# General Certificate of Education Advanced Level Higher 2

Candidate Name ☐

Class ☐

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## CHEMISTRY 9647/01

JC2 Preliminary Examination 23 September 2016
Paper 1 Multiple Choice 1 hour
Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

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**READ THESE INSTRUCTIONS FIRST**

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided.
Shade correctly your FIN/NRIC number.

There are **40** questions in 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 using a **soft pencil** on the separate OMS.
Each correct answer will score one mark.
A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

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

**Answer all questions**

**1** The relative abundances of the isotopes of a sample of titanium are shown in the table below.

| **Relative Isotopic Mass** | 46 | 47 | 48 | 49 | 50 |
|---|---|---|---|---|---|
| **Relative Abundance** | 11.2 | 10.1 | 100.0 | 7.3 | 7.0 |

What is the relative atomic mass of titanium in this sample?

**A** 48.00

**B** 47.92

**C** 47.90

**D** 47.89

**2** To identify an oxide of nitrogen, 0.10 mol of the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.

$$N_xO_y \xrightarrow{H_2(g)} \mathbf{x}NH_3 + \mathbf{y}H_2O$$

The water produced weighs 7.20 g. The ammonia produced is neutralised by 200 $cm^3$ of 1.0 mol $dm^{-3}$ $HCl$.

What is the formula of the oxide of nitrogen?

**A** $N_2O$

**B** NO

**C** $NO_2$

**D** $N_2O_4$

**3** 50 $cm^3$ of a 0.10 mol $dm^{-3}$ solution of a metallic salt was found to react exactly with 25.0 $cm^3$ of 0.10 mol $dm^{-3}$ aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows.

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

What is the new oxidation number of the metal in the salt if its original oxidation number was +3?

**A** +1

**B** +2

**C** +4

**D** +5

**4** Of the following, which is the strongest oxidising agent?

**A** $O_2^+$

**B** $O_2$

**C** $O_2^-$

**D** $O_2^{2-}$

**5** Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The greater the number of unpaired electrons in an atom, the greater the paramagnetism.

Which atom has the greatest paramagnetism?

**A** Oxygen

**B** Chlorine

**C** Scandium

**D** Arsenic

**6** Which of the following is true of both real and ideal gases?

**A** Molecules can be liquefied.

**B** Molecules occupy a finite volume.

**C** Molecules are in constant random motion.

**D** Molecules behave identically at high pressure and low temperature.

**7** The Valence Shell Electron Pair Repulsion Theory (VSEPR) is used to predict the shapes of molecules.

Which shape is correctly predicted by VSEPR?

| | **number of regions of electron density** | **number of lone pairs** | **shape** |
|---|---|---|---|
| **A** | 3 | 1 | Tetrahedral |
| **B** | 3 | 1 | Trigonal pyramidal |
| **C** | 5 | 1 | See-saw |
| **D** | 5 | 1 | Square pyramidal |

**8** The magnitude of the lattice energy of calcium oxide and calcium carbonate is 3414 kJ mol$^{-1}$ and 2814 kJ mol$^{-1}$ respectively. The enthalpy change of decomposition of calcium carbonate is +176 kJ $mol^{-1}$.

Using the information provided, calculate the enthalpy change of the following reaction.

$$CO_3^{2-}(g) \rightarrow O^{2-}(g) + CO_2(g)$$

**A** - 424 kJ $mol^{-1}$

**B** +424 kJ $mol^{-1}$

**C** - 776 kJ $mol^{-1}$

**D** +776 kJ $mol^{-1}$

**9** Primary, secondary and tertiary amine have similarly shaped molecules.

What is the predominant intermolecular force of attraction in methylamine, dimethylamine and trimethylamine?

| | **methylamine** | **dimethylamine** | **trimethylamine** |
|---|---|---|---|
| **A** | hydrogen bonds | hydrogen bonds | hydrogen bonds |
| **B** | hydrogen bonds | permanent dipole – permanent dipole | Instantaneous dipole – induced dipole |
| **C** | permanent dipole – permanent dipole | permanent dipole – permanent dipole | permanent dipole – permanent dipole |
| **D** | hydrogen bonds | hydrogen bonds | permanent dipole – permanent dipole |

**10** The integrated form of first-order rate law is as shown.

$$\ln A = -kt + \ln A_o$$

where A is the activity at time t,
$A_o$ is the initial activity,
k is the rate constant,
t is the time taken.

What is the half-life for a first order reaction if 68% of a substance is reacted within 66s?

**A** 33 s

**B** 40 s

**C** 49 s

**D** 119 s

**11** For which equilibrium is $K_c = K_p$?

**A** $C(s) + H_2O(l) \rightleftharpoons CO(g) + H_2(g)$

**B** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

**C** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

**D** $2NO_2(g) \rightleftharpoons N_2O_4(g)$

**12** The ionic product of water, $K_w$, at two different temperatures is shown below,

| $K_w$ / $mol^2\ dm^{-6}$ | Temperature / K |
|---|---|
| $1.00 \times 10^{-14}$ | 298 |
| $1.44 \times 10^{-14}$ | 303 |

Which statement is correct?

**A** Self-ionisation of water is an exothermic process.

**B** At 303 K, $[H^+] = 0.72 \times 10^{-14}$ mol dm$^{-3}$

**C** $K_w = \dfrac{[H^+][OH^-]}{[H_2O]}$

**D** At 303 K, pH < 7

**13** Calculate the pH of the resulting solution when 10 cm$^3$ of potassium hydroxide with concentration at $7.5 \times 10^{-7}$ mol dm$^{-3}$ is mixed with an equal volume of hydrogen bromide with concentration at $8.5 \times 10^{-8}$ mol dm$^{-3}$.

**A** 4.18

**B** 6.36

**C** 7.64

**D** 9.82

**14** Aqueous hydrochloric acid was electrolysed for ten minutes, 200 cm$^3$ of gas **A** was collected at the anode.

The same current was then applied to concentrated sodium chloride solution in another experiment and 400 cm$^3$ of a gas **B** is collected at the cathode.

Which of these statements is correct?

**A** Gas **B** is pale yellow.

**B** The time taken for the second electrolysis is also ten minutes.

**C** Chlorine gas was collected initially in the first electrolysis system.

**D** Mercury electrodes can be used for the second electrolysis system if gas **B** is to be collected.

**15** Which of the following properties could be predicted for strontium or its compounds?

**A** It does not burn in air.

**B** It forms a soluble sulfate.

**C** It reacts with cold water, liberating hydrogen.

**D** It forms a water-soluble carbonate which does not decompose on heating.

**16** Equal volumes of chlorine gas were bubbled into hot and cold sodium hydroxide separately until reactions were complete.

Which of the following statements is incorrect about the above reactions?

**A** Disproportionation reactions will occur.

**B** Greenish-yellow chlorine gas decolourises in both reactions.

**C** When aqueous silver nitrate is added to the resulting solutions, white precipitate is formed.

**D** Sodium chlorate(VII) and sodium chlorate(I) are formed in the reactions respectively.

**17** Aqueous chlorine is added to aqueous sodium bromide and the mixture is shaken with an equal volume of trichloromethane.

Which observation will be made?

**A** The solution in the test-tube turns colourless.

**B** The solution in the test-tube turns orange.

**C** A colourless layer forms on top of a purple layer.

**D** A colourless layer forms on top of an orange layer.

**18** A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **G** and **H** are copper-containing species.

$$CuSO_4(aq) \xrightarrow[\text{I}]{NH_3(aq)} \textbf{G} \xrightarrow[\text{II}]{\substack{\text{excess} \\ NH_3(aq)}} \textbf{H} \xrightarrow[\text{III}]{Na_4edta(aq)} [Cu(edta)]^{2-}(aq)$$

Which of the following statements is correct?

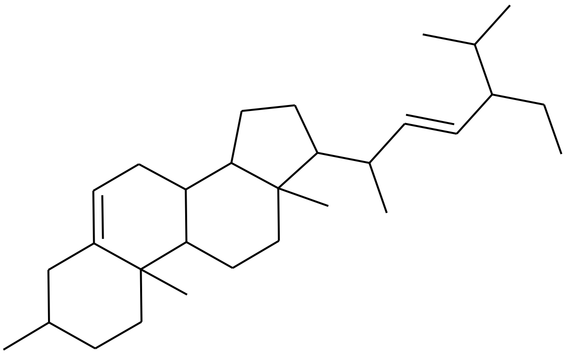
**A** Reaction III is a redox reaction.

**B** $NH_3$ acts as a ligand in reaction I.

**C** **H** is a deep blue solution containing $[Cu(NH_3)_4(H_2O)_2]SO_4$.

**D** The entropy of the system decreases when reaction III occurs.

**19** Stigmasterol is an unsaturated plant sterol occurring in the plant fats of soybean.



How many stereoisomers does stigmasterol have?

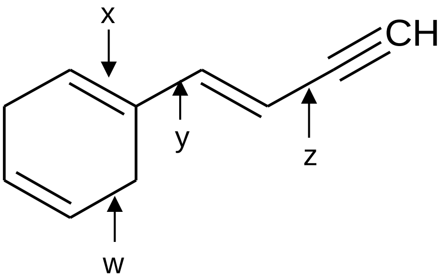
**A** $2^9$

**B** $2^{10}$

**C** $2^{11}$

**D** $2^{12}$

**20.** Four carbon-carbon bonds are labelled in the diagram.



Which bonds are made up of a $sp^2$-$sp^2$ overlap?

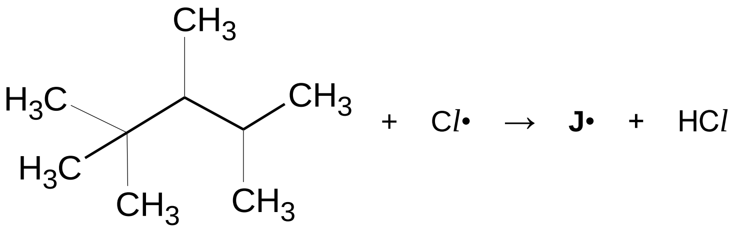
**A** **x** only

**B** **x** and **y** only

**C** **w**, **x** and **y** only

**D** **w**, **y** and **z** only

**21.** When heated with chlorine, the hydrocarbon 2,2,3,4-tetramethylpentane undergoes free radical substitution. In a propagation step, the free radical **J•** is formed by the loss of one hydrogen atom.



How many different forms of **J•** are theoretically possible?

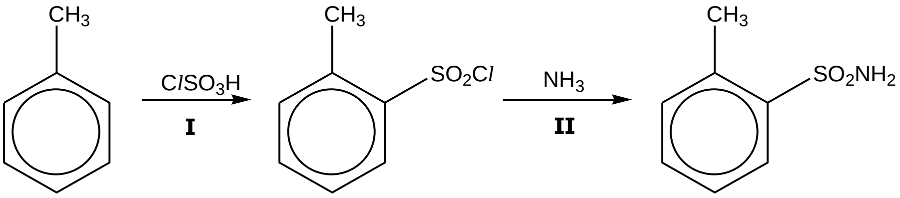
**A** 3

**B** 4

**C** 5

**D** 6

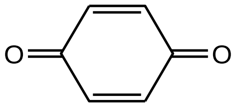
**22** *Saccharin* was an artificial sweetener used in some soft drinks. It was manufactured from methylbenzene by a series of reactions.

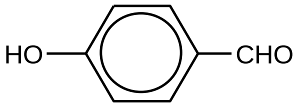


Which of the following shows the correct reaction type for steps **I** and **II**?

| | I | II |
|---|---|---|
| **A** | Electrophilic substitution | Electrophilic addition |
| **B** | Electrophilic substitution | Nucleophilic substitution |
| **C** | Nucleophilic substitution | Nucleophilic substitution |
| **D** | Nucleophilic substitution | Electrophilic substitution |

**23** Which of the following **cannot** be used to distinguish between the following compounds?





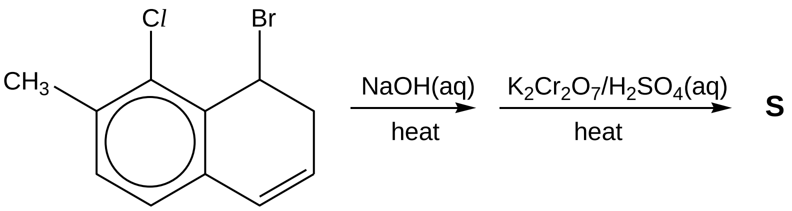
**A** Hot acidified $K_2Cr_2O_7$

**B** Neutral iron(III) chloride

**C** Diammine silver complex

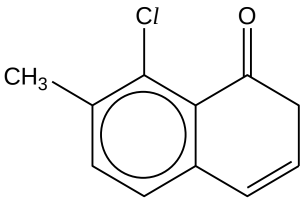
**D** Phenylhydrazine

**24** The reaction scheme below shows the synthesis of compound **S**.

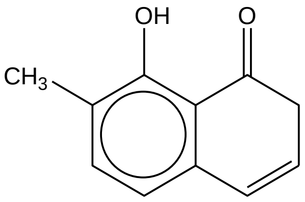


Which of the following can be **S**?

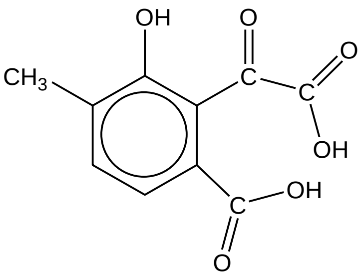
**A**



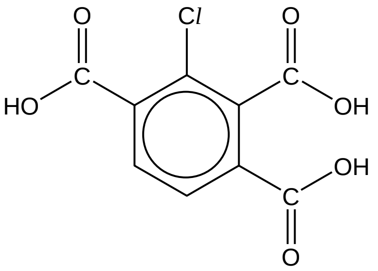
**B**



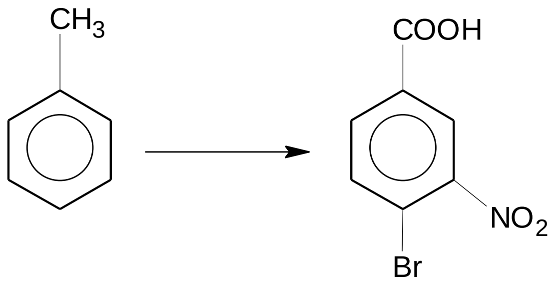
**C**



**D**



**25** The following synthetic route consists of three steps.



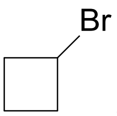
Which sequence of steps would give the highest yield?

| | **Step 1** | **Step 2** | **Step 3** |
|---|---|---|---|
| **A** | $KMnO_4$, $H_2SO_4$, heat | conc $HNO_3$, conc $H_2SO_4$, heat | $Br_2$, Fe, r.t.p |
| **B** | conc $HNO_3$, conc $H_2SO_4$, heat | $Br_2$, Fe, r.t.p | $KMnO_4$, $H_2SO_4$, heat |
| **C** | $Br_2$, $AlBr_3$, r.t.p | conc $HNO_3$, dilute $H_2SO_4$, heat | $KMnO_4$, $H_2SO_4$, heat |
| **D** | $Br_2$, Fe, r.t.p | $KMnO_4$, $H_2SO_4$, heat | conc $HNO_3$, conc $H_2SO_4$, heat |

**26** Ten grams of each of the following was heated with NaOH(aq) for a prolong period of time. Subsequently, dilute $HNO_3$(aq) and $AgNO_3$(aq) were added.

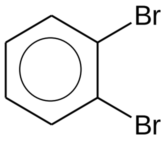
Which compound will produce the greatest mass of silver halide precipitate?

**A**



($M_r$ = 134.9)

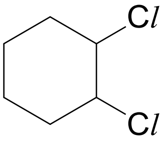
**C**



($M_r$ = 235.8)

**B** $CH_3COCl$
($M_r$ = 78.5)

**D**



($M_r$ = 153.0)

**27** After the reduction using tin and concentrated acid of nitrobenzene to phenylamine, an excess of sodium hydroxide is added.

What is the purpose of the sodium hydroxide?

**A** to dry the product

**B** to liberate the phenylamine

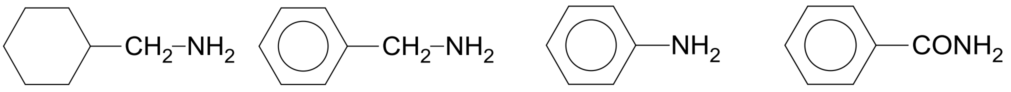
**C** to neutralise the excess acid

**D** to lower the boiling point for subsequent distillation

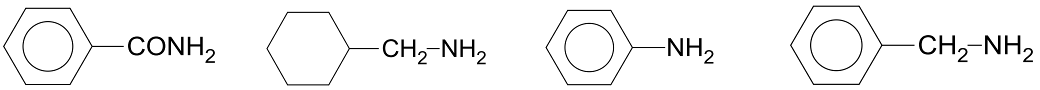
**28** Which of the following shows the correct order of basicity?

**High *pK$_b$*** **Low *pK$_b$***

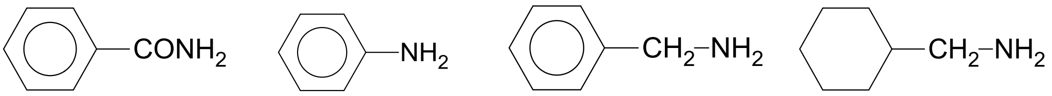
**A**



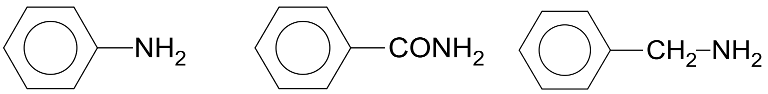
**B**

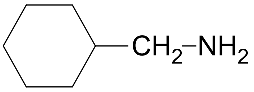


**C**

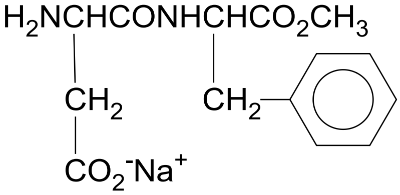


**D**



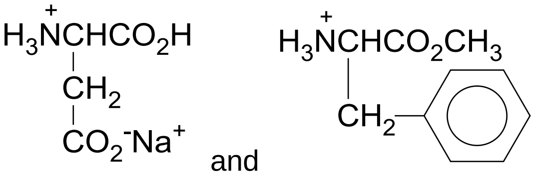


**29** Aspartame is a dipeptide derivatives used as an artificial sweetener. Its general usefulness is restricted because it loses its sweetness after hydrolysis.

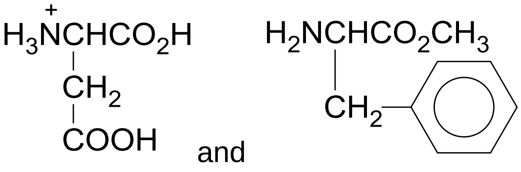


Which product would be formed after prolong acid hydrolysis.

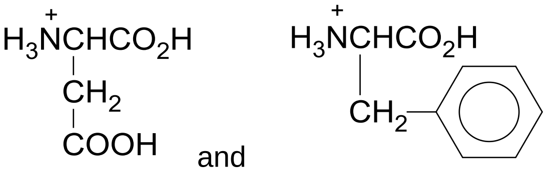
**A**



**B**

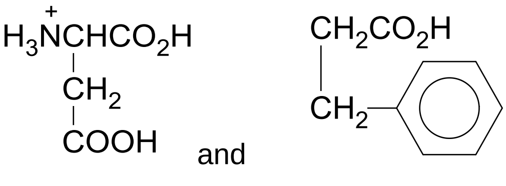


**C**



and $CH_3OH$

**D**



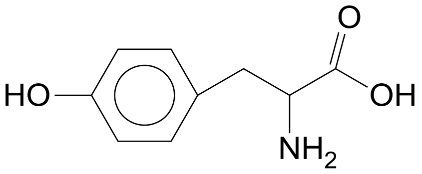
and $CH_3OH$

Turn Over]

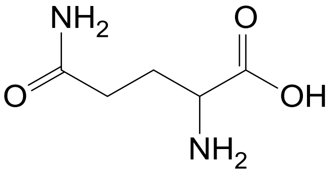
**30** Electrophoresis is a technique of separating and identifying amino acids. amino acids is absorbed into paper that is moistened with a buffer stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species towards the anode.

With a buffer at pH 5, which amino acid will move most readily towards the cathode?

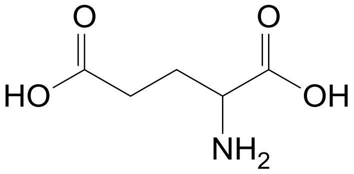
**A**



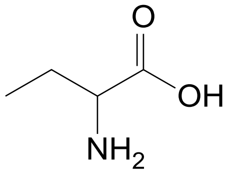
**C**



**B**



**D**

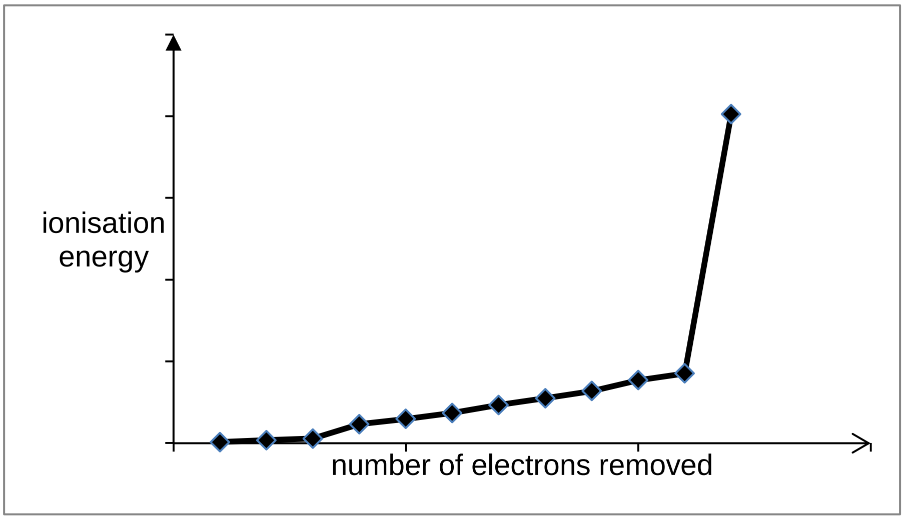


For **questions 31 – 40**, one or more of the numbered statements **1** to **3** may be correct. Decide whether each of the statements is or is not correct. The responses **A** to **D** should be selected on the basis of

| **A** | **B** | **C** | **D** |
|---|---|---|---|
| 1, 2 and 3<br>are correct | 1 and 2 only<br>are correct | 2 and 3 only<br>are correct | 1 only<br>is correct |

No other combination of statements is to be used as correct response.

**31** The graph below shows the first twelve ionisation energies for element **T**.



Which of the following statements are true?

**1** It is in Group I of the Periodic Table.

**2** It forms an oxide which dissolves readily with acid.

**3** It is in the third period (Na to Ar) of the Periodic Table.

**32** The following chemical reactions are listed below.

- Combustion of ethandioic acid
- Evaporation of water
- Atomisation of magnesium
- Photolysis of chlorine

Which of the following statements are correct?

**1** $\Delta S$ is positive for all reactions.

**2** $\Delta G$ is negative for all reactions.

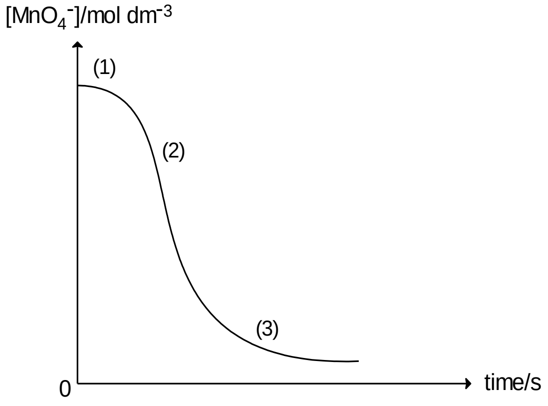
Turn Over]

**3** $\Delta H$ is positive for all reactions.

**33** A reaction in which a product acts as a catalyst is said to be autocatalytic.

$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \xrightarrow{\quad} 2Mn^{2+}(aq) + 10CO_2(g) +$

In the oxidation of ethanedioate ions by manganate(VII) ions, the reaction is accelerated by the $Mn^{2+}$ ions produced during the reaction.



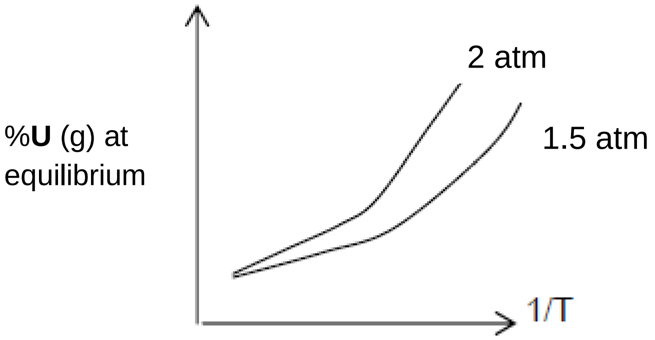
Which of the following statements can be deduced from the graph above?

**1** Initial rate of reaction is the fastest at (1).

**2** Reaction rate increases at (2) as $Mn^{2+}$ is generated.

**3** Reaction rate decreases at (3) as the concentration of the reactants decrease.

**34** The graph below shows how the percentage of reactant **U**(g) that remained in an equilbrium mixture varies with 1/T at pressures of 1.5 atm and 2 atm.



Which of the following statement can be deduced from this information?

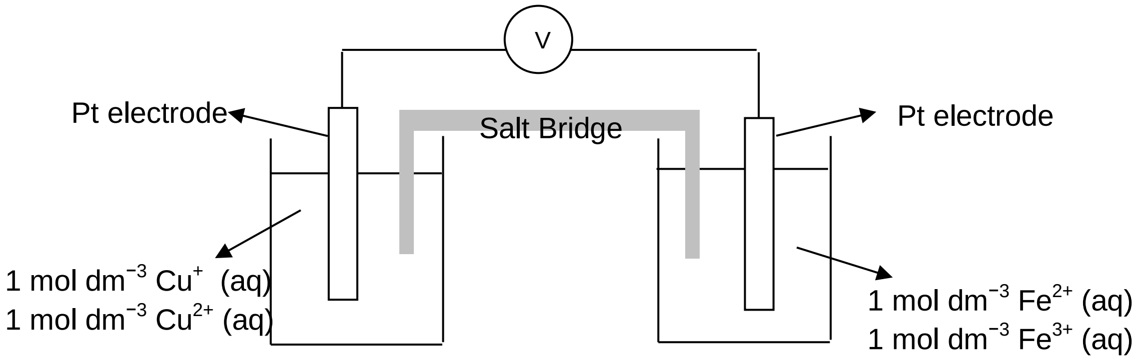
**1** The forward reaction is endothermic.

**2** The equation for the above reaction could be **U**(g) ⇌ **V**(g) + **W**(g).

**3** The equilibrium constant, $K_p$, increases as pressure increases in the system.

| 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 |

**35** A student was investigating the possibility of an electrochemical cell using $Cu^{2+}/Cu^{+}$ and $Fe^{3+}/Fe^{2+}$ half-cells.



Which statements are true of the above set up?

**1** $E^{\ominus}_{cell}$ = +0.62 V.

**2** Copper and iron electrodes cannot be used instead.

**3** When excess sodium hydroxide is added to the $Fe^{2+}/Fe^{3+}$ half-cell, the polarity of the electrodes are reversed.

**36** Barium sulfate is less soluble than magnesium sulfate.

Which of these factors are needed to be considered in order to explain this observation?

**1** $\Delta H_{hyd}$ of barium ion and magnesium ion.

**2** $\Delta H_f$ of barium sulfate and magnesium sulfate.

**3** Atomic radii of barium and magnesium.

**37** Which observation about bromine or its compounds is correct?

**1** When aqueous lead(II) nitrate is added to aqueous sodium bromide, a cream precipitate is observed.

**2** When sodium bromide is treated with concentrated sulfuric acid, a gas that turns moist blue litmus paper red is evolved.

**3** Silver bromide is soluble in both dilute and concentrated ammonia solution.

Turn Over]

| A | B | C | D |
|---|---|---|---|
| 1, 2 and 3<br>are correct | 1 and 2 only<br>are correct | 2 and 3 only<br>are correct | 1 onl<br>is corre |

**38** The catalytic converter is part of the exhaust system of modern cars.

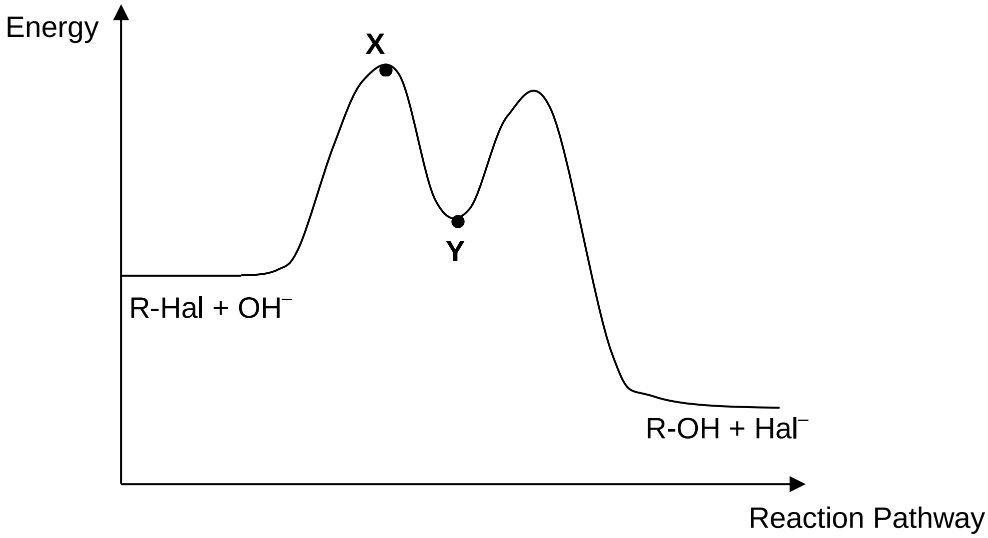
Which reactions occur in the catalytic converter?

**1** $2CO + O_2 \rightarrow 2CO_2$

**2** $2NO + CO \rightarrow N_2 + 2CO_2$

**3** $C_xH_y + (2x+\frac{y}{2})NO \rightarrow xCO_2 + \frac{y}{2}H_2O + (x+\frac{y}{4})N_2$

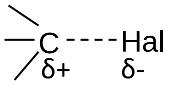
**39** Halogenoalkanes react with aqueous alkali. One mechanism of this reaction has the reaction pathway diagram shown below.



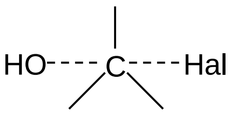
Which statements are true? (---- indicates a partial bond)

**1** The reaction is a type of nucleophilic substitution.

**2** **X** is



**3** **Y** is



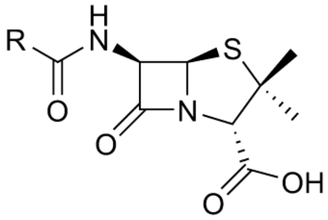
Turn Over]

**40** Which of the following phenomena involves denaturation of proteins?

**1** Heating of egg white.

**2** Production of bean-curd from soy milk.

**3** Dissolving Penicillin in a test tube of hot acid.



Penicillin

**END OF PAPER 1**

# General Certificate of Education Advanced Level Higher 2

Candidate Name

Class

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**CHEMISTRY** **9647/01**
JC2 Preliminary Examination 23 Sep 2016
Paper 1 Multiple Choice 1 hour
Additional Materials: Data Booklet
Optical Mark Sheet (OMS)

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**READ THESE INSTRUCTIONS FIRST**

On the separate multiple choice OMS given, write your name, subject title and class in the spaces provided.
Shade correctly your FIN/NRIC number.

There are **40** questions in 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 using a **soft pencil** on the separate OMS.
Each correct answer will score one mark.
A mark will not be deducted for a wrong answer.

You are advised to fill in the OMS as you go along; no additional time will be given for the transfer of answers once the examination has ended.

Any rough working should be done in this question paper.

***Answer Key:***

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

This document consists of **29** printed pages

## Suggested Worked Solution for MCQs

**1** The relative abundances of the isotopes of a sample of titanium are shown in the table below.

| **Relative Isotopic Mass** | 46 | 47 | 48 | 49 | 50 |
|---|---|---|---|---|---|
| **Relative Abundance** | 11.2 | 10.1 | 100.0 | 7.3 | 7.0 |

What is the relative atomic mass of titanium in this sample?

**A** 48.00
**B** 47.92
**C** 47.90
**D** 47.89

**Answer: B**

Relative atomic mass = $\dfrac{(46\times11.2)+(47\times10.1)+(48\times100)+(49\times7.3)+(50\times7)}{11.2+10.1+100+7.3+7.0}$

$= \dfrac{515.2+474.7+4800+357.7+350}{135.6}$

$= \dfrac{6497.3}{135.6} = 47.92$

**2** To identify an oxide of nitrogen, 0.10 mol of the oxide is mixed with an excess of hydrogen and passed over a catalyst at a suitable temperature.

$$N_xO_y \xrightarrow{H_2(g)} \mathbf{x}NH_3 + \mathbf{y}H_2O$$

The water produced weighs 7.20 g. The ammonia produced is neutralised by 200 $cm^3$ of 1.0 mol $dm^{-3}$ HC*l*.

What is the formula of the oxide of nitrogen?

**A** $N_2O$
**B** NO
**C** $NO_2$
**D** $N_2O_4$

**Answer: D**

Amt of $H_2O$ = $\dfrac{7.2}{18} = 0.40\,\text{mol}$

Amt of $NH_3$ = $\dfrac{200}{1000}\times1 = 0.20\,\text{mol}$

Assuming all gases and using Avogadro's Law

Comparing mole ratio of $N_xO_y$ with $NH_3$

$\dfrac{1}{x} = \dfrac{0.10}{0.20}$ Hence, x = 2

Comparing mole ratio of $N_xO_y$ with $H_2O$

$\dfrac{1}{y} = \dfrac{0.10}{0.40}$ Hence, y = 4

Formula is $N_2O_4$

**3** 50 cm$^3$ of a 0.10 mol dm$^{-3}$ solution of a metallic salt was found to react exactly with 25.0 cm$^3$ of 0.10 mol dm$^{-3}$ aqueous sodium sulfite. In this reaction, the sulfite ion is oxidised as follows.

$$SO_3^{2-}(aq) + H_2O(l) \longrightarrow SO_4^{2-}(aq) + 2H^+(aq) + 2e$$

What is the new oxidation number of the metal in the salt if its original oxidation number was +3?

| | |
|---|---|
| **A** | +1 |
| **B** | +2 |
| **C** | +4 |
| **D** | +5 |

**Answer: B**

Amount of sulphite ions = $\frac{25}{1000} \times 0.10$ = 0.0025 mol

Amount of metallic salt = $\frac{50}{1000} \times 0.10$ = 0.005 mol

Let x be the new oxidation no of metal in salt.

[R]: $M^{3+} + (3-x)e \rightarrow M^x$

Since moles of electrons gained = moles of electrons lost in a redox reaction,

$$\frac{3-x}{2} = \frac{0.0025}{0.005}$$

x = +2

**4** Of the following, which is the strongest oxidising agent?

| | |
|---|---|
| **A** | $O_2^+$ |
| **B** | $O_2$ |
| **C** | $O_2^-$ |
| **D** | $O_2^{2-}$ |

**Answer: A**

Strongest oxidising agent means it will undergo reduction easily and as such will gain electrons.

$O_2^+$ is positively charged and hence is a stronger electron-acceptor than the other species.

**5** Paramagnetism refers to the magnetic state of an atom with one or more unpaired electrons. The greater the number of unpaired electrons in an atom, the greater the paramagnetism.

Which atom has the greatest paramagnetism?

**A** Oxygen
**B** Chlorine
**C** Scandium
**D** Arsenic

**Answer: D**

O: $1s^2 2s^2 2p^4$ → 2 unpaired electrons in the 2p orbital

Cl: $[Ne]3s^2 3p^5$ → 1 unpaired electron in the 3p orbital

Sc: $[Ar]3d^1 4s^2$ → 1 unpaired electron in the 3d orbital

As: $[Ar]3d^{10} 4s^2 4p^3$ → **3 unpaired electrons** in the 4p orbital

**6** Which of the following is true of both real and ideal gases?

**A** Molecules can be liquefied.
**B** Molecules occupy a finite volume.
**C** Molecules are in constant random motion.
**D** Molecules behave identically at high pressure and low temperature.

**Answer: C**
Molecules can be liquefied. (Not true - ideal gas do not exert attractive forces on one another)

Molecules occupy a finite volume. (Not true - the size of the ideal gas molecule is assumed to be negligible compared to the volume of the container it occupies)

Molecules are in constant random motion. (True)

Molecules behave identically at high pressure and low temperature. (Not true – real gases behave most ideally at high temperature and low pressure)

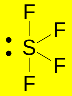
**7** The Valence Shell Electron Pair Repulsion Theory (VSEPR) is used to predict the shapes of molecules.

Which shape is correctly predicted by VSEPR?

| | number of regions of electron density | number of lone pairs | shape |
|---|---|---|---|
| **A** | 3 | 1 | Tetrahedral |
| **B** | 3 | 1 | Trigonal pyramidal |
| **C** | 5 | 1 | See-saw |
| **D** | 5 | 1 | Square pyramidal |

**Answer: C**

5 regions of electron density consisting of 1 lone pair → see-saw shape

For example,  has a see-saw shape

**8** The magnitude of the lattice energy of calcium oxide and calcium carbonate is 3414 kJ mol$^{-1}$ and 2814 kJ mol$^{-1}$ respectively. The enthalpy change of decomposition of calcium carbonate is +176 kJ mol$^{-1}$.

Using the information provided, calculate the enthalpy change of the following reaction.

$$CO_3^{2-}(g) \rightarrow O^{2-}(g) + CO_2(g)$$

| | |
|---|---|
| **A** | - 424 kJ mol$^{-1}$ |
| **B** | +424 kJ mol$^{-1}$ |
| **C** | - 776 kJ mol$^{-1}$ |
| **D** | +776 kJ mol$^{-1}$ |

**Answer: D**

$$\begin{tikzcd}
Ca^{2+}(g) + CO_3^{2-}(g) \arrow[r, "\Delta H_{reaction}"] \arrow[d, "\begin{matrix}LE(CaCO_3)\\ = -2814\end{matrix}"] & O^{2-}(g) + CO_2(g) + Ca^{2+}(g) \arrow[d, "\begin{matrix}LE(CaO)\\ = -3414\end{matrix}"] \\
CaCO_3(s) \arrow[r, "\begin{matrix}\Delta H_{decomposition}\\ = +176\end{matrix}"] & CaO(s) + CO_2(g)
\end{tikzcd}$$

By Hess Law

$\Delta H_{reaction}$ + LE(CaO) = LE($CaCO_3$) + $\Delta H_{decomposition}$ of $CaCO_3$

$\Delta H_{reaction}$ = LE($CaCO_3$) + $\Delta H_{decomposition}$ of $CaCO_3$ – LE(CaO)

$\Delta H_{reaction}$ = - 2814 + 176 + 3414 = +776 kJmol$^{-1}$

Or

Using algebraic method:

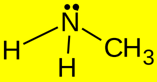
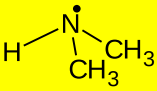
| | |
|---|---|
| (1) $Ca^{2+}$ (g) + $O^{2-}$ (g) → CaO (s) | -3414 |
| (2) $Ca^{2+}$ (g) + $CO_3^{2-}$ (g) → $CaCO_3$ (s) | -2814 |
| (3) $CaCO_3$ (s) → CaO (s) + $CO_2$ (g) | +176 |

Objective : $CO_3^{2-}$ (g) → $O^{2-}$ (g) + $CO_2$ (g) ???

| | | |
|---|---|---|
| (1) reverse | ~~$CaO$ (s)~~ → ~~$Ca^{2+}$ (g)~~ + $O^{2-}$ (g) | +3414 |
| (2) | ~~$Ca^{2+}$ (g)~~ + $CO_3^{2-}$ (g) → ~~$CaCO_3$ (s)~~ | -2814 |
| (3) | ~~$CaCO_3$ (s)~~ → ~~$CaO$ (s)~~ + $CO_2$ (g) | +176 |
| Aim achieved: | $CO_3^{2-}$ (g) → $O^{2-}$ (g) + $CO_2$ (g) | +776 |

| **9** | Primary, secondary and tertiary amine have similarly shaped molecules.<br>What is the predominant intermolecular force of attraction in methylamine, dimethylamine and trimethylamine? | | | |
|---|---|---|---|---|
| | | **methylamine** | **dimethylamine** | **trimethylamine** |
| | **A** | hydrogen bonds | hydrogen bonds | hydrogen bonds |
| | **B** | hydrogen bonds | permanent dipole – permanent dipole | Instantaneous dipole – induced dipole |
| | **C** | permanent dipole – permanent dipole | permanent dipole – permanent dipole | permanent dipole – permanent dipole |
| | **D** | hydrogen bonds | hydrogen bonds | permanent dipole – permanent dipole |

**Answer: D**


(from left to right) the strongest intermolecular force in methylamine, dimethylamine and trimethylamine are hydrogen bonds, hydrogen bonds and permanent dipole – permanent dipole respectively. Trimethylamine does not have hydrogen bonds because there are no hydrogen atoms directly bonded to the nitrogen atom.

| **10** | The integrated form of first-order rate law is as shown.<br>$\ln A = -kt + \ln A_o$<br>where A is the activity at time t,<br>$A_o$ is the initial activity,<br>k is the rate constant,<br>t is the time taken.<br>What is the half-life for a first order reaction if 68% of a substance is reacted within 66s? |
|---|---|
| **A** | 33 s |
| **B** | 40 s |
| **C** | 49 s |
| **D** | 119 s |

**Answer: B**

68% reacted means 32% remain

ln 0.32 = - k(66) + ln 1

k = 0.0172642 $s^{-1}$

Using $t_{1/2} = \dfrac{\ln 2}{k}$ $t_{1/2} = \dfrac{\ln 2}{0.0172642}$ $t_{1/2}$ = 40 second

OR

$C_f/C_o = (1/2)^n$

$32/100 = (1/2)^n$

n = 1.644 one half-life = 66 / 1.644 = 40.15 s

**11** For which equilibrium is $K_c = K_p$?

**A** $C(s) + H_2O(l) \rightleftharpoons CO(g) + H_2(g)$

**B** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

**C** $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

**D** $2NO_2(g) \rightleftharpoons N_2O_4(g)$

**Answer: B**
When there are equal number of moles on each side of the stoichiometric equation
$K_c = K_p$

considering ideal gases, $pV = nRT$ which implies

Concentration of a gas: $\frac{n}{V} = \frac{p}{RT}$

Consider the **reversible** **gaseous** system: $a\mathbf{A}(g) + b\mathbf{B}(g) \rightleftharpoons c\mathbf{C}(g) + d\mathbf{D}(g)$

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b} = \frac{(\frac{p_C}{RT})^c(\frac{p_D}{RT})^d}{(\frac{p_A}{RT})^a(\frac{p_B}{RT})^b} = \frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}(RT)^{(a+b)-(c+d)} = K_p\times(RT)^{(a+b)-(c+d)}$$

**12** The ionic product of water, $K_w$, at two different temperatures is shown below,

| **$K_w$ / mol² dm⁻⁶** | **Temperature / K** |
|---|---|
| $1.00 \times 10^{-14}$ | 298 |
| $1.44 \times 10^{-14}$ | 303 |

Which statement is correct?

**A** Self-ionisation of water is an exothermic process.

**B** At 303 K, $[H^+] = 0.72 \times 10^{-14}$ mol dm$^{-3}$

**C** $K_w = \frac{[H^+][OH^-]}{[H_2O]}$

**D** At 303 K, pH < 7

**Answer: D**
$H_2O \rightleftharpoons H^+ + OH^-$ is an endothermic process.

At 303: $K_w = [H^+][OH^-]$, $1.44 \times 10^{-14} = x^2$ (where x is the $[H^+]$)
$x = 1.2 \times 10^{-7}$ mol dm$^{-3}$
that means $[H^+] = 1.2 \times 10^{-7}$ mol dm$^{-3}$
pH = 6.92 (<7)

**13** Calculate the pH of the resulting solution when 10 cm$^3$ of potassium hydroxide with concentration at $7.5 \times 10^{-7}$ mol dm$^{-3}$ is mixed with an equal volume of hydrogen bromide with concentration at $8.5 \times 10^{-8}$ mol dm$^{-3}$.

| | | |
|---|---|---|
| | **A** | 4.18 |
| | **B** | 6.36 |
| | **C** | 7.64 |
| | **D** | 9.82 |

**Answer: C**
KOH + HBr → KBr + $H_2O$

Amt of KOH = $7.5 \times 10^{-9}$ mol      Amt of HBr = $8.5 \times 10^{-10}$ mol
Since HBr is the limiting reagent and KBr is a neutral salt, the remaining KOH will account for the pH. Thus, the pH of the resulting solution must be greater than 7. Note that there is no buffer solution for strong acid vs strong base reaction.

Amt of KOH left = $6.65 \times 10^{-9}$ mol
$[OH^-] = 6.65 \times 10^{-7} / 0.02 = 3.32 \times 10^{-7}$
Total $[OH^-] = 3.32 \times 10^{-7} + \underline{1 \times 10^{-7}}$ =
(dissociation of water must be considered as the concentration of the base and acid is very low)

pOH = 6.36
pH = 7.64

| | | |
|---|---|---|
| **14** | Aqueous hydrochloric acid was electrolysed for ten minutes, 200 $cm^3$ of gas **A** was collected at the anode.<br>The same current was then applied to concentrated sodium chloride solution in another experiment and 400 $cm^3$ of a gas **B** is collected at the cathode.<br>Which of these statements is correct? | |
| | **A** | Gas **B** is pale yellow. |
| | **B** | The time taken for the second electrolysis is also ten minutes. |
| | **C** | Chlorine gas was collected initially in the first electrolysis system. |
| | **D** | Mercury electrodes can be used for the second electrolysis system if gas **B** is to be collected. |

**Answer: B**
Option A is incorrect because the gas collected at the cathode is $H_2$.
Option C is wrong because the gas collected at the anode is $O_2$.
Option D is wrong because mercury electrodes will cause sodium to be selectively discharged at the cathode of the second electrolysis.

Option B is correct and the following shows the calculation:

| From Expt 1: at the anode | From Expt 2: At the cathode |
|---|---|
| $2H_2O \rightarrow O_2 + 4H^+ + 4e$ | $2H_2O + 2e \rightarrow H_2 + 2OH^-$ |
| $\frac{0.2}{24} = \frac{I \times 10 \times 60}{4 \times 96500}$ solving I = 5.361 A | Considering same current used in Expt 1<br>$\frac{0.4}{24} = \frac{5.361 \times time}{2 \times 96500}$, solving time = 10 min |

| | | |
|---|---|---|
| **15** | Which of the following properties could be predicted for strontium or its compounds? | |
| | **A** | It does not burn in air. |
| | **B** | It forms a soluble sulfate. |

| | | |
|---|---|---|
| | **C** | It reacts with cold water, liberating hydrogen. |
| | **D** | It forms a water-soluble carbonate which does not decompose on heating. |
| **Answer: C**<br>Statement C is correct. Sr reacts vigorously with cold water.<br>$Sr(s) + 2H_2O(\mathit{l}) \rightarrow Sr(OH)_2(aq) + H_2(g)$<br>Sr burns very fast in air to produce a white oxide. $2Sr(s) + O_2(g) \rightarrow 2SrO(s)$<br>$SrSO_4$ is not soluble in water as solubility of Group II sulfate decreases down the Group.<br>$SrCO_3$ is not a water soluble compound and its reasoning is similar to its sulfate. | | |

| | | |
|---|---|---|
| **16** | Equal volumes of chlorine gas were bubbled into hot and cold sodium hydroxide separately until reactions were complete.<br>Which of the following statements is incorrect about the above reactions? | |
| | **A** | Disproportionation reactions will occur. |
| | **B** | Greenish-yellow chlorine gas decolourises in both reactions. |
| | **C** | When aqueous silver nitrate is added to the resulting solutions, white precipitate is formed. |
| | **D** | Sodium chlorate(VII) and sodium chlorate(I) are formed in the reactions respectively. |
| **Answer: D**<br>Hot: $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^-$ (chlorate (V)) + $3H_2O$<br>Cold: $Cl_2 + 2OH^- \rightarrow Cl^- + ClO^-$ (chlorate (I)) + $H_2O$<br>The reactions involved are disproportionation reaction and the greenish yellow chlorine gas will decolourised as it was reacted away. White ppt of silver chloride will be generated when $AgNO_3$ is added. | | |

| | |
|---|---|
| **17** | Aqueous chlorine is added to aqueous sodium bromide and the mixture is shaken with an equal volume of trichloromethane. |

Which observation will be made?

| | |
|---|---|
| **A** | The solution in the test-tube turns colourless. |
| **B** | The solution in the test-tube turns orange. |
| **C** | A colourless layer forms on top of a purple layer. |
| **D** | A colourless layer forms on top of an orange layer. |

**Answer: D**
Chlorine is a strong oxidising agent and the bromide ion will be oxidise to bromine.
$Cl_2 + Br^- \rightarrow Cl^- + Br_2$

When trichloromethane (an organic solvent) is added, the $Br_2$ will dissolve in this organic layer forming an orange layer. The aqueous layer maybe pale yellow (if concentration of bromine formed is high) or colourless (if concentration of bromine is low).

Option C is out as iodine (which is purple) is not formed in this reaction.

Option A and B are out as water and trichloromethane exist as immiscible liquid.

**18** A reaction scheme starting from aqueous copper(II) sulfate solution is shown below. Both **G** and **H** are copper-containing species.

$$CuSO_4(aq) \xrightarrow[\text{I}]{NH_3(aq)} \mathbf{G} \xrightarrow[\text{II}]{\text{excess } NH_3(aq)} \mathbf{H} \xrightarrow[\text{III}]{Na_4edta(aq)} [Cu(edta)]^{2-}(aq)$$

Which of the following statements is correct?

| | |
|---|---|
| **A** | Reaction III is a redox reaction. |
| **B** | $NH_3$ acts as a ligand in reaction I. |
| **C** | **H** is a deep blue solution containing $[Cu(NH_3)_4(H_2O)_2]SO_4$. |
| **D** | The entropy of the system decreases when reaction III occurs. |

**Answer: C**

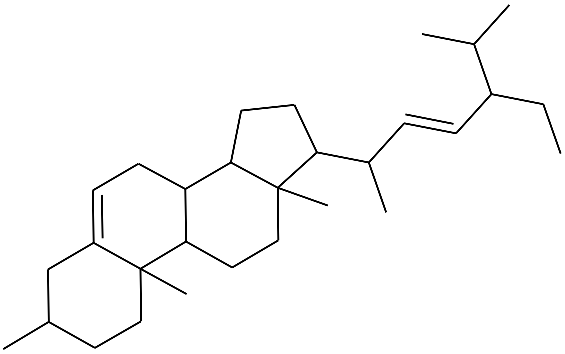
Reaction III is ligand exchange reaction, hence no redox occurs. Also, same no. of bonds and broken and formed, hence no change in entropy.

Reaction I is precipitation reaction, $NH_3 + H_2O \rightleftharpoons OH^- + NH_4^-$
$Cu^{2+} + OH^- \rightleftharpoons Cu(OH)_2$ **(identity of G)**

**G**, $Cu(OH)_2$, is soluble in excess $NH_3$ to form **H**, $[Cu(NH_3)_4(H_2O)_2]SO_4$, a deep blue solution.

When $Na_4$edta was added, ligand exchange reaction occurs
$[Cu(NH_3)_4(H_2O)_2]^{2+} + EDTA^{4-} \rightarrow [Cu(EDTA)]^{2-} + 4NH_3 + 2H_2O$
Entropy of the system increases due to the release of $NH_3$ and water molecules.

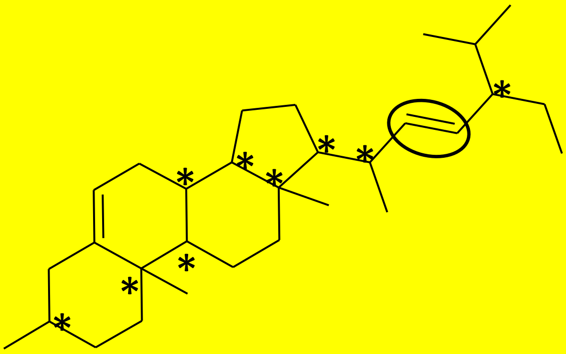
**19** Stigmasterol is an unsaturated plant sterol occurring in the plant fats of soybean.



How many stereoisomers does stigmasterol have?

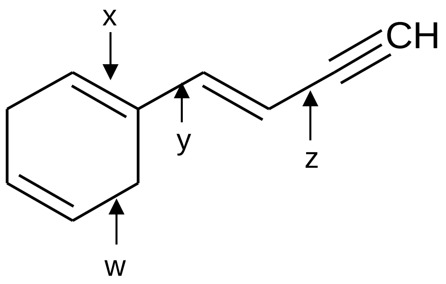
| | |
|---|---|
| **A** | $2^9$ |
| **B** | $2^{10}$ |
| **C** | $2^{11}$ |
| **D** | $2^{12}$ |

**Answer: B**



There are 9 chiral carbon centres and 1 double bond which can exhibit geometrical isomerism. Hence, the total number of stereoisomers is $2^{9+1} = 2^{10}$

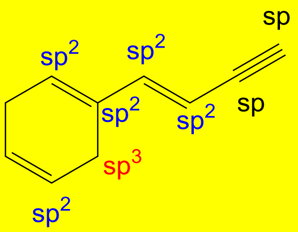
**20.** Four carbon-carbon bonds are labelled in the diagram.



Which bonds are made up of a $sp^2$-$sp^2$ overlap?

| | |
|---|---|
| **A** | **x** only |
| **B** | **x** and **y** only |
| **C** | **w**, **x** and **y** only |
| **D** | **w**, **y** and **z** only |

**Answer: B**

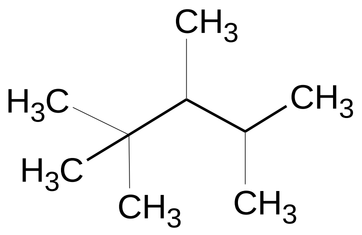


Bond **x** and **y** comprises of $sp^2$ – $sp^2$ overlap.

Bond **w** comprises of $sp^2$ – $sp^3$ overlap.

Bond **z** comprises of $sp^2$ – sp overlap.

**21.** When heated with chlorine, the hydrocarbon 2,2,3,4-tetramethylpentane undergoes free radical substitution. In a propagation step, the free radical **J•** is formed by the loss of one hydrogen atom.

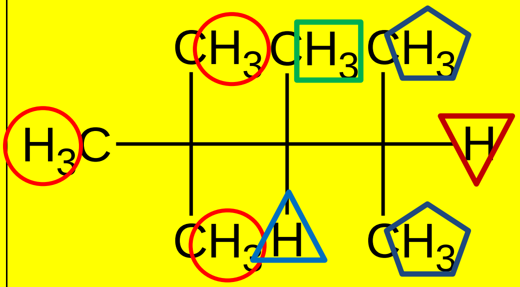


$+ \ Cl\bullet \rightarrow \mathbf{J}\bullet + HCl$

How many different forms of **J•** are theoretically possible?

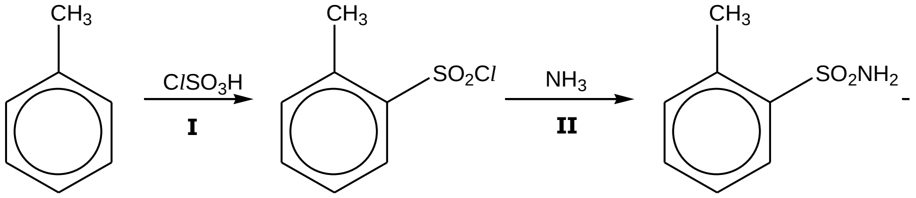
| | |
|---|---|
| **A** | 3 |
| **B** | 4 |
| **C** | 5 |
| **D** | 6 |

**Answer: C**



There are 5 possible sites (as indicated by the shapes) to lose one hydrogen to form different free radical.

**22** *Saccharin* was an artificial sweetener used in some soft drinks. It was manufactured from methylbenzene by a series of reactions.

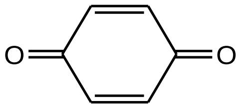


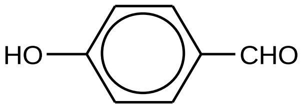
Which of the following shows the correct reaction type for steps **I** and **II**?

| | **I** | **II** |
|---|---|---|
| **A** | Electrophilic substitution | Electrophilic addition |
| **B** | Electrophilic substitution | Nucleophilic substitution |
| **C** | Nucleophilic substitution | Nucleophilic substitution |
| **D** | Nucleophilic substitution | Electrophilic substitution |

**Answer: B**
The first reaction involves the $SO_2Cl^+$ being substituted into the benzene ring.
The second reaction involves the $NH_3$ nucleophilic substitution with the $RSO_2Cl$.

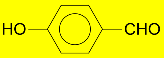
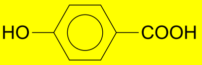
**23** Which of the following **cannot** be used to distinguish between the following compounds?

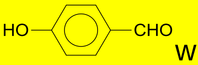


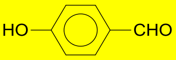


| | |
|---|---|
| **A** | Hot acidified $K_2Cr_2O_7$ |
| **B** | Neutral iron(III) chloride |
| **C** | Diammine silver complex |
| **D** | Phenylhydrazine |

**Answer: D**

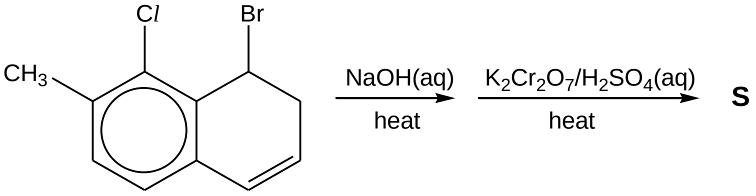
Option A can be used.  undergo oxidation with $Cr_2O_7^{2-}$ to form  .

Option B is possible as  will form a violet complex.

Option C, Tollen's reagent can be used to identify  . A silver mirror will be formed upon heating.

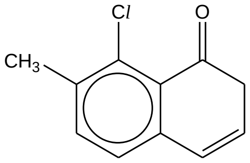
Option D cannot be used as both compounds have carbonyl compound which can form orange ppt with phenylhydrazine.

**24** The reaction scheme below shows the synthesis of compound **S**.

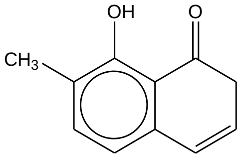


Which of the following can be **S**?

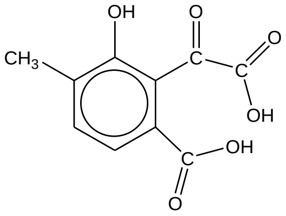
**A**



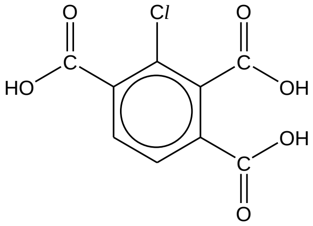
**B**



**C**

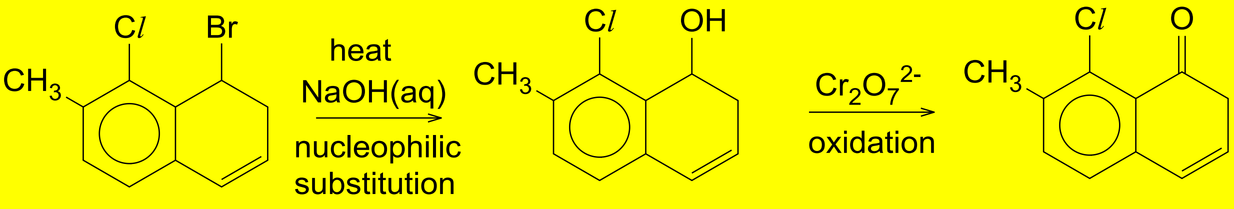


**D**



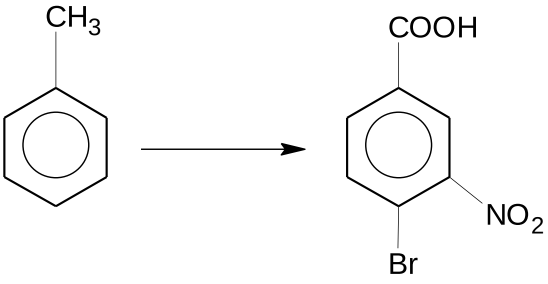
**Answer: A**

The reaction scheme for this question is shown below.



Structure **S**

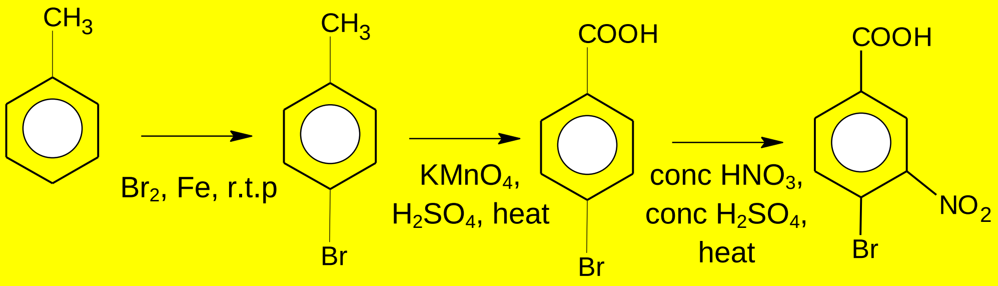
**25** The following synthetic route consists of three steps.



Which sequence of steps would give the highest yield?

| | Step 1 | Step 2 | Step 3 |
|---|---|---|---|
| **A** | $KMnO_4$, $H_2SO_4$, heat | conc $HNO_3$, conc $H_2SO_4$, heat | $Br_2$, Fe, r.t.p |
| **B** | conc $HNO_3$, conc $H_2SO_4$, heat | $Br_2$, Fe, r.t.p | $KMnO_4$, $H_2SO_4$, heat |
| **C** | $Br_2$, *Al*$Br_3$, r.t.p | conc $HNO_3$, dilute $H_2SO_4$, heat | $KMnO_4$, $H_2SO_4$, heat |
| **D** | $Br_2$, Fe, r.t.p | $KMnO_4$, $H_2SO_4$, heat | conc $HNO_3$, conc $H_2SO_4$, heat |

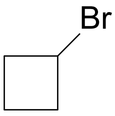
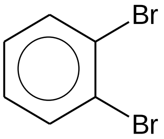
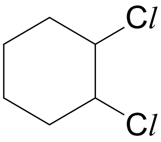
**Answer: D**



Please note that concentrated $HNO_3$ and concentrated $H_2SO_4$ must be used for electrophilic substitution of benzene ring.

**26** Ten grams of each of the following was heated for a prolong period of time with NaOH(aq). Subsequently, dilute $HNO_3$(aq) and $AgNO_3$(aq) were added.

Which compound will produce the greatest mass of AgBr(s)?

| | | | |
|---|---|---|---|
| **A** | <br>($M_r$ = 134.9) | **C** | <br>($M_r$ = 235.8) |
| **B** | $CH_3COCl$<br>($M_r$ = 78.5) | **D** | <br>($M_r$ = 153.0) |

**Answer: D**

Upon heating with NaOH (aq), nucleophilic substitution will occur and all possible halogenoalkanes and acyl halides will undergo nucleophilic substitution.

For Option A
Amount of organic cpd = 10/134.9 = 0.074 mol
Amt of $Br^-$ substituted = 0.074 mol
Mass of AgBr ppted = 0.074 x (108+ 79.9) = 13.9 g

For Option B
Amount of organic cpd = 10/78.5 = 0.127 mol
Amt of $Cl^-$ substituted = 0.127 mol
Mass of AgCl ppted = 0.127 x (108+ 35.5) = 18.3 g

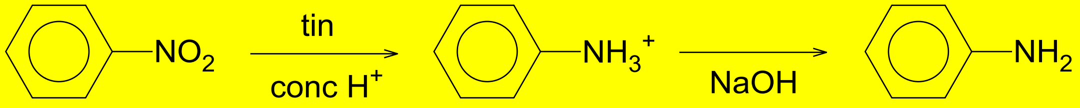
For Option C
No nucleophilic substitution took place.

For Option D
Amount of organic cpd = 10/153 = 0.0653 mol
Amt of $Cl^-$ substituted = 0.0653 x 2 = 0.131 mol
Mass of AgCl ppted = 0.131 x (108+ 35.5) = **18.8 g**

| | |
|---|---|
| **27** | After the reduction using tin and concentrated acid of nitrobenzene to phenylamine, an excess of sodium hydroxide is added. |

| | | |
|---|---|---|
| | What is the purpose of the sodium hydroxide? | |
| | **A** | to dry the product |
| | **B** | to liberate the phenylamine |
| | **C** | to neutralise the excess acid |
| | **D** | to lower the boiling point for subsequent distillation |

**Answer: B**

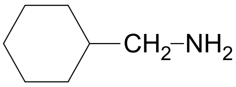
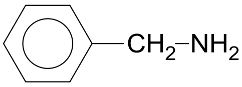
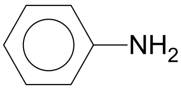
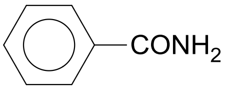
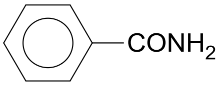
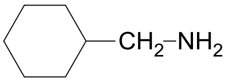
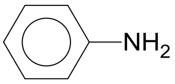
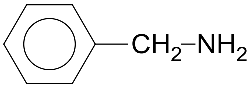
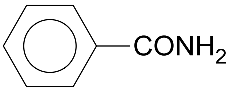
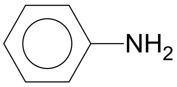
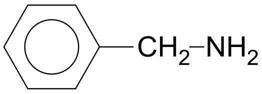
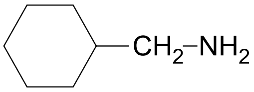
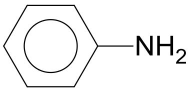
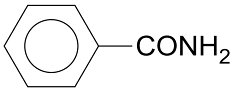
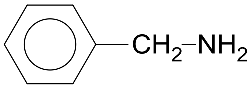
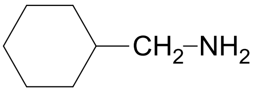


conjugate acid will be formed

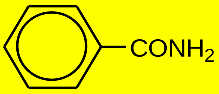
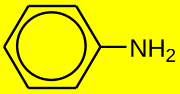
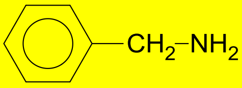
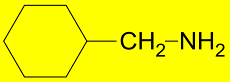
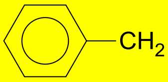
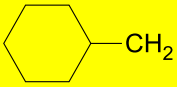
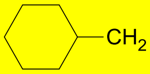
NaOH added to reform phenylamine

The main role of NaOH is not to neutralise the concentrated acid but rather to react with the conjugate acid to form the phenylamine.

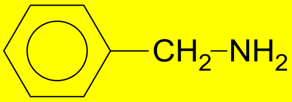
| | |
|---|---|
| **28** | Which of the following shows the correct order of basicity? |

| | | **Weakest base (high $pK_b$)** | | | **Strongest base (Low $pK_b$)** |
|---|---|---|---|---|---|
| | **A** |  |  |  |  |
| | **B** |  |  |  |  |
| | **C** |  |  |  |  |
| | **D** |  |  |  |  |

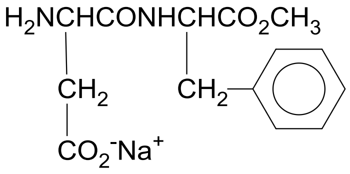
**Answer: C**
**Weakest base** **Strongest base**

| | | | |
|---|---|---|---|
|  |  |  |  |
| This is an amide and it is neutral | The lone pair of electron on the nitrogen atom can delocalised into the benzene ring making it less available for dative bond with the hydrogen protons. | The electron directing cause by the  is not as strong as the  due to the present of the benzene ring | The electron directing effect cause by the  group is the greatest. This cause the lone pair of electrons to be more available for dative bond with $H^+$, resulting in a stronger base |

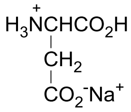
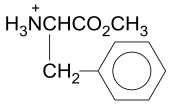
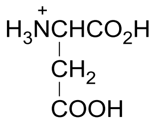
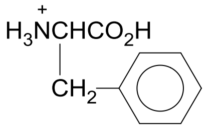
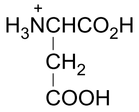
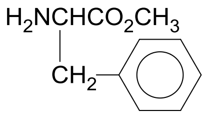
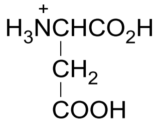
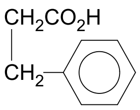
For your knowledge, 2013 Paper 3 Q2(d)

It is know that  ($K_b$ = 2.18 x $10^{-5}$) is less basic than $CH_3NH_2$ ($K_b$ = 5.6 x $10^{-4}$).
The presence of the benzene ring affect the electron donating effect of the R-group.

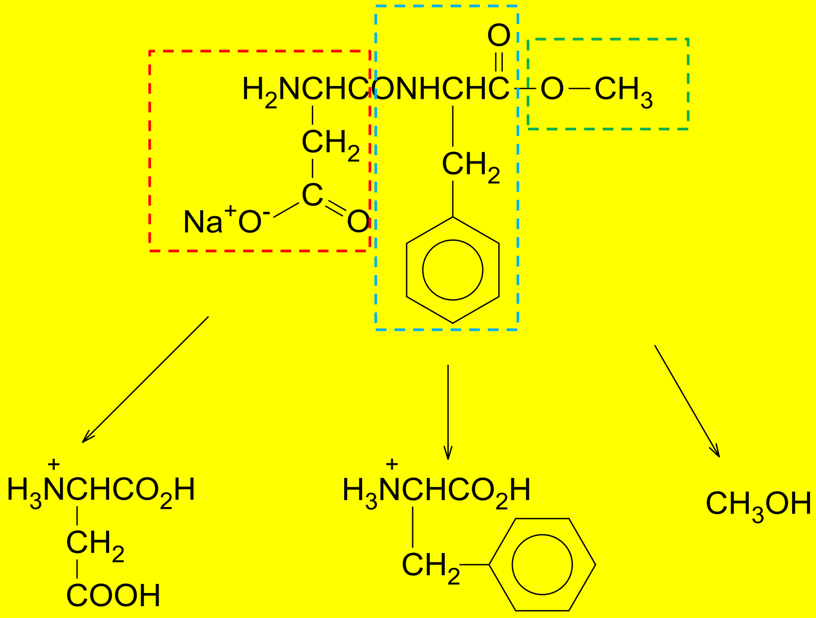
| | |
|---|---|
| **29** | Aspartame is a dipeptide derivatives used as an artificial sweetener. Its general usefulness is restricted because it loses its sweetness after hydrolysis. |



Which product would be formed after prolong acid hydrolysis.

| | | | | |
|---|---|---|---|---|
| **A** | <br>and<br> | **C** | <br>and<br><br>and $CH_3OH$ | |
| **B** | <br>and<br> | **D** | <br>and<br><br>and $CH_3OH$ | |

**Answer: C**

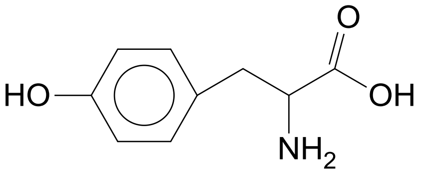
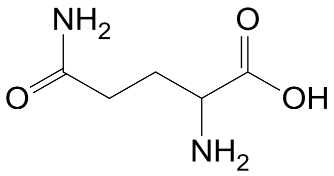
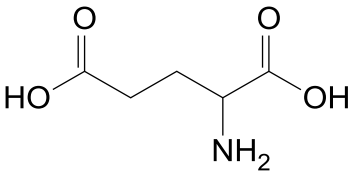
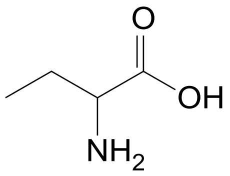


The diagram above shows the acidic hydrolysis reaction of the amide and ester group. Do note that since acid is present, all basic groups (the $NH_2$, the $COO^-Na^+$) will be neutralised.

| **30** | Electrophoresis is a technique of separating and identifying amino acids. A solution of amino acids is absorbed into paper that is moistened with a buffer solution and |
|---|---|

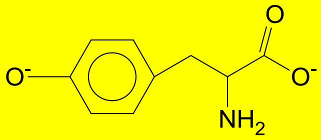
stretched between two electrodes. Positively charged species move towards the cathode, negatively charged species towards the anode.

With a buffer at pH 5, which amino acid will move most readily towards the cathode?

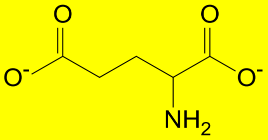
| | | | |
|---|---|---|---|
| **A** |  | **C** |  |
| **B** |  | **D** |  |

**Answer: D**

For A and B since its R-group are acidic, their isoelectric point will be lesser than 5. Thus in buffer at pH 5, they will be in an alkaline environment and will thus behave as an acid generating the anion and thus migrating to the anode.

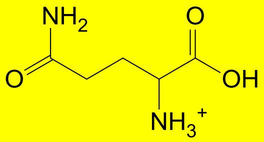


Option A will generate

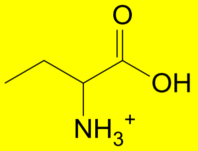


Option B will generate

For C and D their R-group are neutral thus their isoelectric point reside around 7. Thus in buffer at pH 5, they will be in an acidic environment and thus will behave as an alkaline generating the cation and migrating to the cathode.



Option C will generate



Option D will generate

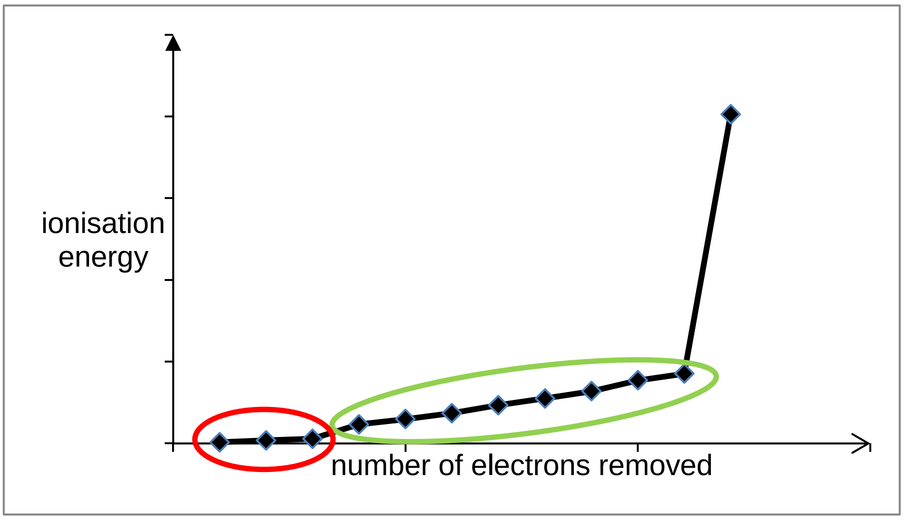
Since D is has a lower $M_r$ as compared to C, it will migrate more readily to towards the cathode.

For **questions 31 – 40**, one or more of the numbered statements **1** to **3** may be correct. Decide whether each of the statements is or is not correct. The responses **A** to **D** should be selected on the basis of

| A | B | C | D |
|---|---|---|---|
| 1, 2 and 3<br>are correct | 1 and 2 only<br>are correct | 2 and 3 only<br>are correct | 1 only<br>is correct |

No other combination of statements is to be used as correct response.

**31** The graph below shows the first twelve ionisation energies for element **T**.



Which of the following statements are true?

| | |
|---|---|
| **1** | It is in Group I of the Periodic Table. |
| **2** | It forms an oxide which dissolves readily with acid. |
| **3** | It is in the third period (Na to Ar) of the Periodic Table. |

**Answer: C**

It is in group III of the Periodic Table as the first 3 consecutive electrons required lower energy. With this idea, Option 1 is definitely wrong and deploying MCQ skill, you should pick Option C (2 and 3) as the correct respond.

Being in group III, and having more than 10 electrons, it could be in the third period.
The group III element could be aluminium whose oxide ($Al_2O_3$) can dissolve readily in acid.

**32** The following chemical reactions are listed below.

- Combustion of ethandioic acid: $C_2H_2O_4\ (l) + O_2\ (g) \rightarrow 2CO_2\ (g) + H_2O\ (l)$
- Evaporation of water: $H_2O\ (l) \rightarrow H_2O\ (g)$
- Atomisation of magnesium: $Mg\ (s) \rightarrow Mg\ (g)$
- Photolysis of chlorine : $Cl_2\ (g) \rightarrow 2Cl\cdot\ (g)$

Which of the following statements are correct?

**1** $\Delta S$ is positive for all reactions.
**2** $\Delta G$ is negative for all reactions.
**3** $\Delta H$ is positive for all reactions.

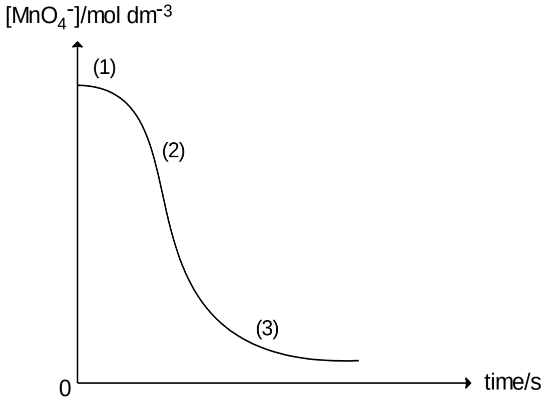
**Answer: D**

| | $\Delta H$ | $\Delta S$ | $\Delta G$ |
|---|---|---|---|
| Combustion of ethandioic acid | Always negative (Exothermic)<br>For combustion, energy is always released. | Positive<br>There is more moles of product than reactant | Since $\Delta H$ is exothermic and $\Delta S$ is positive, $\Delta G$ will always be negative at all temperatures. |
| Evaporation of water | Always positive (Endothermic)<br>Energy need to be absorbed to overcome the intermolecular H-bonding in water. | Positive | $\Delta G = \Delta H - T\Delta S$<br>Dependent on temperature.<br>Since $\Delta H$ and $\Delta S$ is positive, $\Delta G$ will only be negative if temperature increases. |
| Atomisation of magnesium | Always positive (Endothermic)<br>Energy need to be absorbed to change the magnesium solid into magnesium gaseous atoms | Positive | |
| Photolysis of chlorine | Always positive (Endothermic)<br>Energy is absorbed when bonds are broken | Positive | |

**33** A reaction in which a product acts as a catalyst is said to be autocatalytic.

$$2MnO_4^-(aq) + 5C_2O_4^{2-}(aq) + 16H^+(aq) \longrightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$$

In the oxidation of ethanedioate ions by manganate(VII) ions, the reaction is accelerated by the $Mn^{2+}$ ions produced during the reaction.



Which of the following statements can be deduced from the graph above?

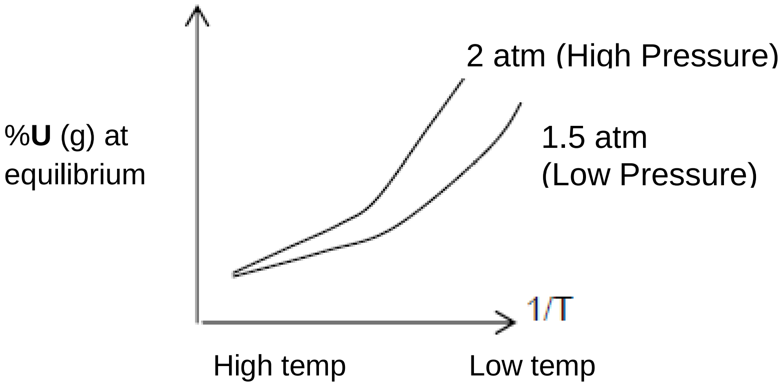
**1** Initial rate of reaction is the fastest at (1).

**2** Reaction rate increases at (2) as $Mn^{2+}$ is generated.

**3** Reaction rate decreases at (3) as the concentration of the reactants decrease.

**Answer: C**
From the graph the gradient at (1) is not the steepest. It is only at region (2) that the reaction rate increases due to the auto-generation of catalyst $Mn^{2+}$. As the reaction progresses, the concentration of reactants decrease and that's when reaction rate starts to dwindle down gradually.

**34** The graph below shows how the percentage of reactant **U**(g) that remained in an equilbrium mixture varies with 1/T at pressures of 1.5 atm and 2 atm.



Which of the following statement can be deduced from this information?

**1** The forward reaction is endothermic.

**2** The equation for the above reaction could be **U**(g) ⇌ **V**(g) + **W**(g).

**3** The equilibrium constant, $K_p$, increases as pressure increases in the system.

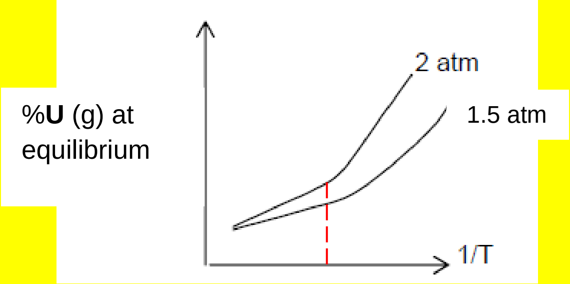
**Answer: B**

The first challenge is to deal with the 1/T axis. One word of advice is to label high temperature and low temperature on the question. This will make things easier.
Do note that **U** is a **REACTANT**!!

Using any curve, as temperature increases while pressure is constant, % U decreases, this means there will be **less reactant U** and forward reaction is favoured As increase in temperature by Le Chatelier's Principle always favour endothermic reaction, forward reaction is endothermic.

From the expression given in option 2 **U**(g) ⇌ **V**(g) + **W**(g)
1mol 2 mol

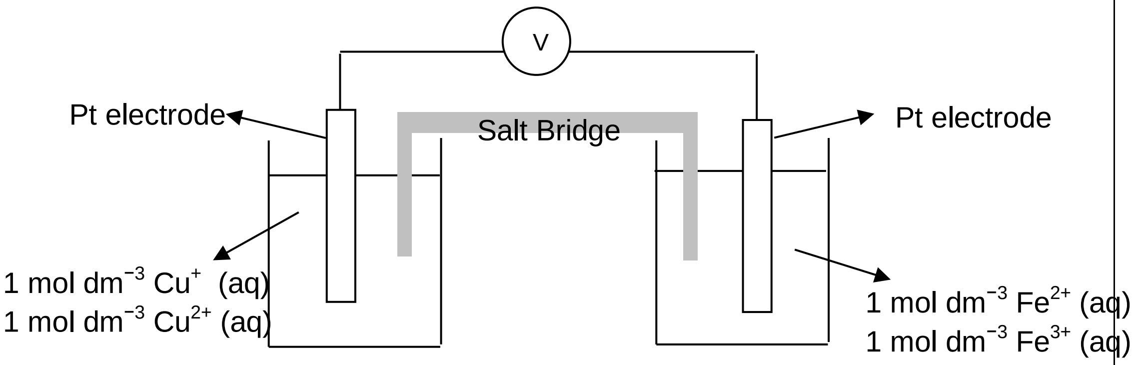
Considering the two curves at separate pressures and at constant temperature



An increase in pressure cause the %U to increase. This means the equilibrium position must shift left. As such the expression in option 2 matches this claim.

Option 3 is wrong as $K_p$ is only temperature dependent.

**35** A student was investigating the possibility of an electrochemical cell using $Cu^{2+}/Cu^{+}$ and $Fe^{3+}/Fe^{2+}$ half-cells.



Which statements are true of the above set up?

**1** $E^{\ominus}_{cell}$ = +0.62 V.
**2** Copper and iron electrodes cannot be used instead.
**3** When excess sodium hydroxide is added to the $Fe^{2+}/Fe^{3+}$ half-cell, the polarity of the electrodes are reversed.

Answer: **A (1 ,2 and 3 only)**

Option 1 is true:
From Data Booklet
$E^{\ominus}(Cu^{2+}/Cu^{+})$ = +0.15 V $E^{\ominus}(Fe^{3+}/Fe^{2+})$ = +0.77 V
$E^{\ominus}_{cell}$ = +0.77 – 0.15 = +0.62 V

Option 2 is true: If copper and iron electrode are used. Other reaction will occur as equilibrium can be established between the metal and their ions.

Option 3 is true:
When $OH^{-}$ is added to the iron half-cell, the half equation becomes
$Fe(OH)_3 + e^{-} \rightleftharpoons Fe(OH)_2 + OH^{-}$ with an $E^{\ominus}$ value of −0.56.
As compared to $E^{\ominus}(Fe^{3+}/Fe^{2+})$ = +0.77V

Thus the iron containing compound half-cell would now undergo oxidation and the $Cu^{2+}/Cu^{+}$ half-cell would now undergo reduction. Hence, the polarity of the electrodes are reversed

**36** Barium sulfate is less soluble than magnesium sulfate.

Which of these factors are needed to be considered in order to explain this observation?

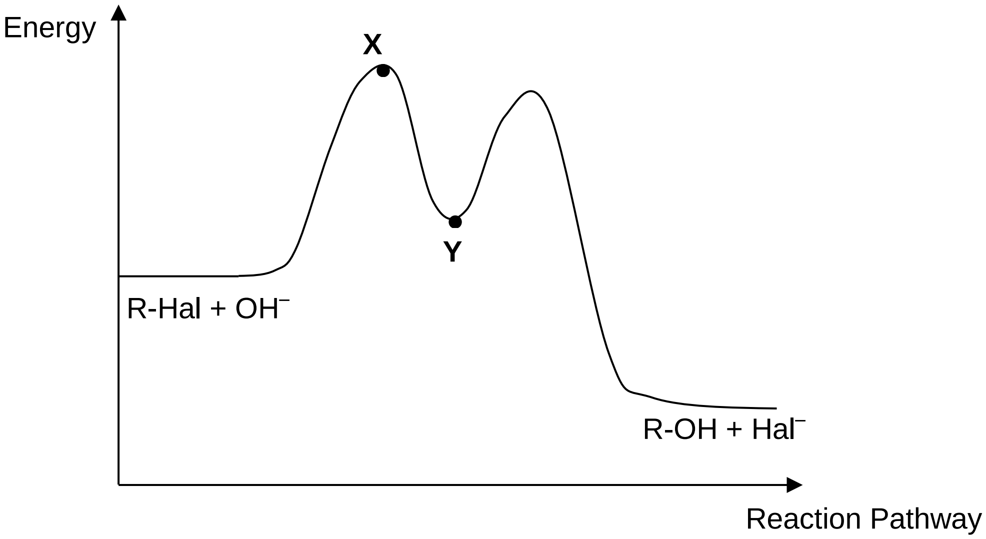
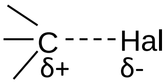
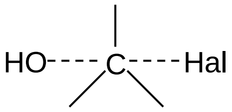
**1** $\Delta H_{hyd}$ of barium ion and magnesium ion.
**2** $\Delta H_f$ of barium sulfate and magnesium sulfate.
**3** Atomic radii of barium and magnesium.

Answer: **D (1 only)**
$\Delta H_{solution} = (\Delta H_{hydration\ of\ cation} + \Delta H_{hydration\ of\ anion}) - \Delta H_{lattice\ energy}$
The more soluble the sulfate, the more exothermic the $\Delta H_{solution}$.
Note that for both $\Delta H_{hydration}$ and $\Delta H_{lattice\ energy}$, these terms are dependent on the ionic radii not the atomic radii.

Option 2 is not feasible as enthalpy change of formation is not required.

| | | |
|---|---|---|
| **37** | Which observation about bromine or its compounds is correct? | |
| | **1** | When aqueous lead(II) nitrate is added to aqueous sodium bromide, a cream precipitate is observed. |
| | **2** | When sodium bromide is treated with concentrated sulfuric acid, a gas that turns moist blue litmus paper red is evolved. |
| | **3** | Silver bromide is soluble in both dilute and concentrated ammonia solution. |
| Answer: **B (1 and 2 only)**<br><br>Option 1: $Pb^{2+}(aq) + Br^{-}(aq) \rightleftharpoons$ **$PbBr_2(s)$**<br>**$PbBr_2(s)$is a cream ppt** (same colour as AgBr ppt)<br><br>Option 2: $NaBr + H_2SO_4 \rightarrow HBr + NaHSO_4$<br>$2HBr + H_2SO_4 \rightarrow$ **$SO_2$ is acidic and turns moist blue litmus paper red** $+ Br_2 + 2H_2O$<br><br>Option 3: AgBr is only soluble in concentrated ammonia. | | |

| | | |
|---|---|---|
| **38** | The catalytic converter is part of the exhaust system of modern cars.<br><br>Which reactions occur in the catalytic converter? | |
| | **1** | $2CO + O_2 \rightarrow 2CO_2$ |
| | **2** | $2NO + CO \rightarrow N_2 + 2CO_2$ |
| | **3** | $C_xH_y + (2x+\frac{y}{2})NO \rightarrow xCO_2 + \frac{y}{2}H_2O + (x+\frac{y}{4})N_2$ |
| | **Answer: A (1,2 and 3)**<br><br>Catalytic converter function to catalyse the<br><br>1. Oxidation of carbon monoxide to carbon dioxide<br>**2.** Reduction of nitrogen oxide to nitrogen and oxygen gas by carbon monoxide.<br>**3.** Complete combustion of hydrocarbons by oxygen or nitrogen oxideReduction of nitrogen oxide to nitrogen and oxygen gas by carbon monoxide. | |

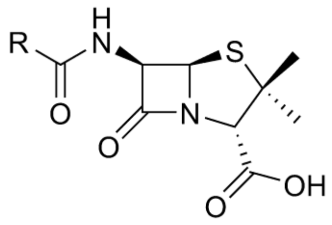
| | | |
|---|---|---|
| **39** | Halogenoalkanes react with aqueous alkali. One mechanism of this reaction has the reaction pathway diagram shown below.<br><br> <br>Which statements are true? (---- indicates a partial bond) | |
| | **1** | The reaction is a type of nucleophilic substitution. |
| | **2** | **X** is  |
| | **3** | **Y** is  |
| | **Answer: B (1 & 2 only)**<br>**Y** is a carbocation intermediate, not a pentavalent transition state. | |

**40** Which of the following phenomena involves denaturation of proteins?

**1** Heating of egg white.

**2** Production of bean-curd from soy milk.

**3** Dissolving Penicillin in a test tube of hot acid.



Penicillin

**Answer: B (1 and 2 only)**

Option 1 involves denaturation:
Heating during cooking causes the **albumin (protein)** in egg white to **denature**. Heating will **disrupt** the **weak Van der Waals forces** (and to a lesser extent, **hydrogen bonds**) holding the **quaternary, tertiary** and **secondary** structures, resulting in a more disordered arrangement.

Option 2 involves denaturation:
Extract from 2010 H2 Paper 3 Q3, “Dofu (bean curd) is made by coagulating soy milk and then pressing the curds between fine cloth to extrude most of the moisture. Coagulating agents that have been used include certain salts, acid or enzymes. **Coagulation is due to the denaturation of the protein in the soy milk**.”

Similar process in food preparation include cheese making, yogurt making and butter making. (Making of Margarine is **not** denaturation but addition of hydrogen into poly unsaturated alkenes)

Option 3 does not involve denaturation as it is merely an acidic hydrolysis process.

**END OF PAPER 1**

# General Certificate of Education Advanced Level Higher 2

| | |
|---|---|
| **CANDIDATE NAME** | |
| **CLASS** | |

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## CHEMISTRY 9647/02

**JC2 Preliminary Examination** **16 September 2016**
**Paper 2 Structured Questions (SPA)** **2hr**

Candidates answer on the Question Paper

Additional Materials: Data Booklet

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**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the 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 work.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer **all** questions.
A Data Booklet is provided.

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

| **For Examiner's Use** | |
|---|---|
| **P1** | / 40 |
| **P2** | / 72 |
| **P3** | / 80 |
| **GRAND TOTAL** | / 192 |
| **%** | |
| **GRADE** | |

| **For Examiner's Use** | |
|---|---|
| **1(P)** | / 12 |
| **2** | / 15 |
| **3** | / 13 |
| **4** | / 11 |
| **5** | / 12 |
| **6** | / 9 |
| **TOTAL P2** | / 72 |

This document consists of **19** printed pages.

**1(P)** When a sparingly soluble salt, calcium hydroxide, $Ca(OH)_2$, is added to water, an equilibrium is established between the undissolved salt and a saturated solution of the salt.

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

The solubility product at laboratory temperature can be found by determining the equilibrium concentration of the hydroxide ions in a saturated solution of calcium hydroxide. This equilibrium concentration can be found by titration with a standard solution of hydrochloric acid.

The numerical value of the solubility product of calcium hydroxide is approximately $5 \times 10^{-6}$.

**(a)** Write an expression for the solubility product of calcium hydroxide, stating its units.

……………………………………………………………………………………………

……………………………………………………………………………………………

[1]

You are required to write a plan to determine the solubility product of calcium hydroxide at laboratory temperature.

You may assume that you are provided with:

- Solid $Ca(OH)_2$
- 0.200 mol $dm^{-3}$ of stock solution of HC*l*
- deionised water
- indicators normally found in a school laboratory
- equipment normally found in a school laboratory

**(b)** **(i)** Calculate the minimum mass of $Ca(OH)_2$ that needs to be weighed in order to obtain 250 $cm^3$ of a saturated solution of $Ca(OH)_2$ at laboratory temperature.

[2]

**(ii)** Assuming that approximately 30.00 $cm^3$ of HC*l* was required to react with 25.0 $cm^3$ of saturated solution of $Ca(OH)_2$, calculate an appropriate concentration of HC*l* required. Hence, calculate the volume of the given solution of HC*l* required to prepare 250 $cm^3$ of this solution.

[2]

Turn over]

**(iii)** Using the information given above and the answers in **b(i)** and **b(ii)**, you are required to write a plan to determine the solubility product of calcium hydroxide.

You are also required to explain how the data you obtain from this experiment may be used to determine the solubility product of calcium hydroxide.

Your plan should include:

- the preparation of 250 $cm^3$ of the saturated solution of calcium hydroxide;
- the preparation of 250 $cm^3$ of standard solution of hydrochloric acid from the stock solution of hydrochloric acid;
- titration procedure;
- how the results obtained can be used to determine the solubility product of calcium hydroxide.

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Turn over]

[7]

Turn over]

[Total: 12]

**2** The manufacture of ammonia from nitrogen and hydrogen takes place in two stages:

First Stage: The manufacture of hydrogen from methane.
Second Stage: The synthesis of ammonia (the Haber Process).

The First Stage occurs via a two-step process.

- *Steam Reforming*
- *Shift Reaction*

Both steps produce hydrogen gas that will be used in the Second Stage for the production of ammonia.

**(a)** *Steam Reforming* is a reaction that converts methane and steam to a mixture of carbon monoxide and hydrogen. There are two possible routes for it:

*Primary Steam Reforming:* Steam is supplied to start the reaction.
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H^\ominus = +210 \text{ kJ mol}^{-1}$ ***eqm* (1)**

*Secondary Steam Reforming:* Some hydrogen is burnt to form steam which then reacts with methane to generate more hydrogen.
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H^\ominus = -482 \text{ kJ mol}^{-1}$
$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H^\ominus = +210 \text{ kJ mol}^{-1}$

**(i)** State if the overall process of *Secondary Steam Reforming* is an exothermic or endothemic process.

…………………………………………………………………………………………..........

[1]

**(ii)** Suggest and explain which steam reforming process (*Primary* or *Secondary*) is favoured by high temperature.

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[2]

Turn over]

**(iii)** The methane gas used usually contains some organic sulfur compounds, R-SH, and hydrogen sulfide, $H_2S$, both of which must be removed or it will poison the catalyst. Hence the methane mixture needs to be p a *desulfurisation unit* first.

- These organic sulfur compounds are first converted into hydrogen sulfide and a hydrocarbon by reduction with hydrogen gas.
- The hydrogen sulfide is reacted with zinc oxide (ZnO) to produce zinc sulfide (ZnS) as one of the products.

Construct two balanced chemical equations showing the reactions that occurred in the *desulfurisation unit*, using R-SH to represent organic sulfur compounds and RH to represent hydrocarbon.

……………………………………………………………………………………………

……………………………………………………………………………………………

[2]

**(b)** In the *Shift Reaction*, the carbon monoxide produced during the *Steam Reforming* process was converted to carbon dioxide and hydrogen gas. *Shift Reaction* is done via a two-step process:

- *High Temperature Shift Reaction* with iron(III) oxide catalyst.
- *Low Temperature Shift Reaction* with thermally unstable copper catalyst at 500 K. The carbon monoxide concentration is further reduced to 0.2%.

The reaction involved in the *Shift Reaction* is illustated in the following equation.

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H^\ominus = -42 \text{ kJ mol}^{-1} \qquad \textbf{\textit{eqm} (2)}$$

**(i)** State the full electronic configuration of iron(III) ion and copper metal.

$Fe^{3+}$: $1s^2$……………………………………

Cu: $1s^2$…………………………………….

[2]

**(ii)** With reference to the *Shift Reaction*, state and explain if iron(III) oxide and copper is functioning as homogeneous or heterogenous catalyst.

……………………………………………………………………………………………

……………………………………………………………………………………………

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……………………………………………………………………………………………

……………………………………………………………………………………………

[2]

Turn over]

**(c)** Traces of carbon dioxide produced in the *Shift Reaction* is subsequently removed by passing it with hydrogen gas over a nickel catalyst at 600 K, a process known as *Methanation*.

$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g)$

Using the enthalpy change values of ***eqm(1)*** and ***eqm(2)***, determine the enthalpy change for this *Methanation* process.

[2]

**(d)** The main process of the Haber Process occurs in a fixed bed reactor.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^{\ominus} = -92\ \text{kJ mol}^{-1}$$

The proportion of ammonia in the equilibrium mixture increases with increasing pressure and with decreasing temperature. Quantitative data are given in the table below.

| **Pressure/atm** | **Percentage of ammonia present at equilibrium at a range of temperature** | | |
|---|---|---|---|
| | **373 K** | **473 K** | **573 K** |
| 10 | - | 50.7 | 14.7 |
| 25 | 91.7 | 63.6 | 27.4 |
| 50 | 94.5 | 74.0 | 39.5 |
| 100 | 96.7 | 81.7 | 52.5 |
| 200 | 98.4 | 89.0 | 66.7 |
| 400 | 99.4 | 94.6 | 79.7 |
| 1000 | - | 98.3 | 92.6 |

**(i)** To obtain a reasonable yield with favourable rate, high pressures, moderate temperatures and a catalyst are used. Using the data, select the temperature and pressure which will result in the highest yield of ammonia.

Temperature …………………… Pressure ………………….. [1]

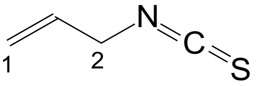
**(ii)** Hence, using the data you have selected in **(d)(i)**, determine the volume of ammonia gas, nitrogen gas and hydrogen gas at equilibrium when 10 cm$^3$ of nitrogen gas is reacted with 30 cm$^3$ of hydrogen gas in the Haber Process. Leave your answer to two decimal places.

[3]

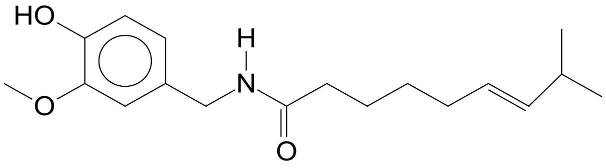
Turn over]

[Total: 15]

**3** **(a)** Allyl isothiocyanate (AITC) is responsible for the pungent taste of wasabi while capsaicin is an active component of chilli pepper and is found in spiced products like curry.



AITC

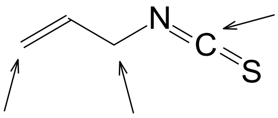


Capsaicin

**(i)** Using your concept of VSEPR, state the shape about the carbon labelled 1 and 2 on AITC.

Carbon 1: …………………….   Carbon 2: ………………….…   [2]

**(ii)** State the type of hybridisation of carbons indicated in AITC.



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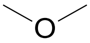
[2]

**(iii)** Besides the ether group  , state the other functional groups that are present in Capsaicin.

………………………………………………………………………………….[3]

**(iv)** Ignoring the effect of the –N=C=S group, write an equation showing how AITC reacts with liquid IBr. Hence, with reference to the *Data Booklet* and given that the bond energy of I-Br to be 180 kJ mol$^{-1}$, determine the enthalpy change of reaction when AITC reacts with liquid IBr.

[2]

**(v)** Using your knowledge in chemical bonding, suggest why the burning sensation of capsaicin cannot be washed away with water.

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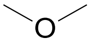
[2]

**(vi)** Draw the structural formula of the products formed when capsaicin is reacted with hot aqueous potassium hydroxide.

[You are to ignore the effect of the  group]

[2]

[Total: 13]

Turn over]

**4** **(a)** Phosgene is a compound with the formula $COCl_2$. It is not to be confused with cobalt(II) chloride with the formula $CoCl_2$.

Phosgene is produced industrially with carbon monoxide and chlorine gas.

$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g) \qquad \Delta H^{\ominus} = -107.6\ \text{kJ mol}^{-1}$$

The $K_p$ of this process is 0.05 $\text{atm}^{-1}$ at 300 K. A mixture contains 2 mol of carbon monoxide and 2 mol of chlorine initially was reacted and allow to reach equilibrium. The equilibrium mixture is found to contain 1.5 mol of phosgene.

**(i)** Draw the Lewis structure of phosgene.

[1]

**(ii)** Write an expression for $K_p$ for the equilibrium between CO, $Cl_2$ and phosgene and hence using the information provided calculate the total pressure of the system at equilibrium.

[3]

**(iii)** Suggest if chlorine or phosgene will deviate more from ideal gas behaviour.

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Turn over]

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[2]

**(b)** Crystals of hydrated cobalt(II) chloride, $CoCl_2.6H_2O$, lose water when thev are heated, forming anhydrous cobalt(II) chloride, $CoCl_2$.

$$CoCl_2.6H_2O(s) \rightarrow CoCl_2(s) + 6H_2O(l)$$

**(i)** The standard enthalpy change for the reaction, $\Delta H^{\ominus}$, is +88.1 kJ mol$^{-1}$. Given that the calculation for entropy change to be similar to that of enthalpy change, use the following entropy data to determine the standard entropy change of the reaction at 298 K. Give your answer to **four** significant figures.

| **Compound** | $S^{\ominus}$ **/ J mol$^{-1}$K$^{-1}$** |
|---|---|
| $CoCl_2.6H_2O$ (s) | 343.0 |
| $CoCl_2$ (s) | 109.2 |
| $H_2O$ ($l$) | 69.9 |
| $H_2O$ (g) | 188.7 |

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[1]

**(ii)** Hence, explain by using calculation, whether hydrated cobalt(II) chloride can be stored at 298K without decomposition.

[2]

**(c)** With the aid of a chemical equation, explain why a solution of cobalt(II) chloride has a pH of 4.6.

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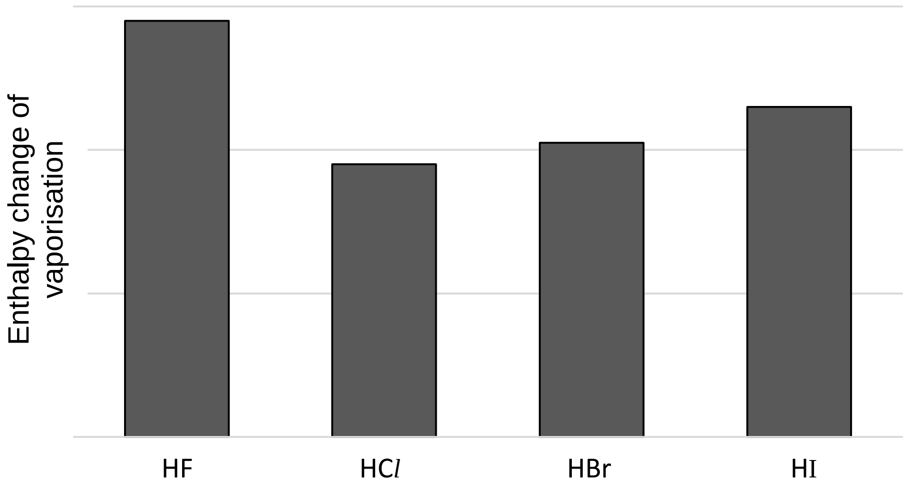
[2]
[Total: 11]

**5** Group VII hydrides are colourless gases at room temperature. The figures below shows the relative enthalpy change of vaporisation of the hydrides.

**Figure 1:** Enthalpy change of vaporisation of H*X*



**(a)** With reference to **Figure 1**, explain the abnormally high enthalpy change of vaporisation of hydrogen fluoride.

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Turn over]

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[2]

**(b)** The table below shows the $pK_a$ of the respective compounds when they are dissolved in water.

| **Compounds** | $\boldsymbol{pK_a}$ | **Compounds** | |
|---|---|---|---|
| | | Hydrogen bromide | -9.00 |
| Hydrogen chloride | -7.00 | Hydrogen iodide | -10.00 |
| Methanoic acid | 3.77 | Water | 7.00 |

**(i)** Using relevant information from the *Data Booklet*, rank the acid strength of aqueous solution containing HC*l*, HBr and HI, in increasing order. Explain your answer.

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Turn over]

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[2]

**(ii)** Account for the relative acidities of methanoic acid and water.

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[2]

**(c)** Unlike other Group VII hydrides, hydrogen fluoride, HF, behaves as a weak acid in water.

A solution of HF was titrated against aqueous potassium hydroxide until 25% of the HF present was neutralised.

**(i)** Write the acid dissociation constant expression, $K_a$, for HF.

[1]

**(ii)** Given that the pH of the resulting solution described above is 2.88, calculate $K_a$ of HF.

Turn over]

[3]

**(d)** One of the most common ways to make hydrogen chloride is to react sodium chloride with concentrated sulfuric acid, $H_2SO_4$ or concentrated phosphoric(V) acid, $H_3PO_4$. Both reactions occur similarly, releasing gas.

**(i)** Construct a balanced equation involving sodium chloride and concentrated phosphoric(V) acid.

……………………………………………………………………………………………….

[1]

**(ii)** In the reaction with sodium bromide, concentrated sulfuric acid produces a reddish-brown solution while concentrated phosphoric(V) acid produces white fumes.

Suggest a reason for the observations above.

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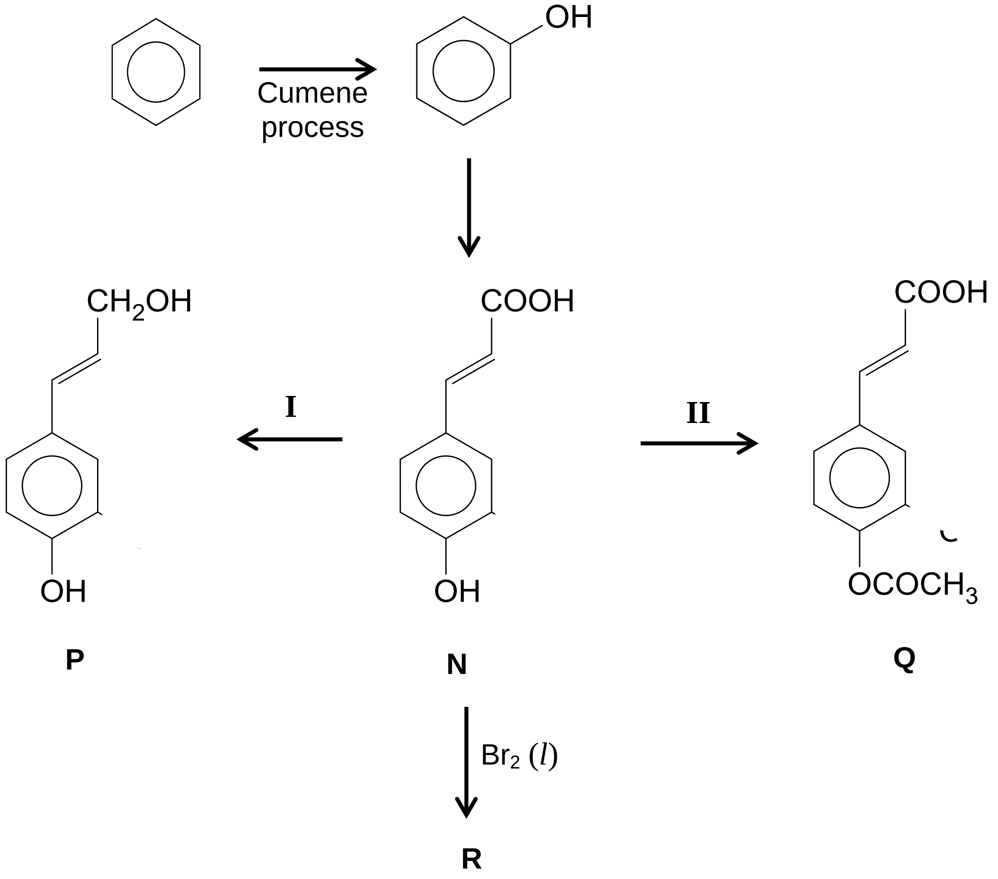
[1]

[Total: 12]

**6** **(a)** The chemical structure and some reactions involving compound **N** are shown below.



**(i)** State the reagents and conditions involved in Steps **I** and **II**.

Step **I**: ……………………….......

Step **II**: ………………………..

[2]

**(ii)** Draw the structure of organic product **R**.

[1]

**(iii)** Propose a chemical test to distinguish between **P** and **N**, in which a positive test is observed for **P only**. Write a balanced chemical equation for the reaction that has occurred.

Test: ………………………………………………………………………………

Observation: ……………………………………………………………………….

Equation:

[3]

**(b)** In the cumene process one mole of benzene reacts with one mole of propene in the presence of oxygen from air to form phenol and organic substance **T**. Substance **T** does not give any positive observation with diammine silver complex or phosphorus pentachloride.

**(i)** From the information provided, identify substance **T**.

[1]

**(ii)** Hence, with an aid of a chemical equation, show how the functional group in substance **T** can be positively identified.

Observation:…………………………………………………………..

Equation:

[2]

[Total: 9]

**END OF PAPER**

## Serangoon Junior College

## 2016 JC2 H2 CHEMISTRY (9647) Paper 2 Suggested Solutions

**1(P)** When a sparingly soluble salt, calcium hydroxide, $Ca(OH)_2$, is added to water, an equilibrium is established between the undissolved salt and a saturated solution of the salt.

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

The solubility product at laboratory temperature can be found by determining the equilibrium concentration of the hydroxide ions in a saturated solution of calcium hydroxide. This equilibrium concentration can be found by titration with a standard solution of hydrochloric acid.

The numerical value of the solubility product of calcium hydroxide is approximately $5 \times 10^{-6}$.

**(a)** Write an expression for the solubility product of calcium hydroxide, stating its units. [1]

$K_{sp} = [Ca^{2+}][OH^{-}]^2$; units: $mol^3\ dm^{-9}$

You are required to write a plan to determine the solubility product of calcium hydroxide at laboratory temperature.

You may assume that you are provided with:

- Solid $Ca(OH)_2$
- $0.200\ mol\ dm^{-3}$ of stock solution of HC*l*
- deionised water
- indicators normally found in a school laboratory
- equipment normally found in a school laboratory

**(b) (i)** Calculate the minimum mass of $Ca(OH)_2$ that needs to be weighed in order to obtain 250 $cm^3$ of a saturated solution of $Ca(OH)_2$ at laboratory temperature. [2]

$K_{sp} \approx 5.0 \times 10^{-6}$

Let the solubility be **x** $mol\ dm^{-3}$.

$(x)(2x)^2 = 5.0 \times 10^{-6}$

$4x^3 = 5.0 \times 10^{-6}$

$x = 0.01077\ mol\ dm^{-3}$

solubility in $g\ dm^{-3} = 0.01077 \times (40.1 + 16.0 \times 2 + 1.0 \times 2) = 0.7982\ g\ dm^{-3}$

Min mass of $Ca(OH)_2$ = $\dfrac{0.7982}{1000} \times 250 = 0.200g$

**(ii)** Assuming that approximately 30.00 $cm^3$ of HC*l* was required to react with 25.0 $cm^3$ of saturated solution of $Ca(OH)_2$, calculate an appropriate concentration of HC*l* required. Hence, calculate the volume of the given solution of HC*l* required to prepare 250 $cm^3$ of this solution. [2]

$Ca(OH)_2 + 2HCl \rightarrow CaCl_2 + 2H_2O$

$$\text{Amount of } Ca(OH)_2 = \frac{25}{1000} \times 0.01077 = 0.0002693\text{mol}$$

$$\text{Amount of HCl} = 0.0002693 \times 2 = 0.0005386\text{mol}$$

$$\text{Concentration of HC}l\text{ required} = \frac{0.0005386}{30} \times 1000 = 0.0180\text{moldm}^{-3}$$

Vol of the given solution needed =

$$\frac{\frac{250}{1000} \times 0.0180}{0.2} = 0.0225\text{dm}^3 = 22.5\text{cm}^3$$

**(iii)** Using the information given above and the answers in **b(i)** and **b(ii)**, you are required to write a plan to determine the solubility product of calcium hydroxide.

You are also required to explain how the data you obtain from this experiment may be used to determine the solubility product of calcium hydroxide.

Your plan should include:

- the preparation of 250 $cm^3$ of the saturated solution of calcium hydroxide;
- the preparation of 250 $cm^3$ of standard solution of hydrochloric acid from the stock solution of hydrochloric acid;
- titration procedure;
- how the results obtained can be used to determine the solubility product of calcium hydroxide.

[7]

**Preparation of saturated solution of calcium hydroxide**

1. **Weigh** approximately **0.200 g** of solid.
2. Using a **measuring cylinder**, place **250 $cm^3$ of deionised water** into a **dry conical flask/beaker**.
3. Add **solid to water** and **stir with a glass rod** to dissolve the solid.
4. **Weigh** and **add more solid** to the water until **excess solid remains / no more solid dissolves.**
5. Allow the mixture to **stand for a period of time** (e.g 30 mins) to establish equilibrium.
6. **Filter** the mixture to obtain the filtrate.

**Preparation of hydrochloric acid form the solution**

1. Fill **a burette** with the stock solution of **hydrochloric acid**. Drain **22.50 $cm^3$** of the hydrochloric acid from the burette into a **250 $cm^3$ volumetric flask**. Top-up the volumetric flask up **to the mark with de-ionised water**. Add the last few drops of de-ionised water using a dropper till the bottom of the meniscus coincides with the mark.
2. **Stopper** the volumetric flask firmly and **shake it** to ensure complete mixing. This is to ensure that a homogeneous solution is obtained.

| | | | |
|---|---|---|---|
| | | | **Titration procedure**<br>1. **Fill a clean burette** with the **hydrochloric acid** solution.<br>2. **Pipette 25.0 $cm^3$ of calcium hydroxide** into a clean **conical flask**.<br>3. Add **2 or 3 drops of methyl orange indicator** into the conical flask and **titrate** this solution with the **hydrochloric acid in the burette** with **constant swirling**, and **add drop-wise** as the titration is **near the end-point**.<br>4. **Stop the titration** immediately when the first **drop of hydrochloric acid** added turns the solution from **yellow to orange**.<br>5. **Repeat the titration** until **two accurate titre readings fall within 0.10 $cm^3$** of each other are obtained |
| | | | **Results**<br>Assume that the volume obtained is **V** $cm^3$<br>Amount of $Ca(OH)_2$ in 25.0 $cm^3$ = $\frac{1}{2}\times(\frac{V}{1000}x0.0180)mol$<br>Concentration of saturated $Ca(OH)_2$ =<br>$\left[\frac{1}{2}(\frac{V}{1000}x0.0180)\div\frac{25}{1000}\right]=z\ moldm^{-3}$<br>$[Ca^{2+}]=z\ mol\ dm^{-3}$<br>$[OH^{-}]=2z\ mol\ dm^{-3}$<br>$K_{sp}=z\times(2z)^2=4z^3\ mol^3\ dm^{-9}$ |
| | | | [Total: 12] |

**2** The manufacture of ammonia from nitrogen and hydrogen takes place in two stages:

First Stage: The manufacture of hydrogen from methane.
Second Stage: The synthesis of ammonia (the Haber Process).

The First Stage occurs via a two-step process.

- *Steam Reforming*
- *Shift Reaction*

Both steps produce hydrogen gas that will be used in the Second Stage for the production of ammonia..

**(a)** *Steam Reforming* is a reaction that converts methane and steam to a mixture of carbon monoxide and hydrogen. There are two possible routes for it:

*Primary Steam Reforming:* Steam is supplied to start the reaction.

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H^\ominus = +210\ \text{kJ mol}^{-1}$ ***eqm* (1)**

*Secondary Steam Reforming:* Some hydrogen is burnt to form steam which then reacts with methane to generate more hydrogen.

$2H_2(g) + O_2(g) \rightarrow 2H_2O(g) \quad \Delta H^\ominus = -482\ \text{kJ mol}^{-1}$

$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad \Delta H^\ominus = +210\ \text{kJ mol}^{-1}$

**(i)** State if the overall process of *Secondary Steam Reforming* is an exothermic or endothemic process.

[1]

Overall is exothermic.

**(ii)** Suggest which steam reforming process (*Primary* or *Secondary*) is favoured by high temperature.

[2]

Primary steam reforming is favoured by high temperature.

For primary steam reforming, process is endothermic. By Le Chatelier's Principle (LCP), high temperature favoured the endothermic reaction which is the forward reaction as excess heat energy is being absorbed.

**(iii)** The methane gas used usually contains some organic sulfur compounds, R-SH, and hydrogen sulfide, $H_2S$, both of which must be removed or it will poison the catalyst. Hence the methane mixture needs to be passed through a *desulfurisation unit* first.

- These organic sulfur compounds are first converted into hydrogen sulfide and a hydrocarbon by reduction with hydrogen gas.
- The hydrogen sulfide is reacted with zinc oxide (ZnO) to produce zinc sulfide (ZnS) as one of the products.

Construct two balanced chemical equations showing the reactions that occurred in the *desulfurisation unit*, using R-SH to represent organic sulfur compounds and RH to represent hydrocarbon

[2]

$R\text{-}SH + H_2 \rightarrow RH + H_2S$

$ZnO + H_2S \rightarrow ZnS + H_2O$

**(b)** In the *Shift Reaction*, the carbon monoxide produced during the *Steam Reforming* process was converted to carbon dioxide and hydrogen gas. *Shift Reaction* is done via a two-step process:

- *High Temperature Shift Reaction* with iron(III) oxide catalyst.
- *Low Temperature Shift Reaction* with thermally unstable copper catalyst at 500 K. The carbon monoxide concentration is further reduced to 0.2%.

The reaction involved in the *Shift Reaction* is illustated in the following equation.

$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H^\ominus = -42\ kJ\ mol^{-1}$ ***eqm* (2)**

**(i)** State the full electronic configuration of iron(III) ion and copper metal. [2]

$Fe^{3+}$: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ Cu: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

**(ii)** With reference to the *Shift Reaction*, state and explain if iron(III) oxide and copper is functioning as homogeneous or heterogenous catalyst. [2]

They are **heterogenous catalysts**

**The availability of partially-filled 3d orbitals allow reactant molecules to be adsorbed onto** the catalyst surface via van der Waals' interactions.

**(c)** Traces of carbon dioxide produced in the *Shift Reaction* is subsequently removed by passing it with hydrogen gas over a nickel catalyst at 600 K, a process known as *Methanation*.

$CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g)$

Using the enthalpy change values of ***eqm(1)*** and ***eqm(2)*** of this question, determine the enthalpy change for this *Methanation* process. [2]

Using algebraic method:
(1) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \qquad \Delta H^\ominus = +210\ kJ\ mol^{-1}$
(2) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \qquad \Delta H^\ominus = -42\ kJ\ mol^{-1}$

Reverse (1) + Reverse (2)
$CO(g) + 3H_2(g) \rightleftharpoons CH_4(g) + H_2O(g) \qquad \Delta H^\ominus = +210\ kJ\ mol^{-1}$
$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g) \qquad \Delta H^\ominus = +42\ kJ\ mol^{-1}$

Overall: $CO_2(g) + 4H_2(g) \rightleftharpoons CH_4(g) + 2H_2O(g) \qquad \Delta H^\ominus = -168\ kJ\ mol^{-1}$
OR
Using energy cycle:

$$\begin{tikzcd}
CO_2(g) + 4H_2(g) \arrow[rr, "\Delta H"] \arrow[dr, "+42"'] & & CH_4(g) + 2H_2O \\
& CO(g) + H_2O(g) + 3H_2(g) \arrow[ur, "-210"'] &
\end{tikzcd}$$

By Hess Law
$\Delta H = +42 - 210 = -168\ kJ\ mol^{-1}$

**(d)** The main process of the Haber Process occurs in a fixed bed reactor.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \Delta H^{\ominus} = -92 \text{ kJ mol}^{-1}$$

The proportion of ammonia in the equilibrium mixture increases with increasing pressure and with falling temperature. Quantitative data are given the table below.

| **Pressure/atm** | **Percentage ammonia present at equilibrium at a range of temperature** | | |
|---|---|---|---|
| | **373 K** | **473 K** | **573 K** |
| 10 | - | 50.7 | 14.7 |
| 25 | 91.7 | 63.6 | 27.4 |
| 50 | 94.5 | 74.0 | 39.5 |
| 100 | 96.7 | 81.7 | 52.5 |
| 200 | 98.4 | 89.0 | 66.7 |
| 400 | 99.4 | 94.6 | 79.7 |
| 1000 | - | 98.3 | 92.6 |

**(i)** To obtain a reasonable yield with favourable rate, high pressures, moderate temperatures and a catalyst are used. Using the data, select the temperature and pressure which will result in the highest yield of ammonia.

[1]

Temperature: 373 K
Pressure: 400 atm

**(ii)** Hence, using the data you have selected in **(a)(i)**, determine the volume of ammonia gas, nitrogen gas and hydrogen gas at equilibrium when 10 cm$^3$ of nitrogen gas is reacted with 30 cm$^3$ of hydrogen gas in the Haber Process. Leave your answer to two decimal places.

[3]

Let x be the volume of $NH_3$ at equilibrium

| | $N_2(g)$ + | $3H_2(g)$ | $2NH_3(g)$ |
|---|---|---|---|
| Initial | 10 | 30 | 0 |
| Change | -0.5x | -1.5x | +x |
| Eqm | 10 – 0.5x | 30 – 1.5x | x |

Total volume of gas at eqm = 10 – 0.5x + 30 – 1.5x + x
= 40 – x

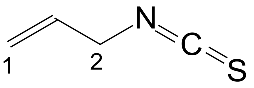
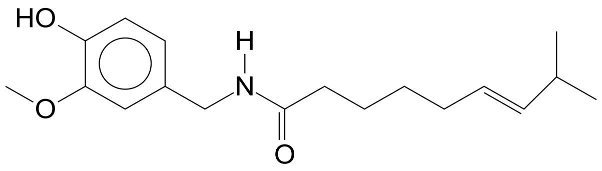
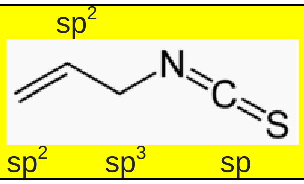
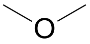
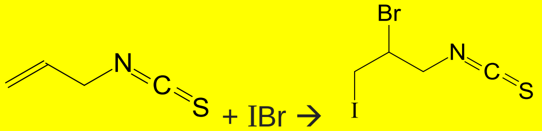
From (a)(i)
Since at 373 K and 400 atm, percentage ammonia present is 99.4%

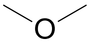
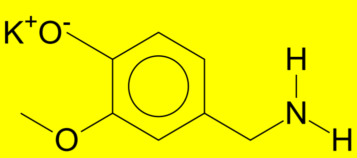
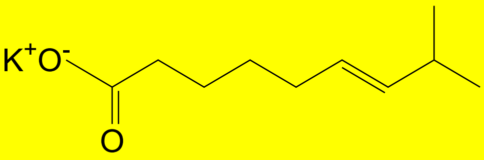
$$99.4 = \frac{x}{40-x} \times 100$$

(0.994)(40-x) = x
39.76 – 0.994x = x
x = 19.94

Hence at eqm:
Volume of $NH_3$ = **19.94 cm$^3$**
Volume of $N_2$ = 10 – 9.97 = **0.03 cm$^3$**
Volume of $H_2$ = 30 – 1.5(19.94) = **0.09 cm$^3$**

[Total: 15]

| | | | |
|---|---|---|---|
| **3** | **(a)** | | Allyl isothiocyanate (AITC) is responsible for the pungent taste of wasabi while capsaicin is an active component of chilli pepper and is found in spiced products like curry.<br> <br>AITC<br> <br>Capsaicin |
| | | **(i)** | Using your concept of VSEPR, state the shape about the carbon labelled 1 and 2 on AITC. [2] |
| | | | Carbon 1: Trigonal planar<br>Carbon 2: Tetrahedral |
| | | **(ii)** | Suggest the type of hybridisation for all carbons present in AITC. [2] |
| | | |  |
| | | **(iii)** | Besides the ether group , state the other functional groups that are present in Capsaicin. [3] |
| | | | Alkene, secondary amide, phenol |
| | | **(iv)** | Ignoring the effect of the –N=C=S group, write an equation showing how AITC reacts with liquid IBr. Hence, with reference to the *Data Booklet* and given that the bond energy of I-Br to be 180 kJ $mol^{-1}$, determine the enthalpy change of reaction when AITC reacts with liquid IBr. [2] |
| | | |  <br>$\Delta H = BE(C=C) + BE(I\text{-}Br) - BE(C\text{-}I) - BE(C\text{-}Br) - BE(C\text{-}C)$<br>$= 610 + 180 - 240 - 280 - 350$<br>$= -80 \text{ kJ mol}^{-1}$ |
| | | **(v)** | Using your knowledge in chemical bonding, suggest why the burning sensation of capsaicin cannot be washed away with water. [2] |
| | | | Capsaicin is a simple molecular structure. There is no favourable solute-solvent interaction between capsaicin and water. Hence, the burning effect could not be washed away with water. |

| | | | |
|---|---|---|---|
| | | **(vi)** | Draw the structural formula of the products formed when capsaicin is reacted with hot aqueous potassium hydroxide.<br>[You are to ignore the effect of the  group]<br>[2] |
| | | |   |
| | | | [Total: 13] |

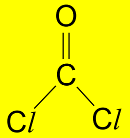
**4** **(a)** Phosgene is the chemical compound with the formula $COCl_2$. It is not to be confused with cobalt(II) chloride with the formula $CoCl_2$.

Phosgene is produced industrially with carbon dioxide and chlorine gas.

$$CO\,(g) + Cl_2\,(g) \rightleftharpoons COCl_2\,(g) \qquad \Delta H^\ominus = -107.6\ \text{kJ mol}^{-1}$$

The $K_p$ of this process is 0.05 $\text{atm}^{-1}$ at 300 K. A mixture contains 2 mol of carbon monoxide and 2 mol of chlorine initially was reacted and allow to reach equilibrium. The equilibrium mixture is found to contain 1.5 mol of phosgene.

**(i)** Draw the Lewis structure of phosgene. [1]



**(ii)** Write an expression for $K_p$ for the equilibrium between CO, $Cl_2$ and phosgene and hence using the information provided calculate the total pressure of the system at equilibrium. [3]

$$K_p = \frac{P_{COCl_2}}{P_{CO}\,P_{Cl_2}}$$

| | $CO\,(g)$ + | $Cl_2\,(g)$ $\rightleftharpoons$ | $COCl_2\,(g)$ |
|---|---|---|---|
| Initial no. of moles | 2 | 2 | 0 |
| Change in no. of moles | -1.5 | -1.5 | +1.50 |
| Eqm. no. of moles | 0.5 | 0.5 | 1.50 |

Total no. of moles of gases at eqm = 0.5 + 0.5 + 1.50 = 2.5

$$K_p = \frac{\left(P_{COCl_2}\right)}{\left(P_{CO}\right)\times\left(P_{Cl_2}\right)}$$

$$0.05 = \left(\frac{1.50}{2.50}\times P_T\right)\div\left(\left(\frac{0.5}{2.50}\times P_T\right)\left(\frac{0.5}{2.50}\times P_T\right)\right)$$

$0.05 = 0.6\ P_T \div (0.2P_T \times 0.2P_T)$

$0.05 = 0.6\ P_T \div (0.04{P_T}^2)$

$0.05 = 15/P_T$

$P_T = 300$ atm

**(iii)** Suggest if chlorine or phosgene will deviate more from ideal gas behaviour. [2]

Phosgene gas deviates more from ideality

The permanent dipole – permanent dipole interaction between phosgene molecules is stronger as compared to the instantaneous dipole – induced dipole between chlorine molecules.

**(b)** Crystals of hydrated cobalt(II) chloride, $CoCl_2.6H_2O$, lose water when they are heated, forming anhydrous cobalt(II) chloride, $CoCl_2$.

$$CoCl_2.6H_2O(s) \rightarrow CoCl_2(s) + 6H_2O(l)$$

**(i)** The standard enthalpy change for the reaction, $\Delta H^{\ominus}$, is +88.1 kJ $mol^{-1}$. Given that the calculation for entropy change to be similar to that of enthalpy change, use the following entropy data to determine the standard entropy change of the reaction at 298 K. Give your answer to **four** significant figures.

| **Compound** | $S^{\ominus}$ **/ J** $mol^{-1}K^{-1}$ |
|---|---|
| $CoCl_2.6H_2O$ (s) | 343.0 |
| $CoCl_2$ (s) | 109.2 |
| $H_2O$ (*l*) | 69.9 |
| $H_2O$ (g) | 188.7 |

[1]

$\Delta S^{\ominus}$ = 109.2 + **6**(69.9) – 343
= +185.6 J $mol^{-1}K^{-1}$ (to 4 s.f.)

**(ii)** Hence, explain by using calculation, whether hydrated cobalt(II) chloride can be stored at 298K without decomposition.

[2]

$\Delta G^{\ominus} = \Delta H^{\ominus} - T\Delta S^{\ominus}$
= $+88.1\times10^3$ – 298(185.6)
= 88100 – 55308.8
= 32791.2
≈ +32800 J $mol^{-1}$

Yes it can be stored without decomposition as $\Delta G^{\ominus}$ is positive.

**(c)** With the aid of a chemical equation, explain why a solution of cobalt(II) chloride has a pH of 4.6.

[2]

(FYI for $Co^{2+}$ charge +2, ionic radius 0.065 nm)
(FYI for $Al^{3+}$: charge +3, ionic radius 0.053 nm)
(FYI for $Mg^{2+}$: charge +2, ionic radius 0.072 nm)

**$Co^{2+}$ ion** has **high charge density** or has **high polarising power** which can distort the electron cloud of the water ligand.

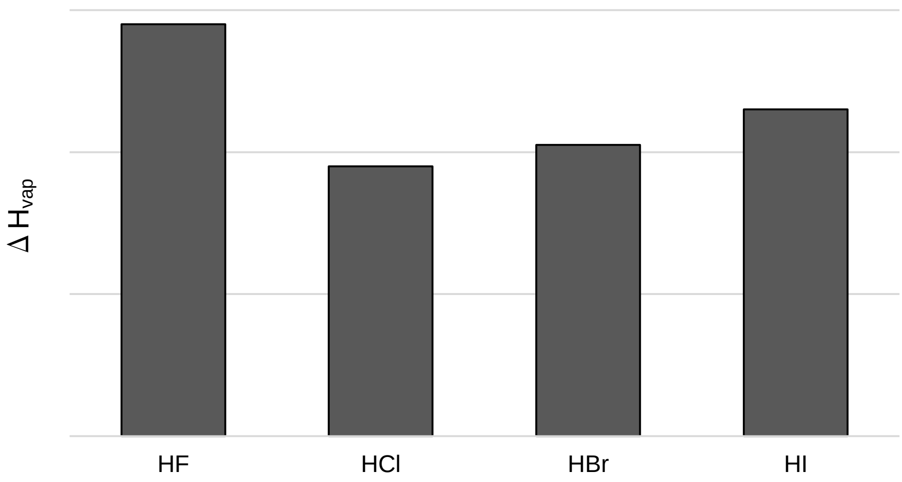
$$[Co(H_2O)_6]^{2+} \rightleftharpoons [Co(H_2O)_5(OH)]^{+} + H^{+}$$

Thus, solution is acidic.

[Total: 11]

**5** Group VII hydrides are colourless gases at room temperature. The figures below shows the relative enthalpy change of vaporisation of the hydrides

**Figure 1:** $\Delta H_{vap}$ of H*X*



**(a)** With reference to **Figure 1**, explain the abnormally high enthalpy change of vaporisation of hydrogen fluoride. [2]

HF molecules are held together by stronger **intermolecular hydrogen bonds** as compared to the other HX molecules held by weaker **permanent dipole-permanent dipole interactions.**

**More energy** is needed to overcome **stronger** intermolecular hydrogen bonds in HF, explaining its abnormally high enthalpy change of vaporisation.

**(b)** The table below shows the $pK_a$ of the respective compounds when they are dissolved in water

| **Compounds** | **$pK_a$** | **Compounds** | **$pK_a$** |
|---|---|---|---|
| | | Hydrogen bromide | -9.00 |
| Hydrogen chloride | -7.00 | Hydrogen iodide | -10.00 |
| Methanoic acid | 3.77 | Water | 7.00 |

**(i)** Using relevant information from the *Data Booklet*, rank the acid strength of aqueous solution containing HC*l*, HBr and HI, in increasing order. Explain your answer. [2]

**From *Data Booklet*, Bond energy**: **H—C*l* (431) > H—Br (366) > H—I (299)**
**Ease of cleavage** of HX bond: **H—C*l* < H—Br < H—I**
Or **energy needed to break HX bond**: **H—C*l* > H—Br > H—I**
Ease of release of $H^+$ ion: HC*l* < HBr < HI
**Acidity : HC*l* < HBr < HI**

**(ii)** Account for the relative acidities of methanoic acid and water. [2]

Methanoic acid is a **stronger acid** than water as its **conjugate base / carboxylate anion** (RCOO$^-$) is resonance **stabilised by the delocalisation of the negative charge over the C atom and both oxygen atoms**.

As such, methanoic acid is less likely to accept a proton from HX than water.

**(c)** Unlike other Group VII hydrides, hydrogen fluoride, HF, behaves as a weak acid in water.

A solution of HF was titrated against aqueous potassium hydroxide until 25% of the HF present was neutralised.

**(i)** Write the acid dissociation constant expression, $K_a$, for HF. [1]

$$K_a = \frac{[H^+][F^-]}{[HF]}$$

**(ii)** Given that the pH of the resulting solution described above is 2.88, calculate $K_a$ of HF. [3]

pH = $-\log_{10}[H^+]$

$[H^+] = 10^{-2.88}$ = **1.32 x 10$^{-3}$ mol dm$^{-3}$**

Let x be the initial [HF]

| | HF ⇌ | $H^+$ + | $F^-$ |
|---|---|---|---|
| Initial/mol dm$^{-3}$ | x | 0 | 0 |
| Change/mol dm$^{-3}$ | -0.25x | +0.25x | +0.25x |
| Eqm/mol dm$^{-3}$ | 0.75x | 0.25x | 0.25x |

$$K_a = \frac{[H^+][0.25x]}{[0.75x]} = \frac{(\mathbf{1.32 \times 10^{-3}})\ x\ \mathbf{1}}{3}$$

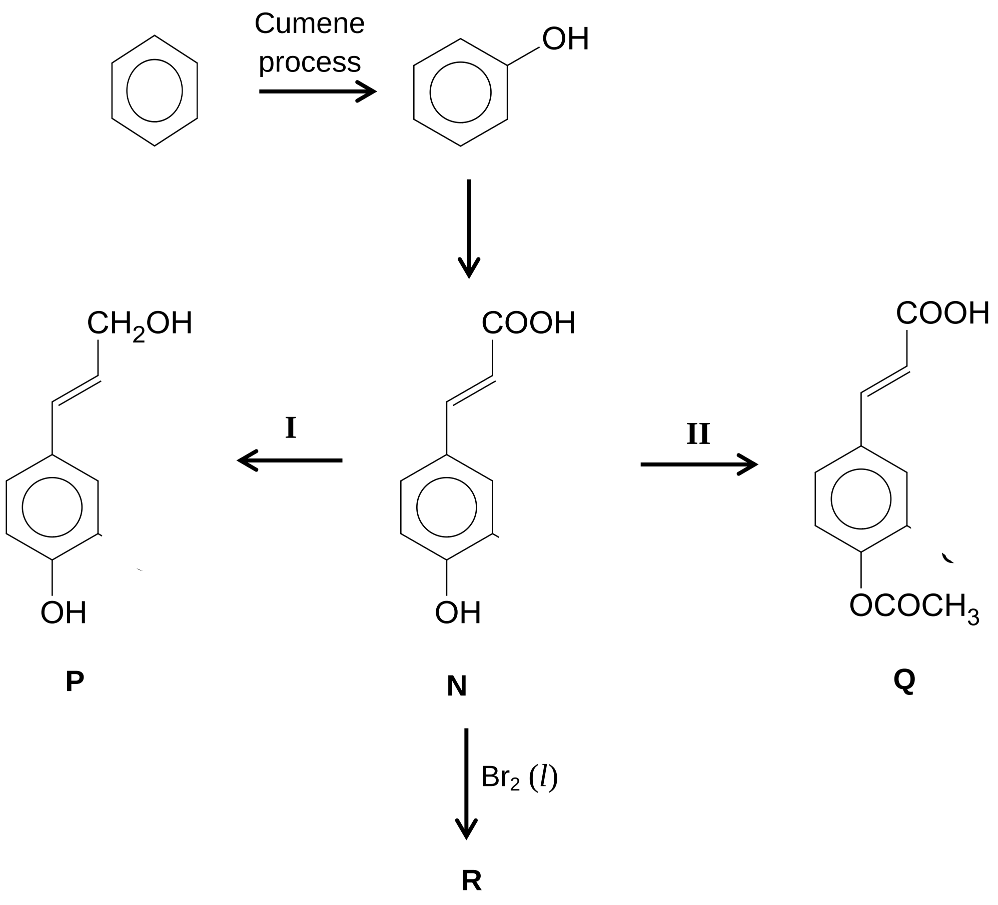
= **4.40 x 10$^{-4}$ mol dm$^{-3}$**

Alternative solution

pH = p$K_a$ + lg {[salt]/[acid]}
2.88 = p$K_a$ + lg {[$F^-$]/[HF]}
2.88 = p$K_a$ + lg (0.25/0.75)
$K_a$ = 4.39 x 10$^{-4}$ mol dm$^{-3}$

| | | | |
|---|---|---|---|
| | **(d)** | One of the most common ways to make hydrogen chloride is to react sodium chloride with concentrated sulfuric acid, $H_2SO_4$ or concentrated phosphoric(V) acid, $H_3PO_4$. Both reactions occur similarly, releasing white fumes of gas. | |
| | | **(i)** | Construct a balanced equation involving sodium chloride and concentrated phosphoric(V) acid.<br>[1] |
| | | | $NaCl + H_3PO_4 \rightarrow HCl + NaH_2PO_4$ |
| | | **(ii)** | In reaction with sodium bromide, concentrated sulfuric acid produces reddish-brown solution while concentrated phosphoric(V) acid produces white fumes.<br>Suggest a reason for the observations above.<br>[1] |
| | | | Concentrated sulphuric acid is able to oxidise $Br^-$ to reddish-brown $Br_2$ while concentrated phosphoric(V) acid cannot. Thus, concentrated phosphoric(V) acid is a **weaker oxidising agent** . |
| | | | [Total: 12] |

**6** **(a)** The chemical structure and some reactions involving compound **N** are shown below.



**(i)** State the reagents and conditions involved in Steps **I** and **II**.

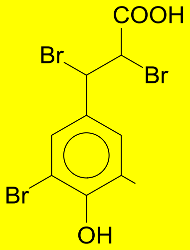
Step **I**:
Step **II**:

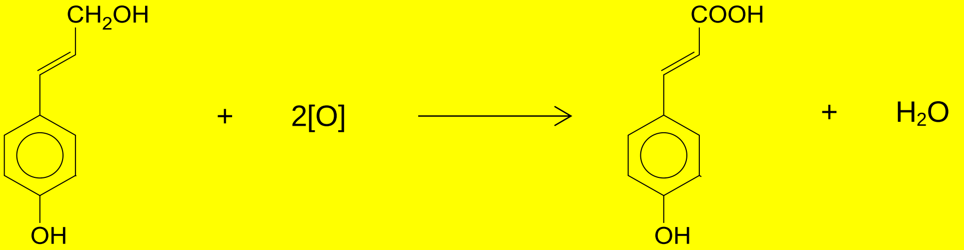
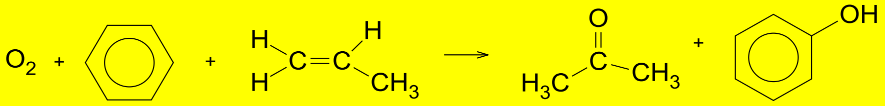
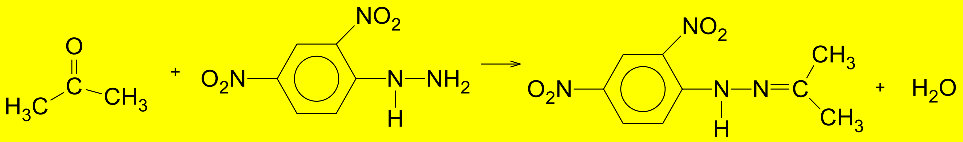
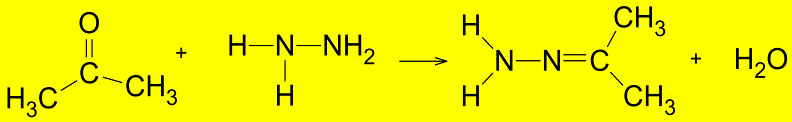
[2]

Step **I:** **LiA*l*H$_4$ in dry ether, rtp**
Step **II:** **CH$_3$COC*l*, rtp**

**(ii)** Draw the structure of organic product **R**.

[1]



| | | | |
|---|---|---|---|
| | | **(iii)** | Propose a chemical test to distinguish between **P** and **N**, in which a positive test is observed for **P only**. Write a balanced chemical equation for the reaction that has occurred.<br>[3] |
| | | | Test: Add **$K_2Cr_2O_7$ in dilute $H_2SO_4$, heat**<br>Observation: **Orange $K_2Cr_2O_7$ turns green**<br><br>**$KMnO_4$ is not suitable as ferulic acid may be [O] as well due to presence of C=C and benzylic H*<br>**distillation with $K_2Cr_2O_7$ to form aldehyde is not preferred when carrying out **simple** chemical tests*<br><br>Equation:<br> |
| | **(b)** | In the cumene process one mole of benzene reacts with one mole of propene in the presence of oxygen from air to form phenol and organic substance **T**. Substance **T** does not give any positive observation with diammine silver complex. | |
| | | **(i)** | From the information provided, identify substance **T**.<br>[1] |
| | | | <br>**T** |
| | | **(ii)** | Hence, with an aid of a chemical equation, suggest how the functional group in substance **T** can be positively identified.<br>[2] |
| | | | **orange ppt** will be observed<br><br>Or<br> |
| | | | [Total: 9] |

**END**

**General Certificate of Education Advanced Level Higher 2**

|  |  |
|---|---|
| **CANDIDATE NAME** |  |
| **CLASS** |  |

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# CHEMISTRY 9647/03

**JC2 Preliminary Examination** **20 September 2016**

**Paper 3 Free Response** **2 hours**

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Papers

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**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the 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 working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

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

This document consists of **14** printed pages

Turn over]

**1** Sodium bisulfite ($NaHSO_3$) is a useful compound to treat chemical waste after organic synthesis. It reacts with methanal, converting it into a non-toxic compound which can be disposed safely. The overall equation is shown below.

$$HSO_3^- + HCOH \longrightarrow CH_2(OH)SO_3^-$$

**(a)** Draw the dot-and-cross diagram of the bisulfite ion, $HSO_3^-$. [1]

**(b)** The initial rate of this reaction can be studied by the "clock" method, using phenolphthalein as a suitable indicator. The sudden appearance of the pink colour indicates the time to stop the stopwatch.

A series of experiments was carried out using different concentrations of $HSO_3^-$ and HCOH. The following results were obtained.

| **experiment number** | **[$HSO_3^-$ ] / mol dm$^{-3}$** | **[HCOH] / mol dm$^{-3}$** | **time for the appearance of the pink colour/ s** |
|---|---|---|---|
| **1** | 0.040 | 0.040 | 60 |
| **2** | 0.040 | 0.050 | 48 |
| **3** | 0.050 | 0.060 | 40 |
| **4** | 0.040 | 0.070 | 34 |

**(i)** What is the simple relationship between the time taken for the pink colour to appear and the initial rate of reaction? [1]

**(ii)** Calculate the initial rate for each of these four experiments and use the results to deduce the order of reaction with respect to the two reactants. Explain your reasoning. [2]

**(iii)** Using your answer in **(b)(ii)**, write the rate equation for the reaction, stating the units of the rate constant. [2]

**(iv)** Sketch the graph of concentration against time for each reactant. [2]

**(c)** Kinetic studies suggests that the mechanism involves the following two steps:

Step 1: Bisulfite reacts with water via an acid-base reaction, forming sulfite, $SO_3^{2-}$.

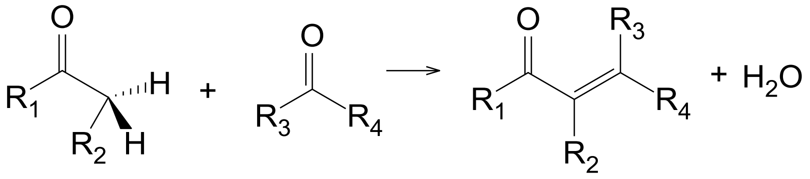
Step 2: The resulting sulfite reacts with methanal to produce the non-toxic compound,$CH_2(OH)SO_3^-$ and hydroxide ion.

**(i)** Write a balanced equation each for step 1 and step 2. [2]

**(ii)** Suggest why phenolphthalein is a suitable indicator to determine the completion of the reaction. [1]

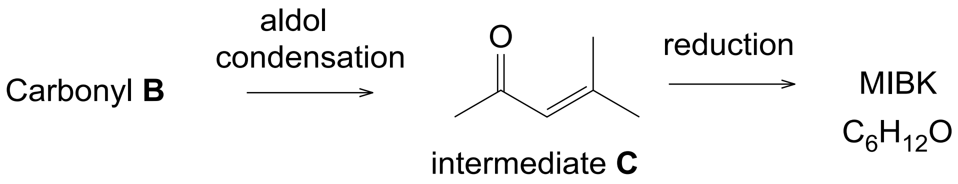
Turn over]

**(d)** Aldol condensations are important in organic synthesis as a good way to form carbon-carbon bonds.



(where $R_1$, $R_2$, $R_3$ and $R_4$ can be alkyl group or hydrogen atom)

The following reaction sequence illustrate how MIBK, a solvent used on paints, could be synthesised from carbonyl compound **B**. It is known that MIBK does not undergo attack by electrophile.



**(i)** Using the information provided, draw the displayed formula carbonyl **B**. [1]

**(ii)** For each of the following reactions, describe the mechanism, showing curly arrows, dipoles and any relevant lone pairs. You are to state the condition required for reaction 2.

Reaction 1: Intermediate **C** with dry hydrogen bromide gas.
Reaction 2: Intermediate **C** with aqueous hydrogen cyanide.

Hence, suggest with explanation if the products formed from the two reactions could rotate plane polarised light.

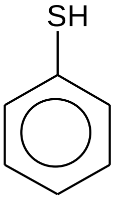
[6]

**(iii)** Deduce the structure of MIBK.

[2]

[Total: 20]

**2(a)** Thiophenol is an organosulfur compound with the formula $C_6H_5SH$. The chemical structure of thiophenol is analogous to phenol, except that the oxygen atom in the hydroxyl group bonded to the aromatic ring is replaced by a sulfur atom.



Thiophenol

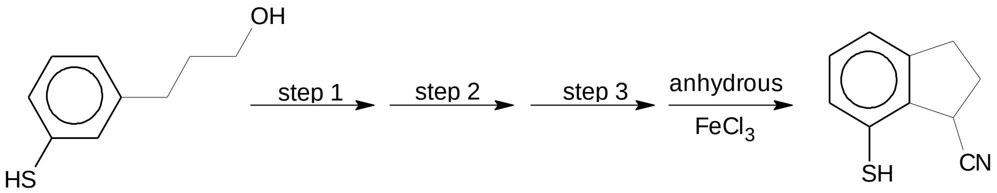
**(i)** Suggest if the C-S-H bond angle in thiophenol will be larger than the C-O-H bond angle in phenol

[1]

**(ii)** Explain why thiophenol has a lower $pK_a$ value than phenol.

[2]

**(iii)** The reaction scheme below shows how one thiophenol derivative could be synthesised into another organic compound in **four** steps using inorganic reagents. Draw the structure of the intermediate compounds and state the reagents and conditions for each step 1, 2 and 3.



[4]

**(b)** The use of *Data Booklet* is relevant in this question.

In an experiment to determine the enthalpy change of combustion of thiophenol, 2.00 $cm^3$ of thiophenol with density of 1.08 g $cm^{-3}$ was burnt as fuel to bring a calorimeter containing 170 $cm^3$ of water at 30°C to boil.

**(i)** Define standard enthalpy change of combustion.

[1]

**(ii)** Calculate the enthalpy change of combustion of thiophenol, $\Delta H_c$, given that the process is 80% efficient.

[2]

**(c)** The use of *Data Booklet* is relevant in this question.

In nuclear magnetic resonance (NMR) spectroscopy, the proton chemical shift can be used to diagnose the structure of an organic molecule.

Compound **D** has a molecular formula of $C_9H_{16}O_3$. When heated with hydrochloric acid, compound **E** and **F** are produced.

Compound **E** has a proton chemical shift of 2.1ppm. When 1 mole of **E** is warmed with alkaline aqueous iodine, 2 mole of yellow precipitates are formed, along with compound **G**. White fumes were also observed when **E** is reacted with thionyl chloride.

Compound **F**, $C_5H_xO_2$, rotates plane polarised light and has a proton chemical shift of 13.0ppm. Compound **F**, however, do not exhibit cis-trans isomerism and will not decolourise oxidising agents.

**(i)** Suggest the structures of **D** to **F**, and explain the observations described above. [9]

**(ii)** Construct a balanced chemical equation of the reaction between **E** and alkaline aqueous iodine. [1]

[Total: 20]

**3** **(a)** Haemoglobin is the iron–containing oxygen transport protein found in the red blood cells.

In general, haemoglobin can be saturated with oxygen molecules (oxyhaemoglobin) or desaturated with oxygen molecules (deoxyhaemoglobin).

The absorption spectra of oxyhaemoglobin and deoxyhaemoglobin differ. The oxyhaemoglobin has significantly lower absorption of the 660 nm wavelength as compared with deoxyhaemoglobin which is valued at 940 nm wavelength. This difference is used for the measurement of the amount of oxygen in a patient's blood by an instrument called a pulse oximeter.

**(i)** With reference to the haemoglobin molecule, describe and explain what is meant by the term *quaternary structure* of proteins. In your answer, you should state the type of bonding or interaction involved.

[2]

**(ii)** Haemoglobin is typically an all alpha-protein consisting of four subunits. However, some of the connecting loops between the helices can sometimes exist in a very short beta-stranded conformation.

With the aid of a diagram, describe how a polypeptide chain is held in the shape of a beta-stranded conformation.

[2]

**(iii)** Using the information from the question, explain if oxyhaemoglobin or deoxyhaemglobin contain the larger energy gap, E, between its d-orbital.

[2]

**(b)** Carbon monoxide mainly causes adverse effects in humans by combining with haemoglobin in the blood.

Human *cytochrome c oxidase* is composed of several subunits. Some of the amino acids found in *cytochrome c oxidase* are listed below.

| **Amino acid** | **Formula of side chain (R in RCH($NH_2$)$CO_2$H** |
|---|---|
| valine (val) | -CH($CH_3$)$_2$ |
| aspartic acid (asp) | -$CH_2$COOH |
| lysine (lys) | -$CH_2CH_2CH_2CH_2NH_2$ |
| cysteine (cys) | -$CH_2$SH |
| asparagine (asp) | -$CH_2CONH_2$ |
| threonine (thr) | -CH(OH)$CH_3$ |

**(i)** Explain how carbon monoxide affects the normal functioning of haemoglobin. [2]

**(ii)** Using the dipeptide segment of **lys-thr** in *cytochrome c oxidase*, give the structural formulae of the products obtained when hot hydrochloric acid is added. [2]

**(iii)** *Cytochrome c oxidase* can undergo denaturation due to various factors, resulting in loss of its biological function.

Identify the site whereby the R group interactions are broken under the following conditions and explain how these interactions are affected in each cases:

**1)** The addition of a reducing agent.
**2)** The addition of a base.

[2]

**(c)** In cyanide poisoning, the enzyme *cytochrome c oxidase* which aid in respiration in human are thought to be adversely affected.

To treat this cases of poisoning, the United State standard cyanide antidote kit was developed and it comprises of a three step process.

Step 1: Inhale small dosage of amyl nitrite.
Step 2: Intravenous of sodium nitrite, $NaNO_2$.
Step 3: Intravenous of sodium thiosulfate.

**(i)** Sodium nitrite is part of the cyanide antidote kit. It decomposes to form an acidic brown gas, a solid residue and a free radical.

When the residual solid was placed in water, it forms a solution of pH 13.

Using the information provided, construct a balanced chemical equation for the decomposition of sodium nitrite. [1]

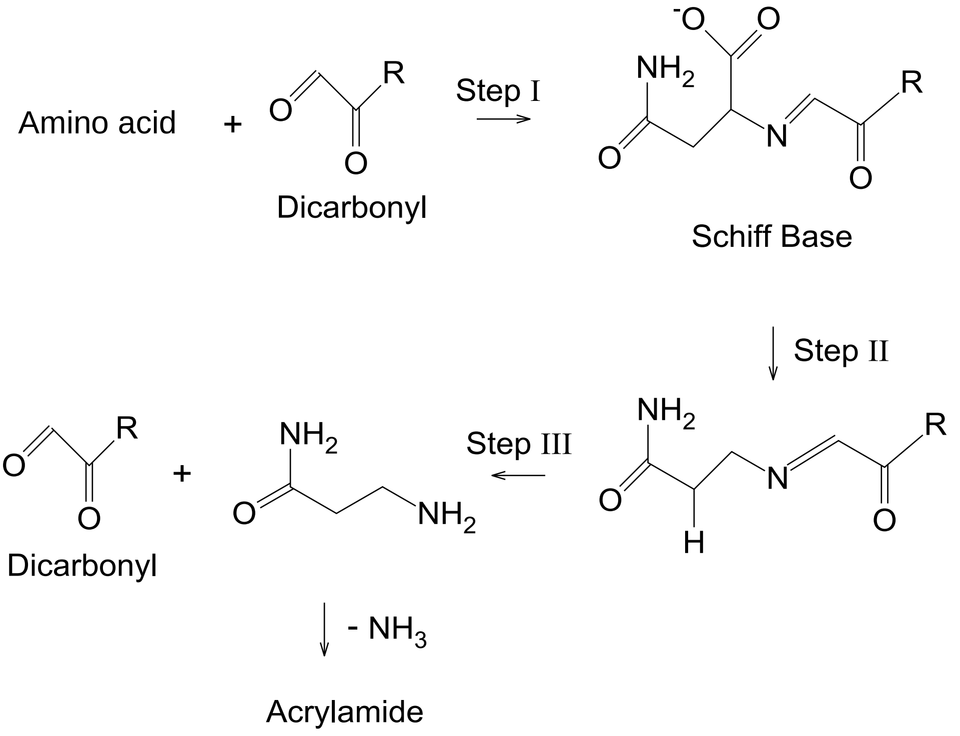
**(ii)** Thiosulfate reacts differently with chlorine and iodine. Using equations only

Turn over]

suggest an explanation for this difference. [2]

**(d)** The Maillard reaction is a chemical reaction between amino acid and reducing sugar that gives browned food its desirable flavour. Pan-fried dumplings, french fries and toasted marshmallows undergo this reaction when heated at high temperature.

Figure 1: The Maillard reaction



Acrylamide, $C_3H_5NO$, a possible human carcinogen, can be generated as a by-product of Maillard reaction between reducing sugars and amino acid.

**(i)** Using the table from **(b)**, state the amino acid that is required in the synthesis of acrylamide.

[1]

**(ii)** Suggest the gas that was produced in Step II and propose how this gas can be identified.

[1]

**(iii)** Suggest the structural formula of acrylamide.

[1]

**(iv)** Propose an isomer of acrylamide which does not evolve ammonia gas on heating with aqueous sodium hydroxide. Hence, state the type of isomerism involved.

[2]

[Total: 20]

Turn over]

**4** **(a)** Limestone is mainly composed of calcite, $CaCO_3$, and is usually white or transparent, shimmering crystals depending on how it is formed. I different colour when exposed to different impurities such as siderite, F

**(i)** Using information from the *Data Booklet*, suggest if calcite or siderite has a lower decomposition temperature.

[2]

**(ii)** Dolomitization is a process by which dolomite, $CaMg(CO_3)_2$, is formed when magnesium ions replaces calcium ions in calcite.

When 1.000 g of an impure sample of dolomite was completely dissolved in excess hydrochloric acid, the carbon dioxide evolved was bubbled into aqueous calcium hydroxide where 0.80 g of white insoluble solid was isolated. Calculate the percentage purity of the dolomite.

[2]

**(b)** Stalagmites and stalactites in limestone caves are created when the calcite is dissolved in rain water and subsequently precipitated when the water drips off the ceiling of the cave to the cave floor.

Dissolution of calcite occurs mainly via the following equilibrium:

$$CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \text{ ---- } (1)$$

However, it is also affected by the amount of atmospheric carbon dioxide present, and it can be represented via these four additional equilibria:

$$CO_3^{2-}\,(aq) + H^+\,(aq) \rightleftharpoons HCO_3^-\,(aq) \text{ ---- } (2)$$
$$HCO_3^-\,(aq) + H^+\,(aq) \rightleftharpoons H_2CO_3\,(aq) \text{ ---- } (3)$$
$$H_2CO_3\,(aq) \rightleftharpoons H_2O\,(l) + CO_2\,(aq) \text{ ---- } (4)$$
$$CO_2\,(aq) \rightleftharpoons CO_2\,(g) \text{ ---- } (5)$$

**(i)** Calculate the enthalpy change of solution of calcite using the information given below.

| | **$\Delta H^\ominus_f$ / kJ mol$^{-1}$** |
|---|---|
| $CaCO_3$ (s) | −1206.9 |
| $Ca^{2+}$ (aq) | −542.8 |
| $CO_3^{2-}$ (aq) | −677.1 |

[1]

**(ii)** Explain how the enthalpy change of solution of calcite would differ from siderite.

[3]

**(iii)** Given that the enthalpy change of atomisation of calcium is 178.2 kJ mol$^{-1}$, and the lattice energy of calcite is −2804 kJ mol$^{-1}$, calculate the enthalpy change of formation of gaseous carbonate ions using an energy level diagram and other relevant information from the *Data Booklet*.

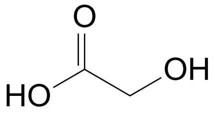
[3]

**(iv)** With reference to the equilibriums given, suggest what would happen to the calcite formations in limestone caves when the acidity of rain and river water increases due to pollutants.

[3]

**(c)** Limescale, which is primarily calcium carbonate is the off-white deposit that is commonly found in kettles. In addition to being unsightly and hard to clean, limescale impairs the operation of medical equipment.

Ethanoic acid and glycolic acid can serve as good descaling agent and are used to remove the limescale.



Glycolic acid

Both organic acids can be treated using the following steps to recover a carbonyl containing compound from limescale.

Step 1: Heat the limescale with the organic acid to ensure all the limescale has reacted.

Step 2: Evaporate the sample and collect the salt.

Step 3: Heat the salt in a test-tube and allow to cool to room temperature. Calcium carbonate will be formed together with a liquid carbonyl containing compound.

Step 4: Separate the calcium carbonate residue from the liquid carbonyl containing compound using vacuum filtration.

**(i)** Propose chemical test to differentiate ethanoic acid and glycolic acid in the school laboratory. You are to state clearly the reagents and condition used and the expected observation to be made.

[2]

**(ii)** Write a balanced equation, for the reaction of limescale and ethanoic acid. Include state symbols in your answer.

[1]

Turn over]

**(iii)** With reference to structure and bonding, suggest why it is possible to isolate the salt via evaporation.

**(iv)** With reference to Step 3, suggest the structural formulae of the organic products formed when calcium ethanoate and calcium glycolate is heated in separate test-tubes.

[2]

[Total: 20]

**5** **(a)** The following table shows some common oxidation numbers of selected metals.

| **Metals** | **Oxidation Numbers** | | |
|---|---|---|---|
| **Sc** | ▨ | ▨ | +3 |
| **Ti** | ▨ | ▨ | +3 |
| **V** | ▨ | +2 | +3 |
| **Fe** | ▨ | +2 | +3 |
| **Cu** | +1 | +2 | ▨ |
| **Zn** | ▨ | +2 | ▨ |

**Table 1**

**(i)** From **Table 1**, state all the ions that are colored.

[1]

**(ii)** Using one of the ions stated in **(a)(i)**, explain why it is colored.

[3]

**(iii)** When dilute aqueous ammonia is added to a solution that contains copper(II) ions, a pale blue precipitate is obtained. This precipitate dissolves to form a deep blue solution when excess ammonia is added.

Give an explanation for these observations using relevant equations.

[3]

**(b)** Iron by mass, is the most common element on Earth, forming much of Earth's outer and inner core. It forms compounds mainly in the +2 and +3 oxidation states. Iron and its compounds are widely used as catalyst.

**(i)** Suggest why iron has the ability to exist in variable oxidation states.

[1]

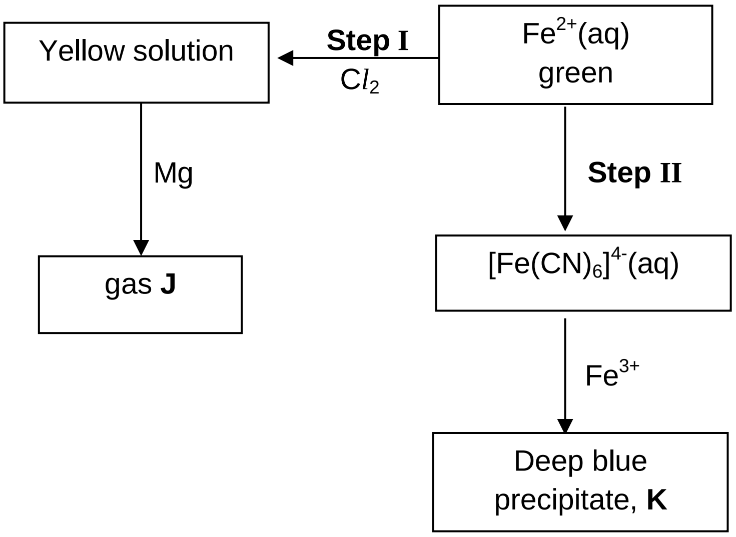
**(ii)** Hydrogen peroxide decompose according to the following equation:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Iron(III) ions can be used to catalyse this decomposition. Using relevant data from the *Data Booklet*, suggest a mechanism for this catalysis, calculating the $E^{\theta}$ values for each step.

[3]

**(iii)** The following diagram shows the reactions of some iron compounds.

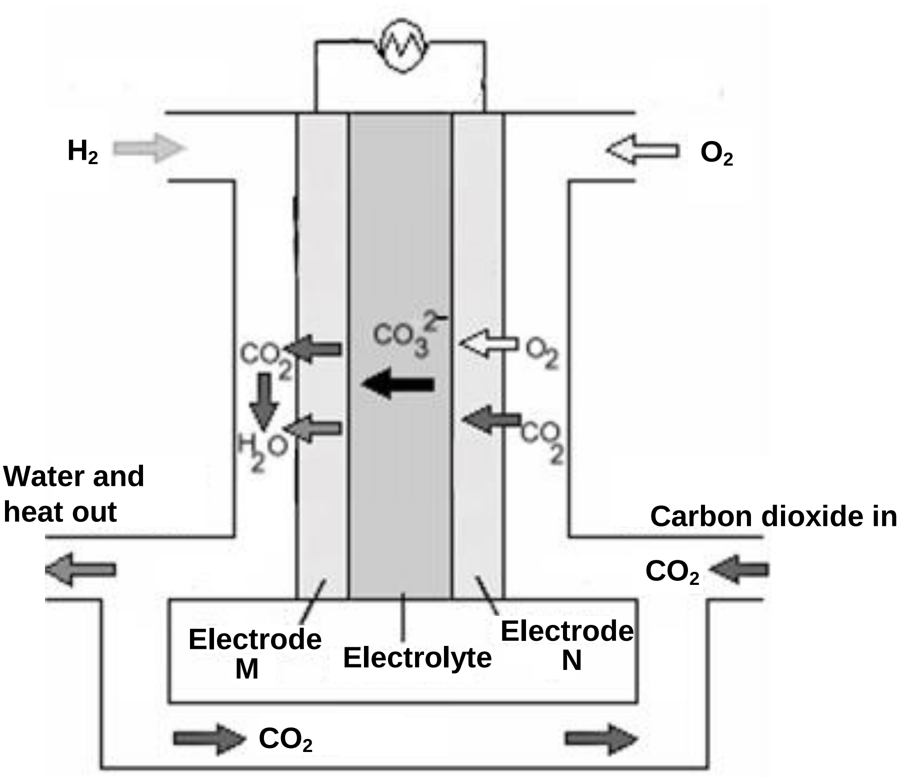


Name the type of reaction in **Step II** and identify gas **J** and precipitate **K**.

[3]

**(c)** Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic matrix.

The following diagram show a MCFC.



At the electrode **N**, carbon dioxide is reacted with oxygen to form carbonate as the only product. The carbonate ions move towards electrode **M** and react with hydrogen to form carbon dioxide and water.

**(i)** Write half-equations for the reactions taking place at the electrodes of the fuel cell and hence, construct the overall equation for the fuel cell reaction. [3]

**(ii)** State the direction of the electron flow with respect to the electrode. [1]

**(iii)** Besides being high in efficiency and high operating cost, suggest one advantage and disadvantage of the molten carbonate fuel cell. [2]

[Total: 20]

**END OF PAPER 3**

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General Certificate of Education Advanced
Level Higher 2

**CANDIDATE NAME**

**CLASS**

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## CHEMISTRY 9647/03

**JC2 Preliminary Examination** **20 Sept 2016**
**Paper 3 Free Response** **2 hours**

Candidates answer on separate paper.

Additional Materials: Data Booklet
Writing Papers

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**READ THESE INSTRUCTIONS FIRST**

Write your name and class on all the 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 working.
Do not use staples, paper clips, highlighters, glue or correction fluid.

Answer any **four** questions.
A Data Booklet is provided.
The use of an approved scientific calculator is expected, where appropriate.
You are reminded of the need for good English and clear presentation in your answers.

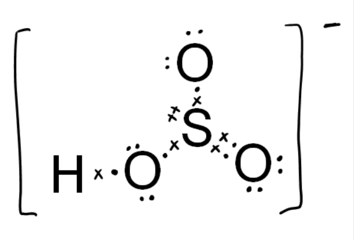
The number of marks is given in the brackets [ ] at the end of each question or part question.
At the end of the examination, fasten all your work securely together with the cover page provided.

# SUGGESTED SOLUTIONS

**1** Sodium bisulfite ($NaHSO_3$) is a useful compound to treat chemical waste after organic synthesis. It reacts with methanal, converting it into a non-toxic compound which can be disposed safely. The overall equation is shown below.

$$HSO_3^- + HCOH \longrightarrow CH_2(OH)SO_3^-$$

**(a)** Draw the dot-and-cross diagram of the bisulfite ion, $HSO_3^-$. [1]



**(b)** The initial rate of this reaction can be studied by the “clock” method, using phenolphthalein as a suitable indicator. The sudden appearance of the pink colour indicates the time to stop the stopwatch.

A series of experiments was carried out using different concentrations of $HSO_3^-$ and HCOH. The following results were obtained.

| experiment number | $[HSO_3^-]$ / mol dm$^{-3}$ | [HCOH] / mol dm$^{-3}$ | time for the appearance of the pink colour/ s |
|---|---|---|---|
| **1** | 0.040 | 0.040 | 60 |
| **2** | 0.040 | 0.050 | 48 |
| **3** | 0.050 | 0.060 | 40 |
| **4** | 0.040 | 0.070 | 34 |

**(i)** What is the simple relationship between the time taken for the pink colour to appear and the initial rate of reaction? [1]

The **shorter the time**, the **faster the initial rate** of reaction.
OR
rate $\propto \frac{1}{t}$

**(ii)** Calculate the initial rate for each of these four experiments and use the results to deduce the order of reaction with respect to the two reactants. Explain your reasoning. [2]

Initial rate for experiments 1: 1/60 = 0.0167 $s^{-1}$
Initial rate for experiments 2: 1/48 = 0.0208 $s^{-1}$
Initial rate for experiments 3: 1/40 = 0.0250 $s^{-1}$
Initial rate for experiments 4: 1/34 = 0.0294 $s^{-1}$
relative rate between experiments 1 and 2: $\frac{0.0208}{0.0167} = 1.25$

Using **experiment 1 and 2**, when the **concentration of $HSO_3^-$ remains constant** and the **concentration of HCOH increases 1.25 times**, the **rate also increases 1.25 times**. Hence the order of reaction with respect to HCOH is **one**.

Let the order of reaction for $HSO_3^-$ be x.
Using the mathematical method for experiment 2 and 3,

$$\frac{rate_2}{rate_3} = \frac{k[HSO_3^-]^x[HCOH]^1}{k[HSO_3^-]^x[HCOH]^1}$$

$$\frac{0.0208}{0.025} = \frac{k[0.04]^x[0.05]^1}{k[0.05]^x[0.06]^1}$$

$$\frac{0.0208}{0.025} = (\frac{4}{5})^x \times \frac{5}{6}$$

$$1 = (\frac{4}{5})^x$$

x = 0

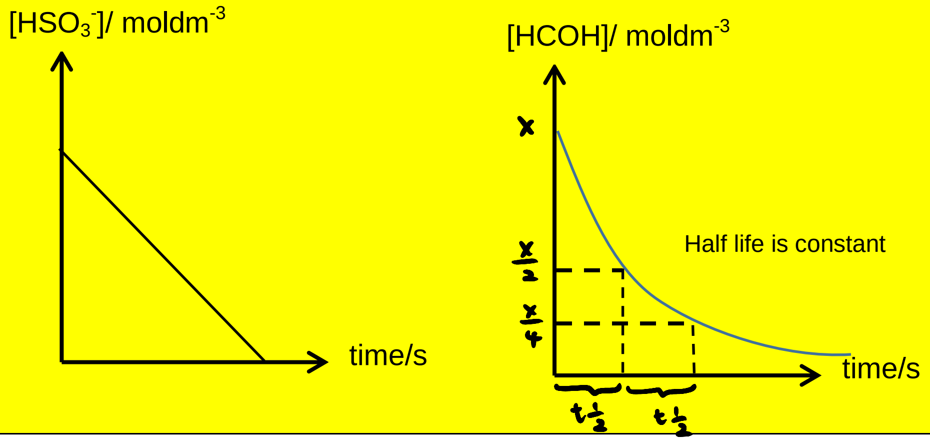
therefore, order of reaction with respect to $HSO_3^-$ is **zero**.

**(iii)** Using your answer in **(ii)**, write the rate equation for the reaction, stating the units of the rate constant. [2]

rate = k[HCOH]

units of rate constant = $\frac{mol\ dm^{-3}s^{-1}}{mol\ dm^{-3}} = s^{-1}$

**(iv)** Sketch the graph of concentration against time for each reactant. [2]



**(c)** Kinetic studies suggests that the mechanism involves the following two steps:

Step 1: Bisulfite reacts with water via an acid-base reaction, forming sulfite, $SO_3^{2-}$.

Step 2: The resulting sulfite reacts with methanal to produce the non-toxic compound, $CH_2(OH)SO_3^-$ and hydroxide ion.

**(i)** Write a balanced equation each for step 1 and step 2. [2]

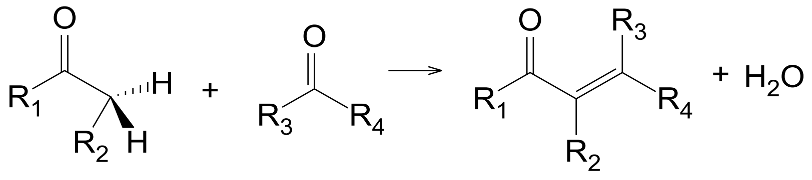
Step 1: $HSO_3^- + H_2O \rightarrow SO_3^{2-} + H_3O^+$

Step 2: $H_2O + SO_3^{2-} + HCOH \rightarrow CH_2(OH)SO_3^- + OH^-$

**(ii)** Suggest why phenolphthalein is a suitable indicator to determine the completion of the reaction. [1]

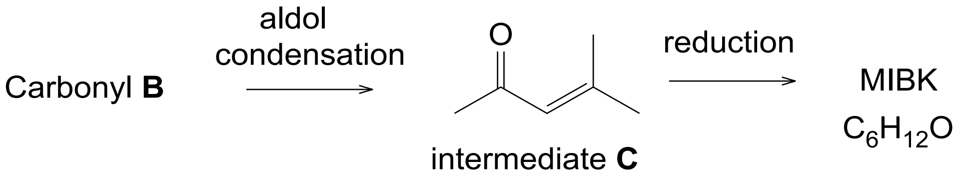
Phenolphthalein is suitable because its **pH transition range** lies **within** the **region of rapid pH change** in the reaction mixture.

**(d)** Aldol condensations are important in organic synthesis as a good way to form carbon-carbon bonds.

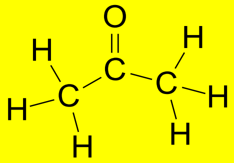


(where $R_1$, $R_2$, $R_3$ and $R_4$ can be alkyl group or hydrogen atom)

The following reaction sequence illustrate how MIBK, a solvent used on paints, could be synthesised from carbonyl compound **B**. It is known that MIBK does not undergo attack by electrophile.



**(i)** Using the information provided, draw the displayed formula carbonyl **B**.



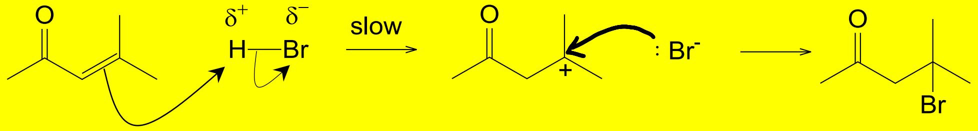
**(ii)** For each of the following reactions, describe the mechanism, showing curly arrows, dipoles and any relevant lone pairs. You are to state the condition required for reaction 2.

Reaction 1: Intermediate **C** with dry hydrogen bromide gas.
Reaction 2: Intermediate **C** with aqueous hydrogen cyanide.

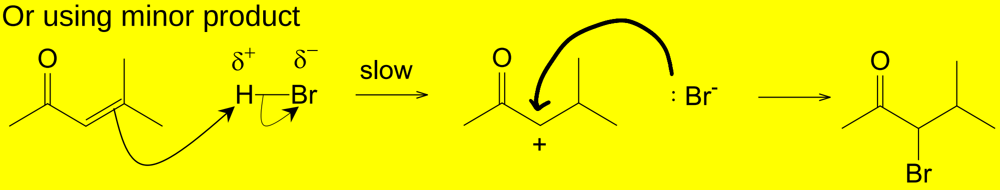
Hence, suggest with explanation if the products formed from the two reactions could rotate plane polarised light.

[6]

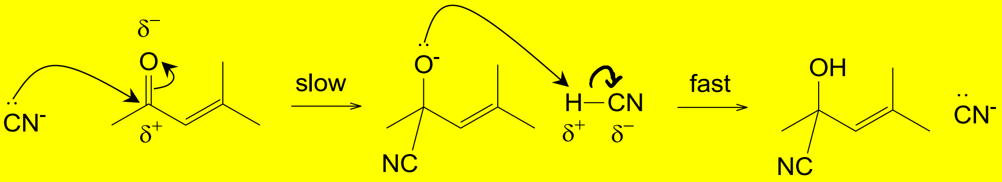
Reaction 1: Electrophilic addition
Either using major product



Or using minor product



Reaction 2: Nucleophilic addition



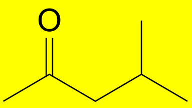
Condition required for reaction 2:
Presence of NaOH(aq) or NaCN, 10°C to 20°C

Reaction 1:
If use major product: No optical activity as there is absence of chiral carbon.
If use minor product: No optical activity as there is presence of racemic mixture
Reaction 2: No optical activity as there is presence of racemic mixture.

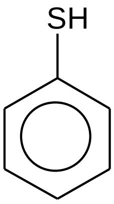
**(iii)** Deduce the structure of MIBK. [2]

To deduce the structure of MIBK:

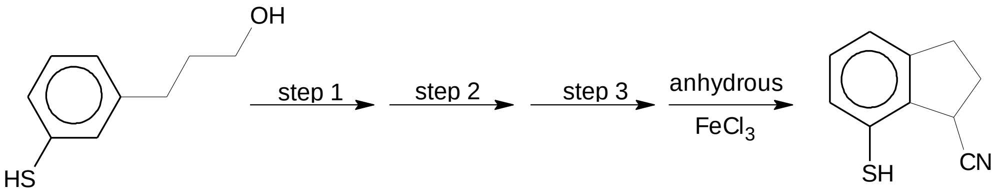
MIBK does **not** undergo **electrophilic addition**
⇨ **alkene** functional group absent

Thus MIBK looks like 

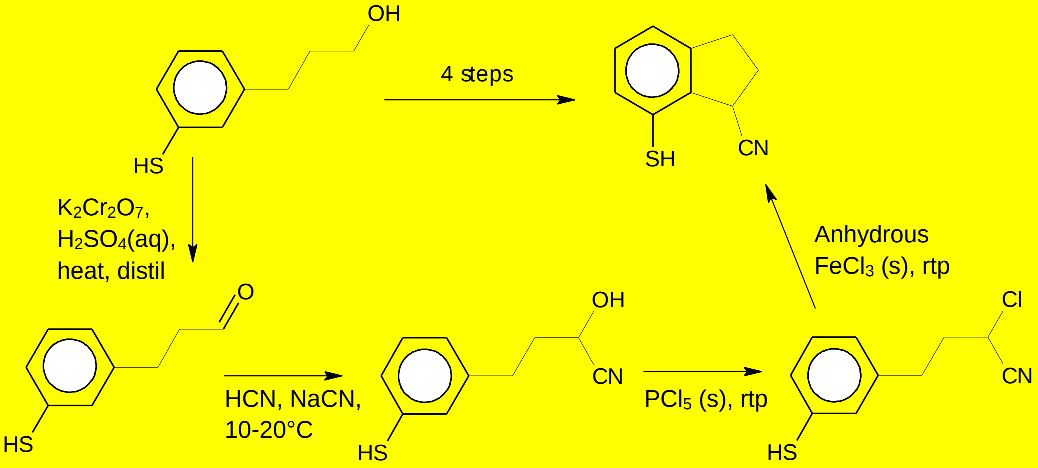
(IUPAC name is 4-methylpentan-2-one)

| | | |
|---|---|---|
| **2(a)** | Thiophenol is an organosulfur compound with the formula $C_6H_5SH$. The chemical structure of thiophenol is analogous to phenol, except that the oxygen atom in the hydroxyl group bonded to the aromatic ring is replaced by a sulfur atom.<br><br>Thiophenol | |
| | **(i)** | Suggest if the C-S-H bond angle in thiophenol will be larger than the C-O-H bond angle in phenol<br>[1] |
| | | **Oxygen is more electronegative than sulfur** thus the electron density around O atom will be greater. The **bond-pair electrons will be nearer to the nucleus resulting in more repulsion**. Thus the bond angle of C-O-H in phenol will be larger. |
| | **(ii)** | Explain why thiophenol has a lower $pK_a$ value than phenol.<br>[2] |
| | | **Thiophenol** has a lower $pK_a$.<br>The sulfur atom is **less electronegative** and the lone pair of electrons on the conjugate base is able to **delocalise** into the benzene ring **more readily** as compared to phenol, thus **stabilising its conjugate base** more than the phenoxide ion. |

**(iii)** The reaction scheme below shows how one thiophenol derivative could be synthesised into another organic compound in **four** steps using inorganic reagents. Draw the structure of the intermediate compounds and state the reagents and conditions for each step 1, 2 and 3.



[4]



**(b)** The use of *Data Booklet* is relevant in this question.

In an experiment to determine the enthalpy change of combustion of thiophenol, 2.00 $cm^3$ of thiophenol with density of 1.08 g $cm^{-3}$ was burnt as fuel to bring a calorimeter containing 170 $cm^3$ of water at 30°C to boil.

**(i)** Define standard enthalpy change of combustion.

[1]

Standard enthalpy change of combustion is the energy **evolved** when **one mole** of substance is **completely burnt in oxygen** under **standard conditions**.

**(ii)** Calculate the enthalpy change of combustion of thiophenol, $\Delta H_c$, given that the process is 80% efficient.

[2]

$Q' = mc\Delta T = 170 \times 4.18 \times (100 - 30)$
$= 49742\text{ J}$

$Q' = \frac{80}{100} Q$

$Q = \frac{100}{80} \times 49742 = 62177.5\text{J}$

$n_{\text{thiophenol}} = \frac{1.08 \times 2.00}{110.1} = 0.01962\text{ mol}$

$\Delta H_c = -\frac{62177.5}{0.01962} = \underline{\mathbf{-3169\text{ kJ mol}^{-1}}}$

**(c)** The use of *Data Booklet* is relevant in this question.

In nuclear magnetic resonance (NMR) spectroscopy, the proton chemical shift can be used to diagnose the structure of an organic molecule.

Compound **D** has a molecular formula of $C_9H_{16}O_3$. When heated with hydrochloric acid, compound **E** and **F** are produced.

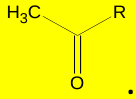
Compound **E** has a proton chemical shift of 2.1ppm. When 1 mole of **E** is warmed with alkaline aqueous iodine, 2 mole of yellow precipitates are formed, along with compound **G**. White fumes were also observed when **E** is reacted with thionyl chloride.

Compound **F**, $C_5H_xO_2$, rotates plane polarised light and has a proton chemical shift of 13.0ppm. Compound **F**, however, do not exhibit cis-trans isomerism and will not decolourise oxidising agents.

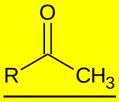
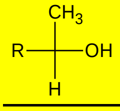
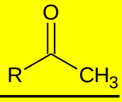
**(i)** Suggest the structures of **D** to **F**, and explain the observations described above. [9]

**D** undergoes **acidic hydrolysis** to form **E** and **F**.
⇒ **D** is an **ester**.
⇒ **E** and **F** are alcohol and carboxylic acid.

**E** has a proton chemical shift of 2.1ppm.

⇒ **E** contains **ketone with this structure**  **.**

**E** undergoes mild **oxidation** with alkaline aqueous iodine to form 2 mol of yellow ppt and **G**.

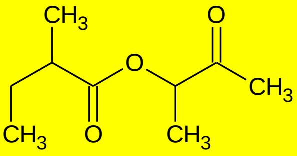
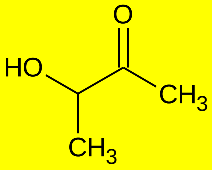
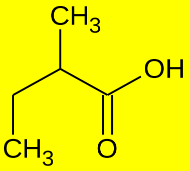
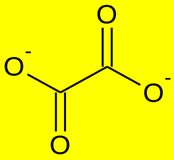
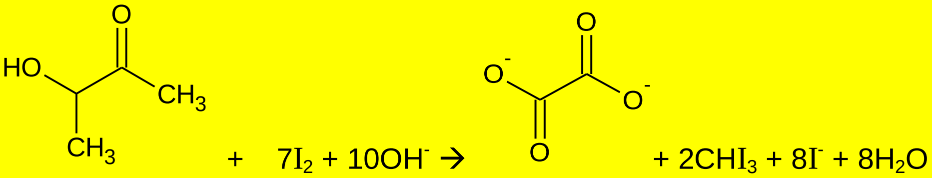
⇒ **E** has  and either  **or** .

⇒ **G** contains carboxylate ion.

**E** undergoes **nucleophilic substitution** with $SOCl_2$.
⇒ **E** has alcohol or carboxylic acid

**F** is **chiral** and has a proton chemical shift of 13.0ppm.
⇒ **C** has **4 different groups attached and is a carboxylic acid**.

**F does not contain alkene as it does not undergo oxidation**

|  |  |  |
|---|---|---|
|  |  | **D**: <br>**E**: <br>**F**: <br>**G**:  |
|  | **(ii)** | Construct a balanced chemical equation of the reaction between **E** and alkaline aqueous iodine. [1] |
|  |  | <br>$+ \quad 7I_2 + 10OH^- \rightarrow$ $+ 2CHI_3 + 8I^- + 8H_2O$ |

**3** **(a)** Haemoglobin is the iron–containing oxygen transport protein found in the red blood cells.

In general, haemoglobin can be saturated with oxygen molecules (oxyhaemoglobin) or desaturated with oxygen molecules (deoxyhaemoglobin).

The absorption spectra of oxyhaemoglobin and deoxyhaemoglobin differ. The oxyhaemoglobin has significantly lower absorption of the 660 nm wavelength as compared with deoxyhaemoglobin which is valued at 940 nm wavelength. This difference is used for the measurement of the amount of oxygen in a patient's blood by an instrument called a pulse oximeter.

**(i)** With reference to the haemoglobin molecule, describe and explain what is meant by the term *quaternary structure* of proteins. In your answer, you should state the type of bonding or interaction involved. [2]

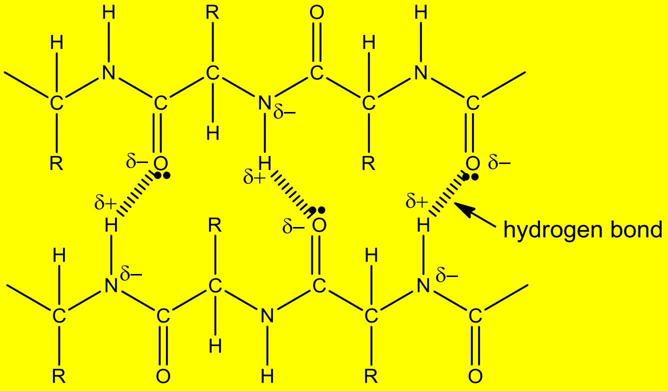
Quaternary structure consists of **more than one polypeptide chain** coming together to form the **complete protein** held together by **ionic bonds**, **hydrogen bonds**, **Van der Waals' interaction** and **disulfide linkages** between the **R groups** of the polypeptides.

The haemoglobin molecule consists of **4** polypeptide chains: **2 α-sub-units** and **2 β-sub-units**, with each sub-unit being **non-covalently** bonded to a **heme** (iron) group.

Each heme group consists of a central $Fe^{2+}$ ion that can bond to one $O_2$ oxygen. **All four components** (4 sub-units and 4 haem groups) **must be present** to form haemoglobin.

**(ii)** Haemoglobin is typically an all alpha-protein consisting of four subunits. However, some of the connecting loops between the helices can sometimes exist in a very short beta-stranded conformation.

With the aid of a diagram, describe how a polypeptide chain is held in the shape of a beta-stranded conformation. [2]



- All peptide linkages are involved in intra-chain hydrogen bonding.
- It is stabilized by hydrogen bonds between the C=O group of a peptide in one strand and the N-H group of another peptide in the adjacent strand.

R groups (side chains) project above and below the sheet and are 90° to the plane of the pleated sheet.

| | | | |
|---|---|---|---|
| | | | |
| | | **(iii)** | Using the information from the question, explain if oxyhaemoglobin or deoxyhaemglobin contain the larger energy gap, E, between its d-orbital.<br>[2] |
| | | | **Wavelength** of light absorbed:<br>oxyhaemoglobin (660nm) < deoxyhaemoglobin (940nm)<br><br>Since E is inversely proportional to wavelength of light<br><br>**Energy** required for d-d transition:<br>oxyhaemoglobin > deoxyhaemoglobin<br><br>Thus, oxyhaemoglobin has a larger energy gap E. |

**(b)** Carbon monoxide mainly causes adverse effects in humans by combining with haemoglobin in the blood.

Human *cytochrome c oxidase* is composed of several subunits. Some of the amino acids found in *cytochrome c oxidase* are listed below.

| **Amino acid** | **Formula of side chain (R in $RCH(NH_2)CO_2H$** |
|---|---|
| valine (val) | $-CH(CH_3)_2$ |
| aspartic acid (asp) | $-CH_2COOH$ |
| lysine (lys) | $-CH_2CH_2CH_2CH_2NH_2$ |
| cysteine (cys) | $-CH_2SH$ |
| asparagine (asp) | $-CH_2CONH_2$ |
| threonine (thr) | $-CH(OH)CH_3$ |

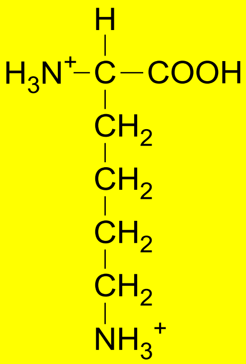
**(i)** Explain how carbon monoxide affects the normal functioning of haemoglobin. [2]

**CO is a stronger ligand** than $O_2$

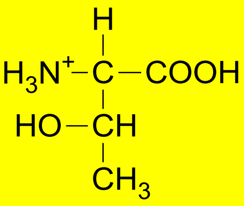
CO **bonds irreversibly** with haemoglobin forming a stable carboxyhaemoglobin complex, thus **preventing the haemoglobin from carrying oxygen**.

This results in carbon monoxide poisoning due to oxygen starvation.

**(ii)** Using the dipeptide segment of **lys-thr** in *cytochrome c oxidase*, give the structural formulae of the products obtained when hot hydrochloric acid is added. [2]

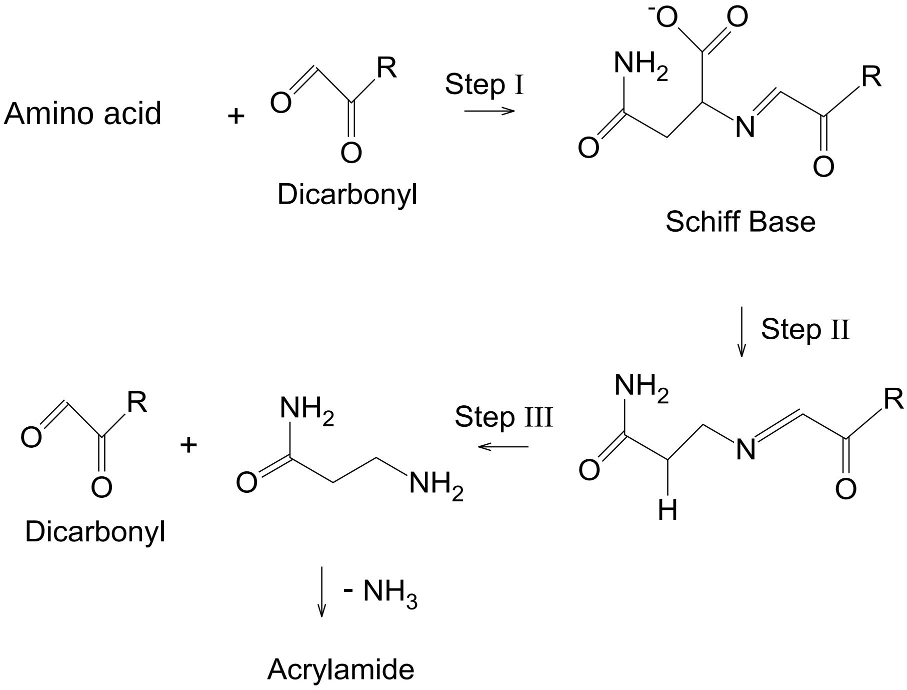
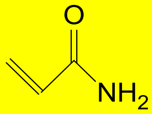


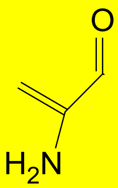
$H_3N^+-CH(COOH)-CH_2-CH_2-CH_2-CH_2-NH_3^+$



$H_3N^+-CH(COOH)-CH(OH)-CH_3$

| | | | |
|---|---|---|---|
| | | **(iii)** | *Cytochrome c oxidase* can undergo denaturation due to various factors, resulting in loss of its biological function.<br>Identify the site whereby the R group interactions are broken under the following conditions and explain how these interactions are affected in each cases: |
| | | | 1) The addition of a reducing agent. |
| | | | Reducing agents **break disulfide linkages** and thus R group interaction at **cysteine** will be affected |
| | | | 2) The addition of a base.<br>[2] |
| | | | The base **will disrupt** the **ionic bonds at asp or lys** holding the **tertiary** and **quaternary** structures. |
| | **(c)** | In cyanide poisoning, the enzyme *cytochrome c oxidase* which aid in respiration in human are thought to be adversely affected.<br>To treat this cases of poisoning, the United State standard cyanide antidote kit was developed and it comprises of a three step process.<br>Step 1: Inhale small dosage of amyl nitrite.<br>Step 2: Intravenous of sodium nitrite, $NaNO_2$.<br>Step 3: Intravenous of sodium thiosulfate. | |
| | | **(i)** | Sodium nitrite is part of the cyanide antidote kit. It decomposes to form an acidic brown gas, a solid residue and a free radical.<br>When the residual solid was placed in water, it forms a solution of pH 13.<br>Using the information provided, construct a balanced chemical equation for the decomposition of sodium nitrite.<br>[1] |
| | | | **$2NaNO_2 \rightarrow NO_2 + Na_2O + NO$** |
| | | **(ii)** | Thiosulfate reacts differently with chlorine and iodine. Using equations only suggest an explanation for this difference.<br>[2] |
| | | | $S_2O_3^{2-}(aq) + 4Cl_2(aq) + 5H_2O(l) \rightarrow 2SO_4^{2-}(aq) + 10H^+(aq) + 8Cl^-(aq)$<br>$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$<br>**$Cl_2$ is a stronger oxidising agent compared to iodine**. Hence, it oxidises S in $S_2O_3^{2-}$ from +2 to +6 while iodine oxidises S in $S_2O_3^{2-}$ from +2 to +2.5. |
| | | | |

| | | | |
|---|---|---|---|
| | **(d)** | The Maillard reaction is a chemical reaction between amino acid and reducing sugar that gives browned food its desirable flavour. Pan-fried dumplings, french fries and toasted marshmallows undergo this reaction when heated at high temperature.<br> <br>Acrylamide, $C_3H_5NO$, a possible human carcinogen, can be generated as a by-product of Maillard reaction between reducing sugars and amino acid. | |
| | | **(i)** | Using the table from **(b)**, state the amino acid that is required in the synthesis of acrylamide. [1] |
| | | | Asparagine |
| | | **(ii)** | Suggest the gas that was produced in Step II and propose how this gas can be identified. [1] |
| | | | $CO_2$<br>Pass the gas into $Ca(OH)_2$, white ppt of $CaCO_3$ will be observed. |
| | | **(iii)** | Suggest the structural formula of acrylamide. [1] |
| | | |  |
| | | **(iv)** | Propose an isomer of acrylamide which does not evolve ammonia gas on heating with aqueous sodium hydroxide. Hence, state the type of isomerism involved. [2] |

| | | | |
|---|---|---|---|
| | | | <br>Functional group isomerism |
| | | | **[Total: 20m]** |

| | | | |
|---|---|---|---|
| **4** | **(a)** | Limestone is mainly composed of calcite, $CaCO_3$, and is usually white or transparent, shimmering crystals depending on how it is formed. It takes on a different colour when exposed to different impurities such as siderite, $FeCO_3$. | |
| | | **(i)** | Using information from the *Data Booklet*, suggest if calcite or siderite has a lower decomposition temperature.<br>[2] |
| | | | **Cationic radius: Fe$^{2+}$ (0.076nm) < Ca$^{2+}$ (0.099nm)**<br>**Charge density: Fe$^{2+}$ > Ca$^{2+}$**<br>**Polarising effect** on the anion: **Fe$^{2+}$ > Ca$^{2+}$**<br>Or<br>**Anion electron cloud distortion: Fe$^{2+}$ > Ca$^{2+}$**<br><br>**Less energy** is required to overcome the **C–O** for **siderite hence lower temperature** is required to decompose the compound. |
| | | **(ii)** | Dolomitization is a process by which dolomite, $CaMg(CO_3)_2$, is formed when magnesium ions replaces calcium ions in calcite.<br><br>When 1.000 g of an impure sample of dolomite was completely dissolved in excess hydrochloric acid, the carbon dioxide evolved was bubbled into aqueous calcium hydroxide where 0.80 g of white insoluble solid was isolated. Calculate the percentage purity of the dolomite.<br>[2] |
| | | | $CaMg(CO_3)_2 + 4HCl \rightarrow CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O$<br>$CO_2 + Ca(OH)_2 \rightarrow CaCO_3 + H_2O$<br><br>Amt of ppt = 0.80 / 100.1 = 0.007992 mol<br>Amt of $CO_2$ produced = 0.007992 mol<br>Amt of dolomite = 0.007992 ÷ 2 = 0.003996 mol<br>Mass of dolomite = 0.003996 x 184.4 = 0.7369 g<br>Percentage purity = (0.7369/1) x 100 = 73.7% |
| | **(b)** | Stalagmites and stalactites in limestone caves are created when the calcite is dissolved in rain water and subsequently precipitated when the water drips off the ceiling of the cave to the cave floor.<br><br>Dissolution of calcite occurs mainly via the following equilibrium: | |

$$CaCO_3\,(s) \rightleftharpoons Ca^{2+}\,(aq) + CO_3^{2-}\,(aq) \quad ---- \quad (1)$$

However, it is also affected by the amount of atmospheric carbon dioxide present, and it can be represented via these four additional equilibria:

$$CO_3^{2-}\,(aq) + H^+\,(aq) \rightleftharpoons HCO_3^-\,(aq) \quad ---- \quad (2)$$
$$HCO_3^-\,(aq) + H^+\,(aq) \rightleftharpoons H_2CO_3\,(aq) \quad ---- \quad (3)$$
$$H_2CO_3\,(aq) \rightleftharpoons H_2O\,(l) + CO_2\,(aq) \quad ---- \quad (4)$$
$$CO_2\,(aq) \rightleftharpoons CO_2\,(g) \quad ---- \quad (5)$$

**(i)** Calculate the enthalpy change of solution of calcite using the information given below.

| | **$\Delta H^\ominus_f$ / kJ mol$^{-1}$** |
|---|---|
| $CaCO_3$ (s) | −1206.9 |
| $Ca^{2+}$ (aq) | −542.8 |
| $CO_3^{2-}$ (aq) | −677.1 |

[1]

$\Delta H_{sol} = -542.8 - 677.1 - (-1206.9)$

$= \mathbf{-13.0\ kJ\ mol^{-1}}$

**(ii)** Explain how the enthalpy change of solution of calcite would differ from siderite.

[3]

**Charge of $Fe^{2+}$ and $Ca^{2+}$ is the same**

**Radii: $Ca^{2+} > Fe^{2+}$**

**$|\Delta H_{latt}|\ )|$: $CaCO_3 < FeCO_3$**

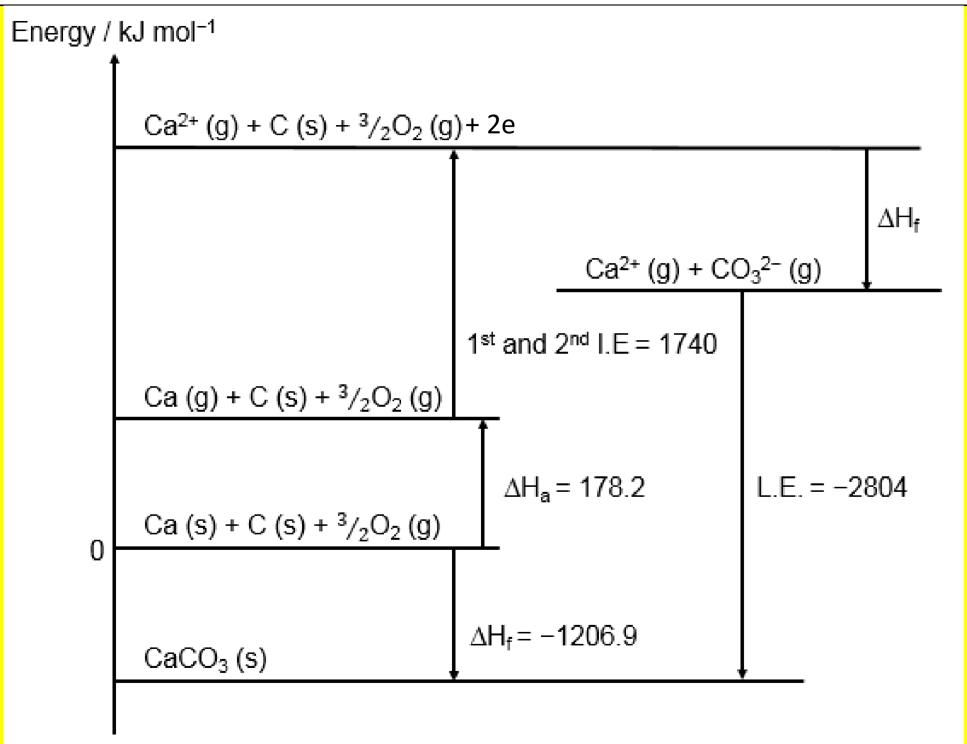
**and $|\Delta H_{hyd}(cation)|$: $Ca^{2+} < Fe^{2+}$**

Due to the **large anionic radius**, the decrease in $|\Delta H_{latt}|$ is **less significant** than the decrease in $|\Delta H_{hyd}(cation)|$.

$\Delta H_{soln}$ of siderite would be **more exothermic**.

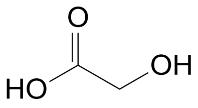
**(iii)** Given that the enthalpy change of atomisation of calcium is 178.2 kJ mol$^{-1}$, and the lattice energy of calcite is −2804 kJ mol$^{-1}$, calculate the enthalpy change of formation of gaseous carbonate ions using an energy level diagram and other relevant information from the *Data Booklet*.

[3]

| | | | |
|---|---|---|---|
| | | |  <br>$\Delta H_f = -1740 - 178.2 + (-1206.9) - (-2804)$<br>$= $ **$-321.1$ kJ mol$^{-1}$** |
| | | **(iv)** | With reference to the equilibriums given, suggest what would happen to the calcite formations in limestone caves when the acidity of rain and river water increases due to pollutants.<br>[3] |
| | | | The calcite formations will be **dissolved/destroyed**.<br>By **LCP**, an **increase in [$H^+$]** would cause the **position of equilibriums of equilibriums (2) to shift right** to **reduce [$H^+$]**, favouring the production of $HCO_3^-$.<br>This then **causes [$CO_3^{2-}$] in equilibrium 2 to decrease** and thus by **LCP**, the **position of equilibrium (1) would then shift right** to **increase [$CO_3^{2-}$]**, **increasing the solubility of $CaCO_3$**. |

**(c)** Limescale, which is primarily calcium carbonate is the off-white deposit that is commonly found in kettles. In addition to being unsightly and hard to clean, limescale impairs the operation of medical equipment.

Ethanoic acid and glycolic acid can serve as good descaling agent and are used to remove the limescale.



Glycolic acid

Both organic acids can be treated using the following steps to recover a carbonyl containing compound from limescale.

Step 1: Heat the limescale with the organic acid to ensure all the limescale has reacted.

Step 2: Evaporate the sample and collect the salt.

Step 3: Heat the salt in a test-tube and allow to cool to room temperature. Calcium carbonate will be formed together with a liquid carbonyl containing compound.

Step 4: Separate the calcium carbonate residue from the liquid carbonyl containing compound using vacuum filtration.

**(i)** Propose chemical test to differentiate ethanoic acid and glycolic acid in the school laboratory. You are to state clearly the reagents and condition used and the expected observation to be made. [2]

Test: Add $KMnO_4$ in dilute $H_2SO_4$, heat

Observation: Purple $KMnO_4$ decolourised in glycolic acid but not ethanoic acid

(Note: Glycolic acid will form $CO_2$ and $H_2O$ upon reaction with acidified $KMnO_4$, heat.)

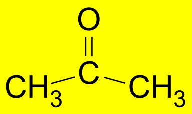
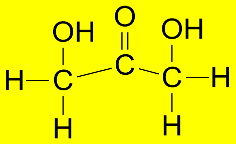
**(ii)** Write a balanced equation, for the reaction of limescale and ethanoic acid. Include state symbols in your answer. [1]

$CaCO_3$ (s) + $2CH_3COOH$ (aq) $\rightarrow$ $2(CH_3COO^-)_2Ca^{2+}$(aq) + $CO_2$ (g) + $H_2O(l)$

**(iii)** With reference to structure and bonding, suggest why it is possible to isolate the salt via evaporation. [1]

Evaporation technique is appropriate as the salt has a **much higher boiling point** than the water.

*The salt has a giant ionic structure with stronger electrostatic forces of attraction between the oppositely charged ions while water is a simple molecular structure with weaker intermolecular hydrogen bonding. Thus by heating the sample, only sufficient energy is supplied to cause the water*

| | | | |
|---|---|---|---|
| | | | *molecule to evaporate leaving behind the salt.* |
| | | **(iv)** | With reference to Step 3, suggest the structural formulae of the organic products formed when calcium ethanoate and calcium glycolate is heated in separate test-tubes.<br>[2] |
| | | | From calcium ethanoate:  $CH_3COCH_3$<br>From calcium glycolate:  |
| | | | [Total: 20] |

**5** **(a)** The following table shows some common oxidation numbers of selected metals.

| **Metals** | **Oxidation Numbers** | | |
|---|---|---|---|
| **Sc** | ▨ | ▨ | +3 |
| **Ti** | ▨ | ▨ | +3 |
| **V** | ▨ | +2 | +3 |
| **Fe** | ▨ | +2 | +3 |
| **Cu** | +1 | +2 | ▨ |
| **Zn** | ▨ | +2 | ▨ |

**Table 1**

**(i)** From **Table 1**, state all the ions that are colored. **[1]**

$Ti^{3+}$, $V^{2+}$, $V^{3+}$, $Fe^{2+}$, $Fe^{3+}$, $Cu^{2+}$

**(ii)** Using one of the ions stated in **(a)(i)**, explain why it is colored. **[3]**

Using $Cu^{2+}$ as example:

- The **d orbitals** of $Cu^{2+}$ are **split into two levels by ligands**.
- The **d electron** undergoes **d-d transition** and is **promoted to a higher energy d orbital**
- In the process, the d electron **absorbs certain wavelength of light energy** from the visible region of the electromagnetic spectrum and **transmits the remaining wavelength** which appears as the colour observed

**(iii)** When dilute aqueous ammonia is added to a solution that contains copper(II) ions, a pale blue precipitate is obtained. This precipitate dissolves to form a deep blue solution when excess ammonia is added.

Give an explanation for these observations using relevant equations. **[3]**

$$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^{+}\,(aq) + OH^{-}\,(aq)$$

$$Cu^{2+}\,(aq) + 2OH^{-}\,(aq) \rightleftharpoons Cu(OH)_2\,(s) \qquad \text{Eqn (1)}$$

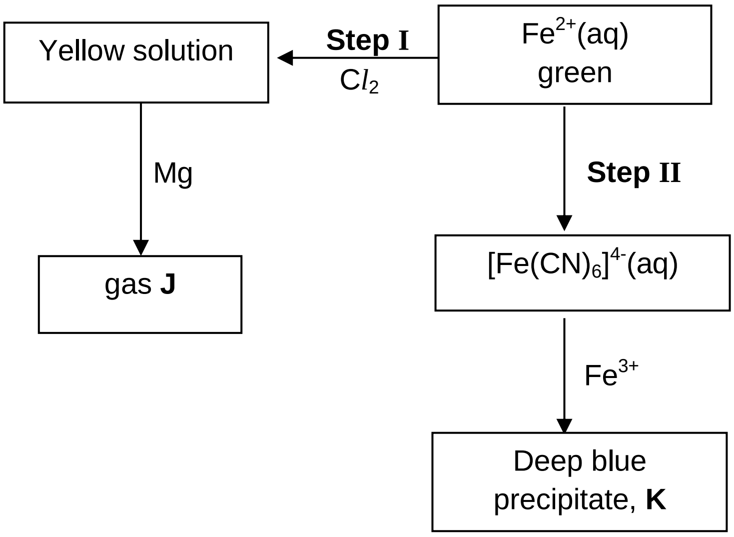
- When **dilute $NH_3$ is added** gradually, **$[OH^{-}]$ increases**.
- **Ionic product of $Cu(OH)_2$ > $K_{sp}$ of $Cu(OH)_2$** or
- Pale blue precipitate of $Cu(OH)_2$ is formed.

$$[Cu(H_2O)_6]^{2+}\,(aq) + 4NH_3\,(aq) \rightleftharpoons [Cu(NH_3)_4(H_2O)_2]^{2+}\,(aq) + 4H_2O\,(l) \qquad \text{Eqn (2)}$$

deep blue

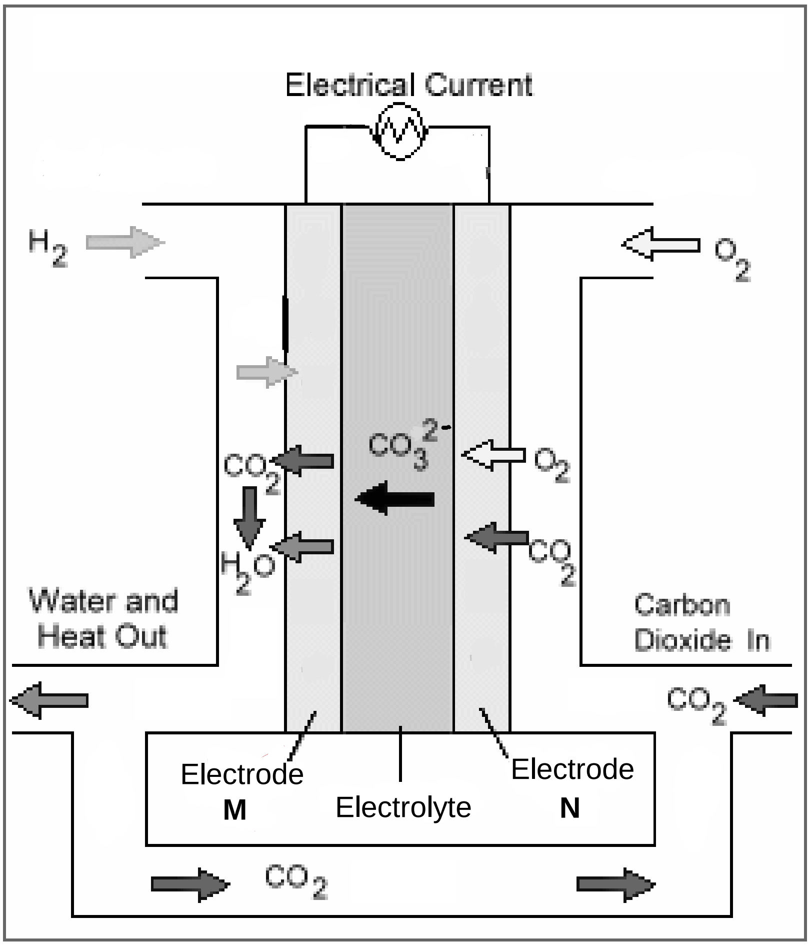
- When excess $NH_3$ is added, **$NH_3$** ligands **replace $H_2O$** ligands to form the **more stable deep blue $[Cu(NH_3)_4(H_2O)_2]^{2+}$** complex.
- **$[Cu^{2+}]$ decreases** as it is used to form the complex.

| | | | |
|---|---|---|---|
| | | | ○ The equilibrium position in Eqn (1) shifts to the **left** to **increase [$Cu^{2+}$]**.<br>○ Thus, the pale blue precipitate dissolves. |
| | **(b)** | Iron by mass, is the most common element on Earth, forming much of Earth's outer and inner core. It forms compounds mainly in the +2 and +3 oxidation states. Iron and its compounds are widely used as catalyst. | |
| | | **(i)** | Suggest why iron has the ability to exist in variable oxidation states.<br>[1] |
| | | | Iron which is a transition metals possess variable oxidation states due to the **small energy level difference between the 3d and 4s electrons**. This results in different numbers of 3d and 4s electrons lost to form stable ions and compounds of different oxidation states. |
| | | **(ii)** | Hydrogen peroxide decompose according to the following equation:<br>$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$<br>Iron(III) ions can be used to catalyse this decomposition. Using relevant data from the *Data Booklet*, suggest a mechanism for this catalysis, calculating the $E^\theta$ values for each step.<br>[3] |
| | | | The relevant half equations are :<br>$H_2O_2 \rightarrow O_2 + 2H^+ + 2e$<br>$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$<br>Step 1: $H_2O_2 + 2Fe^{3+} \rightarrow O_2 + 2H^+ + 2Fe^{2+}$<br>$E^\theta_{cell}$ = 0.77 – 0.68 = +0.09 V<br>Step II: $H_2O_2 + 2H^+ + 2Fe^{2+} \rightarrow 2H_2O + 2Fe^{3+}$<br>$E^\theta_{cell}$ =1.77 – 0.77 = +1.00 V |

| | | | |
|---|---|---|---|
| | | **(iii)** | The following diagram shows the reactions of some iron compounds.<br><br> |
| | | | Name the type of reaction in **Step II** and identify gas **J** and precipitate **K**.<br>[3] |
| | | | **Step II:** ligand exchange<br>**J:** $H_2$<br>**K:** $Fe_4[Fe(CN)_6]_3$ (note cation: $Fe^{3+}$, anion: $[Fe(CN)_6]^{4-}$) |

**(c)** Molten carbonate fuel cells (MCFCs) are high-temperature fuel cells that use an electrolyte composed of a molten carbonate salt mixture suspended in a porous, chemically inert ceramic matrix.

The following diagram show a MCFC:



At the electrode **N**, carbon dioxide is reacted with oxygen to form carbonate as the only product. The carbonate ions move towards electrode **M** and react with hydrogen to form carbon dioxide and water.

**(i)** Write half-equations for the reactions taking place at the electrodes of the fuel cell and hence, construct the overall equation for the fuel cell reaction. [3]

Electrode N (Cathode): $CO_2 + ½O_2 + 2e^- \rightarrow CO_3^{2-}$

Electrode M (Anode): $H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^-$

Overall: $H_2 + ½O_2 \rightarrow H_2O$

| | | | |
|---|---|---|---|
| | | **(ii)** | State the direction of the electron flow with respect to the electrode.<br>[1] |
| | | | Electrons flow from electrode **M** to **N**. |
| | | **(iii)** | Besides being high in efficiency and high operating cost, suggest one advantage and disadvantage of the molten carbonate fuel cell.<br>[2] |
| | | | Advantage:<br>The **product is clean** and it **does not generate greenhouse gas**.<br>Disadvantage:<br>**High temperatures** at which these cells operate and the **corrosive electrolyte** used accelerate component breakdown and corrosion, **decreasing cell life**. |
| | | | [Total: 20] |

**END**