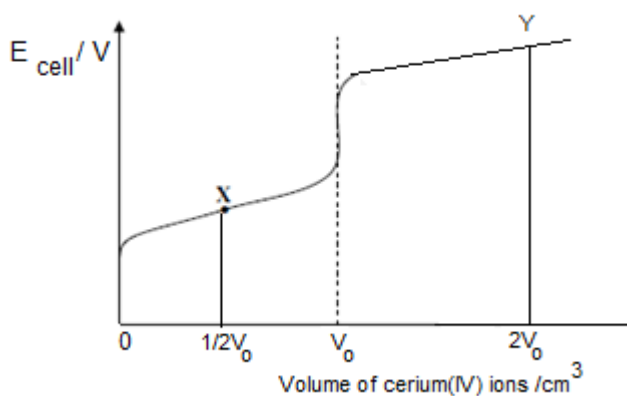
(ii) $[\text{Ce}^{3+}] = [\text{Ce}^{4+}]$.

(i) $E_{\text{cell}} = +0.53 \text{ V}$

(ii) $E_{\text{cell}} = +1.46 \text{ V}$

[1]

(e) If the end-point volume is $V_0 \text{ cm}^3$ of Ce^{4+} , sketch the graph you would expect to obtain. Show clearly in your sketch, the titration volumes in terms of V_0 when you will be obtaining the E_{cell} values calculated in (d)(i) and (d)(ii).

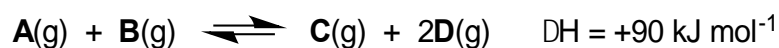


- Shape of titration with axes clearly labelled.
- E_{cell} at X = +0.53 V at $\frac{1}{2}V_0$ when $[\text{Fe}^{2+}] = [\text{Fe}^{3+}]$
- E_{cell} at Y = +1.46 V at $2V_0$ when $[\text{Ce}^{3+}] = [\text{Ce}^{4+}]$

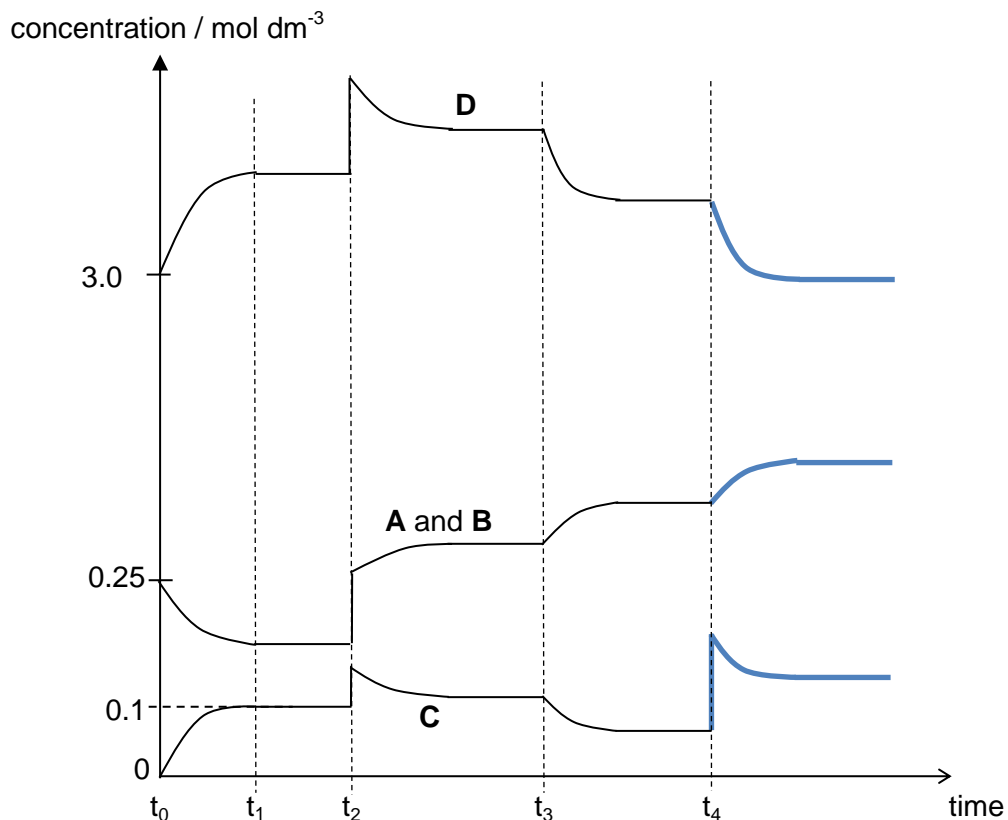
[3]

[Total:12]

2 Gases **A** and **B** react as shown in the equation given.



Gases **A**, **B** and **D** were injected into a vessel at 25 °C and allowed to reach dynamic equilibrium. The graph below (not drawn to scale) shows how the concentration of the four gases varies with time.



(a) (i) Explain what is meant by *dynamic equilibrium*.

- When a reversible reaction reaches a state of dynamic equilibrium, reaction continues to occur but the rates of the forward and backward reactions are equal such that there is no net change in the concentrations of the reactants and products.

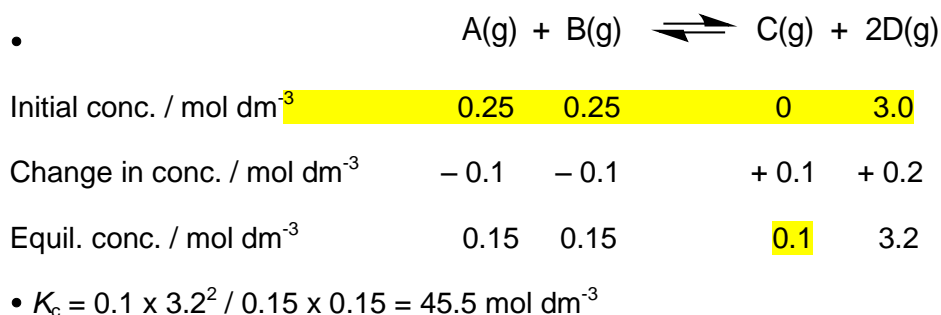
[1]

(ii) Write an expression for K_c for this equilibrium, stating the units.

- $K_c = \frac{[\text{C}][\text{D}]^2}{[\text{A}][\text{B}]} \text{ mol dm}^{-3}$

[1]

(iii) Calculate the value for K_c at time, t_1 .



[2]

(b) (i) State *Le Chatelier's principle*.

- If a system at dynamic equilibrium is subjected to a change which disturbs the equilibrium, the system will respond in such a way so as to counteract the effect of the change so as to re-establish the equilibrium.

[1]

At time, t_2 , the volume of the system was reduced which lead to an increase in concentration of the gases. This causes the position of the equilibrium to shift.

(ii) Suggest and explain what happens to the system between time t_3 to t_4 .

- Position of equilibrium shifts to the left as concentration of A and B increases gradually and concentration of C and D decreases gradually.
- Since the backward reaction is exothermic, hence the temperature of the system must have been decreased at time, t_3 .

[2]

(iii) Sketch on the same axes how the concentration of the four gases will change when more gas **C** was introduced at time, t_4 .

- Sharp increase in [C] followed by decrease in [C], decrease in [D] and increase in [A]&[B]
- Decrease in [D] is twice the increase in [A], [B] and [C]. Equilibrium [C] should not be lower than the initial [C] at t_4 .

[2]

(iv) State and explain the effect of the presence of a catalyst on the equilibrium position and the value of the equilibrium constant.

- A catalyst have no effect on the equilibrium position and the value of K_c .

- The presence of catalyst increases the rate of the forward and backward reaction to the same extent. ($K_C = k_f / k_b \Rightarrow K_c$ constant.)

[2]

- (c) The standard Gibbs free energy change of reaction, ΔG° in J mol^{-1} , is related to the equilibrium constant by the following equation.

$$\Delta G^\circ = -RT \ln (0.02478K_c)$$

- (i) Using your answer in (a)(iii), calculate ΔG° in kJ mol^{-1} .

$$\bullet \Delta G^\circ = \frac{-8.31 \times 298 \times \ln (0.02478 \times 45.5)}{1000} = -0.297 \text{ kJ mol}^{-1}$$

[1]

- (ii) Explain the significance of the sign of your answer in (c)(i).

- Since $\Delta G^\circ < 0$, the reaction is spontaneous at room temperature.

[1]

- (iii) Using your answer in (c)(i) and any other information on page 7, calculate ΔS° .

$$\bullet \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

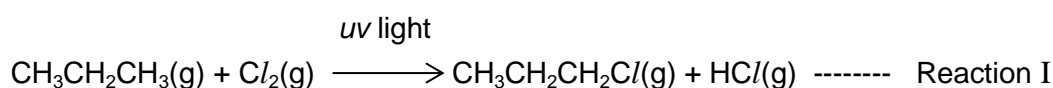
$$\bullet \Delta S^\circ = [90 - (-0.297)] / 298 = +303 \text{ J mol}^{-1} \text{ K}^{-1}$$

Note: sign must be shown

[2]

[Total: 15]

- 3 (a) 1- chloropropane can be synthesized by the following reaction at room temperature.



With reference to the *Data Booklet*, calculate ΔH_r° of Reaction I.

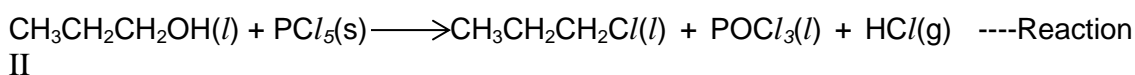
Bonds broken: 1 C-H bond, 1 Cl-Cl bond

Bonds formed: 1 C-Cl bond, 1 H-Cl bond

$$\bullet \Delta H_r^\circ = +(410+244) - (340+431) \\ = -117 \text{ kJ mol}^{-1}$$

[1]

- (b) An alternate method of synthesis of 1-chloropropane is as follows:



- (i) Suggest one reason why Reaction II is a better method to produce 1-chloropropane than Reaction I.

• **Reaction I can undergo further free-radical substitution to give a mixture of halogenoalkanes thus the yield is much lower compared to Reaction II.**

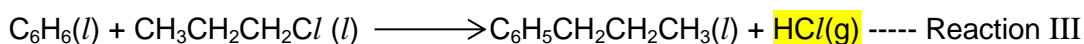
[1]

- (ii) Suggest whether the standard change in entropy of Reaction II is likely to be positive or negative, explaining your reasoning.

• **ΔS° is likely to be positive.**
 • **This is because in the reaction, gaseous molecules are formed & highly disordered. There are more ways to arrange the molecules and distribute the energy.**

[2]

- (c) 1-chloropropane is an important reactant in the synthesis of propylbenzene:



- (i) Define standard enthalpy change of formation.

The **standard enthalpy change of formation** of a substance, ΔH_f° , is the enthalpy change when **one mole** of the substance is formed from **its constituent elements in their standard states at 298 K and 1 atm.**

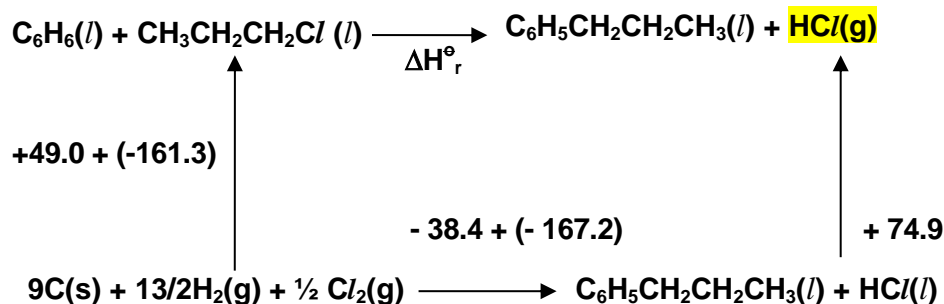
[1]

- (ii) Using the data listed below,

	$\Delta H_f^\circ / \text{kJ mol}^{-1}$
$\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}(l)$	-161.3
$\text{HCl}(l)$	-167.2
$\text{C}_6\text{H}_6(l)$	+49.0
$\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{CH}_3(l)$	-38.4

enthalpy change of vapourisation of HCl is +74.9 kJ mol⁻¹

construct an energy cycle to calculate ΔH_r° of Reaction III.

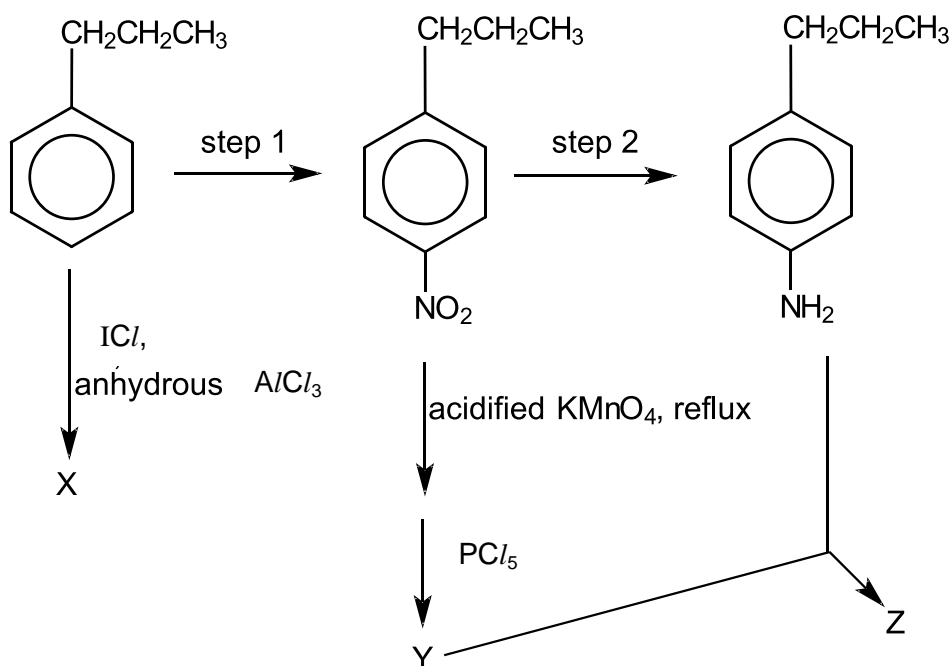


- correct energy cycle (state symbols and coefficients)

$$\left. \begin{array}{l} \bullet \\ \bullet \end{array} \right\} \text{By Hess' Law, } +49.0 + (-161.3) + \Delta H_r^\circ = -38.4 + (-167.2) + 74.9 \\
 \Delta H_r^\circ = -18.4 \text{ kJ mol}^{-1}$$

[2]

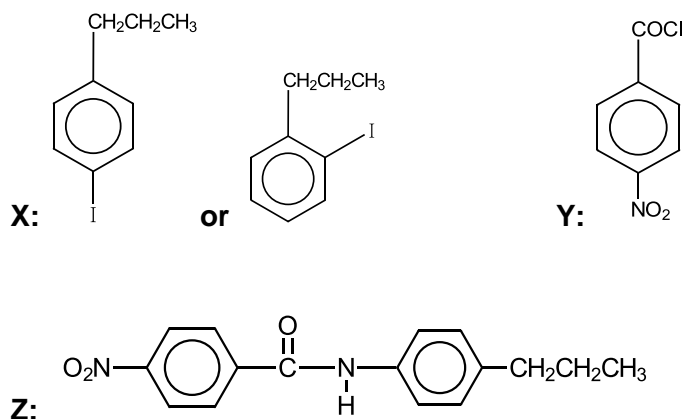
- (d) Propylbenzene is a fuel additive and solvent. It undergoes the following chemical reactions.



- (i) State the reagents and conditions for the following steps:
- Step 1** : Concentrated H_2SO_4 , concentrated HNO_3 , reflux $\leq 60^\circ\text{C}$
- Step 2** : Heat under reflux with Sn, concentrated HCl , followed by NaOH (aq)

[2]

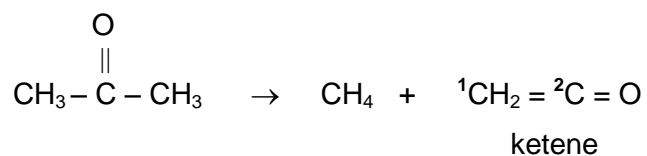
- (ii) Draw the structural formula of the organic compounds X, Y and Z.



[3]

[Total:12]

- 4 When propanone vapour is passed over a heated filament, it breaks down into methane and a reactive substance called ketene.

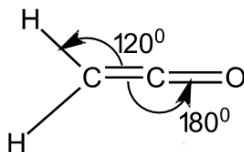


- (a) (i) Draw the hybrid orbitals around each of the 2 carbon atoms, ${}^1\text{C}$ and ${}^2\text{C}$ in ketene molecule. State the type of hybridization for each carbon atom.

Carbon atom ${}^1\text{C}$	Carbon atom ${}^2\text{C}$
Hybridisation: sp^2	Hybridisation: sp

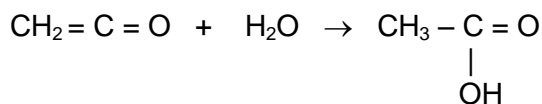
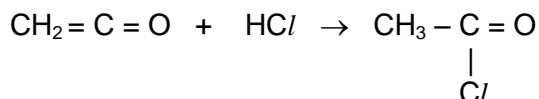
[2]

- (ii) Draw the displayed formula for the ketene molecule and on it show suggested values of the bond angles around ^1C and ^2C atoms.



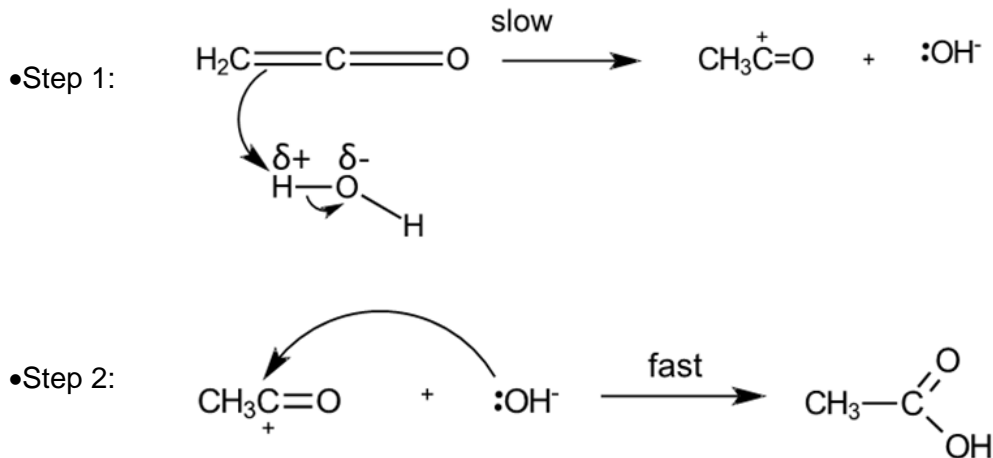
[1]

Ketene is a highly reactive compound. It readily undergoes the reactions shown below.



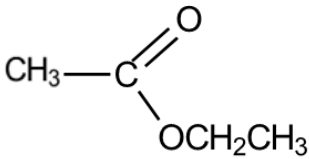
- (b) Name and describe the mechanism for the reaction between ketene and water, showing all charges and using curly arrows to show the movement of electron pairs.

- Name of mechanism: Electrophilic Addition



[3]

- (c) Ketene reacts with ethanol to form a sweet smelling compound **P**, $\text{C}_4\text{H}_8\text{O}_2$, which reacts with LiAlH_4 to give **Q**. Identify **P** and **Q**. Name the type of reaction for the transformation of **P** to **Q**.
-

	$\text{CH}_3\text{-CH}_2\text{OH}$
P	Q

Type of reaction from **P** to **Q**: Reduction

[3]

[Total: 9]

- 5 Ethanedioic acid, $\text{H}_2\text{C}_2\text{O}_4$, reacts with sodium hydroxide to form sodium ethanedioate, $\text{Na}_2\text{C}_2\text{O}_4$. One of the main application of ethanedioate ions is in rust-removal, as ethanedioate forms water-soluble derivatives with iron(III) ions.

- (a) An electrochemical cell is set up using Cu^{2+}/Cu and $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cells. The electrode in $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell is the negative electrode and the cell potential is +0.77 V.

- (i) Using relevant data from the Data Booklet, determine the electrode potential of the $\text{CO}_2/\text{C}_2\text{O}_4^{2-}$ half-cell.

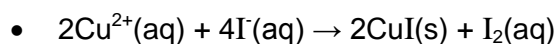
$$\begin{aligned} \bullet \quad E_{\text{Cu}^{2+}/\text{Cu}}^\ominus &= +0.34\text{V} = E_{\text{red}}^\ominus \\ E_{\text{cell}}^\ominus &= E_{\text{red}}^\ominus - E_{\text{ox}}^\ominus \end{aligned}$$

$$+0.77 = +0.34 - E_{\text{CO}_2/\text{C}_2\text{O}_4^{2-}}^\ominus$$

$$\bullet \quad E_{\text{CO}_2/\text{C}_2\text{O}_4^{2-}}^\ominus = -0.43 \text{ V}$$

[2]

- (ii) A small quantity of solid potassium iodide is added to the Cu^{2+}/Cu half-cell. Write an equation and state the observations for the reaction that will occur in this half-cell. Hence, predict and explain the effect on the e.m.f. of the electrochemical cell.

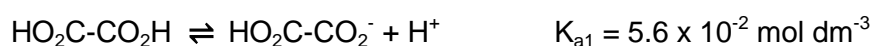


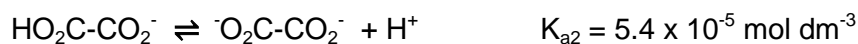
- White ppt in brown solution/ brown ppt observed in the Cu^{2+}/Cu half-cell.

- Since CuI is formed, the $[\text{Cu}^{2+}(\text{aq})]$ will decrease. $E_{\text{Cu}^{2+}/\text{Cu}}$ (E_{red}) will become more negative and the e.m.f. of the electrochemical cell will be less positive/ decrease.

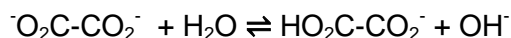
[3]

- (b) The K_a values for the step-wise dissociation of ethanedioic acid are given below.





Calculate the pH of 0.10 mol dm^{-3} of sodium ethanedioate salt, $\text{Na}_2\text{C}_2\text{O}_4$.



- $[\text{OH}^-] = \sqrt{K_{b,c}} = \sqrt{0.10 \times 10^{-14} / (5.4 \times 10^{-5})} = 4.30 \times 10^{-6} \text{ mol}$
- $\text{pH} = 14 - \lg(4.30 \times 10^{-6}) = 8.63$

[2]

- (c) Hydrated salt of magnesium ethanedioate has the formula $\text{MgC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$. When 6.18 g of hydrated magnesium ethanedioate is heated strongly, a white solid **W** and three gases **X**, **Y** and **Z** are generated. Gases **X**, **Y** and **Z** are passed through anhydrous calcium chloride, followed by aqueous sodium hydroxide. The flasks containing anhydrous calcium chloride and aqueous sodium hydroxide had an increase in mass of 1.50 g and 1.83 g respectively. The residual gas **Z** occupied 1 dm^3 at room temperature and pressure. Gas **Z** is poisonous and can be heated with oxygen to give gas **Y**.

- (i) Suggest the identities of **W**, **X**, **Y** and **Z**.

- **W**: MgO , **X**: H_2O
- **Y**: CO_2 , **Z**: CO

Any 2 correct = 1 mark

[2]

- (ii) Hence, determine the value of n , showing your working clearly.

- No. of moles of $\text{CO} = 1/24 = 0.0417 \text{ mol}$
- Mass of $\text{CO} = 0.0417 \times (12.0 + 16.0) = 1.17 \text{ g}$
- Mass of $\text{MgO} = 6.18 - 1.50 - 1.83 - 1.17 = 1.68 \text{ g}$
- No. of moles of $\text{MgO} = 1.68 / (24.3 + 16.0) = 0.0417 \text{ mol}$
- No. of moles of $\text{H}_2\text{O} = 1.50 / 18.0 = 0.0833 \text{ mol}$
- $n = 0.0833 / 0.0417 = 2$

[3]

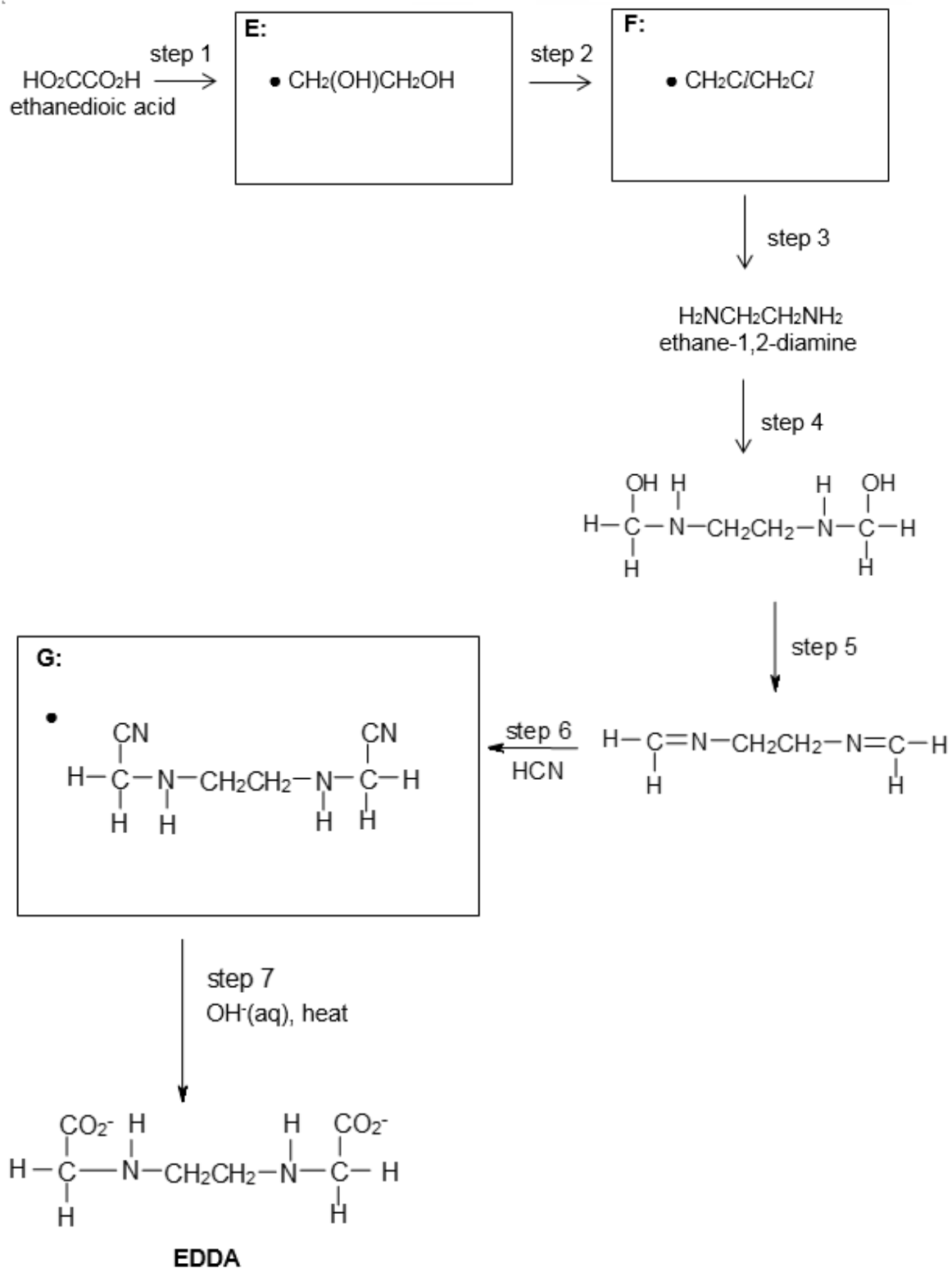
- (iii) Ethanedioate ions form insoluble precipitates with many metal ions, one of which is calcium ethanedioate, a primary constituent of kidney stones.

Calcium ethanedioate decomposes in the same manner as magnesium ethanedioate. Using relevant data from the Data Booklet, deduce whether calcium ethanedioate would decompose at a higher or lower temperature than magnesium ethanedioate. Explain your reasoning.

- Ionic radius of $\text{Ca}^{2+} = 0.099 \text{ nm}$, $\text{Mg}^{2+} = 0.065 \text{ nm}$
- Ca^{2+} is larger than Mg^{2+} , hence possesses smaller charge density / lower polarising power. Electron cloud of $\text{C}_2\text{O}_4^{2-}$ is distorted to a smaller extent and the C-O bond is weakened to a smaller extent.
- Calcium ethanedioate has a higher decomposition temperature.

[3]

- (d) A tetradentate ligand, ethylenediamine-N,N'-diacetate (EDDA) ion, can be synthesised from ethanedioic acid through a series of steps. Ethanedioic acid is first converted to ethane-1,2-diamine through a 3-step synthesis. Steps 4 to 7 represent the mechanism of Skrecker synthesis, which can be used to synthesise amino acids.



- (i) Propose the 3-step synthesis for the formation of ethane-1,2-diamine from

ethanedioic acid, naming the reagents and conditions used in each step. Draw the structures of the intermediate compounds **E** and **F** in the spaces provided in the synthetic route.

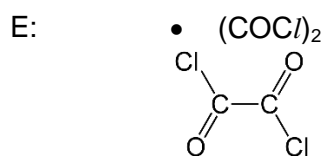
Step 1: • Anhydrous LiAlH₄, dry ether as solvent, room temperature

Step 2: • PCl₅(s), cold

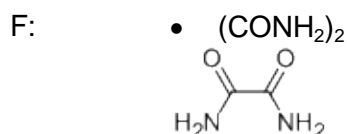
Step 3: • Excess conc NH₃ in ethanol, heat in sealed tube

Alternative Answer:

Step 1: • PCl₅(s), cold



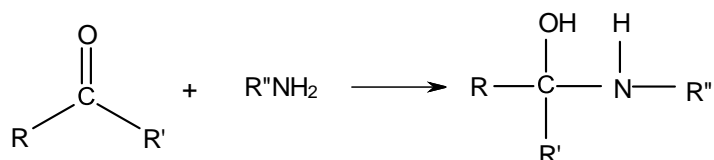
Step 2: • NH₃(g), room temperature



Step 3: • Anhydrous LiAlH₄, dry ether as solvent, room temperature

[5]

(ii) Carbonyl compound and amine react in the following way.



Step 4 of the synthetic route in **(d)** involves the reaction of ethane-1,2-diamine with 2 moles of a carbonyl compound. Identify the carbonyl compound.

• CH₂O

[1]

(iii) Draw the structure of compound **G** in the space provided.

[1]

(iv) State the types of reaction in step 5 and step 7.

Step 5: • Elimination

Step 7: • Alkaline hydrolysis

[2]

[Total: 24]

CHEMISTRY
Paper 3 Free Response

9647/03
13th September 2016
2 hours

Candidates answer on separate paper.

Additional materials: Answer paper
 Graph Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group, Centre number and Index number in the spaces provided on the cover page and on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

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.

This document consists of 15 printed pages.

Answer any **four** questions

1 Ethanedioic acid is a substance found in many plant foods. Cabbage is among the plant foods with high ethanedioic acid content. However, its anion, $\text{C}_2\text{O}_4^{2-}$ can bind to iron to form iron(II) ethanedioate, which renders much of the iron in cabbage unusable by the body.

(a) 50.0 cm³ sample of iron(II) ethanedioate, FeC_2O_4 was extracted from 300 g of cabbage, diluted in water and the solution made up to 250 cm³. A 25.0 cm³ portion of this solution was acidified and required 26.90 cm³ of 0.0100 mol dm⁻³ potassium manganate(VII) for oxidation of iron(II) to iron(III) and ethanedioate ions to carbon dioxide.

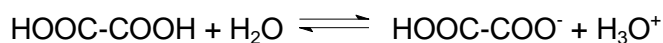
(i) State the change in oxidation number for manganese and carbon in the reaction. [1]

(ii) Write down all the relevant ion-electron half equations and hence the overall redox equation for the reaction between potassium manganate(VII) and iron(II) ethanedioate. [2]

(iii) Calculate the concentration, in mol dm⁻³, of iron(II) ethanedioate in the original sample. [2]

(iv) Calculate the number of moles of iron in each gram of cabbage. [1]

(b) Ethanedioic acid dissociates in water according to the following equation.



The table below compares the K_a values of three organic acids.

	Formula	K_a
Ethanoic acid	CH_3COOH	1.74×10^{-5}
Ethanedioic acid	$\text{HO}_2\text{CCO}_2\text{H}$	6.46×10^{-2}
Oxoethanoic acid	$(\text{CHO})\text{COOH}$	4.79×10^{-4}

With reference to the K_a values, comment on the order of acidity of the three organic acids. [2]

- (c) Compound **A**, with molecular formula C_5H_8O , decolourises aqueous bromine and reacts with PCl_5 giving off white fumes. Upon refluxing **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 mole of **B** also reacts with 1 mole of Na_2CO_3 with effervescence observed. **B** reacts with $NaBH_4$ to form **C**. Deduce the structures of compounds **A**, **B** and **C**, explaining the chemistry of the reactions involved. [8]
- (d) (i) Describe what you see when separate samples of sodium and sulfur are burned in excess air. Write equations for the reactions that occur. [2]
- (ii) The products resulting from the reactions in (d)(i) both react with water. Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution. [2]

[Total: 20]

2 Thallium is a Group III element discovered in 1861, and its toxicity was quickly noted. Thallium isotopes and compounds have useful applications, sometimes despite their toxic nature.

(a) Thallium forms compounds similar to aluminium, and thallium(III) chloride and thallium(III) fluoride have very different structures and bonding.

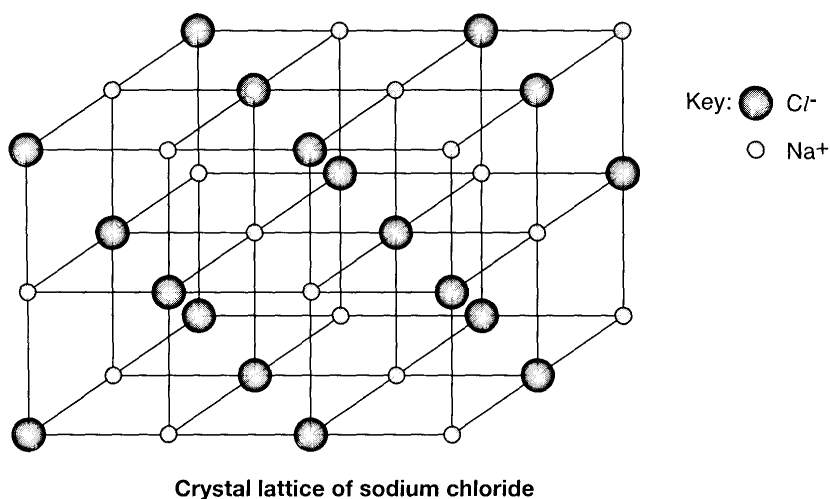
(i) Draw and state the shape of thallium(III) chloride, $TlCl_3$.
[1]

(ii) In gaseous phase, thallium(III) chloride is able to form a compound with a M_r of 621. Draw a dot-and-cross diagram of this compound, and state the $Cl-Tl-Cl$ bond angle.
[2]

(iii) Explain, in terms of structure and bonding, why thallium(III) fluoride has a high melting point of 550 °C.
[2]

(iv) Thallium is also able to form thallium(I) chloride, which is crystalline in nature.

In the crystal lattice of sodium and potassium chlorides, the co-ordination number of each ion is 6. In the crystal lattice of thallium(I) chloride, $TlCl$, the co-ordination number has a different value.



Suggest an explanation for the co-ordination number in the $TlCl$ lattice being different from those in $NaCl$ and KCl .

[1]

(b) Thallium(III) chloride, $TlCl_3$, reacts with hot water to produce thallium(III) oxide precipitate and hydrochloric acid.

(i) Write a balanced equation for the above reaction.
[1]

(ii) In an experiment, a 15 g impure sample of thallium(III) chloride ($M_r = 310.5$) was mixed with hot water, and filtered. Water was then added to the filtrate to make a standard solution in a 250 cm^3 volumetric flask. A 25.0 cm^3 aliquot was titrated against 0.5 mol dm^{-3} aqueous sodium hydroxide, requiring a titre of 22.00 cm^3 . Determine the percentage purity of the sample.

You may assume that the impurities are insoluble in water and are inert.
[2]

(c) Thallium(I) sulfate ($M_r = 504.1$) was often employed as a rodenticide and is highly poisonous. The lethal dosage is 16 ppm of the rat's mass. Assuming a typical rat has a mass of 230 g, determine the number of moles of thallium(I) sulfate needed to kill a rat.
[2]

(d) Thallium(III) ethanoate, $Tl(CH_3CO_2)_3$, is able to react with an alkene through addition. When cyclohexene reacts with thallium(III) ethanoate, a compound with the molecular formula $C_{10}H_{16}O_4$ is formed. Suggest the structural formula of this compound, and state the number of stereoisomers that this compound has.
[2]

(e) ^{201}Tl is an isotope of thallium that is often used in medical diagnostics due to its radioactive decay by electron capture with emission of gamma rays. The electronic configuration of the Tl atom is $[Xe]4f^{14}5d^{10}6s^26p^1$.

Electron capture is a process in which a proton-rich nucleus of an atom absorbs one electron from the first or second quantum shell to change one proton into a neutron.

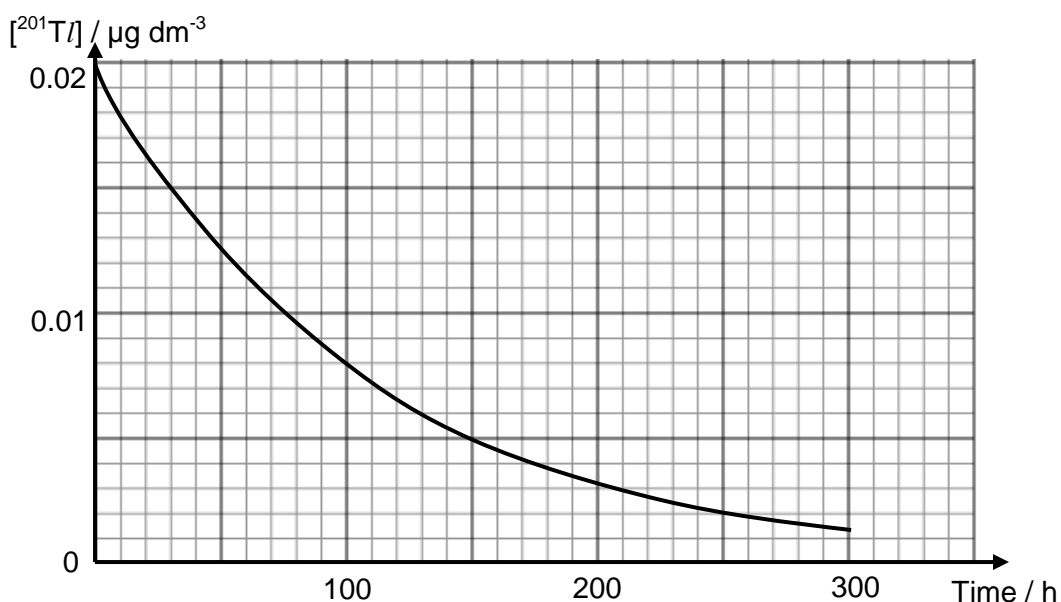
(i) Suggest the species formed, including the nucleon number, when ^{201}Tl undergoes electron capture.
[1]

(ii) The species formed immediately after electron capture is known to be in excited state, before returning to ground state by emitting gamma rays.

Name the orbital where the excited electron is most likely located in, and explain why **high energy** gamma rays are emitted when the species return to ground state.

[2]

- (iii) A patient is typically injected with 0.02 μg of thallium for heart diagnosis. The following graph shows the radioactive decay (through electron capture) of a 0.02 μg sample of ^{201}Tl dissolved in 1 dm^3 of inert solvent.



Using the graph, deduce the order of reaction for the radioactive decay of ^{201}Tl . [2]

- (iv) Hence, write the rate equation for this reaction and determine the rate constant, stating its units. [2]

[Total: 20 m]

- 3 The halogens and organic halides are useful laboratory reagents and have many applications.
- (a) State and explain the difference in the reactions of chlorine and iodine with sodium thiosulfate respectively. Write balanced equations for the reactions. [3]
- (b) Deduce which gas, fluorine or chlorine, would behave more ideally at low pressure. Explain your answer. [1]

Organic halides are a group of compounds comprising alkyl halides, ethenyl halides and aryl halides.

Alkyl halides are used as solvents for relatively non-polar compounds. They are also used as the starting materials for the synthesis of many compounds.

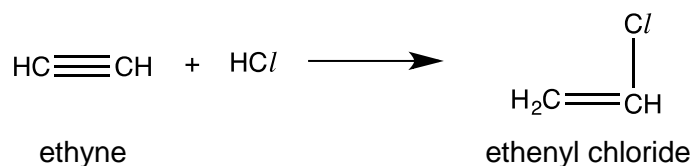
- (c) Alcohols react with hydrogen halides to produce alkyl halides.
- (i) Suggest the type of reaction that occur. [1]
- (ii) 2-iodopropane is formed from propan-2-ol in the presence of sodium iodide and concentrated phosphoric acid.
Explain, with the aid of an equation, why concentrated sulfuric acid is not used. [2]
- (d) 2-chloro-2-methylpropane undergoes alkaline hydrolysis to form 2-methylpropan-2-ol.
- (i) Name and describe the mechanism of the hydrolysis of 2-chloro-2-methylpropane. [3]
- (ii) With the aid of the *Data Booklet*, explain what will happen to the rate of reaction if

2-bromo-2-methylpropane was used instead.

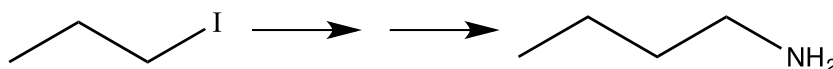
[2]

- (e) Ethenyl chloride is an important industrial chemical mainly used to produce the polymer, PVC.

Ethyne reacts with anhydrous hydrogen chloride gas over a mercuric chloride catalyst to give ethenyl chloride.



- (i) With the aid of the *Data Booklet*, determine the enthalpy change of the reaction. [2]
- (ii) Explain why ethenyl chloride does not undergo alkaline hydrolysis readily. [1]
- (f) 1-iodopropane can be converted to butylamine via a two-stage synthesis. Butylamine is then used as an ingredient in the manufacture of pesticide.



- (i) Suggest reagents and conditions for the two stages. Draw the structure of the intermediate compound. [3]
- (ii) Suggest a chemical test to distinguish between 1-iodopropane and 1-chloropropane. [2]

[Total: 20]

4 Co-Cr alloys are most commonly used to make artificial joints including knee and hip joints due to high wear-resistance and biocompatibility. However in 2010, faulty Co-Cr alloy hip joints manufactured by DePuy was removed from market due to leakage of toxic chromium and cobalt into the body muscles and blood stream.

(a) State the electronic configurations of

(i) an _____ atom of _____ chromium,
[1]

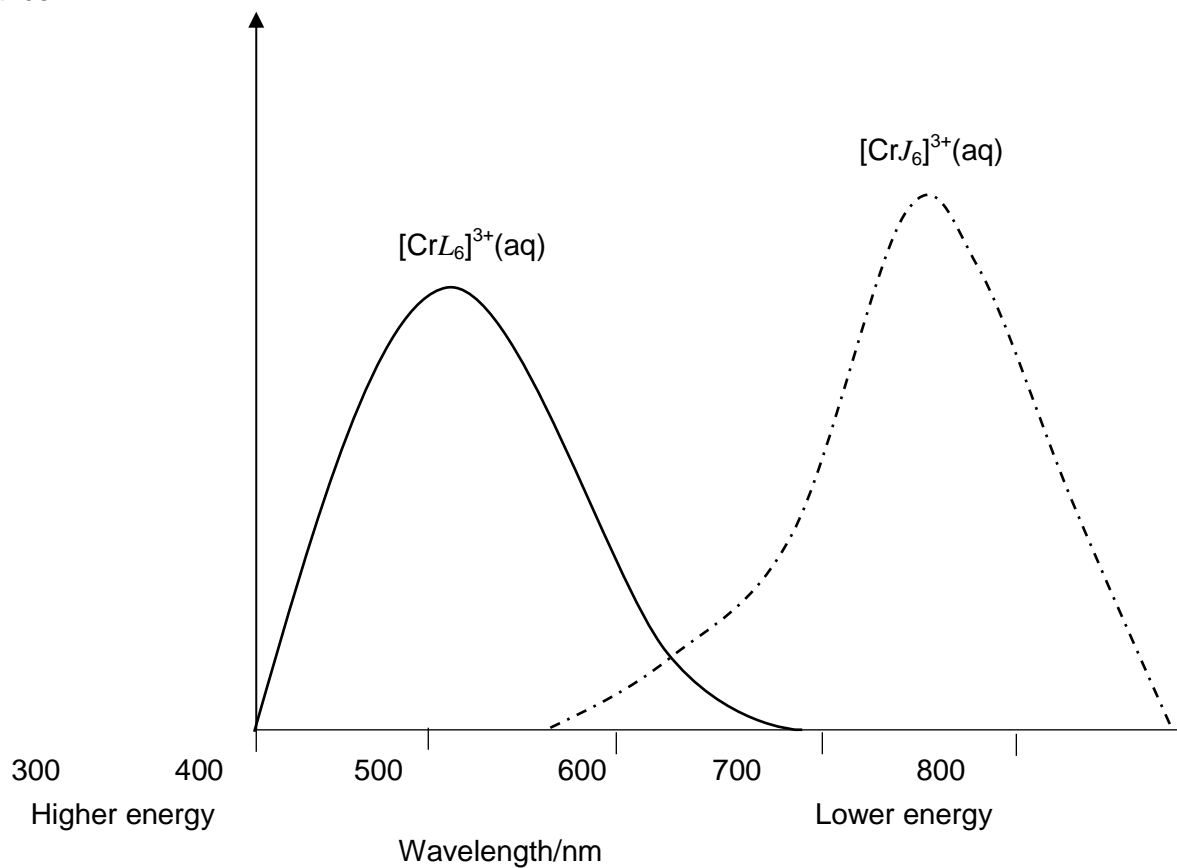
(ii) the Co^{3+} ion. [1]

(b) Why are transition metal complexes coloured? [3]

- (c) The colour of the complexes can be measured by a spectrometer. The amount of light absorbed is expressed as an absorbance value. The higher the absorbance, the more of a particular wavelength of light is being absorbed.

The spectrum below shows the major absorption peaks for $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$.

Relative absorbance



colour	Wavelength/nm
Violet	400-430
Blue	430-490
Green	490-570
Yellow	570-590
Orange	590-620
red	620-750

- (i) What are the colours of $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$?

[2]

- (ii) What deduction can be made from the spectra about the size of the d-orbital splitting in the two complexes?
[2]

Cobalt forms many complexes with ligands such as H_2O , NH_3 and $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$. The most common oxidation states of cobalt are +2 and +3.

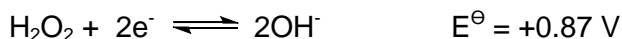
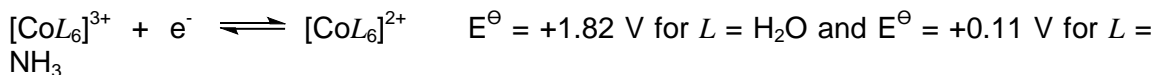
Cations containing cobalt in these two oxidation states have significantly different colours even when the ligands are the same.

- (d) When H_2O_2 is mixed with pink $\text{Co}^{2+}(\text{aq})$ solution, no significant colour change is observed.

When $\text{Co}^{2+}(\text{aq})$ is mixed with excess $\text{NH}_3(\text{aq})$ a slight colour change occurs and cation **Q** is formed.

When cation **Q** is mixed with H_2O_2 , a reddish brown solution is observed.

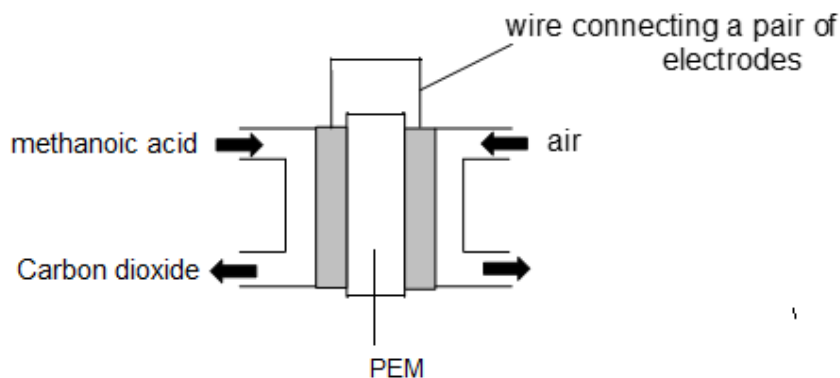
E^\ominus data for the cobalt complex ions and hydrogen peroxide are given below.



Suggest an explanation for the above observations, giving equations where appropriate and identify the cation **Q**.
[5]

- (e) Explain why the neutral complex formed between a Co^{2+} ion and two $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$ ions is soluble in cyclohexane.
[1]

The direct oxidation of methanoic acid in a fuel cell, DFAFC, shown below represents potentially the most efficient method of obtaining useful energy from a renewable fuel.



- (f) The electrons pass around the external circuit to the cathode. The protons produced migrate across the proton exchange membrane, PEM, to the cathode, where they react with oxygen from air, producing water.

Write the equations for the anode and cathode reactions. Hence construct the equation for the overall reaction. [2]

- (g) One method for the construction of DFAFC, involves electroplating a layer of platinum onto the surface of the proton exchange membrane, PEM. The electrolyte for this process is a solution containing $\text{Pt}(\text{NH}_3)_4^{2+}$ and Cl^- ions. The PEM is the cathode in this electrolytic cell.

- (i) Suggest the half-equation for the cathode reaction that deposits platinum on the PEM. [1]

- (ii) In one such preparation, a PEM with a surface area of 25 cm^2 was immersed in an electrolyte bath and a current of 0.0875 A was passed for 95 minutes. Calculate the mass of platinum deposited onto the surface of PEM. [2]

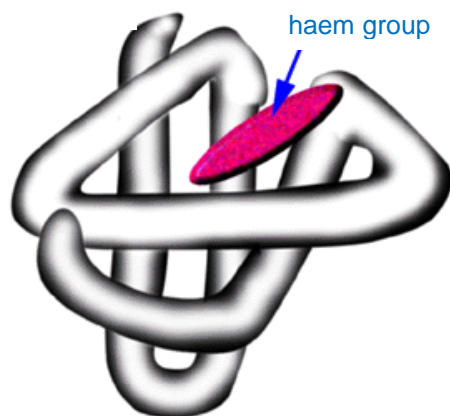
[Total: 20]

- 5 (a) Myoglobin and haemoglobin are globular proteins that serve to bind and deliver oxygen.

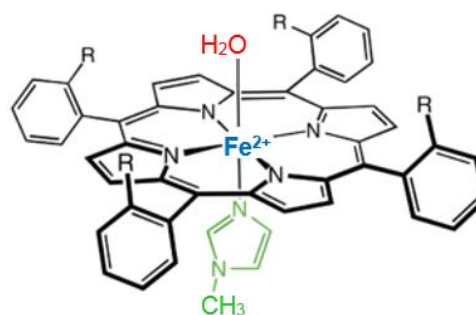
The former serves as an intracellular storage site for oxygen in the muscle tissues, while the latter transports oxygen in the bloodstream.

Each myoglobin molecule contains one haem group.

In deoxygenated myoglobin, a water ligand is weakly bound to the Fe^{2+} of the haem group as shown:



Myoglobin



Haem group in deoxygenated myoglobin

(i) Briefly describe how myoglobin maintains its three-dimensional shape. [2]

(ii) In the presence of the haem group, the polypeptide chain coalesces into a myoglobin molecule.

With the aid of the equation,

$$\Delta G = \Delta H - T\Delta S$$

and by considering the chemical interactions involved, explain why this is a spontaneous process at low temperatures. [2]

(iii) Deoxygenated myoglobin is responsible for the dull purplish red muscle colour, observed in the depth of the muscle. When meat is freshly cut, colour change occurs in two stages:

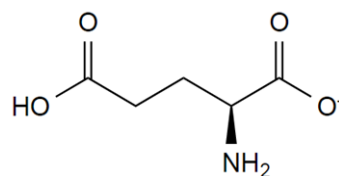
Stage 1: Bright red colour when muscle surface is exposed to air.

Stage 2: With time, the bright red colour slowly changes to an unattractive, dull brown colour associated with stale and spoiled meat.

With reference to the structure of the haem group and the reaction that occurs in each stage, explain the colour changes involved.

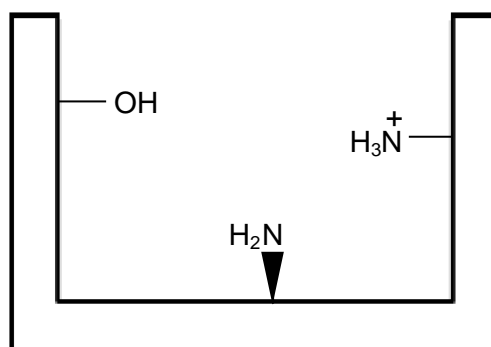
[2]

- (b) One of the isolated compounds that is primarily responsible for the umami (savory) flavor is glutamate, which is a salt formed from glutamic acid that is commonly found in meat.



glutamate

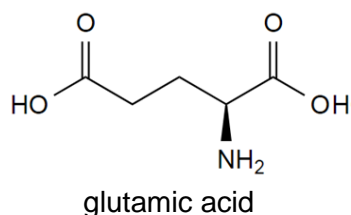
It is thought that glutamate stimulates a specific receptor site located in the taste buds on the tongue, which is essentially a protein molecule. A simplified diagram of the receptor site is shown below:



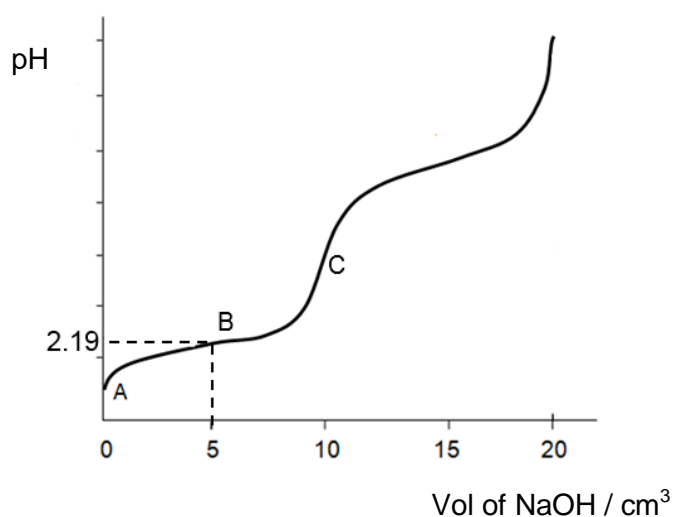
- (i) State **two** different types of interactions that can be formed between glutamate and the receptor protein. Illustrate your answer with labelled diagram(s). [2]
- (ii) To enhance the flavor of food, many retailers in the food industry use monosodium glutamate (MSG) as a food additive, which can be easily synthesized in the laboratory.

Given that laboratory synthesis gives a racemic mixture, explain why 50% of the glutamate synthesized in the laboratory is unable to bind precisely with the correct orientation to the receptor protein. [1]

The structure of glutamic acid is shown below:



10 cm³ of the fully protonated glutamic acid is titrated with 20 cm³ of 1.00 mol dm⁻³ sodium hydroxide solution. Its titration curve is shown below:



(iii) Show that the concentration of glutamic acid is 1.0 mol dm⁻³ at **A**.
[1]

(iv) Hence, calculate the pH of the solution at **A**.
[1]

(v) Identify the specie(s) present at **B**.

With the help of an equation, explain how the solution at **B** can resist a change in pH when a small amount of base is added. [2]

(vi) In a separate experiment, the solution at **B** was reacted with 10.0 cm³ of

0.05 mol dm⁻³ sodium hydroxide.

Calculate the pH of the mixture after the reaction.

You may find it useful to represent the fully protonated glutamic acid as HA.
[2]

(c) Compound **P**, C₉H₁₁NO₂, rotates the plane of polarised light and reacts with the following reagents:

- aqueous bromine to give compound **Q**, C₉H₉NO₂Br₂
- sodium carbonate to give a salt
- PCl₅ to give a 5-membered cyclic compound **R**

Deduce the structural formulae of compounds **P**, **Q** and **R**.
[5]

[Total: 20]

CHEMISTRY
Paper 3 Free Response

9647/03
13th September 2016
2 hours

Candidates answer on separate paper.

Additional materials: Answer paper
 Graph Paper
 Data Booklet

READ THESE INSTRUCTIONS FIRST

Write your name, Civics Group, Centre number and Index number in the spaces provided on the cover page and on all the work you hand in.

Write in dark blue or black pen on both sides of the paper.

You may use a HB pencil for any diagrams, graphs or rough working.

Do not use staples, paper clips, glue or correction fluid.

Answer any **four** questions.

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.

This document consists of 15 printed pages.

Answer any **four** questions

1 Ethanedioic acid is a substance found in many plant foods. Cabbage is among the plant foods with high ethanedioic acid content. However, its anion, $\text{C}_2\text{O}_4^{2-}$ can bind to iron to form iron (II) ethanedioate, which renders much of the iron in cabbage unusable by the body.

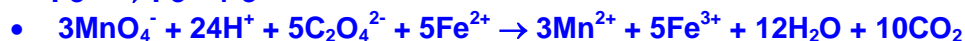
(a) 50.0 cm³ sample of iron(II) ethanedioate, FeC_2O_4 was extracted from 300 g of cabbage, diluted in water and the solution made up to 250 cm³. A 25.0 cm³ portion of this solution was acidified and required 26.90 cm³ of 0.0100 mol dm⁻³ potassium manganate(VII) for oxidation of iron(II) to iron(III) and ethanedioate ions to carbon dioxide.

(i) State the change in oxidation number for manganese and carbon in the reaction. [1]

Mn: From +7 to +2 [Or decrease by 5]

C: From +3 to +4 [Or increase by 1]

(ii) Write down all the relevant ion-electron half equations and hence the overall redox equation for the reaction between potassium manganate(VII) and iron(II) ethanedioate. [2]



(iii) Calculate the concentration, in mol dm⁻³, of iron(II) ethanedioate in the original sample [2]

$$\bullet \text{Number of moles of FeC}_2\text{O}_4 \text{ in } 25.0 \text{ cm}^3 = \frac{5}{3} \times 2.69 \times 10^{-4} \\ = 4.48 \times 10^{-4} \text{ mol}$$

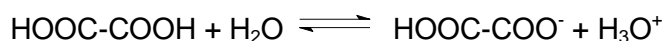
$$\text{Number of moles of FeC}_2\text{O}_4 \text{ in } 250 \text{ cm}^3 = 4.48 \times 10^{-4} \times 250/25.0 \\ = 4.48 \times 10^{-3} \text{ mol}$$

$$\bullet \text{Concentration of FeC}_2\text{O}_4 \text{ in the original sample} = \frac{4.48 \times 10^{-3}}{50 \times 10^{-3}} \\ = 0.0896 \text{ mol dm}^{-3}$$

(iv) Calculate the number of moles of iron in each gram of cabbage. [1]

$$\bullet \text{No. of moles of iron per gram of spinach} = \frac{4.48 \times 10^{-3}}{300} \\ = 1.49 \times 10^{-5} \text{ mol/g}$$

- (b) Ethanedioic acid dissociates in water according to the following equation.



The table below compares the K_a values of three organic acids.

	Formula	K_a
Ethanoic acid	CH_3COOH	1.74×10^{-5}
Ethanedioic acid	$\text{HO}_2\text{CCO}_2\text{H}$	6.46×10^{-2}
Oxoethanoic acid	$(\text{CHO})\text{COOH}$	4.79×10^{-4}

With reference to the K_a values, comment on the order of acidity of the three organic acids. [2]

The bigger the K_a , the stronger the acid. Acid strength is dependent on the stability of the anion formed when the acid ionises. The more stable the anion, the stronger is the acid.

Strength of acid: Ethanedioic acid > Oxoethanoic acid > Ethanoic acid

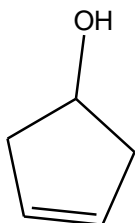
- Oxoethanoic acid is a stronger acid than ethanoic acid as -CHO group is electron withdrawing. The negative charge on the anion is dispersed, thereby stabilizing the ion compared to ethanoate ion.

- Ethanedioic acid is the strongest acid as stabilisation of the monoanion by intramolecular hydrogen bonding with the unionised -COOH group results in the highest K_a value compared with the other two acids.

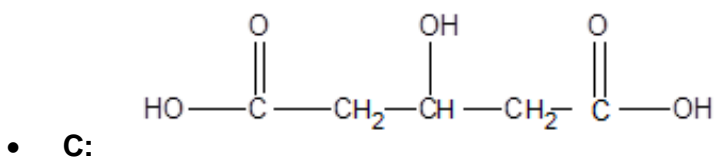
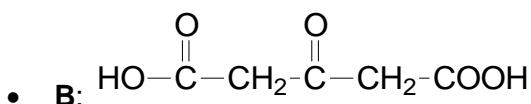
- (c) Compound **A**, with molecular formula $\text{C}_5\text{H}_8\text{O}$, decolourises aqueous bromine and reacts with PCl_5 giving off white fumes. Upon refluxing **A** with acidified potassium manganate(VII), a symmetrical product **B**, $\text{C}_5\text{H}_6\text{O}_5$, is formed. **B** does not give a red precipitate with Fehling's solution but an orange precipitate is observed with 2,4-dinitrophenylhydrazine. 1 mole of **B** also reacts with 1 mole of Na_2CO_3 with effervescence observed. **B** reacts with NaBH_4 to form **C**. Deduce the structures of compounds **A**, **B** and **C**, explaining the chemistry of the reactions involved. [8]

- **A** decolourises aqueous bromine \Rightarrow **C=C** present
- **A** reacts with PCl_5 giving off white fumes of $\text{HCl} \Rightarrow$ **-OH** present
- **A** undergoes oxidation with KMnO_4 where the **-OH** group is oxidised and **C=C** in a ring undergoes total bond cleavage to form **B**
OR **A** undergoes oxidation with KMnO_4 to give a symmetrical product **B** with no loss in **C** atoms \Rightarrow **C=C** is in a ring and **A** is a cyclic compound
- **B** does not give a red precipitate with Fehling's solution but form an orange precipitate with 2,4-dinitrophenylhydrazine \Rightarrow **B** is a ketone and **A** is a 2° alcohol

- 1 mole of B also reacts with 1 mole of $\text{Na}_2\text{CO}_3 \Rightarrow$ B has 2 $-\text{COOH}$ groups.
- B reacts with NaBH_4 to form C \Rightarrow only the carbonyl group in B is reduced but the carboxylic acid groups remain unaffected.



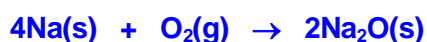
- A:



(9 marking points: Maximum 8)

- (d) (i) Describe what you see when separate samples of sodium and sulfur are burned in excess air. Write equations for the reactions that occur. [2]

Sodium burns readily with a brilliant yellow flame in air or oxygen to form white sodium oxide, Na_2O .



Sulfur burns slowly with a blue flame on heating in air or oxygen to form colourless sulfur dioxide, SO_2 . (Note: SO_3 is not formed)



- Both equations correct
- Both observations correct

- (ii) The products resulting from the reactions in (d)(i) both react with water. Write equations for these two reactions and describe the effect of the resulting solutions on Universal Indicator solution. [2]

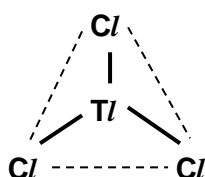
- $\text{Na}_2\text{O(s)} + \text{H}_2\text{O(l)} \rightarrow 2\text{NaOH(aq)}$
Universal Indicator turns violet.
- $\text{SO}_2\text{(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_2\text{SO}_3\text{(aq)}$
Universal Indicator turns red.

[Total: 20]

2 Thallium is a Group III element discovered in 1861, and its toxicity was quickly noted. Thallium isotopes and compounds have useful applications, sometimes despite their toxic nature.

(a) Thallium forms compounds similar to aluminium, and thallium(III) chloride and thallium(III) fluoride have very different structures and bonding.

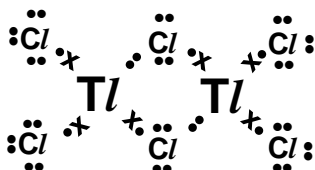
(i) Draw and state the shape of thallium(III) chloride, $TlCl_3$.
[1]



Trigonal planar

(ii) In gaseous phase, thallium(III) chloride is able to form a compound with a M_r of 621. Draw a dot-and-cross diagram of this compound, and state the $Cl-Tl-Cl$ bond angle.
[2]

Based on the M_r , the compound is Tl_2Cl_6 .



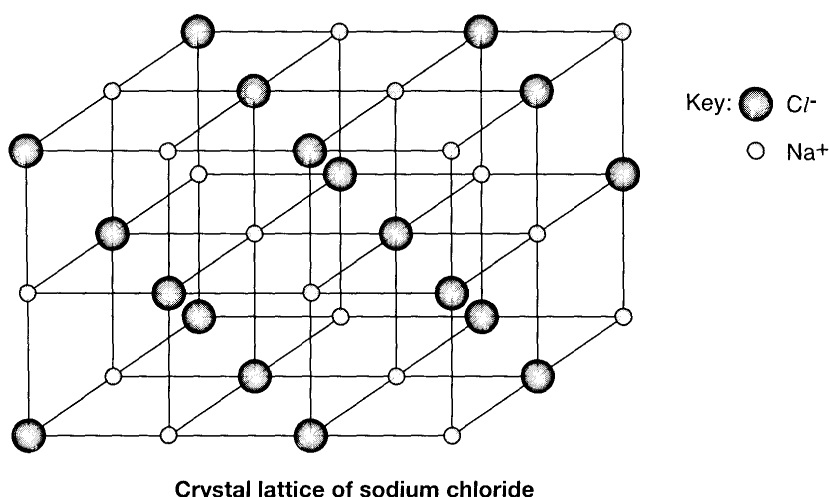
• **109.5°**

(iii) Explain, in terms of structure and bonding, why thallium(III) fluoride has a high melting point of 550 °C.
[2]

- **Thallium(III) fluoride exists as a giant ionic lattice structure and**
- **a large amount of energy is needed to break strong ionic bonds between oppositely charged ions.**

- (iv) Thallium is also able to form thallium(I) chloride, which is crystalline in nature.

In the crystal lattice of sodium and potassium chlorides, the co-ordination number of each ion is 6. In the crystal lattice of thallium(I) chloride, $TlCl$, the co-ordination number has a different value.



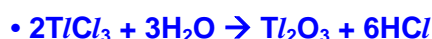
Suggest an explanation for the co-ordination number in the $TlCl$ lattice being different from those in $NaCl$ and KCl .

[1]

- **The size of the Tl^+ cations is larger than the Group I cations such as Na^+ and K^+ . More chloride ions can be packed around the larger Tl^+ cations.**

- (b) Thallium(III) chloride, $TlCl_3$, reacts with hot water to produce thallium(III) oxide precipitate and hydrochloric acid.

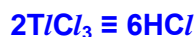
- (i) Write a balanced equation for the above reaction.
- [1]



- (ii) In an experiment, a 15 g impure sample of thallium(III) chloride ($M_r = 310.5$) was mixed with hot water, and filtered. Water was then added to the filtrate to make a standard solution in a 250 cm^3 volumetric flask. A 25.0 cm^3 aliquot was titrated against 0.5 $mol\ dm^{-3}$ aqueous sodium hydroxide, requiring a titre of 22.00 cm^3 . Determine the percentage purity of the sample.

You may assume that the impurities are insoluble in water and are inert.

[2]



$$\text{No of moles of NaOH} = 0.022 \times 0.5 = 0.0110 \text{ mol}$$

$$\text{No of moles of HCl produced from the sample} = 0.0110 \times 10 = 0.110 \text{ mol}$$

$$\text{No of moles of TlCl}_3 \text{ in sample} = 0.110 / 3 = 0.0367 \text{ mol}$$

$$\text{Mass of TlCl}_3 \text{ in sample} = 310.5 \times 0.0367 = 11.4 \text{ g}$$

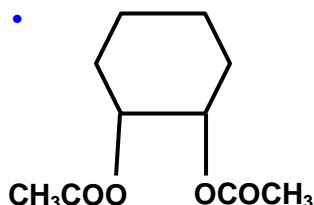
$$\text{Percentage purity of TlCl}_3 \text{ in sample} = 11.4 / 15 \times 100\% = 76.0\%$$

- (c) Thallium(I) sulfate ($M_r = 504.1$) was often employed as a rodenticide and is highly poisonous. The lethal dosage is 16 ppm of the rat's mass. Assuming a typical rat has a mass of 230 g, determine the number of moles of thallium(I) sulfate needed to kill a rat. [2]

- Mass of thallium(I) sulfate needed for lethal dosage = $230 \times 16 / 10^6 = 0.00368 \text{ g}$

- No of moles of thallium(I) sulfate needed = $0.00368 / 504.1 = 7.30 \times 10^{-6} \text{ mol}$

- (d) Thallium(III) ethanoate, $\text{Tl}(\text{CH}_3\text{CO}_2)_3$, is able to react with an alkene through addition. When cyclohexene reacts with thallium(III) ethanoate, a compound with the molecular formula $\text{C}_{10}\text{H}_{16}\text{O}_4$ is formed. Suggest the structural formula of this compound, and state the number of stereoisomers that this compound has. [2]



- This compound has a cis- and a trans-isomer, and the trans-isomer is optically active with two enantiomers. Therefore this compound will have 3 stereoisomers.

- (e) ^{201}Tl is an isotope of thallium that is often used in medical diagnostics due to its radioactive decay by electron capture with emission of gamma rays. The electronic configuration of the Tl atom is $[\text{Xe}]4f^{14}5d^{10}6s^26p^1$.

Electron capture is a process in which a proton-rich nucleus of an atom absorbs one electron from the first or second quantum shell to change one proton into a neutron.

- (i) Suggest the species formed, including the nucleon number, when ^{201}Tl undergoes electron capture. [1]



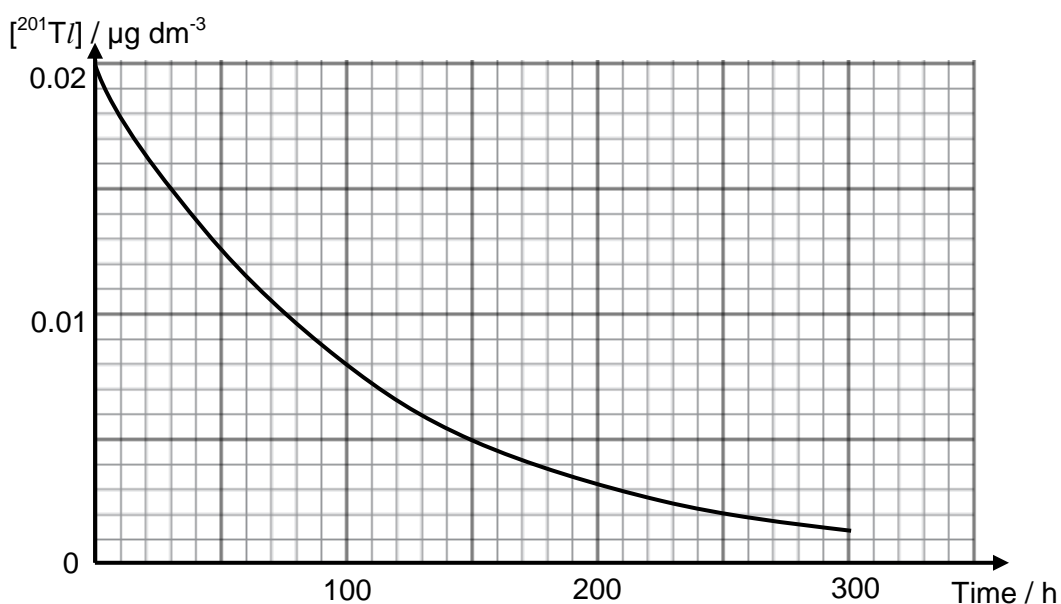
- (ii) The species formed immediately after electron capture is known to be in excited state, before returning to ground state by emitting gamma rays.

Name the orbital where the excited electron is most likely located in, and explain why **high energy** gamma rays are emitted when the species return to ground state.

[2]

- 6p. (can accept any orbital of higher energy than 6p)
- When the electron capture occurs, an inner shell (1 or 2) is now short of an electron. The 6p electron is at a high energy level, and needs to release a large amount of energy to replace the absorbed electron in shell 1 or 2 as the atom returns to ground state.

- (iii) A patient is typically injected with 0.02 μg of thallium for heart diagnosis. The following graph shows the radioactive decay (through electron capture) of a 0.02 μg sample of ^{201}Tl dissolved in 1 dm^3 of inert solvent.



Using the graph, deduce the order of reaction for the radioactive decay of ^{201}Tl .
[2]

- From the graph, $(t_{1/2})_1 = (t_{1/2})_2 = 75 \text{ h}$. Since $t_{1/2}$ is constant,
- order of reaction is 1.

- (iv) Hence, write the rate equation for this reaction and determine the rate constant, stating its units.
[2]

- rate = $k[^{201}\text{Tl}]$
- $k = \ln 2 / t_{1/2} = \ln 2 / 75 \text{ h} = 0.00924 \text{ h}^{-1}$

[Total: 20 m]

3 The halogens and organic halides are useful laboratory reagents and have many applications.

- (a) State and explain the difference in the reactions of chlorine and iodine with sodium thiosulfate respectively. Write balanced equations for the reactions. [3]



• **Oxidising power of the halogens decreases down the group as can be seen from the less positive E value, hence iodine can only oxidise thiosulfate to tetrathionate.**



- (b) Deduce which gas, fluorine or chlorine, would behave more ideally at low pressure. Explain your answer. [1]

• **Fluorine gas will behave more ideally. The electron cloud size of chlorine is larger than fluorine, hence the van der Waals forces of attraction is stronger.**

Organic halides are a group of compounds comprising alkyl halides, ethenyl halides and aryl halides.

Alkyl halides are used as solvents for relatively non-polar compounds. They are also used as the starting materials for the synthesis of many compounds.

- (c) Alcohols react with hydrogen halides to produce alkyl halides.

- (i) Suggest the type of reaction that occur. [1]

• **Nucleophilic substitution**

- (ii) 2-iodopropane is formed from propan-2-ol in the presence of sodium iodide and concentrated phosphoric acid.

Explain, with the aid of an equation, why concentrated sulfuric acid is not used. [2]

• **The hydrogen iodide produced will be readily oxidised by concentrated sulfuric acid to iodine hence will not be available to react with the alcohol.**

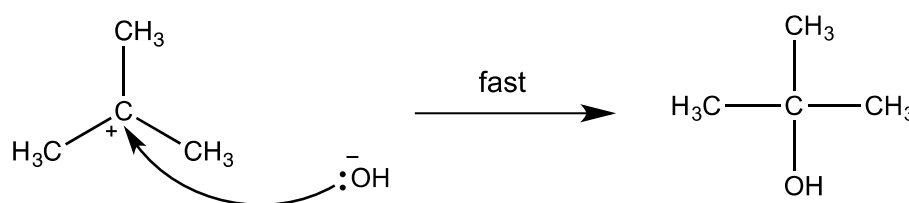
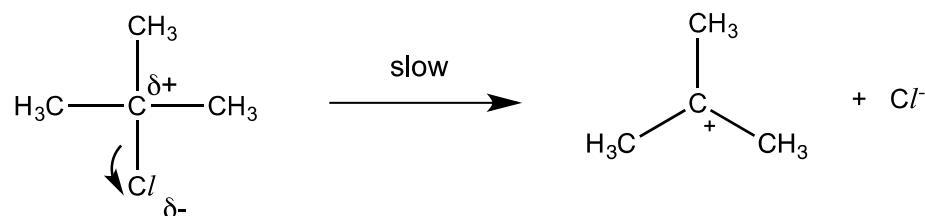


(d) 2-chloro-2-methylpropane undergoes alkaline hydrolysis to form 2-methylpropan-2-ol.

(i) Name and describe the mechanism of the hydrolysis of 2-chloro-2-methylpropane. [3]

• Nucleophilic substitution S_N1

••



(ii) With the aid of the *Data Booklet*, explain what will happen to the rate of reaction if 2-bromo-2-methylpropane was used instead. [2]

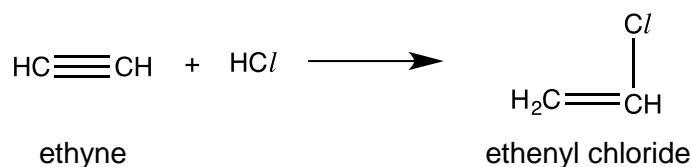
• $BE(C-Cl) = 340 \text{ kJ mol}^{-1}$

$BE(C-Br) = 280 \text{ kJ mol}^{-1}$

• Since bond energy of C-Cl is higher than that of C-Br, the bond strength of C-Cl is greater than that of C-Br. Hence the reactivity of the alkyl halides decreases in the order $RBr > RCl$. The rate of reaction will increase

(e) Ethenyl chloride is an important industrial chemical mainly used to produce the polymer, PVC.

Ethyne reacts with anhydrous hydrogen chloride gas over a mercuric chloride catalyst to give ethenyl chloride.



(i) With the aid of the *Data Booklet*, determine the enthalpy change of the reaction. [2]

•• $\Delta H_r = \text{enthalpy change for bond break} + \text{enthalpy change for bond form}$
 $= BE(H-Cl) + BE(C\equiv C) - [BE(C-Cl) + BE(C-H) + BE(C=C)]$
 $= 431 + 840 - (340 + 410 + 610) = -89 \text{ kJ mol}^{-1}$

(ii) Explain why ethenyl chloride does not undergo alkaline hydrolysis readily. [1]

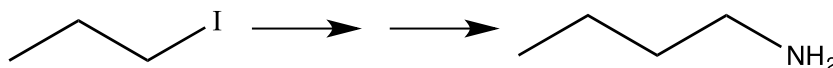
• The lone pair of electrons on chlorine delocalised across the double bond resulting in partial double bond character in C-Cl bond, hence a stronger C-Cl

bond which is harder to break.

OR

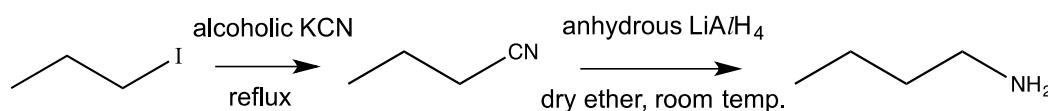
• The nucleophile is unlikely to attack the carbon-carbon double bond as it is electron rich.

- (f) 1-iodopropane can be converted to butylamine via a two-stage synthesis. Butylamine is then used as an ingredient in the manufacture of pesticide.



- (i) Suggest reagents and conditions for the two stages. Draw the structure of the intermediate compound. [3]

•••



- (ii) Suggest a chemical test to distinguish between 1-iodopropane and 1-chloropropane. [2]

• **Procedure:**

Step: (1) Boil RX with NaOH(aq).

(2) Acidify with dilute HNO₃.

(3) Add AgNO₃(aq).

OR

Boil with silver(I) ethanoate in alcohol.

• **White precipitate (AgCl) observed for 1-chloropropane.**

Yellow precipitate (AgI) observed for 1-iodopropane.

[Total: 20]

- 4 Co-Cr alloys are most commonly used to make artificial joints including knee and hip joints due to high wear-resistance and biocompatibility. However in 2010, faulty Co-Cr alloy hip joints manufactured by DePuy was removed from market due to leakage of toxic chromium and cobalt into the body muscles and blood stream.

(a) State the electronic configurations of

- (i) an _____ atom _____ of _____ chromium, [1]



- (ii) the Co^{3+} ion. [1]



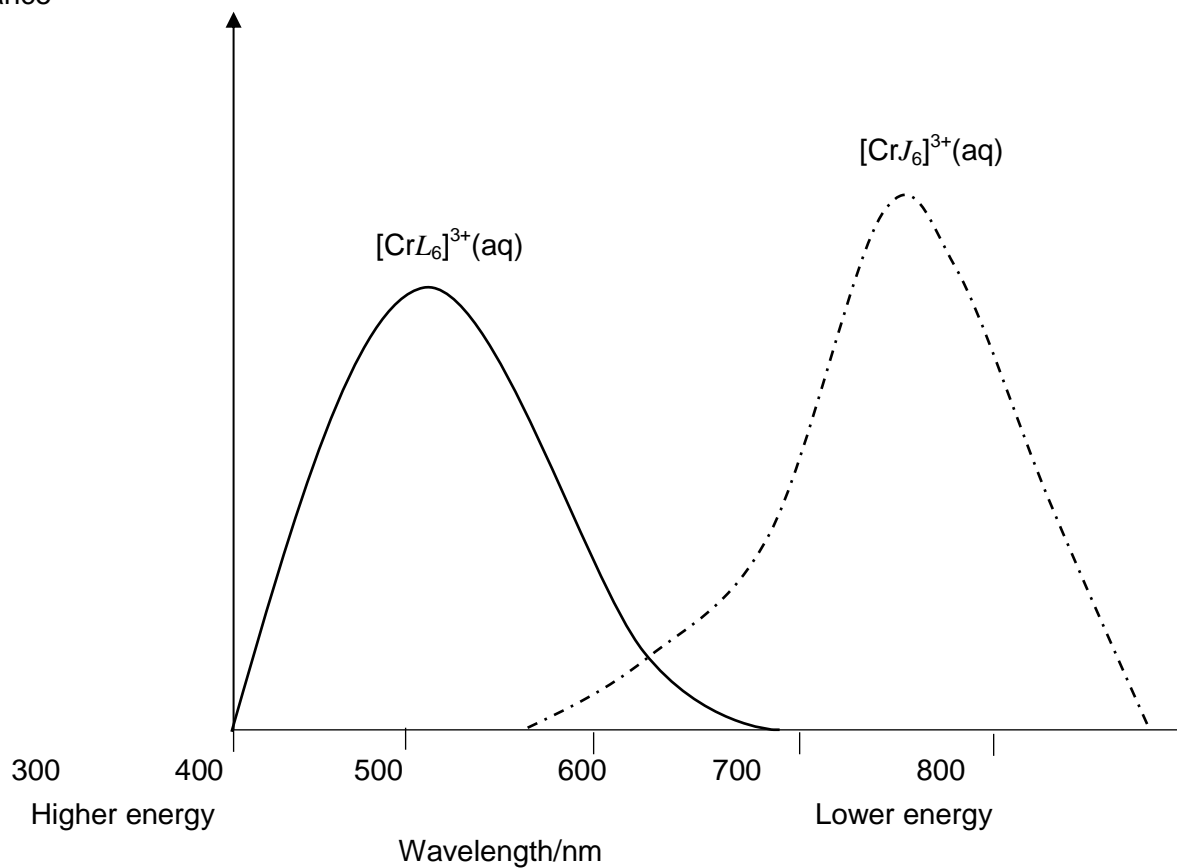
(b) Why are transition metal complexes coloured? [3]

- Transition metal complexes are often coloured due to the presence of partially filled d-orbitals in the metal ion.
- In complexes, the presence of ligands causes a splitting of the energy of d orbitals into 2 groups with an energy gap, ΔE , between them.
- When a d-electron from lower energy group is promoted to the higher energy group (*d-d transition*), radiation in the visible region of the electromagnetic spectrum corresponding to ΔE is absorbed. Light energy that is not absorbed will be seen as the colour of the complex.

- (c) The colour of the complexes can be measured by a spectrometer. The amount of light absorbed is expressed as an absorbance value. The higher the absorbance, the more of a particular wavelength of light is being absorbed.

The spectrum below shows the major absorption peaks for $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$.

Relative absorbance



The wavelengths associated with each colour of light are given below.

colour	Wavelength/nm
Violet	400-430
Blue	430-490
Green	490-570
Yellow	570-590
Orange	590-620
red	620-750

(i) What are the colours of $[\text{CrL}_6]^{3+}(\text{aq})$ and $[\text{CrJ}_6]^{3+}(\text{aq})$? [2]

- $[\text{CrL}_6]^{3+}(\text{aq})$: yellow/orange
- $[\text{CrJ}_6]^{3+}(\text{aq})$: green/blue

(ii) What deduction can be made from the spectra about the size of the d-orbital splitting in the two complexes? [2]

- The d-orbital splitting for $[\text{CrL}_6]^{3+}(\text{aq})$ is larger than $[\text{CrJ}_6]^{3+}(\text{aq})$
- because electrons in lower d-subshell absorbs energy in shorter wavelength and higher energy to excite to higher d-subshell, ΔE is larger.

Cobalt forms many complexes with ligands such as H_2O , NH_3 and $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$. The most common oxidation states of cobalt are +2 and +3.

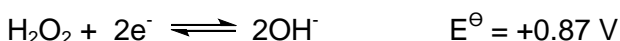
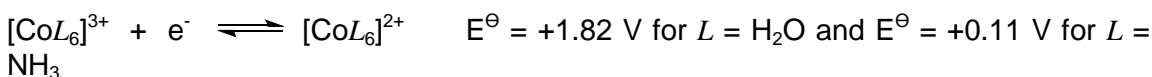
Cations containing cobalt in these two oxidation states have significantly different colours even when the ligands are the same.

(d) When H_2O_2 is mixed with pink $\text{Co}^{2+}(\text{aq})$ solution, no significant colour change is observed.

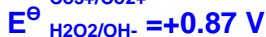
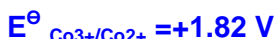
When $\text{Co}^{2+}(\text{aq})$ is mixed with excess $\text{NH}_3(\text{aq})$ a slight colour change occurs and cation **Q** is formed.

When cation **Q** is mixed with H_2O_2 , a reddish brown solution is observed.

E^\ominus data for the cobalt complex ions and hydrogen peroxide are given below.

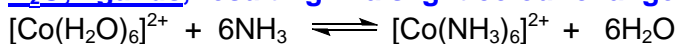


Suggest an explanation for the above observations, giving equations where appropriate and identify the cation **Q**. [5]



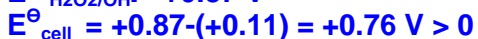
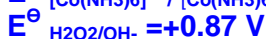
- $E^\ominus_{\text{H}_2\text{O}_2/\text{H}_2\text{O}}$ is less positive than $E^\ominus_{\text{Co}^{3+}/\text{Co}^{2+}}$, H_2O_2 is unable to oxidise $\text{Co}(\text{aq})^{2+}$ to $\text{Co}(\text{aq})^{3+}$ and there is no ligand exchange reaction taking place. Hence, no colour change.

- When excess NH_3 is added, a ligand exchange reaction occurs. NH_3 replaces H_2O , ligands, resulting in a slight colour change.



[explanation & equation: 1m]

- Cation **Q** is $[\text{Co}(\text{NH}_3)_6]^{2+}$.



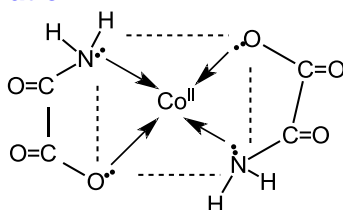
When H_2O_2 is added to Q,

- H_2O_2 oxidises Co^{2+} in $[\text{Co}(\text{NH}_3)_6]^{2+}$ to Co^{3+} in $[\text{Co}(\text{NH}_3)_6]^{3+}$, resulting in a reddish brown solution observed.
- $\text{H}_2\text{O}_2 + 2[\text{Co}(\text{NH}_3)_6]^{2+} \rightarrow 2\text{OH}^- + 2[\text{Co}(\text{NH}_3)_6]^{3+}$

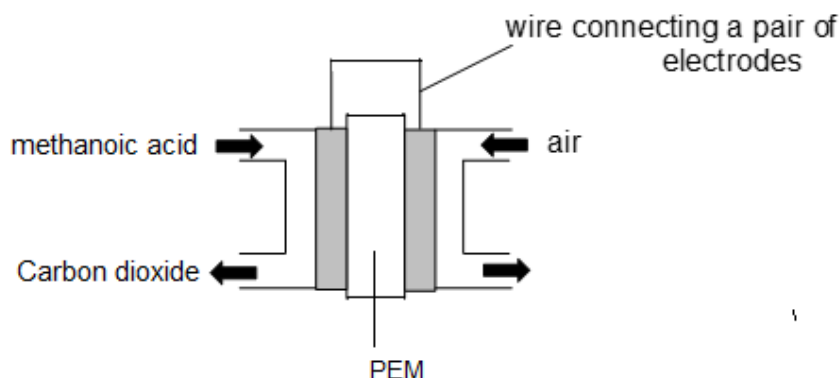
- (e) Explain why the neutral complex formed between a Co^{2+} ion and two $\text{H}_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{CO}_2^-$ ions is soluble in cyclohexane. [1]

It is a simple covalent molecule. The weak van der Waals' forces of attraction formed between Co-complex and cyclohexane molecules liberate sufficient energy to overcome van der Waals' forces of attraction between Co-complex molecules and those between cyclohexane molecules.

For your information:



The direct oxidation of methanoic acid in a fuel cell, DFAFC, shown below represents potentially the most efficient method of obtaining useful energy from a renewable fuel.



- (f) The electrons pass around the external circuit to the cathode. The protons produced migrate across the proton exchange membrane, PEM, to the cathode, where they react with oxygen from air, producing water.

Write the equations for the anode and cathode reactions. Hence construct the equation for the overall reaction. [2]

- $\text{HCO}_2\text{H} \rightarrow \text{CO}_2 + 2\text{H}^+ + 2\text{e}^-$ [Anode]
- $\text{O}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2\text{O}$ [cathode]
- $2\text{HCO}_2\text{H} + \text{O}_2 \rightarrow 2\text{CO}_2 + 2\text{H}_2\text{O}$ [overall reaction]

- (g) One method for the construction of DFAFC, involves electroplating a layer of platinum onto the surface of the proton exchange membrane, PEM. The electrolyte for this

process is a solution containing $\text{Pt}(\text{NH}_3)_4^{2+}$ and Cl^- ions. The PEM is the cathode in this electrolytic cell.

- (i) Suggest the half-equation for the cathode reaction that deposits platinum on the PEM.
[1]



- (ii) In one such preparation, a PEM with a surface area of 25 cm^2 was immersed in an electrolyte bath and a current of 0.0875 A was passed for 95 minutes.

Calculate the mass of platinum deposited onto the surface of PEM.
[2]

- $Q = It = 0.0875 \times 95 \times 60 = 498.75 \text{ C}$
 $\text{No of mol of electrons} = 498.75/96500 = 5.17 \times 10^{-3} \text{ mol}$
 $\text{No of mol of Pt deposited} = 5.17 \times 10^{-3}/2 = 2.58 \times 10^{-3} \text{ mol}$
- $\text{mass of Pt deposited} = 2.58 \times 10^{-3} \times 195 = 0.504 \text{ g}$

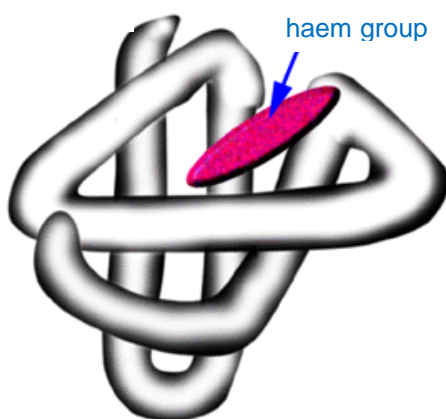
[working : 1m & answer:1m]

[Total: 20]

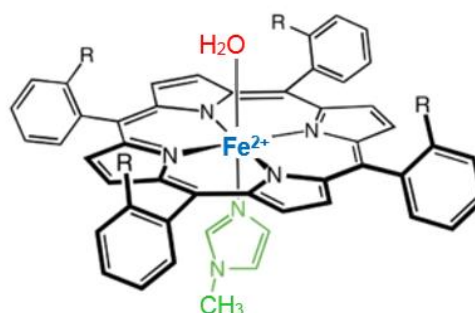
- 5 (a) Myoglobin and haemoglobin are globular proteins that serve to bind and deliver oxygen. The former serves as an intracellular storage site for oxygen in the muscle tissues, while the latter transports oxygen in the bloodstream.

Each myoglobin molecule contains one haem group.

In deoxygenated myoglobin, a water ligand is weakly bound to the Fe^{2+} of the haem group as shown:



Myoglobin



Haem group in deoxygenated myoglobin

- (i) Briefly describe how myoglobin maintains its three-dimensional shape.

[2]

• It is maintained by the interactions between the R-groups of the amino acids, such as • hydrogen bonds between polar groups ($-\text{OH}$, $-\text{NH}_2$), ionic bonds between oppositely charged groups ($-\text{CO}_2^-$ & $-\text{NH}_3^+$), van der Waals' forces of attraction between non-polar side chains (e.g: alkyl group) and disulfide linkages between $-\text{SH}$ groups.

- (ii) In the presence of the haem group, the polypeptide chain coalesces into a myoglobin molecule.

With the aid of the equation,

$$\Delta G = \Delta H - T\Delta S$$

and by considering the chemical interactions involved, explain why this is a spontaneous process at low temperatures.

[2]

• **The bending and folding of the primary structure into a tertiary structure is exothermic (negative ΔH) due to the formation of various interactions between the R-groups of the constituent amino acids.**

• **The process is accompanied by a decrease in entropy (negative ΔS) as the formation of a more ordered myoglobin molecule decreases the degree of disorder because there are now fewer ways in which the molecule and energy can be distributed.**

Hence ΔG is negative at low temperatures.

- (iii) Deoxygenated myoglobin is responsible for the dull purplish red muscle colour, observed in the depth of the muscle. When meat is freshly cut, colour change occurs in two stages:

Stage 1: Bright red colour when muscle surface is exposed to air.

Stage 2: With time, the bright red colour slowly changes to an unattractive, dull brown colour associated with stale and spoiled meat.

With reference to the structure of the haem group and the reaction that occurs in each stage, explain the colour changes involved.

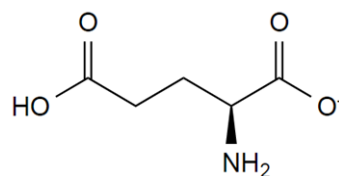
[2]

The colour of meat depends on the ligand attached to the 6th coordinate site in the haem group, and the oxidation stage of the iron centre.

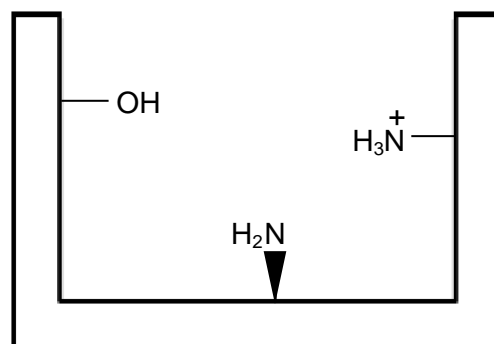
• **When the meat is exposed to oxygen from the air, ligand exchange (oxygenation) occurs to form oxymyoglobin. O_2 replaces H_2O ligand and is dative bonded to the haem group, which gives the bright red colour observed.**

• **When meat has been stored for too long, the Fe^{2+} in the haem group undergoes oxidation to form Fe^{3+} , which gives rise to the dull brown colour.**

- (b) One of the isolated compounds that is primarily responsible for the umami (savory) flavor is glutamate, which is a salt formed from glutamic acid that is commonly found in meat.

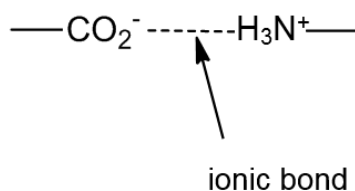
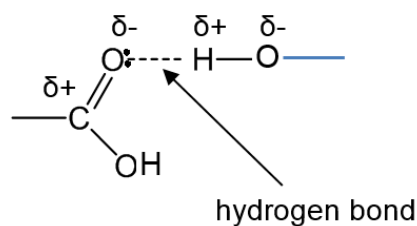
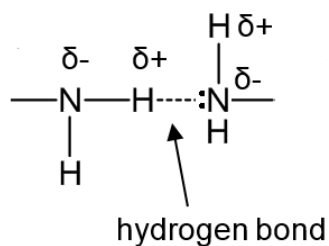


It is thought that glutamate stimulates a specific receptor site located in the taste buds on the tongue, which is essentially a protein molecule. A simplified diagram of the receptor site is shown below:



- (i) State **two** different types of interactions that can be formed between glutamate and the receptor protein. Illustrate your answer with labelled diagram(s). [2]

••Any two illustrated

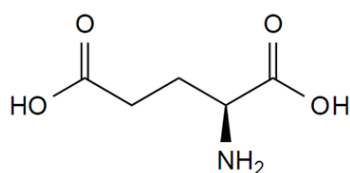


- (ii) To enhance the flavor of food, many retailers in the food industry use monosodium glutamate (MSG) as a food additive, which can be easily synthesized in the laboratory.

Given that laboratory synthesis gives a racemic mixture, explain why 50% of the glutamate synthesized in the laboratory is unable to bind precisely with the correct orientation to the receptor protein. [1]

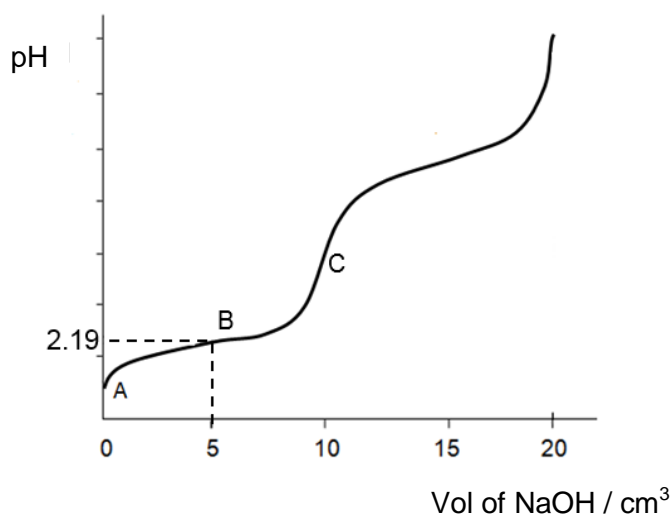
- Only one mirror image form of glutamate synthesized provides the desired biological effect as it has the correct orientation to bind to the protein receptors. The other form is inactive.

The structure of glutamic acid is shown below:



glutamic acid

10 cm³ of the fully protonated glutamic acid is titrated with 20 cm³ of 1.00 mol dm⁻³ sodium hydroxide solution. Its titration curve is shown below:



- (iii) Show that the concentration of glutamic acid is 1.0 mol dm⁻³ at A. [1]

$$n(\text{NaOH}) \text{ used to reach 1}^{\text{st}} \text{ endpoint} = 0.010 \text{ mol}$$

$$n(\text{glutamic acid}) = 0.010 \text{ mol}$$

$$\bullet [\text{glutamic acid}] = 0.010/0.0100 = 1.0 \text{ mol dm}^{-3}$$

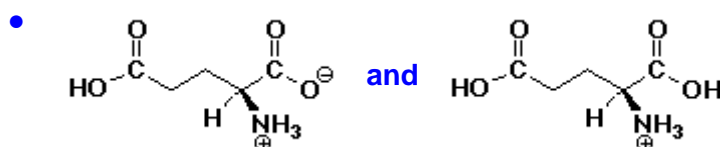
- (iv) Hence, calculate the pH of the solution at **A**.
[1]

$$[\text{H}^+] = \sqrt{K_{a1} \times c} = \sqrt{10^{-2.19} \times 1.0} = 0.0804 \text{ mol dm}^{-3}$$

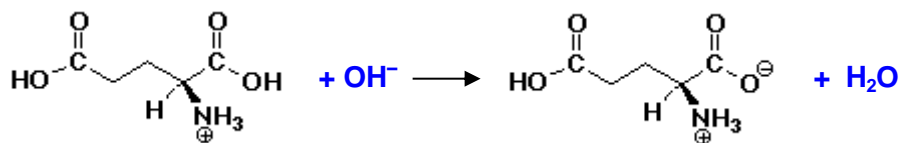
$$\bullet \text{pH at A} = -\log_{10}(0.0804) = 1.10$$

- (v) Identify the specie(s) present at **B**.

With the help of an equation, explain how the solution at **B** can resist a change in pH when a small amount of base is added. [2]



• When a small amount of alkali is added,



Negligible change in pH as OH^- ions are removed.

- (vi) In a separate experiment, the solution at **B** was reacted with 10.0 cm^3 of 0.05 mol dm^{-3} sodium hydroxide.

Calculate the pH of the mixture after the reaction.

You may find it useful to represent the fully protonated glutamic acid as HA. [2]



$$\text{At point B, } n_{\text{HA}} = n_{\text{A}^-} = 0.010 / 2 = 0.005 \text{ mol}$$

$$\text{Number of moles NaOH added} = 0.05 \times 10/1000 = 5.00 \times 10^{-4} \text{ mol}$$

$$\text{Number of moles HA at equilibrium} = 0.005 - 5.00 \times 10^{-4} \text{ mol} = 0.0045 \text{ mol}$$

$$\text{Number of moles A}^- \text{ at equilibrium} = 0.005 + 5.00 \times 10^{-4} \text{ mol} = 0.0055 \text{ mol}$$

$$\bullet \text{pH} = \text{pK}_a + \lg [\text{salt}]/[\text{acid}]$$

$$= 2.19 + \lg \{(0.0055/0.025) / (0.0045/0.025)\} = 2.28$$

- (c) Compound **P**, $\text{C}_9\text{H}_{11}\text{NO}_2$, rotates plane polarised light and reacts with the following reagents:

- aqueous bromine to give compound **Q**, $\text{C}_9\text{H}_9\text{NO}_2\text{Br}_2$
- sodium carbonate to give a salt
- PCl_5 to give a 5-membered cyclic compound **R**

Deduce the structural formulae of compounds **P**, **Q** and **R**.

[5]

• P rotates plane polarised light \rightarrow P contains a chiral carbon; has no plane of symmetry and a non-superimposable mirror image.

• P reacts with aq Br_2 to give compound Q, $\text{C}_9\text{H}_9\text{NO}_2\text{Br}_2$

\rightarrow P is phenylamine or phenol

\rightarrow one of the 2, 4, 6 positions relative to first substituent on benzene is occupied with another substituent

• P reacts with sodium carbonate to give a salt \rightarrow P contains a $-\text{COOH}$ group.

(Hence, P can't be phenol as molecular formula only contains 2 O atoms)

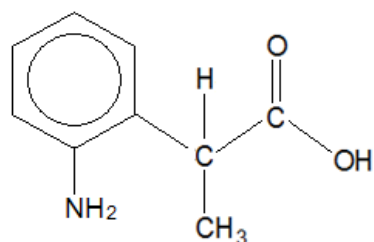
• $-\text{OH}$ in $-\text{COOH}$ reacts with PCl_5 to give $-\text{COCl}$. Formation of 5-membered ring

\rightarrow $-\text{NH}_2$ group in P attacks the electron deficient carbonyl C in the $-\text{COCl}$ group.

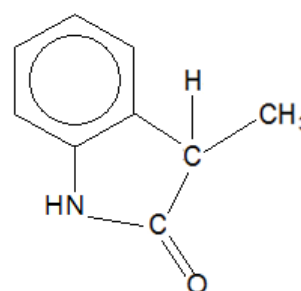
\rightarrow $-\text{NH}_2$ group & the other substituent on benzene ring are ortho to each other.

[4 marking points, max 2 marks]

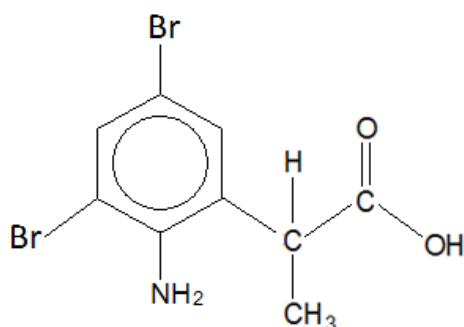
P:



R:



Q:



[1m for each structure]

[Total: 20]