JC2 PRELIMINARY
EXAMINATION HIGHER 2

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| CANDIDATE NAME | |

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**CHEMISTRY** **9647/01**

Paper 1 Multiple Choice **23 September 2016**

**1 hour**

Additional Materials: Multiple Choice Answer Sheet
Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

Write in soft pencil.
Do not use staples, paper clips, highlighters, glue or correction fluid.
Write your name, Centre number and index number on the Answer Sheet in the spaces provided unless this has been done for you.

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.

This document consists of 20 printed pages

## Section A

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

**1** Which of the following quantities is equal to the Avogadro constant?

**A** the number of atoms in 24 $dm^3$ of nitrogen gas at r.t.p. condition

**B** the number of molecules in 1 $dm^3$ of oxygen at 273 K and 1 atm

**C** the number of electrons removed to form $Ne^+$ ions from $6.02 \times 10^{-23}$ mol of Ne atoms

**D** the number of ions in 83.5 g of $[Co(NH_3)_5Cl]Cl_2$

**2** Which of the following species has no unpaired electrons?

**A** Fe **B** $Ge^{2+}$ **C** Si **D** $Ti^{3+}$

**3** Why is the molecule of $BCl_3$ planar, whereas the molecule of $PH_3$ is pyramidal?

**A** The repulsion between chlorine atoms is greater than that between hydrogen atoms.

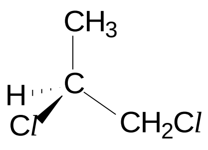
**B** The covalent radius of chlorine is greater than that of hydrogen.

**C** The boron atom is $BCl_3$ has six electrons in its valence shell, whereas the phosphorus atom in $PH_3$ has eight**.**

**D** The boron atom has no d-orbitals available for bonding.

**4** In which pair do the isomers have identical boiling points?

**A**



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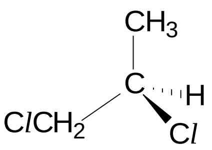
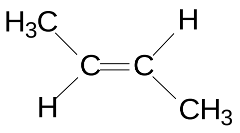


**B**



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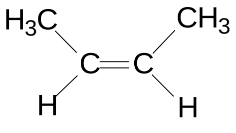


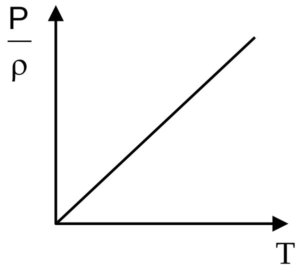
**C** $CH_3CH_2CH_2CH_2OH$ and $(CH_3)_2CHCH_2OH$

**D** $CH_3(CH_2)_4CH_3$ and $(CH_3)_2CHCH(CH_3)_2$

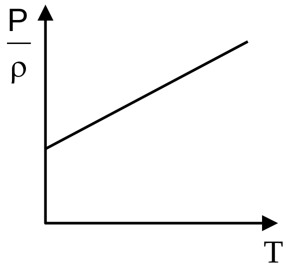
**5** Which of the following shows a graph of $\frac{P}{\rho}$ against T for an ideal gas?

(P = pressure; $\rho$ = density; T = temperature in °C).

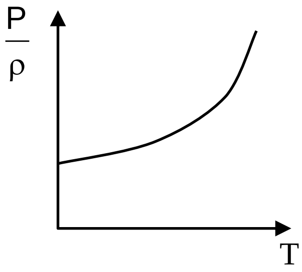
**A**



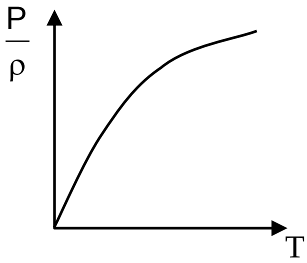
**B**



**C**



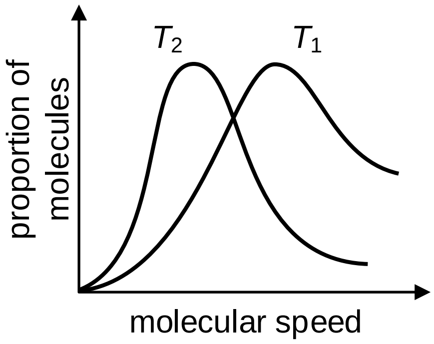
**D**



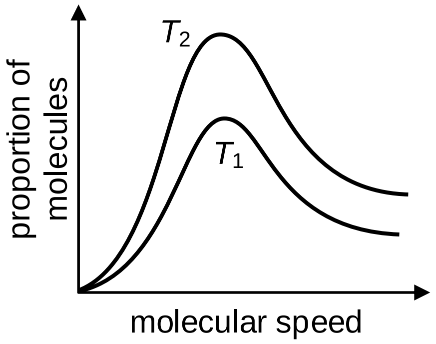
**6** One mol of neon gas at temperature $T_1$ was added to another one mol of neon and the temperature was increased to $T_2$.

Which of the following diagrams correctly represents the Boltzmann distribution of molecular speeds before and after the changes were made?

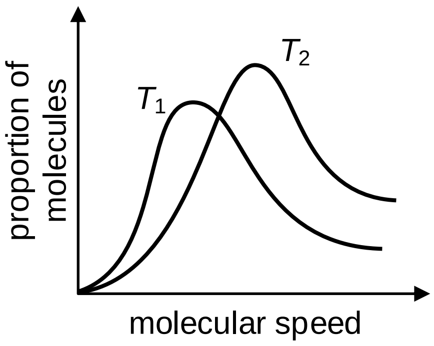
**A**



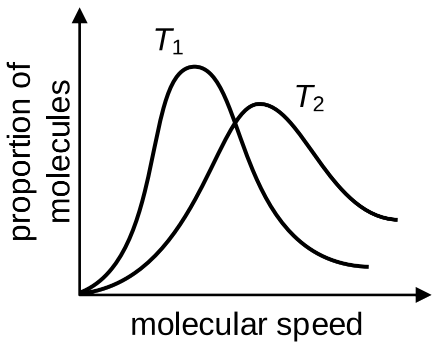
**B**



**C**



**D**



**7** *Use of Data Booklet is relevant to this question.*

Dinitrogen oxide burns in ethyne to produce water vapour, carbon dioxide and nitrogen gas as the only products.

$$5N_2O(g) + C_2H_2\ (g) \rightarrow H_2O(g) + 2CO_2(g) + 5N_2(g)$$

Given that the N=N and N=O bond energies in dinitrogen oxide are +418 kJ $mol^{-1}$ and +686 kJ $mol^{-1}$ respectively, what is the enthalpy change of the reaction?

**A** +1670 kJ $mol^{-1}$

**B** +1710 kJ $mol^{-1}$

**C** –1670 kJ $mol^{-1}$

**D** –1710 kJ $mol^{-1}$

**8** Quarter-life, $t_{1/4}$, of a radioactive isotope is defined as the time taken for the sample to decay to ¼ its original amount.

Potassium-argon dating is used to determine the age of a rock. $^{40}K$ is a radioactive isotope of potassium and it decays to $^{40}Ar$ with a constant $t_{1/4}$ of 2.50 x $10^9$ years. A sample of moon rock was found to contain 6.25% of the original amount of $^{40}K$.

How old is the rock?

**A** 2.50 x $10^9$ years

**B** 5.00 x $10^9$ years

**C** 7.50 x $10^9$ years

**D** 1.00 x $10^{10}$ years

**9** During electrolysis, 0.785 g of chromium is deposited on the cathode when 8690 C of electricity is passed into a chromium-containing electrolyte.

Which of the following could have been the electrolyte?

**A** $CrCl_2$

**B** $CrCl_3$

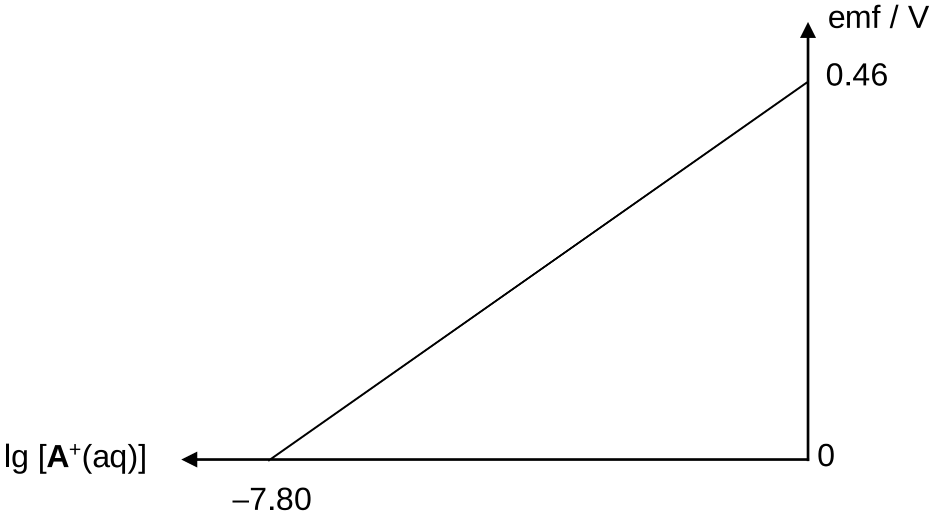
**C** $K_2CrO_3$

**D** $K_2Cr_2O_7$

**10** *Use of the Data Booklet is relevant to this question.*

The graph below shows the variation in electromotive force (emf) of the following electrochemical cell with lg [**A**$^+$(aq)] at 298 K.

Cu(s) | Cu$^{2+}$(aq, 1 mol dm$^{-3}$) || **A**$^+$(aq) | **A**(s)



Which of the following statements is incorrect?

**A** Cu(s) is the negative electrode.

**B** The direction of electron flow in the external circuit will be reversed when the concentration of **A**$^+$(aq) is 1.00 x 10$^{-7}$ mol dm$^{-3}$.

**C** The standard electrode potential of the **A**$^+$(aq) | **A**(s) half-cell is +0.80 V.

**D** The emf of the given cell under standard conditions will be +0.46 V.

**11** Gas **D** dissociates on heating to set up the equilibrium below:

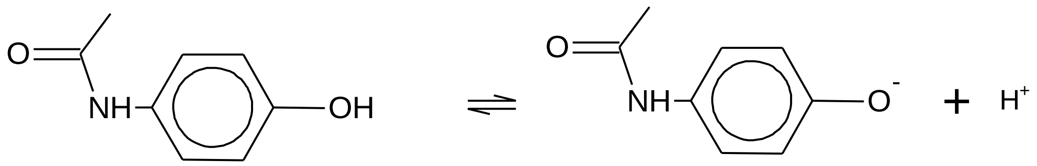
$$\mathbf{D}(g) \rightleftharpoons \mathbf{E}(g) + \mathbf{F}(g)$$

A quantity of **D** was heated at a constant pressure, p, at a certain temperature. The equilibrium partial pressure of **D** was found to be $\frac{1}{7}$p.

What is the equilibrium constant, $K_p$, at this temperature?

**A** $\frac{6p}{7}$ **B** $\frac{9p}{7}$ **C** $\frac{36p}{7}$ **D** 6p

**12** Paracetamol (p$K_a$ = 9.5) is a widely used over-the-counter pain reliever and fever reducer. Its solubility in water is 12.78 mg cm$^{-3}$ at 25 °C. ($M_r$ of Paracetamol = 151.0)



paracetamol

What is its pH in water at 25 °C?

**A** 1.07

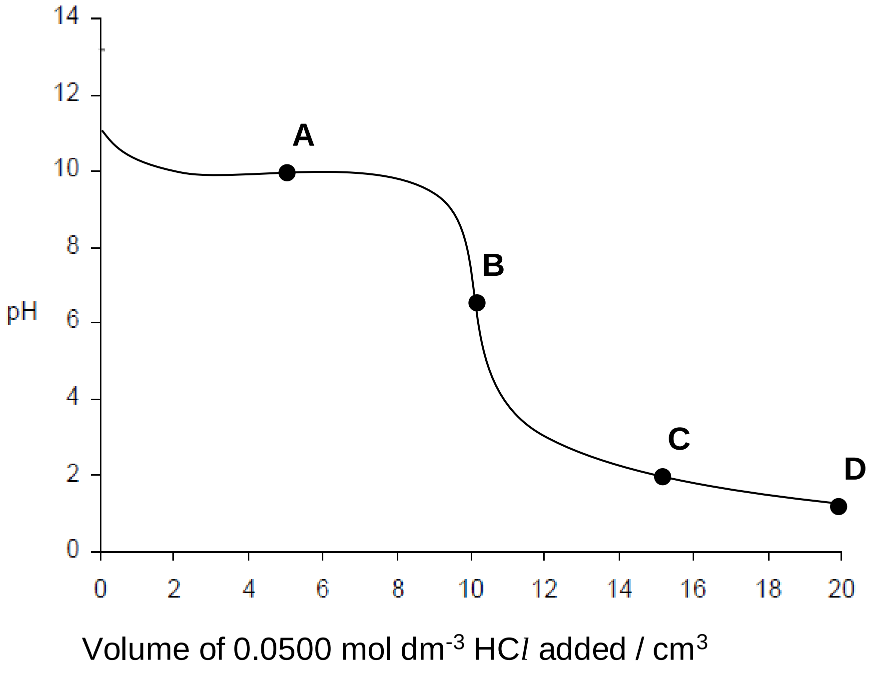
**B** 5.29

**C** 6.79

**D** 8.71

**13** The pH change when 0.0500 mol dm$^{-3}$ HC*l* is added dropwise to 5.00 cm$^3$ of 0.100 mol dm$^{-3}$ $CH_3NH_2$ (aq) is shown in the graph below.

At which point on the graph is pH= 14 - p$K_b$, where $K_b$ is the base dissociation constant of the weak base?



**14** Which of the following statements explains the observations that magnesium hydroxide dissolves in ammonium chloride, but not in aqueous sodium chloride?

**A** The ammonium ion changes the solubility product of $Mg(OH)_2$.

**B** $NH_4^+$ ion is first formed, and then acts through a common ion effect.

**C** $NH_4Cl$ dissociates less fully than $NaCl$.

**D** The $NH_4^+$ ion acts as an acid.

**15** A saturated solution of $Ca(OH)_2$ is found to have a pH of 12.3 at 25 °C.

Which of the following statements is incorrect?

**A** The $K_{sp}$ of $Ca(OH)_2$ is $4 \times 10^{-6}$ mol$^{\mathbf{3}}$ dm$^{-9}$.

**B** The solubility of $Ca(OH)_2$ would increase when temperature is raised to 35 °C.

**C** The solubility of $Ca(OH)_2$ will decrease when solid $Na_2O$ is added.

**D** The pH of the solution would increase when $Ca(NO_3)_2$ is added

**16** *Use of the Data Booklet is relevant to this question.*

Natural water in reservoirs often contains very finely divided solid particles of between 1 and 100 nm in diameter which have negative charges on their surface.

One stage in the water purification process consists of adding salt solutions containing high charge-density cations which will neutralise the negative charges and cause the solid particles to join together and be precipitated out.

Which compound, in aqueous solution, would be the most effective in precipitating the finely divided solid particles?

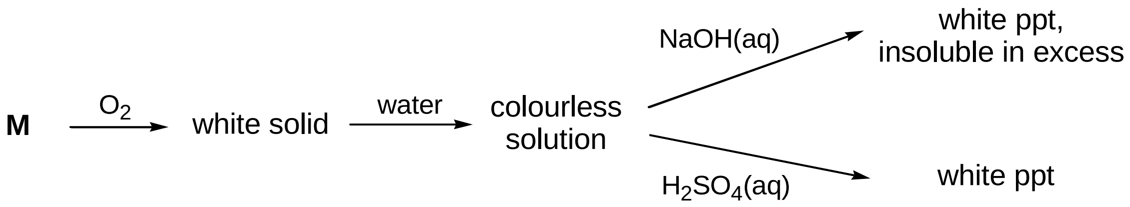
**A** $AlCl_3$

**B** $MgCl_2$

**C** $SiCl_4$

**D** $PCl_3$

**17**



Based on the information above, what could element **M** be?

**A** aluminium

**B** calcium

**C** potassium

**D** silicon

**18** HC*l* is stable to heat, but HI decomposes into its elements when heated.

What is the reason for this difference?

**A** HI is a stronger reducing agent than HC*l*.

**B** C*l*–C*l* bond is stronger than I–I bond.

**C** H–C*l* bond is stronger than H–I bond.

**D** HI is more volatile than HC*l*.

**19** *Use of the Data Booklet is relevant to this question.*

Which of the following solutions would result in a colour change when left to stand in the atmosphere?

**A** an acidified solution of cobalt(II) nitrate

**B** a solution of potassium hexacyanoferrate(III)

**C** an acidified solution of tin(II) chloride

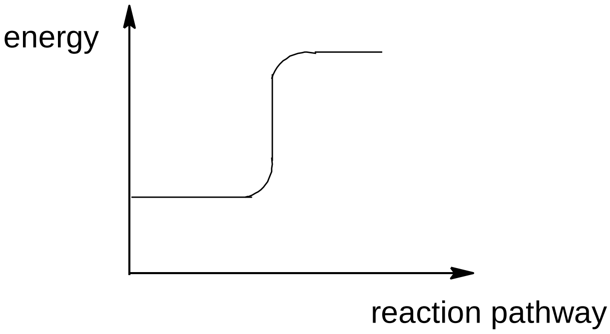
**D** an acidified solution of vanadium(II) sulfate

**20** Adding concentrated $HCl(aq)$ to $CuSO_4(aq)$ causes the colour of the solution to change from blue to green.

Which of the following row correctly shows the number of d-electrons and the energy gap between the d-orbitals, before and after the reaction?

| | number of d-electrons | energy gap between the d-orbitals |
|---|---|---|
| **A** | changes | changes |
| **B** | changes | remains the same |
| **C** | remains the same | changes |
| **D** | remains the same | remains the same |

**21** In the reaction of methane with chlorine in the presence of light, the following energy level diagram (for single reaction step) is obtained.



To which of the following steps does this diagram apply?

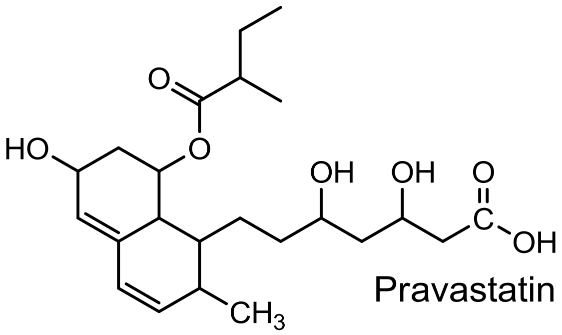
**A** $\bullet CH_3 + \bullet CH_3 \longrightarrow C_2H_6$

**B** $CH_4 + \bullet Cl \longrightarrow CH_3Cl + \bullet H$

**C** $\bullet CH_3 + Cl_2 \longrightarrow CH_3Cl + \bullet Cl$

**D** $Cl_2 \longrightarrow \bullet Cl + \bullet Cl$

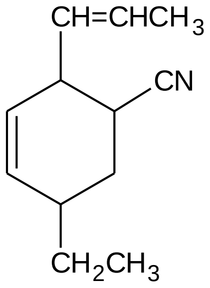
**22** The cholesterol-lowering agents called statins, such as pravastatin, are among the most widely prescribed drugs in the world.



How many chiral centres are present in the product when pravastatin was treated with $H_2$, Ni catalyst at 200 $^0$C?

**A** 6 **B** 7 **C** 8 **D** 9

**23**



compound **P**

Which of the following statements about compound **P** is incorrect?

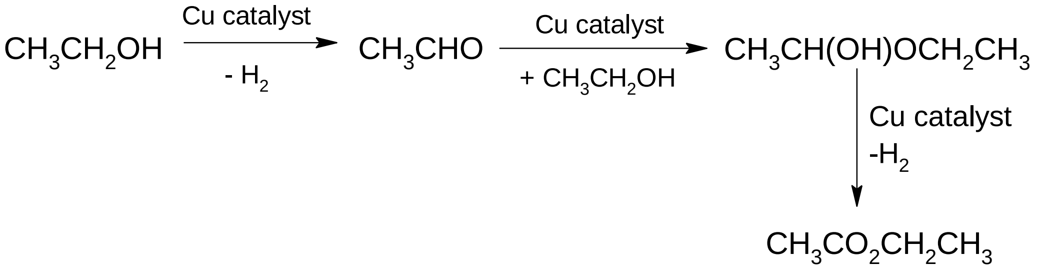
**A** There is only one *sp* hybridised carbon atom in a molecule of **P**.

**B** A molecule of **P** contains four $\pi$ bonds.

**C** After **P** reacts with HC*l*(g), all but one carbon atom in the product formed are $sp^3$ hybridised.

**D** After **P** reacts with LiA*l*$H_4$, all the carbon atoms in the product formed are $sp^3$ hybridised.

**24** Industrially, ethyl ethanoate may be prepared from cheap, low-grade ethanol as follows:



Which process is included in the above reaction sequence?

**A** disproportionation

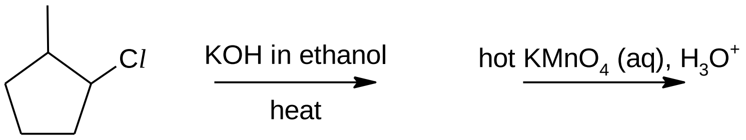
**B** electrophilic addition

**C** nucleophilic addition

**D** reduction

**25** Which process will **not** give a good yield of $CH_3CO(CH_2)_3CO_2H$?

**A**



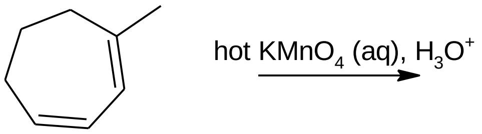
**B**

$H_2NCO(CH_2)_3CHClCH_3 \xrightarrow[\text{heat}]{\text{KOH(aq)}} \xrightarrow{\text{hot } KMnO_4 \text{ (aq), } H_3O^+}$

**C**

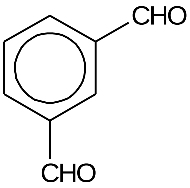
$CH_3CH(OH)(CH_2)_3CH_2Cl \xrightarrow[\text{heat}]{\text{NaOH in ethanol}} \xrightarrow{\text{hot } KMnO_4 \text{ (aq), } H_3O^+}$

**D**



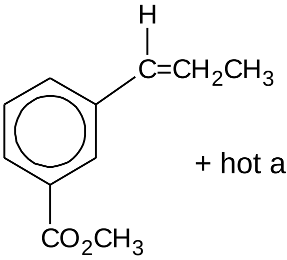
**26** Which of the following reactions would **not** produce 1,3-dicarboxylic acid?

**A**



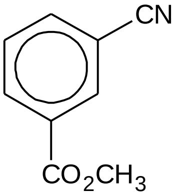
+ Fehling's solution followed by acidification

**B**



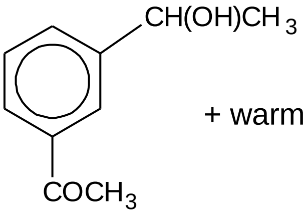
+ hot acidified potassium manganate(VII)

**C**



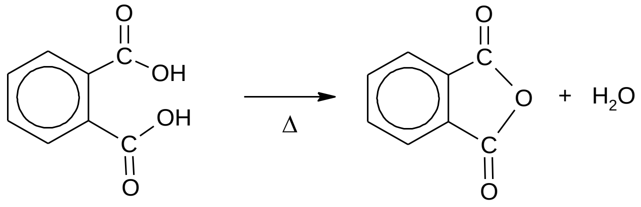
+ aq $H_2SO_4$, heat

**D**



+ warm, alkaline aqueous iodine followed by acidification

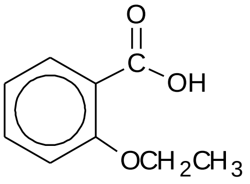
**27** When heated strongly, phthalic acid undergoes condensation reaction to form phthalic anhydride.



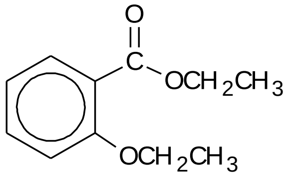
phthalic acid    phthalic anhydride

On reaction with water, the anhydride gives phthalic acid. What would be formed when phthalic anhydride reacts with ethanol instead of water?

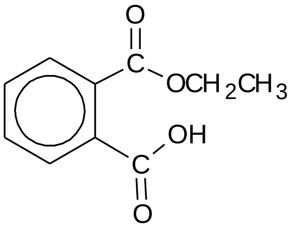
**A**



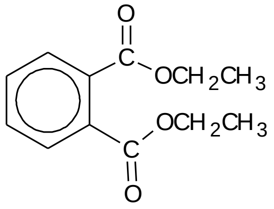
**B**



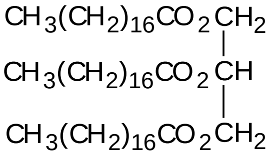
**C**



**D**

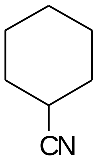


**28** Experiments are carried out on three compounds **Q**, **R**, and **S**.



$$\begin{array}{l} CH_3(CH_2)_{16}CO_2CH_2 \\ CH_3(CH_2)_{16}CO_2CH \\ CH_3(CH_2)_{16}CO_2CH_2 \end{array}$$

**Q**



**R**

$BrCH_2CH_2CH_2Br$

**S**

A sample of 0.01 mol of each compound is heated under reflux with 50 $cm^3$ of 1 mol $dm^{-3}$ aqueous NaOH (in excess) until hydrolysis is completed and any ammonia gas produced was expelled from the solution. The excess NaOH was then titrated in each case and was found to require 20 $cm^3$, 30 $cm^3$ and 40 $cm^3$ of 1 mol $dm^{-3}$ HC*l* for neutralisation.

Which sequence of compounds matches these results?

| | 20 $cm^3$ | 30 $cm^3$ | 40 $cm^3$ |
|---|---|---|---|
| **A** | **Q** | **R** | **S** |
| **B** | **Q** | **S** | **R** |
| **C** | **R** | **S** | **Q** |
| **D** | **S** | **R** | **Q** |

**29** Why are amides, $RCONH_2$, less basic than amines, $RNH_2$?

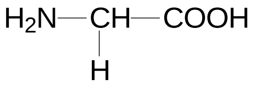
**A** Amides form zwitterion in which the nitrogen atom carries a positive charge.

**B** Amides have a resonance structure involving the movement of a pair of electrons from the nitrogen atom to the oxygen atom.

**C** Electrons on the nitrogen atom move on the C-N bond giving it some double bond character so that it is more difficult to break.

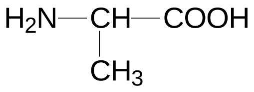
**D** The amide carbonyl group withdraws electrons from the $NH_2$ group to make the hydrogen atoms more acidic.

**30** Silk fibroin is a type of fibrous protein made up almost entirely of β–pleated sheets. The main amino acids found in silk fibroin are alanine, glycine, serine and cysteine. The structures of these amino acids are given below.



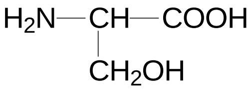
$H_2N-\underset{\underset{H}{|}}{CH}-COOH$

*glycine*



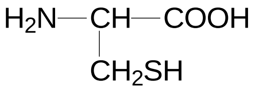
$H_2N-\underset{\underset{CH_3}{|}}{CH}-COOH$

*alanine*



$H_2N-\underset{\underset{CH_2OH}{|}}{CH}-COOH$

*serine*



$H_2N-\underset{\underset{CH_2SH}{|}}{CH}-COOH$

*cysteine*

Which of the following statements about the type of interactions present in silk fibroin is incorrect?

**A** The β–pleated sheets are held together by hydrogen bonding.

**B** There are van der Waals' forces between glycine and alanine in the protein.

**C** There are disulfide linkages present in silk fibroin.

**D** Serine forms ionic bonds with another serine amino acid in the protein.

## Section B

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 that 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** A 0.0200 mol sample of an oxochloride of **T**, **T**OC$l_y$ required 10.00 cm$^3$ of 0.400 mol dm$^{-3}$ acidified potassium manganate(VII) for oxidation to **T**O$_3^-$ ions.

Which of the following statements are correct?

**1** 5 mol **T**OC$l_y$ react with 1 mol MnO$_4^-$.

**2** The change in oxidation state of **T** in the reaction is +1.

**3** The value of y in **T**OC$l_y$ is 2.

**32** The ion **U**$^{5+}$ has 38 electrons and 46 neutrons.

Which of the following statements are correct?

**1** In an electric field, the ion **U**$^{5+}$ will be deflected to the same extent as the yttrium ion, $^{89}Y^{5+}$.

**2** The electronic configuration of **U**$^{5+}$ is [Kr] 4d$^2$.

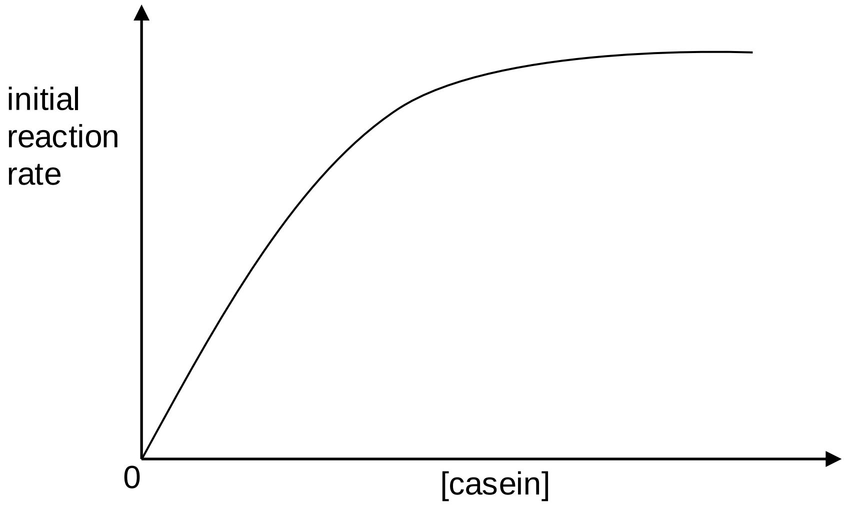
**3** The third ionisation energy of element **U** is significantly higher than its second ionisation energy.

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 graph shows the results of an investigation of the initial rate of hydrolysis of casein by the enzyme trypsin. In the experiments, the initial concentration of casein was varied but that of trypsin was kept constant.



Which conclusions can be deduced from these results?

**1** When [casein] is low, the rate is first order with respect to [casein].

**2** When [casein] is high, the rate is dependent of [trypsin].

**3** When [casein] is high, the rate is dependent of [casein].

**34** Button cells are tiny cells used to power small electronic devices such as wrist watches and calculators. One such cell consists of lithium electrode and a paste of manganese(IV) oxide electrode dipped in an organic electrolyte. The e.m.f. produced by the cell is 3.00 V. In discharging the cell, $LiMnO_2$ will be formed.

Which of the following statements about the Li-$MnO_2$ cell are correct?

**1** Electrons flow from the lithium electrode to the manganese(IV) oxide electrode.

**2** The equation for the reaction at the cathode is $MnO_2 + e \rightarrow MnO_2^-$.

**3** Water is added to manganese(IV) oxide to form the paste.

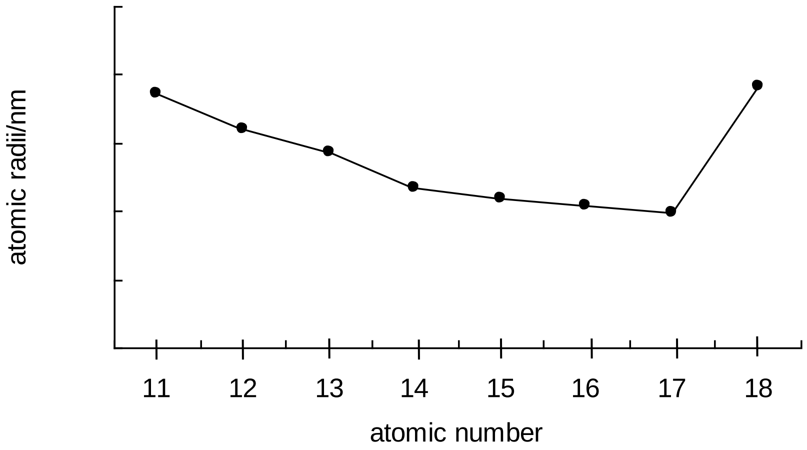
The responses **A** to **D** should be selected on the basis of

| 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 |

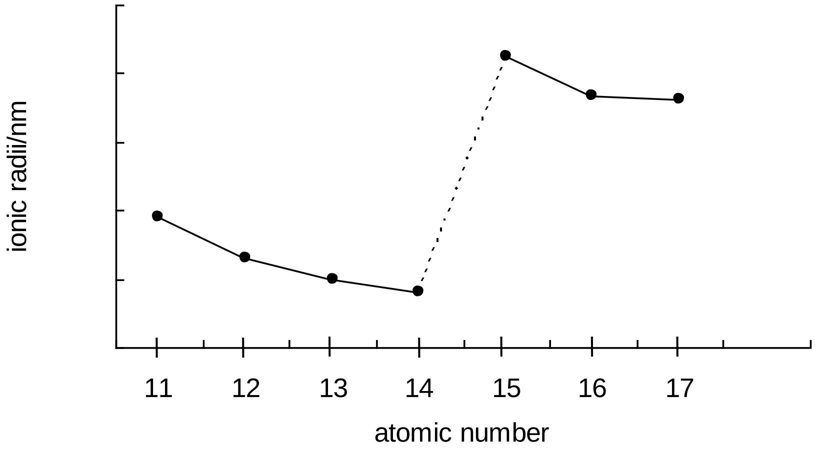
No other combination of statements is used as a correct response.

**35** Which of the following graphs correctly represents the variation in the specified property of the elements in Period 3?

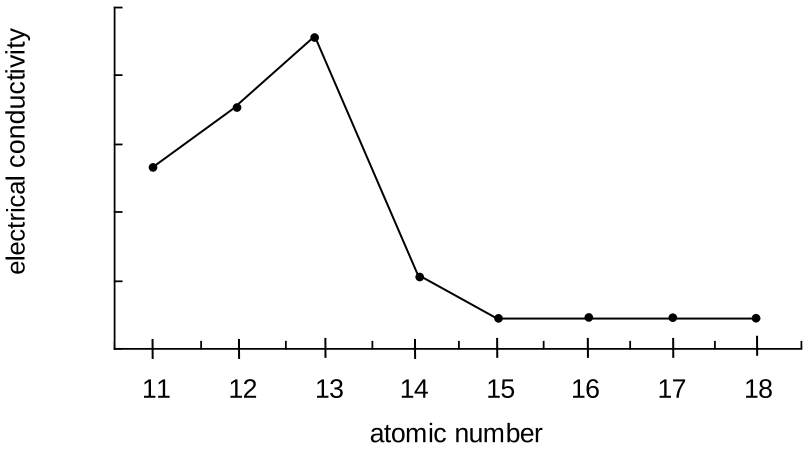
**1**



**2**



**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.

**36** For the reaction,

$(CH_3)_3CX + CH_3CH_2O^- \rightarrow (CH_3)_3COCH_2CH_3 + X^-$ (where X = C*l*, Br or I)

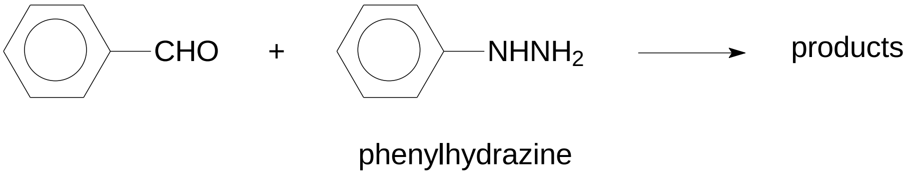
which of the following statements are likely to be correct?

**1** The reaction involves an electrophilic attack by $CH_3CH_2O^-$.

**2** The rate determining step involves the formation of a carbocation.

**3** The reaction will take place more rapidly when X is I than when X is C*l*.

**37** The reaction of phenylhydrazine is similar to that of 2,4-dinitrophenylhydrazine.



Which changes in bonding occur in the reactants and products during the reaction above?

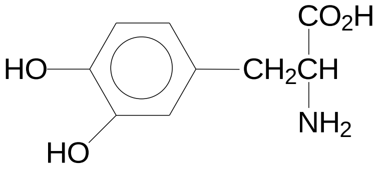
| | **Bond broken** | **Bond formed** |
|---|---|---|
| **1** | C–H | C–C |
| **2** | N–H | O–H |
| **3** | C=O | C=N |

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** *Dopamine* is a neurotransmitter found in many animals, including vertebrates and invertebrates.



*Dopamine*

Which of the following statements are **correct**?

**1** 1 mole of *dopamine* reacts with 3 moles of acyl chloride

**2** 1 mole of *dopamine* reacts with 1.5 moles of $Br_2$(aq).

**3** 1 mole of *dopamine* reacts with 3 moles of $Na_2CO_3$.

**39** Compound **V**, with molecular formula $C_6H_{12}$, was reacted with acidified potassium manganate(VII) and the resultant mixture obtained was colourless. The mixture was thereafter distilled to form distillate **W** and residual solution **X**.

Distillate **W** is able to form a yellow precipitate with alkaline aqueous iodine. Residual solution **X** reacts with sodium carbonate to form a colourless gas.

Which of the following statements are **true**?

**1** Compound **V** will decolourise aqueous bromine.

**2** Distillate **W** can form an orange precipitate with 2,4-dinitrophenylhydrazine.

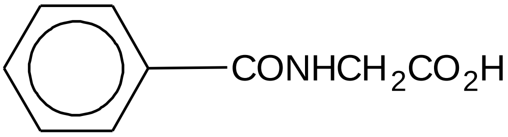
**3** Residual solution **X** can form white fumes with $PCl_5$.

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** Benzoylglycine (hippuric acid) was first isolated from stallions' urine.



Benzoylglycine

Which properties does this compound possess?

**1** It can be hydrolysed to produce an amino acid.

**2** It can be made by reacting benzoyl chloride with aminoethanoic acid.

**3** It can be neutralised by reaction with cold aqueous sodium hydroxide.

**End of Paper**

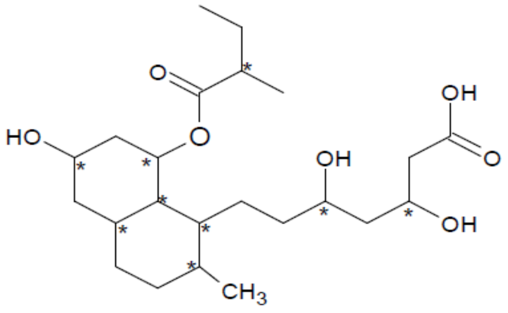
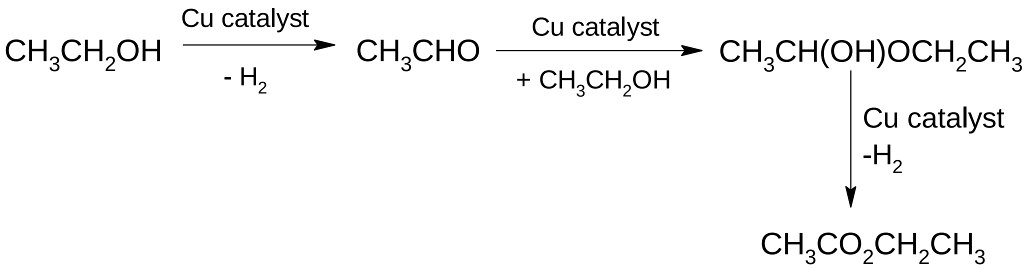
## H2 Chemistry Preliminary Examination Paper 1 Worked solution

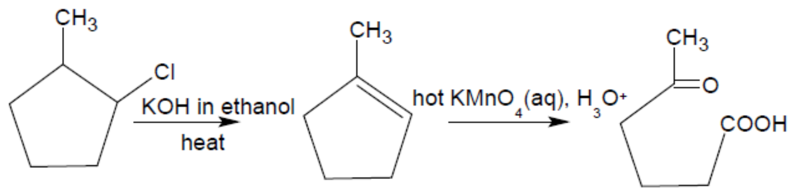
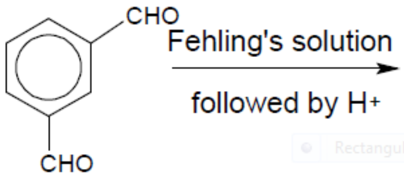
| | | |
|---|---|---|
| **1** | D | **Option A** is wrong: the number of atoms in 24 $dm^3$ of nitrogen gas at r.t.p. condition<br>24 $dm^3$ $N_2 \equiv$ 1 mol $N_2 \equiv$ 2 mol N $\equiv$ 2 x L<br><br>**Option B** is wrong: the number of molecules in 1 $dm^3$ of oxygen at 273 K and 1 atm<br>1 $dm^3$ $O_2 \equiv$ 1/22.4 mol $O_2 \equiv$ 1/22.4 x L<br><br>**Option C** is wrong: the number of electrons removed to form $Ne^+$ ions from 6.02 x $10^{-23}$ mol of Ne atoms<br>No of electrons removed = (6.02 x $10^{23}$) x (6.02 x $10^{-23}$) = $6.02^2$ electrons<br><br>**Option D is correct**: the number of ions in 83.5 g of $[Co(NH_3)_5Cl]Cl_2$<br>Amount = 83.5/250.4 = 1/3 mol<br>1 mol $[Co(NH_3)_5Cl]Cl_2 \equiv$ 3 mol ions<br>1/3 mol $[Co(NH_3)_5Cl]Cl_2 \equiv$ 1 mol ions = L |
| **2** | B | **Option A** is wrong: ${}_{26}Fe$ : [Ar] $3d^6$ $4s^2$ (one unpaired d-orbital)<br>**Option B is correct**: ${}_{32}Ge^{2+}$ : [Ar] $3d^{10}$ $4s^2$ (no unpaired, all paired)<br>**Option C** is wrong: ${}_{14}Si$ : [Ne] $3s^2$ $3p^2$ (two unpaired p-orbitals)<br>**Option D** is wrong: ${}_{22}Ti^{3+}$ : [Ar] $3d^1$ (one unpaired d-orbital) |
| **3** | C | By VSEPR theory, $BCl_3$ has 3 bond pairs, and no lone pairs. This give rise to trigonal planar structure.<br>$PH_3$ has 3 bond pairs and 1 lone pair, therefore it is trigonal pyramidal structure. |
| **4** | A | The molecules in option **A** are a pair of enantiomers. Enantiomers are known to have identical chemical and physical properties, with the exception of its ability to rotate plane polarised light. Therefore the enantiomers will have identical boiling point. |
| **5** | B | **Option A** is wrong : $P = \frac{\rho RT}{M_r}$<br>$\frac{P}{\rho} = kT = k$ (t °C + 273) (similar to y = mx + c)<br>Plot wrong as y-intercept is zero. Note temp axis is in °C and y-intercept = 273$k$.<br>**Option B is correct**: $\frac{P}{\rho} = kT = k$ (t + 273) (similar to y = mx + c)<br>**Option C** is wrong: Not a linear plot of y = mx + c<br><br>**Option D** is wrong: Not a linear plot of y = mx + c |

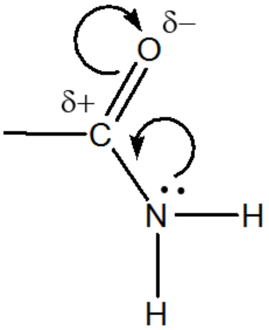
<table>
<tr><td>**6**</td><td>C</td><td>One mol of neon gas at temperature $T_1$ was added to another one mol of neon and the temperature was increased to $T_2$.<br>As such, the area under the curve should increase since there is an increase in the number of moles of gases.<br>When temperature increases to $T_2$, the curve should tend to the right as the molecular speed should increase at a higher temperature.<br>**Option C** is correct</td></tr>
<tr><td>**7**</td><td>C</td><td>ΔH = (5(BE(N=N) + BE(N=O)+2BE(C-H) + BE(C≡C)) – (2BE(O-H) + 4BE(C=O) + 5(N≡N))<br>= (5(418 + 686)+2(410) + (840)) – (2(460) + 4(740) + 5(994))<br>= - 1670 kJ $mol^{-1}$</td></tr>
<tr><td>**8**</td><td>B</td><td><table>
<tr><th>No. of quarter life</th><th>Amount of $^{40}K$ left</th></tr>
<tr><td>0</td><td>100%</td></tr>
<tr><td>1</td><td>25%</td></tr>
<tr><td>2</td><td>6.25%</td></tr>
</table>
Since two quarter life have passed, the time required would be $2.5 \times 10^9 \times 2 = 5.0 \times 10^9$ years</td></tr>
<tr><td>**9**</td><td>D</td><td>0.785 g Cr ≡ 0.0151 mol Cr<br>8690 C ≡ 0.09005 mol e<br>0.0151 mol Cr ≡ 0.09005 mol e<br>1 mol Cr ≡ 5.96 mol e ≡ 6 mol e<br><br>$Cr^{n+} + ne \rightarrow Cr$<br>n = 6<br>**Option A** is wrong : OS of Cr = +2<br>**Option B** is wrong : OS of Cr = +3<br>**Option C** is wrong : OS of Cr = +4<br>**Option D is correct**: : OS of Cr = +6</td></tr>
<tr><td>**10**</td><td>B</td><td>Cu(s) | $Cu^{2+}$(aq, 1 mol $dm^{-3}$) || **A**$^+$(aq) | **A**(s)<br>**Option A** is wrong as statement is correct : The $Cu^{2+}$/Cu half-cell is the anode and Cu is the negative electrode<br>**Option B** is correct as statement is incorrect : [**A**$^+$(aq)] = $1.00 \times 10^{-7}$ and log [**A**$^+$(aq)] = -7. From the graph, emf > 0 and the direction of electron flow will **not** be reversed.<br>**Option C** is wrong as statement is correct : $E^{\ominus}_{cell} = E^{\ominus}_{red} + E^{\ominus}_{ox}$ $+0.46 = E^{\ominus}_{red} + (-0.34)$ $E^{\ominus}_{red} = +0.80V$<br>**Option D** is wrong as statement is correct : At std conditions, [**A**$^+$(aq)] = 1.00 mol $dm^{-3}$<br>log [**A**$^+$(aq)] = 0<br>emf = +0.46 V (from graph)</td></tr>
</table>

| | | |
|---|---|---|
| **11** | B | $\mathbf{D}(g) \rightleftharpoons \mathbf{E}(g) + \mathbf{F}(g)$<br>Initial pressure/atm: p, 0, 0<br>Eqm pressure/atm: $\frac{1p}{7}$, $\frac{3p}{7}$, $\frac{3p}{7}$<br>Note : Total pressure = p (constant)<br>$K_p = \dfrac{(\frac{3}{7}\text{ atm})^2}{(\frac{1}{7}\text{ atm})}$ = 9p/7 atm |
| **12** | B | Method 1: Calculation –confirmation method<br>$pK_a = 9.5$<br>$K_a = 10^{-9.5}$<br>[paracetamol] = $[(12.78 \times 10^{-3})/151] / (1 \times 10^{-3}) = 0.084 \text{ mol dm}^{-3}$<br>$K_a = \dfrac{[\text{anion}][\text{H}^+]}{[\text{paracetamol}]}$<br>$10^{-9.5} = \dfrac{[\text{anion}][\text{H}^+]}{[0.0846]}$<br>$[H^+] = 5.17x10^{-6}$<br>$pH = -\lg[H^+] = 5.29$<br><br>Method 2: Elimination method – smart guess<br>• Paracetamol behaves as weak acid, which undergoes partial dissociation<br>• hence pH must be near to 7<br>• Most probable pH is 5.29 |
| **13** | A | $pH = 14 - pK_b$<br>$pK_b = 14 - pH$<br>$pK_b = pOH$<br>i.e. max buffer capacity<br><br>Option A is correct |
| **14** | D | $NH_4^+$ is the conjugate acid of a weak base, $NH_3$.<br><br>$NH_4^+$ dissociates partially in water to produce $H_3O^+$ as follows:<br>$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$<br><br>$Mg(OH)_2(s)$ then undergoes an acid–base reaction (neutralisation) with the $H_3O^+$ ions produced.<br>$Mg(OH)_2(s) + 2H_3O^+(aq) \longrightarrow Mg^{2+}(aq) + 4H_2O(l)$ |

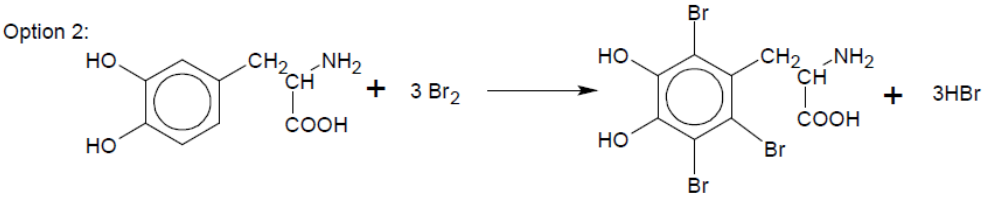
|  |  |  |
|---|---|---|
| **15** | D | A saturated solution of $Ca(OH)_2$ is found to have a pH of 12.3 at 25 °C.<br>$Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^-$….. eqm (1)<br>Option A is correct: $K_{sp}$ of $Ca(OH)_2 = [Ca^{2+}][OH^-]^2 = (1/2 \text{ x } 10^{-1.7})(10^{-1.7})^2 = 4 \times 10^{-6}$ mol$^3$ dm$^{-9}$.<br>Option B is correct: The solubility of $Ca(OH)_2$ would increase when temperature is raised to 35 °C.<br>Option C is correct: When solid $Na_2O$ is added, NaOH is formed, hence $[OH^-]$ increases. As such, POE of eqm (1) above will shift to the left, hence $[OH^-]$ decrease. The solubility of $Ca(OH)_2$ will decrease.<br>**Option D is incorrect**: When $Ca(NO_3)_2$ is added, $[Ca^{2+}]$ increases. As such, POE of eqm (1) above will shift to the left, hence $[OH^-]$ decrease. The pH of the solution would decrease. |
| **16** | A | • Important information in question : high charge-density cations<br>• Only $AlCl_3$ and $MgCl_2$ will dissolve in water to give cations, $Al^{3+}$ and $Mg^{2+}$<br>• Hence, most effective high charge-density cation is $Al^{3+}$ |
| **17** | B | • All of the elements burns in presence of oxygen to give respective oxides. All the metal oxides formed will be soluble in water but $SiO_2$ is insoluble in water.<br>• $Al_2O_3$ is amphoteric oxide which reacts with NaOH, ie soluble in excess NaOH through formation of the following complex<br>$Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow 2Na[Al(OH)_4](aq)$<br>• Both $K_2O$ and CaO are basic oxide which do not react with NaOH, thus remains as white ppt.<br>• However, only CaO will react with $H_2SO_4$ to give a sparingly soluble white ppt.<br>$CaO(s) + H_2SO_4(aq) \rightarrow CaSO_4(s) + H_2O(l)$ |
| **18** | C | • Thermal decomposition of hydrogen halides, HX, involves the breaking of the covalent H-X bond.<br>• General trend of Group VII halides: Going down Group VII, the valence np orbital of the halogen atom is larger and more diffused. Thus, the overlap of orbitals between the 1s orbital of H and the np orbital of halogen atom becomes less effective. Consequently, the H-X bond is longer and weaker as indicated by the bond energies. Less energy is required to break the H-X bond going down the group, i.e. thermal stability decreases.<br>• Conclusion : H–C$l$ bond is stronger than H–I bond. |
| **19** | D | **Option A** : $E_{cell}$ = -0.59V, reaction is not feasible.<br>**Option B:** hexacyanoferrate(III) cannot be further oxidised.<br>**Option C**: Sn is not a transition element, therefore while it can be oxidised from $Sn^{2+}$ to $Sn^{4+}$, there is no color change.<br>**Option D is correct**: $E_{cell}$ = 0.97V, therefore reaction is feasible. $V^{2+}$ is green, and it changes to $V^{3+}$ which is violet. |

| | | |
|---|---|---|
| **20** | C | $[Cu(H_2O)_6]_{2+} + 6\ Cl^- \rightarrow [CuCl_4]^{2-} + 6H_2O$<br>Blue yellow<br>The oxidation state of Cu is +2 in both complexes; therefore the number of d electrons will be the same.<br>Different ligand splits the field differently and thus accounting for the different colors. The energy gap is going to be different.<br>Thus **option C** is the only correct answer. |
| **21** | D | The graph shows that the reactants are of lower energy than the products. Hence, the best possible answer will be option **D** as the reactant which is $Cl_2$ will be of lower energy than the product which are the highly reactive radicals. |
| **22** | D | When treated with $H_2$, Ni cat at 200 °C, the product will be<br><br> <br>As shown in the diagram, there are 9 chiral carbons in the product. |
| **23** | D | **Option A**: The –CN in compound **P** has sp hybridised carbon atom. (Correct)<br>**Option B**: The 2 pi bonds in the two double bonds + 2 pi bonds in C≡N. (Correct)<br>**Option C**: Reaction with $HCl(g)$ will lead to all the alkenes in the compounds to undergo electrophilic addition and the carbon will become a $sp^3$ hybridised except for -C≡N. (Correct)<br>**Option D**: $LiAlH_4$ will not be able to reduce the C=C, hence not all the carbons in the product formed will not be $sp^3$ hybridised. (Incorrect) |
| **24** | C | <br> <br>First step: oxidation<br>Second step: nucleophilic addition<br>Third step: oxidation |

| | | |
|---|---|---|
| **25** | C | Option A:  <br>Option B: $H_2NCO(CH_3)_3CHClCH_3 \xrightarrow[\text{heat}]{\text{KOH(aq)}} {}^{-}OOC(CH_3)_3CH(OH)CH_3 \xrightarrow{\text{hot KMnO}_4\text{(aq), H}_3\text{O}^+} CH_3CO(CH_2)_3COOH$<br>Option C: $CH_3CH(OH)(CH_2)_3CH_2Cl \xrightarrow[\text{heat}]{\text{NaOH in ethanol}} CH_3CH(OH)(CH_2)_2CH{=}CH_2$<br>$\downarrow$ hot $KMnO_4$(aq), $H_3O^+$<br>$CH_3CH(OH)(CH_2)_2COOH$ (major product)<br>Option D: The compound oxidises to $CH_3CO(CH_2)_3COOH$. |
| **26** | A | The rest of the options will produce 1,3-dicarboxylic acid.<br>Option A:  <br>Will not be able to oxidise the compound. Only Tollens' reagent can oxidise this compound to 1,2-dicarboxylic acid. |
| **27** | C | Using the example of phthalic anhydride producing phthalic acid with water, ethanol should follow the same reaction as water. The general formula of the reaction is shown in the equation below.<br>$C_6H_4(CO)_2O$ (anhydride) + ROH → $C_6H_4(COOH)COOR$ [R – $CH_3CH_2$-] |
| **28** | B | **Q** 1 mol of Q requires 3 mol of NaOH for the hydrolysis process.<br>Amount of NaOH left after hydrolysis = (50/100 x 1) – 0.03 = 0.02 mol<br>1 mol NaOH requires 1 mol of HCl for neutralisation<br>Vol of HCl required to neutralise the remaining NaOH = 0.02 / 1 = 0.02dm$^3$ = 20cm$^3$<br>**R** 1 mol of R requires 1 mol of NaOH for the hydrolysis process.<br>Amount of NaOH left after hydrolysis = (50/100 x 1) – 0.01 = 0.04 mol<br>1 mol NaOH requires 1 mol of HCl for neutralisation<br>Vol of HCl required to neutralise the remaining NaOH = 0.04 / 1 = 0.04dm$^3$ = 40cm$^3$<br>**S** 1 mol of S requires 2 mol of NaOH for substitution of 2 Br.<br>Amount of NaOH left after hydrolysis = (50/100 x 1) – 0.02 = 0.03 mol<br>1 mol NaOH requires 1 mol of HCl for neutralisation<br>Vol of HCl required to neutralise the remaining NaOH = 0.03 / 1 = 0.03dm$^3$= 30cm$^3$ |

| | | |
|---|---|---|
| **29** | B | Option A: Amino acids form zwitterions not amides.<br><br>Option B: Basicity depends on the availability of lone pairs of electron on nitrogen for coordination with proton. The lone pair of electrons on the N atom can be delocalised with the $\pi$ electrons of the C=O double bond. This creates the resonance structure. This makes the amides less basic than amines.<br> <br>Option C: Need to concentrate on the availability of lone pairs of electrons on nitrogen, not on how it is more difficult to break the C-N bond.<br><br>Option D: The powerful **electron-withdrawing effect of the carbonyl group C=O** reduces the electron density on the N atom, making it less effective as a proton acceptor. Not make the hydrogen atoms more acidic. |
| **30** | D | Option A: True<br><br>Option B: Both glycine and alanine have non polar R groups, hence would have van der Waals' forces between them.<br><br>Option C: Cystein is a sulfur containing amino acid which is capable of forming disulfide linkages between the cysteine molecules.<br><br>Option D: Serine forms hydrogen bonds with another serine amino acid in the protein as the side group is an alcohol group. |
| **31** | A | Option 1 is correct : 0.0200 mol **T** ≡ 0.00400 mol $MnO_4^-$<br>5 mol **T** ≡ 1 mol $MnO_4^-$<br><br>Option 2 is correct : 5 mol **T** ≡ 1 mol $MnO_4^-$ ≡ 5 mol e<br>1 mol **T** ≡ 1 mol e<br>1 mol **T** lost 1 mol e<br>Change in OS of **T** = +1<br><br>Option 3 is correct : $\mathbf{T}OCl_y \rightarrow \mathbf{T}O_3^-$<br>+4 +5<br>OS of **T** in $\mathbf{T}OCl_y$ = +4<br>In $\mathbf{T}OCl_y$, $+4 + (-2) + (y(-1)) = 0$<br>$y = 2$ |

| | | |
|---|---|---|
| **32** | A | Option 1 is correct: The ion **$U^{5+}$** has the symbol $^{89}_{43}U^{5+}$ and thus the same charge by mass ratio as yttrium ion, $^{89}Y^{5+}$. Both deflected to same extent.<br>Option 2 is correct: **U** is the technetium, **$T_c$**. Electronic configuration of **$T_c$** is [Kr] $4d^5$ $5s^2$ and that of **$U^{5+}$** is [Kr] $4d^2$.<br>Option 3 is correct : **$U^{2+}$** (g) → **$U^{3+}$** (g) + e (3rd IE)<br>[Kr] $4d^5$ [Kr] $4d^4$<br>The energy required to remove the a mol of e from **$U^{2+}$** (g) will be significantly higher than 2nd IE as it involves the removal of electron from an inner quantum shell. |
| **33** | B | Trypsin is an enzyme that catalyses the reaction. When the [substrate] (casein) is low, increasing the concentration of casein will increase the rate of reaction as there are plenty of active sites available on the catalyst, therefore its first order with respect to casein.<br>However, as the concentration of casein rise, the active sites in the enzyme will be saturated, and therefore, increasing the concentration of casein will have no effect on the rate of reaction, thus it's a zero order reaction. |
| **34** | B | Option 1 is correct: In discharging the cell, $Li^+$ $MnO_2^-$ will be formed. Li is oxidised to $Li^+$ and electrons released will flow to the $MnO_2$ electrode.<br>Option 2 is correct: At the $MnO_2$ electrode (cathode), $MnO_2$ gains electron and is reduced to $MnO_2^-$.<br>Option 3 is wrong: Water cannot be used as it will react with Li, a Group I metal. |
| **35** | A | Graph 1 is correct: (Explanation can be found in Pg 4 Periodicity notes)<br>• The atomic radii of the elements **decrease** across period 3 gradually. Across a period, there is an increase in the **effective nuclear charge**, due to increasing **number of protons** in the nucleus and approximately constant shielding effect.<br>• The radius of Ar is, in fact, the van der Waals' radius between two atoms. Hence, largest radius.<br>Graph 2 is correct: explanation will use actual element and its ion to minimise confusion (Pg 4 Periodicity notes)<br>• The cationic radius decreases from atomic number 11 to 14 (which is actually $Na^+$ to $Si^{4+}$) (Electronic configuration: **$1s^2$ $2s^2$ $2p^6$**).<br>- Nuclear charge increases from $Na^+$ to $Si^{4+}$ due to an increase in protons.<br>- Shielding effect remains approximately constant as these cations are isoelectronic.<br>- Due to the increase in nuclear charge, the valence electrons in these ions are held more tightly to the nucleus, accounting for a smaller cationic radius.<br>• The anionic radius decreases from $Si^{4-}$ to $Cl^-$ (Electronic configuration: **$1s^2$ $2s^2$ $2p^6$ $3s^2$ $3p^6$**)<br>- Similarly for the anions ($Si^{4-}$, $P^{3-}$, $S^{2-}$ and $Cl^-$) are isoelectronic (constant shielding). The decrease in anionic radii is also due to the increase in nuclear charge.<br>• Radii of anions > Radii of cations because of an **extra shell** of electrons in the anions. |

| | | |
|---|---|---|
| | | Graph 3 is correct: Explanation can be found in Pg 5 Periodicity notes<br>- Na, Mg and A*l* are metals.<br>Conductivity increases from Na to A*l* due to an **increase** in the number of valence electrons donated to the delocalised electron cloud by the metal atoms.<br>- Si is a metalloid (having both properties of metals and non-metals). It has low conductivity. It is a semi-conductor.<br>- P, S and C*l* are non-metals. The electrons are localised in covalent pairs and are unable to move to conduct electricity. They have very low conductivities. They are non-conductors (insulators).<br>Na Mg A*l* Si $P_4$ $S_8$ $Cl_2$<br>← Metals → Metalloid ← Non-Metals → |
| **36** | C | Option 1: The reaction involves nucleophilic attack not electrophilic attack.<br>Option 2: The RX compound is a tertiary RX hence it will be undergoing $SN_1$ mechanism which involves the formation of a carbocation in the slow step.<br>Option 3: The reaction involves the cleaving of C-X bond so if the X is I, the reaction will take place rapidly as the C-I bond is weaker than C-C*l* bond. |
| **37** | C | During the reaction, C=O bond from benzaldehyde and 2 N-H bonds from phenylhydrazine will be broken. The products will have C=N bond and O-H (from water) being formed. |
| **38** | D | Option 1: One mole of dopamine has 1 $–NH_2$ group and 2 –OH groups. Hence, one mole of dopamine will react with 3 moles of RCOCl. ( the $–NH_2$ group will form amide with RCOCl and the –OH group will form ester with RCOCl).<br>Option 2: Dopamine will undergo electrophilic substitution with 3 moles of $Br_2$(aq) wrt to the two phenol groups.<br> <br>Option 3: One mole of dopamine will react with one mole of $Na_2CO_3$ as only the –COOH group in the compound will react. |
| **39** | A | Distillate W forms a yellow ppt with alkaline aq iodine – W has –C=O group.<br>X reacts with $Na_2CO_3$ – X has –COOH group.<br>Option 1: Given the formula of V, V should have unsaturated bonds in it so it should be able to decolourise aq bromine.<br>Option 2: W is a carbonyl compound so it should be able to form orange ppt with 2,4-DNPH.<br>Option 3: X has –COOH group so it should be able to react with $PCl_5$. |
| **40** | A | Option 1: It can be hydrolysed to form Benzoic acid and aminoethanoic acid.<br>Option 2: Benzoyl chloride and aminoethanoic acid can undergo nucleophilic substitution/condensation to form benzoylglycine and HCl as the products.<br>Option 3: Cold NaOH(aq) can react with –COOH group through acid-base reaction. |

PIONEER JUNIOR COLLEGE

JC2 PRELIMINARY EXAMINATION
HIGHER 2

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|---|---|
| CANDIDATE NAME | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| CT GROUP | 1 | 5 | S | | | INDEX NUMBER | | | | | |

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**CHEMISTRY** **9647/02**

Paper 2 Structured **13 September 2016**

**2 hours**

Additional Materials: Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

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

Answer **all** questions.

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** | |
|---|---|
| **Paper 2** | |
| 1 | /12 |
| 2 | /12 |
| 3 | /14 |
| 4 | /8 |
| 5 | /9 |
| 6 | /17 |
| Penalty | sf units |
| Total | **/72** |

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This document consists of **17** printed pages.

Answer **all** questions in the spaces provided.

## 1 Planning (P)

The formation of a cobalt(II) complex ion, from $Co^{2+}$ and an unknown ligand($L^-$), is accompanied by the appearance of a blue colouration.

$$Co^{2+} + 4L^- \rightarrow [CoL_4]^{2-}$$

A machine, known as a spectrometer, is able to measure the amount of light that is absorbed when a specific wavelength of visible light is shone through a few $cm^3$ of the solution. The amount of light absorbed is then expressed as an absorbance value, and the absorbance value is proportional to the concentration of the cobalt(II) complex ion.

This technique can be used to confirm the formula of the cobalt(II) complex ion. A series of solutions containing varying volume ratios of $L^-$ to $Co^{2+}$, both of the same concentration, while keeping the total volume of the $Co^{2+}$ and $L^-$ constant, is prepared. A spectrometer is used to measure the absorbance of the solutions. A graph of absorbance value against volume of $L^-$ is then plotted.

Using the graph of absorbance value against volume of $L^-$, the ratio of $L^-$ to $Co^{2+}$ equal to that in the cobalt(II) complex ion can be then determined from the maximum point. This is known as the “Job’s Method”.

**(a)** The spectrometer is set to use the wavelength of the light that is absorbed most strongly by the complex ion.

| **Colour** | **Wavelengths (nm)** |
|---|---|
| Red | 620-750 |
| Orange | 590-620 |
| Yellow | 570-590 |
| Green | 495-590 |
| Cyan | 475-495 |
| Blue | 450-475 |
| Violet | 380-450 |

Suggest a wavelength in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

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[2]

**(b)** Using the information given above, you are required to write a plan to confirm the formula of the cobalt(II) complex ion as $[CoL_4]^{2-}$.

You may assume that you are provided with:

- solid cobalt(II) nitrate, $Co(NO_3)_2.6H_2O$;
- solution of $L^-$, of concentration 0.100 mol dm$^{-3}$;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of 250 cm$^3$ of 0.100 mol dm$^{-3}$ aqueous cobalt(II) nitrate;
- the preparation of five 50 cm$^3$ complex ion solutions containing varying volume ratios of $L^-$ to $Co^{2+}$;
- how the absorbance values would be obtained;
- a sketch of the graph of absorbance value against volume of $L^-$ that you would expect to obtain;
- how the calculation can be performed to determine the formula of $[CoL_4]^{2-}$.

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[10]
[Total: 12]

**2** The mission of the Hydrogen and Fuel Cells Programme by the U.S. Department of Energy (DoE) is to reduce petroleum use, greenhouse gas emissions, and air pollution and to contribute to a more diverse and efficient energy infrastructure by enabling the widespread commercialisation of hydrogen and fuel cell technologies.

One such technology involves creating an energy system concept that stores hydrogen in the form of metal hydrides. Magnesium hydride ($MgH_2$) is one of the compounds currently being researched on its viability on hydrogen storage. One way to release hydrogen from metal hydrides is to react them with water, where a hydroxide is formed as a side product.

The other way to obtain hydrogen is through the thermal decomposition of the metal hydride $\mathbf{M}H_2$. When hydrogen is needed, these metal hydrides can be heated to release molecular hydrogen.

$$\mathbf{M}H_2 \rightleftharpoons \mathbf{M} + H_2$$

This adsorption and desorption of hydrogen in metals serves like a ‘hydrogen bank’. The rate of desorption of hydrogen is proportional on the strength of ionic bonds formed between the metal and hydride ions.

Apart from $MgH_2$, other Group II hydrides are also being studied and researched on the same purpose. The table below shows some properties of the Group II hydrides.

| | $\mathbf{MgH_2}$ | $\mathbf{CaH_2}$ | $\mathbf{SrH_2}$ | $\mathbf{BaH_2}$ |
|---|---|---|---|---|
| **Percentage of H / % by mass of H** | 7.7 | 4.8 | 2.2 | 1.4 |
| **Density / g cm$^{-3}$** | 1.74 | 1.54 | 2.64 | 3.62 |
| **Melting point / ˚C** | 650 | 842 | 777 | 727 |
| **$\Delta H_f$ / kJ mol$^{-1}$** | -114 | -144 | -119 | -118 |

**(a)** **(i)** Write an equation for the reaction between solid $MgH_2$ and water.

…………………………………………………………………………………………..

[1]

**(ii)** Draw the dot-and-cross diagram for $MgH_2$.

[1]

**(b)** **(i)** Explain, with reasoning, the trend on the rate of desorption of hydrogen for the Group II metal hydrides from $CaH_2$ to $BaH_2$.

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[2]

**(ii)** Which metal hydride, $CaH_2$ or $BaH_2$, would you expect to decompose more readily? Explain your answer by using relevant data from the above table.

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[2]

**(iii)** Using relevant information from the *Data Booklet* and the information given below, construct a Born-Haber cycle to calculate the lattice energy for $CaH_2$.

(The first electron affinity for hydrogen is -72.8 kJ mol$^{-1}$ and the enthalpy change of atomisation of calcium is +178 kJ mol$^{-1}$)

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[3]

**(c)** A car company is planning to develop cars that run on hydrogen fuel produced by $MgH_2$.

The following information is for a typical petrol-fuelled car.

| | |
|---|---|
| Weight of vehicle / kg | 1088 |
| Fuel tank / L | 42 |
| Fuel consumption / km $L^{-1}$ | 17 |
| Energy consumption of petrol / kJ $kg^{-1}$ | 46.4 |
| Density of petrol / g $cm^{-3}$ | 0.8 g |

**(i)** Calculate the energy produced by a petrol-fuelled car running at full tank.

[1]

**(ii)** It was found that 1 kg of hydrogen produce 3 times more energy than petrol with the same mass.

Assuming 100% efficiency, calculate the amount of magnesium metal needed to store the hydrogen as the hydride to provide the same amount of energy in the hydrogen-fuelled car. (1 L = 1000 $cm^3$)

$$MgH_2 \rightleftharpoons Mg + H_2$$

[2]

[Total: 12]

**3** **(a)** In the presence of excess oxygen, a liquid alcohol, compound **A**, $C_xH_yO$, undergoes complete combustion to produce 3.19 $dm^3$ of hot gases at a temperature of 250 °C at a pressure of 1 atm,

Upon cooling to room temperature, the volume contracted to 836 $cm^3$. The gases were then passed through aqueous sodium hydroxide and the final volume remaining was 100 $cm^3$.

**(i)** Fill in the following blanks for the equation for the complete combustion of **A**.

$$\mathbf{C_xH_yO + \boxed{\phantom{xxxxxx}}\ O_2 \longrightarrow \boxed{\phantom{xx}}\ CO_2 + \boxed{\phantom{xx}}\ H_2O}$$

[1]

**(ii)** Using the *ideal gas equation*, find the amount of $CO_2$ and amount of $H_2O$ that was produced respectively from the complete combustion of compound **A**.

[3]

**(iii)** Using your answer to **(a)(i)** and **(a)(ii)**, calculate the value of x and y and hence, write down the empirical formula for **A**.

[1]

**(ii)** The actual number of moles of gases obtained from the combustion is found to be higher than that calculated when using the *ideal gas equation*.

Account for the difference between the two results.

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………………………………………………………………………………………… [1]

**(b)** Methane can be obtained when carbon monoxide is heated to 900 °C with hydrogen gas as shown in the following equation.

$$\mathbf{CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)}$$

**(ii)** Write an expression for the $K_c$ of the reaction, stating its units.

[1]

**(iii)** 1 mol of carbon monoxide was heated with 4 mol of hydrogen gas in a 10 dm$^3$ vessel. At equilibrium, the vessel contained 0.387 mol of methane.

Calculate the $K_c$ for the reaction of carbon monoxide.

[2]

**(iv)** Suggest, with an explanation, how the position of equilibrium might alter when 1 mol of helium was added into the vessel.

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[1]

**(c)** Anhydrous aluminium sulfate is commonly used in organic reactions to remove water. It decomposes at 600 °C to produce an insoluble white solid and misty fumes. The white solid dissolves in both aqueous sodium hydroxide and aqueous hydrochloric acid while the misty fumes turn moist blue litmus red.

**(i)** Suggest the identities of the white solid and the misty fumes. Hence, write a balanced equation for the decomposition of aluminium sulfate.

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[2]

**(ii)** Write equations for the reactions of the white solid with aqueous sodium hydroxide and hydrochloric acid.

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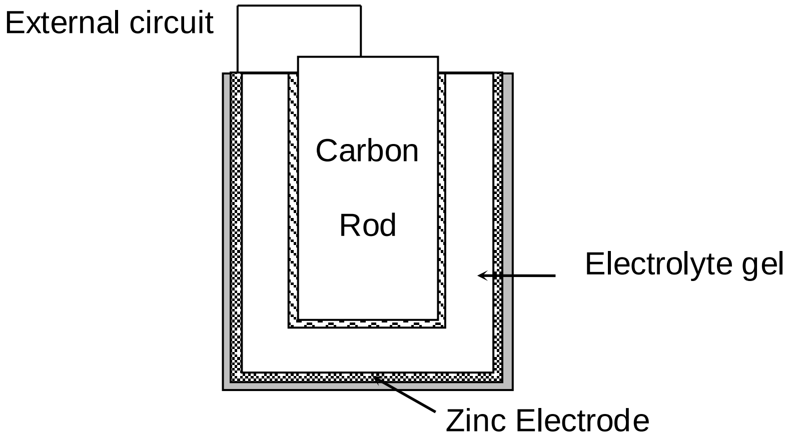
[2]

[Total: 14]

4 Batteries for hearing aids comprise of zinc and carbon electrodes. These electrodes in an electrolyte, maintained at a pH of 11, forms a galvanic cell in which zinc is oxidised and oxygen from the air is reduced.



**(a)** Write a balanced equation for the overall chemical reaction and calculate the $E^{\theta}_{cell}$ of this cell.

[2]

**(b)** Indicate, on the diagram on page 10, the polarity of both electrodes and the direction of electron flow in the external circuit.

[2]

**(c)** Explain how the e.m.f. of the cell would change if the pH of the electrolyte decreases.

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[2]

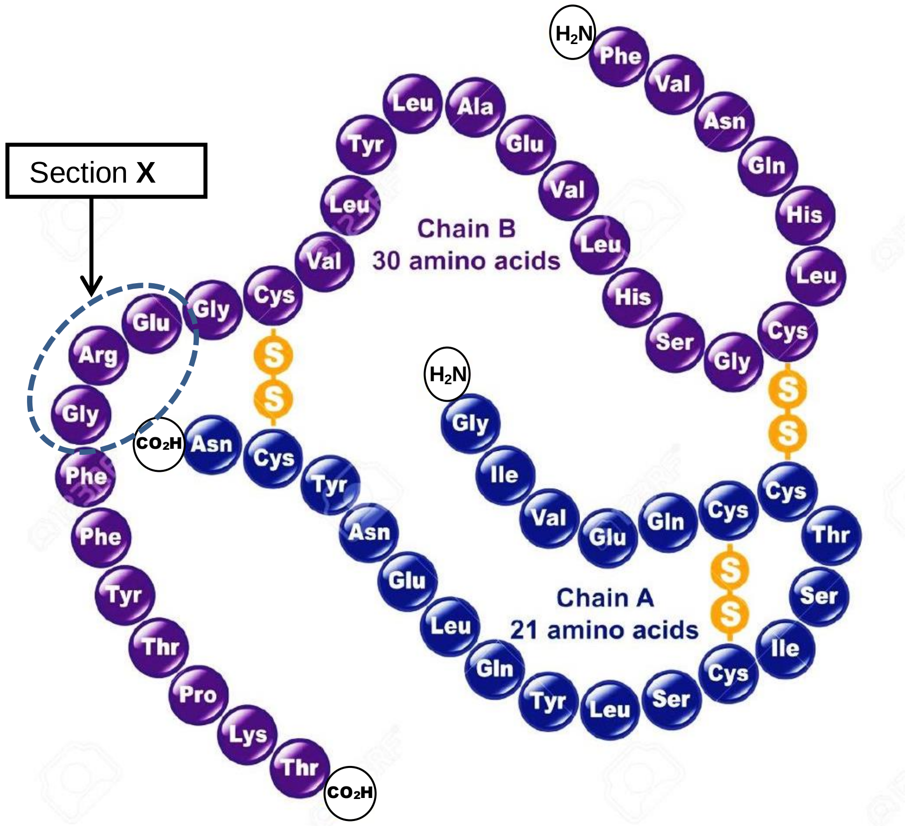
**(d)** If a current of 4 x $10^{-5}$ A was drawn from the cell, calculate how long a zinc electrode weighing 2 g will last before it needs to be replaced. Give your answer correct to the nearest day.

[2]

[Total: 8]

**5** Insulin is a hormone made by the pancreas that allows your body to use glucose from carbohydrates in the food that you eat for energy. Insulin helps keeps your blood sugar level from getting too high or too low.

The insulin molecule consists of 51 amino acid residues, in two polypeptide chains.



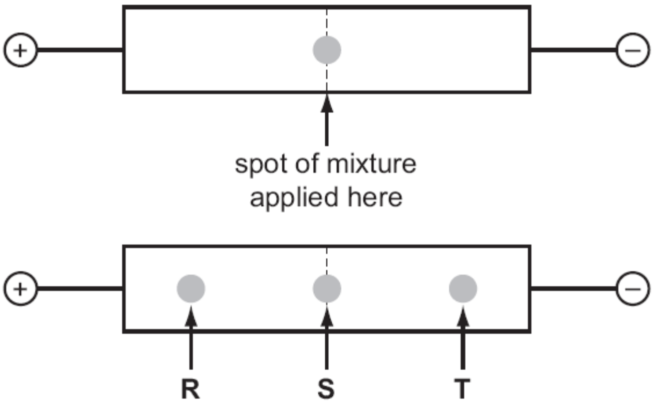
Some information on the amino acids of insulin is given below.

| amino acid | Abbreviated name | Formula of side chain (**R** in **R**CH($NH_2$)$CO_2H$) | pI |
|---|---|---|---|
| arginine | arg | $-(CH_2)_3NHC(NH_2)=NH$ | 10.76 |
| cysteine | cys | $-CH_2SH$ | 5.07 |
| glutamic acid | glu | $-CH_2CH_2COOH$ | 3.22 |
| glycine | gly | $-H$ | 5.97 |

**(a)** Draw the structural formula of section **X** in insulin.

[1]

**(b)** The diagram shows the results of electrophoresis on a mixture of the amino acids obtained from hydrolysis of section **X** at pH 6.0.



Draw the structure of the species responsible for the spots labelled **R**, **S** and **T**.

| **R** | **S** | **T** |
|---|---|---|
| | | |

[3]

**(c)** The polypeptide chains of insulin coil to form short sections of α-helix which stabilises the secondary structure.

Describe with the aid of a sketch, how a polypeptide chain is held in the shape of an α-helix.

[3]

**(d)** The three-dimensional structure of insulin is further stabilised by disulfide linkages. Write an equation for the formation of such linkage and state the type of reaction involved.

.......................................................................................................................

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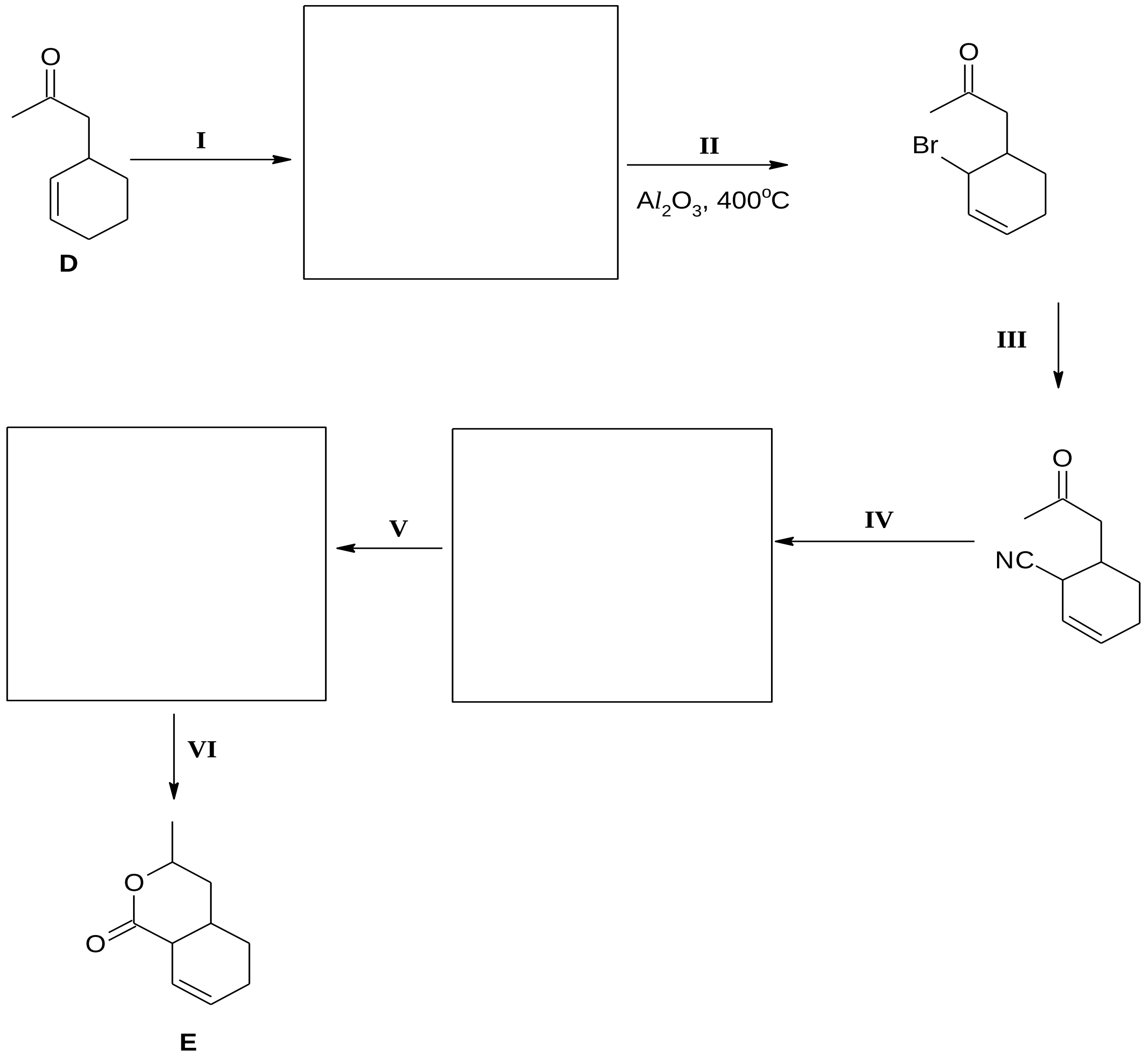
[2]
[Total: 9]

**6** Lactones are cyclic esters. They are formed by intramolecular esterification of the corresponding hydroxycarboxylic acids.

**(a)** **(i)** The reaction scheme below shows how lactone **E** is synthesised from compound **D**.

Complete the reaction scheme by giving the structural formulae of the intermediate organic products in the spaces provided and stating the reagents and conditions for steps **I**, **III**, **IV**, **V** and **VI**.



| Step | Reagents and conditions |
|---|---|
| I | |
| III | |
| IV | |
| V | |
| VI | |

[8]

**(ii)** Suggest a simple chemical test to distinguish compound **D** from **E**.

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[2]

**(iii)** Name and outline the mechanism when compound **D** is treated with HCN in the presence of aqueous NaOH at 10 $^{o}$C.

[3]

**(b)** Lactones with three- or four-membered rings are very reactive compared to five- or six-membered rings, making their isolation difficult.

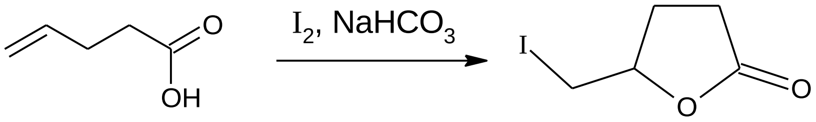
Suggest why lactones with three- or four-membered rings are very reactive.

……………………………………………………………………………………………

……………………………………………………………………………………………
[1]

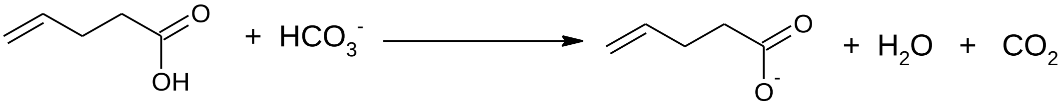
**(c)** Iodolactonisation reaction was first reported by M. J. Bougalt in 1904 and has since become one of the most effective ways to synthesise lactones.

An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown below.

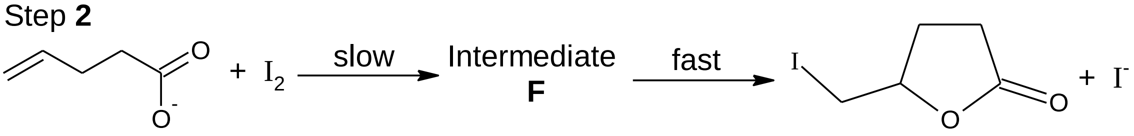


Two simplified steps in the iodolactonisation mechanism are given below.

Step **1**



Step **2**



**(i)** Suggest the role of $HCO_3^-$ in step **1** of the mechanism.

……………………………………………………………………………………..
[1]

**(ii)** The type of reaction in Step **2** of the mechanism is electrophilic addition.

Draw the structure of intermediate **F**.

[1]

**(iii)** Suggest the structural formulae of the final organic product formed when $CH_2=CHCH(CH_3)CH_2CH_2COOH$ undergoes iodolactonisation in a similar process as above.

[1]
[Total: 17]

**End of Paper**

JC2 PRELIMINARY
EXAMINATION HIGHER 2

CANDIDATE NAME

| | | | | | |
|---|---|---|---|---|---|
| CT GROUP | 1 | 5 | | | |

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| INDEX NUMBER | | | | |

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**CHEMISTRY** **9647/02**

Paper 2 Structured **13 September 2016**

**2 hours**

Additional Materials: Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

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| **FOR EXAMINER'S USE** | | | |
|---|---|---|---|
| **Paper 2** | | | |
| 1 | / 12 | 5 | / 9 |
| 2 | / 12 | 6 | / 17 |
| 3 | / 14 | Penalty | sf units |
| 4 | / 8 | Total | / 72 |

This document consists of **19** printed pages and **1** BLANK page.

Answer **all** questions in the spaces provided.

**1** **Planning (P)**

The formation of a cobalt(II) complex ion, from $Co^{2+}$ and an unknown ligand ($L^-$), is accompanied by the appearance of a blue colouration.

$$Co^{2+} + 4L^- \rightarrow [CoL_4]^{2-}$$

A machine, known as a spectrometer, is able to measure the amount of light that is absorbed when a specific wavelength of visible light is shone through a few $cm^3$ of the solution. The amount of light absorbed is then expressed as an absorbance value, and the absorbance value is proportional to the concentration of the cobalt(II) complex ion.

This technique can be used to confirm the formula of the cobalt(II) complex ion. A series of solutions containing varying volume ratios of $L^-$ to $Co^{2+}$, both of the same concentration, while keeping the total volume of the $Co^{2+}$ and $L^-$ constant, is prepared. A spectrometer is used to measure the absorbances of the solutions. A graph of absorbance against volume of $L^-$ is then plotted.

Using the graph of absorbance against volume of $L^-$, the ratio of $L^-$ to $Co^{2+}$ equal to that in the cobalt(II) complex ion can be then determined from the maximum point. This is known as the “Job’s Method”.

**(a)** The spectrometer is set to use the wavelength of the light that is absorbed most strongly by the complex ion.

| Colour | Wavelengths (nm) |
|---|---|
| Red | 620-750 |
| Orange | 590-620 |
| Yellow | 570-590 |
| Green | 495-590 |
| Cyan | 475-495 |
| Blue | 450-475 |
| Violet | 380-450 |

Suggest a wavelength in the visible spectrum from which a suitable wavelength of light might be chosen. Explain your answer.

[2]

**Any value from 591 to 619 nm.**

**The observed colour of the cobalt complex ion is blue thus the colour complementary to blue, orange, will be absorbed.**

**(b)** Using the information given above, you are required to write a plan to confirm the formula of the cobalt(II) complex ion as $[CoL_4]^{2-}$.

You may assume that you are provided with:

- solid cobalt(II) nitrate, $Co(NO_3)_2.6H_2O$;
- solution of $L^-$, of concentration 0.100 mol $dm^{-3}$;
- access to a spectrometer and instructions for its use;
- graph paper;
- the apparatus and chemicals normally found in a school or college laboratory.

Your plan should include details of:

- the preparation of 250 $cm^3$ of 0.100 mol $dm^{-3}$ aqueous cobalt(II) nitrate;
- the preparation of five 50 $cm^3$ complex ion solutions containing varying volume ratios of $L^-$ to $Co^{2+}$;
- how the absorbance values would be obtained;
- a sketch of the graph of absorbance against volume of $L^-$ that you would expect to obtain;
- how the calculation can be performed to determine the formula of $[CoL_4]^{2-}$.

[10]

**Preparation of aqueous $Co^{2+}$**

**$M_r$ of cobalt nitrate = 290.9**
**Amount of cobalt nitrate in 250 $cm^3$ = (0.1 / 1000) x 250 = 0.0250 mol**
**Mass of cobalt nitrate required = 0.0250 x 290.9 = 7.27 g**

**Using a clean and dry weighing boat / bottle, weigh accurately 7.27 g of solid cobalt nitrate with an electronic balance.**
**Transfer the solid into a 100 $cm^3$ beaker.**
**Rinse the weighing boat with deionised water and transfer the washings into the beaker.**
**Dissolve the solid with deionised water.**
**Transfer the solution into a 250 $cm^3$ graduated flask with the aid of a filter funnel and a glass rod.**
**Rinse the beaker with deionised water and transfer the washings into the graduated flask.**
**Top the graduated flask to the mark with deionised water.**
**Cap the graduated flask and shake well to ensure the solution is well mixed.**

**Preparation of 4 solutions**

| Flask | Vol of $L^-$ / $cm^3$ | Vol of $Co^{2+}$ / $cm^3$ |
|---|---|---|
| 1 | 25.00 | 25.00 |
| 2 | 35.00 | 15.00 |
| 3 | 40.00 | 10.00 |
| 4 | 42.00 | 8.00 |
| 5 (max 6:1 ratio) | 45.00 | 5.00 |

- **5 solutions**
- **Total volume = 50 $cm^3$**
- **At least 2 volume smaller or greater than 40 $cm^3$ of $L^-$**
- **No volume of $L^-$ or $Co^{2+}$ should be 0 $cm^3$.**

## Procedure

- Fill a burette with the prepared $Co^{2+}$ solution and another with the $L^-$ solution.
- Transfer 25 $cm^3$ of $Co^{2+}$ solution into a 100 $cm^3$ conical flask, followed by 25 $cm^3$ of $L^-$ solution.
- Swirl the solution to ensure it is homogeneous
- Repeat steps 1 to 3 for with the stated volumes of solutions for Flask 2 to 4.
- Set up the spectrometer to absorb yellow light.
- Measure and record the absorbance of each of the 4 solutions.
- Plot a graph of absorbance against volume of $L^-$ solution.

## Calculations

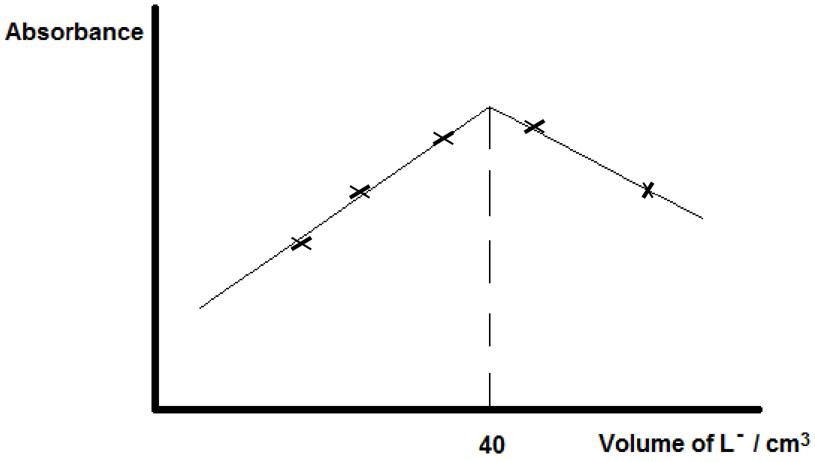
Maximum of point = 40 $cm^3$ of $L^-$

Amount of $L^-$ = (40 / 1000) x 0.1 = 0.00400 mol

Amount of $Co^{2+}$ = (10 / 1000) x 0.1 = 0.00100 mol

Ratio of $L^-$ to $Co^{2+}$ = 4:1

## Graph



[10]
[Total: 12]

**2** The mission of the Hydrogen and Fuel Cells Programme by the U.S. Department of Energy (DoE) is to reduce petroleum use, greenhouse gas emissions, and air pollution and to contribute to a more diverse and efficient energy infrastructure by enabling the widespread commercialisation of hydrogen and fuel cell technologies.

One such technology involves creating an energy system concept that stores hydrogen in the form of metal hydrides. Magnesium hydride ($MgH_2$) is one of the compounds currently being researched on its viability on hydrogen storage. One way to release hydrogen from metal hydrides is to react them with water, where a hydroxide is formed as a side product.

The other way to obtain hydrogen is through the thermal decomposition of the metal hydride **M**$H_2$. When hydrogen is needed, these metal hydrides can be heated to release molecular hydrogen.

$$\mathbf{M}H_2 \rightleftharpoons \mathbf{M} + H_2$$

This adsorption and desorption of hydrogen in metals serves like a ‘hydrogen bank’. The rate of desorption of hydrogen is proportional on the strength of ionic bonds formed between the metal and hydride ions.

Apart from $MgH_2$, other Group II hydrides are also being studied and researched on the same purpose. The table below shows some properties of the Group II hydrides.

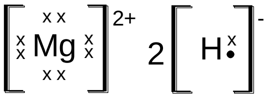
| | **$MgH_2$** | **$CaH_2$** | **$SrH_2$** | **$BaH_2$** |
|---|---|---|---|---|
| **Percentage of H / % by mass of H** | 7.7 | 4.8 | 2.2 | 1.4 |
| **Density / g $cm^{-3}$** | 1.74 | 1.54 | 2.64 | 3.62 |
| **Melting point / ˚C** | 650 | 842 | 777 | 727 |
| **$\Delta H_f$ / kJ $mol^{-1}$** | -114 | -144 | -119 | -118 |

**(a)** **(i)** Write an equation for the reaction between solid $MgH_2$ and water.

**$MgH_2(s) + 2H_2O(l) \rightarrow Mg(OH)_2(s) + 2H_2(g)$**

[1]

**(ii)** Draw the dot-and-cross diagram for $MgH_2$.



[1]

**(b)** **(i)** Explain, with reasoning, the trend on the rate of desorption of hydrogen for the Group II metal hydrides from $CaH_2$ to $BaH_2$.

**Strength of ionic bond** $\propto \dfrac{q_+ q_-}{r_+ + r_-}$

**Radius of cation, $r_+$ : $Ca^{2+} < Sr^{2+} < Ba^{2+}$**
**Strength of ionic bond : $BaH_2 < SrH_2 < CaH_2$**
**Rate of desorption of hydrogen from $CaH_2 < SrH_2 < BaH_2$ (fastest)**

[2]

**(ii)** Which metal hydride, $CaH_2$ or $BaH_2$, would you expect to decompose more readily? Explain your answer by using relevant data from the above table.

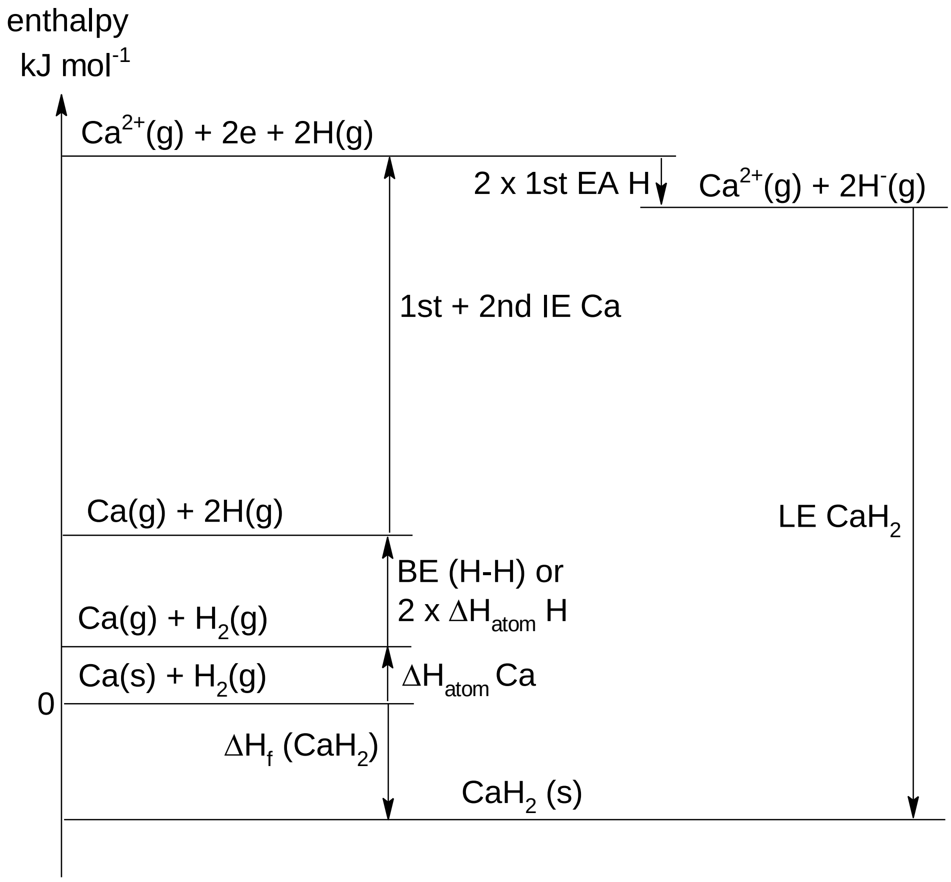
**$\Delta H_f$ becomes less exothermic from $CaH_2$ to $BaH_2$**
**$-\Delta H_f$ becomes less endothermic from $CaH_2$ to $BaH_2$**

**Hence,**
**Ease of decomposition: $CaH_2 < BaH_2$**

[2]

**(iii)** Using relevant information from the *Data Booklet* and the information given below, construct a Born-Haber cycle to calculate the lattice energy for $CaH_2$.

(The first electron affinity for hydrogen is -72.8 kJ mol$^{-1}$ and the enthalpy change of atomisation of calcium is +178 kJ mol$^{-1}$)



$$\Delta H_f^{\ominus}(CaH_2) = \Delta H_{at}^{\ominus}(Ca) + 2\Delta H_{at}^{\ominus}(H) + 1^{st}\,IE(Ca) + 2^{nd}\,IE(Ca) + 2 \times 1^{st}\,EA(H) + \Delta H_{latt}^{\ominus}(CaH_2)$$

$$-144 = 178 + 436 + 590 + 1150 + 2(-72.8) + \Delta H_{latt}^{\ominus}(CaH_2)$$

**LE= $\underline{-2.35 \times 10^{3}\ \text{kJ mol}^{-1}}$**

[3]

**(c)** A car company is planning to develop cars that run on hydrogen fuel produced by $MgH_2$.

The following information is for a typical petrol-fuelled car.

| | |
|---|---|
| **Weight of vehicle / kg** | 1088 |
| **Fuel tank / L** | 42 |
| **Fuel consumption / km $L^{-1}$** | 17 |
| **Energy consumption of petrol / kJ $kg^{-1}$** | 46.4 |
| **Density of petrol / g $cm^{-3}$** | 0.8 g |

**(i)** Calculate the energy produced by a petrol-fuelled car which is running at full tank.

**Mass of fuel at full tank = 42 x 1000 x 0.8 = 33600 g**

**Energy produced by the petrol at full tank = 33600/1000 x 46.4**
**= 1559.04 kJ**

**[1]**

**(ii)** It was found that 1 kg of hydrogen produce 3 times more energy than petrol with the same mass.

Assuming 100% efficiency, calculate the amount of magnesium metal needed to store the hydrogen as the hydride to provide the same amount of energy in the hydrogen-fuelled car. (1 L = 1000 $cm^3$)

$$MgH_2 \rightleftharpoons Mg + H_2$$

**1 kg petrol produces 46.4 kJ of energy**
**1 kg $H_2$ produces (46.4 x 3) = 138.9 kJ of energy**

**Hence to produce 1559.04 kJ of energy,**
**mass of hydrogen required = 1559.04/138.9 =11.15 kg**

**or**
**Mass of H2 = 33600 / 3 = 11.2 kg**

**$Mg + H_2 \rightarrow MgH_2$**
**Number of mole of $H_2$ needed = 11.15 x 1000/2 = 5575 or 5600**

**$Mg \equiv H_2$**
**Number of mole of Mg needed = 5575**

**Mass of Mg metal needed = 5575 x 0.0243**
**= 135 kg or 136 kg**

[2]
[Total: 12]

**3** **(a)** In the presence of excess oxygen, a liquid alcohol, compound **A**, $C_xH_yO$, undergoes complete combustion to produce 3.19 $dm^3$ of hot gases at a temperature of 250 °C at a pressure of 1 atm,

Upon cooling to room temperature, the volume contracted to 836 $cm^3$. The gases were then passed through aqueous sodium hydroxide and the final volume remaining was 100 $cm^3$.

**(i)** Fill in the following blanks for the equation for the complete combustion of **A**.

$$\mathbf{C_xH_yO + \boxed{(x + \tfrac{1}{4}y - 1)}O_2 \rightarrow \boxed{x}CO_2 + \boxed{(y/2)}H_2O}$$

**[1]**

**(ii)** Using the *ideal gas equation*, find the amount of $CO_2$ and amount of $H_2O$ that was produced respectively from the complete combustion of compound **A**.

**Amount of gases in hot gases = $(101000 \times 3.19 \times 10^{-3}) / (8.31 \times 523)$**
**= 0.0741 mol**

**Volume of $CO_2$ = 836 – 100 = 736 $cm^3$**
**Amount of $CO_2$ = $(101000 \times 736 \times 10^{-6}) / (8.31 \times 298)$ = 0.0300 mol**

**Volume of $O_2$ = 100 $cm^3$**
**Amount of $O_2$ = $(101000 \times 100 \times 10^{-6}) / (8.31 \times 298)$ = 0.00408 mol**

**Amount of $H_2O$ = 0.0741 – 0.0300 – 0.00408 = 0.0401 mol**

[3]

**(iii)** Using your answer to **(a)(i)** and **(a)(ii)**, solve for **x** and **y** in $C_xH_yO$ and hence determine the empirical formula of **A**.
**Amount of C = 0.0300 mol**
**Amount of H = 0.0401 x 2 = 0.0802 mol**

**Empirical ratio (C:H) = 0.0300 : 0.0802**
**x = 3; y = 8**

**Empirical formula = $C_3H_8O$**

[1]

**(ii)** The actual number of moles of gases obtained from the combustion is found to be higher than that calculated when using the *ideal gas equation*.

Account for the difference between the two results.

**Significant intermolecular forces exists between the gas molecules, hence the gases deviates from ideality.**

[1]

**(b)** Methane can be obtained when carbon monoxide is heated to 900 °C with hydrogen gas as shown in the following equation.

$$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g)$$

**(ii)** Write an expression for the $K_c$ of the reaction, stating its units.

$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$ **mol$^{-2}$ dm$^6$**

[1]

**(iii)** 1 mol of carbon monoxide was heated with 4 mol of hydrogen gas in a 10 dm$^3$ vessel. At equilibrium, the vessel contained 0.387 mol of methane.

Calculate the $K_c$ for the reaction of carbon monoxide.

| | **CO** | **$3H_2$** | $\rightleftharpoons$ | **$CH_4$** | **$H_2O$** |
|---|---|---|---|---|---|
| **Initial mol** | **1** | **4** | | **0** | **0** |
| **Δ mol** | **-0.387** | **-1.161** | | **+0.387** | **+0.387** |
| **Eq mol** | **0.613** | **2.839** | | **0.387** | **0.387** |
| **[ ] mol dm$^{-3}$** | **0.0613** | **0.284** | | **0.0387** | **0.0387** |

$K_c = \frac{(0.0387)(0.0387)}{(0.0613)(0.284)^3}$ **= 1.07 mol$^{-2}$ dm$^6$**

[2]

**(iv)** Suggest, with an explanation, how the position of equilibrium might alter when 1 mol of helium was added into the vessel.

**When an inert gas is added, the total pressure increase but the partial pressure of the reactants and products do not change. There would not be any change to the position of equilibrium.**

**OR**
**When an inert gas is added, since the volume of the vessel remains the same, the concentration of the reactants and products do not change. There would not be any change to the position of equilibrium.**

[1]

**(c)** Anhydrous aluminium sulfate is commonly used in organic reactions to remove water. It decomposes at 600 °C to produce only an insoluble white solid and misty fumes. The white solid dissolves in both aqueous sodium hydroxide and aqueous hydrochloric acid while the misty fumes turn moist blue litmus red.

**(i)** Suggest the identities of the white solid and the misty fumes. Hence, write a balanced equation for the decomposition of aluminium sulfate.

**White solid: $Al_2O_3$ Misty fumes: $SO_3$**

$Al_2(SO_4)_3 \rightarrow Al_2O_3 + 3SO_3$

[2]

**(ii)** Write equations for the reactions of the white solid with aqueous sodium hydroxide and hydrochloric acid.

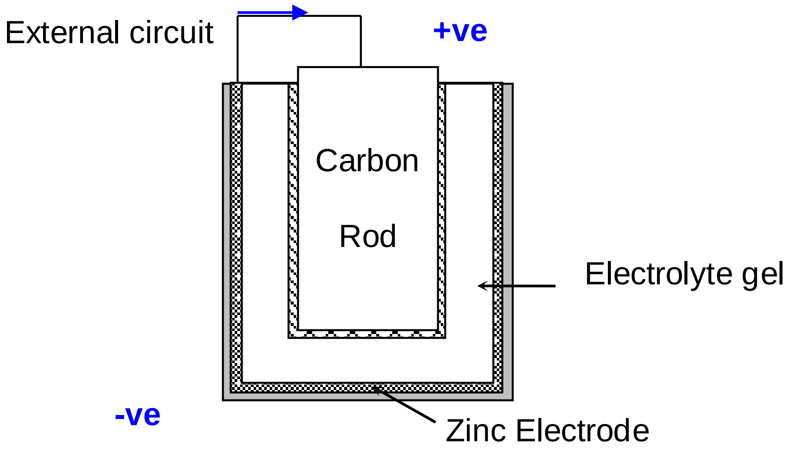
$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$ **[1]**

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na[Al(OH)_4]$ **[1]**

[2]

[Total: 14]

**4** Batteries for hearing aids comprise of zinc and carbon electrodes. These electrodes in an electrolyte, maintained at a pH of 11, forms a galvanic cell in which zinc is oxidised and oxygen from the air is reduced.



**(a)** Write a balanced equation for the overall chemical reaction and calculate the $E^{\theta}_{cell}$ of this cell.

**$2\ Zn + O_2 + 2H_2O \rightarrow 2\ Zn^{2+} + 4OH^-$ [or $2\ Zn(OH)_2\ (s)$]**

**$E^{\theta}_{cell} = +0.40 + (+0.76) = +1.16\ V$**

[2]

**(b)** Indicate, on the diagram above, the polarity of both electrodes and the direction of electron flow in the external circuit.

[2]

**(c)** Explain how the e.m.f. of the cell would change if the pH of the electrolyte decreases.

**When pH decreases, $[OH^-]$ falls and so, position of equilibrium of the reduction half-cell shifts to the right. Hence, $E_{reduction}$ becomes more positive, making e.m.f. more positive.**

[2]

**(d)** If a current of 4 x $10^{-5}$ A was drawn from the cell, calculate how long a zinc electrode weighing 2 g will last before it needs to be replaced. Give your answer correct to the nearest day.

**Amount of Zn =** $\frac{2}{65.4}$ **= 0.03058 mol**

**$Zn \rightarrow Zn^{2+} + 2\ e^-$**

**Amount of electrons = 2 × 0.03058 = 0.06116 mol**

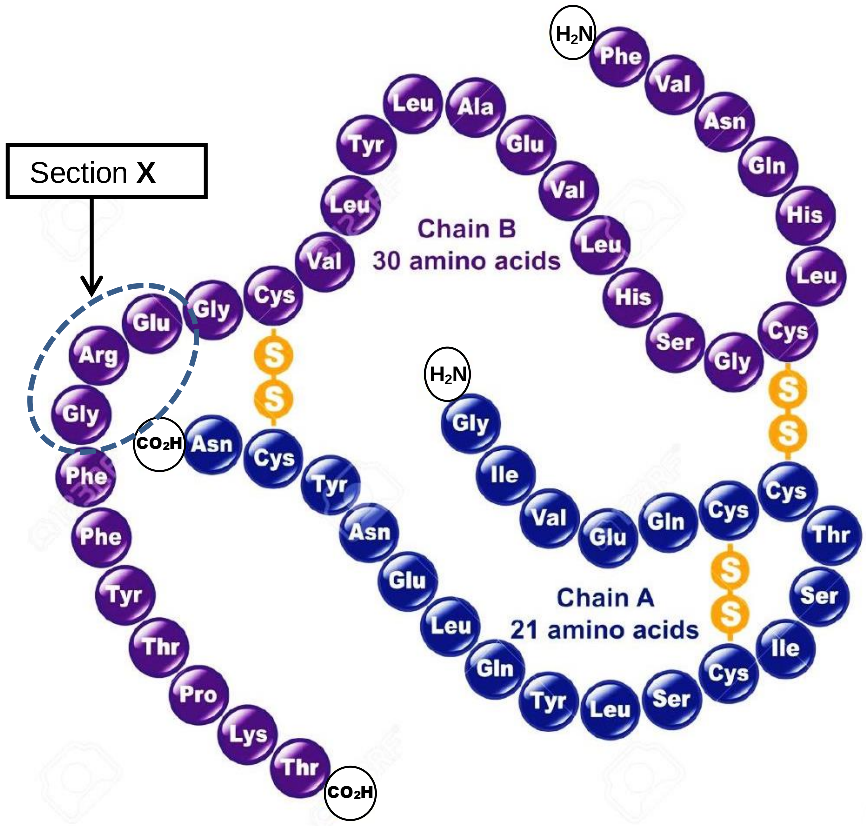
**$\therefore$ Q = 0.06116 × 96500 = 5902 C**

$$t = \frac{Q}{I} = \frac{5902}{4 \times 10^{-5}} = 1.476 \times 10^{8}\ s = \underline{1708\ days}$$

[2]
[Total: 8]

**5** Insulin is a hormone made by the pancreas that allows your body to use glucose from carbohydrates in the food that you eat for energy. Insulin helps keeps your blood sugar level from getting too high or too low.

The insulin molecule consists of 51 amino acid residues, in two polypeptide chains.

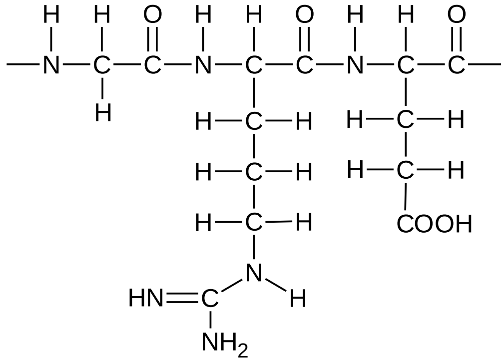


Some information on the amino acids of insulin is given below.

| amino acid | Abbreviated name | Formula of side chain (**R** in **R**$CH(NH_2)CO_2H$) | pI |
|---|---|---|---|
| arginine | arg | $-(CH_2)_3NHC(NH_2)=NH$ | 10.76 |
| cysteine | cys | $-CH_2SH$ | 5.07 |
| glutamic acid | glu | $-CH_2CH_2COOH$ | 3.22 |
| glycine | gly | $-H$ | 5.97 |

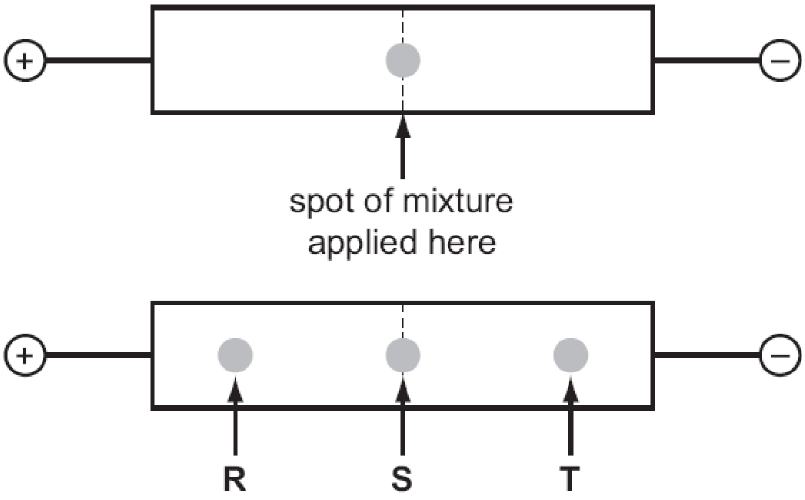
**(a)** Draw the structural formula of section **X** in insulin.

**Formula must start with N terminus, showing R groups, ending with C terminus:**

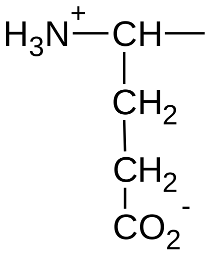
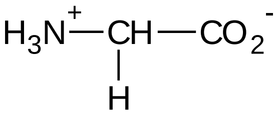
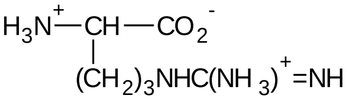


[1]

**(b)** The diagram shows the results of electrophoresis on a mixture of the amino acids obtained from hydrolysis of section **X** at pH 6.0.



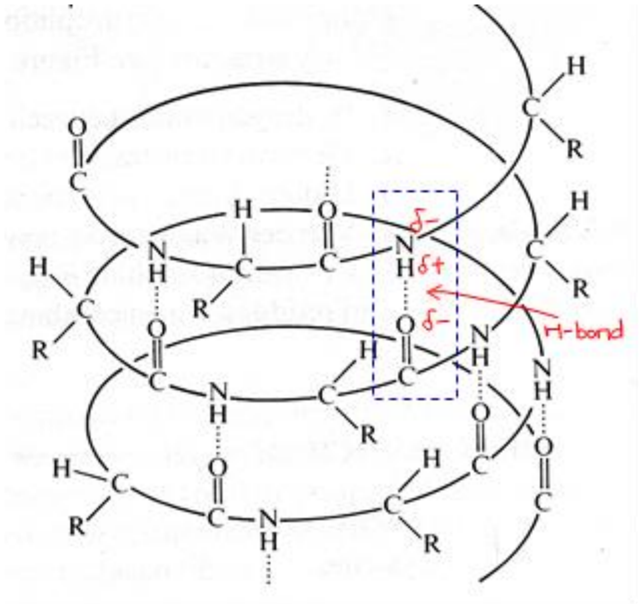
Draw the structure of the species responsible for the spots labelled **R**, **S** and **T**.

| **R** | **S** | **T** |
|---|---|---|
| <br>$H_3\overset{+}{N}-CH(CH_2CH_2CO_2^-)-CO_2^-$<br>**k** | <br>$H_3\overset{+}{N}-CH(H)-CO_2^-$ | <br>$H_3\overset{+}{N}-CH((CH_2)_3NHC(NH_3)^+{=}NH)-CO_2^-$<br>**Accept protonation on any basic amine group of side chain. (more than 1 protonation also allowed)** |

[3]

**(c)** The polypeptide chains of insulin coil to form short sections of α-helix which stabilises the secondary structure.

Describe with the aid of a sketch, how a polypeptide chain is held in the shape of an α-helix.



[3]

**(d)** The three-dimensional structure of insulin is further stabilised by disulfide linkages.

Write an equation for the formation of such linkage and state the type of reaction involved.

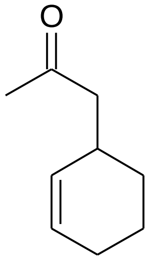
**Type of reaction: oxidation**

**$-CH_2S-H + H-SCH_2- \rightarrow -CH_2-S-S-CH_2- + 2[H]$ (*or* $H_2$)**
**OR**
**$-CH_2S-H + H-SCH_2- + [O]$ (*or* $\frac{1}{2} O_2$) $\rightarrow -CH_2S-SCH_2- + H_2O$**

[2]
[Total: 9]

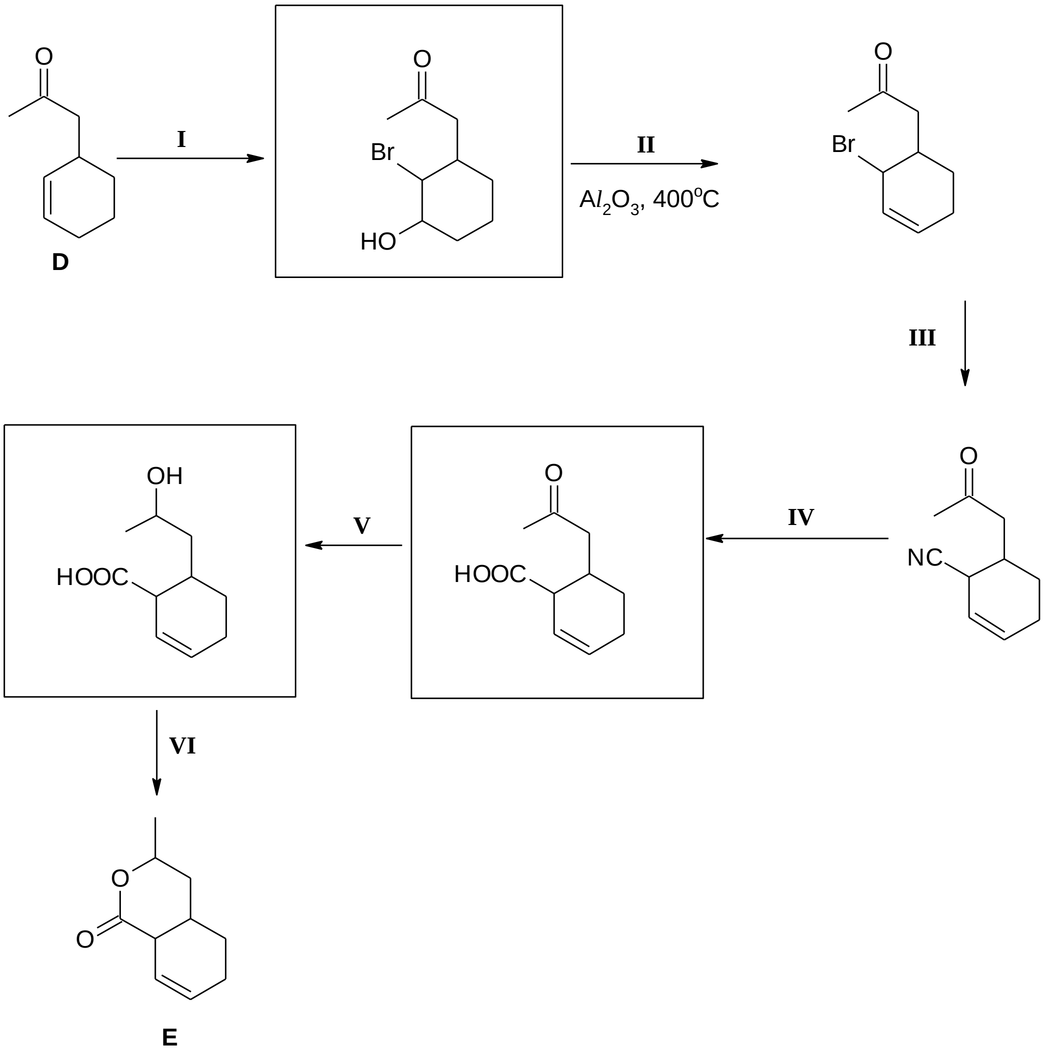
**6** Lactones are cyclic esters. They are formed by intramolecular esterification of the corresponding hydroxycarboxylic acids.

**(a)** **(i)** The reaction scheme below shows how lactone **E** is synthesised from compound **D**.



**D**

Complete the reaction scheme by giving the structural formulae of the intermediate organic products in the spaces provided and stating the reagents and conditions for steps **I**, **III**, **IV**, **V** and **VI**.



| Step | Reagents and conditions |
|---|---|
| I | $Br_2(aq)$ |
| III | NaCN/KCN in ethanol, heat |
| IV | $H_2SO_4$ (aq), heat |
| V | $NaBH_4$ in methanol |
| VI | concentrated $H_2SO_4$, heat |

[8]

**(ii)** Suggest a simple chemical test to distinguish compound **D** from **E**.

**Reagents and conditions: 2,4-dinitrophenylhydrazine**

**Observations:**

**For compound D, orange ppt is formed.**

**For compound E, no orange ppt is formed (or no observable change)**

**Or**

**Reagents and conditions: $K_2Cr_2O_7$, $H_2SO_4$(aq), heat**

**Observations:**

**For compound D, orange solution remains (or no observable change)**

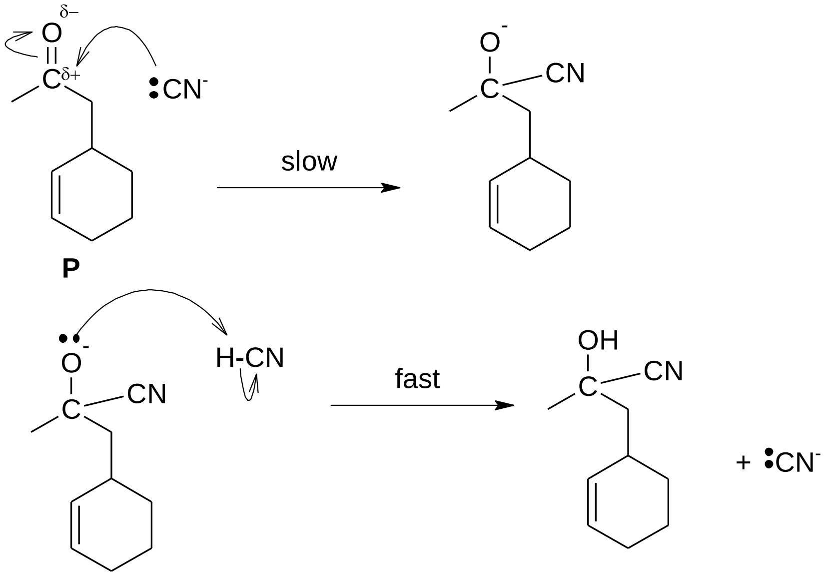
**For compound E, orange solution turned green.**

[2]

**(iii)** Name and outline the mechanism when compound **D** is treated with HCN in the presence of aqueous NaOH at 10 °C.

**Name of mechanism: Nucleophilic Addition**

**$NaOH(aq) + HCN(aq) \rightarrow H_2O(l) + Na^+(aq) + CN^-(aq)$**



[3]

**(b)** Lactones with three- or four-membered rings are very reactive compared to five- or six-membered rings, making their isolation difficult.

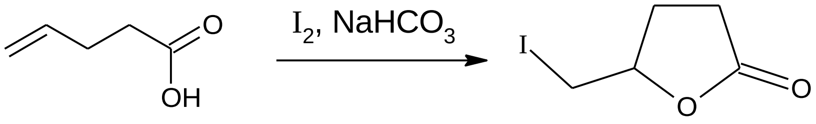
Suggest why lactones with three- or four-membered rings are very reactive.

**Three- or four-membered rings have significant ring/angle strain.**

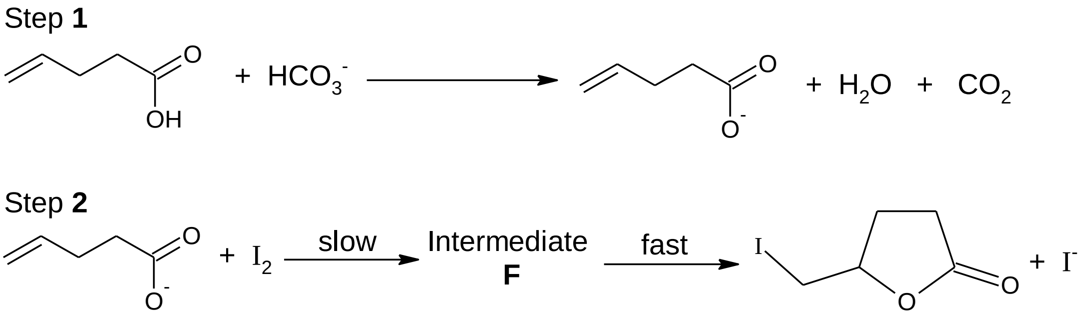
[1]

**(c)** Iodolactonisation reaction was first reported by M. J. Bougalt in 1904 and has since become one of the most effective ways to synthesise lactones.

An example of the iodolactonisation is the reaction of 4-pentenoic acid as shown below.



Two simplified steps in the iodolactonisation mechanism are given below.



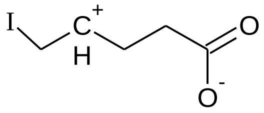
**(i)** Suggest the role of $HCO_3^-$ in step **1** of the mechanism.

**It acts as a base to abstract $H^+$ from the carboxylic acid.**

[1]

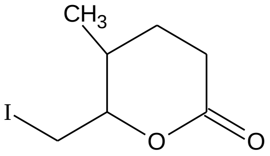
**(ii)** The type of reaction in Step **2** of the mechanism is electrophilic addition.

Draw the structure of intermediate **F**.



[1]

**(iii)** Suggest the structural formulae of the final organic product formed when $CH_2{=}CHCH(CH_3)CH_2CH_2COOH$ undergoes iodolactonisation in a similar process as above.



[1]

[Total: 17]

**End of Paper**

JC2 PRELIMINARY
EXAMINATION HIGHER 2

CANDIDATE NAME

CT GROUP | 1 | 5 | S | | |

INDEX NUMBER | | | | |

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**CHEMISTRY** **9647/03**

Paper 3 Free Response **15 September 2016**

**2 hours**

Candidates answer on separate paper.

| | |
|---|---|
| Additional Materials: | Answer Paper<br>Graph Paper<br>Data Booklet<br>Cover Page |

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**READ THESE INSTRUCTIONS FIRST**

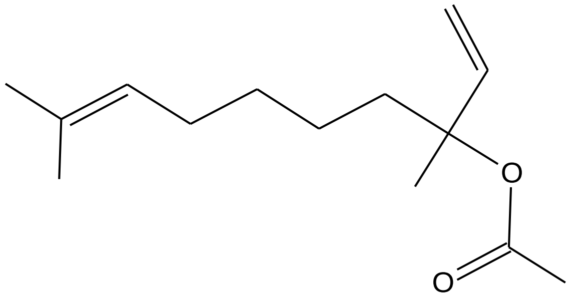
Write your class, index number and name on all work that you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together.

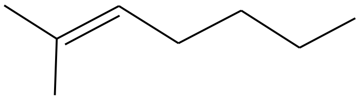
Answer any **four** questions.
Begin **each** question on a fresh piece of writing paper.

**1** **(a)** Linalyl acetate is a naturally occurring phytochemical found in many flowers. It is one of the principal components of the essential oils of bergamot and lavender. It has the following structure.



Linalyl acetate can be synthesised by the reaction of carboxylate anion with an alkyl halide as shown below:

$$CH_3CO_2^-Na^+ + RC(CH_3)(CH=CH_2)I \rightarrow NaI + RC(CH_3)(CH=CH_2)OCOCH_3$$

where R = 

The kinetics of this reaction was determined by measuring the concentration of the remaining $RC(CH_3)(CH=CH_2)I$ with time.

The initial concentrations of $RC(CH_3)(CH=CH_2)I$ and $CH_3CO_2^-Na^+$ were 0.0050 mol dm$^{-3}$ and 0.100 mol dm$^{-3}$ respectively. The following data was obtained.

| Time/ min | $[RC(CH_3)(CH=CH_2)I]$ / mol dm$^{-3}$ |
|---|---|
| 0 | 0.0050 |
| 15 | 0.0040 |
| 30 | 0.0032 |
| 45 | 0.0026 |
| 60 | 0.0021 |
| 75 | 0.0017 |

**(i)** Plot a suitable graph to show that the order of reaction with respect to $RC(CH_3)(CH=CH_2)I$ is one. [3]

**(ii)** A new set of experiment was carried out and the initial concentrations of $RC(CH_3)(CH=CH_2)I$ and $CH_3CO_2^-Na^+$ was increased to 0.0100 mol dm$^{-3}$, and 0.200 mol dm$^{-3}$ respectively. When a similar graph was plotted, it was found that the gradient at each point doubled.

Deduce the order of reaction with respect to $CH_3CO_2^-Na^+$, and explain your answer. [2]

**(iii)** Construct a rate equation for the reaction between $CH_3CO_2^-Na^+$ and $RC(CH_3)(CH=CH_2)I$, stating the units for the rate constant. [1]

**(iv)** Using your answer in **(a)(iii)**, suggest the mechanism for the reaction between $CH_3CO_2^-Na^+$ and $RC(CH_3)(CH=CH_2)I$ that leads to the formation of the ester, $RC(CH_3)(CH=CH_2)OCOCH_3$.
[3]

**(b)** An example of a homogeneous catalyst is $Fe^{2+}$(aq), which is used in the oxidation of sodium ethanedioate, $Na_2C_2O_4$, with acidified potassium manganate(VII), $KMnO_4$. Ethanedioate is oxidised to carbon dioxide.

**(i)** What do you understand by the term *homogeneous* catalyst? [1]

**(ii)** Write an overall equation for the reaction of sodium ethanedioate with acidified potassium manganate(VII). [1]

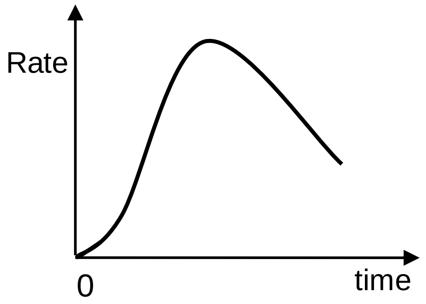
**(iii)** The $E^{\ominus}_{cell}$ of the reaction between sodium ethanedioate with acidified potassium manganate(VII) is +2.01 V. However, the reaction is found to proceed at a very slow rate.

Explain why the reaction between sodium ethanedioate and acidified potassium manganate(VII) is slow. [1]

**(iv)** By considering suitable $E^{\ominus}$ values from the *Data Booklet* and the data given below, explain how $Fe^{2+}$ functions as a catalyst for the reaction between sodium ethanedioate with acidified potassium manganate(VII), writing equations where appropriate.

$$2CO_2(g) + 2e^- \rightleftharpoons C_2O_4^{2-}(aq) \qquad E^{\theta} = -0.49V$$ [3]

**(v)** In the absence of a $Fe^{2+}$ catalyst, the rate of reaction between potassium manganate(VII), and sodium ethanedioate is shown in the graph below.

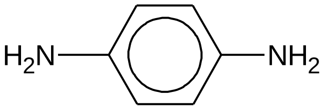


Explain the shape of the graph. [2]

**(c)** The rate of a chemical reaction is usually increased at elevated temperatures.

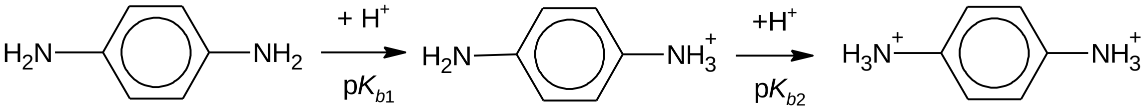
Explain, with the aid of a Boltzmann Distribution graph, why an increase in temperature increases the rate of reaction. [3]
[Total: 20]

**2** **(a)** Ammonia and *para*-phenylenediamine, $H_2NC_6H_4NH_2$, are *Bronsted-Lowry bases* that are used widely in permanent hair dyes. *Para*-phenylenediamine has the structure shown below:



*para*-phenylenediamine

*Para*-phenylenediamine, $H_2NC_6H_4NH_2$, can ionise in stages.



The two p$K_b$ values associated with *para*-phenylenediamine are shown in the table below.

| Base | formula | p$K_{b1}$ | p$K_{b2}$ |
|---|---|---|---|
| ammonia | $NH_3$ | 4.7 | - |
| *para*-phenylenediamine | $H_2NC_6H_4NH_2$ | 7.7 | 11.0 |

**(i)** Explain what is meant by the term *Bronsted-Lowry base*. [1]

**(ii)** Suggest a reason why the p$K_{b1}$ value of *para*-phenylenediamine is higher than the p$K_{b1}$ of ammonia. [1]

**(iii)** Suggest a reason why the p$K_{b1}$ value of *para*-phenylenediamine is lower than p$K_{b2}$. [1]

**(iv)** Explain what is meant by a *buffer solution*. [1]

**(v)** Assuming that a solution at pH 6.5 contains only $[H_2NC_6H_4NH_2]$ and $[H_2NC_6H_4NH_3^+]$, calculate the ratio of $\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$ in the solution.

(ignore the effect of p$K_{b2}$ of *para*-phenylenediamine on the pH) [2]

**(vi)** Calculate the pH of solution containing equimolar amount of $H_2NC_6H_4NH_3^+$ and $^+H_3NC_6H_4NH_3^+$ [2]

**(b)** Ammonia is commonly used in qualitative analysis of halides in aqueous solutions, such as detecting the presence of chloride and bromide ions in natural water sources such as rivers, lakes and streams.

**(i)** 5 $cm^3$ of 0.0100 mol $dm^{-3}$ of silver nitrate is added to a 30 $cm^3$ sample of river water containing chloride ions.

What is the minimum concentration, in mol $dm^{-3}$, of chloride ions present in the river water when the first trace of precipitate appears?

Given solubility product of the silver chloride is $2.0 \times 10^{-10}$ $mol^2$ $dm^{-6}$.

[2]

**(ii)** To a test tube containing another river sample containing bromide ions, describe what you would see when aqueous silver nitrate is added to the sample, followed by excess aqueous ammonia to the resulting mixture. [1]

**(iii)** Explain, with aid of appropriate equation(s), the observations in **(b)(ii)**.

You should use the concepts of Le Chatelier's Principle and solubility product, $K_{sp}$, to explain your answer. [4]

**(c)** **(i)** When iodine reacts with sodium hydroxide, iodide and iodate(V) are formed.

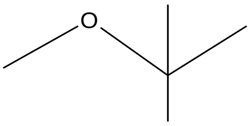
Write a balanced ionic equation, with state symbols, for the formation of $IO_3^-$ when iodine reacts with sodium hydroxide. Name the type of reaction taking place. [2]

**(ii)** When Group II iodates(V), **M**$(IO_3)_2$, are heated at high temperature, it form the metal oxide, iodine vapour and a colourless gas that relights glowing splinter.

It was observed that Group II iodates(V) down the group have to be heated more strongly before the iodine vapour appears. Explain why thermal stability increases down the group for Group II iodate(V). [3]

[Total: 20]

**3** **(a)** Liquid methyl t-butyl ether, **MTBE**, is a fuel additive that is used as an oxygenate to raise the octane number in fuel. This will help the fuel to burn completely and reduce air pollution.



**MTBE**

**(i)** What is meant by the term *standard enthalpy change of formation* of **MTBE**? [1]

**(ii)** Use the following data and relevant data from *Data Booklet* to construct an appropriate energy cycle, find the standard enthalpy change of formation of **MTBE**.

| | |
|---|---|
| Standard enthalpy change of atomisation of C(s) | +715 kJ $mol^{-1}$ |
| Standard enthalpy change of atomisation of **MTBE**($l$) | +6822 kJ $mol^{-1}$ |

[4]

**(iii)** Given that the standard enthalpy change of vaporisation of **MTBE** is +30.4 kJ $mol^{-1}$ and using relevant data from the *Data Booklet and* **(a)(ii)**, calculate the bond energy of C-O in **MTBE**. [2]

**(iv)** Suggest a reason for the difference in the C-O bond energy in **(a)(iii)** from the value given in the *Data Booklet*. [1]

**(b)** **MTBE** can be produced from methanol and but-1-ene by the following equation. The reaction has a standard entropy change of reaction of -281 J $mol^{-1}$ $K^{-1}$.

$$CH_3OH(l) + C_4H_8(l) \rightarrow \underset{\textbf{MTBE}}{C_5H_{12}O(l)} \qquad \Delta H^{\theta}$$

The table below lists the $\Delta H^{\theta}_f$ (standard enthalpy change of formation) values for some compounds.

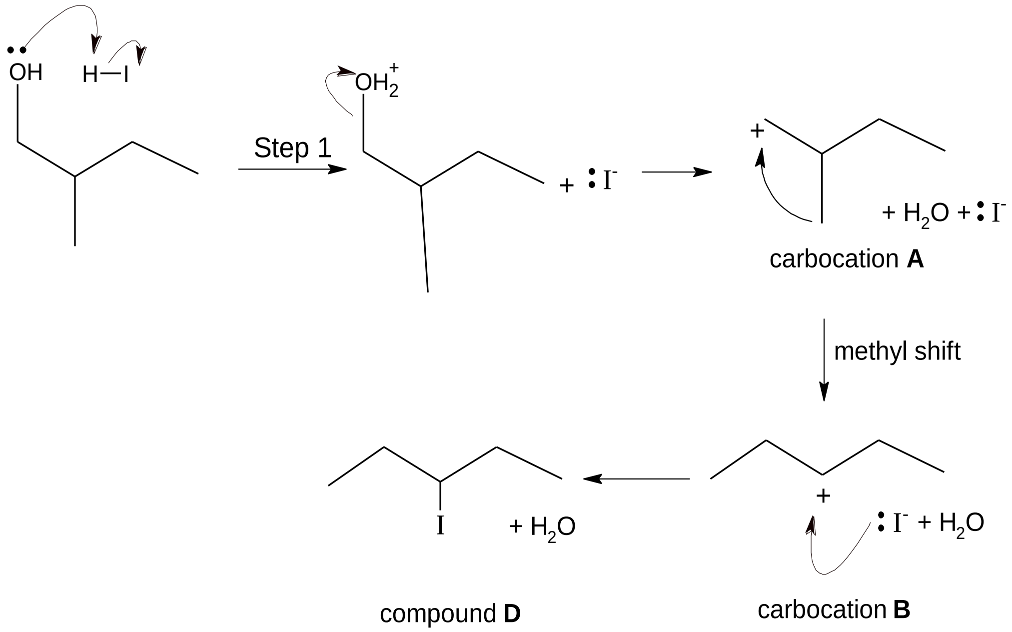
| compound | $\Delta H^{\theta}_f$ / kJ $mol^{-1}$ |
|---|---|
| $CH_3OH(l)$ | -239 |
| $C_4H_8(l)$ | -0.4 |

**(i)** Calculate the $\Delta H^{\theta}_f$ for the reaction in **(b)** using the values from the table above and your answer to **(a)(ii)**. [1]

**(ii)** Determine the feasibility of the production of **MTBE** from methanol and but-1-ene at 298 K. [2]

**(c)** Methyl shift can occur in organic chemistry reactions in reactions involving carbocation intermediates.

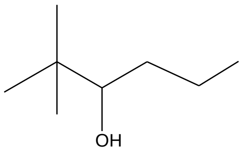
An example of a methyl shift in a reaction between an alcohol and HI is shown below. In this reaction compound **D** is produced as the major product.



**(i)** What is the role of HI in step 1? [1]

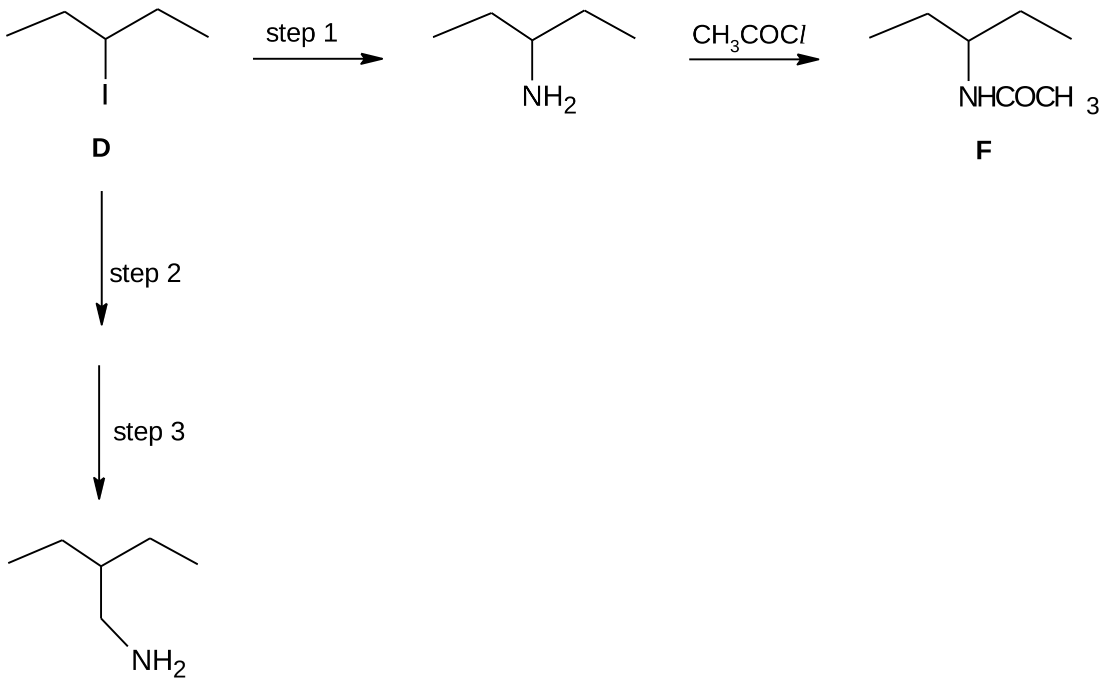
**(ii)** Suggest a reason why there is a methyl shift to produce carbocation **B** from carbocation **A**. [1]

**(iii)**

The structure of compound **E** is .

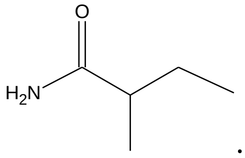
Predict the major final product formed when compound **E** reacts with HBr based on the methyl shift reaction given in **(c)**. [1]

**(iv)** Compound **D** undergoes the following reactions.



Suggest suitable reagents for steps 1, 2 and 3. [3]

**(v)** Suggest one simple chemical test which would enable you to distinguish between compound **F** and



.

You should state the reagents and conditions for the test and describe the observations.

[3]

[Total: 20]

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**4** **(a)** Compound **G**, $C_{10}H_{15}NO_3$, is a natural stimulant made in the adrenal gland of the kidney and is carried in the bloodstream and affects the autonomous nervous system, which controls functions such as heart rate and dilation of the pupils.

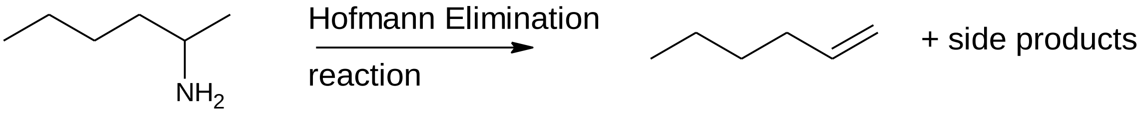
**G** is soluble in dilute sodium hydroxide and dilute hydrochloric acid but does not react with sodium carbonate.

**G** undergoes reaction with hot acidified potassium dichromate(VI) to form **J**. **J** gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not give a silver mirror with Tollens' reagent. Upon heating with concentrated $H_2SO_4$, **G** forms **K**, $C_{10}H_{13}NO_2$. **K** does not react with $PCl_5$. On heating with acidified potassium manganate(VII), **K** forms three compounds, **L**, $C_7H_6O_4$, **M**, $C_2H_4O_2$, and an ammonium salt, $CH_3NH_3^+$.

Deduce the structures for each compound, **G** to **M**, and give an account of the chemistry involved. [10]

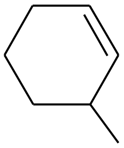
**(b)** Like alcohols and halogenoalkanes, amines can be converted into alkenes by an elimination reaction known as Hofmann elimination.

For example, 1-methyl-pentylamine is converted into hex–1–ene as shown.



An interesting feature of the Hofmann elimination is that it gives a **less substituted alkene** compared to other elimination reactions.

**(i)** Draw the likely structure of the starting amine if the following alkene **N** is the main product formed when the amine undergoes a Hofmann elimination reaction.



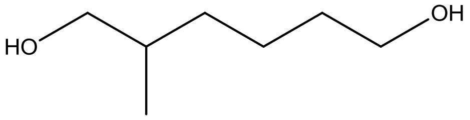
**N**

[1]

**(ii)** Suggest, in no more than 3 steps, a suitable synthetic pathway to convert **N** into the following compounds.

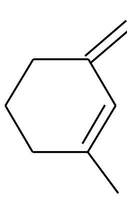
For each step, state clearly the reagents and conditions, indicating the structural formula of all intermediate compounds formed.

**(I)**



[2]

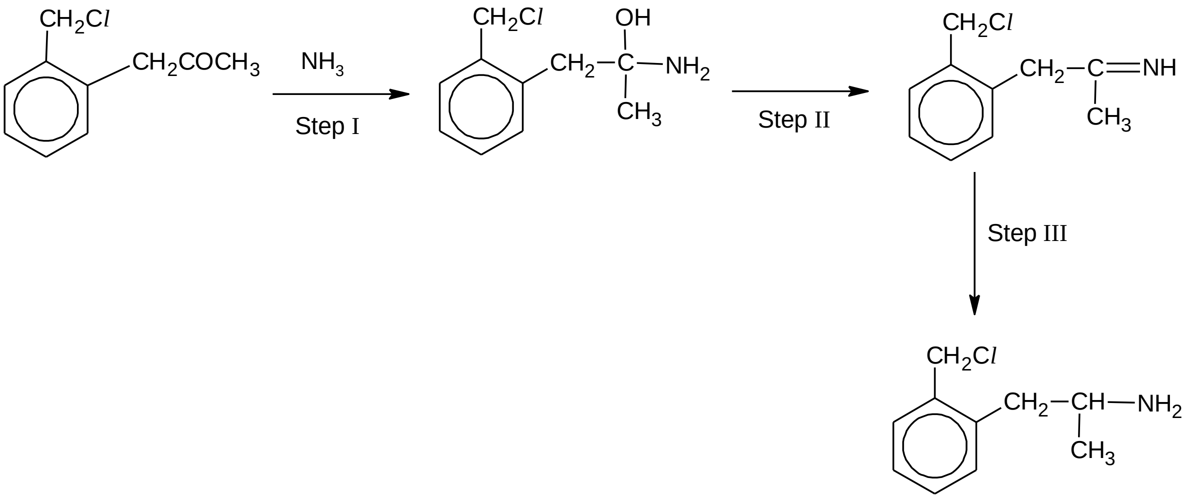
**(II)**



[3]

**(c)** Amines can be formed by reductive amination of an aldehyde or ketone with ammonia or amine in the presence of reducing agent.

A reductive amination to produce an amine **P** takes place in the pathway shown.



**P** ($C_{10}H_{14}NCl$)

**(i)** Suggest the type of reaction that occurs in steps I and II. [2]

**(ii)** Suggest the reagents and conditions for step III. [1]

**(iii)** On heating, **P** forms **Q**, $C_{10}H_{13}N$. Suggest a structure for **Q**.

[1]
[Total: 20]

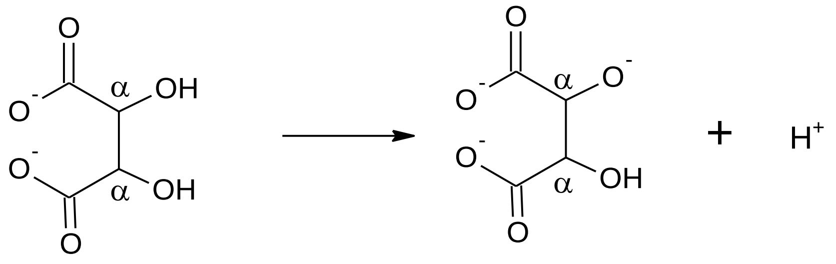
**5** **(a)** An electrochemical cell involving tartaric acid, $(CH(OH)CO_2H)_2$, has the following cell diagram notation.

$Pt(s)|(CH(OH)CO_2H)_2\ (aq)\ |CO_2(g)\ |H^+(aq)\ ||\ Co^{3+}(aq), Co^{2+}(aq)|Pt(s)$

**(i)** Given that the e.m.f of the cell is +0.80 V and using relevant data from the *Data Booklet*, determine the standard electrode potential of the $CO_2(g)|(CH(OH)CO_2H)_2(aq)$ half-cell. [2]

**(ii)** Draw a labelled diagram of the above electrochemical cell. [3]

**(b)** Fehling's solution is made by adding equal volumes of a blue solution **A** containing aqueous copper(II) sulfate and a colourless solution **B** containing potassium sodium tartrate and sodium hydroxide. In a strong base, an alpha-hydroxy group in the tartrate ion, $(CH(OH)CO_2^-)_2$, deprotonates as shown in the diagram below.



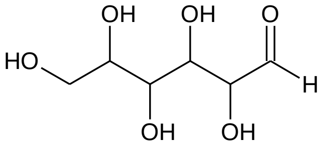
Deprotonated tartrate ion

The deprotonated tartrate ion acts as a bidentate ligand and binds to the $Cu^{2+}(aq)$ using both oxygen atoms from the **alpha-hydroxy groups**. A square planar bistartratocuprate(II) complex, $[Cu(tart)_2]^{4-}$, forms, and a deep blue solution is seen.

[tart = deprotonated tartrate ion]

**(i)** Draw the shape of $[Cu(tart)_2]^{4-}$ complex, indicating clearly the type of bonds formed between the $Cu^{2+}$ and the ligands. [2]

**(ii)** The open straight chain form of D–glucose, a reducing sugar, is shown.



D–glucose

State what would be observed when D–glucose solution is warmed with a few drops of Fehling's solution. Hence, or otherwise, write the balanced equation for the reaction described above. [2]

**(iii)** Explain why there is a need to form the $[Cu(tart)_2]^{4-}$ complex in the Fehling's solution test. [1]

**(iv)** Explain why the Fehling's solution is deep blue while potassium sodium tartrate solution is colourless. [4]

**(v)** Stronger field ligands are known to give rise to a larger energy gap between the two sets of d-orbitals in a transition metal complex.

| | | | | | |
|---|---|---|---|---|---|
| Violet | Blue | Green | Yellow | Orange | Red |

400 nm 430 nm 480 nm 560 nm 590 nm 630 nm 750 nm

$\longrightarrow$

. Energy of light decreases

To test for proteins, Biuret reagent which also contains the $[Cu(tart)_2]^{4-}$ complex is used. In the presence of peptides, it undergoes ligand exchange to form $[Cu(peptide)_2]^{2+}$. The deep blue solution turns violet.

Using the above electromagnetic spectrum of visible light, state the relative field strength of peptides and deprotonated tartrate ions. Explain your answer. [3]

**(c)** Adolf Kolbe first published a method describing the preparation of an alkane from the electrolysis of an aqueous solution of sodium salt of a monoprotic acid, using inert electrodes.

In the Kolbe electrolysis of sodium propanoate, butane was formed at the anode in the following reaction.

$$2CH_3CH_2CO_2^- \rightarrow CH_3CH_2CH_2CH_3 + 2CO_2 + 2e^-$$

**(i)** Write the half equation for the reaction at the cathode during the electrolysis of sodium propanoate. Hence write an equation for the **overall** reaction. [2]

**(ii)** A student tried to synthesise another hydrocarbon using an aqueous solution of a sodium salt of a diprotic acid, succinic acid, $(CH_2CO_2H)_2$. The succinate ion, $(CH_2CO_2^-)_2$ ,undergoes a similar reaction as propanoate ion at the anode.

$$(CH_2CO_2^-)_2 \rightarrow \mathbf{R} + 2CO_2 + 2e^-$$

Suggest an identity of the hydrocarbon **R**. [1]

[Total : 20]

**End of Paper**

JC2 PRELIMINARY
EXAMINATION HIGHER 2

CANDIDATE NAME: ANSWER SCHEME

CT GROUP: 1 5

INDEX NUMBER:

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# CHEMISTRY

**9647/03**

Paper 3 Free Response

**15 September 2016**

**2 hours**

Candidates answer on separate paper.

| | |
|---|---|
| Additional Materials: | Answer Paper<br>Data Booklet<br>Cover Page |

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**READ THESE INSTRUCTIONS FIRST**

Write your class, index number and name on all work that you hand in.
Write in dark blue or black pen on both sides of the paper.
You may use a soft pencil for any diagrams, graphs or rough workings.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
You are reminded of the need for good English and clear presentation in your answers.

The number of marks is given in brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together.

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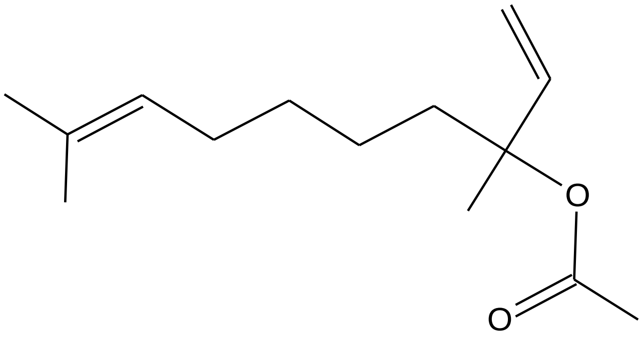
This document consists of 22 printed pages.

Answer any **four** questions.
Begin **each** question on a fresh piece of writing paper.

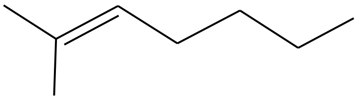
**1** **(a)** Linalyl acetate is a naturally occurring phytochemical found in many flowers. It is one of the principal components of the essential oils of bergamot and lavender. It has the following structure.



Linalyl acetate can be synthesised by the reaction of carboxylate anion with an alkyl halide as shown below:

$$CH_3COO^-Na^+ + RC(CH_3)(CH{=}CH_2)I \rightarrow NaI + RC(CH_3)(CH{=}CH_2)OCOCH_3$$

where R =



The kinetics of this reaction was determined by measuring the concentration of the remaining $RC(CH_3)(CH{=}CH_2)I$ with time. The initial concentrations of $RC(CH_3)(CH{=}CH_2)I$ and $CH_3COO^-Na^+$ were 0.0050 mol dm$^{-3}$ and 0.100 mol dm$^{-3}$ respectively . The following data was obtained.

| Time/ min | $[RC(CH_3)(CH{=}CH_2)I]$ / mol dm$^{-3}$ |
|---|---|
| 0 | 0.0050 |
| 15 | 0.0040 |
| 30 | 0.0032 |
| 45 | 0.0026 |
| 60 | 0.0021 |
| 75 | 0.0017 |

**(i)** Plot a suitable graph to show that the order of reaction with respect to $RC(CH_3)(CH{=}CH_2)I$ is one. [3]

constant $t_{½}$ (at about 48.25 minutes) first order

**(ii)** A new set of experiment was carried out and the initial concentrations of $RC(CH_3)(CH=CH_2)I$ and $CH_3CO_2^-Na^+$ was increased to 0.0100 mol dm$^{-3}$, and 0.200 mol dm$^{-3}$ respectively. When a similar graph was plotted, it was found that the gradient at each point doubled.

Deduce the order of reaction with respect to $CH_3CO_2^-Na^+$, and explain your answer. [2]

The reaction was zero order with respect to $CH_3COO^-Na^+$.

Gradient of a concentration-time graph gives the rate of reaction.

The reaction is first order with respect to $RC(CH_3)(CH=CH_2)I$, and doubling the concentration will double the rate. This implies that changing the concentration of $CH_3CO_2^-Na^+$ has no effect on the rate of reaction.

**(iii)** Construct a rate equation for the reaction between $CH_3COO^-Na^+$ and $RC(CH_3)(CH=CH_2)I$, stating the units for the rate constant. [1]

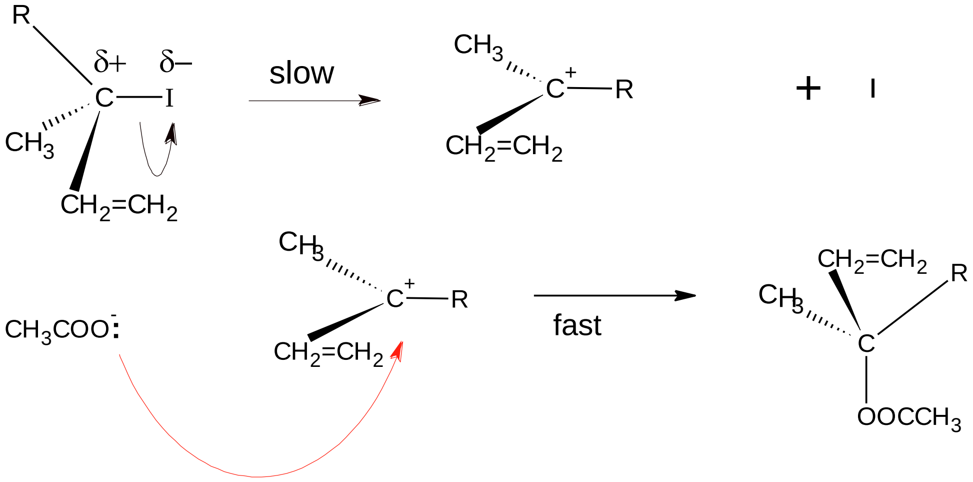
Rate = $k[RC(CH_3)(CH=CH_2)I]$

Units of k = min$^{-1}$

**(iv)** Using your answer in **(iii)**, suggest the mechanism for the reaction between $CH_3CO_2^-Na^+$ and $RC(CH_3)(CH=CH_2)I$ that leads to the formation of the ester, $RC(CH_3)(CH=CH_2)OCOCH_3$.

[3]

Nucleophilic substitution ($S_N1$)



**(b)** An example of a homogeneous catalyst is $Fe^{2+}(aq)$, which is used in the oxidation of sodium ethanedioate, $Na_2C_2O_4$, with acidified potassium manganate(VII), $KMnO_4$. Ethanedioate is oxidised to carbon dioxide.

**(i)** What do you understand by the term *homogeneous* catalyst. [1]

A homogeneous catalyst is a catalyst that exists in the same phase as the reactants.

**(ii)** Write an overall equation for the reaction of sodium ethanedioate with acidified potassium manganate(VII). [1]

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \text{-->} 2Mn^{2+} + 8H_2O + 10CO_2$

**(iii)** The $E^\ominus_{cell}$ of the reaction between sodium ethanedioate with acidified potassium manganate(VII) is +2.01 V. However, the reaction is slow.

Explain why the reaction is slow. [1]

High activation energy due to the repulsion between two negatively charged ions $MnO_4^-$ and $C_2O_4^{2-}$ to react, the rate of reaction is very slow.

**(iv)** By considering suitable $E^\ominus$ values from the *Data Booklet* and the data given below, explain how $Fe^{2+}$ functions as a catalyst for the reaction between sodium ethanedioate with acidified potassium manganate(VII), writing equations where appropriate.

$$2CO_2(g) + 2e^- \rightleftharpoons C_2O_4^{2-}(aq) \qquad E^\theta = -0.49V$$

[3]

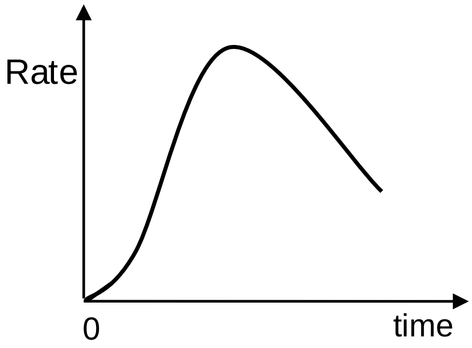
$Fe^{2+}$ can speed up the rate of reaction as it is able to attract the oppositely charged ions in the following equations:

$MnO_4^- + 8H^+ + 5Fe^{2+} \text{------>} 5Fe^{3+} + 4H_2O + Mn^{2+}$ $\quad E^\theta = +0.75V$

$C_2O_4^{2-} + 2Fe^{3+} \text{-------->} 2CO_2 + 2Fe^{2+}$ $\quad E^\theta = +1.26V$

Since the $E^\theta$ is positive for both reactions, they are energetically feasible.

**(iv)** In the absence of a $Fe^{2+}$ catalyst, the rate of reaction between potassium manganate(VII), and sodium ethanedioate is shown in the graph below.



Explain the shape of the graph. [2]

The rate of reaction is slow at the beginning of the reaction.

As the reaction proceeds, $[Mn^{2+}]$ increases, which catalyses the reaction. The rate of reaction increases.

The rate of reaction will eventually decrease as [reactants] decreases to very low levels despite the increasing concentration of the $Mn^{2+}$ catalyst.

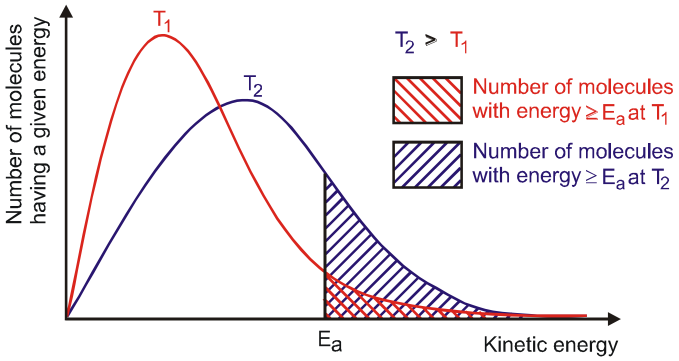
**(c)** The rate of a chemical reaction is usually increased at elevated temperatures.

Explain, with the aid of a Boltzmann Distribution graph, why an increase in temperature increases the rate of reaction. [3]

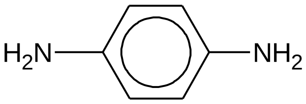
[Total: 20]

At a higher temperature, the average kinetic energy of the particles is higher. The particles move faster and collide with each other more frequently.

In addition, the number of particles with energy $\geq E_a$ increases exponentially, resulting in a greater number of effective collisions per unit time. This gives rise to a large increase in the rate of reaction.

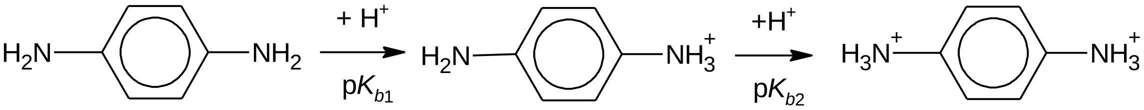


**2** **(a)** Ammonia and *para*-phenylenediamine, $H_2NC_6H_4NH_2$, are *Bronsted-Lowry bases* that are used widely in permanent hair dyes. *Para*-phenylenediamine has the structure shown below:



*para*-phenylenediamine

*Para*-phenylenediamine, $H_2NC_6H_4NH_2$, can ionise in stages.



The two $pK_b$ values associated with *para*-phenylenediamine are shown in the table below.

| Base | formula | $pK_{b1}$ | $pK_{b2}$ |
|---|---|---|---|
| ammonia | $NH_3$ | 4.7 | - |
| *para*-phenylenediamine | $H_2NC_6H_4NH_2$ | 7.7 | 11.0 |

**(i)** Using ammonia, $NH_3$, explain what is meant by the term *Bronsted-Lowry base*.

[1]

Ammonia, $NH_3$, has a lone pair of electrons which acts as a base to accept a proton.

**(ii)** Suggest a reason why the $pK_{b1}$ value of *para*-phenylenediamine is higher than the $pK_{b1}$ of ammonia. [1]

The lone pair of electrons on N of $H_2NC_6H_4NH_2$ can be delocalized into the bezene ring, making it less available to accept a proton, compared to $NH_3$. Hence $pK_{b1}$ value of *para*-phenylenediamine is larger than the $pK_{b1}$ of ammonia.

**(iii)** Suggest a reason why the $pK_{b1}$ value of *para*-phenylenediamine is lower than $pK_{b2}$. [1]

More energy is required to accept another $H^+$ by $H_2NC_6H_4NH_3^+$, from $H_2O$ to form $H_3NC_6H_4NH_3^{2+}$, which is electrostatically unfavourable. Hence $pK_{b1}$ value of *para*-phenylenediamine is lower than $pK_{b2}$.

OR

The lone pair of electrons on $NH_2$ of $H_2NC_6H_4NH_3^+$ can be delocalized into the bezene ring to a greater extent, making it less available to accept a proton. Hence $pK_{b1}$ value of *para*-phenylenediamine is lower than the $pK_{b2}$.

**(iv)** Explain what is meant by a *buffer solution*. [1]

A buffer solution is one which is able to ***resist*** a change in pH (i.e. maintain an almost constant pH) upon the addition of a ***small*** amount of acid or alkali, or on dilution.

**(v)** Assuming that a solution at pH 6.5 contains only [$H_2NC_6H_4NH_2$] and [$H_2NC_6H_4NH_3^+$], calculate the ratio of $\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$ in the solution.

[2]

pH + pOH = 14
pOH = 14 - 6.5 = 7.5

$$pOH = pK_1 + \lg\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$$

$$7.5 = 7.7 + \lg\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]}$$

$$\frac{[H_2NC_6H_4NH_3^+]}{[H_2NC_6H_4NH_2]} = 0.63$$

**(vi)** Calculate the pH of solution containing equimolar amount of $H_2NC_6H_4NH_3^+$ and $^+H_3NC_6H_4NH_3^+$.

[2]

when equimolar amount of $H_2NC_6H_4NH_3^+$ and $H_3NC_6H_4NH_3^{2+}$ is formed,
[$H_2NC_6H_4NH_3^+$] = [$^+H_3NC_6H_4NH_3^+$]

This is the maximum buffer capacity at second stage of neutralization.
Hence

$$pOH = pK_2 + \lg\frac{[H_3NC_6H_4NH_3^{2+}]}{[H_2NC_6H_4NH_3^+]}$$

pOH = $pK_2$
pOH = 11
pH = 3

**(b)** Ammonia is commonly used in qualitative analysis of halides in aqueous solutions, such as detecting the presence of chloride and bromide ions in natural water sources such as rivers, lakes and streams.

**(i)** 5 $cm^3$ of 0.0100 mol $dm^{-3}$ of silver nitrate is added to a 30 $cm^3$ sample of river water containing chloride ions.

What is the minimum concentration, in mol $dm^{-3}$, of chloride ions present in the river water when the first trace of precipitate appears?

Given solubility product of the silver chloride is $2.0 \times 10^{-10}$ $mol^2\ dm^{-6}$.

[2]

$$Ag^+(aq) + X^-(aq) \rightarrow AgX(s)$$

The ppt is AgX.
$[Ag^+]$ at point of mixing = no. of moles of $Ag^+$ before mixing ÷ total vol
= (0.0100 x 5/1000) ÷ 35/1000
= $1.428 \times 10^{-3}$ mol $dm^{-3}$

$[Cl^-]$ at point of mixing = no. of moles of $X^-$ before mixing ÷ total vol.
= ($[Cl^-]_{initial}$ x 30/1000) ÷ 35/1000 mol $dm^{-3}$

For precipitation to take place,
Ionic product (AgC*l*) ≥ Ksp(AgC*l*)

( $[Ag^+][Cl^-]$ ) at point of mixing $\geq 2.0 \times 10^{-10}$

$$(1.428\times10^{-3})\times\left(\frac{[Cl^-]_{initial}\times\frac{30}{1000}}{\frac{35}{1000}}\right) \geq 2.0 \times 10^{-10}$$

$$[Cl^-]_{initial} \geq 1.63 \times 10^{-7}$$

Hence, minimum concentration is $1.63 \times 10^{-7}$ mol $dm^{-3}$

**(ii)** To a test tube containing another river sample containing bromide ions, describe what you would see when aqueous silver nitrate is added to the sample, followed by excess aqueous ammonia to the resulting mixture

[1]

$Br^-$: cream ppt of AgBr observed; insoluble in excess $NH_3$(aq)

**(iii)** Explain, with aid of appropriate equation(s), the observations in **(b)(ii)**.

You should use the concepts of Le Chatelier's Principle and solubility product, $K_{sp}$, to explain your answer.

[4]

$Ag^+(aq) + Br^-(aq) \rightleftharpoons AgBr(s)$ ....(1)
Precipitate of AgBr is observed when I.P> $K_{sp}$

$Ag^+(aq) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq)$ ….(2)
When excess $NH_3$ is added (high $[NH_3]$) to AgBr(s), the position of equilibrium (2) shifts to the **right** in order to reduce the effect of excess $NH_3(aq)$. OR complex $[Ag(NH_3)_2]^+$ is formed

$[Ag^+]$ decreases hence equilibrium (1) shifts to the left.
but the ionic product of AgBr is still **larger than** $K_{sp}(AgBr)$,
AgBr remains insoluble.
OR
$AgBr(s) + 2NH_3(aq) \rightleftharpoons [Ag(NH_3)_2]^+(aq) + Br^-(aq)$

**(c)** **(i)** When iodine reacts with sodium hydroxide, iodide and iodate(V) are formed.

Write a balanced ionic equation, with state symbols, for the formation of $IO_3^-$ when iodine reacts with sodium hydroxide. Name the type of reaction taking place. [2]

$3I_2(s) + 6OH^-(aq) \rightarrow 5I^-(aq) + IO_3^-(aq) + 3H_2O(l)$

Disproportionation

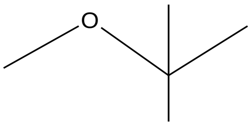
**(ii)** When Group II iodates(V), $\mathbf{M}(IO_3)_2$, are heated at high temperature, it form the metal oxide, iodine vapour and a colourless gas that relights glowing splinter.

It was observed that Group II iodates(V) down the group have to be heated more strongly before the iodine vapour appears. Explain why thermal stability increases down the group for Group II iodate(V). [3]

[Total: 20]

- Cationic size of $M^{2+}$ increases down Group II resulting in decreasing charge density and/or hence decreasing polarising power.
- Thus the electron cloud of the $IO_3^-$ is less distorted and thus less weakening effect on the I-O bond in $IO_3^-$.
- More energy required to bring about decomposition of $M(IO_3)_2$, resulting in higher temperature required for the purple iodine vapour to be observed.
- Thermal stability of $M(IO_3)_2$ increases down the group.

**3** **(a)** Methyl t-butyl ether, **MTBE**, is a fuel additive that is used an oxygenate to raise the octane number in fuel. This will help the fuel to burn more completely and reduce air pollution.



Methyl t-butyl ether, **MTBE**

**(i)** What is meant by the term *standard enthalpy change of formation* of **MTBE**?

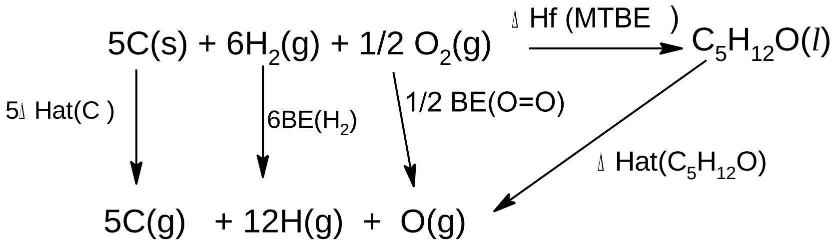
[1]

*Standard enthalpy change of formation* of **MTBE** is the heat change when 1 mole of a **MTBE** is formed from its constituent elements in their standard states under standard conditions of 298 K and 1 atmospheric pressure.

**(ii)** Use the following data and relevant data from *Data Booklet* to construct an appropriate energy cycle, find the standard enthalpy change of formation of **MTBE**.

| | |
|---|---|
| Standard enthalpy change of atomisation of C(s) | +715 kJ mol$^{-1}$ |
| Standard enthalpy change of atomisation of **MTBE**(*l*) | +6822 kJ mol$^{-1}$ |

[4]



By Hess' Law,

$\Delta H^{\theta}_{f}$ (MTBE) = $5\Delta H^{\theta}_{at}$ (C) + 6BE($H_2$) + ½BE ($O_2$) – $\Delta H_{at}$ ($C_5H_{12}O$)

$\Delta H^{\theta}_{f}$ (MTBE) = *5(715) + 6BE(H-H) + ½BE(O=O) - 6822*

$\Delta H^{\theta\theta}_{f}$ (MTBE) = *3575 + (6 x 436) + ½ (496) - 6822*

**$\Delta H^{\theta}_{f}$ (MTBE) = -383 kJ mol$^{-1}$**

**(iii)** Given that the standard enthalpy change of vaporisation of **MTBE** is +30.4 kJ mol$^{-1}$ and using relevant data from the *Data Booklet and* **(a)(ii)**, calculate the bond energy of C-O in **MTBE**.

Bond energy of $C_5H_{12}O$ involves breaking a total of:
2(C-O), 3(C-C) and 12(C-H) bonds.

$\Delta H^{\theta}_{at}$ ($C_5H_{12}O$) = $\Delta H^{\theta}_{vap}$ ($C_5H_{12}O$) + 2BE(C-O) + 3BE(C-C) + 12BE(C-H)
6822 = 30.4 + 2BE(C-O) + 3BE(C-C) + 12BE(C-H)
6791.6 = 2BE(C-O) + (3 x 350) + (12 x 410)
6791.6 = 2BE(C-O) + 5970
BE(C-O) = **+411 kJ mol$^{-1}$**

**(iv)** Suggest a reason for the difference in the C-O bond energy in **(a)(iii)** from the value given in the *Data Booklet*. [1]

The bond energy values from the Data Booklet are **average values**. The actual bond dissociation energy values depend on the specific chemical and electronic environment that a bond is in.

**(b)** **MTBE** can be produced from methanol and but-1-ene by the following equation. The reaction has a standard entropy change of reaction of -281 J mol$^{-1}$ K$^{-1}$.

$$CH_3OH(l) + C_4H_8(l) \rightarrow \underset{\textbf{MTBE}}{C_5H_{12}O(l)} \qquad \Delta H^{\theta}$$

The table below lists the $\Delta H^{\theta}_f$ (standard enthalpy change of formation) values for some compounds.

| compound | $\Delta H^{\theta}_f$ / kJ mol$^{-1}$ |
|---|---|
| $CH_3OH(l)$ | -239 |
| $C_4H_8(l)$ | -0.4 |

**(i)** Calculate the $\Delta H^{\theta}$ for the reaction in **(b)** using the values from the table above and your answer to **(a)(ii)**. [1]

$$\begin{aligned}\Delta H^{\theta} &= \sum m\Delta H^{\theta}_f(\text{products}) - \sum n\Delta H^{\theta}_f(\text{reactants}) \\ &= -383 - (-239 - 0.4) \\ &= -143.6 \text{ kJ mol}^{-1} \\ &= -144 \text{ kJ mol}^{-1}\end{aligned}$$

**(ii)** Determine the feasibility of the production of **MTBE** from methanol and but-1-ene at 298 K. [2]

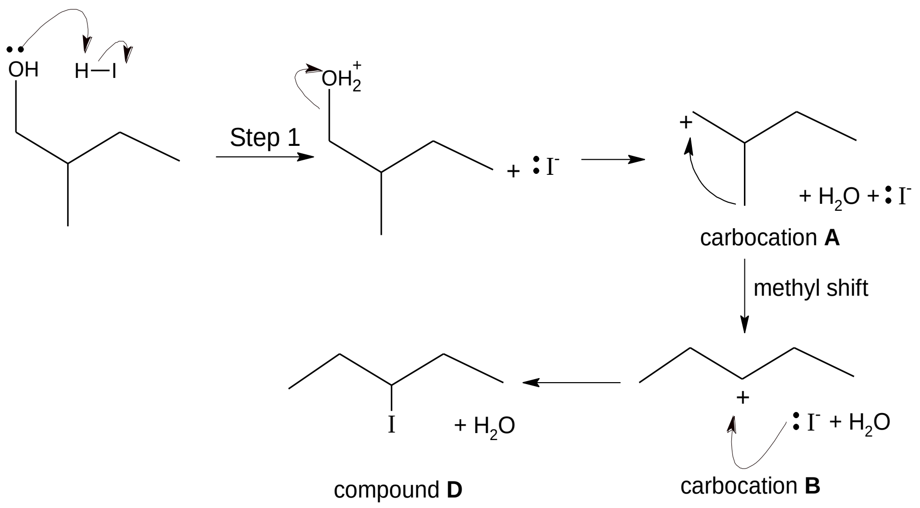
$$\begin{aligned}\Delta G^{\theta} &= \Delta H^{\theta} - T\Delta S^{\theta} \\ &= -143.6 - 298(-281 \times 10^{-3}) \\ &= -59.9 \text{ kJ mol}^{-1} < 0\text{, reaction is energetically feasible at 298 K.}\end{aligned}$$

(ECF)

Final answer and statement on energetically feasible.

**(c)** Methyl shift can occur in organic chemistry reactions in reactions involving carbocation intermediates.

An example of a methyl shift in a reaction between an alcohol and HI is shown below. In this reaction compound **D** is produced as the major product.



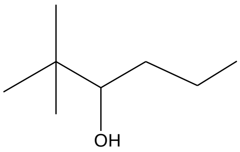
**(i)** What is the role of HI in step 1?

acid

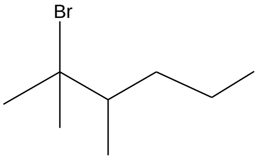
**(ii)** Suggest a reason for the methyl shift to produce carbocation **B** from carbocation **A**. [1]

**B** is a <u>secondary carbocation</u> which is <u>more stable</u> than the **A** which is a <u>primary carbocation</u>. Hence, a more stable carbocation **B** is formed as an intermediate during the reaction.

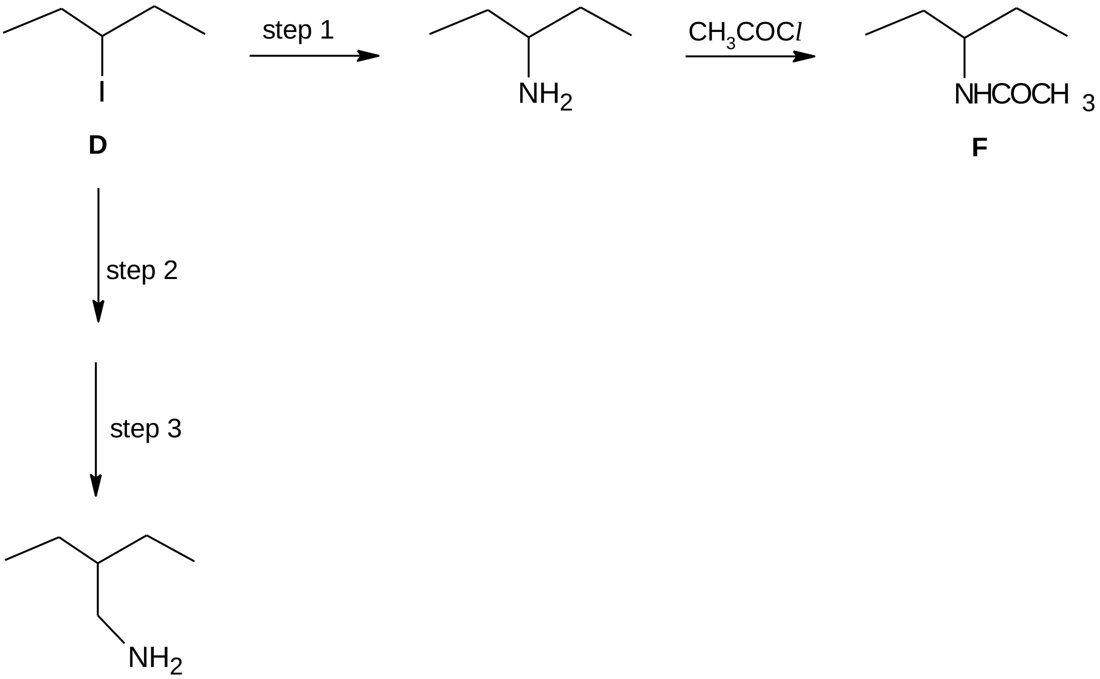
**(iii)**

The structure of compound **E** is  .

Predict the major final product formed when compound **E** reacts with HBr based on the methyl shift reaction in **(c)**. [1]



**(iv)** Compound **D** undergoes the following reactions.

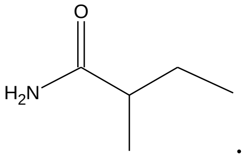


**D**

**F**

Suggest suitable reagents for steps 1, 2 and 3. [3]

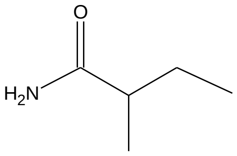
step 1: excess $NH_3$ in ethanol and heat it in sealed tube.
step 2: NaCN in ethanol, heat
step 3: $LiAlH_4$ in dry ether / $H_2$, Ni cat, $200^0C$.

**(v)** Suggest one simple chemical test which would enable you to distinguish between compound **F** and  .

You should state the reagents and conditions for the test and describe the observations.

[Total: 20]

Reagents and conditions: NaOH(aq), heat

Observation:  the gas liberated which is $NH_3$ turns moist red litmus paper blue.

For **F**, moist red litmus paper remains red

**4** **(a)** Compound **G**, $C_{10}H_{15}NO_3$, is a natural stimulant made in the adrenal gland of the kidney and is carried in the bloodstream and affects the autonomous nervous system, which controls functions such as heart rate, dilation of the pupils.

**G** is soluble in dilute sodium hydroxide and dilute hydrochloric acid but does not react with sodium carbonate.

**G** undergoes reaction with hot acidified potassium dichromate(VI) to form **J**. **J** gives an orange precipitate with 2,4-dinitrophenylhydrazine but does not give a silver mirror with Tollens' reagent. Upon heating with concentrated $H_2SO_4$, **G** forms **K**, $C_{10}H_{13}NO_2$. **K** does not react with $PCl_5$. On heating with acidified potassium manganate(VII), **K** forms three compounds, **L**, $C_7H_6O_4$, **M**, $C_2H_4O_2$, and an ammonium salt, $CH_3NH_3^+$.

Deduce the structures for each compound, **G** to **M**, and give an account of the chemistry involved.

**[10]**

**G** is soluble in dilute sodium hydroxide and dilute hydrochloric acid but does not react with sodium carbonate. **G** contains **basic/amine groups** and **phenol**

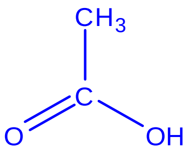
**G** undergoes **oxidation** with acidified potassium dichromate(VI) to form **J**, which undergoes **condensation** with 2, 4 - DNPH.

=> **J** is a **ketone**
=> **G** contains **secondary alcohol**

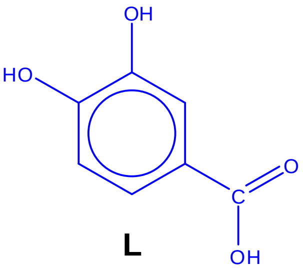
**G** undergoes **elimination** with concentrated $H_2SO_4$, heat to form **K**, $C_{10}H_{14}NO_2$
=> **G** is confirmed to be a secondary alcohol.
=> **K** is an **alkene**

**K** does not react with $PCl_5$
=> **K** is a **has 2 phenol groups**

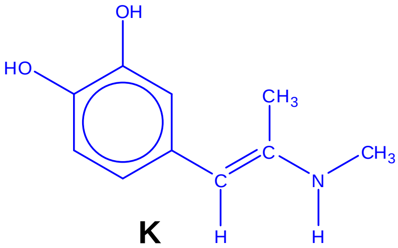
**K** undergoes **oxidation** and **acidic hydrolysis** with acidified potassium manganate to form **L, M** and $\mathbf{CH_3NH_3^+}$.



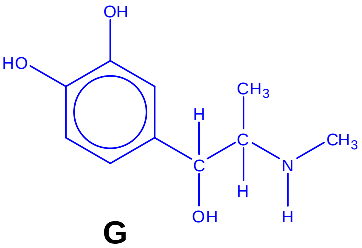
**M**



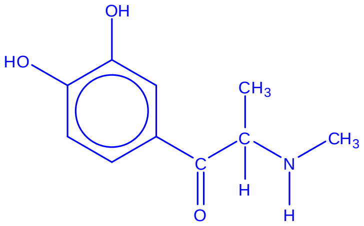
**L**



**K**



**G**



**J**

*The position of the substituent is not important in this question.

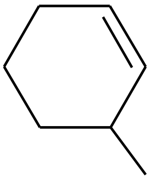
**[1 for each of the compound]**

**(b)** Like alcohols and halogenoalkanes, amines can be converted into alkenes by an elimination reaction known as Hofmann elimination.

For example, 1-methyl-pentylamine is converted into hex–1–ene as shown.

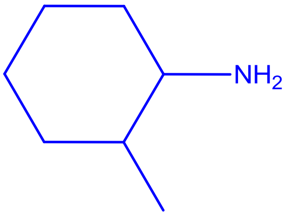
An interesting feature of the Hofmann elimination is that it gives a **less substituted alkene** compared to other elimination reactions.

**(i)** Draw the likely structure of the starting amine if the following alkene **N** is the main product formed when the amine undergoes a Hofmann elimination reaction.



**N**

**[1]**

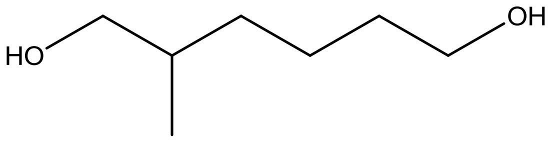


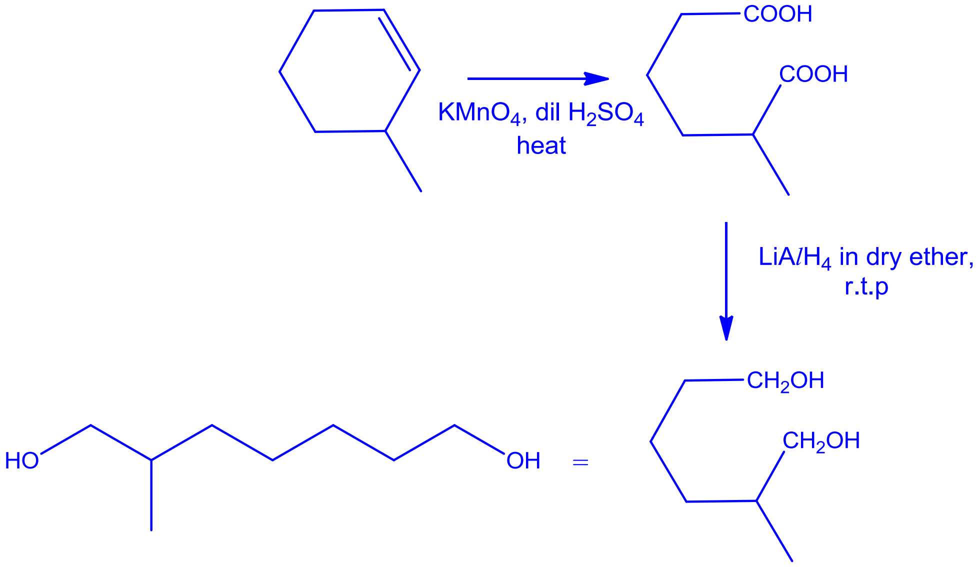
**(ii)** Suggest, in no more than 3 steps, a suitable synthetic pathway to convert **N** into the following compounds.

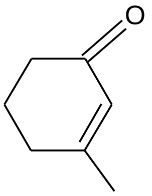
For each step, state clearly the reagents and conditions, indicating the structural formula of all intermediate compounds formed.

**[5]**

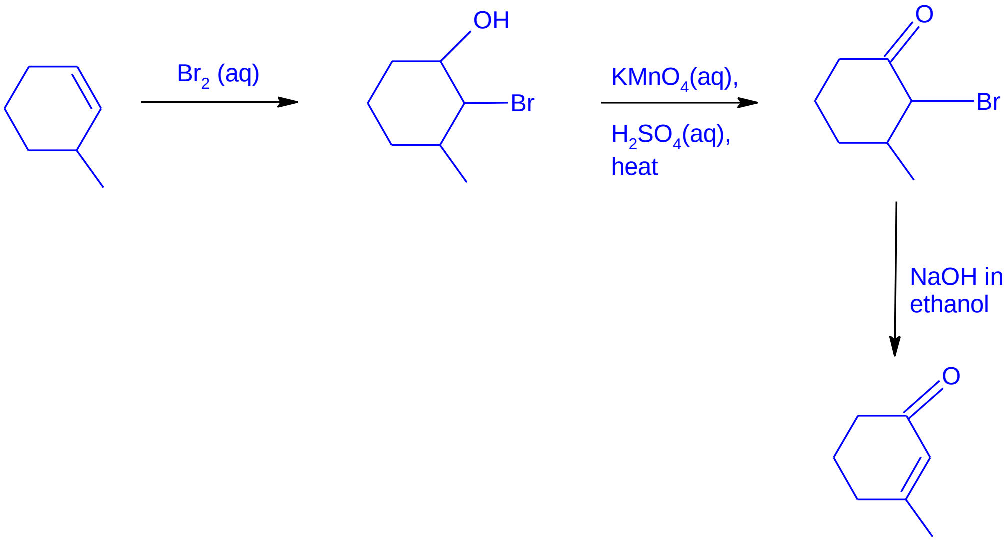
**(I)**




COOH
COOH
KMnO4, dil H2SO4
heat
LiA/H4 in dry ether,
r.t.p
HO
OH
=
CH2OH
CH2OH

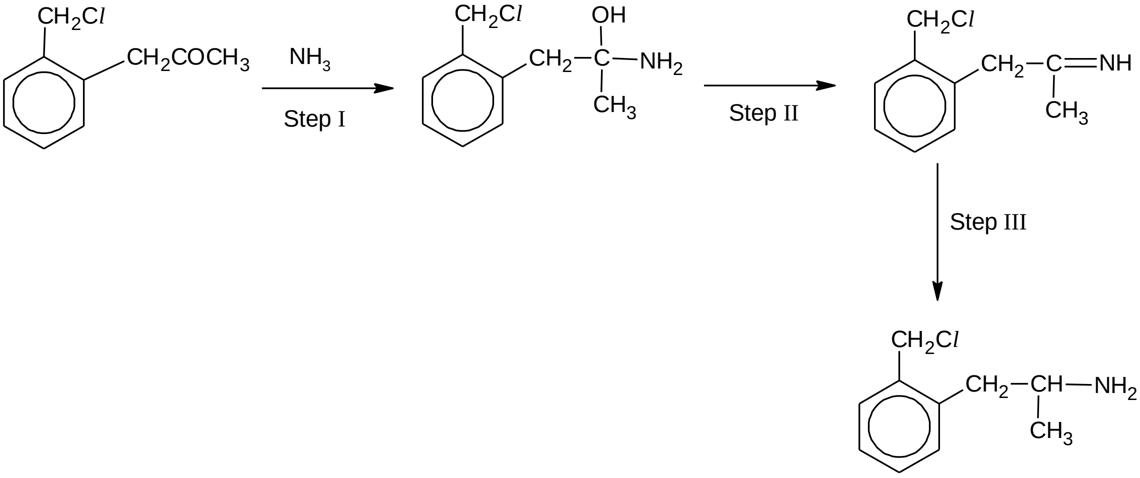


**(II)**


Br2 (aq)
OH
Br
KMnO4(aq),
H2SO4(aq),
heat
O
Br
NaOH in
ethanol
O

**(c)** Amines can be formed by reductive amination of an aldehyde or ketone with ammonia or amine in the presence of reducing agent.

A reductive amination to produce an amine **P** takes place in the pathway shown.



**P** ($C_{10}H_{14}NCl$)

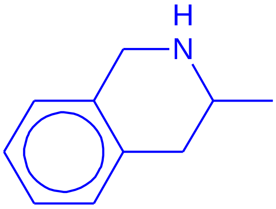
**(i)** Suggest the type of reaction that occurs at steps I and II. **[2]**

Step I – **Nucleophilic addition**
Step II - **Elimination**

**(ii)** Suggest the reagents and conditions for step III. **[1]**

$H_2$ in nickel catalyst, 200°C, $LiAlH_4$

**(iii)** On heating, **P** forms **Q,** $C_{10}H_{13}N$. Suggest a structure for **Q**. **[1]**



**[Total: 20]**

**5** **(a)** An electrochemical cell involving tartaric acid, $(CH(OH)CO_2H)_2$, has the following cell diagram notation.

$Pt(s)|(CH(OH)CO_2H)_2\ (aq)\ |CO_2(g)\ |H^+(aq)\ ||\ Co^{3+}(aq),\ Co^{2+}(aq)|Pt(s)$

**(i)** Given that the e.m.f of the cell is +0.80 V and using relevant data from the *Data Booklet*, determine the standard electrode potential of the $CO_2(g)|(CH(OH)CO_2H)_2(aq)$ half-cell.

At the cathode, $E^\ominus_{red}$ $(Co^{3+}(aq), Co^{2+}(aq))$ = +1.82 V

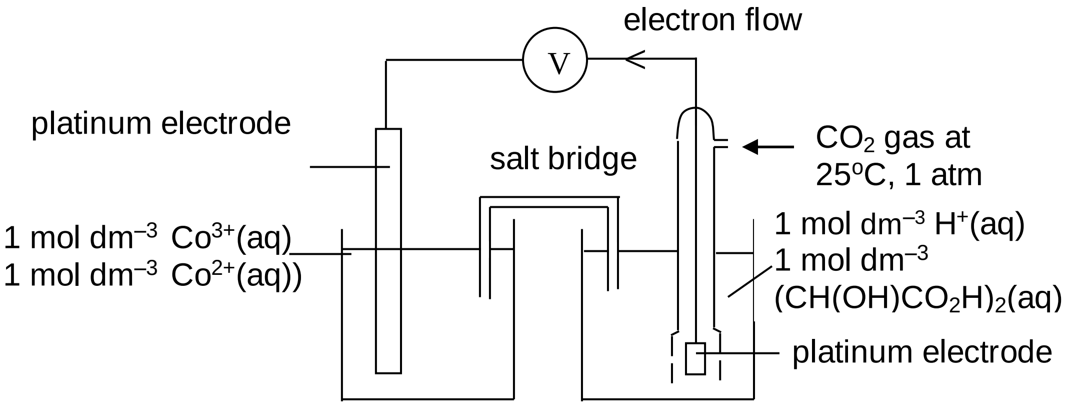
Since e.m.f. of cell = +0.80 V, and $E^\ominus_{cell} = E^\ominus_{red} + E^\ominus_{oxid}$

$\therefore\ E^\ominus_{oxid} = E^\ominus_{cell} - E^\ominus_{red}$

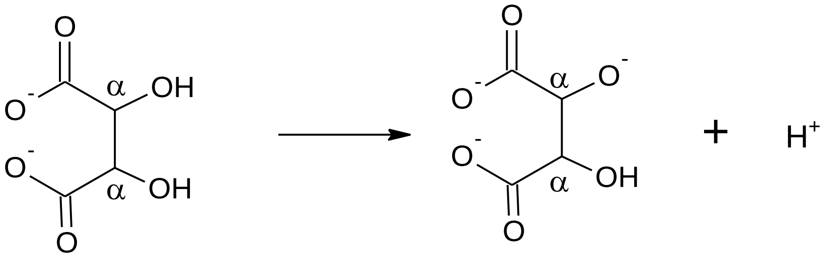
$= +0.80 - (+1.82) = -1.02$ V

At the anode, $E^\ominus_{red}$ = +1.02 V

**(ii)** Draw a labelled diagram of the electrochemical cell.



**(b)** Fehling's solution is made by adding equal volumes of a blue solution **A** containing aqueous copper(II) sulfate and a colourless solution **B** containing potassium sodium tartrate and sodium hydroxide. In a strong base, an alpha-hydroxy group in the tartrate ion, $(CH(OH)CO_2^-)_2$, deprotonates as shown in the diagram below.



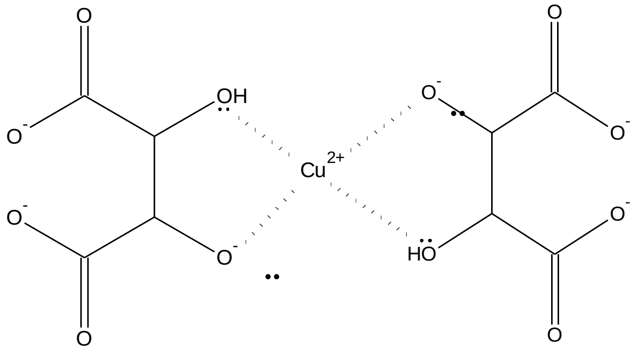
Deprotonated tartrate ion

The deprotonated tartrate ion acts as a bidentate ligand and binds to the $Cu^{2+}(aq)$ using both oxygen atoms from the **alpha-hydroxy groups**. A square planar bistartratocuprate(II) complex, $[Cu(tart)_2]^{4-}$, forms, and a deep blue solution is seen.
[tart = deprotonated tartrate ion]

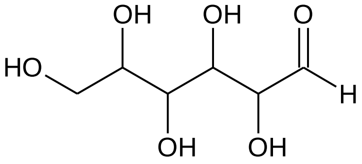
**(i)** Draw the shape of $[Cu(tart)_2]^{4-}$ complex, indicating clearly the type of bonds formed between the $Cu^{2+}$ and the ligands.

(may want to include coordination number)

[2]



**(ii)** The open straight chain form of D–glucose, a reducing sugar, is shown.



**D–glucose**

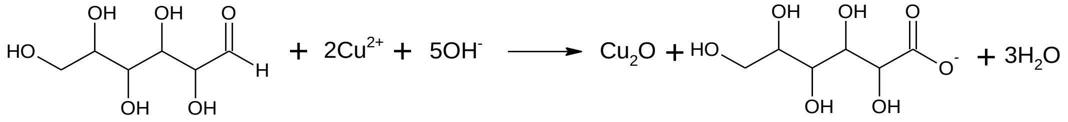
State what would be observed when D–glucose solution is warmed with a few drops of Fehling's solution.

Write the balanced equation for the reaction described above.

[2]

Observation: Brick-red/reddish–brown precipitate of $Cu_2O$ observed

Equation:



**(iii)** Explain why there is a need to form the $[Cu(tart)_2]^{4-}$ complex in the Fehling's solution test.

[1]

The deprotonated tartrate ions, by complexing with $Cu^{2+}$ prevents the precipitation of $Cu^{2+}$ as solid $Cu(OH)_2$ from the reaction of $CuSO_4$ and NaOH.

The $Cu^{2+}$ in the complex can then be reduced to $Cu^+$ in the form of copper(I) oxide, $Cu_2O$.

$$2Cu^{2+} + H_2O + 2e^- \rightarrow Cu_2O + 2H^+$$

**(iv)** Explain why the Fehling's solution is deep blue while potassium sodium tartrate solution is colourless.

[4]

In the presence of ligands, the partially filled 3d-orbitals of $Cu^{2+}$ split into 2 sets of different energy levels.

The small difference in energy between the two sets of orbitals corresponds to the energy of visible light in the electromagnetic spectrum

On absorbing energy from the visible light, an electron from a lower d-orbital gets promoted to a vacant / half-filled orbital of higher energy.

The colour observed is complementary to that absorbed.

For a compound of Group I, the metal ion does not have electrons in the 3d-orbitals and hence the d-d electron transitions would not occur. Hence, the solution of this compound is colourless.

**(v)** Stronger field ligands are known to give rise to a larger energy gap between the two sets of d-orbitals in a transition metal complex.

| Violet | Blue | Green | Yellow | Orange | Red |
|---|---|---|---|---|---|

400 nm 430 nm 480 nm 560 nm 590 nm 630 nm 750 nm

Energy of light decreases →

To test for proteins, Biuret reagent which also contains the $[Cu(tart)_2]^{4-}$ complex is used. In the presence of peptides, it undergoes ligand exchange to form $[Cu(peptide)_2]^{2+}$. The deep blue solution turns violet.

Using the above electromagnetic spectrum of visible light, state the relative ligand field strength of peptides and deprotonated tartrate ions. Explain your answer.

[3]

Peptides are stronger field ligands than the deprotonated tartrate ions.

$[Cu(tart)_2]^{4-}$ appears blue because it absorbs orange light. $[Cu(peptide)_2]^{2+}$ appears violet because it absorbs yellow light.

Yellow light has higher energy than orange light, the energy gap between the d orbitals of $[Cu(peptide)_2]^{2+}$ is larger than that of $[Cu(tart)_2]^{4-}$.

**(c)** Adolf Kolbe first published a method describing the preparation of an alkane from the electrolysis of an aqueous solution of sodium salt of a monoprotic acid, using inert electrodes.

In the Kolbe electrolysis of sodium propanoate, butane was formed at the anode in the following reaction.

$2CH_3CH_2CO_2^- \rightarrow CH_3CH_2CH_2CH_3 + 2CO_2 + 2e^-$

**(i)** Write the half equation for the reaction at the cathode during the electrolysis of sodium propanoate. Hence write an equation for the **overall** reaction.

[2]

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

Overall reaction:

$2CH_3CH_2CO_2^- + 2H_2O \rightarrow CH_3CH_2CH_2CH_3 + 2CO_2 + H_2 + 2OH^-$

**(ii)** A student tried to synthesise another hydrocarbon using an aqueous solution of a sodium salt of a diprotic acid, succinic acid, $(CH_2CO_2H)_2$. The succinate ion, $(CH_2CO_2^-)_2$ ,undergoes a similar reaction as propanoate ion at the anode.

$(CH_2CO_2^-)_2 \rightarrow$ **R** $+ 2CO_2 + 2e^-$

Suggest an identity of the hydrocarbon **R**.

[1]

$CH_2{=}CH_2$ OR $C_2H_4$ [1]

[Total : 20]

**End of Paper**